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EDITED BY

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AND

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THE THEORY OF ALLOTROPY

BY

A. SMITS, PH.D.

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF AMSTERDAM

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WITH 239 FIGURES IN THE TEXT

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PREFACE

WHEN the author, about fourteen years ago, stated in an inaugural lecture that systems of one component were then and for several years had been considered to be governed by the Phase Rule, he expressed the opinion generally held by physical chemists.[1]

It was believed, in fact, that one-component systems had been completely investigated, and that new points of view could only be obtained by the study of more complicated systems. It was not even suspected that many mysteries still remained unsolved, even in one-component systems, which only the Phase Rule could elucidate. At that time every conception was lacking in the light of which monotropy and enantiotropy and all the various phenomena associated with them could be surveyed from a single point of view.

Four years later, in 1910, the author came to the conclusion that the theoretical knowledge gained in the phase study of more complicated systems made possible a rational explanation of these problems, and in this way the Theory of Allotropy originated. Since that time this theory has been further developed by the author, who, with the assistance of his co-workers, has also tested it in several directions.

Meanwhile, the introduction of the principles underlying this theory into the domain of electro-chemistry has resulted in the development of a new theory of electromotive equilibrium, by means of which anodic and cathodic polarisation, over-voltage and passivity can be simply and consistently explained. Subsequent experimental investigation led to results which, both from the purely chemical point of view as well as from the electrical standpoint, were in complete harmony with the theory. Amongst those who were interested in this region, many at first gained the impression that the interpretation of X-ray spectra given at that time could not be brought into satisfactory agreement with the Theory of Allotropy. As a matter of fact this was indeed the case; but, from the chemical point of view, such serious objections could be brought against the original explanation that a modification of this interpretation appeared to be absolutely necessary. Fortunately it can

[1] Inaugural Lecture, Delft, 1906, "De algemeneene chemie en hare beteekenis voor de praktyk," p. 14.

now be stated, as is made evident in the last chapter of the theoretical portion of the book, that a change in the above-mentioned interpretation has very recently begun, and hence it is now possible to look forward to the speedy removal of the original difference of opinion between chemists and physicists. Under these auspicious circumstances the hope is justified that the continued investigation of the X-ray spectra of solids will contribute in no small measure to the future development of the Theory of Allotropy.

With regard to the method of representation employed the following observation may be made. The pseudo-components referred to consist of different molecular species, and although the idea of "different molecular species" must be interpreted in the widest possible sense, as indeed has been expressly emphasised in Chapter I., in the discussion of the space diagrams the subject will be treated as though only isomeric or polymeric molecules could enter into the question. It must be noticed, however, that whatever these molecular species may be, the graphic method of representation always remains essentially the same.

It should be stated that the author had hoped to be able more closely to limit the number of sections of the space model considered in Chapter I. On further reflection, however, this appears undesirable; on the one hand, in order to explain many phenomena sections of different types must be considered, and, on the other hand, the complete position of the unary system in the pseudo-system only emerges clearly when the question is thoroughly discussed.

Referring again to the method of representation, it may be observed that in these considerations gaseous or liquid phases have been first discussed, and the molecular properties of these phases have then been applied to the solid phase. But the consequence of setting out from the other side, thus making the solid phase the starting-point, has also been considered. If one proceeds in this way it seems not impossible for the complexity, which in the author's opinion is a necessary condition for the appearance of allotropy, to consist in the existence of particles which must be considered to be different, solely because of their position or orientation in the space lattice.

But if this were the only kind of complexity in the whole system it would only occur in the solid phase, and this circumstance would give rise to peculiar difficulties. For although this complexity in the solid phase enables us plausibly to explain allotropic changes and certain retardation phenomena in solids, it would not be possible in this way satisfactorily to explain the influence of the previous history of the gaseous or liquid phase on the solidification phenomena or on the

properties of the newly formed solid phase. To make this possible it would be necessary, in the author's opinion, to attribute to the gas and to the liquid another kind of complexity suitable to these phases; but the uniformity of the method of treatment would then be lost.

Although naturally there is no contradiction here of the Theory of Allotropy, still it is evident that a uniform method of treatment possesses great advantages, so that only very cogent reasons could lead to the abandonment of the method adopted.

Finally it may be pointed out that this book does not purport to deal with investigations into the phenomena of allotropy; it is only concerned with the Theory of Allotropy, and only those experiments which make it possible to test the theory or which have been applied to that purpose are discussed.

Shortly after the appearance of the German edition of this book the author learned of the successful extension of Brereton Baker's classical researches on perfectly dried substances to liquids and solids. The results of these experiments are of great importance from the point of view of the theory developed here, for, not only do they afford it valuable support, but they show at the same time that the method of intensive drying furnishes us with one of the most beautiful means of establishing the complexity of unary phases. In addition, this method makes it possible more closely to penetrate into the essential nature of this complexity. On account of their great importance a special chapter has been devoted to Baker's recent investigations.

It should be mentioned that in the English translation many alterations have been made and new matter has been introduced.

A. SMITS.

Amsterdam,
February, 1922.

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THE THEORY OF ALLOTROPY

PART I—THEORETICAL

CHAPTER I

THE PRINCIPLES OF THE THEORY AND THE METHOD OF REPRESENTATION

1. General Remarks concerning the Hypothesis on which the Theory of Allotropy is based.[1]

IF a one-component system ($n = 1$) containing m different kinds of molecules is considered, in which, in consequence of reversible changes, an equilibrium may be established, the velocities of these changes determine whether the system will behave under a given experimental treatment as a *one-component* system (unary) or as a *poly-component* system, the highest possible number of components being m.

By the term "components" is meant the independently variable constituents of a system, and since the molecular species to which reference has just been made are not independent, it is of course out of the question, in the case under consideration, to speak of several components.

It often happens, however, that, by working rapidly or by the use of negative catalysts, transformation between the different molecular species occurs to so slight an extent during the experiment, that the system behaves as though it consisted of several components. Hence the different molecular species are also called pseudo-components. In the above-mentioned case, then, one may speak of the pseudo-binary, pseudo-ternary, and pseudo-quaternary behaviour of an essentially unary system.

The occurrence of different molecular species of one and the same substance is in no way exceptional; on the contrary, when the extraordinarily frequent occurrence of association and dissociation and the very widespread phenomenon known as tautomerism are considered, the statement seems to be justified that it is not the exception but the rule for the liquid phase of a substance to be composed of different kinds of molecules, ions and electrons being reckoned as such. In other words, liquid phases are complex in character. Various workers,

[1] *Chem. Weekblad*, **7**, 79 and 155 (1910); *Kon. Akad. v. Wet.*, **18**, 808 (1910); *Zeitschr. f. physik. Chemie*, **76**, 421 (1911).

amongst whom Drucker[1] may be specially mentioned, have emphasised that this statement also holds good for gaseous phases, but very little attention has been given to the solid phase. This must not be taken to mean that it has never been assumed, in special cases, that the solid phase too may be built up from molecules of different kinds.

Thus, in the case of selenium, this opinion has already been advanced by Marck,[2] but, possibly through too narrow an interpretation of the idea "complexity" as applied to a phase, the phenomenon has not been considered to be of frequent occurrence, and still less has any causal connection been sought between it and Allotropy.

The theory that will be discussed in this book maintains that, if the existence of a substance in different homogeneous phases is called *Phase Allotropy*, this phenomenon and that of *Phase complexity* must be causally connected with each other, in the case of the same substance, and in this way: *The origin of Phase Allotropy is always to be found in the complexity of the phase.* This phase complexity consists then in the occurrence of different molecular species. The expression "different molecular species" is to be interpreted in the widest possible sense, for by it is meant not only the different kinds of molecules of a substance, isomeric or polymeric molecules, but also their electrically charged dissociation products, ions and electrons, whilst in the case of metals atoms also are included.[3]

The different molecular species will be represented by α, β, γ, etc., and thus the category to which these molecular species belong is left undecided in the general preliminary discussion.

The existence of different molecular species of an element or of a compound, using the term in the narrower sense (isomeric or polymeric molecules), in any phase of this substance may be called *Molecular Allotropy*, so that, in accordance with the view developed here, it may often be said that the origin of *Phase Allotropy* is to be found in *Molecular Allotropy*.

The hypothesis on which this theory is based consists of two parts.

The first part states *that every phase and therefore also every crystalline phase of an allotropic substance is a state which, under certain circumstances, can behave as a poly-component phase.*

The second part, based principally on the analogy which exists between the solid, liquid and gaseous states of aggregation, states *that the cause of this behaviour must be assumed to be the complexity;* i.e. *the existence of different molecular species, which are in inner equilibrium when the behaviour of the system is unary, or in other words when it behaves as a one-component system.*

The term inner equilibrium means the equilibrium between the different molecular species of one and the same substance.

The hypothesis maintains, therefore, that the transition point,

[1] *Zeitschr. f. physik. Chemie*, **68**, 616 (1909).

[2] *Zeitschr. f. anorg. Chem.*, **37**, 459 (1903).

[3] The possibility is also not excluded, that in some cases particles may be different in the above sense, solely because of a different arrangement or orientation in the space lattice.

melting point, boiling point, critical point, etc., of such a unary allotropic substance relate, not to a *single* molecular species, but to an inner equilibrium between molecules of *different* kinds.

2. The Derivation of the *T X* Diagram by Means of the ζ Line.

This conception can be most easily elucidated by the deduction, with the aid of Gibbs' Equilibrium Principle, of the T X diagram for a binary pseudo-system together with that of the unary system situated within it.

This principle states that at constant temperature and pressure a system tends to change into such a state that the thermodynamic potential (ζ function) becomes a minimum.

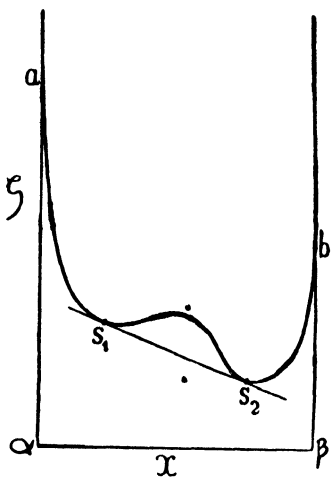


FIG. 1.

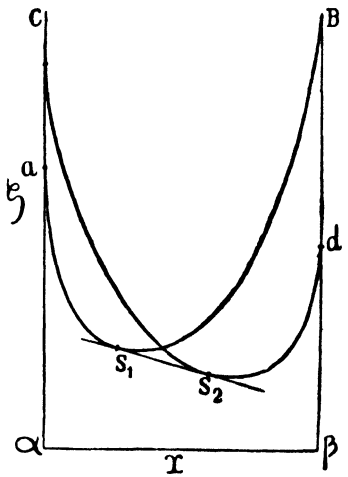


FIG. 2.

This general principle, which has so often been applied with success, provides in this instance again the safest means of deducing the connection between the pseudo and the unary systems.

Still, in so applying it, several fundamental questions must be taken into account.

In our hypothesis it is assumed that the pseudo-components are more or less miscible in the solid state, otherwise inner equilibrium would be impossible. From the great analogy between the behaviours of liquid mixtures and mixed crystals, Bakhuis Roozeboom[1] in 1891 made the assumption that, when the mixed crystal series exhibits a gap, the ζx curve will have a form such as that represented in Fig. 1 by the line *a b*.

This indicates a continuity, although in the labile region, between

[1] *Zeitschr. f. physik. Chemie*, **33**, 385 (1899). Bakhuis Roozeboom made this assumption. Afterwards, van Rÿn van Alkemade, *Zeitschr. f. physik. Chemie*, **11**, 289 (1893), did the same for the co-existence of salt solutions with solid phases.

the two series of mixed crystals, to which the two pseudo-components α and β give rise, and which have, in general, different crystalline forms.

It is, however, not improbable that in many cases this continuity does not exist, and that the two portions of the ζx line relating to mixed crystals of different crystalline forms are unconnected with each other, but that each *per se* proceeds continuously from one axis to the other, as is shown in Fig. 2. The curve $c\,d$ then relates to one species of mixed crystals, and indicates the values of ζ for different mixed crystals in which the pseudo-component α under the influence of β crystallises in the same form as the latter, whilst the line $a\,b$ refers to mixed crystals in which, conversely, β, under the influence of α, crystallises in the α form.

These conditions would naturally be realisable to an unlimited extent if the pseudo-components were *isodimorphous*, but the assumption would then have to be made that, solely because of different orientations of one and the same molecular species in the space lattice, the pseudo-components might appear in different crystalline forms.

It is questionable, however, whether yet another interpretation is not possible. It is clear that the stability of the space lattice of the pseudo-component α will diminish as more of β is taken up, and thus it is possible that at a definite composition the space lattice becomes so unstable that finally an entirely new orientation appears. The question now is, What form will the ζx curve take in this case? Thus it is possible that the ζx line $a\,b$, Fig. 3, proceeding from the α axis, instead of continuing towards the other axis, asymptotically approaches the line $r\,s$; that is to say, a mixed crystal of composition r is impossible since this crystal would require the value of ζ to be infinitely great.

Similarly the ζx line $d\,c$ would then become asymptotic to $p\,q$. The formula

$$\left(\frac{d\zeta}{dx}\right)_{PT} = \mathrm{RT}\log\frac{x}{1-x} + \int_{v}\left(\frac{dp}{dx}\right)_{v,\,T} dv\,*$$

in this case becomes *infinite* for a definite value of x, since the second term on the right-hand side then becomes infinitely great.

Finally, there is still another possibility. That is, the ζx lines in the diagram may end abruptly, as is shown in Fig. 4. Naturally in this case the end-point may occur before the curve attains its minimum value. Thus the diagram shows that the possibility of the existence of mixed crystals having the same crystalline form ceases suddenly at the points b and c, and that the continuation of these lines, which might indeed be *imagined*, has, thermodynamically, absolutely no further significance.

Which of these interpretations is the correct one we do not know, and fortunately, so far as the following considerations are concerned, the question is quite immaterial.

For the sake of simplicity the first interpretation will be adopted.

When the case is considered in which the pseudo-components are

* See van der Waals-Kohnstamm, *Thermodynamik*, **2**, p. 630.

miscible in all proportions in the *liquid* state, the ζx curve for the liquid mixtures, *i.e.* the curve, Fig. 5, containing the point L, exhibits no peculiarities; it is always convex towards the x axis and has only *one* minimum. In Figures 5–11 A and B have been written instead of α and β.

In the first place, the following question now arises:—

If a homogeneous phase of a pseudo-binary system is in inner equilibrium, where will this equilibrium be found on the corresponding ζx curve?

Every point of a ζx curve represents the smallest ζ value of a definite mixture under constant temperature and pressure.

At the minimum point of a ζx curve the ζ value of a corresponding mixture is smaller than that of other neighbouring mixtures, and if

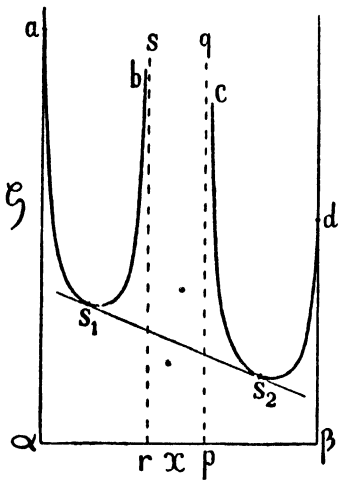


FIG. 3.

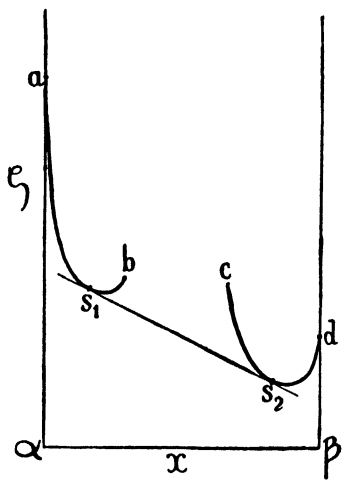


FIG. 4.

a reaction between α and β is possible, in accordance with Gibbs' Equilibrium Principle, this reaction will continue until that composition is reached which corresponds with a minimum point. Then, however, the composition remains unchanged, and inner equilibrium sets in. For this inner equilibrium, therefore, the following expression holds good:—

$$\left(\frac{d\zeta}{dx}\right)_{PT} = 0.$$

The total differential of the ζ function of a binary mixture is

$$d\zeta = -\eta dT + vdp + \mu_1 dm_1 + \mu_2 dm_2.$$

If it is now supposed that the two components can be mutually transformed, as is indicated by the equation

$$\nu_1 A \rightleftarrows \nu_2 B$$

it is seen that

$$dm_1 = \nu_1 dm$$

and

$$dm_2 = \nu_2 dm,$$

so that the following expression may be written :—

$$d\zeta = -\eta d\mathrm{T} + vdp + (\Sigma\nu\mu)dm.$$

Hence it follows, that in the equilibrium state

$$\Sigma\nu\mu = 0.$$

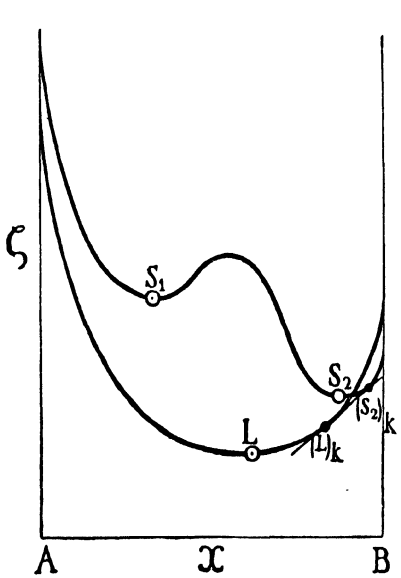


FIG. 5.

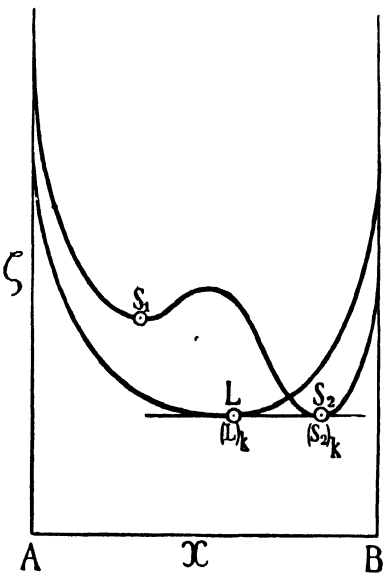


FIG. 6.

On the mixed crystal line, which consists of two branches, each of which passes through a minimum, and which are connected in the diagram by a partly metastable, partly labile intermediate portion, there are two points outside the labile region where $\left(\frac{d\zeta}{dx}\right)_{PT} = 0$, so that this curve points to the existence of two inner equilibria in the solid phase, whilst from the liquid curve in the preceding case it appears that only one inner equilibrium can occur. It may, however, be pointed out that this would also be true of the solid state, if there too α and β were miscible in all proportions; but in that event, as will presently be shown, most of the interest would be lost.

If a temperature somewhat lower than the melting point of β is considered, the ζx curves for solid and liquid will intersect on the β

side, as is shown in Fig. 5, for under these conditions pure β and mixtures rich in β are solid.

The co-existence thus conditioned between a mixed crystal phase and a liquid phase can be found, as is well known, by drawing the common tangent to the two curves.

Thus, at the constant temperature and pressure assumed, reading from left to right, the following series of phases occurs in the binary system: liquid—liquid co-existing with mixed crystals—mixed crystals. If, however, inner equilibrium is established, the state which has the lowest potential appears, and this is the liquid L (Fig. 5). In order to

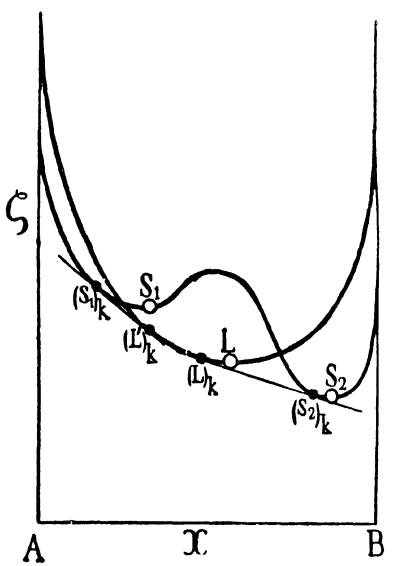


FIG. 7.

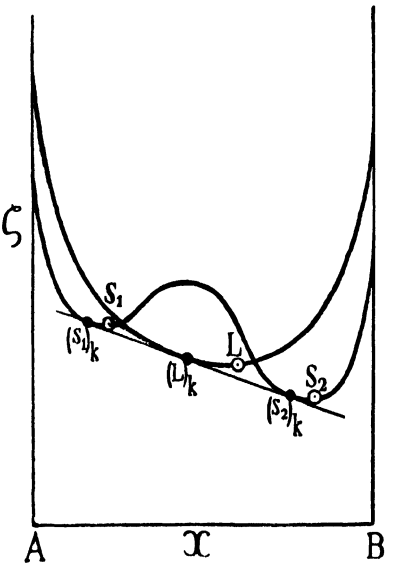


FIG. 8.

ascertain the influence of temperature on the position of the ζx curve let us consider the equation

$$d\zeta = vdp - \eta d\Gamma,$$

from which it follows, that

$$\left(\frac{d\zeta}{d\Gamma}\right)_p = -\eta.$$

When the temperature is lowered the ζx curves consequently rise, and since now the liquid curve rises more rapidly than that for the solid phase, at a definite temperature the state of affairs indicated in Fig. 6 is obtained.

In the binary system $(L)_k$ and $(S_2)_k$ also co-exist here, but there is now the peculiarity that both these points are minimum points of

exactly equal value, so that the heterogeneous equilibrium continues to exist unchanged even when inner equilibrium sets in.

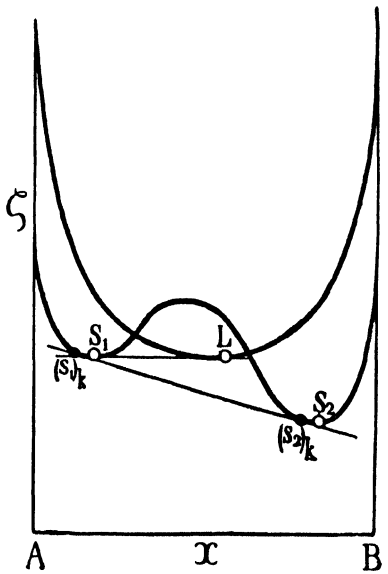


FIG. 9.

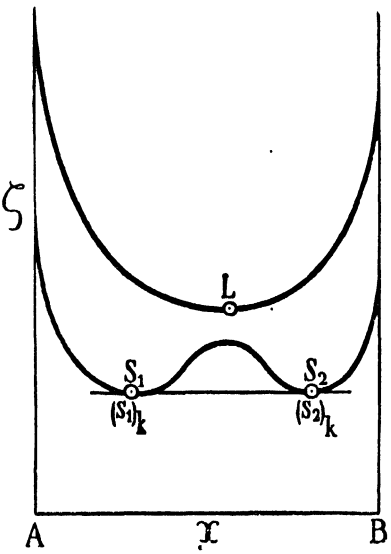


FIG. 10.

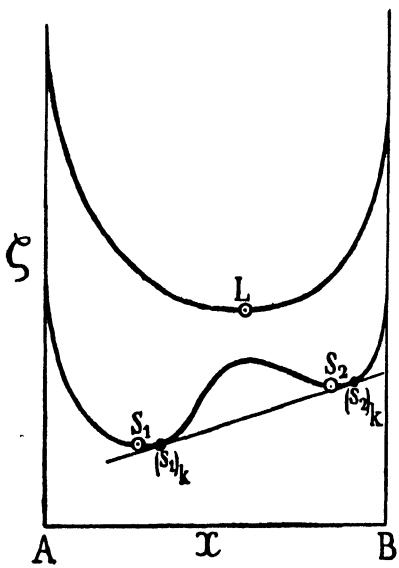


FIG. 11.

The temperature at which this happens is the *stable unary melting point.* If the temperature is supposed to have fallen below the melting point the ζ x diagram then takes the form shown in Fig. 7. In the binary system two two-phase equilibria between liquid and mixed crystals now appear, but in inner equilibrium the most stable state S_2 is formed, a solid phase.

At the three-phase temperature, at which the three co-existing phases in the pseudo-binary system $(S_1)_k$, $(L)_k$ and $(S_2)_k$ lie on a common tangent, as in Fig. 8, inner equilibrium gives rise to no special phenomena; the solid phase S_2 is still always the most stable.

On lowering the temperature

still further the liquid phase in the pseudo-binary system will also become metastable, and at a definite temperature the peculiar position indicated in Fig. 9 is obtained; that is to say, the metastable minimum points S_1 and L have a common tangent, which means that these two metastable inner equilibrium states can co-exist, and hence it follows that a *metastable unary melting point* may also appear.

Even though S_2 is still always the most stable phase in the unary system, and may continue to be so when the temperature is lowered still further, it is nevertheless possible for a sudden change to occur.

Thus, if the right branch of the ζ curve for the solid phase rises more rapidly than the left when the temperature is reduced, the remarkable case results, that at a certain definite temperature (Fig. 10) the minima S_1 and S_2 have the same tangent, so that the solid phases $(S_1)_k$ and $(S_2)_k$, which can co-exist in the binary system, also co-exist when inner equilibrium is established. The temperature at which this occurs is the *unary transition point*, for at this temperature the two solid phases S_1 and S_2 exchange their respective stabilities. That is, if the temperature is allowed to fall just a little more, the minimum point S_1 will lie below the minimum point S_2, as is shown in Fig 11, or, in other words, S_2 is now no longer the most stable state of the unary system; its place has been taken by S_1.

If only the ζx curves for the solid phases are considered, it is seen from the diagrams already discussed that at higher temperatures the phase S_1 is metastable with regard to the phase S_2, for the ζ-value of S_2 is smaller than that of S_1.

The phenomenon of *Enantiotropy* is characterised by the reversal of this relationship at a definite temperature, which lies *below* the stable unary melting point, in consequence of S_2 rising more rapidly than S_1. The converse case might, however, also have been considered, *viz.* that in which at high temperatures S_2 is metastable with respect to S_1, this relationship being reversed through the more rapid rise of the *metastable* point S_1 than of the point S_2. In the latter case, therefore, the transition point would lie above the unary melting point, *i.e.* the phenomenon known as *Monotropy* would occur.

Finally, it may be pointed out that the minimum shown on the left-hand side of the ζx curve for the solid phase may also be completely missing. Then neither *Monotropy* nor *Enantiotropy* occurs, but only Molecular Allotropy.

3. The $(T X)_p$ Figures.

If this result is further represented by means of a T X figure, the diagrams shown in Figs. 12 and 13 are obtained, in which the pseudo-binary diagram is indicated by faint lines, the heavy lines referring to the unary system.

The points L_2 and S_2 indicate the co-existing liquid and solid phases at the stable unary solidifying point, while L_1 and S_1 mark the co-existing phases at the metastable unary solidifying point. The co-existing solid phases at the unary transition point are shown by the points S_1'

and S_2'. In Fig. 12, which illustrates the phenomenon of Enantiotropy, this co-existence is stable, and in Fig. 13, which represents the case of Monotropy, metastable.

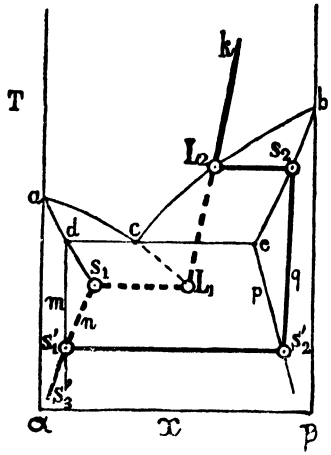


FIG. 12.

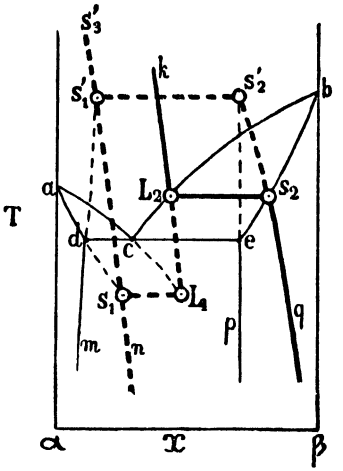


FIG. 13.

The lines kL_2, S_2S_2' and $S_1'S_3'$ specify the inner equilibria in the liquid and in the two solid phases respectively, at different temperatures,

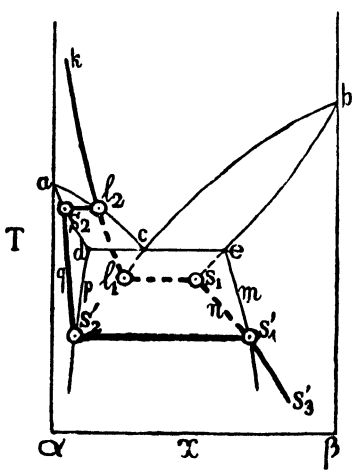


FIG. 14.

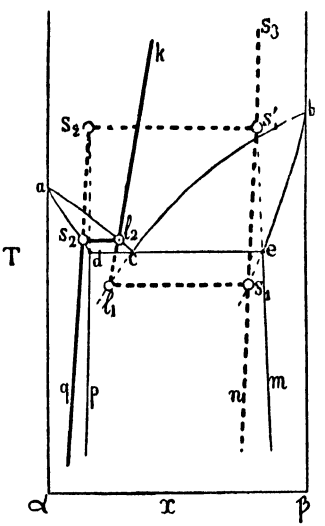


FIG. 15.

but under constant pressure. In the cases under consideration here, the line relating to the inner equilibria in the liquid meets the melting

line *b c*. It is, however, also possible for this line to meet the melting line *a c*, and the T X diagrams shown in Figs. 14 and 15 are then obtained.

Since it is thus seen that this new Theory of Allotropy may with advantage be discussed with the help of ζx curves, the case will now be considered in which the three-phase temperature in the pseudo-binary system lies between the melting points of the components.

The T X diagrams for this case are given in Figs. 16 and 17, the pressure being assumed to remain constant.

It is at once seen that Fig. 16 refers to *Enantiotropy* and Fig. 17 to *Monotropy*. Here also it is possible for the line relating to inner equilibrium in the liquid phase to meet the melting line *a c*, as is shown in Fig. 18. The drawing of these figures from the ζx curves is again

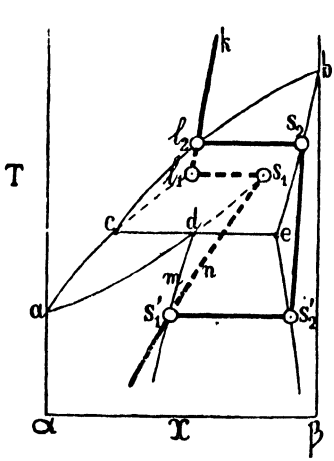


FIG. 16.

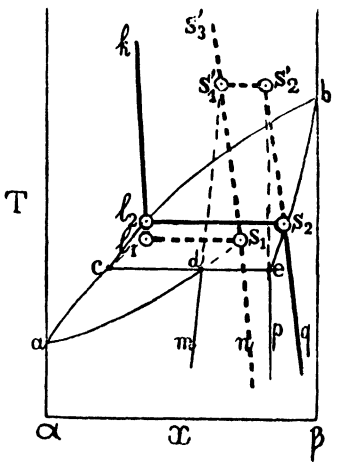


FIG. 17.

very simple if one only bears in mind that the liquid point L (see Fig. 10) now lies to the left of $(S_1)_k$ and not *between* the two co-existing solid phases.

From the assumption that the pseudo-components are more or less miscible in the solid state, it necessarily follows thermodynamically that the solid phase which co-exists with a liquid phase which is in inner equilibrium must be situated at the minimum of the ζx curve for the mixed crystals.

From this it may at once be concluded that the solid phase also is in inner equilibrium. This may, however, be shown in the following manner. When the liquid phase is in inner equilibrium the following expression is true

$$(\nu_1\mu_1)_L = (\nu_2\mu_2)_L.$$

For the heterogeneous equilibrium between the liquid and the solid phases

$$(\mu_1)_L = (\mu_1)_s$$

and

$$(\mu_2)_L = (\mu_2)_S$$

or

$$(\nu_1\mu_1)_L = (\nu_1\mu_1)_S$$

and

$$(\nu_2\mu_2)_L = (\nu_2\mu_2)_S$$

and hence it follows that

$$(\nu_1\mu_1)_S = (\nu_2\mu_2)_S$$

or, stated in words, the solid phase is also in inner equilibrium.

It has already been pointed out that the form of the ζx line for the solid mixtures determines the possibility of the appearance of allotropy.

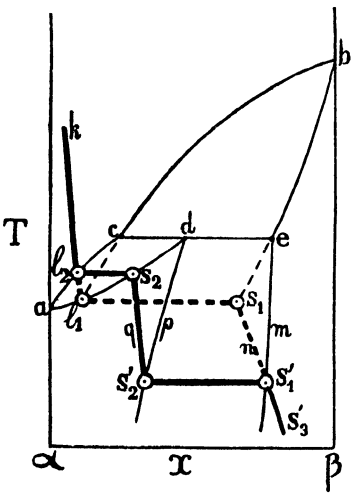


FIG. 18.

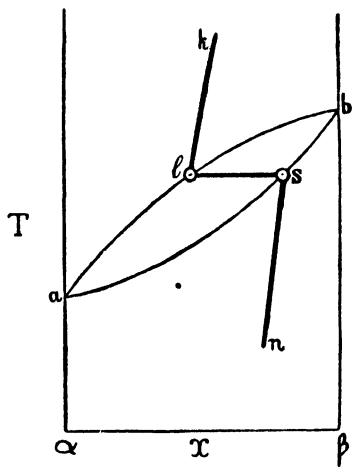


FIG. 19.

That is to say, if the series of mixed crystals is continuous and a T X section such as is shown in Fig. 19 is obtained, allotropy cannot occur.

4. Benedicks' Types of Allotropy.

Although unacquainted with the Theory of Allotropy, Benedicks,[1] in the year 1912, postulated the following four "Types of Allotropy," in which any given property is represented as a function of the temperature.

Benedicks was of opinion that Type 2a, Fig. 20, occurs when a solid solution of the second modification in the first stable at high temperatures is formed before the transition point is reached. In the case of Type 2b, on the other hand, a solid solution of the first in the second modification is formed above the transition point. Type 3 represents a combination of Types 2a and 2b, and in Type 4 the

[1] *Journal of the Iron and Steel Institute*, **2**, 242 (1912).

transition point disappears and only a continuous change now exists between the solid solutions richer in the first and second pseudo-components respectively.

It is clear that these different *Types of Allotropy* follow immediately from the Theory of Allotropy, yet at the same time it must here be emphasised that according to this Theory the peculiar course of the line *a b* in Type 2a, for example, can only be explained in the following way: Before the transition temperature is reached a very definite displacement of the inner equilibrium commences, as a result of which the concentration increases of that molecular species which is richer in the second modification than the first.

If this were a solution of the second *modification* in the first, the solid solution in a state of equilibrium would certainly be *binary*, whilst here phenomena are dealt with which appear even when the behaviour is unary. Hence it follows

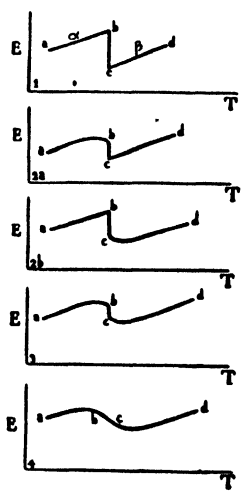


FIG. 20.

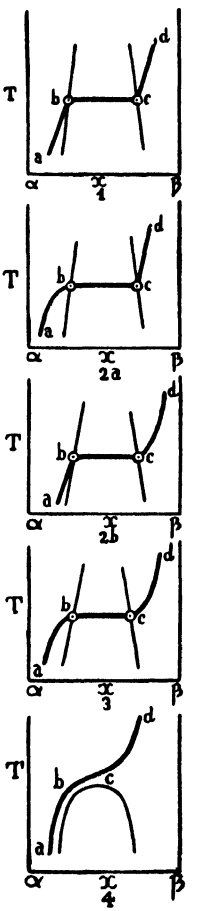


FIG. 21.

that the inner equilibrium between different molecular species in the solid state must here be displaced.

In Fig. 21 Benedicks' Types of Allotropy are considered in the light of the Theory of Allotropy; in this diagram only the lower portion of the pseudo-figure, *i.e.* the region referring to decomposition in the solid state, has been drawn.

Type 1, Fig. 21, corresponds with Benedicks' Type 1 (Fig. 20).

Types 2a, 2b and 3 of Fig. 20 occur when, as Types 2a, 2b and 3 of Fig. 21 show, the inner equilibrium in one of the two solid modifications, or in both, changes markedly with the temperature in the neighbourhood of the transition point. It is clear, that is to say, that every temperature function which is dependent on the internal composition will follow a course similar to that of the inner equilibrium line.

Type 4, Fig. 20, may occur, as Type 4 (Fig. 21) shows, if the inner equilibrium curve passes through the region of a continuous series of mixtures and the inner equilibrium undergoes considerable displacement.

This form will doubtless make its appearance when the line referred to traverses the region which lies somewhat above a critical mixture point for the solid state.

5. Equilibria under the Vapour Pressure.

Hitherto only equilibria under constant pressure and in the absence of the vapour phase have been discussed; equilibria under varying vapour pressures will now be considered.

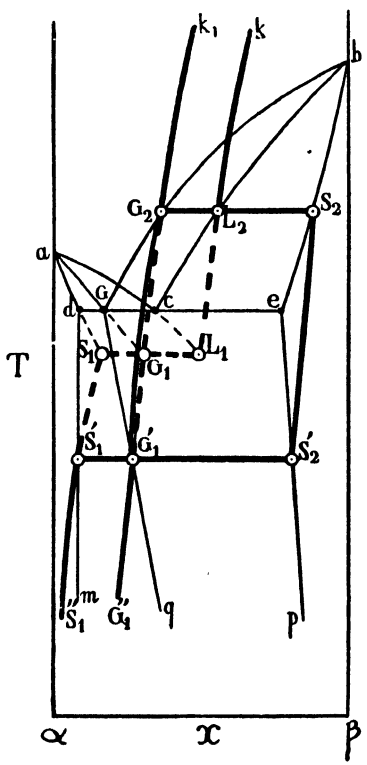


FIG. 22.

For this purpose Fig. 22 represents the projection of the three-phase areas of the pseudo-binary system and of the two-phase area of the unary system on the T X plane.

The three-phase area indicated by the lines *a d*, *a* G and *a c* refers to the co-existence of α-mixed crystals *a d*, the gaseous phase *a* G, and the liquid phase *a c*. The three-phase area *b e*, *b c*, *b* G, represents the co-existence of β-mixed crystals *b e*, the liquid phase *b c*, and the co-existing gas phase *b* G.

The third three-phase area relates to the co-existence of the mixed crystal phase *e p*, the gaseous phase G *q*, and the α-mixed crystal phase *d m*.

In the unary system the two-phase area for the liquid-vapour equilibrium is bounded by the lines kL_2L_1 and $k_1G_2G_1$, whilst the two-phase area in which β-mixed crystals co-exist with their proper vapour is shown by the lines S_2S_2' and G_2G_1', and the two-phase area for the equilibrium between α-mixed crystals and the vapour belonging thereto is indicated by the lines S_1S_1'' and G_1G_1''.

At the junction of two two-phase areas of the unary system a three-phase equilibrium is formed, which must naturally lie in one of the three-phase areas of the pseudo-binary system.

Fig. 22 shows three such junctions. The meeting of the two-phase area for liquid and vapour with that for the β-mixed crystals and vapour produces the three-phase equilibrium between the solid phase S_2, the liquid phase L_2 and the gas phase G_2. This is the stable melting equilibrium of a substance which behaves as a unary system under its own vapour pressure.

At the junction of the two-phase area for the β-mixed crystal phase and the co-existing vapour with that for the α-mixed crystal phase and the vapour belonging to it, the three-phase equilibrium between the α-mixed crystal phase S_1', the vapour phase G_1', and the β-mixed crystal phase S_2' is formed. This is the transition equilibrium under the pressure of the vapour, and it must naturally be found in the three-phase area of the pseudo-system relating to the two solid mixed crystal phases and the co-existing vapour.

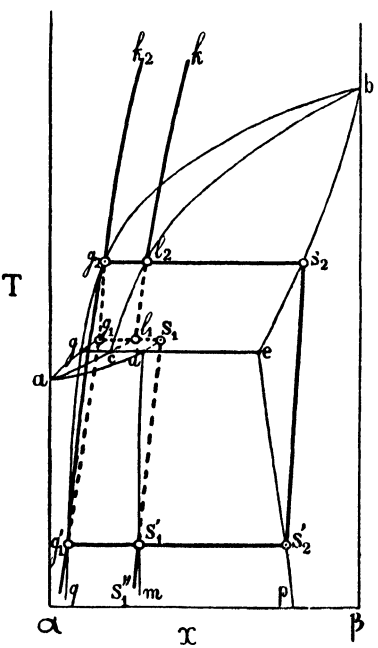


FIG. 23.

Finally, the junction of the two-phase area for liquid and vapour with that for the unary α-mixed crystals and vapour has still to be considered.

This meeting takes place below the stable unary melting equilibrium and above the unary transition equilibrium, and therefore it concerns the metastable portions of the above-mentioned two-phase areas. The three-phase equilibrium represented by this junction is, therefore, also metastable, and the three co-existing phases S_1, G_1 and L_1 consequently represent the metastable unary melting equilibrium under the vapour pressure of the system; these three co-existing phases are naturally to be found in the metastable part of the three-phase area for mixed crystals, vapour and liquid. It may here be pointed out that in every unary three-phase equilibrium three two-phase areas of the unary system come together, of which two only have as yet been discussed. The two-phase areas which have not yet been mentioned refer to unary equilibria in the absence of vapour, and are consequently omitted here. It is evident that a two-phase area proceeds from the points S_2 and L_2 relating to the co-existence of β-mixed crystals and liquid, *i.e.* to the stable melting equilibria at higher

pressures, and from S_1 and L_1 there arises a similar area for the equilibrium between α-mixed crystals and liquid. The latter two-phase area represents the metastable melting equilibria under higher pressures.

There is also still another two-phase area relating to the co-existence of α- and β-mixed crystal phases; it takes its origin from S_1' and S_2', and represents the transition equilibria which appear at higher pressures.

The T X projection of the three-phase areas of the pseudo-binary system and the two-phase areas of the unary system have here been considered in their mutual relationships, for the case in which *Enantiotropy* appears. From this the corresponding relationship may be deduced for the case of *Monotropy* without further discussion.

The relationships which appear when the pseudo-system contains no eutectic and the temperature of the four-phase equilibrium lies between the triple points of the components are so simple, that it is sufficient to give the T X projection shown in Fig. 23.

It may here be emphasised that both in the case of Enantiotropy and Monotropy the two solid phases exist with vapours of different compositions, except at the transition point.

6. The *P T X* Space Model.

The P T X space model of the pseudo-binary system consists, as is well known, of various surfaces, which are related to one another in pairs. At the intersection of two similar surfaces three phases can co-exist, and at the point where three such surfaces come together four phases can co-exist. The P T X space model of a unary system is likewise built up from a number of surfaces representing inner equilibria, and at the intersection of one of these surfaces with a similar surface belonging to the pseudo-binary system a two-phase co-existence in the unary system makes its appearance. Thus, for example, the surface relating to inner equilibrium in the liquid cuts the surface which represents the co-existence of liquid and vapour in the pseudo-binary system. Every point of this line of intersection therefore represents a liquid which co-exists with vapour in the unary system. Similarly the intersection of the surface for the inner equilibrium in the vapour with the surface relating to the co-existence of liquid and vapour in the pseudo-binary system produces a line of intersection, every point of which defines a vapour which co-exists with liquid in the unary system.

These co-existing vapours and liquids of the unary system have, however, at the same temperature and pressure, different compositions, so that the equilibrium between liquid and vapour is indicated, in the P T X space model of the unary system, by two lines, for the co-existing points of which the corresponding x values are different. This naturally holds good for every other two-phase equilibrium in the unary system. It is clear that the P T projection allows

this peculiarity of the unary system to be concealed; in this projection the difference in the compositions of co-existing phases cannot be expressed, for in this method of representation every pair of lines relating to the co-existence of two phases will be projected as a single line.

It is therefore of interest to consider several P X sections of the pseudo-binary P T X space model, and in these sections to indicate the position of the unary system.

For this purpose it is not necessary to draw the space figure. The P T projection is sufficient, and this projection will therefore now be considered.

In connection with previous remarks it may again be emphasised here that two cases can be distinguished. In the first place the pseudo-components α and β may be *isomers*, and secondly β may represent a *polymer* of α.[1]

In the first case the P T X space model may contain a eutectic melting line, whilst in the second case this line will not appear.

7. The *P T* Projection of the *P T X* Space Model of the Pseudo-binary and the Unary Systems, when α and β are Isomers and a Eutectic Melting Line Appears.

This projection is given in Fig. 24, which is here the determining diagram. The faint lines are the three-phase lines of the pseudo-binary system and the two-phase lines of the pseudo-components, whilst the heavily drawn lines relate to the two-phase lines of the unary system. For greater clearness the phases of the unary system are indicated by means of the suffix u, thus :—S_u, L_u and G_u.

The point at which the vapour pressure curve of the unary system $K_u D$ indicated by $L_u + G_u$ meets the three-phase line $S_{\beta_M} + L + G$, which therefore refers to β-mixed crystals, liquid and vapour, is the unary solidifying point under the vapour pressure of the system. This occurs at the point D; at this triple point, then, two new inner equilibrium lines belonging to the unary system appear, the melting line D E, which is more closely defined by $S_{u_2} + L_u$, and the sublimation line D A′, on which $S_{u_2} + G_u$ co-exist.

At the point B in the diagram this sublimation line cuts the three-phase line $S_{\alpha_M} + S_{\beta_M} + G$ of the pseudo-binary system, that is to say, the assumption has here been made that a transition point also appears under the vapour pressure of the system.

From this triple point B, therefore, besides the sublimation line, $S_{u_2} + G_u$, two other inner equilibrium lines belonging to the unary system proceed, namely, the sublimation line A B of the new modification, representing the co-existence $S_{u_1} + G_u$ and the transition curve B C for the co-existence $S_{u_1} + S_{u_2}$.

At the point of intersection of the metastable prolongation of the

[1] Other cases of different molecular species exhibit no essential differences.

vapour pressure line $L_u + G_u$ and the three-phase line $S_{\alpha_M} + L + G$, that is to say at D', is situated the metastable melting point determined under the vapour pressure of the system. From this triple point two other metastable inner equilibrium lines relating to the unary system must naturally take their origin, namely the metastable melting line D' E' for the co-existence $S_{u_1} + L_u$ and the sublimation line D' A of the first solid modification, which is metastable as far as the point B; this line represents the co-existence $S_{u_1} + G$.

From the fact that the four three-phase lines which meet, in the pseudo-system, at the quadruple point e_2 have been indicated by $S_{\alpha_M} + L + G$, $S_{\beta_M} + L + G$, $S_{\alpha_M} + S_{\beta_M} + G$ and $S_{\alpha_M} + S_{\beta_M} + L$,

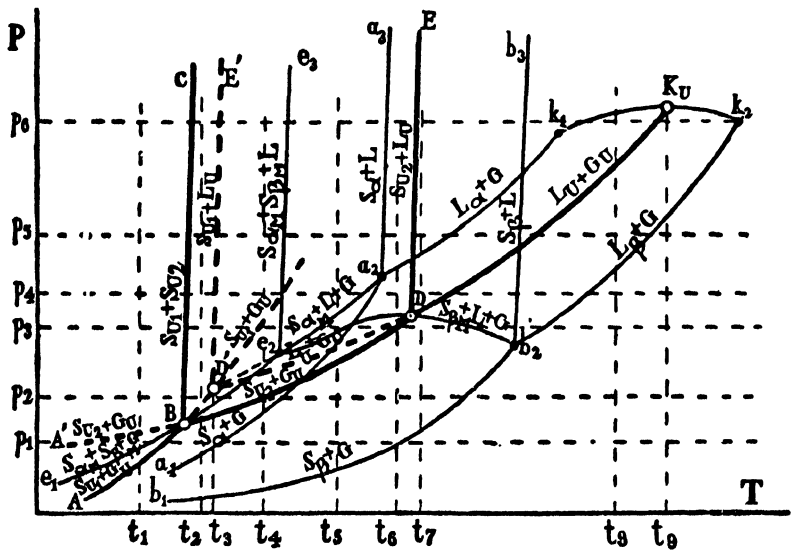


FIG. 24.

expressly to emphasise that the solid phase is here a mixed crystal phase, the application of the Theory of Allotropy in this P T projection at once follows.

If this were not the case, this P T projection would be in perfect agreement with that advanced by Schoevers [1] for the case of allotropy, but the diagram would then contradict the theory developed here.

The P T projection is quite unsuitable for the purpose of elucidating the considerations which have been put forward, for, as has already been noticed, it completely veils the most important factor, the difference in composition of the phases. This projection will, therefore, only be used here to indicate which P X sections of the space model should be considered.

[1] *Dissertation*, Amsterdam.

8. $(PX)_T$ Sections of the Space Model.

Just like the $(TX)_P$ figures, the $(PX)_T$ figures are naturally derived from the ζx diagrams, but with the difference that from the equation

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

it follows that

$$\left(\frac{d\zeta}{dT}\right)_P = -\eta,$$

i.e. at constant pressure the ζx lines fall when the temperature is raised, that is when η is positive, while the relation

$$\left(\frac{d\zeta}{dp}\right)_T = v$$

shows that, at constant temperature, the ζx lines rise as the temperature is increased.

Since, however, in the derivation of the ζx figures the relative displacement of the ζx lines is exclusively employed, this is of secondary importance only, and therefore the thermodynamical derivation of the $(PX)_T$ figure need not be further entered into here.

The question how the inner equilibrium lines will run in the PX section of the unary system is more interesting.

Although the position of the inner equilibrium lines will be fully discussed in a separate chapter, it appears desirable to notice here that the displacement of the inner equilibrium by pressure is given by Planck's well-known equation,

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

As is well known, this formula only holds when the concentrations are given, not per unit of volume but in molar fractions.

From this expression it is clear that the sign of Δv determines the direction of the displacement. It has been assumed here that the pseudo-components are isomers and hence it follows naturally that the PX lines for the inner gaseous equilibria run vertically in the PX figure. This does not hold, however, for the lines referring to inner equilibrium in the liquid or solid phases, since in general the value of b in van der Waals' equation of state are not the same for isomeric substances. However, in the figures which follow, the PX lines of the unary system are, *for greater simplicity*, drawn vertically in all phases.

In Fig. 25, the PX section at the temperature t_1 (see Fig. 24) is considered. Here the pseudo-binary figure is again drawn faintly, the heavy lines relating to the unary figure.

The line $G_{u_0} G_u$ indicates the inner equilibrium in the gaseous phase. At G_u this line is intersected by the vapour pressure curve aG of the pseudo-binary system. This, if the gas over G_u is compressed, and assuming that no metastable states appear, results in the formation of the mixed crystal phase S_{u_1}, which, just like the gaseous

phase G_{u_1} will be in inner equilibrium if the behaviour is unary. If after the gas has disappeared the compression is continued, an increase of pressure occurs and only the solid phase will then remain; the inner equilibrium in this solid phase is represented by the line $S_{u_1} S_{u_1}'$.

If, however, the solid phase should not be formed on compressing out the gas above G_u the metastable prolongation of the line *b* G may be reached; *i.e.* if no retardation occurs, on continued compression the metastable solid phase S_{u_2} will appear, which, in the case of unary behaviour, is likewise in inner equilibrium. When the vapour has completely disappeared, further compression will in this case also result

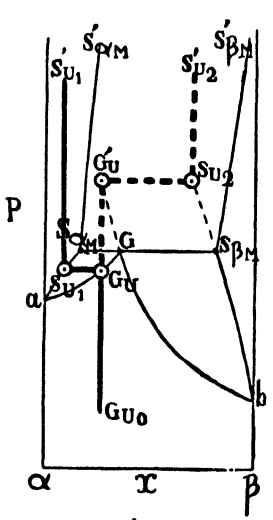


FIG. 25.

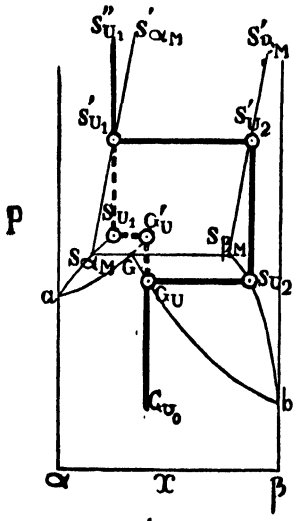


FIG. 26.

in an increase of pressure, and the inner equilibrium in the metastable solid phase will be correspondingly displaced along the line $S_{u_2} S_{u_2}'$.

At the temperature here selected the unary solid phase S_{u_1} remains stable under all pressures, and S_{u_2} metastable, and hence it may be said that at this temperature the system exhibits the phenomenon of *monotropy*.

Just as it is possible for a system to be monotropic under its own vapour pressure and enantiotropic under higher pressures, so a system which is monotropic at lower temperatures may at higher temperatures exhibit enantiotropy.

If it is assumed, as in the present instance, that enantiotropy occurs under the vapour pressure, this is actually the case. That is, if t_2 is chosen as the second temperature, the P X section shown in Fig. 26 is obtained.

The change in the position of the unary system relative to the pseudo-binary system, produced by increase of temperature, is noteworthy. The line for the inner equilibrium in the vapour is displaced towards the right in relation to the pseudo-binary system, and as a result the intersection with the pseudo-binary figure, which previously took place on the vapour line *a* G, now occurs on the vapour line *b* G.

At any temperature between t_1 and t_2 naturally an intermediate state of affairs is obtained, and if a suitable temperature is chosen the intersection may occur exactly at the point G, and G_u will therefore coincide with G. Hence, at this temperature, two solid and a vapour phase may co-exist in the unary system, and these phases are all in inner equilibrium; i.e. *this temperature at once represents the transition point when the system is under its own vapour pressure.*

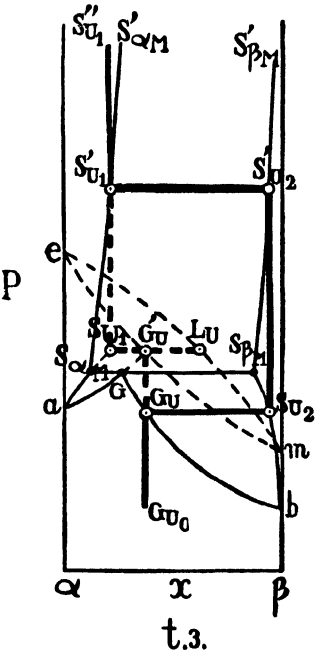


FIG. 27.

The temperature t_2, which lies somewhat above this temperature, yields the P X section, Fig 26, from which it appears that the lines for the inner equilibrium in the stable solid modification S_{u_2}, and in the metastable modification S_{u_1}, intersect the mixed crystal lines S_{β_M} S_{β_M}' and S_{α_M} S_{α_M}' of the pseudo-system at S_{u_2}' and S_{u_1}'. This means that at that point a conversion of the solid phase S_{u_2}' into S_{u_1}' will take place under constant pressure, if the behaviour is unary and provided no retardation occurs. Thus the modification S_{u_1} which is metastable at low pressures becomes stable for the first time.

If the phase S_{u_2}' is entirely transformed, further compression will result in an increase of pressure, and the inner equilibrium in the stable phase is now moved along the line S_{u_1}' S_{u_1}''. At the temperature t_2, therefore, change of pressure produces enantiotropy.

Fig. 27 refers to the temperature of the metastable melting point D of the unary system. The only peculiarity shown by this P X section as compared with the preceding one lies in this: the metastable prolongation of the inner equilibrium line for the vapour passes exactly through the point, where in the pseudo-binary system the metastable prolongation of the vapour line *a* G cuts the vapour line for the metastable liquid–vapour equilibrium. Consequently in the unary system, solid, liquid and vapour, *viz.* $S_{u_1} + G_u' + L_u$, co-exist in a metastable condition, or, in other words, *in this section the metastable melting equilibrium under the vapour pressure of the system appears.*

Fig. 28 holds good for t_4, which lies a little below the eutectic point of the pseudo-binary system.

In the light of the preceding discussion, this diagram is immediately intelligible. Fig. 29 relates to a temperature t_5, which lies a little above the eutectic temperature of the pseudo-binary system. The P X section

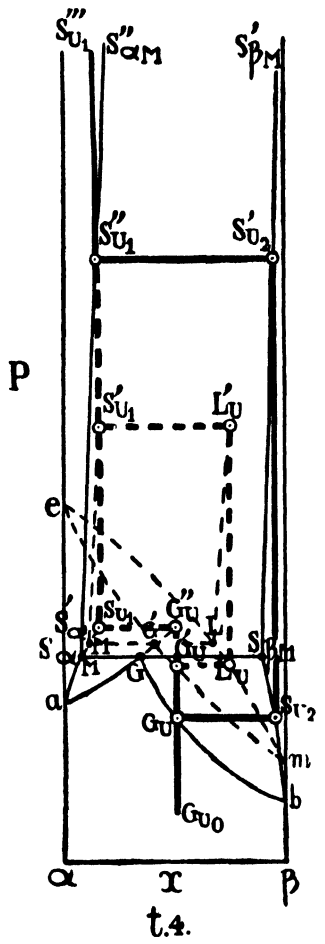


FIG. 28.

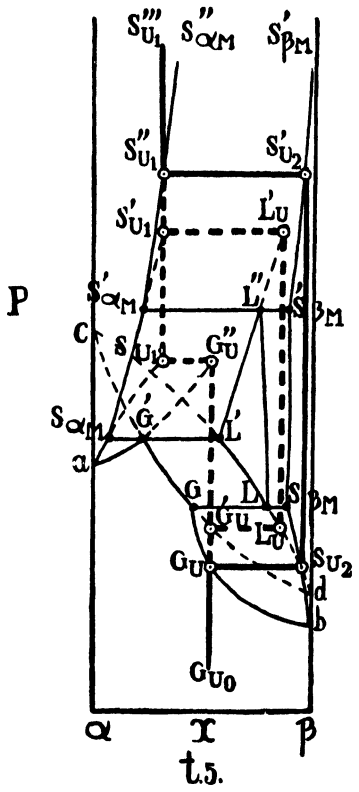


FIG. 29.

of the pseudo-system shows, therefore, amongst other things, a region for the stable co-existence of liquid, L L′, and vapour, G G′; of S_α-mixed crystals, $S_{\alpha_M} S_{\alpha_M}'$, and liquid, L″ L′, and finally of S_β-mixed crystals, $S_{\beta_M}' S_{\beta_M}$, and liquid, L″ L. The unary figure is again quite intelligible without further description. The higher the temperature selected, naturally, the higher will be the pressure at which the transition point

occurs. This could not be indicated in the diagrams, however, on account of their small dimensions, and for this reason these figures are very schematic in character.

The following P X sections, Figs. 30 and 31, refer to temperatures t_6 and t_7, which lie a little below and a little above the stable unary melting point D respectively.

These figures differ from one another inasmuch as, whilst in Fig. 30 the inner

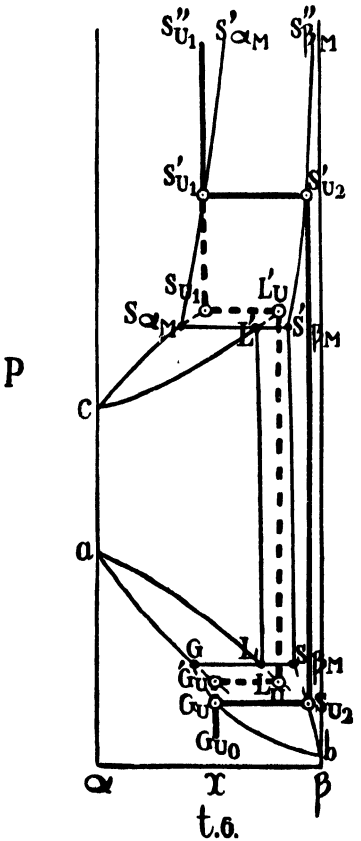


FIG. 30.

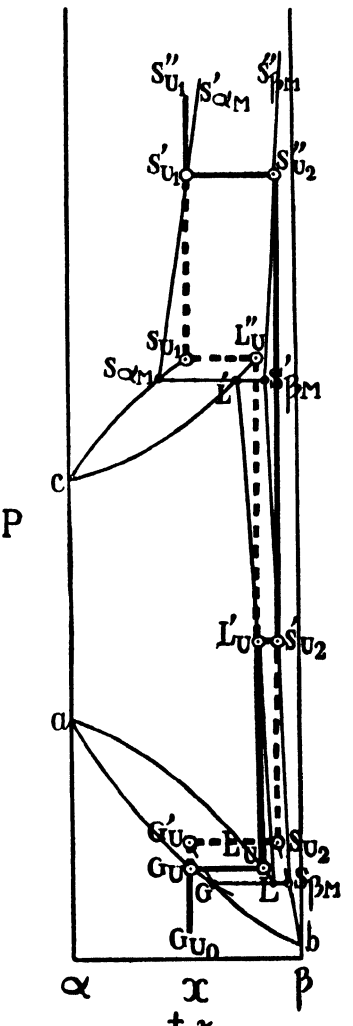


FIG. 31.

equilibrium line for the vapour intersects the vapour curve *b* G of the pseudo-binary system, *i.e.* the curve characterising the vapour which co-exists with the β-mixed crystal phase, in Fig. 31 the line for the inner vapour equilibrium meets the vapour line indicating the vapour

phase which co-exists in the pseudo-binary system with a series of liquids. At the intermediate temperature of the stable unary melting point, the intersection referred to takes place exactly at the point G, which represents the vapour which co-exists with the liquid L and the mixed crystal phase S_{β_M}; so that at this temperature these three phases will also co-exist in the unary system, which simply means that *this temperature represents the stable unary melting point.*

If the system is now considered at the temperature t_8, which lies below the critical temperature of the pseudo-components, Fig. 32 is obtained, in which the course of the curve at the critical temperature t_9

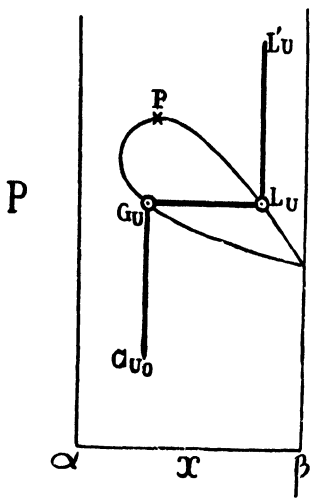


FIG. 32.

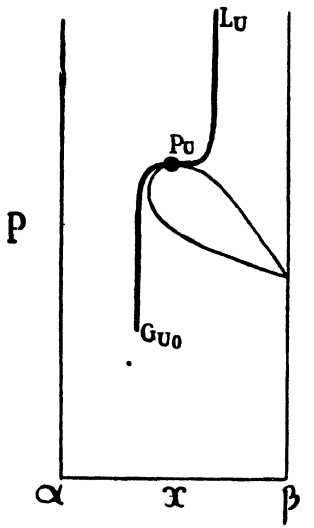


FIG. 33.

may already be recognised. At this temperature, that is to say, the points G_u and L_u, representing the co-existing vapour and liquid phases, coincide at the critical point P, as is shown in Fig. 33, which means that at this point vapour and liquid pass without discontinuity the one into the other.

This section shows a point of inflexion in the line representing inner equilibrium in the fluid[1] phase at which the tangent is horizontal, and which is therefore characterised by the expressions :—

$$\frac{dp}{dx} = 0 \text{ and } \frac{d^2p}{dx^2} = 0.$$

[1] The term fluid phase is used here, because at this point the vapour and the liquid phases in the stable region pass into one another without discontinuity.

9. (TX_P) Sections of the Space Model with Eutectic Lines.

In 3 several T X diagrams have already been deduced by means of the ζx lines for a constant pressure above that corresponding to the two three-phase lines S + L + G in the pseudo-binary system.

Naturally lower pressures could also have been considered, but the derivation of the T X figures would then have been less simple.

Now that the P T projection and the P X sections of the space figure have been discussed, however, the T X sections with the T X

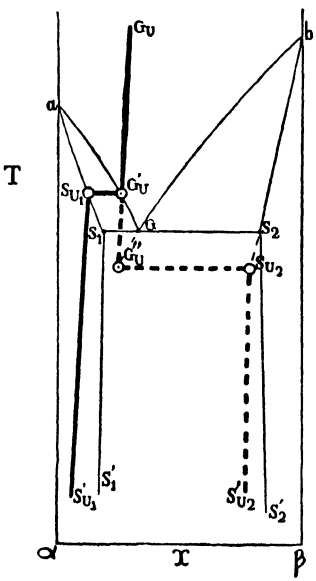


FIG. 34.

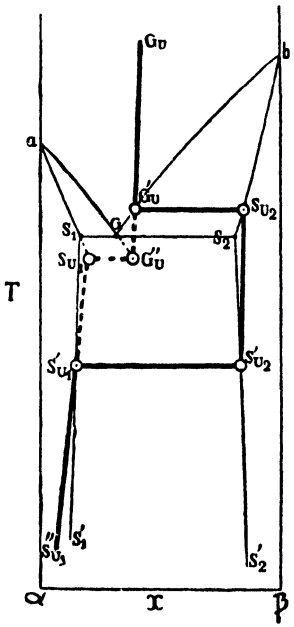


FIG. 35.

diagrams of the unary system situated therein may easily be constructed for any arbitrary pressure.

In drawing the inner equilibrium lines it is assumed that the change $\alpha \rightarrow \beta$ is an endothermic one and that the total heat effect in the condensed phase, including the heats of mixture, in this transformation remains endothermic. According to the formula

$$\frac{d \ln k}{dT} = -\frac{q^*}{RT^2}$$

* q is the decrease of energy per gram-molecule, or the thermo-chemical heat, when the transformation takes place in an infinitely large quantity of the homogeneous phase.

since q is negative, at higher temperatures all the inner equilibrium lines tend towards the β side. These lines will be considered more closely in Chapter II.

The pressures considered here are indicated in the P T projection. At the pressure p_1 the T X diagram shown in Fig. 34 is obtained, which is quite analogous to the melting diagram for higher pressures; yet instead of a liquid and a gaseous phase only a solid and a gaseous phase appear. This is also the case at the pressure p_2, to which Fig. 35

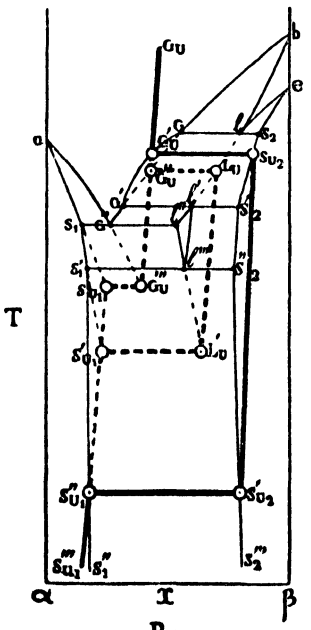


FIG. 36.

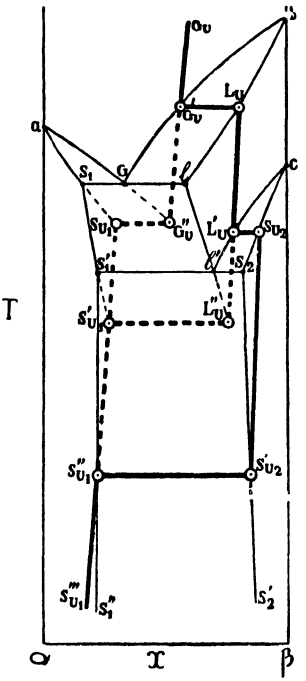


FIG. 37.

refers. The difference between these two diagrams lies in the existence of monotropy at the pressure p_1, whilst at the higher pressure p_2 enantiotropy appears. This comes about because at the pressure p_1 the inner equilibrium line for the gaseous phase intersects the vapour line a G, whilst at the pressure p_2 it cuts the vapour line b G.

At the pressure p_3 equilibria containing liquid appear at higher temperatures in accordance with Fig. 36. In the unary system, however, this is only true for metastable states.

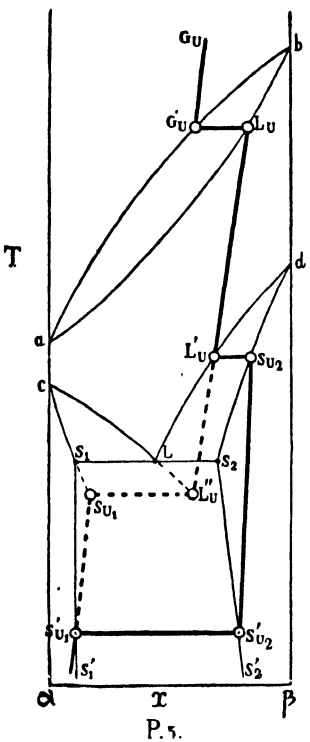
At the higher pressure p_4, Fig. 37, however, stable liquid phases also appear in the unary system, for this pressure lies above that corresponding to the stable unary triple point solid—liquid—vapour.

The T X section for the pressure p_5 has the familiar form and is shown in Fig. 38. At the critical pressure of the unary system this peculiar phenomenon again appears: the inner equilibrium line relating to the liquid phase has a point of inflexion at the critical temperature at which the tangent is horizontal;[1] this is evident from Fig. 39. The critical point is therefore defined mathematically by the expressions

$$\frac{d\mathrm{T}}{dx} = 0 \text{ and } \frac{d^2\mathrm{T}}{dx^2} = 0.$$

The T X figure corresponding to the pressure p_6 need not be given here.

When, contrary to the assumption here made, enantiotropy does not occur under the vapour pressure of the system, but monotropy, it is possible that enantiotropy may appear at higher pressures.



P. 5.

FIG. 38.

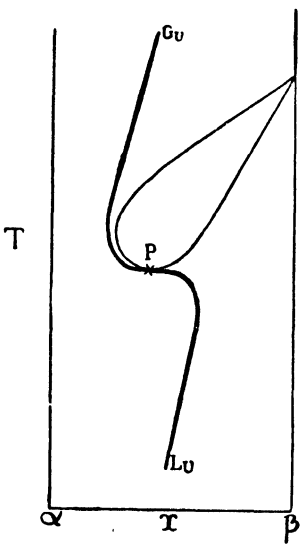


FIG. 39.

The connection between the pseudo-binary and the unary systems is, however, so easy to trace that this case will not be examined more closely here. It is sufficient to show how the change from monotropy under the vapour pressure to enantiotropy under higher pressures is expressed in the P T projection of the unary system when the PT projection of the pseudo-system is also considered. For this purpose

[1] It is here assumed that the critical point K_2 is situated at a higher pressure than K_1.

only the most essential portions of the complete projection need be reproduced (see Fig. 40).

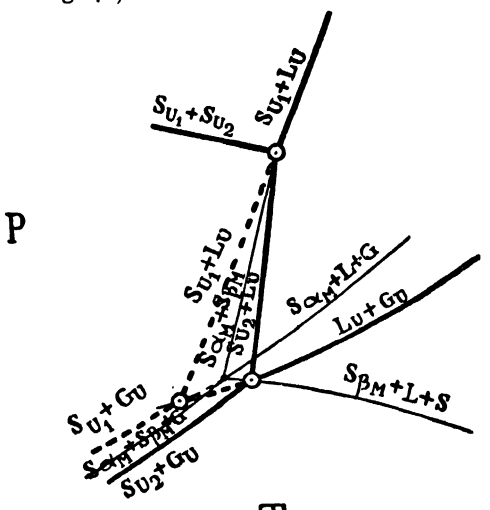


FIG. 40.

10. The *PX* Projection of the *PTX* Space Model of the Pseudo-binary and the Unary Systems, when the Second Component is a Polymer of the First.[1]

If it is now further imagined that the unary system possesses a transition point under the vapour pressure, the P T projection (Fig. 41) is obtained, which is immediately intelligible.

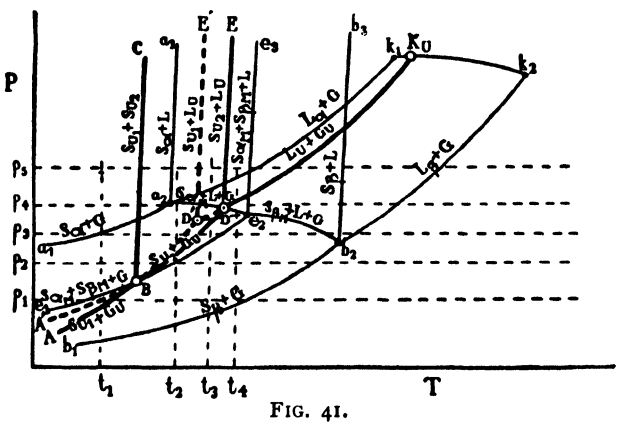


FIG. 41.

[1] The reason for the non-appearance of a eutectic fusion line in this case will be explained in Chapter III.

11. $(PX)_T$ Sections of the Space Diagram.

It has been assumed that the second component is a polymer of the first, and consequently the position of the inner equilibrium lines in the P X section will be determined by the fact that, in accordance with the equation :—

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

the inner equilibrium in the gaseous phase is displaced by increase of pressure towards the side of the polymer. The direction of the line relating to the inner equilibrium in the liquid, and also in the solid phase, will depend on whether the total molecular volume decreases or increases with the dissociation of the

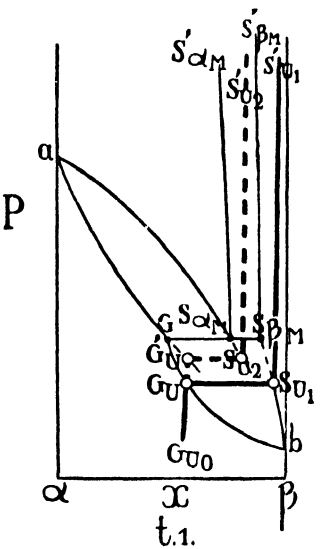


FIG. 42.

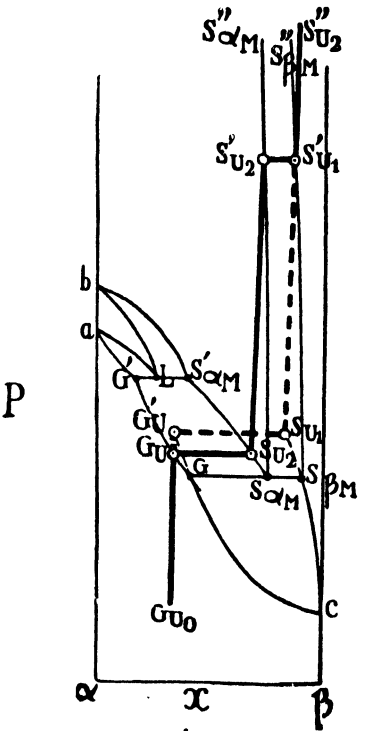


FIG. 43.

polymer a_n into na. As a rule, however, it may be assumed that the molecular volume decreases for the reaction

$$na \rightarrow a_n$$

and that therefore

$$\Delta v > 0.$$

In this case the lines for the inner equilibria in the liquid and the

solid phases will be displaced by increase of pressure towards the side of the polymer, and the following P X figures have been drawn in accordance with this circumstance. It must not be overlooked, however, that in the case of water, as van Laar[1] has shown, the double molecule H_4O_2 appears to possess a greater molecular volume than two molecules H_2O, so that for this substance the lines relating to the inner

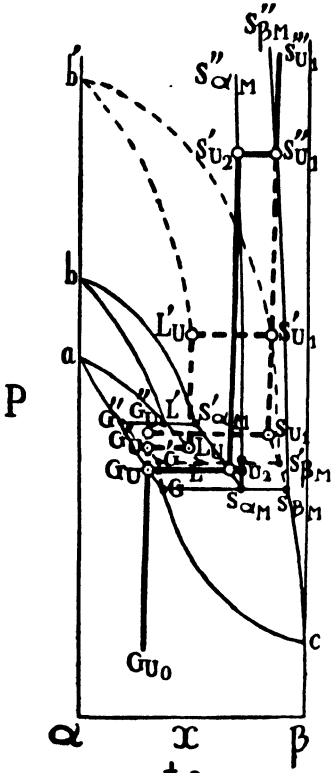


FIG. 44.

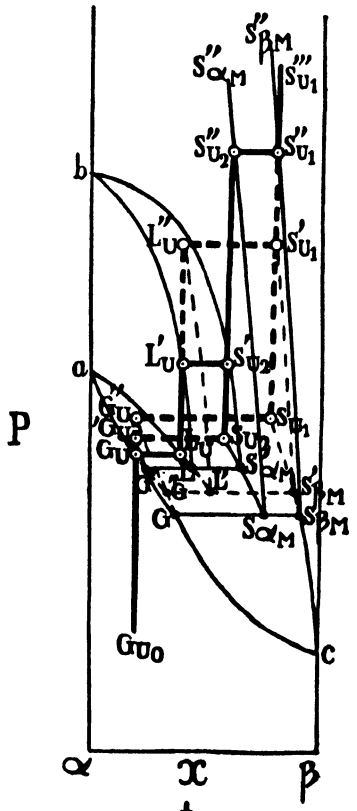


FIG. 45.

equilibria in the liquid and solid phases are displaced by increase of pressure towards the side of the simple pseudo-component H_2O.

At a temperature t_1, below the transition point B under the vapour pressure, the P X section has the form shown in Fig. 42.

The unary system at this constant temperature exhibits the phenomenon of *monotropy* when the pressure is increased. The solid phase S_{u_1} is the stable modification under the vapour pressure, and S_{u_2} is the

[1] *Archives Teyler*, Serie II., T. XI. Troisième, partie 1 (1908).

metastable modification. At a temperature above that of the point B, *e.g.* at t_2, increase of pressure is accompanied by the appearance of enantiotropy. This is illustrated in Fig. 43.

Under the vapour pressure of the system, S_{u_2} is now the stable form and S_{u_1} is metastable. At higher pressures, however, this relationship is reversed, and at a certain definite pressure, the *transition pressure*, both modifications exist in equilibrium with each other. This equilibrium is indicated by $S_{u_2}' S_{u_1}'$.

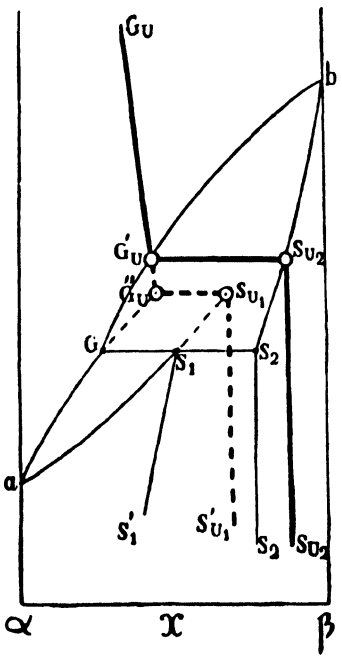


FIG. 46.

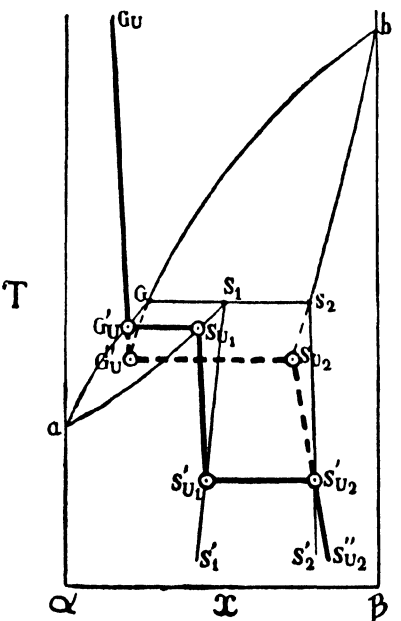


FIG. 47.

At the temperature t_3, which lies above the metastable triple point D′ and below the stable triple point D, all the main features still remain the same; but if it is desired to show the metastable inner equilibria of the unary figure, the diagrams will be less simple; still by going into the matter somewhat more deeply the connections become considerably clearer.

Thus, in Fig. 44, as regards the unary system, besides the stable equilibrium $S_{u_2} + G_u$, and the transition equilibrium $S_{u_2}' + S_{u_1}''$, three metastable equilibria occur; namely

$$G_u' + L_u, \quad G_u'' + S_{u_1} \text{ and } L_u' S_{u_1}'.$$

At a temperature t_4, situated above the stable triple point D, there

appear in the unary system, as is evident from Fig. 45, starting from low pressures, first the stable unary condensation equilibrium $G_u + L_u$, then the metastable unary sublimation equilibrium for S_{u_2}, *viz.* $(G_u' + S_{u_2})$, followed by that for S_{u_1}, $(G_u'' + S_{u_1})$, then the stable melting equilibrium of S_{u_2}, $(S_{u_2}' + L_u')$, and at a higher pressure the metastable melting equilibrium for S_{u_1}, and finally at a still higher pressure the unary transition equilibrium $(S_{u_2}'' + S_{u_1}'')$.

12. $(T\,X)_P$ Sections of the Space Model, without Eutectic Lines.

The $(T\,X)_P$ sections of this space model in which no eutectic appears naturally differ from those which contain a eutectic, such as have

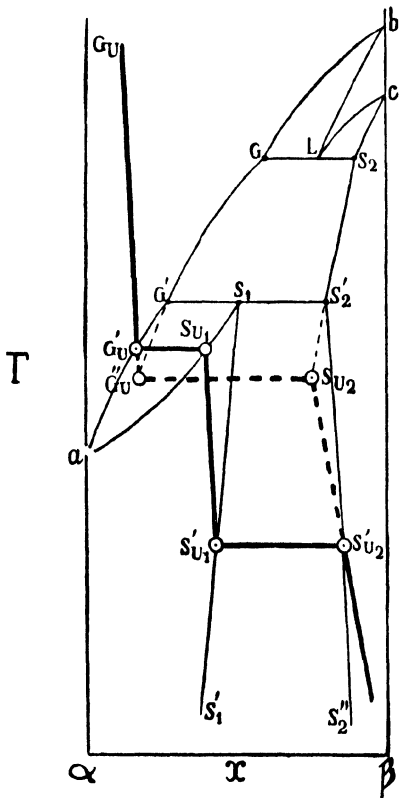


FIG. 48.

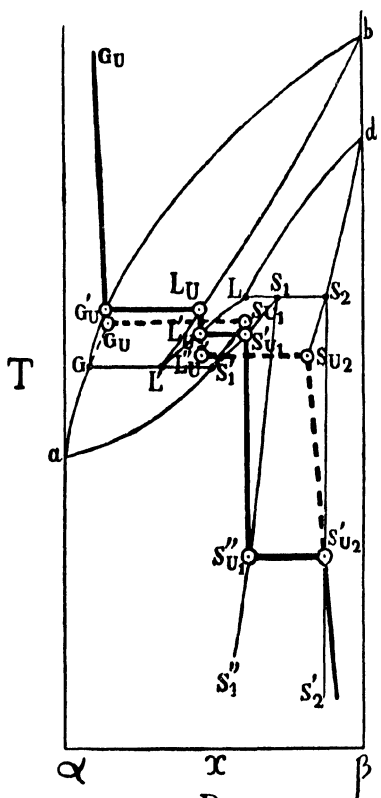


FIG. 49.

just been discussed. Taken in conjunction with the foregoing considerations, however, these (T X) sections may be readily understood. Figs. 46, 47, 48, 49 and 50 represent these T X sections for the pressures p_1, p_2, p_3, p_4, and p_5 respectively.

It should be particularly noticed here that the inner equilibrium in the gaseous phase is displaced by increase of temperature, in accordance with the formula

$$\frac{d \ln k}{dT} = - \frac{q}{RT^2},$$

towards the side of the simple pseudo-component, if the second component is a polymer of the first and the transformation $n\alpha \rightarrow \alpha_n$ is exothermic, and that as a rule the appearance of a transition point is conditioned by the fact that at low pressures the inner equilibrium line for the gaseous phase intersects the vapour line belonging to the β-mixed crystals, as shown in Fig. 46, whilst at a higher pressure, on the other hand, it intersects the vapour line appertaining to the α-mixed crystals, as in Fig. 47.[1] As a necessary consequence of this, Fig. 50 is finally obtained for the pressure p_5, in which the line for the inner equilibrium in the liquid phase cuts the melting line of the α-mixed crystals and not that for β-mixed crystals.

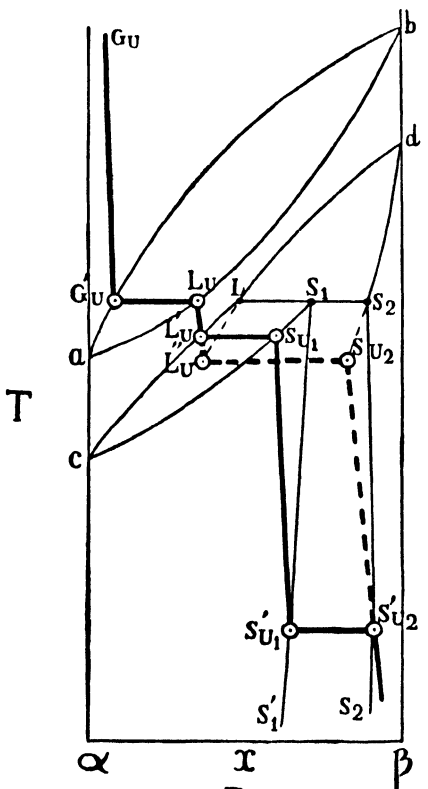


FIG. 50.

On the other hand, if the phenomenon of monotropy under the vapour pressure of the system occurs, at low pressures the line representing inner equilibrium in the vapour may intersect the vapour curves of both the α- and β-mixed crystals.

At higher pressures the same consideration holds good for the inner equilibria in the liquid; for this curve can then meet the melting curves for both β- and α-mixed crystals.

[1] It must be emphasised here that in this case pressure exerts an influence which is opposed to the temperature influence, and that in particular cases the pressure influence predominates. When this occurs the inner equilibrium in the vapour which co-exists with solid is not displaced by increase of temperature in the direction of the simple pseudo-component, but towards the polymeric pseudo-component. This case will be more fully considered in Chapter II.

13. Another Position in the Pseudo-binary System for the *P T* Figure of the Unary System.

It is clear that the vapour-pressure line of the stable unary solid phase need not intersect the line $S_{\alpha_M} + S_{\beta_M} + G$ of the pseudo-binary system, and that no transition point will then appear. This case

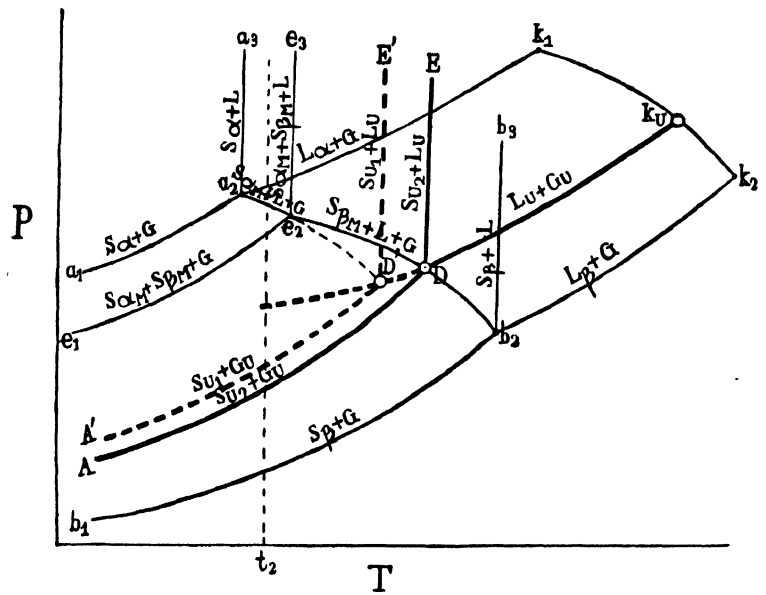


FIG. 51.

has been illustrated in Fig. 51, because later a PX section will have to be considered at the temperature t_2, which is indicated in this diagram.

14. The Pseudo-system Contains a Compound.

It may be pointed out here that the pseudo-components may form a compound. In this case a melting line for the compound will appear in the pseudo-binary TX figure, the maximum point of which may lie either in the stable or in the metastable region.

Both these cases are considered in Figs. 52 and 53, and indeed in these pseudo-binary figures such a position has been chosen for the unary system that two transition equilibria appear; namely $S_1' \rightleftarrows S_2'$ and $S_2'' \rightleftarrows S_3'$, where S_2' and S_2'' are mixed crystals in inner

equilibrium, the compositions of which differ but slightly from the composition of the compound, whilst the unary solid phases S_1' and S_3' lie nearer to the β and α sides respectively.

It should be emphasised that this representation only permits of the total composition being shown. If the compound dissociates both

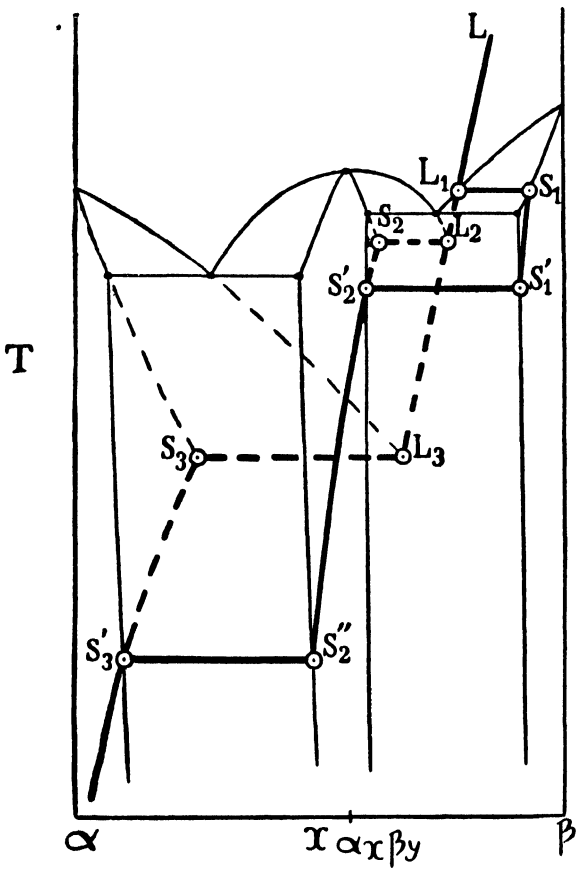


FIG. 52.

in the liquid and in the solid state, as is here assumed, and if it is desired to indicate the concentrations of the different constituents in the various phases, then the ternary representation of the pseudo-system must be undertaken and the dissociation surfaces for the liquid and solid mixtures must be drawn. The above deductions are, however, sufficient for our purpose.

A more important circumstance here is that the last diagram, Fig. 53, is also obtained, when the series of mixtures of α and β is twice

interrupted. Naturally the middle melting line does not then relate

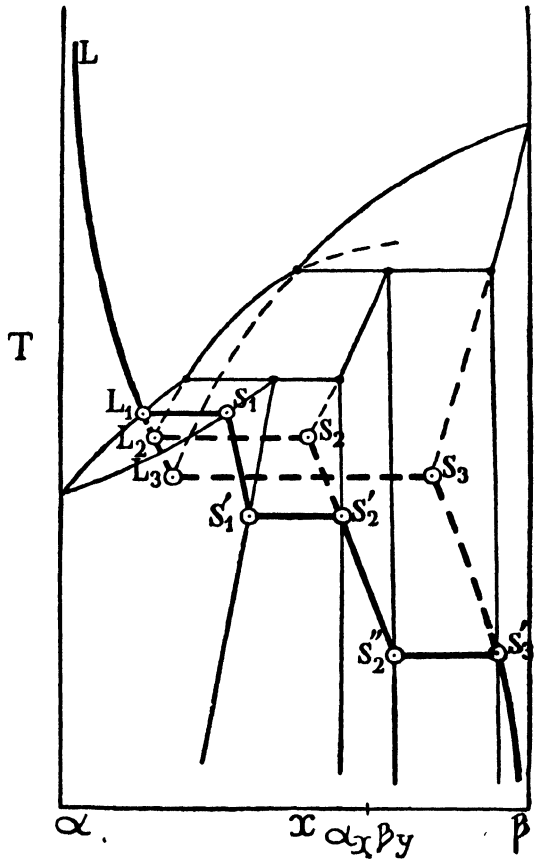


FIG. 53.

to a compound, but to the intermediate portion of the discontinuous series of mixed crystals.

CHAPTER II

A More Detailed Consideration of the Position of the Inner Equilibrium Lines in Gaseous and Condensed Phases

1. The $(PX)_T$ Lines.

The position of the inner equilibria in dilute gaseous phases may easily be indicated by applying the laws which hold good for equilibria in dilute solutions. The composition of the gaseous phase may then be found by means of the equilibrium constant, which depends, when concentrations are expressed in molar fractions, not only on the temperature, but also on the pressure. The relation deduced by Gibbs thermodynamically may be written in the following form :—

$$K_x = AT^{\Sigma\nu} \cdot e^{\frac{E_1 - E_2}{RT}} P^{-\Sigma\nu} \quad . \quad . \quad . \quad (1)$$

which becomes for constant temperature

$$(K_x)_T = \Lambda' P^{-\Sigma\nu} \quad . \quad . \quad . \quad . \quad (2)$$

This last determinative equation for the displacement of the equilibrium by pressure also follows directly from the application of the Law of Mass Action, and this method of deduction brings out clearly the connection between the quantities K_c or K_p and K_x.

If the concentrations of the reacting components of the equilibrium

$$\nu_1 A_1 + \nu_2 A_2 + \ldots \rightleftarrows \nu_1' A_1' + \nu_2' A_2' + \ldots$$

are expressed in mols. per litre, the following equation is obtained for the equilibrium constant :—

$$K_c = \frac{C_{A_1'}^{\nu_1'} \cdot C_{A_2'}^{\nu_2'} \ldots}{C_{A_1}^{\nu_1} \cdot C_{A_2}^{\nu_2} \ldots} \quad . \quad . \quad . \quad . \quad (3)$$

This constant K_c is independent of the pressure. When the partial pressures are taken as a measure of the concentrations this expression results :—

$$K_p = \frac{p_{A_1'}^{\nu_1'} \cdot p_{A_2'}^{\nu_2'} \ldots}{p_{A_1}^{\nu_1} \cdot p_{A_2}^{\nu_2} \ldots} = K_c(RT)^{\Sigma\nu} \quad . \quad . \quad . \quad (4)$$

since

$$p = CRT,$$

consequently

$$\Sigma\nu \ln p = \Sigma\nu \ln C + \Sigma\nu \ln RT$$

or

$$\ln K_p = \ln K_c + \ln RT^{\Sigma\nu}.$$

This quantity K_p is also independent of the pressure.

If, however, the partial pressure is expressed as the product of the total pressure and the molar fraction, we get

$$K_p = \frac{(PX_{A_1'})^{\nu_1'} \cdot (PX_{A_2'})^{\nu_2'} \ldots}{(PX_{A_1})^{\nu_1} \cdot (PX_{A_2})^{\nu_2} \ldots} \quad . \quad . \quad . \quad (5)$$

and since

$$K_x = \frac{(X_{A_1'})^{\nu_1'} \cdot (X_{A_2'})^{\nu_2'} \ldots}{(X_{A_1})^{\nu_1} \cdot (X_{A_2})^{\nu_2} \ldots} \quad . \quad . \quad . \quad . \quad (6)$$

therefore

$$K_x = K_p P^{-\Sigma\nu}. \quad . \quad . \quad . \quad . \quad (7)$$

This formula is identical with (2), and it shows that K_x depends on the pressure.

Moreover it follows from this expression for K_x that the displacement of the equilibrium depends exclusively on the change in the number of molecules.

So long as the Gas Laws are valid, equilibria between isomers ($\Sigma\nu = 0$) are uninfluenced by pressure. If, however, the second molecular species is a polymer of the first, the inner equilibrium

$$na \rightleftarrows a_n$$

will depend on the pressure, and the greater n is the greater the influence of pressure will be. If equation (5) is now applied, the total number of molecules of a_n being represented by X and of a by $1 - X$, the following equation is obtained:—

$$K_p = \frac{PX}{\{P(1-X)\}^n}$$

or

$$K_p = \frac{X}{P^{n-1}(1-X)^n} \quad . \quad . \quad . \quad . \quad (8)$$

if now

$$n > 1$$

then for

$$P = 0, \quad X = 0,$$

i.e. in any dissociation equilibrium, the dissociation is complete at zero pressure. The inner equilibrium line therefore passes through the origin $X = 0$.

As P increases X also increases, and when $P = \infty$, $X = 1$. The

fact should not, however, be overlooked that when the values for P become too high the simple Gas Laws no longer hold good.

The form of the inner equilibrium line in the $(P\,X)_T$ figure is not, however, completely determined by these considerations, for there are several possibilities, two of which are shown in Figs. 54 and 55.

Bakhuis Roozeboom[1] gives Fig. 54 in his discussion of the equilibrium

$$\text{Acetaldehyde} \rightleftarrows \text{Paraldehyde},$$

and Aten,[2] considered that Fig. 55 represented a general type. These two curves have different coefficients of direction at the point

$$P = 0, \quad X = 0.$$

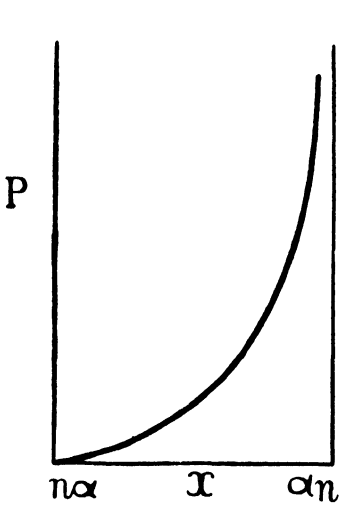


FIG. 54.

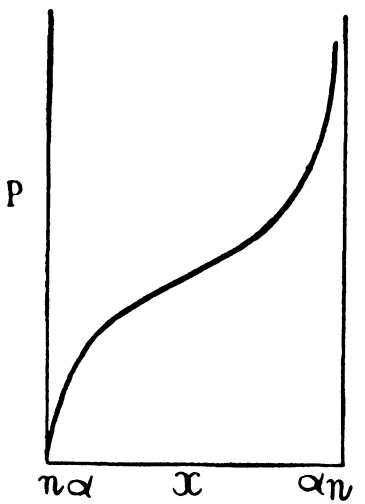


FIG. 55.

If the curve defined by the following equation is considered

$$\frac{X}{P^{n-1}(1-X)^n} = K_p$$

and if this expression is differentiated logarithmically, this equation results

$$\frac{1}{X} - \frac{n-1}{P}\frac{dP}{dX} + \frac{n}{1-X} = 0$$

or

$$\frac{dP}{dX} = \frac{1+(n-1)X}{n-1}\,\frac{P}{X(1-X)} \quad . \quad . \quad . \quad (9)$$

[1] *Versl. Kon. Akad. v. Wet.*, **11**, 283 (1902).
[2] *Die Het. Gleichgew.*, Bakhuis Roozeboom, II, **3**, p. 10.

so that

$$\operatorname{Lim}\left(\frac{dP}{dX}\right)_{X=0} = \frac{1}{n-1}\frac{P_0}{X_0}. \quad . \quad . \quad . \quad (10)$$

If now X_0 is eliminated by means of the equation

$$K_p = \frac{X_0}{P_0^{n-1}}$$

into which (8) transforms, when $X = O$, the following result is obtained:—

$$\operatorname{Lim}\left(\frac{dP}{dX}\right)_{X=0} = \frac{1}{n-1}\frac{P_0^{2-n}}{K_p}.$$

Three cases may now be distinguished:—

1. $1 < n < 2.$

In this case

$$\operatorname{Lim}\left(\frac{dP}{dX}\right)_{X=0} = o,$$

and the $(P\,X)_T$ line has a form corresponding with Fig. 54.

2. $n = 2.$

From equation (10) it then follows that

$$\operatorname{Lim}\left(\frac{dP}{dX}\right)_{X=0} = \frac{1}{K_p}$$

and the $(P\,X)_T$ line will follow the course indicated in Fig. 56.

3. $n > 2.$

For this case

$$\operatorname{Lim}\left(\frac{dP}{dX}\right)_{X=0} = \infty$$

and the $(P\,X)_T$ line must have the form illustrated in the accompanying Fig. 55.

The curve now follows a vertical course, not only at high pressures, but also when the pressure is very low, so that at some intermediate pressure a point of inflection must occur. In Fig. 54 this point lies in the origin; in Fig. 56, however, it has completely disappeared.

As a check on these conclusions the value of X at the point of inflection may be calculated as a function of n. To do this, equation (9) is again made the starting point, and by logarithmic differentiation the following is obtained:—

$$\frac{1}{\frac{dP}{dX}}\cdot\frac{d^2P}{dX^2} = \frac{n-1}{1+X(n-1)} - \frac{1}{X} + \frac{1}{1-X} + \frac{1}{P}\frac{dP}{dX}$$

$$= \frac{n-1}{1+X(n-1)} - \frac{1}{X} + \frac{1}{1-X} + \frac{1+X(n-1)}{n-1}\cdot\frac{1}{X(1-X)}.$$

If this expression is now equated to zero, after several transformations we get

$$2(n-1)^2X^2 + 4X(n-1) + (2-n) = 0$$

or $$X = -\frac{2 \pm \sqrt{2n}}{2(n-1)}.$$

A root greater than 0 will consequently be found if $\sqrt{2n} > 2$, *i.e.* if $n > 2$. For $n = 2$ the abscissæ at the point of inflection will be negative.

Consequently the curve suggested by Bakhuis Roozeboom will *not* appear in the unary system

Acetaldehyde $\rightleftarrows$ Paraldehyde

because in this case $n = 3$; it has previously been proved that the line indicated by Aten *only* holds good when $n > 2$.

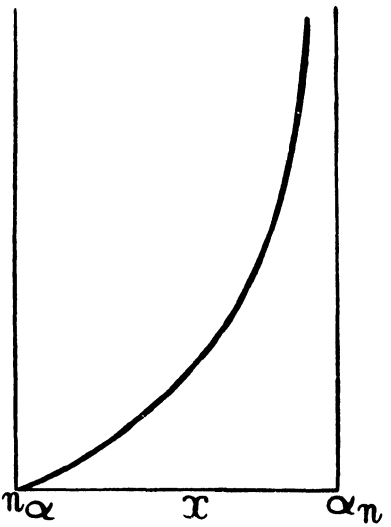


FIG. 56.

2. The $(TX)_P$ Lines.

The displacement of the homogeneous equilibrium with the temperature is determined by the energy change which, at constant volume, is measured as thermochemical heat.

By applying the equation

$$\left(\frac{d \ln K_x}{dT}\right)_P = \frac{E_1 - E_2}{RT^2} \quad . \quad . \quad . \quad . \quad (11)$$

to the reaction

$$na \rightleftarrows a_n + q \text{ cal.}$$

if it is considered that $E_1 - E_2 = q$ and that $K_x = \frac{X}{(1-X)^n}$, the following conclusions may be arrived at.

When q is positive, $\frac{dX}{dT}$ will be negative,

When $q = 0$, $\frac{dX}{dT} = 0$,

When q is negative $\frac{dX}{dT}$ will be positive.

Here again two cases may be distinguished.

1. $n = 1$, or, in other words, the two pseudo-components are isomers.

At the most the heat effect in this case can only be small, and consequently $\frac{dX}{dT}$ will be very small. The sign of this quantity naturally changes with that of q.

When $q = 0$ the T X line has a vertical tangent.

2. $n > 1$, *i. e.* the second pseudo-component is a polymer of the first.

If the polymer is *exothermic*, *dissociation* is increased by raising the temperature, *i.e.* $\frac{dX}{dT}$ will be negative.

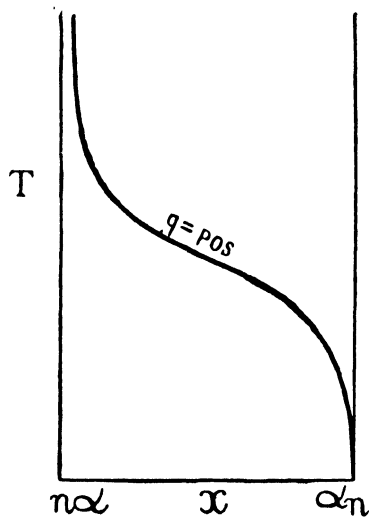


FIG. 57.

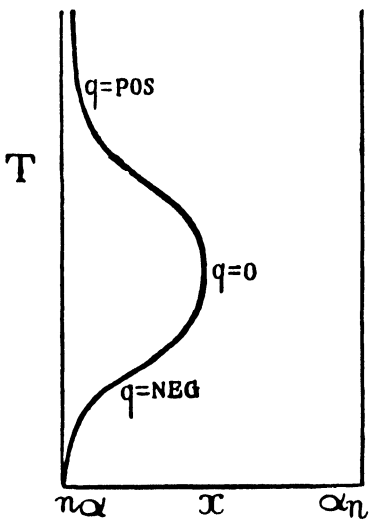


FIG. 58.

If, on the other hand, the polymer is *endothermic*, *polymerisation* increases with increase of temperature, *i.e.* $\frac{dX}{dT}$ is positive.

Since, however, as is well known, when dissociation occurs the number of degrees of freedom and hence the heat capacity increases, and consequently an $n\alpha$ molecule possesses a greater heat capacity than α_n, the polymerisation will become less endothermic as the temperature rises, and it may be conjectured that at still higher temperatures q will become equal to 0 and will finally become negative.

From (1) it follows that in the case of the existence of an exothermic polymer, when $T = 0°$, $K_x = \infty$, since then $\Sigma v = 1 - n$, and is therefore negative. Hence when $T = 0°$, $X = 1$.

If, on the other hand, the polymer is *endothermic*, when $T = 0°$, since the exponential factor predominates in the expression $\infty . e^{-\infty}$

$$K_x = 0 \text{ and } X = 0.$$

As $T \rightarrow \infty$, K_x and consequently x also approximate ever more closely to the value 0.

The two cases discussed here are illustrated in Figs. 57 and 58.

3. The *TX* and *PX* Projections of the Gaseous Phases of the Unary Equilibria $S \rightleftarrows G$ and $L \rightleftarrows G$.

Since $\frac{dP}{dT}$ is always positive both for the sublimation line and for the vapour pressure line of the liquid phase of a unary system, the P X and T X projections of the gaseous phase do not differ in any essential respect, and hence it will be sufficient to discuss the T X projection.

The possibility should, however, first be noticed of the polymer being so strongly endothermic that the heat of sublimation or of evaporation becomes negative and that, in consequence, the sign of $\frac{dP}{dT}$ changes. The projections under discussion then differ from one another in that the P X projections contain a pressure maximum.

The stable unary equilibria S + G and L + G are represented in Fig. 59, and the position of the vapour lines GG_1 and $G_1'G_1$ will now be considered for the region in which the Gas Laws are valid.

Along these two lines both the pressure and the temperature increase, hence in considering this matter both these influences must be borne in mind.

This double influence has already been discussed during the consideration of the $(PX)_T$ and the $(TX)_P$ figures. It was there noticed that when α and β are isomers change of pressure exerts no influence on the position of the inner equilibria in the gaseous phase, whilst, as a general rule, the temperature influence proved to be small. Hence, since X is here independent of the pressure, the form of the T X projection agrees with that of the $(TX)_P$ figure.

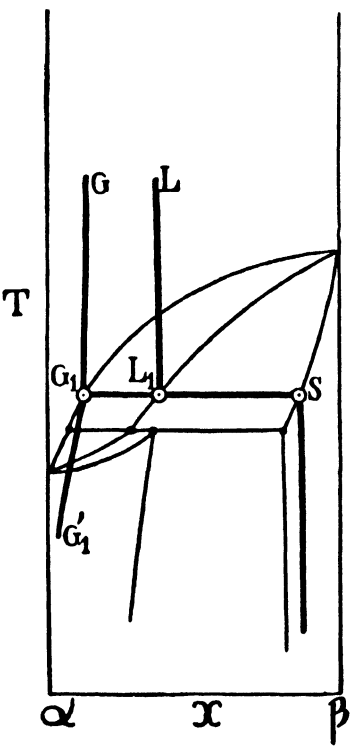


FIG. 59.

When $\beta = \alpha_n$, and is therefore a polymer of α, increase of pressure causes a displacement of the inner equilibrium towards the α_n side, whilst rise of temperature displaces it towards the α side if the polymer is exothermic, and towards the α_n side when it is endothermic. In the

latter case pressure and temperature act in the same direction, and $\frac{dX}{dT}$ is therefore certainly positive.

In the case of a polymer which is exothermic, however, the unary vapour line will run towards the right when the pressure influence predominates, but towards the left when the influence of temperature has the greater effect.

Before considering this case more closely the following predictions may already be made :—

1. The temperature influence will be promoted by high values for q.
2. The influence of pressure will be favoured by high n values.
3. At the point G_1, the vapour point of the unary melting equilibrium under the vapour pressure of the system, the vapour line $G_1'G_1$ will run more strongly towards the right than G_1G, since in the unary system

$$\frac{dP}{dT_{SG}} > \frac{dP}{dT_{LG}}.$$

This also follows from the $(PX)_T$ section of the pseudo-binary PTX figure, situated a little above or below the three-phase equilibrium at present under discussion.

The matter may now be discussed somewhat more fully.

From the equation

$$\left(\frac{d \ln K_X}{dT}\right) = \left(\frac{d \ln K_X}{dT}\right)_p + \left(\frac{d \ln K_X}{dp}\right)_T \cdot \frac{dp}{dT} \quad . \quad . \quad (12)$$

it follows, if for

$$\left(\frac{d \ln K_X}{dT}\right)_p \text{ and } \left(\frac{d \ln K_X}{dp}\right)_T$$

values obtained from (1) are substituted, that

$$\frac{d \ln K_X}{dT} = -\frac{E_1 - E_2}{RT^2} - \frac{\Sigma\nu}{p} \cdot \frac{dp}{dT}$$

or, since $\Sigma\nu = 1 - n$, and $E_1 - E_2 = q$

$$\frac{d \ln K_X}{dT} = \frac{-q}{RT^2} - \frac{1-n}{p} \cdot \frac{dp}{dT} \quad . \quad . \quad . \quad (13)$$

now according to Clapeyron's equation

$$\frac{1}{p} \frac{dp}{dT} = \frac{\lambda}{RT^2} \cdot \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where λ denotes the heat of sublimation or of vaporisation of the unary substance.

Since in (12) and (13) $\frac{dp}{dT}$ refers to the gaseous phase of the sublimation or evaporation equilibrium, the value for $\frac{dp}{dT}$ obtained from (14) may be substituted in (13).

Equation (15) then results

$$\frac{d \ln K_x}{dT} = - \frac{q - (n-1)\lambda}{RT^2} \quad . \quad . \quad . \quad (15)$$

From this equation it becomes clear that

$\frac{dX}{dT}$ is positive when $q - (n-1)\lambda < 0$,

$\frac{dX}{dT}$ is negative when $q - (n-1)\lambda > 0$

and finally $\frac{dX}{dT} = 0$, when $q = (n-1)\lambda$.

This condition holds good, therefore, for the temperature at which the product of the heat of sublimation or evaporation and the factor $(n-1)$ is equal to the heat of transformation of the pseudo-components in the gaseous state.

Now in order that $\frac{dX}{dT}$ may be negative, q must be large and λ small. But since these values are mutually connected and λ increases with q, it is desirable to consider the numerator of the second term of equation (15) rather more closely.

With this object λ may be resolved into the amount of heat λ_x which is necessary for the conversion of liquid of the composition x_L into gas of the same composition, and the chemical heat λ_i necessary to establish inner equilibrium in the vapour.

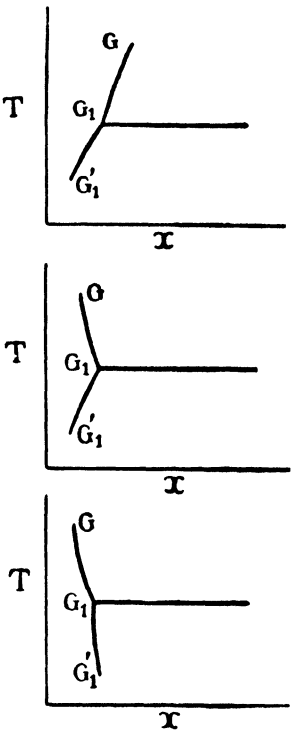


FIG. 60.

We may therefore write

$$\lambda_i = (X_L - X_G)q$$

and

$$q - (n-1)\lambda = q - (n-1)\{\lambda_x + (X_L - X_G)q\} \quad . \quad . \quad (16)$$

It is seen that the following conditions will increase the negative values of $\frac{dX}{dT}$.

1. Low values of $X_L - X_G$ or $X_S - X_G$.
2. A low value for n; and if equation (16) is written in the form

$$q - (n-1)\lambda = q\{1 - (X_L - X_G)(n-1)\} - (n-1)\lambda_x, \quad . \quad (17)$$

it is obvious that the negative value of $\frac{dX}{dT}$ is also increased by

3. High values of q, assuming that

$$(X_L - X_G)(n-1) < 1.$$

Summarising these results, the following possible positions illustrated in Fig. 60 are obtained for the two lines relating to inner equilibria in the vapour, which intersect at the point where the system melts under its own vapour pressure.

$q - (n-1)\lambda_{LG} < 0$ $q - (n-1)\lambda_{SG} < 0$	The pressure influence predominates for both lines.
$q - (n-1)\lambda_{LG} > 0$	The influence of temperature predominates.
$q - (n-1)\lambda_{SG} < 0$	Pressure exerts the greater influence.
$q - (n-1)\lambda_{LG} > 0$ $q - (n-1)\lambda_{SG} > 0$	In the case of both lines the influence of temperature predominates.

Naturally it is also possible for one or more extreme values for X to appear, since ultimately q may equal $(n-1)\lambda$.

4. The *T X* Projection for the Gaseous Phase in the Neighbourhood of the Unary Critical Point.

If the vapour line G_1G is produced to the critical point K (see Fig. 61), it is seen that, since at K the vapour line passes without

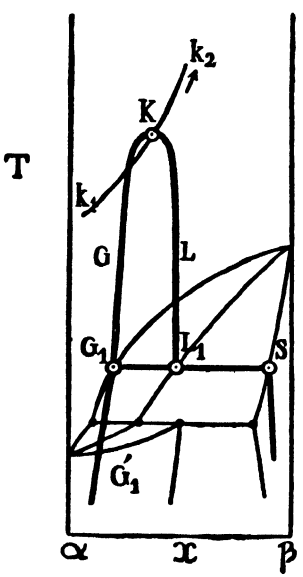


FIG. 61.

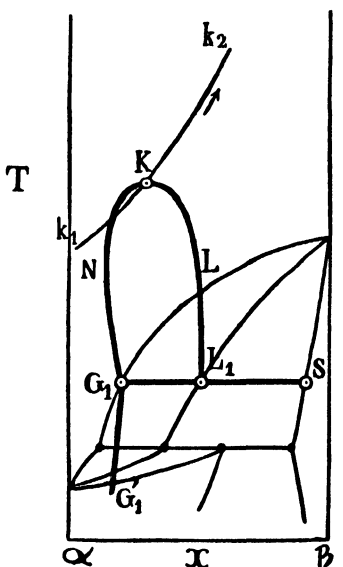


FIG. 62.

discontinuity into the liquid line, and the continuous curve so obtained must have a horizontal tangent at the point K, the vapour line in the neighbourhood of K must in all cases run towards the right, which was also its previous direction.

If, therefore, at lower temperatures the vapour line runs towards the

left, quite independently of the values of q and n, a point N must appear on the vapour line, the tangent at which is vertical; above this point the line will run towards the right, as is shown in Fig 62.

This position is realised in the cases of acetic acid and nitrogen tetroxide.

Examples of the type illustrated in Fig. 61, in which the vapour line tends towards the right at lower temperatures also, are provided by alcohol and water.

The marked change in the value of X in the neighbourhood of the critical point may be explained as follows:—

Let us write

$$\left(\frac{dX}{dT}\right)_{LG} = \left(\frac{dX}{dT}\right)_{v} + \left(\frac{dX}{dV}\right)_{T}\left(\frac{dV}{dT}\right)_{LG} \quad . \quad . \quad (18)$$

where X and v relate to the gaseous phase.

Now it is well known that on the bounding line at the critical point, $\left(\frac{dV}{dT}\right)_{LG}$, *i.e.* the rate at which the volume increases with the temperature $= -\infty$, it is equally well known that $\left(\frac{dX}{dV}\right)_{T}$ has at this point a finite negative value and that $\left(\frac{dX}{dT}\right)_{v}$ is finitely positive. Hence it may be concluded that at the critical point the expression $\left(\frac{dX}{dT}\right)_{LG}$ for the bounding vapour line $= \infty$.

With regard to the liquid line, it may be stated that as it approaches the critical point this line must incline strongly towards the left in consequence of the rapid decrease in density of the liquid phase. By applying equation (18) to the liquid line (X and V then refer to liquid) it may be shown that $\left(\frac{dV}{dT}\right)_{LG}$ at the critical point is equal to $+\infty$. If at lower temperatures the liquid curve should run to the right, which can only occur in the case of an endothermic polymer, the tangent at the point N will be vertical, as in Fig. 63, for, in contrast to what has been stated concerning the gaseous phase, the influence of pressure on the liquid phase is so small when compared with the temperature influence that it may be disregarded.

The PX projection shown in Fig. 64 applies to the case in which the polymer is still endothermic even at the critical temperature. This figure is to be found in the portion of Bakhuis Roozeboom's work, *Die Heterogenen Gleichgewichte usw.*, written by Aten, Vol. II., Part 3, p. 65, where the following remark occurs:—

"When by raising the temperature the number of complex molecules is increased, temperature and pressure exert an influence in the same direction. In the case of the unary vapour and the unary liquid a higher temperature, and consequently increased pressure, must inevitably result in an increase in the number of complex molecules. Both branches of the unary bounding curve incline therefore

towards the right. If this continues to be the case until the critical temperature is reached the unary bounding curve must have, at the unary critical point, a cusp at which point the tangent is horizontal, as in the curve $E_1E_2C_3C_2C_1$, Fig. 33." (This is here Fig. 64.)

This conclusion, however, is incorrect. From the increase in the temperature and the pressure, Aten thus infers that an increase occurs in the concentration of the complex molecules for the liquid branch of the bounding curve as the critical point is approached.

But the dissociation will be determined in the main by the molecular volume, and only in a secondary degree by the external pressure, and just in the neighbourhood of the critical point this is very evident, since along the liquid bounding line increase of pressure is associated with increase of volume.

Naturally X may also be considered, in accordance with the hypothesis, as a function of the

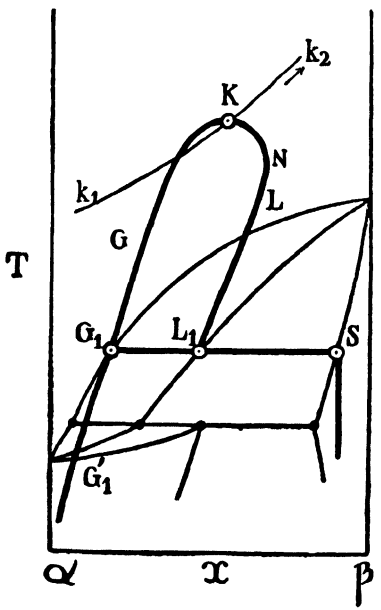


FIG. 63.

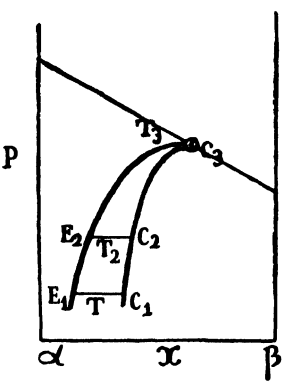


FIG. 64.

independent variables P and T, instead of as a function of V and T, as has been done here, then, however, the deduction must be made in the following way.

The following equation may be written:—

$$\left(\frac{dX}{dT}\right)_{LG} = \left(\frac{dX}{dT}\right)_{P} + \left(\frac{dX}{dP}\right)_{T}\left(\frac{dP}{dT}\right)_{LG} \quad . \quad . \quad . \quad (19)$$

In order that $\left(\frac{dX}{dT}\right)_{P}$ may be considered more closely, this quantity is split up in the following way:—

$$\left(\frac{dX}{dT}\right)_{p} = \left(\frac{dX}{dT}\right)_{v} + \left(\frac{dX}{dV}\right)_{T} \cdot \left(\frac{dV}{dT}\right)_{p}.$$

After substitution equation (20) is obtained.

$$\left(\frac{dX}{dT}\right)_{LG} = \left(\frac{dX}{dT}\right)_{v} + \left(\frac{dX}{dV}\right)_{T} \cdot \left(\frac{dV}{dT}\right)_{p} + \left(\frac{dX}{dP}\right)_{T} \left(\frac{dP}{dT}\right)_{LG} \quad . \quad (20)$$

Now as the critical point is approached along the bounding curve, $\left(\frac{dV}{dT}\right)_{P}$ increases to infinity, and this, combined with the fact that at the critical point $\left(\frac{dX}{dV}\right)_{T}$ is negative, leads to the conclusion that the second term on the right-hand side of the equation is equal to $-\infty$.

On the other hand, the differential quotient $\left(\frac{dX}{dP}\right)_{T}$ becomes $+\infty$ at the critical point, for the following reasons :—

1. $$\left(\frac{dX}{dP}\right)_{T} = \left(\frac{dX}{dV}\right)_{T} \cdot \left(\frac{dV}{dP}\right)_{T}.$$

2. At the critical point $\left(\frac{dV}{dP}\right)_{T} = -\infty$, while, as has already been stated, $\left(\frac{dX}{dV}\right)_{T}$ has there a finite negative value; hence the third term of the above equation must equal $+\infty$, for $\left(\frac{dP}{dT}\right)_{LG}$ has, at the critical point, a finite value.—The first term of the right-hand side of the equation is finitely positive at the critical point; denoting this value by a we get $\left(\frac{dX}{dT}\right)_{LG} = a - \infty + \infty$.

Hence the value of $\left(\frac{dX}{dT}\right)_{LG}$ at the critical point cannot be arrived at in this way.

In order to find the limiting value of $\left(\frac{dX}{dT}\right)_{LG}$ at the critical point in this way, the following further substitution must be made in equation (20):—

$$\left(\frac{dX}{dP}\right)_{T} = \left(\frac{dX}{dV}\right)_{T} \left(\frac{dV}{dP}\right)_{T}.$$

The following is then obtained :—

$$\left(\frac{dX}{dT}\right)_{LG} = \left(\frac{dX}{dT}\right)_{v} + \left(\frac{dX}{dV}\right)_{T} \left\{\left(\frac{dV}{dT}\right)_{p} + \left(\frac{dV}{dP}\right)_{T} \left(\frac{dP}{dT}\right)_{LG}\right\}$$

or

$$\left(\frac{dX}{dT}\right)_{LG} = \left(\frac{dX}{dT}\right)_{v} + \left(\frac{dX}{dV}\right)_{T} \left(\frac{dV}{dT}\right)_{LG}$$

and this is equation (18), from which the value of $\left(\frac{dX}{dT}\right)_{LG}$ at the critical point was obtained.

It is seen, therefore, that if these considerations are to be extended to the critical point, it is absolutely necessary to eliminate pressure as an independent variable.

Reference must not be omitted to the following possibility. When the pseudo-components differ very markedly from one another in volatility, the difference must be so great that the critical point of α lies far below the triple point of β, the unary system may contain, besides the stable critical point, two further metastable critical points, one above it and one below, but both lying below the stable unary melting point under the vapour pressure.

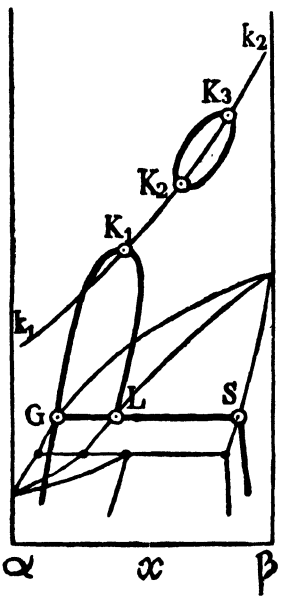


FIG. 65.

This case arises if the pseudo-system belongs to the ether-anthraquinone type,[1] *i.e.* if the plait point curve of the pseudo-binary system intersects the three-phase area for S + L + G.

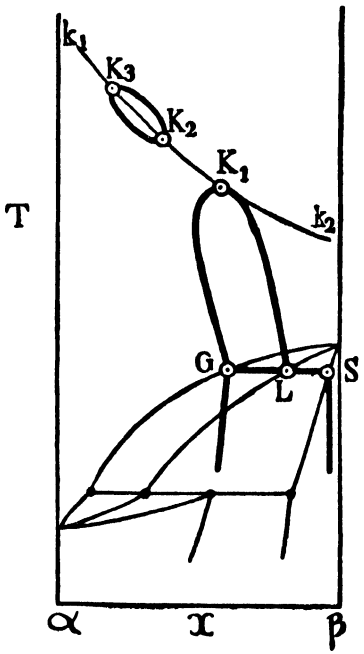
An example of this extremely interesting case is furnished by the cyanogen system, and in discussing cyanogen in the experimental portion this phenomenon will therefore be dealt with more fully. This arrangement is all the more suitable since there it is absolutely necessary to use these less simple systems to explain the relationships in question. Nevertheless, a simpler and therefore more easily represented consequence of this case must be briefly discussed here.

The pseudo-binary idea contains the possibility of the plait point curve for the pseudo-binary system intersecting the two-phase area for liquid and vapour twice. Three stable critical points would then appear in the unary system, two upper and one lower; this means that after the substance has reached its critical temperature and the fluid phase has been formed, at a higher temperature it will split up again into liquid and vapour, and finally at a still higher temperature one single phase will again be formed.

The TX projection may then have peculiar forms. Fig. 65 is improbable, inasmuch as increase of temperature displaces the position of the inner equilibrium in the liquid phase towards the β side, although β is a polymer of α; β would therefore have to be an endothermic polymer. This disadvantage is avoided in Fig. 66, yet this position too must be unconditionally rejected, for here β, which exhibits the higher triple point temperature, would have the lower critical temperature. In Fig. 67, on the other hand, all these difficulties

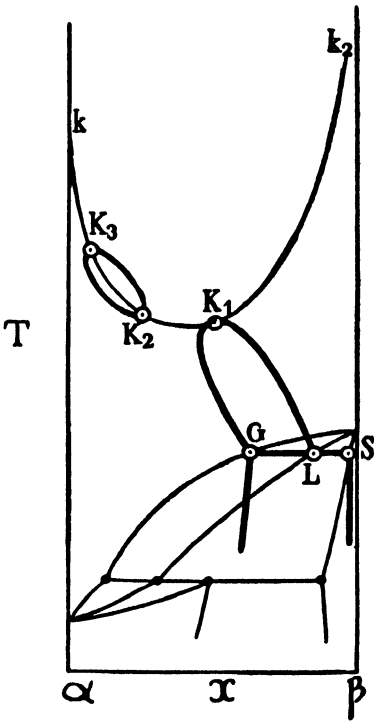
[1] *Zeitschr. f. physik. Chemie*, **51**, 193 (1905); **52**, 587 (1905).

disappear, for here it is supposed that the plait point curve has a minimum.



b

FIG. 66.



c

FIG. 67.

The critical points K_2 and K_3 lie to the left of the minimum, whilst K_1 may be found either to the left or to the right of it. In the first case, at all three critical temperatures, in the P X figure the unary

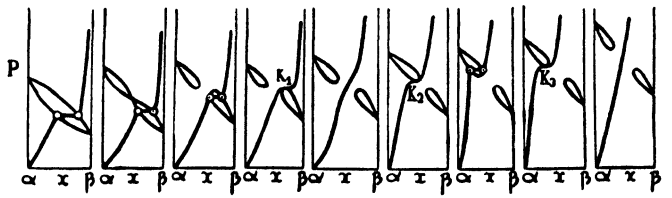


FIG. 68.

inner equilibrium line touches the part of the loop, representing L + G in the pseudo-binary system, which runs towards the left. In the second case, however, at the first critical temperature the

critical point lies on the portion of the loop, relating to the liquid vapour equilibrium in the pseudo-binary system, which runs towards the right.

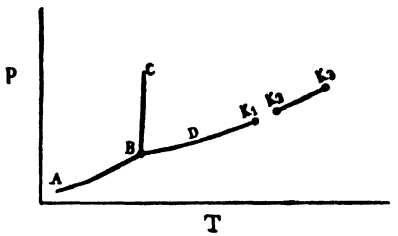


FIG. 69.

These relationships are illustrated by a series of P X diagrams, Fig. 68, which relate to temperatures extending over the whole interval between the three critical points.

The P T projection of the unary system is given in Fig. 69; it shows that the vapour pressure line consists of two portions, of which the first portion ends at the critical point K_1, whilst the second portion originates at the critical point K_2, and ends at the critical point K_3.

An example of the case under discussion has not yet been realised, and further, it will not be an easy matter to realise it, for it is extremely peculiar. We are now, however, prepared for a phenomenon, which formerly, *i.e.* before the establishment of this theory, would have caused the greatest perplexity.

5. Inner Equilibria in Condensed Phases.

The T X projection of the liquid line of the unary liquid-vapour equilibrium has already been mentioned in the course of the discussion

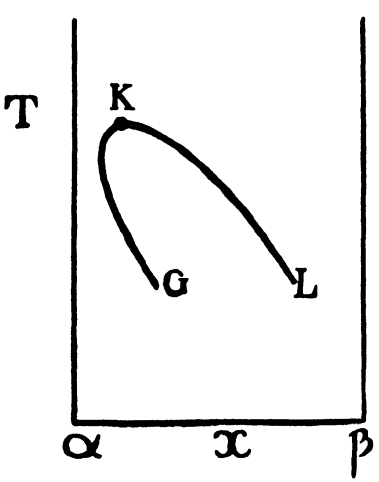


FIG. 70.

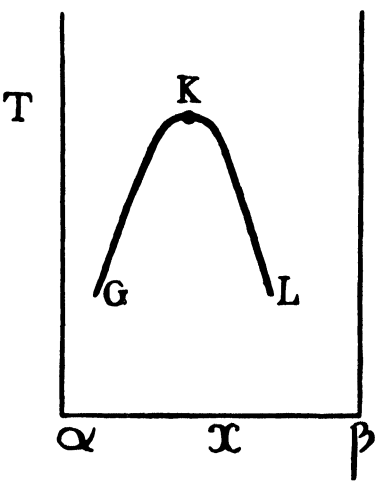


FIG. 71.

of the co-existing vapour line. The following possibilities were found for the liquid line:—

1. The liquid line runs towards the left until the critical temperature is reached (q is positive).

2. The liquid line runs towards the left, but before the critical point is reached a change of direction occurs (q is negative).

For the vapour line the following cases were distinguished:—

1. For positive values of q the vapour line may always run towards the right, or at lower temperatures it may run towards the left to begin with, bending back somewhere below the critical temperature (q is positive).

2. For negative values of q the vapour line runs continuously to the right.

By combining these possible forms for the vapour and liquid lines the types indicated in Figs. 70, 71 and 72 are obtained.

In agreement with these considerations, Figs. 70 and 71 are to be found in van der Waals-Kohnstamm's *Thermodynamics*, Vol. I, p. 173; for there it is assumed that q is positive. The formula

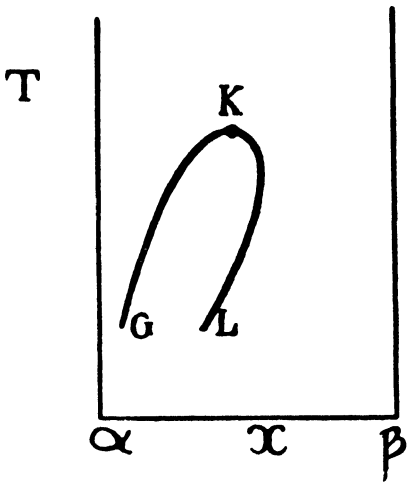


FIG. 72.

$$\frac{1+X}{X(1-X)}T\left(\frac{dX}{dT}\right)_{Lim} = -\frac{E}{R_2T} - \frac{T}{V-b}\cdot\left(\frac{dV}{dT}\right)_{Lim}$$

deduced on page 171 of the second volume yields our Fig. 72 when E is negative.

This is quite clear without further explanation, for at low values of T the first factor of the second term on the right-hand side of the equation is the predominating factor, so that $\left(\frac{dX}{dT}\right)_{Lim}$ is positive, whilst at higher temperature $\left(\frac{dV}{dT}\right)_{Lim}$ increases, to become infinity at the critical temperature. The other factor of the second term then predominates, its sign being positive for the liquid line and negative for the vapour line. On the liquid line, therefore, the sign of $\left(\frac{dX}{dT}\right)_{Lim}$ must change somewhere below the critical point.

6. The $(TX)_P$ Figures for Condensed Phases.

(a) *The pseudo-component β is a polymer of α.*

The position of the inner equilibrium line in the $(TX)_P$ figure is given by the formula

$$\left(\frac{d\ln K_x}{dT}\right)_P = -\frac{q}{RT^2}.$$

Now the heat effect of the transformation $\alpha \rightleftarrows \beta$ taking place in a mixed crystal phase may be resolved into

1. The quantity of heat absorbed when one molecule of an infinitely large amount of the mixed crystal phase is withdrawn. This is equal to $-q_\alpha$.

2. The quantity of heat developed in the transformation

$$\alpha \rightarrow \beta + q_R.$$

3. The quantity of heat set free by the mixture of one molecule of β with an infinitely large amount of the mixed crystal phase; $= q_\beta$.

The quantities q_α and q_β are, therefore, differential heats of mixture, whilst q_R denotes the heat of reaction. We may therefore write

$$q_{S_1} = -q_{\alpha_{S_1}} + q_R + q_{\beta_{S_1}} \quad . \quad . \quad . \quad . \quad (21)$$

In the case of polymers q_R is, as a rule, positive and much greater than the heats of mixture, so that q is also positive. The inner equilibrium line for the solid phase will therefore incline towards the left when the temperature is increased. This is also true for the case in which the condensed phase is a liquid. If now the neighbourhood of the transition point is considered and the question is asked, Which of the co-existing phases at the transition temperature will be the stable modification at higher temperatures? the answer can immediately be given, as a result of these considerations, that the stable modification will be the one whose formation is associated with an absorption of heat.

Let the phase rich in α be called S_1, the phase rich in β, S_2, and the quantity of heat set free by the conversion of S_1 into S_2, $q_{S_1S_2}$; it should be noted that the heat effect associated with this *heterogeneous* transformation may also be resolved.

For this purpose let us *first* imagine that so much α has been withdrawn from the mixed crystal phase S_1 that the composition of the phase corresponds with the point S_3, lying between S_1 and S_2. This point S_3 has been so chosen, that after in the *second* place the quantity of α so withdrawn has been converted into β, and *thirdly* this amount of β has been again added to the mixed crystal phase S_3, a mixed crystal phase of the composition S_2 results. The heat effects of these three processes will be designated by q_α', q_R', and q_β'. The last-mentioned quantity also includes the heat effect associated with the change of crystalline form when the two phases are not isomorphous.

The following can, therefore, be written for the heat of transformation $q_{S_1S_2}$:—

$$q_{S_1S_2} = -q_\alpha' + q_R' + q_\beta'.$$

The quantities q_α' and q_β' are not differential heats of mixture, as in equation (21), but *mean values* for the differential heat of mixture of α in phases whose compositions lie between S_1 and S_3, or of β in phases whose compositions lie between S_3 and S_2. This can be indicated in the following way:—

$$q_{S_1S_2} = -q^{\alpha'}{}_{\overline{S_1S_3}} + q_R' + q_\beta{}'_{\overline{S_3S_2}} \quad . \quad . \quad . \quad . \quad (22)$$

Finally, the course of the transformation $S_1 \rightarrow S_2$ may also be such that in the phase S_1 an infinitely small amount of α is converted into β, so that the composition of this phase is displaced to an infinitely small extent towards S_2. This process may be imagined to be repeated so often that the composition of the phase S_2 is reached.

In this manner $q_{S_1S_2}$ is obtained as a mean value of the heat of transformation in phases whose compositions lie between S_1 and S_2. Thus we write:—

$$q_{S_1S_2} = q_{\overline{S_1S_2}} \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Moreover the separate parts constituting the right-hand side of equation (21) may be imagined to be subdivided, as the result of which $q_{S_1S_2}$ appears as the sum of the heat of reaction q_R and two average values for the differential heats of mixture of α and β respectively, in phases the compositions of which lie between S_1 and S_2. Consequently,

$$q_{S_1S_2} = -q_\alpha{}'_{\overline{S_1S_2}} + q_R{}' + q_\beta{}'_{\overline{S_1S_2}} \quad . \quad . \quad . \quad (24)$$

If the pseudo-component β is a polymer of α, it is probable that on the right-hand sides of equations (22) and (24) the positive heat of transformation $q_R{}'$ predominates.

In this case, therefore, $q_{S_1S_2}$ is positive, *i.e.* the transformation $S_1 \rightarrow S_2$ takes place with evolution of heat, so that S_1 is the stable phase at higher temperatures, as is shown in Fig. 73. Since the resulting phase, the formation of which takes place with absorption of heat, lies to the left of the other, it may be called here "left-lying transition equilibrium."

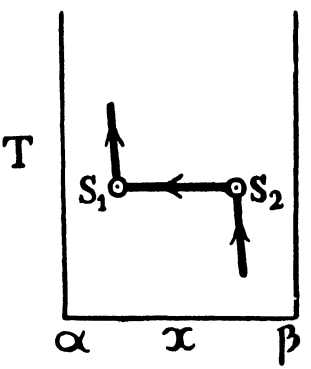


FIG. 73.

The conclusion has already been arrived at that the inner equilibrium line runs towards the left when the pseudo-components are polymers, and that consequently the TX figure for the transformation equilibrium and its neighbourhood has the form outlined in Fig. 73.

It is clear that these relative positions also hold for the metastable transformation equilibrium and for the metastable inner equilibrium lines, and consequently Aten's Fig. 68 in Bakhuis Roozeboom's *Die Heterogenen Gleichgewichte*, Vol. II, part 3, p. 130, is inaccurate.

(b) *The pseudo-components are isomers.*

When α and β are isomers, the heats of reaction in (21), (22) and (24) may be rather small; they will therefore not usually predominate.

In the first place, if the position of the inner equilibrium lines is considered, it is noticed that since the heats of mixture q_α and q_β in

equation (21) are dependent on the composition of the mixed crystal phase, the total heat of transformation in the solid phase may be different for phases of different compositions.

Thus for a given phase

$$q_R - q_\alpha + q_\beta \text{ may be } < 0$$

or

$$q_\alpha - q_\beta < q_R.$$

Further, it is known that the total heat effect of an inner equilibrium line, and hence $\left(\frac{dX}{dT}\right)$, may also have a different sign when the composition remains the same, though at a different temperature.

However, in this case also, the heat of reaction and the heat of mixture continue to vary in a regular manner with the temperature and the composition, so that repeated change of sign is very improbable.

(c) *A right-lying transition equilibrium combined with inner equilibrium lines which run towards the left.*

When the average total heat of transformation in phases situated between S_1 and S_2 is negative, and therefore $q_{\overline{S_1 S_2}} < 0$, whilst the

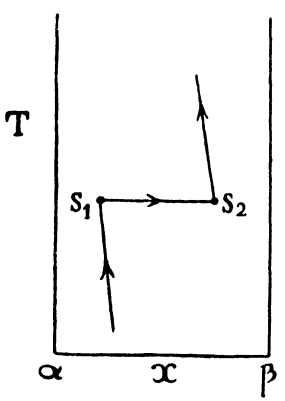


FIG. 74.

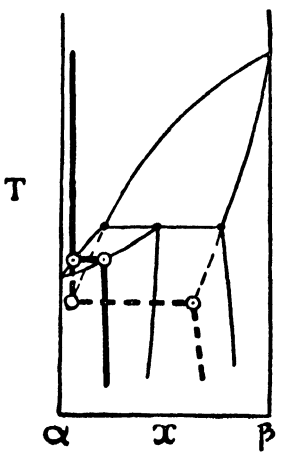


FIG. 75.

total heat in each of the phases S_1 and S_2 is positive, and therefore q_{S_1} is > 0 and $q_{S_2} > 0$, the position represented in Fig. 74 is obtained.

Since q_{S_1} and q_{S_2} are positive, while $q_{\overline{S_1 S_2}}$ is negative, it may be concluded that the total heat effect q between S_1 and S_2 passes at least twice through zero. The straight line $S_1 S_2$ therefore cuts the geometrical locus $q = 0$ at least twice, and in any case an even number of times between S_1 and S_2. It is seen, therefore, that with the

help of equation (23) an indication may be obtained from the position of the transformation equilibrium (right- or left-lying) regarding the existence of points in the neighbourhood of which q must = o, and conclusions may thus be drawn which could not result from a consideration of the inner equilibrium lines alone. Similarly it is obvious without further discussion that a T X figure, in which a line of constant temperature or constant composition can be drawn in such a way that the geometrical locus is intersected many times, is improbable, since q_s does not undergo a frequent change of sign in consequence of changes in temperature or composition, any more than the expression into which, according to (21), it may be resolved. It is clear that resolution of the total heat of transformation in accordance with (22) and (24) is only an

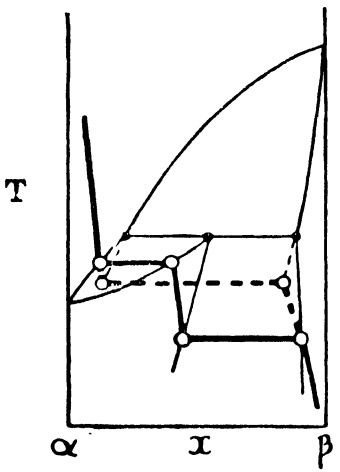


FIG. 76.

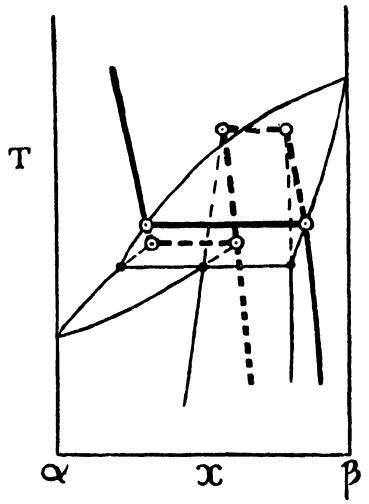


FIG. 77.

advantage when several of the resolved fragments are to be calculated, and another can be either experimentally determined, neglected or estimated.

This is possible in pseudo-systems in which the unary equilibrium can only be established with the aid of catalysts.

In the deduction of the various possible and complete T X figures the different possible positions of the inner equilibrium lines must naturally be combined with the possible forms of the T X sections. If the pseudo-components are isomeric none of the possible combinations is excluded. If, however, the heat of reaction preponderates, as in the case of polymerisation, for exclusively left-running equilibrium lines and left-lying transformation equilibria, and if the binary pseudo-figure is of simple form (only a disintegration region for the solid state) the three cases previously indicated are obtained, to which Figs. 75, 76 and 77 refer.

(d) *The form of the* $(PX)_T$ *figures for condensed phases.*

As has already been mentioned, the influence of pressure is given by Planck's formula

$$\left(\frac{d \ln K_X}{dP}\right)_T = -\frac{\Delta V}{RT} \quad . \quad . \quad . \quad . \quad (25)$$

Little is known of the differential increase of volume ΔV.

It can only be said that, as a rule, polymerisation is accompanied by decrease of volume, in which case the unary PX lines run towards the right; sometimes, however, polymerisation is associated with an increase of volume, as in the case of water, and then the unary PX lines run towards the left.

If the pseudo-components are isomers nothing can be said with regard to the sign of ΔV.

All that is known is, that for condensed phases ΔV will in general be small, so that for the unary lines $\left(\frac{dP}{dT}\right)_T$ will be very great.

It will only be possible to draw any conclusions from formulæ (11) and (25) regarding the form of the figures under discussion when an equation of state applicable to the solid state has been discovered.

(e) *The relation between strong and weak dissociation and the phenomena of enantiotropy and monotropy.*

The above considerations have shown that enantiotropy and monotropy may be explained perfectly logically from the same point of view.

On the other hand, Tammann [1] is of opinion that the monotropic forms of a substance stand in an entirely different relation to one another than the enantiotropic forms.

He speaks of two crystals of the same group as being monotropic, and calls two crystals of different groups enantiotropic, and in his opinion this assertion may be supported by an empirical principle put forward by him, which states that from normal liquids only members of a group which are similar to each other are formed, or, in other words, from normal liquids only monotropic forms separate, while abnormal liquids may yield enantiotropic forms.

Examination of Eötvös' Rule has shown that the product $\gamma(Mv)^{\frac{2}{3}}$, which is proportional to the molecular surface energy, is approximately a linear function of the temperature for different so-called normal liquids, and that it varies only slightly with the nature of the liquid.

For these liquids the temperature coefficient of the molecular surface energy

$$-\frac{d\gamma(Mv)^{\frac{2}{3}}}{dT}, \text{ is greater than } 2,$$

while for other liquids, the so-called abnormal liquids, the change of

[1] *Nach. K. Gesell. d. Wissenschaft Göttingen Math.-physik. Klasse*, 13 Mai, 1911, and 15 Juli, 1911.

$\gamma(Mv)^{\frac{2}{3}}$ increases with the temperature, and varies to a considerable extent with the nature of the liquid, as the following table shows.

Substance	$\frac{d\{\gamma(Mv)^{\frac{2}{3}}\}}{dT}$	$\frac{d^2\{\gamma(Mv)^{\frac{2}{3}}\}}{dT^2}$	
	So-called normal liquids		
Aniline	2·05	0	
Carbon tetrachloride	2·10	0	Monotropy
Methyl alcohol	2·12	0	,,
Carbon dioxide	2·22	0	Enantiotropy
Nitrobenzene	2·23	0	
Benzene	2·37	0	
Benzophenone	2·63	0	Monotropy
	Abnormal substances		
Water	0·88		Enantiotropy
Sulphur	1·51		,,
Phenol	1·80		,,
Formanilide	1·66		Monotropy
o-Cresol	1·93		Enantiotropy

In the second series of liquids the temperature coefficient of the molecular surface energy is less than 2, and moreover it increases with the temperature, *i.e.* at higher temperatures it approximates to the normal value.

Now it is quite true that as a rule so-called normal liquids deposit monotropic forms; abnormal liquids, on the other hand, often give rise to enantiotropic forms, and from this Tammann is of opinion that the conclusion must be drawn that monotropic and enantiotropic modifications are constituted essentially differently.

In the light of our considerations, however, the empirical principle previously mentioned must be interpreted in quite a different way.

In the first place, it must be emphasised that even at the present time surface tension measurements will not enable us to decide with certainty whether a liquid is quite normal. Eötvös' Rule is insufficient definitely to decide this question. The study of surface tension at different temperatures has made it clear that association is probably a general phenomenon.

Amongst the liquids so far investigated, however, there are a considerable number which appear to associate but slightly. Hence it may be stated that *experience shows that only those liquids which are slightly associated frequently deposit monotropic forms, whilst more strongly associated liquids often yield enantiotropic forms.*

This empirical principle can now be very simply explained on the basis of the following considerations. Let us suppose that β is a polymer of α, and that the pseudo-binary system has a eutectic; then, according to Fig. 22, the gaseous phase on the line ag contains a greater concentration of polymer than the co-existing solid phase on the line ad.

This is extremely improbable, and thus the figure must fail in the case of polymerisation. This difficulty is avoided, however, if the pseudo T X figure contains no eutectic, as in Fig. 23. Both the liquid and the solid phases then contain more of the polymeric substance than the co-existing gas phase, as might be expected. Whilst therefore in the case of isomerism the T X figures may belong to different types, when polymerisation occurs no eutectic will appear, and confirmation of this conclusion has already been found in various pseudo-binary systems.

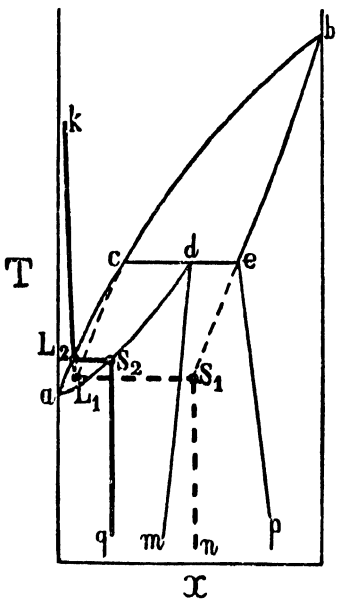


FIG. 78.

Thus the T X figures for the systems acetaldehyde—paraldehyde, paraldehyde—metaldehyde, acetaldehyde —metaldehyde have no eutectic,[1] nor does the system methyl sulphocyanide — its tri-polymer.[2]

On the basis of this result the empirical principle previously mentioned can now easily be explained. That is to say, if the accompanying T X diagram (Fig. 78) represents the pseudo-system, and if the liquid is only slightly associated, it is well known that the line relating to the inner equilibrium in the liquid phase lies very much to one side, and hence the line for the stable inner equilibrium in the solid state approximates to the nearest pseudo-component.

When association occurs to a less extent, the line $k\,L_2$ lies, in fact, close to the axis of the unassociated pseudo-component having the lower melting point.

Now it is evident that the intersection of the lines $S_2 q$ and $d\,m$ or $S_1 n$ and $e\,p$ has, in general, some special significance, so that on the basis of these considerations it may at once be assumed that the phenomenon of monotropy will occur more frequently than that of enantiotropy, and this is in fact the case.

If slightly and very slightly associated liquids are considered from this point of view, it is immediately seen that, in consequence of the extremely one-sided position of the line relating to inner equilibrium in the solid state, the chance of intersection taking place is reduced to a minimum, so that in the case of these substances monotropy exclusively may be expected as a general rule, and this is also in complete agreement with Tammann's general principle.

[1] *Zeitschr. f. physik. Chemie*, **77**, 269 (1911).
[2] Gillis, *Chem. Weekblad*, **15**, 48 (1918).

CHAPTER III

PSEUDO-TERNARY SYSTEMS AND SYSTEMS CONTAINING MORE THAN THREE PSEUDO-COMPONENTS

1. The Ternary Space-representation.

THE case will now be considered in which the pseudo-system is ternary and the unary system contains a transition point.

The pseudo-ternary system consists of three pseudo-binary systems $\alpha - \beta$, $\beta - \gamma$, and $\alpha - \gamma$. In the accompanying TX diagram, Fig. 79, it is assumed that each of the three binary (TX) figures has a eutectic. As is evident from the figure, at the ternary eutectic point the three mixed crystal phases, S_{α_M}, S_{β_M}, S_{γ_M}, co-exist with the liquid phase *l*.

Now in order that the position of the unary diagram in the pseudo-ternary system may be arrived at, let us in the first place consider each of the three pseudo-binary systems separately, indicating in these figures the positions of the lines relating to inner equilibrium.

This has already been done, as may be seen from the diagram, and the lines $L_2 S_2$, $L_3 S_3$, and $L_4 S_4$ represent the stable unary melting equilibria in the pseudo-systems $\alpha - \beta$, $\beta - \gamma$, and $\alpha - \gamma$, whilst $L_1 S_1$ relates to the metastable unary melting equilibrium in the first-mentioned system.

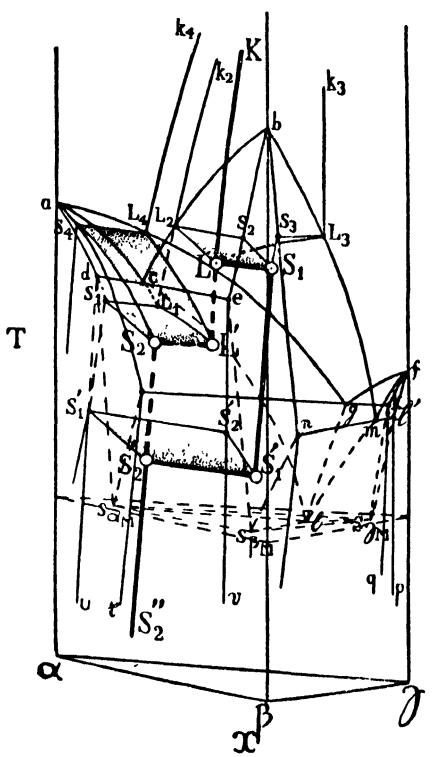


FIG. 79.

Let us now suppose that α and β undergo transformation the one into the other with great velocity, while γ behaves as a true component.

If then the unary melting equilibrium $S_2 L_2$ is taken as the starting point, and to it γ is added, this melting equilibrium will be depressed, as might be expected, and thus it is evident that for the melting equilibria obtained by the addition of increasing quantities of the component γ, a two-phase area $S_2 S_1$, $L_2 L_1$ is obtained which continues in space as far as the melting plane of S_{β_M}, and which relates to the co-existence of S_{β_M} and L. In just the same way β and γ may be imagined to undergo mutual transformation with great velocity, whilst α behaves as a true component. Proceeding then from the unary melting equilibrium $S_3 L_3$ and adding α, a second two-phase area relating to $S_{\beta_M} + L$ is obtained, namely $S_3 S_1 L_3 L$, which likewise extends to the fusion plane for S_{β_M}.

This two-phase area intersects the first in the line $S_1 L$, and the significance of this fusion equilibrium is easily seen. In the first-mentioned area originating at $S_2 L_2$ the inner equilibrium $\alpha \rightleftarrows \beta$ exists, whilst in the second, which originates at $S_3 L_3$, the inner equilibrium $\beta \rightleftarrows \gamma$ predominates. The line of intersection of these two two-phase areas will consequently represent two co-existing phases $S_1 + L$, in which the inner equilibrium $\alpha \rightleftarrows \beta \rightleftarrows \gamma$ prevails. This fusion equilibrium $S_1 \rightleftarrows L$ is the stable unary melting equilibrium of the pseudo-ternary system, whence it follows that L must be a point on the line representing the inner equilibrium in the liquid phase of the pseudo-ternary system. In the diagram the curve K L represents this line. Its prolongation in the direction of lower temperatures indicates the metastable pseudo-ternary inner equilibrium in the super-cooled liquid, whilst the line $S_1 S_1'$ relates to the pseudo-ternary inner equilibrium in the solid state.

The fusion equilibrium $S_4 L_4$ and the metastable fusion equilibrium in the pseudo-binary system $\alpha - \gamma$ have still to be considered.

Using the method indicated above, it may be shown that a two-phase area originates at $S_4 L_4$, on which the equilibrium $\alpha \rightleftarrows \gamma$ exists when β behaves as a true component, and that similarly a two-phase area extends into space from $S_1 L_1$, in which the equilibrium $\alpha \rightleftarrows \beta$ exists when γ has the properties of a true component. These two two-phase areas also intersect each other, and the line of intersection $S_2 L'$ again indicates a fusion equilibrium, between the mixed crystal phase S_2 and the liquid L', both of which are in inner equilibrium, and therefore belong to the unary system. Since, however, the line of intersection $S_2 L'$ now represents the intersection of two metastable two-phase areas (*i.e.* the two-phase area arising from $S_4 L_4$ will be intersected in its metastable portion), the unary fusion equilibrium $S_2 \rightleftarrows L'$ is metastable. It is clear that the point L' must lie on the metastable prolongation of the inner liquid line K L, just as is here shown. S_2 denotes a metastable unary solid phase situated in the pseudo-ternary system, and is the starting point of a line which indicates the position of the inner equilibrium in this phase at lower temperatures. If, now, no further complications arise, the phenomenon known as monotropy occurs; in the diagram, however, enantiotropy is assumed to exist.

That is to say, the existence has been assumed of a transition equilibrium $S_1' S_2'$ in the pseudo-binary system $\alpha - \beta$. In these two co-existing solid phases, an α- and a β-mixed crystal phase, the inner equilibrium $\alpha \rightleftarrows \beta$ therefore prevails. Supposing γ to behave as a true component, and that in consequence of the addition of γ the temperature of the transition equilibrium is lowered, a two-phase area is obtained which may be called a transition surface, in the co-existing phases of which the equilibrium $\alpha \rightleftarrows \beta$ prevails. This surface intersects the curve representing the stable and the metastable inner solid equilibria in S_1' and S_2', which means that $S_1' S_2'$ represents the position of the unary transition equilibrium in the pseudo-ternary system, at which the solid mixed crystal phases S_1' and S_2', both of which are in a state of inner equilibrium, co-exist. The line $S_2' S_2''$ naturally refers here to the stable inner equilibrium in the solid state below the transition point.

(a) *Simplified methods of representation.*

From this example it appears that pseudo-ternary systems are more intricate than pseudo-binary systems; still, use must often be made of the method of representation indicated here, in order to explain observed phenomena. In this connection, however, it must be emphasised that help may frequently be obtained from a pseudo-binary diagram provided that it is remembered that such a pseudo-binary system is based on one that is pseudo-ternary or perhaps even more complicated.

This will be more fully explained in connection with the pseudo-ternary diagram given here. In order to simplify matters it may be assumed that two of the three pseudo-components, *e.g.* α and β, undergo mutual transformation with so great a velocity that the system $\alpha \rightleftarrows \beta$ always remains in a state of equilibrium. In this case α and β together behave as a *single* pseudo-component, which may be designated α'.

Thus the first pseudo-component is α' and the second γ (see Fig. 80). On the α axis a denotes the temperature of the stable fusion equilibrium $S_2 \rightleftarrows L_2$ of Fig. 79, b the temperature of the metastable fusion equilibrium $S_1 \rightleftarrows L_1$, and c the temperature of the transition equilibrium $S_1' \rightleftarrows S_2'$.

The melting line $a\,g$ and the mixed crystal line $a\,f$ now define the stable two-phase fusion area which, according to Fig. 79, commences at $S_2 L_2$. The metastable melting line $b\,g'$ and the mixed crystal line $b\,d'$, on the other hand, indicate the metastable two-phase fusion area originating at $S_1 L_1$ in the same figure, whilst the transition lines $c\,f'$ and $c\,d'$ show the two-phase transition area in the pseudo-ternary representation.

If in this new pseudo-binary T X figure the lines relating to inner equilibria in the unary system are drawn, the following heavy lines are obtained: K L' representing inner liquid equilibria, which from L to L' are metastable, $S_1 S_1'$ relating to the inner equilibria in the solid

state, which are stable at temperatures above that of the transition equilibrium, whilst $S_2' S_2''$ represents similar equilibria at temperatures lower than the transition equilibrium temperature. The line $S_2 S_2'$ refers to the solid state, which is metastable above the temperature of the transition equilibrium. This pseudo-binary representation has been obtained by assuming that the equilibrium $\alpha \rightleftarrows \beta$ is always established. Similar diagrams may naturally be deduced if, instead, it is

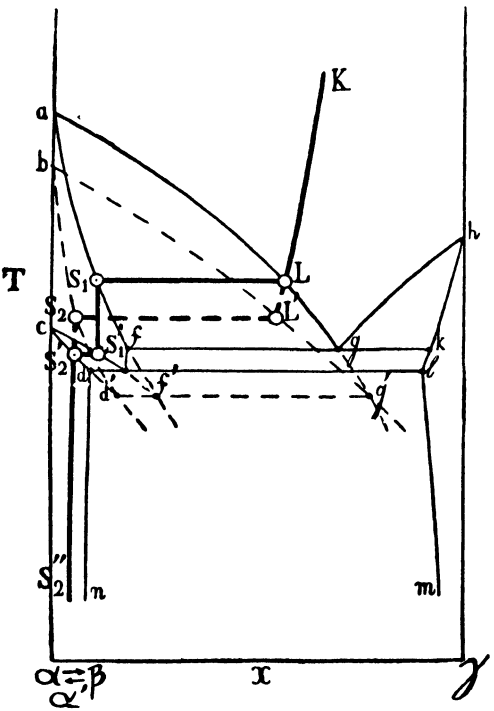


FIG. 80.

assumed that the equilibria $\alpha \rightleftarrows \gamma$ or $\beta \rightleftarrows \gamma$ are established with great velocity.

It is clear that by following this method diagrams are obtained which make it possible to explain observed phenomena in a simple manner. Also when the pseudo-system is more complicated, every three dimensional representation may be reduced by the application of this principle to one of two dimensions.

(b) *The isothermal figure for constant pressure.*

Notwithstanding the above statement, however, it will often be convenient to refrain from applying this simplified method of

representation, and if the pseudo-system is ternary, to make use of a ternary diagram; in such a case the tracing out of a three dimensional space model is not at once commenced, but sections are first of all considered, *e.g.* for a constant temperature; thus the isothermal figure is studied, and in this way an accurate view is soon obtained of the connection between the unary and the pseudo-systems. This will be more fully described when considering the system acetaldehyde—paraldehyde—metaldehyde, which will be discussed later.

At present the discussion of the subject will be limited to a few remarks of a general nature.

Assuming that the pseudo-system is ternary, and that the pseudo-components are isomers, the inner equilibrium in a gaseous, liquid or solid phase may be indicated at any given temperature in the following way.

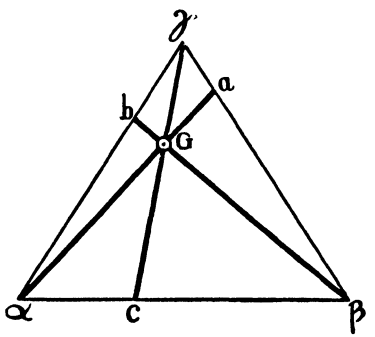


FIG. 81.

In the triangular diagram, Fig. 81, α, β and γ are the pseudo-components whilst a, b and c mark the positions of the inner gaseous equilibria in the three pseudo-binary systems.

Let us assume for a moment that γ and β attain a state of inner equilibrium very rapidly, but that α behaves as a true component; the position of the equilibrium $\gamma \rightleftarrows \beta$ after the addition of different quantities of α may then be shown on this diagram. Since γ and β are isomers, the equilibrium between these two molecular species will not be displaced by the addition of α, and a straight line connecting the point a with α will therefore define the equilibrium position.

In the same way, it may be assumed that α and β are always associated in inner equilibrium, and that γ behaves as a true component. The inner equilibrium $\alpha \rightleftarrows \beta$ will then remain unaltered by the addition of γ to the system $\alpha + \beta$, which is in inner equilibrium, and hence the system will again move along a straight line, in this case from c towards γ. The two straight lines thus obtained intersect in the point G; consequently at this point the equilibria $\beta \rightleftarrows \gamma$ and $\alpha \rightleftarrows \beta$ both exist, and hence also the tri-molecular inner equilibrium $\alpha \rightleftarrows \beta \rightleftarrows \gamma$ which belongs to the unary system. From this inner equilibrium relationship it follows that α is also in inner equilibrium with γ, even though this equilibrium is only reached through β, and consequently the point b must be so situated that a straight line drawn from β through G also passes through this point. Now it is always possible that this equilibrium can only be attained by way of β. In this case the tri-molecular inner equilibrium $\alpha \rightleftarrows \beta \rightleftarrows \gamma$ may be said to be linear. If, however, the equilibrium $\alpha \rightleftarrows \gamma$ can be established

directly, the tri-molecular inner equilibrium is represented in the following manner:—



and it may then be described as a triangular inner equilibrium.

If α, β and γ are polymers, very little difference is to be noticed. If the pseudo-components are represented by α, α_m and α_n, and if, for example, $n > m > 1$, the following statement may be made. When α_m and α_n reach a state of inner equilibrium very quickly and α is a true component, the equilibrium $m\alpha_n \rightleftarrows n\alpha_m$ will be displaced towards the right by the addition of α, and indeed, when the dilution due to the addition of α has become very great, it is displaced practically completely to the α_m side. Hence it follows that the line $a - mn_\alpha$ now has a form such as that depicted in Fig. 82, and that it touches the side $mn_\alpha - n\alpha_m$ at the point mn_α. In the same way the position outlined here for the two other equilibrium lines can be explained. Finally it should be noticed that at the apices of the triangle mn_α, $n\alpha_m$ and $m\alpha_n$ have been written, in order to show that the different transformations are actually possible with the quantities of the pseudo-components indicated at the apices. On considering the liquid and solid phases similar results are obtained.

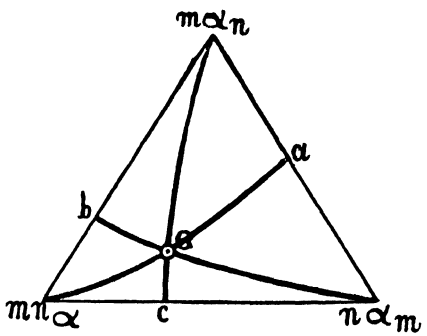


FIG. 82.

CHAPTER IV

ALLOTROPIC SUBSTANCES IN THE PRESENCE OF A SOLVENT

1. General Considerations.

IF the allotropic substance consists of two pseudo-components it will form with a solvent an essentially binary system, which, however, constitutes a pseudo-ternary system at the least.

Thus, in order to explain the behaviour of such a system, it is necessary to imagine it to be ternary and to indicate the position of the binary system in this pseudo-ternary system. With this object the solution isotherms for the solid phase at a definite temperature and pressure have been drawn in the accompanying diagram, Fig. 83.[1]

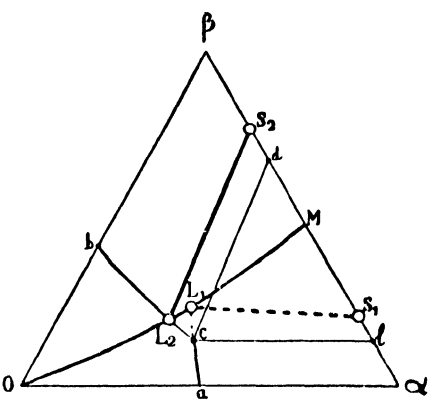


FIG. 83.

The temperature assumed here lies below the eutectic temperature of the system α—β and the pressure is assumed to be greater than the highest vapour pressure. O refers to the solvent, whilst α and β denote the pseudo-components.

The isotherm $a\,c$ represents saturated solutions which co-exist with the mixed crystal phase $a\,l$ and the isotherm $b\,c$ relates to saturated solutions which co-exist with the mixed crystal phase $\beta\,d$.

Consequently c indicates the saturated solution which co-exists with the two mixed crystal phases d and l. The curve O M represents the equilibria between α and β in solutions of different concentrations.

In the figure under discussion this line intersects the isotherm $b\,c$, and therefore, when α and β are in equilibrium with each other in the solution, the only stable saturated solution is L_2.

If now α and β are in equilibrium with each other in the saturated solution, and this saturated solution is stable, the co-existing solid phase is also stable and is in inner equilibrium. Since this co-existing solid

[1] It is here assumed that no compound of the pseudo-components can separate out.

phase is indicated by S_2, this must be the stable solid phase in the unary system $\alpha + \beta$. Now, in general, however, there will also be a metastable solid phase in the unary system, and this may easily be found in the following way. Thus, when L_2 is not too far removed from c, the curve for the homogeneous equilibrium in the solution also intersects in L_1 the metastable prolongation of the isotherm relating to mixed crystals rich in α. Now this solution co-exists in the metastable state with the metastable solid phase S_1—that is to say, this phase S_1 is the metastable solid phase of the unary system $\alpha + \beta$.

Whilst, therefore, L_2 and S_2 represent the co-existing phases of the stable saturation equilibrium in the binary system $O + (\alpha \rightleftarrows \beta)$, L_1 and S_1 refer to the co-existing phases of the metastable saturation equilibrium in the same binary system.

From these considerations the result follows that the intersection of

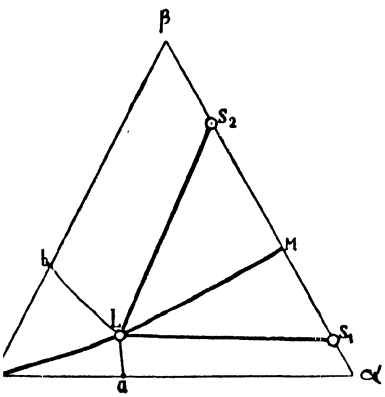


FIG. 84.

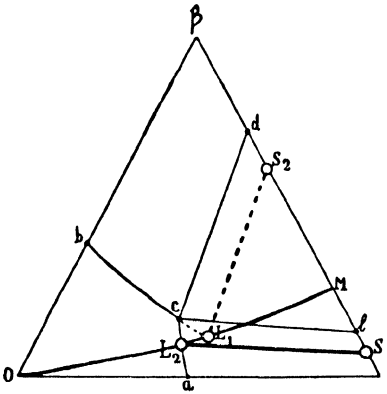


FIG. 85.

the equilibrium curve O M with the stable portion of the solution isotherm for mixed crystals rich in β, and the metastable portion of the solution isotherm for mixed crystals rich in α, is connected with the circumstance that in the unary system $(\alpha + \beta)$ a mixed crystal phase rich in β is the metastable modification.

If it is now assumed that enantiotropy exists in the unary system $(\alpha + \beta)$, and that the temperature of the investigation lies below the transition point, the change that will appear if the temperature is supposed to be raised to the transition temperature is at once evident.

When the temperature is raised the points L_2, c and L_1 approach each other. Consequently, the points S_2 and d, and S_1 and e are also crowded together, and when the equilibrium curve O M just passes through the point c two mixed crystal phases in inner equilibrium with each other co-exist in the binary system, *i.e.* the two modifications of the unary system $(\alpha + \beta)$ co-exist with one and the same saturated solution, or, in other words, the transition point is then reached. The form of the ternary diagram is then represented by Fig. 84.

At a temperature above the transition point the equilibrium curve intersects the solution isotherm relating to mixed crystal phases rich in α, and then the stable modification is no longer S_2, but S_1, as is evident from Fig. 85.

2. The Study of those Allotropic Organic Substances known as "Tautomers."

The allotropic substances known as tautomers are frequently transformed but slowly, and hence the influence of solvents on several tautomeric equilibria has already been thoroughly investigated.

Van't Hoff[1] has deduced a formula for the change in the equilibrium caused by the solvent, and Dimroth[2] has carried out extremely interesting investigations in this direction. Not only has a systematic study not yet been carried out of allotropic substances capable of being transformed by a solvent, *i. e.* of systems which, according to the foregoing considerations, are pseudo-ternary, and in which the position of the isotherm characterising the inner equilibrium in the liquid phase makes it possible to decide which solid phase is stable at a given temperature and which metastable, but, in addition, the subject has not yet received sufficient theoretical consideration.

In connection with the ideas developed here I have gone into the problem somewhat closely.[3] Before proceeding to these considerations, however, Dimroth's researches will first be mentioned.

In his investigations Dimroth made use of van't Hoff's formula relating to the variation in the equilibrium caused by the solvent, which is as follows:—

$$\frac{C_A}{C_B} = \frac{L_A}{L_B} G \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In this expression C_A and C_B denote the concentrations of the substances A and B, which are in inner equilibrium, at a given temperature.

L_A and L_B are the saturation concentrations of A and B in the pure solvent at the same temperature, and G is a constant which is independent of the solvent.

Dimroth makes reference to the fact that interesting conclusions may be drawn from this relationship, conclusions which are of great importance in the preparation of isomers which undergo mutual transformation. He says: "If it is assumed that at a given temperature $G = 1$, it then follows that if at this temperature any arbitrary solvent is saturated with both isomers A and B, and solid A and solid B lie at the bottom, the whole system will remain in equilibrium unchanged." Here it should be noticed that the temperature at which this is the case is the temperature of the transition point between A and B, and

[1] *Vorlesungen über theoretische phys. Chem.*, p. 219.

[2] *Lieb. Ann.* **337**, 133 (1910), and **399**, 115 (1913).

[3] *Versl. Kon. Akad. v. Wet.* **24**, 283 (1915); *Zeitschr. f. physik. Chemie*, **92**, 34 (1916).

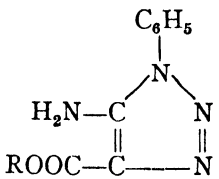
consequently the temperature at which the two solid phases A and B are in equilibrium with each other.

If $G < 1$, then $\frac{C_A}{C_B}$ is $< \frac{L_A}{L_B}$. In this case the solution saturated with the two solid isomers A and B will contain more A than corresponds with equilibrium conditions. The consequence of this is that A is converted into B in the liquid, from which the latter form crystallises out; solid A goes into solution until this form has completely disappeared. When $G > 1$ the converse takes place. As a result of these considerations Dimroth says: "If therefore two isomers which undergo mutual transformation with sufficient velocity are together introduced into a quantity of solvent insufficient to dissolve them, if van't Hoff's principle holds good the direction of the process of isomerisation must depend exclusively on the constant G, and must therefore be entirely independent of the nature of the solvent."

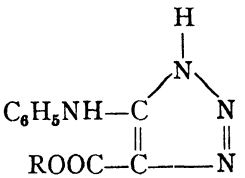
This, however, Dimroth says, is contrary to experience, for it is often possible to convert isomers the one into the other by treating them with different solvents. In this connection he refers particularly to the work of E. Bamberger[1] on the isomers of nitro-formaldehyde-hydrazone, of which the α form is converted into the β modification by means of water or alcohol, whilst, conversely, this β modification is transformed into the α form by treatment with benzene, chloroform or ligroin.

In this connection Dimroth states emphatically: "There can be no doubt that these experiments, which are successfully practised in the laboratory, contradict van't Hoff's principle."

This expression of opinion seems rather strange, for Dimroth himself, in an investigation of the amino-derivatives of triazol-carbonic ester, which exhibits the following transformation,



1-Phenyl 5-amino-triazol-carbonic ester (neutral).



5-Anilino-triazol-carbonic ester (acid).

found a very beautiful confirmation of van't Hoff's Law, so that doubt as to the correct interpretation of so-called laboratory practice was rather to be expected.

Dimroth determined the concentrations C_A and C_B of the two isomers in different solvents after equilibrium had been established at 60° under the catalytic influence of a trace of acid.

The solubility of each of the isomers, and consequently L_A and L_B, was determined, in addition, at the same temperature and in the

[1] *Ber. d. d. chem. Ges.*, **34**, 2061 (1901).

same solvent, and by means of equation (1) the value of G was then calculated.

The investigation of the isomers of the ethyl and methyl esters furnished the following interesting results (see the table below).

In general a very constant value was calculated for G. Since it chances that in the case of the ethyl ester the value of G is > 1 and in the case of the methyl ester < 1, it may be predicted that if the two isomers of the ethyl ester are left in contact with the saturated solution at 60° the neutral form will completely disappear, whilst in the case of the methyl ester exactly the opposite must take place.

Solvent.	$\frac{C_a}{C_n}$.	$\frac{L_a}{L_n}$.	G.
Ethyl Ester			
Ether	20·7	8·4	2·4
Ethyl Alcohol	4·56	2·1	2·4
Toluene	1·53	0·74	2·1
Benzene	1·2	0·6	2·4
Nitrobenzene	0·85	0·33	2·6
Chloroform	0·32	0·19	1·7
Methyl Ester			
Ether	20·7	53·0	0·4
Methyl Alcohol	2·3	7·0	0·33
Toluene	1·8	4·3	0·33
Benzene	1·02	3·2	0·32
Nitrobenzene	0·8	2·2	0·36
Chloroform	0·32	1·1	0·32

With these conclusions experiment was found to be in complete agreement, so that the investigation of these isomers furnished a beautiful confirmation of van't Hoff's principle.

3. A Generally Valid Relationship, applicable both to Isomers and Polymers, by means of which it may be ascertained in a very Simple Way which is the Stable Modification.

The substances discussed here exhibit the phenomenon known as molecular allotropy, for they are built up from two different molecular species. Moreover, since the substance appears in two solid phases, it also furnishes an example of phase allotropy. In the absence of a solvent, therefore, the substance constitutes a system belonging to the pseudo-binary type, and it only functions as a unary system when, in the homogeneous phases, the different molecular species are in inner equilibrium with each other.

If the two modifications are studied in the presence of a solvent a pseudo-ternary system has to be dealt with, which will be binary when the two pseudo-components are in inner equilibrium with each

other in the homogeneous phase. In order that the cases discussed by Dimroth may be considered in the clearest manner, use is again made of the triangular method of representation.

At the apices of the equilateral triangle (Fig. 86), the letters A, B and C are placed; of these A and B represent the pseudo-components which are miscible to a limited extent in the solid state, whilst C refers to the solvent.

Amongst other things the following isotherms are indicated in this triangle for a definite temperature:—the solubility isotherm for the mixed crystal series A A_1, represented by the curve *a* L, and for the series of mixed crystals B B_1, to which the curve *b* L refers. Thus the point of intersection L indicates the saturated solution which can co-exist with the mixed crystal phases A_1 and B_1.

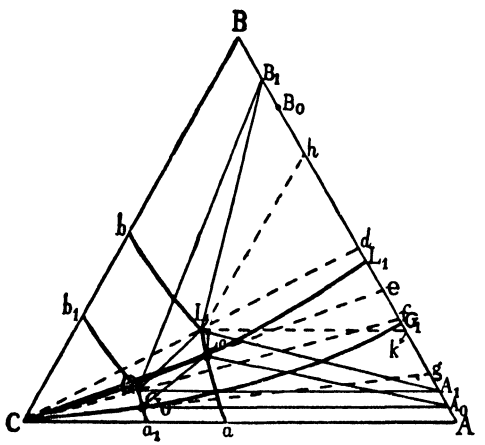


FIG. 86.

Let us now imagine the solution to be also in equilibrium with its vapour, in consequence of which naturally the vapour pressure is not constant.

The vapour isotherm corresponding to the solubility isotherm *a* L is indicated by the line a_1 G, that corresponding to the solubility isotherm *b* L by b_1 G, so that G denotes the vapour phase which co-exists in the four-phase equilibrium with the saturated solution L and the two solid phases A_1 and B_1.

Since now CL_0L_1, which represents the isotherm relating to inner equilibrium in the liquid, *i.e.* the line showing how the inner equilibrium between A and B in the liquid phase is displaced in consequence of any change in the concentration of the solvent C, intersects the solubility isotherm *a* L of the mixed crystal series A A_1 in the point L_0, it is immediately seen that as regards inner equilibrium between A and B, of all the saturated solutions only that represented by L_0 is stable; this then will naturally co-exist with a mixed crystal phase which is likewise in inner equilibrium, and which is indicated here by the point A_0.

In addition, the isotherm relating to inner equilibrium in the vapour is indicated by $C G_0 G_1$, and it follows at once from this, that of all the saturated vapours only that represented by G_0 is stable so far as inner equilibrium is concerned, so that in the stable three-phase equilibrium solid—liquid—vapour the phases A_0, L_0 and G_0 co-exist.

As is well known, the composition of any arbitrarily chosen phase is very easily indicated. Thus the composition of the liquid phase L is

found by drawing a line through this point parallel to C B and another one parallel to C A, as in Fig. 86. The first parallel cuts the side A B at h, the second at k. The number of gram-molecules of A, say x, is now represented by B h, the number of gram-molecules of B, or y, by A k, whilst the number of gram-molecules of the solvent C, $1 - x - y$, is indicated by $h\,k$.

Furthermore, when only the concentration ratio between A and B is in question, *e. g.* at the same point L, this may be found very simply. If a straight line is drawn through the points C and L this line cuts the side A B in d, and at every point on the line C d the concentration ratio between A and B is the same, and consequently it has the same value at d as at L.

At d this ratio is

$$\frac{Bd}{Ad} = \frac{Bh}{Ak} = \frac{x}{y}.$$

It is now quite clear that, when the isotherm relating to inner equilibrium in the liquid passes exactly through the point L, *i.e.* through the point of intersection of the two liquid isotherms, this indicates that at the observed temperature, A and B are in equilibrium in the solution which is saturated with the mixed crystal phases A_1 and B_1.

From this it also follows immediately that in this case the co-existing solid phases will be in inner equilibrium, and that the equilibrium $A \rightleftarrows B$ will likewise prevail in the vapour which co-exists with L. In this case, therefore, the vapour pressure G at the point of intersection of the two vapour isotherms must also lie on the isotherm relating to equilibrium in the vapour.

Consequently, at the transition point of the two modifications, the points L_0 and L, G_0 and G, A_0 and A_1, and B_0 and B_1 coincide, and this is also true of the points e and d, and g and f, which indicate the concentration ratios of A and B in the liquid and vapour phases.

For the sake of simplicity the composition of the phases will be indicated by small letters when the system is in inner equilibrium, and by capitals when inner equilibrium does not exist.

In the liquid L, therefore, the concentration ratio between A and B is denoted by $\frac{X_L}{Y_L}$ and at the liquid point L_0 by $\frac{x_L}{y_L}$.

In agreement with this, the ratio between A and B in the vapour G will be indicated by $\frac{X_g}{Y_g}$ and in the vapour G_0 by $\frac{x_g}{y_g}$.

Similarly in the solid phase A the concentration ratio A/B will be represented by $\frac{X_{s_1}}{Y_{s_1}}$, and the corresponding ratio in the phase A_0 by $\frac{x_{s_1}}{y_{s_1}}$; at B_1, on the other hand, this ratio will be indicated by $\frac{X_{s_2}}{Y_{s_2}}$ and at B_0 by $\frac{x_{s_2}}{y_{s_2}}$.

At the transition temperature the following simple relationships now hold good:—

$$\frac{x_L}{y_L} = \frac{X_L}{Y_L} \quad . \quad . \quad . \quad (2) \qquad \frac{x_{s_1}}{y_{s_1}} = \frac{X_{s_1}}{Y_{s_1}} \quad . \quad . \quad . \quad (4)$$

$$\frac{x_g}{y_g} = \frac{X_g}{Y_g} \quad . \quad . \quad . \quad (3) \qquad \frac{x_{s_2}}{y_{s_2}} = \frac{X_{s_2}}{Y_{s_2}} \quad . \quad . \quad . \quad (5)$$

At any other temperature, however, the following expressions are obtained:—

$$\frac{x_L}{y_L} = f_1 \frac{X_L}{Y_L} \quad . \quad . \quad . \quad (6) \qquad \frac{x_{s_1}}{y_{s_1}} = f_3 \frac{X_{s_1}}{Y_{s_1}} \quad . \quad . \quad . \quad (8)$$

$$\frac{x_g}{y_g} = f_2 \frac{X_g}{Y_g} \quad . \quad . \quad . \quad (7) \qquad \frac{x_{s_2}}{y_{s_2}} = f_4 \frac{X_{s_2}}{Y_{s_2}} \quad . \quad . \quad . \quad (9)$$

Regarding the factors f it is only necessary here to state that they are connected with each other and that at the transition temperature they become simultaneously equal to 1.

Expressions (6) to (9) possess *general validity*, and equation (6) is most suitable for the purpose of determining which is the stable modification at a given temperature.

If it is assumed that $f_1 > 1$, the case represented in Fig. 86 occurs.

The inner equilibrium L_0 then requires a greater concentration of A than exists in the solution L.

Consequently, if at the outset the saturated solution L co-exists with the two mixed crystal phases A_1 and B_1 the transformation

$$B \rightarrow A$$

will take place in the solution, and as a result it becomes unsaturated with regard to the B mixed crystals and supersaturated with A mixed crystals; in consequence of this, B mixed crystals dissolve and A mixed crystals separate out. This process continues until the B mixed crystals have completely disappeared and a solution remains in which A and B are in inner equilibrium, and which co-exists with a mixed crystal phase A_0, which is likewise in inner equilibrium.

When $f < 1$ the reverse process occurs.

It is clear that the same result will be attained by discussing equations (7), (8), or (9).

All these expressions have, of course, the advantage of being *generally* valid.

It will often happen that it is not known which of the two modifications of a substance is the stable form at a given temperature; equation (6) then furnishes, as has just been shown, an extremely simple method of deciding the matter.

The concentrations of A and B are determined, at the required temperature, in a solution *saturated with both the solid phases* A_1 *and* B_1 (which will be mixed crystals) and in this way the value of $\frac{X_L}{Y_L}$ is found.

Now the peculiarity of this method lies in the fact that $\frac{x_L}{y_L}$ *relates, not to any solution in which* A *and* B *are in inner equilibrium, but specially to the solution* L_0. *A further portion of the saturated solution is therefore taken and treated with a few small crystals of each of the solid phases, and it is then left at the same temperature until inner equilibrium becomes established, as a result of which one variety of crystals disappears* (except at the transition point).

The concentrations of A and B in this solution are then determined, and in this way $\frac{x}{y}$ is found; for this purpose it is quite immaterial whether the concentration is large or small.

The following quotient is then calculated :—

$$\frac{x_L}{y_L} \Big/ \frac{X_L}{Y_L} = f_1,$$

and from this we know with *absolute certainty* that if $f > 1$, *without exception* A is stable, and that B is stable if $f < 1$.

In this method it is quite unimportant whether A and B are isomers or polymers, what molecular weight is assumed in calculating the concentration ratios between A and B, or whether this value is the correct one or not; all these are irrelevant to the question, since they do not affect the factor f_1.

4. Van't Hoff's Equation in the Case of Isomers.

The relationship

$$\frac{C_A}{C_B} = \frac{L_A}{L_B} G$$

does not possess general validity, and this is immediately apparent, for instead of $\frac{X_L}{Y_L}$, the fraction $\frac{L_A}{L_B}$ is used here, in which L_A and L_B denote the solubilities of A and B respectively in the pure solvent. Thus $\frac{L_A}{L_B}$ does not represent the concentration ratio between A and B in the liquid L, which is saturated with A and B (see Fig. 86), but :—

$$L_A = \frac{Ca}{Aa} \quad \text{and} \quad L_B = \frac{Cb}{Bb}.$$

From this it is clear that van't Hoff's formula is only valid in the ideal case, in which the laws of dilute states are applicable to solutions and vapour phases saturated with the solid phases, so that any mutual influence between A and B is excluded.

It is not surprising, therefore, that van't Hoff's formula holds good only to a very limited extent. Against this, however, must be placed the fact that in these ideal cases it may express more.

This will be illustrated in Fig. 87, which relates to such an ideal system. This diagram differs from Fig. 86 in that, amongst other things, the solubility and vapour isotherms are straight lines so far as they refer to stable states. These are the lines connecting the points a and a_1 with the apex B, and the points b and b_1 with the apex A. This means that so far as solubility and partial pressure are concerned the substances A and B are without influence on each other. It should also be noticed that since the assumption is here made that A and B are isomers, the isotherms relating to inner equilibria in the liquid and in the vapour are likewise straight lines. And finally, according to this hypothesis, A and B do not form mixed crystals.

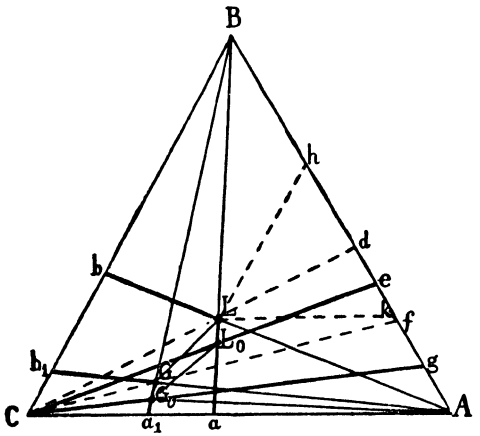


FIG. 87.

Consequently, the same conditions hold good for inner equilibrium in the liquid phase as exist at L_0, that is to say,

$$K_{L_0} = \frac{x_L}{y_L} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and in the same way the inner equilibrium in the co-existing vapour phase is subject to the same regularity as applies to G_0, that is

$$K_{g_0} = \frac{x_g}{y_g} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

If now the laws for ideal solutions and gases can be applied, as is assumed in the above case, Henry's Law will be valid, as regards both A and B, for all the co-existing liquid and vapour phases to be considered here, no matter whether these phases are in inner equilibrium or not.

If it is now supposed that in the application of Henry's Law concentrations must be indicated per unit of volume, the following is obtained: If one gram-molecule of the liquid contain x_L gram-molecules of A, and if this quantity occupies v_L c.c., the concentration of A per litre of solution is

$$\frac{1000\, x_L}{v_L}.$$

Further, if one gram-molecule of the co-existing vapour contains x_g gram-molecules of A, and if this one gram-molecule of gas occupies v_g c.c. under the conditions of temperature and pressure under

consideration here, the concentration of A in the vapour, reckoned in terms of one litre of the gaseous mixture, is

$$\frac{1000\,x_g}{v_g}.$$

If Henry's Law is now applied we can write :—

$$\frac{\dfrac{1000\,x_L}{v_L}}{\dfrac{1000\,x_g}{v_g}} = \frac{\dfrac{1000\,X_L}{V_L}}{\dfrac{1000\,X_g}{V_g}} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

and

$$\frac{\dfrac{1000\,y_L}{v_L}}{\dfrac{1000\,x_L}{v_L}} = \frac{\dfrac{1000\,Y_L}{V_L}}{\dfrac{1000\,X_g}{V_g}} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

If now the quotients of the first terms of equations (12) and (13) denote the concentration ratio of A and B in the co-existing phases L_0 and G_0, which are in inner equilibrium, and are therefore saturated with solid A, it is seen that these quotients are equal to the corresponding ratios for the co-existing phases L and G, which are not in inner equilibrium, and which are saturated with both solid A and solid B.

From equations (12) and (13) this expression now follows :—

$$\frac{\dfrac{x_L}{y_L}}{\dfrac{x_g}{y_g}} = \frac{\dfrac{X_L}{Y_L}}{\dfrac{X_g}{Y_g}} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

i.e. in the ideal case the factors f_1 and f_2 in equations (6) and (7) are equal to each other, and therefore *the relative difference between the concentrations of* A *and* B *in the co-existing liquid and vapour phases* L *and* G *in the four-phase equilibrium of the pseudo-ternary system will then be just as great as the relative difference in the inner equilibria* L_0 *and* G_0 *in the binary system.*

With regard to Fig. 87, however, equation 14 states that

$$\frac{\dfrac{Be}{Ae}}{\dfrac{Bg}{Ag}} = \frac{\dfrac{Bd}{Ad}}{\dfrac{Bf}{Af}} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

If equation (14) is now written in the form

$$\frac{x_L}{y_L} = \frac{X_L}{Y_L} \cdot \frac{x_g}{y_g} \cdot \frac{X_g}{Y_g} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

and

$$\frac{x_g}{y_g} \cdot \frac{X_g}{Y_g} = G,$$

this expression is obtained :—

$$\frac{x_L}{y_L} = \frac{X_L}{Y_L} \cdot G \quad . \quad . \quad . \quad . \quad . \quad (17)$$

for which van't Hoff writes :—

$$\frac{C_A}{C_B} = \frac{L_A}{L_B} G \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Here, however, X_L and Y_L represent the concentrations of A and B in the solution L (see Fig. 87), which is saturated with both A and B, whilst L_A and L_B, on the other hand, represent the saturation concentrations of A and B respectively in the pure solvent. In general, naturally the quantities $\frac{X_L}{Y_L}$ and $\frac{L_A}{L_B}$ are not equal to each other, but this may very well occur when, as in the ideal case, the solubilities of A and B are uninfluenced by the presence of each other. This is evident from Fig. 87, for there it is immediately seen that

$$\frac{L_A}{L_B} = \frac{Bh}{Ak} = \frac{X_L}{Y_L} \quad . \quad . \quad . \quad . \quad (19)$$

so that for the ideal case van't Hoff's formula is quite accurate.

In conclusion it must still be mentioned here that in contrast to equation (6) the quotients $\frac{x_L}{y_L}$ in equation (17) and $\frac{C_A}{C_B}$ in equation (18) represent the concentration ratio between A and B in any arbitrary solution in which A and B are in inner equilibrium.

5. Relationships Applicable to Polymerism.

Until now it has been assumed that A and B are isomers, yet the same considerations are applicable to cases of polymerisation also. Thus let it be supposed that B is a polymer of A and that the inner equilibrium is represented by

$$B \rightleftarrows 2A,$$

then the method of deduction just described can also be applied here. But it must be remembered that in order to obtain a formula analogous to equation (16), *i.e.* one containing the equilibrium constants for the liquid and gaseous phases, Henry's Law must be applied to those concentrations of A and B which occur in the equation for the equilibrium constant.

Consequently the concentration x^2 of A and y of B are considered, and in this way the following relationship is arrived at :—

$$\frac{x_L^2}{y_L} = \frac{X_L^2}{Y_L} \cdot \frac{x_g^2}{y_g} \cdot \frac{X_g^2}{Y_g} \quad . \quad . \quad . \quad . \quad (20)$$

which indeed expresses the same thing as equation (16), which is applicable to isomers, though its form is different. Naturally this

equation also is only applicable to ideal cases, and it can then only be written and applied in the form

$$\frac{x_L^2}{y_L} = \frac{X_L^2}{Y_L} \cdot h. \quad . \quad . \quad . \quad . \quad (21)$$

in order to establish which modification is the stable one at a given temperature. This, however, is only possible when the magnitudes of the different molecular species are known. Here the great advantage of equation (6) becomes clearly evident, for this can be applied even though the molecular magnitudes of A and B are unknown.

An attempt has been made here to treat the problem in the simplest possible manner. The relationships obtained will now be deduced thermodynamically.

6. The Thermodynamical Derivation of the Relation between the Saturation Concentration and the Inner Equilibrium.

Let us now consider the case in which, in a homogeneous phase, gaseous or solution, the following equilibrium exists between two molecular species of a substance at a definite temperature and pressure :—

$$\nu_1 A \rightleftarrows \nu_2 B \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Let us further suppose that in two separate spaces the solid substances A and B are also in equilibrium with their saturated vapours or saturated solutions at the same temperature, and that consequently :—

$$A_s \rightleftarrows A_g \quad . \quad . \quad . \quad . \quad . \quad (23)$$

$$B_s \rightleftarrows B_g \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Now let us imagine ν_1 molecules of solid A to be converted into ν_2 molecules of solid B by way of the homogeneous gaseous or liquid phase.

In the first process, which will now be considered more closely, let the homogeneous phase be gaseous and in a state of inner equilibrium, and in the second process let it be supposed that the homogeneous phase is a solution in which the molecular species A and B are likewise in inner equilibrium. In both cases the increase in the molecular potential $\Sigma\nu\mu$ must be the same.

Now, before proceeding to the consideration of the first process, it may be pointed out that for the increase of the molecular potential

$$\Sigma(\nu\mu)_s = \nu_2\mu_{s_B} - \nu_1\mu_{s_A} \cdot \quad . \quad . \quad . \quad . \quad (25)$$

the following expression can be written :—

$$\left.\begin{aligned}\Sigma(\nu\mu)_s = \nu_2\mu_{s_B} - \nu_1\mu_{s_A} = \nu_2\mu_{s_B} - \nu_2\mu_{G_B} + \nu_2\mu_{G_B} - \nu_1\mu_{G_A} \\ + \nu_1\mu_{G_A} - \nu_1\mu_{s_A}\end{aligned}\right\} \quad (26)$$

in which μ_{G_A} and μ_{G_B} represent the molecular potentials of A and B in the saturated vapour.

The following expressions hold good for the heterogeneous equilibria between solid A and vapour and solid B and vapour :—

$$\mu_{S_B} = \mu_{G_B} \quad \text{or} \quad \nu_2\mu_{S_B} = \nu_2\mu_{G_B} \quad . \quad . \quad . \quad (27)$$

and

$$\mu_{S_A} = \mu_{G_A} \quad \text{or} \quad \nu_1\mu_{S_A} = \nu_1\mu_{G_A} \quad . \quad . \quad . \quad (28)$$

Combining equations (26) and (28) we get

$$\Sigma(\nu\mu)_S = \nu_2\mu_{G_B} - \nu_1\mu_{G_A} \quad . \quad . \quad . \quad . \quad (29)$$

If now the inner equilibrium potentials of A and B in the gaseous state are denoted by

$$\mu'_{G_A} \quad \text{and} \quad \mu'_{G_B},$$

when inner equilibrium is established

$$\nu_1\mu'_{G_A} = \nu_2\mu'_{G_B},$$

so that instead of (29) we may also write

$$\Sigma(\nu\mu)_S = \nu_2\mu_{G_B} - \nu_2\mu'_{G_B} + \nu_1\mu'_{G_A} - \nu_1\mu_{G_A} \quad . \quad . \quad (30)$$

In this equation $\nu_2\mu_{G_B} - \nu_2\mu'_{G_B}$ denotes the change in the thermodynamic potential when ν_2 molecules of gaseous B, having the potential of the saturated vapour, are brought to the equilibrium potential; and in the same way $\nu_1\mu'_{G_A} - \nu_1\mu_{G_A}$ represents the change in the thermodynamic potential when ν_1 molecules of gaseous A are brought from the equilibrium potential to that of the saturated vapour. These changes can also easily be indicated in another way, if it is assumed that the vapours under consideration obey the gas laws, and that the molecular species A and B are without influence on each other.

We can then write

$$d\mu = -\eta dT + vdp,$$
$$(d\mu)_T = vdp,$$

or :—

$$(\mu)_T = \int vdp = RT \ln p + C,$$

whence it follows that :—

$$\mu'_{G_A} = RT \ln p'_A + C \quad . \quad . \quad . \quad . \quad (31)$$

and

$$\mu_{G_A} = RT \ln p_A + C \quad . \quad . \quad . \quad . \quad (32)$$

or :—

$$\mu'_{G_A} - \mu_{G_A} = RT \ln \frac{p'_A}{p_A} = RT \ln \frac{C'_{A_G}}{C_{A_G}} \quad . \quad . \quad (33)$$

consequently

$$\nu_1\mu'_{G_A} - \nu_1\mu_{G_A} = \nu_1 RT \ln \frac{C'_{A_G}}{C_{A_G}} \quad . \quad . \quad . \quad (34)$$

In the same way this expression is obtained :—

$$\nu_2\mu_{G_B} - \nu_2\mu'_{G_B} = \nu_2 RT \ln \frac{C_{G_B}}{C'_{G_B}} \quad . \quad . \quad . \quad (35)$$

so that equation (30) now assumes the form

$$\Sigma(\nu\mu)_s = \nu_2 \, RT \ln \frac{C_{B_G}}{C'_{B_G}} + \nu_1 RT \ln \frac{C'_{A_G}}{C_{A_G}} \quad . \quad . \quad (36)$$

The same considerations can be employed when the homogeneous phase, in which inner equilibrium prevails, is a solution (second process); in this case, instead of (36), the following equation is obtained:—

$$\Sigma(\nu\mu)_s = \nu_2 \, RT \ln \frac{C_{B_L}}{C'_{B_L}} + \nu_1 \, RT \ln \frac{C'_{A_L}}{C_{A_L}} \quad . \quad . \quad (37)$$

Since now $\Sigma(\nu\mu)_s$ must have the same value in both cases, the second term of equation (36) must equal the second term of equation (37).

Thus it follows from equations (36) and (37) that

$$\frac{C'^{\nu_1}_{A_L}}{C'^{\nu_2}_{B_L}} = \frac{C^{\nu_1}_{A_L}}{C^{\nu_2}_{B_L}} \cdot \frac{C'^{\nu_1}_{A_G}}{C'^{\nu_2}_{B_G}} \div \frac{C^{\nu_1}_{A_G}}{C^{\nu_2}_{B_G}} \quad . \quad . \quad . \quad . \quad (38)$$

In this equation the concentrations marked with a dash refer to inner equilibria, whilst the unaccented C indicates saturation concentrations. It must here be emphasised, however, that this result is only rigidly valid when the pseudo-components A and B behave as ideal substances. If they are now supposed to be isomers,

$$\nu_1 = \nu_2 = 1,$$

and consequently

$$\frac{C'_{A_L}}{C'_{B_L}} = \frac{C_{A_L}}{C_{B_L}} \cdot \frac{C'_{A_G}}{C'_{B_G}} \div \frac{C_{A_G}}{C_{B_G}} \quad . \quad . \quad . \quad . \quad (39)$$

which, however, is identical with equation (16).

If the case is one of polymerisation, and if, for example,

$$\nu_1 = 2 \quad \text{and} \quad \nu_2 = 1,$$

the general equation (38) transforms into

$$\frac{C'^2_{A_L}}{C'_{B_L}} = \frac{C^2_{A_L}}{C_{B_L}} \cdot \frac{C^2_{A_G}}{C'_{B_G}} \div \frac{C^2_{A_G}}{C_{B_G}} \quad . \quad . \quad . \quad . \quad (40)$$

which is identical with equation (20).

7. An Apparent Contradiction between Theory and Practice.

Dimroth[1] in his examination of van't Hoff's formula

$$\frac{C'_{A_L}}{C'_{B_L}} = \frac{C_{A_L}}{C_{B_L}} \cdot G \quad . \quad . \quad . \quad . \quad . \quad (41)$$

pointed out that since the direction of the isomeric change depends exclusively on the factor G, this quantity must be independent of the nature of the solvent. He is of opinion that this is contrary to

[1] *Lieb. Ann.* **337**, 127 (1910).

experience, since isomers may be converted the one into the other by treatment with different solvents.

In considering Dimroth's statement it must be noticed, as has been emphasised on a former occasion, that, in the first place, one can only speak of a test of formula (41) if a solution saturated with A and B and in contact with both solid phases is used as the starting point. Under these conditions in one case only will no change occur, that is when the temperature of the system is exactly the transition temperature for the two solid phases. In every other case a transformation will take place, quite independently of the solvent, in which the metastable solid modification disappears and the stable form remains. There are naturally some systems in which this transformation proceeds slowly, but efforts can then be made to accelerate the process catalytically. It may be shown in a very simple way that practice is, in fact, in agreement with theory, by applying equation (6), which has general validity, in the manner shown above.

$$\frac{x_L}{y_L} = f_1 \frac{X_L}{Y_L}.$$

The conversion of isomers into one another by treatment with different solvents is quite a different phenomenon. If, for example, the α form is dissolved in a given solvent, and then by some means the solution is caused to crystallise, it will only be stated that the β form appears, whilst when another solvent is used the reverse process takes place.

It must be carefully noticed here that the formula now under discussion relates to equilibrium conditions, whilst the last-mentioned phenomenon is dependent on the nuclear number and on spontaneous crystallisation.

These phenomena will be discussed in a subsequent chapter, and consequently it will there be possible for the first time to explain this apparent contradiction.

8. The Influence of the Solvent on the Position of the Homogeneous Equilibrium.[1]

The following considerations were first published by the author in 1916, but the ideas on which they are based have been developed in his lectures for many years. They refer to all homogeneous equilibria, and consequently they must also apply to the special case of inner equilibrium.

It is well known that homogeneous equilibria are often strongly influenced by the solvent. This, amongst other things, has been established by Dimroth's[2] investigation of the behaviour of triazolcarbonic ester in different solvents, by Halban's[3] study of the transformation of parabromphenyldimethylallylammonium bromide, and finally by the researches of Kurt Meyer[4] on the keto- and enol-forms

[1] Smits, *Versl. Kon. Akad. v. Wet.*, **25**, 641 (1916).
[2] *Loc cit.*
[3] *Zeitschr. f. physik. Chemie*, **67**, 129 (1909).
[4] *Ber.* **47**, 832 (1914).

of aceto-acetic ester. The following is the author's explanation of this interesting phenomenon.

Starting from the thermodynamic equation

$$Z = E - TH + PV \quad . \quad . \quad . \quad . \quad (1)$$

and differentiating at constant temperature and pressure with respect to n_1, the following is obtained :—

$$\left(\frac{dZ}{dn_1}\right)_{PT} = \left(\frac{dE}{dn_1}\right)_{PT} - T\left(\frac{dH}{dn_1}\right)_{PT} + P\left(\frac{dV}{dn_1}\right)_{PT} \quad . \quad . \quad (2)$$

$$\left(\frac{dZ}{dn_1}\right)_{PT} = \mu_1 = \text{molecular thermodynamic potential} \quad . \quad (3)$$

Since solutions are here considered, the last differential quotient $\left(\frac{dV}{dn_1}\right)_{PT}$ is very small.

Similarly P is also very small if the vapour pressure of the solvent is small and if the work is carried out in a vacuum. Even when open vessels are used, and P is therefore equal to one atmosphere, the term $P\left(\frac{dV}{dn_1}\right)_{PT}$ is so small that it may safely be neglected.

Now in the case of dilute solutions, entropy may be resolved into a portion independent of the concentration and a concentration term, and thus for the increase of entropy produced by the reversible addition of the dissolved substance

$$\left(\frac{dH}{dn_1}\right)_{PT} = \left(\frac{dH}{dn_1}\right)_{\substack{PT \\ C=1}} - R \ln C_1 * \quad . \quad . \quad . \quad (4)$$

* This formula is derived in the following way :—

Starting with the relationship

$$\left(\frac{dH}{dn_1}\right)_{PT} = \left(\frac{dH'}{dn_1}\right)_{PT} - \frac{d}{dn_1} pR\{(1-x-y-\ldots)\ln(1-x-y-\ldots) + x\ln x + y\ln y + \ldots\}$$

which holds good for the addition of dn_1 mol. of the dissolved substance to p mol. of the solution, and writing $\frac{d}{dn_1} pA$ for the last term, so that

$$\frac{d}{dn_1} pA = A\frac{dp}{dn_1} + p\frac{dA}{dn_1} = A + p\frac{dA}{dx} \cdot \frac{dx}{dn_1} .$$

For dilute solutions, in which case $\frac{dx}{dn_1} = \frac{1}{p}$, this expression transforms into

$$\frac{d}{dn_1} pA = A + \frac{dA}{dx},$$

or

$$\frac{d}{dn_1} pA = R\{(1-x-y-\ldots)\ln(1-x-y-\ldots) + x\ln x + y\ln y + [-\ln(1-x-y-\ldots) + \ln x]\}$$

$$= \ln x + \text{quantities which can be neglected here.}$$

Thus we get—

$$\left(\frac{dH}{dn_1}\right)_{PT} = \left(\frac{dH'}{dn_1}\right)_{PT} - R\ln x = F(v \,.\, T) - R\ln c = \left(\frac{dH}{dn_1}\right)_{\substack{PT \\ C=1}} - R\ln C.$$

from which, after substitution, this equation is obtained

$$\mu = \left(\frac{dE}{dn_1}\right)_{PT} - T\left(\frac{dH}{dn_1}\right)_{\substack{PT \\ C=1}} + RT \ln C_1 . \quad . \quad . \quad (5)$$

If now all the reacting constituents are summed, reckoning molecular numbers on the right of the sign of equality as positive and those on the left as negative, equation (6) is obtained :—

$$\Sigma\nu\mu = \Sigma\nu\left(\frac{dE}{dn_1}\right)_{PT} - T\Sigma\nu\left(\frac{dH}{dn_1}\right)_{\substack{PT \\ C=1}} + RT\Sigma\nu \ln C_1 . \quad . \quad (6)$$

If the increase of energy and the entropy increase per gram-molecule are denoted by E_1 and $H_{1_{C=1}}$ respectively, *i.e.* if we write

$$\left(\frac{dE}{dn_1}\right)_{PT} = E_1 \quad \text{and} \quad \left(\frac{dH}{dn_1}\right)_{\substack{PT \\ C=1}} = H_{1_{C=1}}$$

this expression is obtained :—

$$\Sigma\nu\mu = \Sigma\nu_1 E_1 - T\Sigma\nu_1 H_{1_{C=1}} + RT\Sigma\nu_1 \ln C_1 \quad . \quad . \quad (7)$$

If it is further supposed that under equilibrium conditions

$$\Sigma\nu\mu = 0 \quad \text{and} \quad RT\Sigma\nu_1 \ln C_1 = RT \ln K_C$$

equation (7) gives rise to

$$RT \ln K_C = - \Sigma\nu_1 E_1 + T\Sigma_1 H_{1_{C=1}}$$

or

$$\ln K_C = - \frac{\Sigma\nu_1 E_1}{RT} + \frac{\Sigma_1 \nu_1 H_{1_{C=1}}}{R} \quad . \quad . \quad . \quad (8)$$

It must be specially emphasised here that the expression $\Sigma\nu_1 E_1$, which represents the energy change at the *observed temperature*, is practically independent of the temperature, and can therefore be looked upon as a constant, for the sum of the specific heats of those constituents on the right-hand side of the equation for the reaction, minus the sum of the specific heats of the constituents on the left, yields a quantity which, according to Scheffer,[1] may be completely neglected here. Thus it has been assumed that, *provided that the influence on the dissolved substance is exclusively physical in character, the sum of the molecular entropies* $\Sigma\nu_1 H_{1_{C=1}}$ *is equally great for different solvents.*

Consequently if equation (8) is applied to the same equilibrium in two different solvents I and II, it follows from the assumption just mentioned that in the equations

$$\ln K_I = - \frac{\Sigma(\nu_1 E_1)_I}{RT} + C_I \quad . \quad . \quad . \quad (9)$$

[1] *Versl. Kon. Akad. v. Wet.* **25**, 592 (1916).

and

$$\ln K_{II} = -\frac{\Sigma(\nu_1 E_1)_{II}}{RT} + C_{II} \quad . \quad . \quad . \quad (10)$$

$$C_I = C_{II}$$

so that if, instead of the decrease of energy, the thermochemical heat q is written

$$\ln \frac{K_I}{K_{II}} = \frac{q_I - q_{II}}{RT} \quad . \quad . \quad . \quad . \quad (12)$$

This formula states therefore that the difference in the position of the chemical equilibrium in the two solvents must be attributed to the difference in the total heat of transformation of the substance in the dissolved state, and it at once becomes clear that a difference in the thermal effect of the same reaction in different solvents must be due to a difference in the heats of mixture of the reacting constituents in the different solvents.

Let us now consider the simple transformation

$$A \rightleftarrows B + q;$$

the total heat of transformation q may be resolved into three factors:—

1. The differential heat of disintegration of A, that is to say the heat of mixture with the negative sign, $= -q_{M_A}$;

2. The heat of reaction when one gram-molecule of liquid A is converted into liquid B $= q_R$;

3. The differential heat of mixture of B, $= q_{M_B}$; consequently

$$q = -q_{M_A} + q_R + q_{M_B}.$$

For the total heats of transformation in the two solvents the following expressions are obtained:—

$$q_I = -q_{M_{A_I}} + q_R + q_{M_{B_I}} \quad . \quad . \quad . \quad (13)$$

and

$$q_{II} = -q_{M_{A_{II}}} + q_R + q_{M_{B_{II}}} \quad . \quad . \quad . \quad (14)$$

so that

$$q_I - q_{II} = (q_{M_{A_{II}}} - q_{M_{A_I}}) - (q_{M_{B_{II}}} - q_{M_{B_I}}) \quad . \quad . \quad (15)$$

If now the difference between the heats of mixture of A in the two solvents be called $q_{M_{A_{II-I}}}$ and that of B $q_{M_{B_{II-I}}}$, equation (12) assumes the following form:—

$$\ln \frac{K_I}{K_{II}} = \frac{q_{M_{A_{II-I}}} - q_{M_{B_{II-I}}}}{RT} \quad . \quad . \quad . \quad (16)$$

(*a*) *Hence it appears in the first place that the influence of the solvent on the position of the chemical equilibrium has its origin in the different heats of mixture of the reacting constituents in these different solvents.*

In order to test this conclusion, it will now be sufficient if, in

addition to the equilibrium constants, the heats of solution of the reacting substances in the different solvents are also determined; because the difference between the heats of solution of a substance in different solvents is equal to the difference between the heats of mixture.

This supposition leads to yet another conclusion. It follows from equation (12) that when $K_I > K_{II}$, $q_I > q_{II}$.

If equation (12) is now differentiated with respect to T, this expression is obtained

$$\frac{d \ln \frac{K_I}{K_{II}}}{RT} = \frac{q_{II} - q_I}{RT^2} = \text{negative} \quad . \quad . \quad . \quad (17)$$

(*b*) *This indicates, therefore, that if* $K_I > K_{II}$ *the difference in* $K_I - \ln K_{II}$ *will decrease with increase of temperature,* i.e. *the difference in the equilibrium position in the two solvents becomes smaller as the temperature rises.*

It is almost superfluous to point out that if the assumption in equation (11), namely that $C_I = C_{II}$, is *not* made, by subtracting (10) from (9) the following equation is obtained :—

$$\ln \frac{K_I}{K_{II}} = \frac{q_I - q_{II}}{RT} + C_I - C_{II} \quad . \quad . \quad . \quad (18)$$

which when differentiated with respect to T likewise gives

$$\frac{d \ln \frac{K_I}{K_{II}}}{dT} = \frac{q_{II} - q_I}{RT^2};$$

still, this equation teaches us *nothing*. Only from equation (12) may the conclusion be drawn that when $K_I > K_{II}$ the relationship $q_I > q_{II}$ exists, and this first led to conclusion (*b*).

CHAPTER V

Systems containing a Liquid Crystal Phase

A Brief Discussion.

In the case of commonly occurring crystalline substances the melting point is the temperature at which liquefaction is associated with the disappearance of a definite orientation.

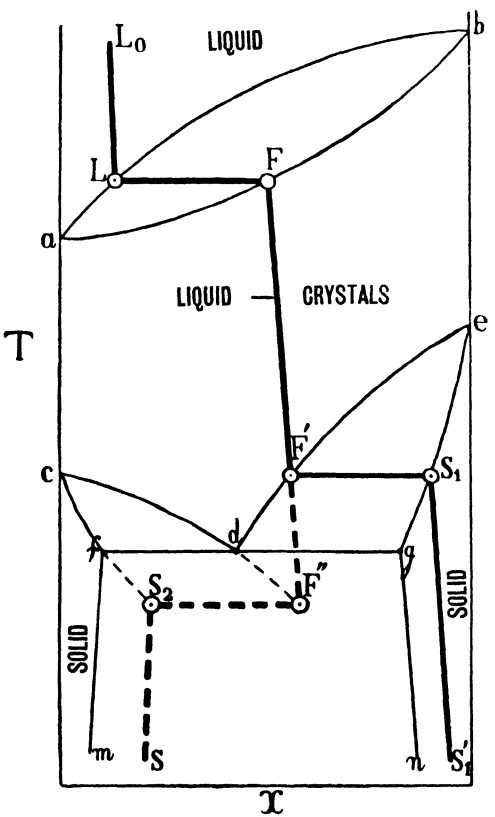


Fig. 88.

Substances which form liquid crystals are, however, peculiar in that the phenomenon of melting takes place in stages; that is to say,

the two processes just mentioned do not occur at the same temperature, but liquefaction first occurs, and afterwards, at a higher temperature, the oriented state disappears. The first point may be called the liquefying- or the de-liquefying-point, whilst the second may be called the de-orientation- or the orientation-point.

Lehmann, to whom we are indebted for the greater part of our knowledge of the liquid crystalline state, has repeatedly emphasised

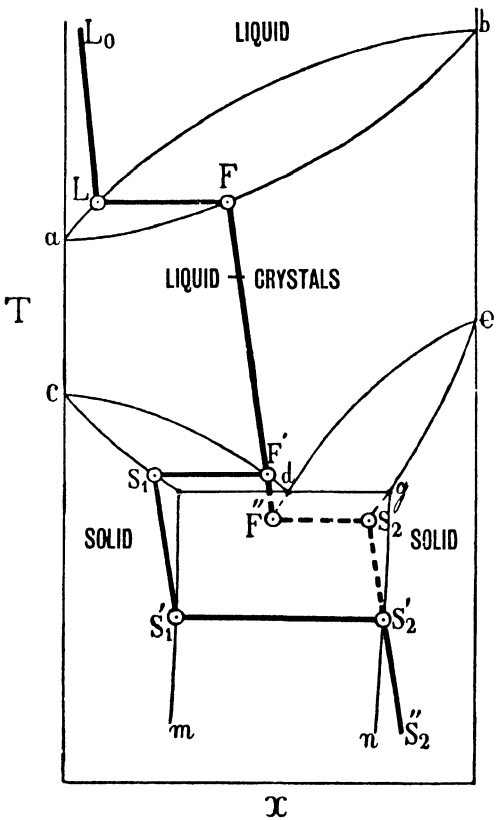


FIG. 89.

that substances which form liquid crystals are of a complex nature. According to the Theory of Allotropy, this is the case for every phase of an allotropic substance, and since allotropy is very general amongst substances which exist as liquid crystals, the above-mentioned theory must also be applicable to these bodies.

It will therefore be supposed that the pseudo-system consists, in the case of substances which form liquid crystals, of at least two pseudo-components, each of which melts in stages, and it will also be assumed that both exhibit the phenomenon of melting in stages.

To commence with, the case will be considered in which the two pseudo-components mix in all proportions in the liquid crystalline state, but are only partially miscible in the ordinary crystalline condition. The following state of affairs is thus obtained (see Fig. 88).

The points *a* and *b* are the orientation-points and *c* and *e* the crystallising-points. The existence of a eutectic has been assumed in the crystallisation diagram. The heavy lines relate to the unary system,

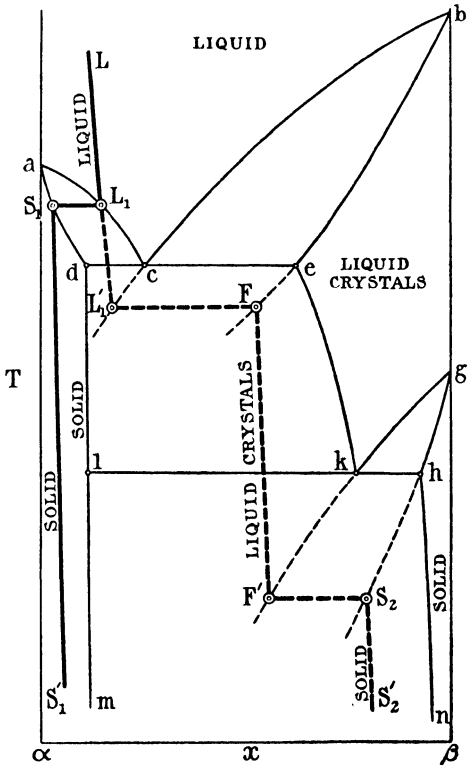


FIG. 90.

and from them it is seen that the liquid phase L deposits the liquid crystalline phase F, and that the latter has its stable crystallising-point at F′ and its metastable crystallising-point at F″, so that in the ordinary crystalline state the system is allotropic, and indeed monotropic.

When enantiotropy occurs in the usual crystalline state the diagram will resemble Fig. 89.

Now it may also happen that one of the pseudo-components melts in stages, whilst the other does not. This possibility is illustrated in Fig. 90, in which *a* represents the melting point of the pseudo-component α, while *b* and *g* indicate the orientation- and crystallising-

points respectively of β. Here again the pseudo-figure is drawn faintly and thus d, c, e represents the three-phase equilibrium between a solid, a liquid and a liquid crystalline phase, whilst l, k, h indicates the co-existence of a liquid crystal phase (k) and two phases (l and h) which possess the ordinary crystalline structure. The heavily drawn lines show that when the behaviour is unary the ordinary solidifying point

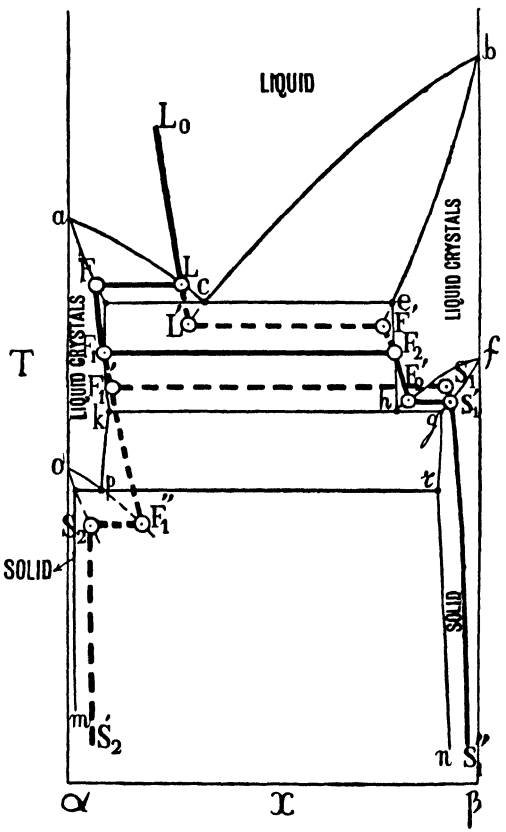


FIG. 91.

appears at L_1 and the stable solid phase S_1 is formed. At L_1' the super-cooled liquid passes into the liquid crystal phase F, which has its crystallising point at F', and which is transformed there into the metastable modification S_2, which forms crystals of the ordinary type. Thus, as regards its unary behaviour, as has already been observed, the substance exhibits a liquid crystal phase in the metastable state.

The case will now be considered in which the pseudo-components are also miscible, to a limited extent only, in the liquid crystalline state. If the pseudo-components lower the orientation- and crystallising-points

of each other, Fig. 91 may arise. The peculiarity of this diagram lies in the appearance of a transition point in the liquid crystalline state, represented by the points F_1 and F_2, below which at F_2' crystallisation occurs and the solid phase S'_1 is formed. Here, however, a second peculiarity may be distinguished, consisting in the fact that if the transition point in the liquid crystalline state fails to appear, at F''_1 a metastable crystalline modification S_2 will be deposited from the first metastable liquid crystal phase.

From this short discussion it follows that these new views may be applied without difficulty to systems containing liquid crystal phases.

CHAPTER VI

PHENOMENA WHICH MAY BE PREDICTED FROM THE THEORY OF ALLOTROPY

1. General Considerations.

ACCORDING to this theory an inner equilibrium exists in every unary phase of an allotropic substance, which, speaking generally, changes with temperature, pressure, etc.

If the pressure is kept constant and the temperature is changed, it will naturally depend on the velocity with which equilibrium is established and on the rate of change of the temperature whether for practical purposes inner equilibrium always exists.

If the temperature changes so rapidly that the inner equilibrium cannot adjust itself to it, inner equilibrium is not realised but disturbed conditions are obtained, which are naturally metastable, and the properties of which, *e g.* specific gravity, refractive index, viscosity, specific conductivity, solubility, transition point, melting point, boiling point, critical point, etc., deviate from those of the equilibrium state.

The same considerations naturally hold good when the pressure is varied at constant temperature, and also when both temperature and pressure are simultaneously changed.

2. Displacement of the Solidifying and Melting Points in consequence of the Retarded Establishment of Inner Equilibrium.

Let it be supposed that a liquid p, Fig. 92, is cooled rapidly under constant pressure; then, if the rate of cooling is sufficiently great, the liquid will not follow the equilibrium line $p\,L_2$, but some other line, for example $p\,L_3$. If this liquid, which is not in inner equilibrium, can be cooled below the melting line of the pseudo-binary system, it will, in addition, be metastable in the pseudo-binary sense. If for the sake of simplicity the assumption is here made that no appreciable retardation occurs in the pseudo-binary system, the substance will commence to solidify at L_3, *i. e.* at too low a temperature, and if no internal transformation takes place during solidification a solid phase is formed, having the composition indicated by the point P.

During solidification, however, the temperature changes to a much less extent than during the cooling of the liquid phase, and hence a certain amount of internal change must be assumed to take place in the course of solidification. If this assumption is made, the total composition of the system will be displaced during this process along

the line $L_3 S_3'$, so that $L_3' S_3'$ represents the solidification end-point, and consequently when solidification is complete a solid phase, having the composition S_3', is formed. From this point the temperature again falls rapidly, and here, according to our hypothesis, internal transformation is again practically completely suspended.

It must be particularly emphasised here that the retarded solidification which occurs in the case of slow lowering of the temperature is quite a different phenomenon. This is the more easily recognised because inner equilibrium in the liquid phase may be realised over a certain range of temperature, which lies below the unary solidifying temperature, and consequently in the supercooled unary liquid (see

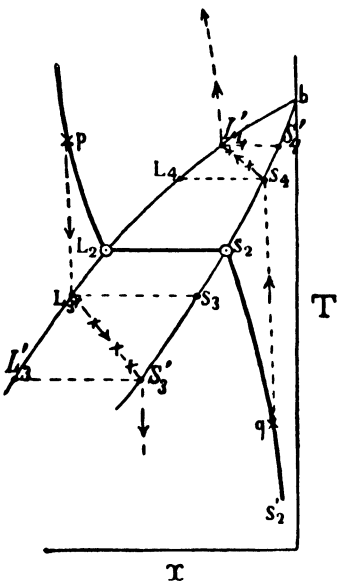


FIG. 92.

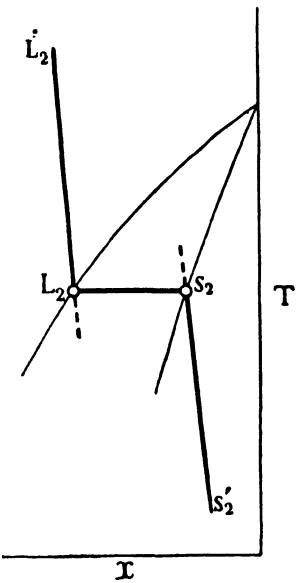


FIG. 93.

Fig. 93). Hence we are not concerned here with a retardation of the inner equilibrium, but with retardation of the *heterogeneous* equilibrium.

This retardation of the heterogeneous equilibrium always leads to displacement of the initial solidifying point in the direction of lower temperature. If now, as is here assumed, retarded establishment of the inner equilibrium is likewise associated with a lowering of the temperature at which solidification begins, a special method of procedure must be employed in order correctly to explain the observed phenomenon. When the retardation affects the heterogeneous equilibrium only it may be corrected by inoculation. If, on the other hand, the observed retardation has its origin in a displacement of the inner equilibrium, the liquid below the solidifying point is not undercooled, as is clear from Fig. 92, and consequently crystallisation cannot be

induced by inoculation. Inoculation thus provides a means of investigating to which type the observed depression of the solidifying point belongs.

If the solid inner equilibrium q is taken as the starting point, when this solid phase is heated so quickly that the inner equilibrium is unable to adjust itself to the temperature, according to Fig. 92, fusion commences at a higher temperature than that of the unary melting equilibrium.

In the diagram fusion begins at S_4; if as a result change takes place in the direction of the establishment of inner equilibrium, the total composition will change to correspond with the line $S_4 L_4'$, and therefore at L_4' the fusion of the solid is just complete. Thus the initial melting point is indicated by the line $S_4 L_4$, and the temperature at which fusion is complete by the line $S_4' L_4'$.

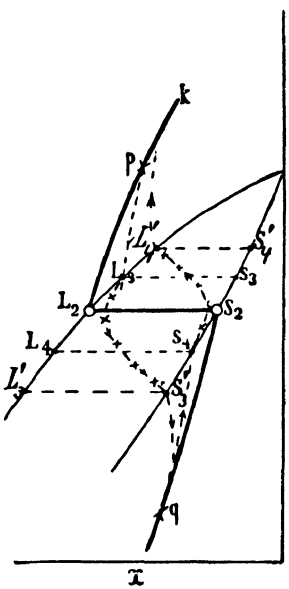


FIG. 94.

Now it is also conceivable that when the substance is gradually heated liquefaction first occurs at a temperature above that of the unary melting point. If this happens it should be possible in Fig. 93 to proceed along the metastable prolongation of the inner equilibrium line $S_2' S_2$ without fusion occurring; this would furnish an example of supersolidification. Such a retardation has never been established with certainty in the case of heterogeneous equilibrium in a unary system, and furthermore it will not be easy to realise. As a rule heterogeneous equilibria are not retarded in this direction, and this, so far as gradual heating is concerned, may easily be demonstrated. If, therefore, it is found that when heated quickly the substance begins to melt at a higher temperature than the unary melting point, this phenomenon points to retarded establishment of the inner equilibrium, and the T X diagram will occupy some such position in the pseudo-binary system as is indicated in Fig. 92.

The case is more interesting when the position of the inner equilibrium line is as outlined in Fig. 94. The peculiarity in this case is that when cooled rapidly the liquid p solidifies over the temperature range $L_3 S_3$ to $L_3' S_3'$, and the initial solidifying temperature thus lies above that of the unary solidification equilibrium $L_2 S_2$.

When the solid phase q is heated rapidly the substance melts, strange to say, over the range of temperature $S_4 L_4$ to $S_4' L_4'$, and the initial melting point thus lies below the temperature of the unary fusion equilibrium.

From the consideration of Figs. 92 and 94 it follows, therefore, that *absolutely pure* substances may melt or solidify over a range of temperature when they are heated or cooled relatively quickly, and this, in all probability, frequently happens in the case of organic substances, in which, generally speaking, inner equilibrium is only slowly established.

3. Displacement of the Transition Point by Rapid Change of Temperature.

The change in the transition temperature may be immediately understood from Fig. 95 in conjunction with the foregoing discussion.

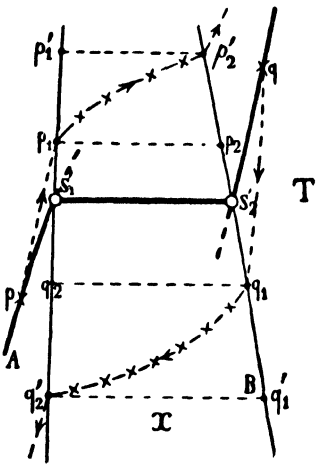


FIG. 95.

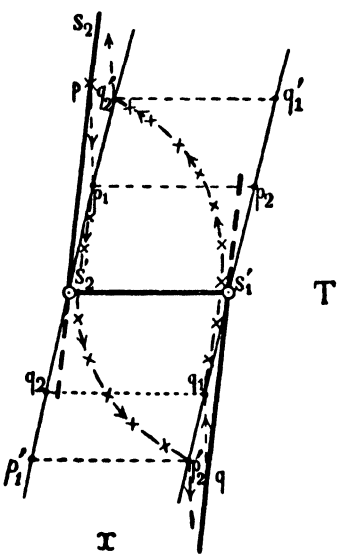


FIG. 96.

In this connection it should be noticed, however, that if the transition point can also be overstepped without a change of phase setting in when the temperature is very slowly changed, so far as unary behaviour is concerned, this is evidence of retardation in the heterogeneous transformation. If the position of the unary T X diagram is assumed to be that represented in Fig. 95, retarded establishment of the homogeneous inner equilibrium would lead qualitatively to the same result as retarded establishment of the heterogeneous equilibrium, *i.e.* both phenomena cause the temperature at which the transformation process begins to be displaced in the same direction. In this case, in order finally to decide whether the observed displacement is at least partly due to retarded establishment of the inner equilibrium, further experiments are necessary. Thus different inner equilibrium states, situated a little above or below the unary transformation equilibrium, may be taken

as starting points, and the question investigated whether, when the temperature is rapidly changed, these differences exert any influence on the initial transition temperature. If this should prove to be the case it is evidence of retardation in the establishment of inner equilibrium.

If, however, Fig. 96 represents the position of the T X diagram in the pseudo-figure, retarded establishment of the heterogeneous equilibrium exerts a contrary influence to that exerted by a retarded establishment of the inner equilibrium. That is to say, the latter gives rise to too high an initial transition temperature when the direction of the temperature change is from higher to lower temperatures, and to too low an initial transition temperature when the temperature changes in the opposite direction. If this phenomenon is observed, this fact alone furnishes definite proof of the complexity of the system, and that the relative positions are such as are here indicated.

4. Change of Vapour Pressure in Consequence of Rapid Evaporation.

Another phenomenon which may here be mentioned is the following: Let it be supposed for a moment that a solid or a liquid phase is

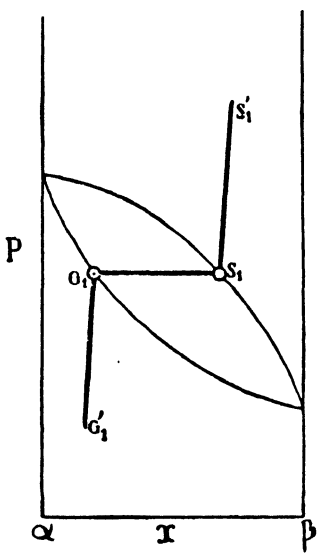


FIG. 97.

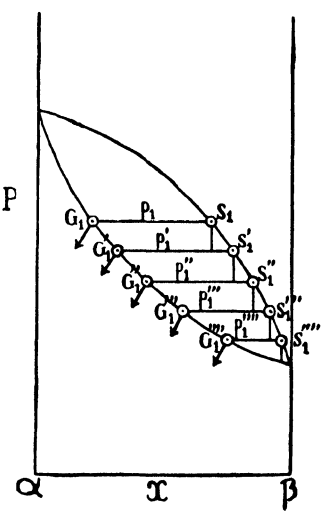


FIG. 98.

rapidly evaporated in a vacuum, at so low a temperature that the inner equilibrium only adjusts itself slowly. If now the accompanying P X diagram, Fig. 97, holds good at the assumed temperature, and if S_1 represents the solid phase which, in the unary system, is in equilibrium with its vapour, it may be demonstrated that if the vapour G_1 is

removed, provided the behaviour of the system remains unary, a new vapour of the same composition will be formed, in which, as well as in the solid phase, the reaction $\beta \rightarrow \alpha$ takes place. As a result of this reaction the solid phase retains the same composition and vapour pressure.

If, however, evaporation is allowed to take place, as was originally assumed, at such a temperature that the possibility of unary behaviour is excluded, fractional evaporation will occur, and as a result of the continual removal of the vapour phase, the residual solid phase gets richer and richer in the less volatile pseudo-component β.

Thus, as Fig. 98 shows, the vapour pressure will continuously diminish. Whilst the pressure falls from p_1 to p_1'''', the composition of the solid phase changes from S_1 to S_1''''.

5. Change of Solubility in Consequence of Rapid Solution.

If, for the sake of simplicity, it is again assumed that a solid phase consisting of two pseudo-components is brought into contact with a solvent, a saturated solution will be formed in which the pseudo-components are in equilibrium with each other, in a concentration ratio which in general does not correspond with that which prevails in the inner equilibrium in the solid phase.

If the position is as indicated in Fig. 99, the ratio in the solution L_2 is $\frac{\beta N}{\alpha N}$; in the stable modification S_2, however, the ratio is $\frac{\beta S_2}{\alpha S_2}$.

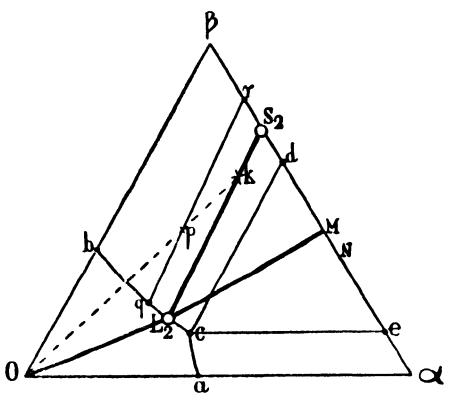


FIG. 99.

If we now imagine so much solvent O to be added to the two-phase system $S_2 + L_2$, the total composition of which is given by the point *k*, that the total composition becomes equal to *p*, the point *p* will lie on the *nodal line qr*. This means that the co-existing phases in the pseudo-system having this total composition are *q* and *r*. Hence it follows that instead of the original phases S_2 and L_2, if solution has been sufficiently rapid, the phases *q* and *r* are now obtained, *i.e.* the solid phase has become poorer in that pseudo-component which was present in greater concentration in the co-existing liquid solution than in the mixed crystals.

When inner equilibrium is only slowly established, therefore, the solubility of the solid substance can be changed by the continual addition of fresh solvent.

6. The Order in which New Phases are Formed. Ostwald's Law of Successive Transformations.[1]

Frankenheim[2] in 1836 first pointed out that when the vapour of a pure substance is cooled down, the nature of the phases which separate out is not solely dependent on the temperature; for example, it cannot be stated that the new phase will be solid or liquid according as the temperature lies above or below the melting point. Thus it frequently happens that, although the temperature lies below the melting point, instead of a solid phase a liquid separates out; *e.g.* phosphorus vapour when cooled down to 20° C. deposits a supercooled liquid phase, and not the solid white modification.

This behaviour corresponds with another phenomenon which has been observed by a number of investigators, namely that supersaturated solutions, from which a variety of substances may crystallise, frequently deposit the most soluble of these substances first.

This phenomenon also occurs when the supersaturation is not the result of cooling down in the usual way, but is brought about by the addition of a second solvent in which the substance is less soluble. If, for example, water is added to a solution of mercuric iodide in methyl alcohol, as Bancroft[3] observed, the yellow modification separates out at ordinary temperatures; of these two forms (yellow and red) this is the metastable variety and consequently the more soluble.

This behaviour led Bancroft to write: "It appears as if the generalisation might be made that when sudden precipitation occurs the least stable form is the first to appear."

Ostwald[4] showed from Frankenheim's observations that similar phenomena also occur when the change in the state of aggregation is accompanied by a chemical process. In this connection Ostwald refers to phosphorus. He recalls that phosphorus vapour does not condense directly into the stable modification, red phosphorus,[5] but that it passes first of all into a liquid, and from this into the yellow modification. In the same way the vapour of cyanic acid yields on condensation metastable liquid cyanic acid.

Ostwald met with similar phenomena in the case of chemical changes, and as a result he became convinced that such changes must obey some law. This law he called the *Law of Successive Transformations,* and he stated it in the following terms: "When a given chemical system is left in an unstable state, it tends to change not into the most stable form, but into the form the stability of which most nearly resembles its own; *i.e.* into that transient or permanently stable modification whose formation from the original state is accompanied by the smallest loss of free energy."

[1] Smits, *Zeitschr f. physik. Chemie*, **84**, 385 (1913).
[2] *Pogg. Ann.* **39**, 380 (1836).
[3] *Journ. Physik u. Chemie*, **1**, 142 (1896).
[4] *Zeitschr. f. physik. Chemie*, **22**, 306 (1897).
[5] It was not known at that time that the *violet* modification is the stable form of phosphorus.

The introduction to this section has been extended to some length in order to show that in spite of repeated investigation the phenomena here dealt with still remain entirely unexplained.

Unfortunately, however, even at the present day it is still impossible to treat this problem in an exact manner, and consequently the following *very vague* indications are given with some hesitation. It has been decided to include them because they may serve to point the *direction* in which, in my view, the explanation is to be found.

Two cases must here be distinguished, for the new phase may be formed in two different ways. In the first place, it may appear as the result of *slow cooling or some other slow process*, and secondly it may be formed by *suddenly cooling* a vapour, or by the addition of a liquid to a solution, whereby the dissolved substance is *suddenly* precipitated. To the latter case, without doubt the simpler, the term *fixation* may be applied.

The less simple case will, however, first be considered. According to the Theory of Allotropy different phases have different compositions. The appearance of phases having definite compositions proves, however, that of *all the possible* compositions *these* are most favoured. In the following consideration it is assumed that this favouring tendency has its origin in the mother phase, *i.e.* in the phase from which the new phases may be deposited. In so doing use is made of an assumption, due to Boltzmann and employed by Reinganum, but which has been applied more especially by van der Waals to explain deviations from the equation of state. Reference is here made to the idea of pseudo-associations (Schein assoziationen).

Pseudo-associations are molecular aggregations or complexes consisting of a number of molecules which may vary within narrow limits. For example, a pseudo-association containing ten molecules on the average may at one moment contain eight, at another moment twelve molecules.

If, now, the conception of the pseudo-association is introduced into the Theory of Allotropy, it is but a step to the assumption that the pseudo-associations may be built up from different molecular species, and that consequently pseudo-associations of every possible composition must exist.

As has already been stated, the appearance of phases of different compositions points to the fact that definite compositions are favoured. A further step can now be taken, and we may recognise in the pseudo-associations the materials from which those nuclei are built up which give rise to the formation of new phases; *i.e.* it is assumed that the tendency in favour of certain compositions has already manifested itself in the formation of the pseudo-associations. In other words, it is assumed *that every phase is prepared for the formation of possible new phases, and that this preparation becomes apparent in molecular complexes or pseudo-associations.*

If as a first very simple example the case is considered of a gas which is cooled under a constant pressure greater than the triple point pressure, the following conclusions may be drawn: If in Fig. 100 *a* G *b*

and $a\,L\,b$ represent the vapours and liquids which co-exist with each other in the pseudo-binary system, and if $G_0\,G$ represents the inner equilibrium in the gaseous phase and $L\,L_1$ the inner equilibrium in the liquid phase, this diagram shows that under the pressure assumed here, and so far as unary behaviour is concerned, the vapour G will condense at the temperature $t°$, at which point it passes into the liquid L. It is now assumed that in the vapour G pseudo-associations of every possible composition are present. It is then evident from the diagram that two of these compositions correspond with a state of inner equilibrium, and this means that, as regards molecular effects, these, of all the possible compositions, will be most favoured. Hence it may be concluded that, as compared with the others, pseudo-associations of these two compositions are also favoured. Consequently if the concentration of the pseudo-association is represented as a function of the composition, a

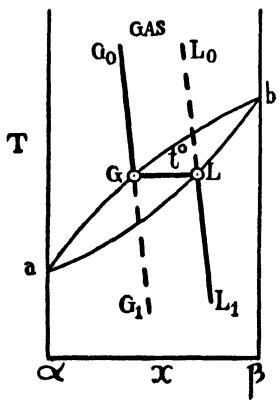


FIG. 100.

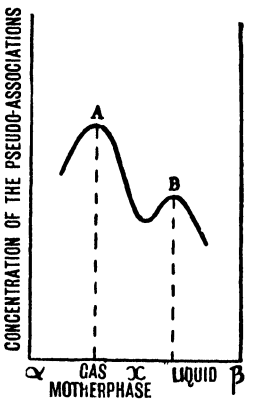


FIG. 101.

curve containing *two* maxima may be expected. As regards the relative heights of these maxima it is probable that one maximum will be so much the lower the more the composition corresponding to it deviates from the composition of the mother phase. The pseudo-association, having the same composition as the mother phase, is therefore present in the greatest concentration. The graphical expression of these considerations gives rise to Fig. 101. If this diagram holds good for the condensation temperature $t°$, the second maximum B corresponds to a liquid phase, and on condensing the gas the A pseudo-associâtions will undergo transformation into pseudo-associations of the type B to such an extent as is characteristic of the liquid state.[1]

Similar curves are obtained for higher temperatures, and hence it follows that in any gas conditions are met with which may be considered to be preparatory to the formation of the liquid phase.

[1] It is clear that in general the composition of the co-existing phases will not be in complete agreement with the x values of the maxima, but for the sake of simplicity this will not be repeatedly and expressly emphasised here.

The positions of the maxima are displaced by changes of temperature; thus the position of the maximum A changes as the temperature changes because the inner equilibrium in the gaseous phase varies with the temperature, and since the two maxima are undoubtedly connected with each other, the position of the maximum B will also undergo change. When the temperature is reduced the maxima will rise, for theoretically a fall in temperature must result in an increased formation of pseudo-associations.[1] If the position of the maximum B at different temperatures is introduced into the T X diagram, Fig. 100, the dotted line $L_0 L$ is obtained, whilst the maximum A is displaced along the line $G_0 G$. The conditions which hold good for the gaseous phase are also applicable, of course, to the liquid phase, and so it must be assumed that the pseudo-association curve for the liquid L, boiling at $t°$, exhibits two maxima, of which the higher A now has the same composition as the liquid L, as is shown in Fig. 102. As the temperature is reduced the maximum A is displaced along the line $L L_1$, Fig. 100, and the maximum B along the dotted line $G G_0$.

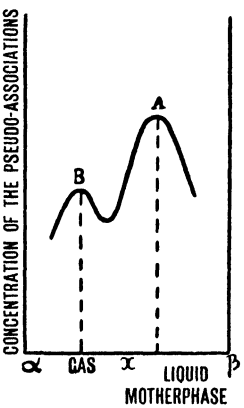


FIG. 102.

Whether the dotted lines are connected in any way with the curve relating to the continuity of the gaseous and liquid states is beyond the present discussion.

If the gas is now cooled down under a constant pressure somewhat lower than the pressure at the triple point, the line relating to the inner equilibrium in the stable gaseous phase meets the pseudo P T X diagram in a vapour surface which co-exists with a solid phase. If, however, the separation of the solid is delayed, the line under discussion will be realisable beyond this point, and plunging deeper into the diagram, it ultimately meets, at a lower temperature, a second and now metastable vapour surface belonging to a liquid which is likewise metastable.

One of the possible positions for this case has already been indicated in the section given in Fig. 36, but this diagram is somewhat complicated because the pressure there considered is higher than the triple point pressure of the pseudo-component β. If, on the other hand, the pressure is imagined to be lower than the vapour pressure of this pseudo-component, Fig. 103, which is of particular interest here, is obtained.

The inner equilibrium moves along the line $G_0 G$ and at $t°$, provided no retardation occurs, the solid substance S is deposited. If, however, the separation of this substance is delayed, at $t_1{}^0$ the liquid L

[1] If an association of pseudo-associations is also possible, it is necessary to employ a triangular system of co-ordinates, and consequently Fig. 101 no longer gives a clear indication of the state of affairs.

appears, and this phase has a different inner equilibrium from that of the solid substance S.

In order to explain this behaviour, let it be assumed that the

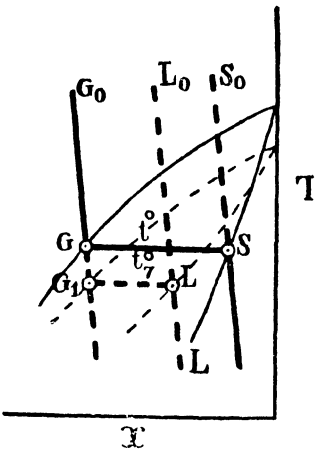


FIG. 103.

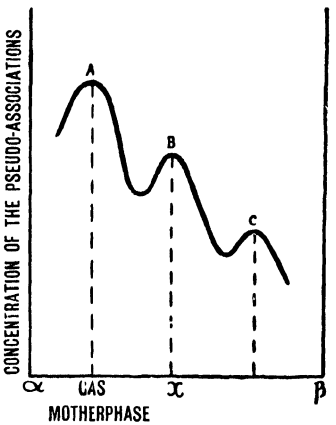


FIG. 104.

concentration curve for the pseudo-associations contains not two but three maxima, and that at the temperature $t°$ the third maximum

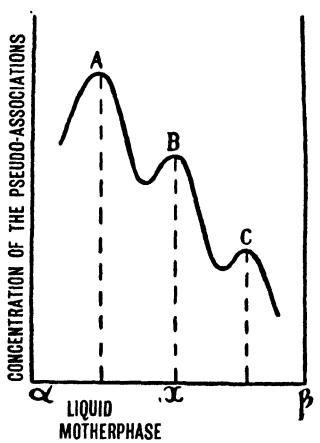


FIG. 105.

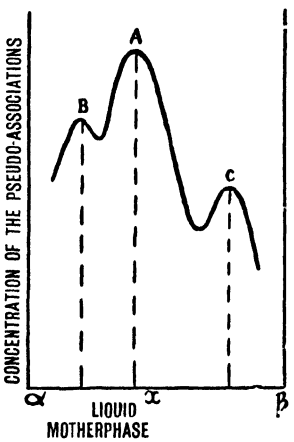


FIG. 106.

corresponds to the composition of the solid phase S. A curve is then obtained of the form indicated in Fig. 104. The maximum A is situated at the composition of the inner equilibrium in the gaseous

phase, B lies at the composition of the unary liquid, and C corresponds to the composition of the unary solid phase.

The case will now be considered in which two solid substances may separate out from a liquid when it is cooled under constant pressure.

It must then be assumed that the pseudo-association curve for this liquid exhibits three maxima. As regards the positions of these maxima it should be noticed, however, that two cases may arise. Both the solid phases lie on the same side in relation to the liquid, as in the case of systems the pseudo-components of which are *polymers*, this is also the case as regards the maxima B and C (see Fig. 105). If, however, the

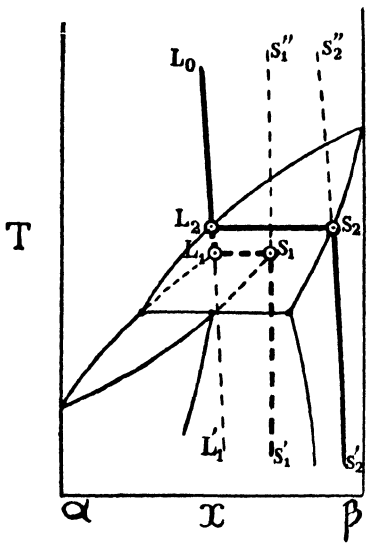


FIG. 107.

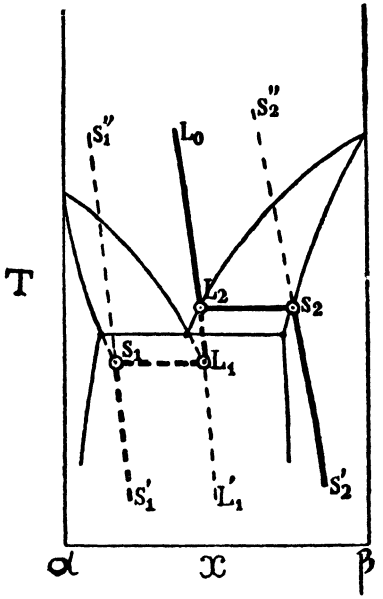


FIG. 108.

pseudo-components are *isomers*, the solid phases may not only both lie on the same side, but they may also be disposed on either side of the liquid line, and the two maxima will then be situated one on each side of A, as in Fig. 106. The maxima B and C are displaced by variations of temperature at constant pressure in the same direction as A, and at the solidifying point of each modification the corresponding maximum is situated at the composition of the solid phase concerned.

The lines relating to pseudo-associations are also shown in the T X diagrams, Figs. 107 and 108.

As has been stated, pseudo-associations may be looked upon as preparatory to the formation of new phases, and consequently the question must now be answered as to how the formation of a solid phase from these pseudo-associations may be imagined. This question

may be provisionally answered in the following way. It is known that the kinetic state of the molecules changes as the result of change of temperature, and the pseudo-associations may be expected to behave in a similar way; now at a certain definite temperature, the solidifying point, this kinetic state and the density become such that orientation may suddenly occur, and crystallisation then follows.

The pseudo-associations in which orientation has begun are called *nuclei*, by which we mean the points from which crystallisation commences and afterwards proceeds with a greater or less velocity depending on the temperature. As Tammann [1] has already pointed out, it depends mainly on the nuclear number which of the possible solid phases will first be deposited from a supercooled liquid. It may here be recalled that the *nuclear number* for a liquid at a given temperature denotes the number of nuclei formed in a given time in a definite volume when the liquid is suddenly cooled from a temperature above the solidifying point to the temperature at which the nuclear number is required and which lies below the solidifying point.

It must now be assumed that when the nuclear number exceeds a certain limit the metastability of the liquid becomes so great that *spontaneous* crystallisation occurs. This limit may be called the critical nuclear number. The question may now be asked, What conclusions can be drawn from this conception of the nuclear number?

The above considerations lead to the assumption that the nuclear number is proportional to the concentration of the pseudo-associations, and that therefore we may write:—

$$K = fC$$

where K is the nuclear number, C the concentration of the pseudo-association, and f is a factor of proportionality or the orientation constant which is dependent only on the temperature. It should be kept in mind, however, that, according to Tammann, when represented as a function of the supercooling, the nuclear number passes through a maximum. These facts may now perhaps be explained in the following way. Theoretically, pseudo-association increases as the temperature falls, and consequently the concentration C of the pseudo-associations will increase when the temperature is reduced. If, now, it is assumed for a moment that the orientation velocity diminishes as the temperature falls, f and C will vary in opposite directions. If C predominates at the commencement, which always appears to be the case, as the temperature is reduced, K will increase at the outset. In all probability, however, temperature exerts a very great influence on the value of f, and, as in the case of every reaction, it will finally become the most important factor; thus the appearance of a maximum in the nuclear number can be readily understood.[2] It is evident without further discussion, as Tammann has already conjectured, that the

[1] *Zeitschr. f. physik. Chemie*, **25**, 422 (1898); see also *Krystallisieren und Schmelzen*.

[2] It is also possible, however, as will be emphasised later, for f to exhibit this course.

viscosity, which increases as the temperature falls, often becomes an important factor.

If, now, in accordance with the assumption which has been made, a liquid deposits two solid phases, it will depend on the expressions

$$K_{S1} = f_1 C_B$$

and

$$K_{S2} = f_2 C_C$$

which modification will first spontaneously crystallise.

But, as has been seen, spontaneous crystallisation first occurs when the critical nuclear number is reached, and this critical nuclear number will vary for different modifications. *If, however, at a given moment the existing nuclear numbers are widely different, it may be stated with a high degree of probability that the modification having the greater nuclear number will first be deposited.*

Before proceeding further with this explanation, however, the factor f must be considered rather more closely.

This factor is probably quite different in character from a reaction velocity constant, and so it is possible that as the temperature falls, even below the solidifying point, it first increases, reaches a maximum value and then diminishes. Only the final fall seems certain.

As regards the factor f for the pseudo-associations of different modifications, it can only be stated that the greater the difference between the solidifying points of the two forms, the greater will be the probability that the value of f for the modification having the higher solidifying point will be least at a point slightly below the solidifying point of the form having the lower melting point.

It follows, further, that the pseudo-association concentration of the modification the composition of which most nearly approaches the composition of the liquid will exceed the concentration of the pseudo-associations corresponding to the other modification. Even though the factor f is disregarded, the result is arrived at that the nuclear number of the modification whose composition approximates most closely to the composition of the liquid first attains its critical value, and consequently this modification is deposited.

However, both the factor f and the critical nuclear number are here determinative, and hence, for the present, it is only possible to suggest a probable rule. The more the compositions of the different pseudo-associations differ from one another, the greater will be the difference between C_B and C_C, and the less will be the effect of differences in the values of f.

Taking these considerations as a basis, therefore, the following rule is obtained. *If the modifications of an allotropic substance differ widely, as regards their compositions, from a liquid which is supercooled with respect to the different modifications, that modification will, as a rule, first spontaneously separate out the composition of which most nearly approximates to the composition of the liquid.*

Only when the solidifying points of the different modifications are also

widely separated can the difference in the values of f exert a predominating influence, and in special cases this difference may cause the deposition to follow a different order.

According to this statement of the Law of Successive Transformations, which differs entirely from Ostwald's wording, it will often happen that the modification whose composition lies nearest to the composition of the liquid is the stable and not the metastable form; consequently, the phenomena observed will then be the exact reverse of what, according to Ostwald, should be expected.

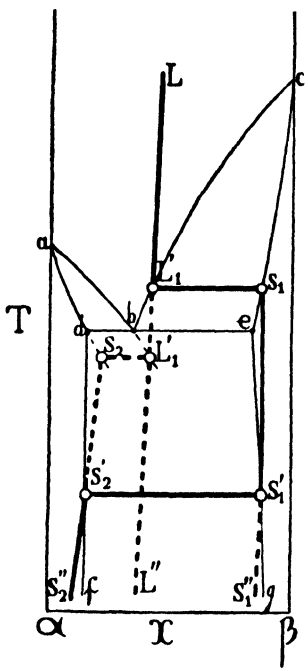


FIG. 109.

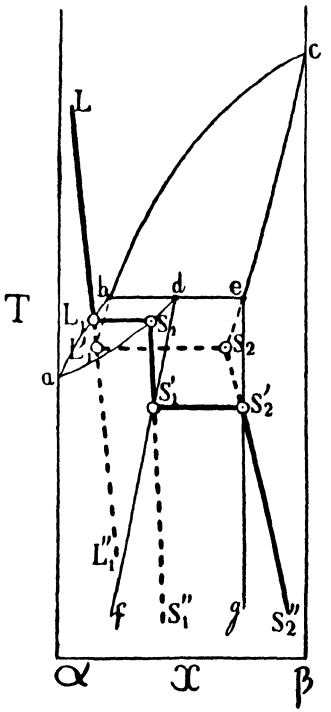


FIG. 110.

This result will be further illustrated by means of T X diagrams.

Fig. 109 shows that above the transition temperature and below the metastable unary solidifying point the metastable modification approximates most closely in composition to the liquid, whilst below this point exactly the reverse is the case. In this instance, therefore, at temperatures higher than the transition point, as a rule the metastable form will first separate out; below the transition point, however, the stable form will first make its appearance.

When the position is as outlined in Fig. 110 these relationships are reversed. From these examples the difference between Ostwald's formulation of the Law and that given here can clearly be seen.

The case must now be considered in which the vapour is assumed to be the mother phase and the pressure is supposed to lie below the triple point pressure of the modification having the lowest melting point. On cooling, either the stable solid phase, the metastable solid phase, or the metastable liquid phase may be deposited first.

In order that this case may be adequately treated, condensation and sublimation nuclei must also be discussed; according to the point of view adopted here these nuclei consist of pseudo-associations the kinetic state and density of which either correspond with or approximate very closely to these values for liquid or solid phases. These nuclei are formed at constant pressure when the temperature is lower than the boiling point, and at constant temperature when the pressure exceeds the pressure of the saturated vapour. In this case, therefore, the three following expressions must be considered:—

$$K_L = f_L C_L,$$
$$K_{s_1} = f_{s_1} C_{s_1},$$
$$K_{s_2} = f_{s_2} C_{s_2}.$$

Here again f_L, f_{s_1}, and f_{s_2} are velocity constants relating to nucleus formation, and they are doubtless temperature functions. But at the present time nothing is known as to how these velocities vary as the temperature falls. All that is known is, that the velocity of condensation or of sublimation is always very great, so that the quantities K_L, K_{s_1}, and K_{s_2} always reach their critical values very rapidly.

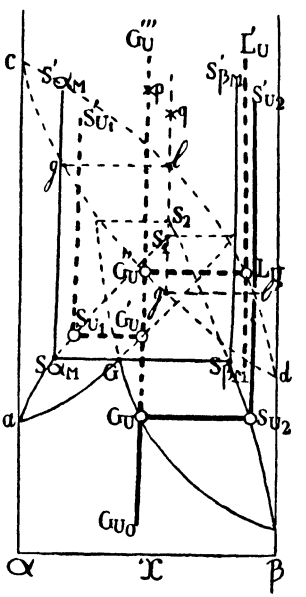


FIG. 111.

It might be thought, since the formation of condensation nuclei appears to be simpler than the formation of sublimation nuclei, for in the latter case adjustment of the molecular motion is necessary, that the formation of the liquid phase will always be favoured.

This is highly probable, and consequently it will be advisable to pay particular attention to this possibility.

In order that a rule may be deduced, however, the circumstances must be so chosen that the factors f_L, f_{s_1}, and f_{s_2} can exert the least possible influence, and this will be the case when the concentrations of the pseudo-associations are widely different, or, in other words, when the liquid phase and the solid modification differ considerably from one another in composition.

Thus the following rule is obtained and is found to be in agreement with the foregoing considerations.

When the phases which may be formed from the supersaturated vapour

differ markedly from one another in composition, that phase will first appear the composition of which most nearly approaches to the composition of the vapour.

If, however, the differences in composition are small, in consequence of preferential nucleus formation liquid will as a rule first be formed,

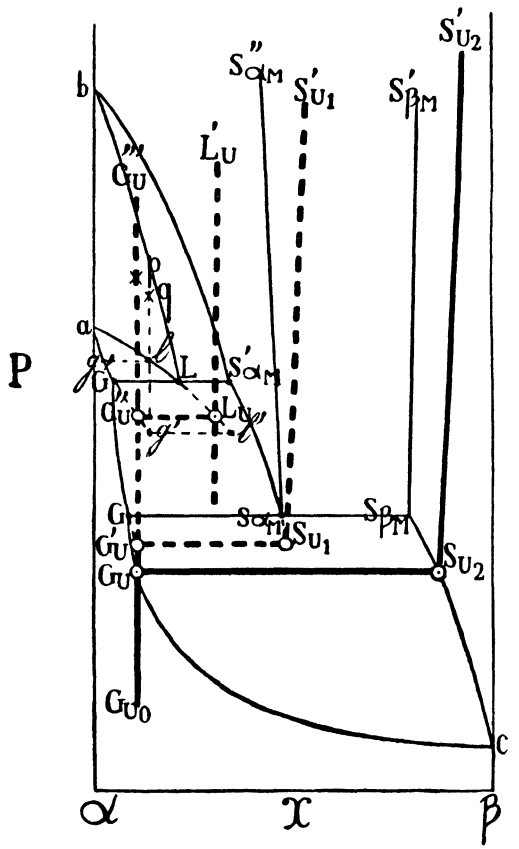


FIG. 112.

and this liquid may remain for some time. If the liquid phase is obtained first the rule already given will apply to this case.

Before proceeding further these results will be illustrated by P X diagrams.

If the pseudo P T X diagram contains a eutectic line and if, for example, a P X section is considered corresponding to a temperature slightly below the metastable melting point under the vapour pressure (see also Fig. 26), this diagram will furnish information as to what will happen when a supersaturated vapour phase is transformed. In

order to make the matter quite clear, only that portion of Fig. 26 which is of interest here has been reproduced in Fig. 111.

Let us now imagine a vapour phase to be supersaturated in respect to both the solid phases and also the liquid phase. This supersaturated vapour phase, which will be supposed to be in inner equilibrium, is denoted, for example, by the point *p*. When this phase undergoes transformation, its behaviour being unary, various two-phase systems may be formed. In the first place the metastable liquid phase L_u may separate out, so giving rise to the metastable two-phase system L_u G_u''; the metastable solid phase S_{u_1} may, however, be deposited, in which case the metastable two-phase equilibrium $S_{u_1} + G_u'$ is formed, and finally the stable solid phase S_{u_2} may appear, as a result of which the stable two-phase equilibrium $S_{u_2} + G_u$ is established. Previous considerations now justify the statement that the metastable solid phase will probably be deposited first, for this phase approximates most closely by far to the composition of the vapour. The case will now be investigated in which the P T X space model contains no eutectic line, as, for example, in Fig. 51. If now a P X section is again chosen at a temperature t_2 which lies below the metastable unary melting point under the vapour pressure of the system, the position illustrated in Fig. 112 is obtained.

Next, let us investigate the vapour *p* which is supersaturated with respect to the stable solid, metastable solid and the metastable liquid phases. The liquid phase here approaches most nearly to the composition of the vapour, and therefore the metastable liquid phase L_u will first be deposited. The order in which the solid phases appear may be determined as follows. Both solid phases lie on the same side of the liquid phase, but the metastable solid phase S_{u_1} is by far the nearer, and so separation of the metastable solid phase may be expected first. This will be the more probable the greater the difference between the solidifying temperatures, for in that case so much the greater will be the chance of the metastable modification having the higher *f* value.

The less simple case, *i.e.* that of *slow* cooling, has been considered first because it necessitated the introduction of a new hypothesis, namely that every phase is prepared, in consequence of the existence of pseudo-associations, for the formation of possible new phases. As regards this extension of the discussion, it is at present only possible *broadly* to indicate the order in which the crystallisation of allotropic systems occurs, and even to-day we are obliged to content ourselves with this result, for our knowledge of the internal condition of supercooled liquids and supersaturated vapours has not yet advanced sufficiently far for an exact elaboration and proof of any hypothesis in this field to be possible.

(a) *The sudden cooling of a vapour.*

The processes which occur in consequence of the sudden cooling of a vapour are much simpler to treat, especially if it is supposed that the phases thereby caused to separate out are fixed as regards their total composition.

If the vapour of a substance belonging to the pseudo-binary type is suddenly cooled down in a closed vessel so that the vapour becomes supersaturated, and the state of affairs at a given moment corresponds with the point q in Fig. 111, and if the cooling process takes place so rapidly that the substance can only behave in a purely pseudo-binary manner, a denser phase must be deposited from the supersaturated vapour, but the total composition, as in the case of all normal binary processes, remains unaltered.

In the PX diagram, Fig. 111, the lines $c\,L_u\,d$ and $c\,G_u''\,d$ indicate the metastable co-existence of liquid and vapour, and thus it is seen that the point q lies in a metastable liquid region. Besides this, however, it also lies in the region for the co-existence of α and β mixed crystals in the pseudo-system. As a result of this it may be concluded from Fig. 111 that when fixation occurs, either a metastable liquid phase or one or two metastable mixed crystal phases will be deposited.

Which of these possibilities will in fact occur depends exclusively on the velocity factor relating to nucleus formation, and since the formation of sublimation nuclei is probably a more complex process than the formation of condensation nuclei, in this case the *liquid* phase will probably be deposited first.

Since the pressure falls during this condensation, and the composition of the liquid simultaneously changes, a liquid phase is obtained lying on the line $c\,d$ and a vapour which co-exists with it. Every temperature passed through in the course of this rapid cooling corresponds with another PX section, but in each of these sections the liquid lies on the line $c\,l\,d$ and the vapour on the line $c\,g\,d$, whilst the total composition remains unchanged. Consequently in every PX section the liquid phase lies between l and l' and the vapour phase between g and g'. If the cooling is stopped inner equilibrium is established, and finally the two-phase system $L_u + G_u''$, corresponding to the prevailing temperature, is established.

Afterwards the phenomena appear which have been discussed in the case of slow cooling. Now, however, it frequently happens that even during rapid cooling the pseudo-binary metastable two-phase system liquid + vapour changes into the pseudo-binary stable three-phase equilibrium; that is, into mixed crystal phases rich in α and β respectively, together with vapour (indicated in Fig. 111 by S_{α_M} S_{β_M}, and G). If the cooling is stopped at this stage, the change into the stable unary two-phase equilibrium $S_{u_2} + G_u$ thereupon takes place with greater or less velocity, and in the course of this change the α-mixed crystal phase is completely transformed into the β-mixed crystal phase.

If the pseudo-binary system contains no eutectic, a different order may be followed in the last case. If, for example, the system liquid—vapour has been formed (in Fig. 112 liquid is indicated by the line $l\,l'$ and vapour by the line $g\,g'$) during the cooling process a change may take place in the pseudo-binary stable two-phase system α mixed crystals + vapour, as the result of which the first phase must lie on the

line $S_{\alpha_M}' S_{\alpha_M}$ and the second on the line G′G; if rapid cooling is now stopped inner equilibrium will be again established, and thus the metastable unary two-phase equilibrium $S_{u_1} + G_u'$ arises, representing the unary sublimation equilibrium for the metastable phase. Finally the stable unary sublimation equilibrium appears, represented here by S_{u_1} and G_u.

In this case therefore phases appear in the following order: vapour, liquid, metastable solid, stable solid.

(b) *The sudden cooling of a liquid.*

When a liquid is suddenly cooled the problem is much simpler. If, for example, the TX diagram, Fig. 113, in which monotropy is

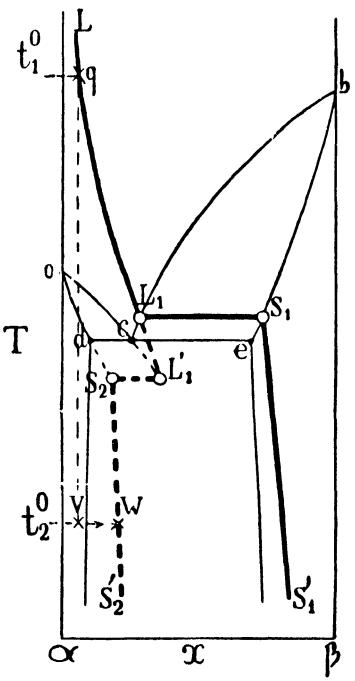


FIG. 113.

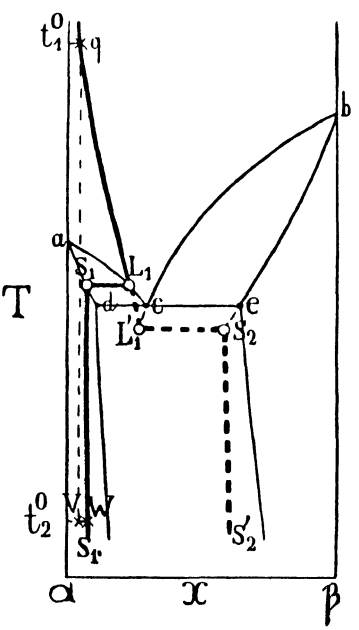


FIG. 114.

assumed, holds good for a given pressure, and if the liquid *q*, which at $t_1°$ is in inner equilibrium, is cooled down to $t_2°$ so quickly that the possibility of internal change is excluded, the mixed crystal phase V will be formed, which afterwards, in consequence of a scarcely perceptible internal change, passes into the metastable solid modification W.

In this case rapid cooling furnishes a certain means of obtaining the metastable modification. Consequently, on rapid cooling the phases appear in this case in the order: liquid, metastable solid, stable

solid. If, however, the position is as illustrated in Fig. 114, conversely, rapid cooling always results in the crystallisation of the stable modification.

(c) *Fixation by the addition of a bad solvent, deposition of the metastable modification.*

In conclusion, a little space will be devoted to the question of the fixation of a dissolved substance by the addition of a bad solvent.

In the section entitled "Allotropic Substances in the Presence of a Solvent" the isothermal diagram showing the connection between the

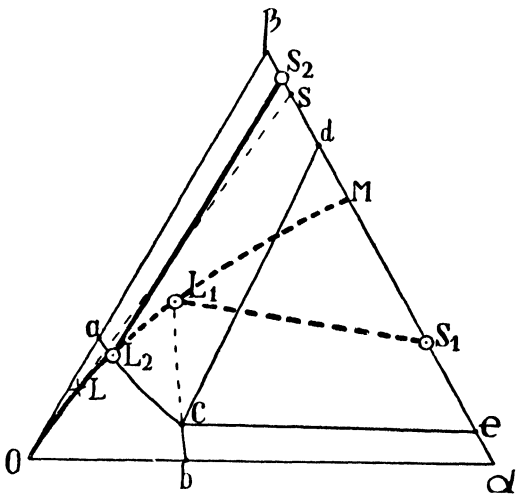


FIG. 115.

ternary and the binary systems formed by an allotropic substance and a solvent has already been discussed.

Figs. 115 and 116 are connected with the diagram referred to. Taking Fig. 115, let us start from the unsaturated solution L which, since in this solution the molecular species α and β are in inner equilibrium, must lie on the curve O M. The question now is, What will happen if this solution is poured into a large quantity of another liquid in which the substance dissolved in the first liquid is practically insoluble? Clearly in this case the dissolved pseudo-components α and β will be deposited in the same proportion in which they are present in the solution. This ratio is immediately found by drawing a straight line O through L and prolonging it until it cuts the axis $\alpha - \beta$. The point of intersection so obtained, denoted in the diagram by s, gives the ratio sought. The precipitated solid is apparently identical with the solid phase S, which lies in the β-mixed crystal region.

The stable modification is also a β-mixed crystal phase, but of different composition. It is represented by the point S_2.

Thus, in this case, the precipitated solid, the mixed crystal phase S, will be indistinguishable from the stable modification, and yet, at the outset, it does not correspond with this form. An internal change takes place, however, as a result of which, perhaps imperceptibly, the precipitated mixed crystal phase passes into the stable modification.

A second possibility is indicated in Fig. 116. The isotherm may lie very much to one side, and it is then found that the stable saturated solution in the binary system solvent—allotropic substance contains α molecules almost exclusively, whilst the stable form is a β-mixed crystal phase.

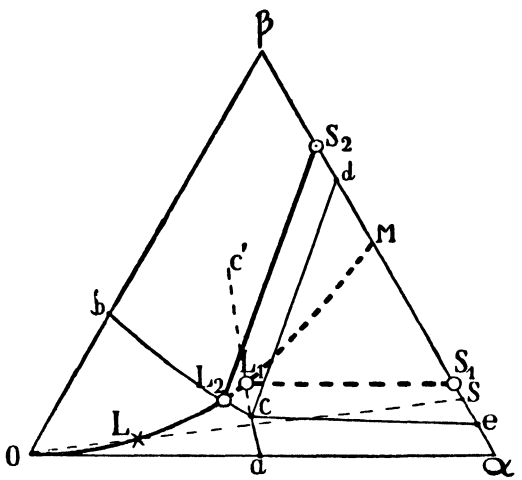


FIG. 116.

Thus in Fig. 116 it is seen that the stable modification co-exists with the saturated solution L_2, which is extremely rich in α molecules. The unsaturated solution L is a little richer still in α molecules, and if this solution again is supposed to be poured into another liquid which is an indifferent solvent as regards the substance under consideration, solid S will separate out, and this now, unlike the stable modification, consists not of β-mixed crystals, but of metastable α-mixed crystals. The precipitated substance now differs but slightly—for the most part the difference is imperceptible—from the metastable modification, S_1, into which it passes by a scarcely noticeable change.

In this very interesting case, therefore, on addition of a bad solvent the metastable modification separates out first.

Between the two extremes here discussed there must be a large number of transitional cases, in which at the commencement of the precipitation a conglomerate of the two mixed crystal phases *d* and *e* is deposited, which thereupon changes into the stable modification.

(d) *Appearance of the metastable modification in the case of slow cooling.*

From the preceding discussion it has been seen that fixation of the metastable modification by the introduction of a bad solvent does not involve any contradiction between theory and practice, but that the process is in complete agreement with theoretical considerations.

Now the preceding isotherm, Fig. 116, shows that in the case of slow crystallisation also the metastable modification may appear first. In this diagram S_2 denotes the stable modification and L_2 the saturated solution, in which α and β are in equilibrium with each other. This saturated solution now contains a preponderance of the α-pseudo-component, *i.e.* the component present in the greater concentration in the metastable modification S_1.

According to these views regarding the order in which new phases appear, it might be expected that the modification whose composition lies nearest to the relative composition of the supersaturated solution with respect to α and β would often be deposited first from supersaturated solutions containing the pseudo-components α and β in equilibrium. Thus if the equilibrium isotherm is displaced considerably to one side, and if the saturated solution markedly approaches the metastable modification, it will often happen that over a certain temperature range the power of the metastable modification for spontaneous crystallisation is the greater. The equilibrium isotherm O M may have very different positions in different solvents, and consequently it may occur that, whilst the stable modification crystallises first from one solvent, from another the metastable form is deposited first.

It must be concluded, therefore, that, contrary to Dimroth's opinion, no contradiction to theoretical principles is involved here.

Finally, if the equilibrium between α and β cannot be established sufficiently quickly during crystallisation by isothermal evaporation, and if for instance the metastable modification S_1 is formed first, the co-existing saturated solution changes along the solubility isotherm $a\,c\,c'$ in the direction $a \rightarrow c'$, becoming in consequence continually richer in β, and thus, naturally, the mixed crystals formed will also be richer in β. Since now this change in the saturated solution steadily increases the supersaturation with respect to β, at a given moment spontaneous crystallisation of β-mixed crystals will occur, and these will subsequently change into the stable modification. In this case therefore α-mixed crystals are first obtained, β-mixed crystals being obtained afterwards.

CHAPTER VII

The Application of the Theory of Allotropy to Electromotive Equilibria[1]

1. General Considerations.

When the theory here developed is applied to metals, every phase of the metal must be assumed to be complex. There may also be various kinds of complexity. It may be due, for example, to the existence, in every phase of the metal, of an ionisation equilibrium such as the following:—

$$M \rightleftarrows M^{\nu\cdot} + \nu\theta \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This equilibrium between atoms of the metal, metallic ions, and the electrons contained in the solid metal is comparable with ionisation equilibria in electrolytes, with the difference, however, that in the case of metals the negatively charged particles are not ions but free electrons.

The above-mentioned ionisation equilibrium represents what is probably the simplest case, for several ionisation equilibria may exist side by side in any given metal. This is the case when, for example, the metal gives rise to ions of different valencies. If these ions are represented by $M^{\cdot\cdot}$ and $M^{\cdot\cdot\cdot}$, the ionisation equilibria will run thus:—

$$M \rightleftarrows M^{\cdot\cdot} + 2\theta \quad \text{and} \quad M \rightleftarrows M^{\cdot\cdot\cdot} + 3\theta \quad . \quad . \quad (2)$$

A third possibility arises from the presence in the metal of different ions, carrying the same quantity of electricity per atom, it is true, but varying in size. The state of the metal is then more complex, as will be seen from the following example:—

$$\left.\begin{array}{l} M \rightleftarrows M^{\cdot\cdot} + 2\theta \\ M_2 \rightleftarrows M_2^{\cdot\cdot} + 4\theta \\ M_2 \rightleftarrows 2M \end{array}\right\} \quad . \quad . \quad . \quad . \quad (3)$$

Because of the great analogy between ionisation equilibria in electrolytes and the metallic ionisation equilibrium indicated here, the author has not hesitated to base the last-mentioned equilibria on those laws, the application of which to electrolytic ionisation equilibria has met with such great success.

[1] Smits, *Versl. Kon. Akad. v. Wet.*, **22**, 642 (1913); *Zeitschr. f. physik. Chemie*, **88**, 743 (1914). Smits and Aten, *Zeitschr. f. physik. Chemie*, **90**, 723 (1915); **92**, 1 (1916). Smits and Byvoet, *Versl. Kon. Akad. v. Wet.*, **27**, 311 (1918). Smits, *Versl. Kon. Akad. v. Wet.*, **27**, 1 (1918); **27**, 981 (1919); **27**, 1470 (1919).

Thus, the new ideas regarding electromotive equilibria, polarisation, overvoltage, and passivity rest, in the first place, on the application of the principles of the Theory of Allotropy, and secondly on the assumption that when a metal is brought into contact with an electrolyte, not only metallic ions, but electrons also, may pass into the solution, and that consequently the laws of dilute solutions hold good for the electrons in the electrolyte.

Only a very small number of free electrons can be present in any electrolyte, for if the conductivity of an electrolyte should be due to electrons to any appreciable extent, Faraday's Law would no longer hold good. Later calculations will show that the number of electrons in aqueous solutions is in fact so small that they cannot contribute appreciably to the conveyance of the current.

2. The Electromotive Equilibrium, Metal—Electrolyte.

If a metal, in which the equilibrium

$$M \rightleftarrows M^{\cdot\cdot} + 2\theta$$

prevails, is dipped into water, M atoms will go into solution until the saturation equilibrium is established; *i.e.* until just as many atoms of the metal go into solution every second as are deposited on the metal from the solution. This heterogeneous non-electrical equilibrium may be represented by the equation

$$\begin{matrix} M_S \\ \downarrow\uparrow \\ M_L \end{matrix} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now it might be thought that a similar equilibrium would be established between metallic ions and electrons; but the case is really quite different, since here electrically charged particles are dealt with, and these have a different solubility.

If we assume that the metallic ions have the greater solubility, and that to begin with all these ions go into solution, the electrolyte will thus become positively and the metal negatively charged. The positive charge of the electrolyte would then exert an attractive influence on the electrons in the metal; the negative charge of the metal, on the other hand, would repel them, so that electrons would likewise be forced into the solution. From these considerations we see, therefore, that to begin with a solution of metallic ions and electrons in equivalent proportions is obtained, which remains essentially unchanged until the least soluble constituent, in this case the electron, has attained its saturation concentration. When this moment arrives, however, the saturation concentration of the metallic ions has not yet been reached, and they will still be going into solution. The consequence of this is, that the electrolyte becomes positively and the metal negatively charged, and thus the ions in the solution are subjected to an attractive force.

If the metallic ions could reach their saturation concentration, exactly as many ions would pass per second from the metal into the

solution as would migrate in the opposite direction, *without any particular force being operative.*

But in consequence of the negative charge on the metal, which at a given moment prevents the further solution of the ions, saturation cannot occur; yet, *just because of this attractive force,* a point will here be reached at which exactly as many metallic ions go into the electrolyte per second as pass in the reverse direction, although *the electrolyte is still unsaturated with respect to metallic ions.*

As has already been mentioned, the electrons in the metal are under the influence of the positive charge on the electrolyte. Naturally this positive electrolytic charge acts in such a way that, at the moment when the electrons in the electrolyte attain their saturation concentration, some electrons are still going into solution, and thus the solution becomes *supersaturated* with respect to electrons. This process continues until a point is reached at which exactly as many electrons pass every second from the metal to the solution as are deposited on the metal from the solution. Consequently heterogeneous equilibria are also established between metallic ions and electrons in the metal and in the electrolyte, which may be represented thus :—

$$\begin{matrix} M_S^{\bullet\bullet} \\ \downarrow\uparrow \\ M_L^{\bullet\bullet} \end{matrix} \quad \text{and} \quad \begin{matrix} \theta_S \\ \downarrow\uparrow \\ \theta_L \end{matrix} \qquad . \quad . \quad . \quad . \quad (5)$$

and since these equilibria are associated with a difference of potential they will be called electromotive equilibria.

3. The Difference of Potential Considered Thermodynamically.

Electromotive equilibria will now be considered from the standpoint of thermodynamics.

From the condition for equilibrium

$$\Sigma \nu\mu = 0 \qquad . \quad . \quad . \quad . \quad . \quad (6)$$

the relationship

$$\mu_{M_S} = \mu_{M_L}$$

is obtained for the equilibrium between the uncharged atoms in the metal and in the electrolyte.

This equilibrium condition cannot be applied without further discussion to the equilibrium between the metallic ions in the metal and those in the electrolyte, or to the equilibrium between the electrons in the metal on the one hand and those in the electrolyte on the other, for, as we have already seen, an electrical force enters into these equilibria, the origin of which is to be found in the different solubilities of the electrically charged particles.

Hence the assumption is next made that no potential difference exists between the metal and the co-existing electrolyte, an assumption which might be realised in the case of certain metals.

If the molecular thermodynamic potential of the metallic ions in the metal, the potential difference Δ being o, is denoted by

$$(\mu_{M_S^{\nu\cdot}})_{\Delta=0}$$

and that of the metallic ions in the co-existing electrolyte by

$$(\mu_{M_L^{\nu\cdot}})_{\Delta=0},$$

the equilibrium, which is now in fact a saturation equilibrium, will naturally be represented by the following expression :—

$$(\mu_{M_S^{\nu}})_{\Delta=0} = (\mu_{M_L^{\nu\cdot}})_{\Delta=0}.$$

If, however, Δ is not zero, but a definite potential difference exists, as is generally the case, it may be imagined that the equilibrium

$$\begin{matrix} M_S \\ \uparrow\downarrow \\ M_L \end{matrix}$$

is established, simply by virtue of the difference of potential, in a similar way to the establishment of equilibrium between the water inside an osmotic cell and the water outside, in consequence of the difference in the hydrostatic pressures.

If, therefore, we wish to apply the condition for equilibrium to the electrically charged particles, the molecular electrical potential of the metallic ions, both in the metal and in the electrolyte, must also be taken into consideration. If V_S denotes the electrical potential of the metal, and V_L that of the electrolyte, the molecular electric potential of the metallic ions in the metal will be νFV_S and in the electrolyte νFV_L, where F is the electrical charge on a monovalent ion. Hence, for the heterogeneous equilibrium between metal and electrolyte, the equilibrium condition leads to the relationship

$$(\mu_{M_S^{\nu\cdot}})_\Delta + \nu FV_S = (\mu_{M_L^{\nu\cdot}})_\Delta + \nu FV_L \quad . \quad . \quad (7)$$

from which it follows that

$$V_S - V_L = -\frac{(\mu_{M_S^{\nu\cdot}})_\Delta - (\mu_{M_L^{\nu\cdot}})_\Delta}{\nu F}$$

or if Δ is written instead of $V_S - V_L$ and the index Δ is omitted,

$$\Delta = -\frac{\mu_{M_S^{\nu\cdot}} - \mu_{M_L^{\nu\cdot}}}{\nu F} \quad . \quad . \quad . \quad . \quad (8)$$

If the electronic equilibrium is considered, this relationship is obtained :—

$$(\mu_{\theta_S})_\Delta - FV_S = (\mu_{\theta_L})_\Delta - FV_L \quad . \quad . \quad . \quad (9)$$

or

$$\Delta = \frac{\mu^\theta_S - \mu_{\theta_L}}{F} \quad . \quad . \quad . \quad . \quad (10)$$

These considerations differ from the well-known views of Nernst, in

that the assumption has here been made that the ions and electrons of the metal are in heterogeneous equilibrium with the ions and electrons of the electrolyte; whilst formerly only the atoms of the metal and the ions of the electrolyte were taken into consideration in the deduction of the potential difference.

These new considerations now make it possible to derive a formula for the potential difference, in which not only the concentration of the metal or of the electrons in the electrolyte appears, but in which account is also taken of the concentrations of these constituents in the metal. For this purpose the well-known resolution of the molecular thermodynamic potential into a concentration term and a term which is independent of the concentration,

i.e.

$$\mu = \mu' + RT \ln C \quad . \quad . \quad . \quad . \quad (11)$$

is applied, not only to the metallic ions and the electrons in the electrolyte, but also to the metallic ions and the electrons in the metal.

From equation (8) the following equation is thus obtained :—

$$\Delta = \frac{\mu'_{M_S^{\nu\cdot}} - \mu'_{M_L^{\nu\cdot}} + RT \ln (M_S^{\nu\cdot}) - RT \ln (M_L^{\nu\cdot})}{\nu F} \quad . \quad (12)$$

If we now put

$$\mu'_{M_S^{\nu\cdot}} - \mu'_{M_L^{\nu\cdot}} = RT \ln K'_{M^{\nu}} \quad . \quad . \quad . \quad (13)$$

we get

$$\Delta = -\frac{RT}{\nu F} \ln \frac{K'_{M^{\nu\cdot}}(M_S^{\nu\cdot})}{(M_L^{\nu\cdot})} \quad . \quad . \quad . \quad . \quad (14)$$

In an exactly analogous way, by making equation (10) the starting point, an electronic formula is obtained for the potential difference.

Thus

$$\Delta = \frac{\mu'_{\theta_S} - \mu'_{\theta_L} + RT \ln (\theta_S) - RT \ln (\theta_L)}{F} \quad . \quad . \quad (15)$$

Putting

$$\mu'_{\theta_S} - \mu'_{\theta_L} = RT \ln K'_{\theta} \quad . \quad . \quad . \quad (16)$$

the following expression results :—

$$\Delta = \frac{RT}{F} \ln \frac{K'_{\theta}(\theta_S)}{(\theta_L)} \quad . \quad . \quad . \quad . \quad (17)$$

The products $K'_{M^{\nu\cdot}}(M^{\nu\cdot})$ and $K'_{\theta}(\theta_S)$ have a very simple physical significance. Thus it is well known when

$$\Delta = 0,$$

in which case, as has already been seen,

$$(\mu_{M_S^{\nu\cdot}})_{\Delta=0} = (\mu_{M_L^{\nu\cdot}})_{\Delta=0}$$
$$(\mu_{\theta_S})_{\Delta=0} = (\mu_{\theta_L})_{\Delta=0}$$

and therefore

$$K'_{M^{\nu\cdot}}(M^{\nu\cdot}_S) = (M^{\nu\cdot}_L)$$

and

$$K'_{\theta}(\theta_S) = (\theta_L).$$

If the metal behaves in a unary manner, $K'_{M^{\nu\cdot}}(M^{\nu\cdot}_S)$ and $K'_{\theta}(\theta_S)$ are constants, and instead of these products $K_{M^{\nu\cdot}}$ and K_{θ} can then be written; in this way the following equations are obtained for Δ:—

$$\Delta = -\frac{RT}{\nu F}\ln\frac{K_{M^{\nu\cdot}}}{(M^{\nu\cdot}_L)} \quad . \quad . \quad . \quad . \quad (18)$$

and

$$\Delta = \frac{RT}{F}\ln\frac{K_{\theta}}{(\theta_L)} * \quad . \quad . \quad . \quad . \quad (19)$$

Hence it follows that $K_{M^{\nu\cdot}}$ represents the *saturation concentration of the metallic ions*, and K_{θ} *the saturation concentration of the electrons* in the electrolyte.

Thus two equations have been derived for the potential difference, of which the first (18) is in agreement with Nernst's formula,

$$\Delta = -\frac{RT}{\nu F}\ln\frac{P}{C}$$

with this difference, however, that instead of P, *i.e.* the *solution tension*, the quantity $K_{M^{\nu\cdot}}$ appears, and this has the significance of a saturation concentration.

Van Laar[1] first derived formula (18) in a somewhat different way. He considered the atoms only in the metal and applied the resolved molecular thermodynamic potential exclusively to the ions in the electrolyte; this explains why he obtained equation (18) but not equation (14).

After van Laar had published his derivation in 1903, the author,[2] in 1906, pointed out the physical significance of the quantity $K_{M^{\nu\cdot}}$ which appears here instead of the solution tension P.

It is at once seen that the electronic formula (19) is in complete agreement with formula (18). That is to say, if a metal is taken, the ions of which in the electrolyte can never reach their saturation concentration,

$$K_{M^{\nu\cdot}} \text{ is always } > (M^{\nu\cdot}_L)$$

and consequently the potential difference is always negative.

* In a postscript [*Zeitschr. f. physik. Chemie*, **78**, 228 (1911)] Haber and Zawadsky emphasise that by introducing the electronic concentration into Nernst's formula by means of the constant product of ions and electrons a similar formula can be deduced. The constant which they obtain in place of the ionic solution tension they call the transition tension of the electrons.

[1] *Versl. Kon. Akad. v. Wet.*, February 1903. "Lehrb. der theoretischen Elektrochemie."

[2] *Versl. Kon. Akad. v. Wet.*, April 1906, p. 859.

The same result follows from the electronic formula, for in this case the electrolyte is always supersaturated with respect to electrons, so that

$$K_\theta \text{ is always } < (\theta_L)$$

and this again necessitates a negative value for Δ. It also follows from the electronic formula that by increasing the ionic concentration, Δ is rendered less negative or more strongly positive, for in this case the equilibrium

$$M_L \rightleftarrows M_L^{\nu\cdot} + \nu 0_L$$

will be displaced from right to left, and this results in a decrease of the electron concentration.

It may here be emphasised, however, that equations (18) and (19) cannot be used in the case of polarisation phenomena nor yet when changes of potential appear as the result of chemical action! *In these cases use is made of the new formulæ* (14) *and* (17), *which have been obtained by applying the Theory of Allotropy to electromotive equilibria.*

4. Introduction of the Ideas: Solubility Product of a Metal and Solubility Quotient of a Non-Metal.

It has been assumed that the constituents of a metal pass to some extent into the electrolyte, and that in consequence a similar equilibrium to that existing in the metal is established in the electrolyte; so that, in addition to the heterogeneous equilibrium, two homogeneous equilibria occur, the one in the metal and the other in the electrolyte. The complete equilibrium may therefore be represented in the following way:—

$$\begin{array}{ccc} M_S \rightleftarrows M_S^{\nu\cdot} + \nu\theta_S \\ \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \\ M_L \rightleftarrows M_L^{\nu\cdot} + \nu\theta_L \end{array} \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Proceeding now from the perfectly justifiable assumption that the Law of Mass Action, which holds good for equilibria between molecules and ions, can also be applied to equilibria between ions and electrons, by applying this law to the equilibrium in the liquid phase the following expression is obtained:—

$$K = \frac{M_L^{\nu\cdot}(\theta_L)^\nu}{(M_L)} . \quad . \quad . \quad . \quad . \quad (21)$$

Since now the liquid is saturated in respect of atoms of metal, at any given temperature and pressure (M_L) will be constant, and therefore we can write

$$K' = (M_L^{\nu\cdot})(\theta_L)^\nu = L_M \quad . \quad . \quad . \quad . \quad (22)$$

L_M may be called the *solubility product* of the metal.

If now, to take a specific example, a saturated solution of chlorine

in water or any other electrolyte is considered at a definite temperature and pressure, the following equilibrium will exist:—

$$Cl2_L + 2\theta_L \rightleftarrows 2Cl'_L \quad . \quad . \quad . \quad . \quad (23)$$

If to this equilibrium the Law of Mass Action is applied, equation (24) is obtained

$$K = \frac{(Cl'_L)^2}{(Cl2_L)(\theta_L)^2} \quad . \quad . \quad . \quad . \quad (24)$$

or

$$K(Cl2_L) = \frac{(Cl'_L)^2}{(\theta_L)^2}.$$

Since the quantity (Cl_2) is constant if the temperature and pressure are kept constant, this formula may be written

$$Q = \frac{(Cl'_L)^2}{(\theta_L)^2} \quad . \quad . \quad . \quad . \quad . \quad (25)$$

in which Q may be called the *solubility quotient* of chlorine under a pressure of one atmosphere. If the chlorine pressure amounts to p atmospheres the following expression will hold good:—

$$Q_p = \frac{(Cl'_L)^2}{(\theta_L)^2} \quad . \quad . \quad . \quad . \quad . \quad (26)$$

5. The Equation for the Difference between the Potential Differences of Two Metals.

Suppose two metals to be taken and dipped, each into an aqueous solution of one of its salts; the potential differences are then given by the equations

$$\Delta_{M_1-L_1} = \frac{\mu_{\theta_{S_1}} - \mu_{\theta_{L_1}}}{F}$$

and

$$\Delta_{M_2-L_2} = \frac{\mu_{\theta_{S_2}} - \mu_{\theta_{L_2}}}{F}.$$

Hence it follows that the difference between these potential differences is

$$\Delta_{M_1-L_1} - \Delta_{M_2-L_2} = \frac{\mu_{\theta_{S_1}} - \mu_{\theta_{S_2}} - \mu_{\theta_{L_1}} + \mu_{\theta_{L_2}}}{F} \quad . \quad . \quad (27)$$

or

$$\Delta_{M_1-L_1} - \Delta_{M_2-L_2} = \frac{\mu_{\theta_{S_1}} - \mu_{\theta_{S_2}} - \mu'_{\theta_{L_1}} - RT \ln(\theta_{L_1}) + \mu'_{\theta_{L_2}} + RT \ln(\theta_{L_2})}{F} \quad (28)$$

or

$$\Delta_{M_1-L_1} - \Delta_{M_2-L_2} = -\frac{RT}{F} \ln \frac{(\theta_{L_1})}{(\theta_{L_2})} + \frac{\mu_{\theta_{S_1}} - \mu_{\theta_{S_2}}}{F} \quad . \quad (29)$$

since the quantities $\mu'_{\theta_{L_1}}$ and $\mu'_{\theta_{L_2}}$ are equal for one and the same solvent.

6. The Experimental Electric Potential.[1]

Before making further use of the above formula, it may be pointed out that the measurement of the potential difference metal-electrolyte is carried out by means of a standard electrode, *e.g.* a calomel or hydrogen electrode. In other words, an electrical cell is constructed which is closed during the measurement. The electromotive force of this cell, in which the diffusion potential between L_1 and L_2 may be imagined to be compensated, is then

$$E = \Delta_{M_1-L_1} - \Delta_{M_2-L_2} - \Delta_{M_1-M_2} \quad . \quad . \quad . \quad (30)$$

where $\Delta_{M_1-M_2}$ denotes the *Volta effect*.

If the values for $\Delta_{M_1-L_1}$ and $\Delta_{M_2-L_2}$ from equation (18) are now substituted, we obtain

$$E = -\frac{RT}{\nu_1 F}\ln\frac{K_{M_1}^{\nu_1}}{(M_{1L}^{\nu_1})} + \frac{RT}{\nu_2 F}\ln\frac{K_{M_2}^{\nu_2}}{(M_{2L}^{\nu_2})} - \Delta_{M_1-M_2}$$

If $\Delta_{M_2-L_2}$ is the potential difference in the case of the normal hydrogen electrode and this is called Δ_0, the following equation is obtained:—

$$E = -\frac{RT}{\nu_1 F}\ln\frac{K_{M_1}^{\nu_1}}{(M_{1L}^{\nu_1})} - \Delta_0 + \Delta_{M_1-M_2} \quad . \quad . \quad (31)$$

in which E may be called the *experimental electric potential*.

Thus, this expression still contains the *Volta effect*, and so long as this is unknown and no further assumptions as to its magnitude are introduced, the potential difference $\Delta_{M_1-L_1}$ cannot be determined *per se* by this method, nor yet can the saturation concentration K_M^{ν} for the metallic ions, which is equivalent to the "solution tension" of Nernst, and which was formerly calculated from the formula:—

$$E = -\frac{RT}{\nu F}\ln\frac{K_M^{\nu}}{(M_L^{\nu})} - \Delta_0 \quad . \quad . \quad . \quad (32)$$

$\Delta_{M_1-M_2}$ being neglected.

Hence, so long as the *Volta effect* is unknown, it is impossible to draw any conclusion from the so-called electromotive series with regard to the order followed by the metallic ions when arranged according to their saturation concentrations. From the fact that the metal M_1 is more negative in a normal solution of one of its salts than is M_2 when similarly dipped into a normal solution of one of its salts, it is usually concluded that

$\Delta_{M_1-L_1}$ is more negative than $\Delta_{M_2-L_2}$,

but this conclusion is incorrect, for the measurement merely shows that

$\Delta_{M_1-L_1} - \Delta_{M_1-M_1}$ is more strongly negative than $\Delta_{M_2-L_2}$.

It has here been shown that the equation for the experimental electric potential containing the "saturation concentration" or the "solution

[1] Smits and Bijvoet, *loc. cit.*

tension" has the disadvantage of being subject to the as yet unknown Volta effect.

As regards the new electron formula, however, as we shall soon see, the case is quite different, and this is also true of the new formulæ containing the solubility product of the metal, or the solubility quotient in the case of non-metals.

It has already been shown that

$$\Delta_{M_1-L_1} - \Delta_{M_2-L_2} = -\frac{RT}{F}\ln\frac{(\theta_{L_1})}{(\theta_{L_2})} + \frac{\mu_{\theta_{M_1}} - \mu_{\theta_{M_2}}}{F},$$

but we actually measure

$$E = \Delta_{M_1-L_1} - \Delta_{M_2-L_2} - \Delta_{M_1-M_2},$$

and since the Volta effect

$$\Delta_{M_1-M_2} = \frac{\mu_{\theta_{M_1}} - \mu_{\theta_{M_2}}}{F}$$

the following expression is obtained :—

$$E = -\frac{RT}{F}\ln\frac{(\theta_{L_1})}{(\theta_{L_2})} \quad . \quad . \quad . \quad . \quad (33)$$

In this formula the Volta effect does not appear.

7. The Introduction of the "Solubility Product" and the "Solubility Quotient" into the Equation for the Experimental Electric Potential.

If we now imagine that

$$L_{M_1} = (M_{1L_1}^{\nu_1\cdot})(\theta_{L_1})^{\nu_1}$$

and

$$L_{M_2} = (M_{2L_2}^{\nu_2})(\theta_{L_2})^{\nu_2},$$

the following equations are obtained :—

$$\ln(\theta_{L_1}) = \frac{1}{\nu_1}\ln\frac{L_{M_1}}{(M_{1L_1}^{\nu_1\cdot})}$$

and

$$\ln(\theta_{L_2}) = \frac{1}{\nu_2}\ln\frac{L_{M_2}}{(M_{2L_2}^{\nu_2\cdot})},$$

so that on substitution equation (33) becomes

$$E = -\frac{RT}{\nu_1 F}\ln\frac{L_{M_1}}{(M_{1L_1}^{\nu_1\cdot})} + \frac{RT}{\nu_2 F}\ln\frac{L_{M_2}}{(M_{2L_2}^{\nu_2\cdot})} \quad . \quad . \quad (34)$$

If, instead of the solubility product of the metal M_1 the solubility quotient of a non-metal under atmospheric pressure is now introduced, and that for the general case in which the following equilibrium prevails in the solution :—

$$N n_L + n\nu\theta_L \rightleftarrows n N_L^{\nu\prime},$$

so that

$$Q_N = \frac{(N_L^{\nu'})^n}{(\theta_L)^{n\nu}}$$

$$Q_N = \frac{(N_L^{\nu'})^n}{(\theta_L)^{n\nu}}$$

and

$$\ln(\theta_L) = \frac{1}{n\nu} \ln \frac{(N_L^{\nu'})^n}{Q_N},^*$$

the following expression is derived from equation (33)

$$E \frac{RT}{n\nu_1 F} \ln \frac{Q_N}{(N_{L_1}^{\nu_1'})^n} + \frac{RT}{\nu_2 F} \ln \frac{L_{M_2}}{(M_{2L_2}^{\nu_2})} . \quad . \quad . \quad (35)$$

Both these equations, (33) and (35), make it possible to deduce the ratio of the solubility products or the solubility quotients from the electromotive force, *inasmuch as these equations no longer contain the Volta effect.*

8. The Determination of the "Solubility Products" of Metals and the "Solubility Quotients" of Non-Metals.

In the practical application of equation (34) the metal M_2 is replaced by the normal hydrogen electrode under atmospheric pressure, and in this way the experimental electric potential is determined for the metal M_1 in relation to the normal hydrogen electrode. $(M_{2L_2}^{\nu_2})$ is then put = 1. In applying formula (35) a similar mode of procedure is followed.

Introducing common logarithms, and putting $T = 273° + 18°$, the following equation is obtained for metals :—

$$E = -\frac{0{\cdot}058}{\nu_1} \log \frac{L_{M_1}}{(M_{1L_1}^{\nu_1})} + \frac{0{\cdot}058}{\nu_2} \log L_{H_2} \quad . \quad . \quad (36)$$

and for non-metals

$$E = \frac{0{\cdot}058}{\nu_1 n} \log \frac{Q_N}{(N_L^{\nu_1'})^n} + \frac{0{\cdot}058}{\nu_2} \log L_{H_2} \quad . \quad . \quad (37)$$

It should here be noticed that in considering the solubility product of metals, it was assumed, for the sake of simplicity, that the neutral particles emitted by metals are atoms. Hence, for the solubility product of a monovalent metal, we must write

$$L_M = (M)^* \times (\theta).$$

* Since oxygen reacts with water to form an anion, we write

$$O_2 + 2H_2O + 4\theta \rightleftarrows (4OH)'$$

and then

$$Q_{\theta_2} = \frac{(OH)^4}{(\theta)^4}.$$

If, however, as in the case of hydrogen, the uncharged particles are the molecules H_2, the solubility product becomes

$$L_{H_2} = (H^{\cdot})^2 (\theta)^2$$

The product $(H^{\cdot})$ (θ), which, on account of the monovalent nature of hydrogen, one might be inclined to look upon as the solubility product, is therefore in reality the square root of the solubility product.

The quantity ν indicates the number of electrons split off from a neutral particle in the process of ionisation. As it has been assumed here that the neutral particles consist of hydrogen molecules, in this case $\nu = 2$, and we may write

$$E = -\frac{0{\cdot}058}{\nu} \log \frac{L_M}{(M_L^{\nu\cdot})} + \frac{0{\cdot}058}{2} \log L_{H_2} \quad . \quad . \quad (36a)$$

Thus the experimental potential of a metal includes its solubility product, the concentration of the metallic ions, and the solubility product of hydrogen.

If now the solubility product of hydrogen were known, all the others could be calculated from the experimental potential by means of the last equation.

Now it may safely be said that the solubility product of the most negative metal, namely *lithium*, has the highest value, and that the concentration of the ions and the electrons in the solution would not be greater than in the pure metal, assuming the latter to be completely ionised.

Supposing metallic lithium to be completely dissociated into ions and electrons, since the metal does not contain 100 gram-atoms per litre (the atomic weight is 7 and the specific gravity 0·6) the product (L_{Li}) (θ) will always be less than 10^4.

We can therefore write

$$L_{Li} = a \,.\, 10^4, \quad . \quad . \quad . \quad . \quad . \quad (38)$$

where a is a factor which is < 1. If now for the sake of simplicity the value 1 is assigned to a, and consequently 10^4 is substituted for L_{Li} in the above equation, the solubility product of hydrogen can be calculated from the experimental potential of *lithium* relative to the normal hydrogen electrode for a known concentration of lithium ions.

The potential necessary for this calculation is the experimental *normal potential* of lithium, *i.e.* the experimental potential relative to the normal hydrogen electrode, and this is obtained when the concentration of the lithium ions = 1. This experimental normal potential, which is not easily measured directly, but which can easily be calculated, is equal to − 3·02 V. If E denotes the experimental normal potential

$$E = -\frac{0{\cdot}058}{\nu} \log L_M + \frac{0{\cdot}058}{2} \log L_{H_2} \quad . \quad . \quad (36b)$$

If in this expression 10^4 is substituted for L_M, − 3·02 V for E, and 1 for ν, we get

$$-3{\cdot}02 = +0{\cdot}058 \times 4 + \frac{0{\cdot}058}{2} \log L_{H_2}$$

or

$$\log L_{H_2} = 2 \times -48.$$

If the value thus obtained for the solubility product of hydrogen is introduced into formula (36*b*) for the experimental normal potential of a metal, equation (39) is obtained.

$$E = -\frac{0{\cdot}058}{\nu} \log L_M - 2{\cdot}8 \quad . \quad . \quad . \quad (39)$$

In the same way, if it is assumed that the concentration of the non-metallic ions $(N_L^{\nu_1'}) = 1$, the equation for the normal experimental potential of a non-metal, which is obtained from (37), gives rise to the following expression :—

$$E = \frac{0{\cdot}058}{n\nu} \log Q_N - 2{\cdot}8 \quad . \quad . \quad . \quad (40)$$

These two equations place us in a position to determine the solubility product of a metal or the solubility quotient of a non-metal in relation to the hydrogen electrode, in a very simple way, from the normal experimental potential of the metal or the non-metal, as the case may be. The values given in the accompanying table are thus obtained.

Metal.	E.	ν.	log L_M.	Metal.	E.	ν.	log L_M.
Li	− 3·02	1	+ 4	Co	− 0·29	2	2 × − 43
K	− 2·92	1	+ 2	Ni	− 0·19	2	2 × − 45
Ba	− 2·8	2	0	Pb	− 0·12	2	2 × − 46
Na	− 2·71	1	− 1·3	Sn	− 0·10	2	2 × − 46·3
Sr	− 2·7	2	2 × − 1·5	H_2	0	2	2 × − 48
Ca	− 2·5	2	2 × − 5	Sb	+ 0·1	3	3 × − 50
Mg	− 1·55	2	2 × − 21·3	Bi	+ 0·2	3	3 × − 51
Mn	− 1·0	2	2 × − 31	As	+ 0·3	3	3 × − 53
Zn	− 0·76	2	2 × − 35	Cu	+ 0·34	2	2 × − 54
Cr	− 0·60	2	2 × − 38	Ag	+ 0·80	1	− 61·9
Fe	− 0·43	2	2 × − 40·7	Hg_2	+ 0·80	2	2 × − 61·9
Cd	− 0·40	2	2 × − 41·2	Pd	+ 0·82	2	2 × − 62·2
Tl	− 0·33	1	− 42·4	Au	+ 1·5	1	− 74

Non-metal.	E	ν.	log Q_N.
S	− 0·55	2	2 × 39
O_2	+ 0·41	4	4 × 55 *
I_2	+ 0·54	2	2 × 57·4
Br_2	+ 1·08	2	2 × 67
Cl_2	+ 1·36	2	2 × 71·5
F_2	+ 1·9	2	2 × 81

* Here $Q_{O_2} = \frac{(OH)^4}{(\theta)^4}$.

It has been shown that since the measured electromotive force always contains the as yet unknown Volta effect, it is impossible to

compare the potential differences metal-electrolyte and non-metal-electrolyte with each other.

It has, however, been proved that by introducing the solubility product of metals or the solubility quotient in the case of non-metals, formulæ may be deduced for the electromotive force, in which the unknown Volta effect no longer occurs. The new formulæ contain ideas which are easily realised, and they are therefore especially suited to practical application.

The electromotive force produced when the normal hydrogen electrode is made the second electrode has been called the experimental electric potential of the first electrode. The formula for this electric potential is, therefore, at the ordinary temperature

$$E = -0{\cdot}058 \log (\theta_L) - 2{\cdot}8 \quad . \quad . \quad . \quad (40a)$$

Thus for a metal

$$E = -\frac{0{\cdot}058}{\nu} \log \frac{L_M}{(M_L^{\nu\cdot})} - 2{\cdot}8 \quad . \quad . \quad . \quad (41)$$

and for a non-metal

$$E = \frac{0{\cdot}058}{n\nu} \log \frac{Q_N}{(N_L^{\nu'})^n} - 2{\cdot}8 \quad . \quad . \quad (42)$$

Thus for O_2

$$E_{O_2} = \frac{0{\cdot}058}{4} \log \frac{Q_{O_2}}{(OH')^4} - 2{\cdot}8.$$

It may be perceived from equation (41) that as the concentration of the metallic ions ($M_L^{\nu\cdot}$) increases, the potential becomes less negative or more positive. In this connection it should be noticed that for most metals L_M is so small, and consequently log L_M has so great a negative value, that the first term on the right-hand side of our equation is nearly always positive. Still, the value of L_M for most of the base metals in a state of inner equilibrium is too great, even when ($M_L^{\nu\cdot}$) is raised to the maximum value attainable in saturated salt solutions, for the first term of the right-hand side of equation (41) to predominate, and for the experimental potential to be positive in consequence.

From equation (42) it follows that the experimental potential of a non-metal becomes more strongly negative, or less positive, as the concentration of the non-metallic ions in the electrolyte is increased.

These considerations already permit the great advantages offered by the introduction of the idea of the solubility product of a metal and the solubility quotient of a non-metal to be clearly recognised. Frequent confirmation of this will be found later.

We have already seen that this conception makes it possible to deduce extremely simple and suitable formulæ for the experimental potential, which, unlike the formula formerly applied, equation (31), no longer contain the unknown Volta effect. In equation (31) this effect has always been disregarded, although no accurate knowledge as to its magnitude has yet been obtained.

The lack of knowledge regarding the Volta effect makes the establishment of a series for the saturation concentrations of the metallic ions impossible, though this can be very easily carried out for the solubility products of the metals and the solubility quotients of the non-metals.

9. Calculation of the Dissociation Constants for Ionisation Equilibria in the Case of Metals.

By applying the electronic equation, the potential difference between two metals dipping into an electrolyte is found to be

$$E = -\frac{RT}{F}\ln\frac{(\theta_{L_1})}{(\theta_{L_2})}.$$

If now two non-corrodible electrodes are taken, one of which dips into a ferro-ferri solution whilst the other forms a hydrogen electrode, and if (θ_{L_1}) denotes the electron concentration in the equilibrium

$$Fe^{\cdot\cdot} \rightleftarrows Fe^{\cdot\cdot\cdot} + \theta$$

and (θ_{L_2}) the electron concentration in the hydrogen ionisation equilibrium

$$H_2 \rightleftarrows 2H^{\cdot} + 2\theta,$$

if the solutions are so chosen that the ionic concentrations $(Fe^{\cdot\cdot})$ $(Fe^{\cdot\cdot\cdot})$ and $(H^{\cdot})$ are all equal to unity, it follows from

$$K = \frac{(Fe^{\cdot\cdot\cdot})(\theta)}{(Fe^{\cdot\cdot})} \quad . \quad . \quad . \quad . \quad . \quad (43)$$

that

$$K = (\theta)_{Fe} = (\theta_{L_1}) \quad . \quad . \quad . \quad . \quad (44)$$

and since

$$I_{H_2} = (H^{\cdot})^2(\theta)^2 = 10^{2\times-48} \text{ and } (H^{\cdot}) = 1,$$
$$(\theta)_{H_2} = 10^{-48}.$$

Consequently, as in (40*a*)

$$E = -0{\cdot}058 \log (\theta_{L_1}) - 2{\cdot}8,$$

so that in this case

$$E = -0{\cdot}058 \log K - 2{\cdot}8 \quad . \quad . \quad . \quad (45)$$

In this way the values of K for several ionisation equilibria have been calculated.

Ionisation Equilibrium.	E.	log K.
$Cr^{\cdot\cdot} \rightleftarrows Cr^{\cdot\cdot\cdot} + \theta$	$-0{\cdot}4$	-41
$Cu^{\cdot} \rightleftarrows Cu^{\cdot\cdot} + \theta$	$0{\cdot}18$	-51
$Sn^{\cdot\cdot} \rightleftarrows Sn^{\cdot\cdot\cdot\cdot} + 2\theta$	$0{\cdot}2$	$2\times-51{\cdot}4$
$Fe^{\cdot\cdot} \rightleftarrows Fe^{\cdot\cdot\cdot} + \theta$	$0{\cdot}75$	-61
$Hg_2^{\cdot\cdot} \rightleftarrows 2Hg^{\cdot\cdot} + 2\theta$	$0{\cdot}92$	2×-64
$Co^{\cdot\cdot} \rightleftarrows Co^{\cdot\cdot\cdot} + \theta$	$1{\cdot}8$	-79

10. Polarisation of a Metal containing one kind of Ion only.

The foregoing considerations, which serve to render the reader conversant with the principles of the new theory, enable us now to proceed to the discussion of polarisation.

In the investigation of this phenomenon use is made of one of the two new equations (14) and (17) for the potential difference :—

$$\Delta = -\frac{RT}{\nu F} \ln \frac{K'_{M}{}^{\nu\cdot}(M_S^{\nu\cdot})}{(M_L^{\nu\cdot})}$$

or

$$\Delta = \frac{RT}{F} \ln \frac{K'_{\theta}(\theta_S)}{(\theta_L)}.$$

These equations are equally valid whether the metal is in inner equilibrium or not. If the insulated metal is in inner equilibrium the internal condition is perfectly definite at constant temperature and pressure, and consequently $(M_S^{\nu\cdot})$ and (θ_S) and also (M_S) are then constants. Moreover, it is known that

$$\nu(M_S^{\nu\cdot}) = (0_S)$$

when the insulated metal is uncharged.

If the metal is brought into contact with an electrolyte, the above equation is naturally no longer *perfectly* valid; since, however, an extremely small deviation from this equation corresponds to a large charge on the metal, the *concentration change* in question is so extremely small under the circumstances here considered, that it may without hesitation be neglected.

11. Anodic Polarisation.

If the metal M is made the anode, the following results are obtained :—

The inner equilibrium

$$M_S \rightleftarrows M_S^{\nu\cdot} + \nu\theta_S$$

exists in the metal, whilst in the corresponding electrolyte the following equilibrium occurs :—

$$M_L \rightleftarrows M_L^{\nu\cdot} + \nu\theta_L.$$

As has already been mentioned, these two homogeneous equilibria are connected together by three heterogeneous equilibria, so that the complete equilibrium may be represented by the symbol

$$\begin{array}{ccc} M_S \rightleftarrows M_S^{\nu\cdot} + \nu\theta_S \\ \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \\ M_L \rightleftarrows M_L^{\nu\cdot} + \nu\theta_L \end{array}$$

In analogy with Nernst's observations on ordinary heterogeneous equilibria, the heterogeneous electromotive equilibrium between the

ions in the metal and in the bounding surface of the electrolyte, and similarly the heterogeneous electromotive equilibrium between the electrons in the metal and those in the bounding surface of the electrolyte will be established with great velocity.

If the metal is made the anode, electrons are withdrawn from it, and as a result the equilibrium will be disturbed. This disturbance may be compensated in various ways:

1. By a further ionisation of the atoms of the metal, whereby the electrons withdrawn are again replaced, whilst at the same time the newly formed ions go into solution.

This process is known as *anodic solution.*

2. As a result of the replacement of the electrons abstracted from the metal by electrons which pass from the electrolyte to the metal.

Since the concentration of free electrons in the liquid is so extremely small, the electrons furnished by the electrolyte must doubtless be split off from the anions. In this case, therefore, anodic solution is not observed, but, if the deposition pressure of the non-metal is reached, *deposition of the anion* takes place.

From these considerations it follows that when the potential of the metal is more negative than the deposition potential of the anion, the second process will appear first if the first process does not occur, or if it does not take place sufficiently quickly.

Thus anodic solution is the primary phenomenon.

It consists of the heterogeneous processes

$$\uparrow \quad \text{and} \quad \begin{matrix} M^{\nu\cdot}_{S} \\ \downarrow \\ M^{\nu\cdot}_{L} \end{matrix}$$
$$\nu\theta_S$$

and the subsequent homogeneous reaction

$$M_S \rightarrow M^{\nu\cdot}_{S} + \nu\theta_S.$$

Since it is known that these heterogeneous processes must take place with very great velocity, it will depend solely on the velocity with which inner equilibrium is re-established in the metal, which phenomenon will be observed when the metal is made the anode.

If this velocity is very great, naturally the composition of the metal will not change. If now the composition of the electrolyte also remains unaltered, in consequence of the deposition of metal on the cathode, for example, or because the volume of electrolyte used is very large, the potential of the anode will remain constant during anodic solution. This state of affairs is very nearly realised in the case of silver, and except when the current density is rather great, or, in other words, except when electrons are taken from the metal fairly rapidly, the potential only changes very slightly.

It should be pointed out here, however, that a small change of potential can always be caused by change in the concentration of the

metal ions in the bounding surface metal-electrolyte; since, however according to equation (14)

$$\Delta = -\frac{0{\cdot}058}{\nu} \log \frac{K'_{M^{\nu\cdot}}(M^{\nu\cdot}_S)}{(M^{\nu\cdot}_L)}$$

the potential only becomes $\frac{0{\cdot}058}{\nu}$ volts less negative or more positive when the concentration of the metallic ions $(M^{\nu\cdot}_L)$ is increased *ten*-fold, the influence of change of concentration must be very slight.

In other cases, however, it is found that when electrons are withdrawn very rapidly delays occur which, according to the new view, are due to the fact that the dissociation

$$M_S \rightarrow M^{\nu\cdot}_S + \nu\theta_S$$

takes place too slowly to allow the electrons withdrawn and the ions which have gone into solution to be replaced in time. The metal then becomes superficially poorer, both in ions and in electrons, and it then becomes clear from equation (14) that the potential difference will be less negative or more positive on account of the decrease of M_S, whilst at the same time $(M^{\nu\cdot}_L)$ remains constant. In other words, *anodic polarisation* appears.

Equation (17)

$$\Delta = \frac{RT}{F} \ln \frac{K_\theta'(\theta_S)}{(\theta_L)}$$

then furnishes the following information concerning the electronic concentrations.

When inner equilibrium cannot be established in the metal by the process of anodic solution, the electron concentration diminishes to a greater extent in the electrolyte than in the metal.

12. Cathodic Polarisation.

It is self-evident that a theory which claims to give an explanation of anodic polarisation, rational in every respect, only really represents an advance if it can at the same time satisfactorily explain cathodic polarisation. This demand is met by the views developed here. If an electrode is made the cathode, it will supply electrons, and as a result metallic ions from the electrolyte will be instantaneously deposited on the cathode, whereupon the formation of atoms of the metal takes place. Thus the whole process can be represented in the following way:—

$$\begin{array}{c} \nu\theta \\ \downarrow \\ M^{\nu\cdot}_S + \nu\theta_S \rightarrow M_S. \\ \uparrow \\ M^{\nu\cdot}_L \end{array}$$

If now the reaction

$$M^{\nu\cdot}_S + \nu\theta_S \rightarrow M_S$$

does not take effect sufficiently quickly, the freshly deposited metal will contain too many ions and electrons; it is still in the *state of formation*, and in this case, therefore, exactly the reverse phenomena occur to those previously noticed at the anode.

Thus it follows from equation (18) that the potential difference at the cathode will be less positive or more negative owing to the increase of $M^{\nu\cdot}_S$, whilst $M^{\nu\cdot}_L$ remains constant. So far as the electron concentration is concerned, it can be shown, by a similar method to that indicated above, that (θ_L) now increases more markedly than (θ_S).

13. Change in the Volta Effect in consequence of Polarisation.

We have here investigated the influence of anodic solution and cathodic deposition of a metal on the potential difference metal-electrolyte, when the current density is too great to allow inner equilibrium to be established in the metal.

Since, however, as has already been discussed, the potential difference is not measured, but the experimental electric potential, containing the Volta effect, we must investigate how this effect depends on anodic and cathodic polarisation.

For the potential difference in the case of a metal behaving in a unary manner, *i.e.* a metal which is always in inner equilibrium, this equation holds good:—

$$\Delta_{M_U-L} = -\frac{0{\cdot}058}{\nu} \log \frac{K'_{M^{\nu\cdot}}(M^{\nu\cdot}_S)_U}{M^{\nu\cdot}_L}.$$

while the potential difference for the same metal when polarised is given by

$$\Delta_{M_P-L} = -\frac{0{\cdot}058}{\nu} \log \frac{K'_{M^{\nu\cdot}}(M^{\nu\cdot}_S)_P}{(M^{\nu\cdot}_L)}.$$

Hence it results that

$$\Delta_{M_U-L} - \Delta_{M_P-L} = -\frac{0{\cdot}058}{\nu} \log \frac{(M^{\nu\cdot}_S)_U}{(M^{\nu\cdot}_{SP})} \quad . \quad . \quad (46)$$

Now for the Volta effect between two metals, 1 and 2, we have this expression:—

$$\Delta_{M_1-M_2} = \frac{\mu_{\theta M_1} - \mu_{\theta M_2}}{F} \quad . \quad . \quad . \quad . \quad (47)$$

and hence it may be concluded, just as in the deduction of the potential difference metal-electrolyte, that

$$\Delta_{M_1-M_2} = 0{\cdot}058 \log \frac{K'_\theta(\theta_{M_1})}{(\theta_{M_2})} \quad . \quad . \quad . \quad (48)$$

so that the change which the Volta effect undergoes when M_1 exists at one time in the unary state and at another time in a polarised condition is given by the relationship

$$\Delta_{M_1U-M_2} - \Delta_{M_1P-M_2} = 0{\cdot}058 \log \frac{(\theta_{M_1})_U}{(\theta_{M_1})_P} \quad . \quad . \quad (49)$$

If we now write

$$\frac{(M_{1_S^{\nu}})_U}{(M_{1_S^{\nu}})_P} = n$$

$$\frac{(\theta_{M_1})_U}{(\theta_{M_1})_P} = n$$

and hence it arises that when the change in the potential difference metal-electrolyte due to polarisation is

$$\frac{0{\cdot}058}{\nu} \log n,$$

the change in the Volta effect amounts to

$$0{\cdot}058 \log n,$$

and is therefore ν times as great.

We measure the sum of these two changes, that is to say

$$\frac{\nu + 1}{\nu} 0{\cdot}058 \log n,$$

and of this total change the portion $\frac{\nu}{\nu + 1}$ is due to the Volta effect. In the case of monovalent metals this fraction has the value $\frac{1}{2}$, for divalent metals the value $\frac{2}{3}$, and so on. Hence it follows that the *Volta effect may vary considerably*.

It is well known that many physicists are of opinion that the Volta effect only amounts to a few millivolts, and that the electromotive force of a galvanic element is exclusively conditioned by the potential difference metal-electrolyte, and that consequently this only need be considered.

Thus our considerations place the Volta effect in a new light, for they lead to the conclusion that if the Volta effect for metals which are in a state of inner equilibrium is, in fact, zero or very small, which means that the thermodynamic potentials of the electrons in the metals are equal or approximately equal, according to the electron theory this should be a characteristic property of metals in a state of inner equilibrium.

After the publication of these theoretical considerations the author has become acquainted with the interesting investigations of Gaede[1] and of Wertheimer[2] on the "Polarisation of the Volta Effect," and on the influence of the silent discharge on the Volta effect. As a result of this work it is clear that although the continuation and extension of these experiments is very desirable, the results already obtained are in surprisingly good agreement with the theory here developed.

[1] Gaede, *Ann. d. Phys.*, **14**, 641 (1904).
[2] Wertheimer, *Verh. d. Deutsch. Phys. Ges.*, **15**, 1333 (1913).

14. The Change in the Experimental Electric Potential produced by Polarisation.

Thus the conclusion is reached that the change measured in experiments on polarisation is magnified by the Volta effect. The consideration of the potential difference metal-electrolyte, therefore, only allows the phenomena of polarisation to be treated qualitatively; but it is often desirable, even in the qualitative treatment, to discuss these phenomena in the light of the new equations containing the solubility product of the metals and the solubility quotient in the case of non-metals, for in these formulæ, as is now well known, the Volta effect does not occur.

We only need to know the direction in which these products or quotients change as a result of polarisation. Since equations (14) and (17) are quite independent of whether the metal is in inner equilibrium or not, it is quite clear that they will also hold good when the metal becomes polarised.

Now it follows from these two equations that

$$\frac{(M_S^{\nu\cdot})\,(\theta_S)^{\nu\cdot}}{(M_L^{\nu\cdot})\,(\theta_L)^{\nu\cdot}} = K \quad . \quad . \quad . \quad . \quad (50)$$

and since the numerator of this fraction is diminished by anodic polarisation, the denominator must also decrease. The numerator of this fraction is, however, increased as a result of cathodic polarisation, and in this case the denominator must also increase. But the denominator is the solubility product of the metal, and so the conclusion is reached that *the solubility product of a metal is diminished by anodic polarisation and increased by cathodic polarisation.*

If now equation (41) is once more considered,

$$E = -\frac{0{\cdot}058}{\nu} \log \frac{L_M}{(M_L^{\nu\cdot})} - 2{\cdot}8$$

we see that the experimental electric potential of a metal will become less negative or more positive in consequence of anodic polarisation, and less positive or more strongly negative as a result of cathodic polarisation.

15. Polarisation Phenomena in the case of Hydrogen during the Electrolytic Evolution of this Gas.

It is clear that the phenomena here mentioned will also be exhibited when hydrogen is evolved, for according to our theory there is no essential difference between the evolution of this gas and the deposition of a metal.

When hydrogen is evolved the following reaction must take place at the cathode

$$2H^{\cdot}_G + 2\theta_G \rightarrow H_{G2};$$

if, however, this does not proceed quickly enough, a gaseous phase in

the *state of formation*[1] will be deposited; this phase contains too many ions and electrons, and so the solubility product is increased and the hydrogen phase exhibits a more negative potential difference than hydrogen which is in inner equilibrium. This polarisation of hydrogen is called *overvoltage*.

In order to differentiate between this and the overvoltage which may appear when hydrogen is evolved as the result of chemical action, the overvoltage just mentioned will be called "electrolytic overvoltage."

It should be mentioned here that the theory requires that the hydrogen dissolved in the coexisting metallic phase should here also be in the state of formation.

16. The Metal contains Positive Ions of Different Valencies.

The case will now be considered in which the metal contains two kinds of positive ion of different valencies.

If the metal behaves in the unary manner the following equilibria may be expected both in the metal and in the co-existing electrolyte :—

$$\begin{aligned} M &\rightleftarrows M^{\nu_1\cdot} + \nu_1\theta \\ M &\rightleftarrows M^{\nu_2\cdot} + \nu_2\theta \end{aligned}$$

so that for the complete system we obtain

$$\begin{array}{ccc} M_S & \rightleftarrows & M_S^{\nu_1\cdot} + \nu_1\theta_S \\ \uparrow\downarrow & & \uparrow\downarrow \quad\quad \uparrow\downarrow \\ M_L & \rightleftarrows & M_L^{\nu_1\cdot} + \nu_1\theta_L \end{array}$$

and

$$\begin{array}{ccc} M_S & \rightleftarrows & M_S^{\nu_2\cdot} + \nu_2\theta_S \\ \uparrow\downarrow & & \uparrow\downarrow \quad\quad \uparrow\downarrow \\ M_L & \rightleftarrows & M_L^{\nu_2\cdot} + \nu_2\theta_L \end{array}$$

whence the result is obtained that the following equilibrium prevails both in the metal and in the liquid :—

$$M^{\nu_1\cdot} \rightleftarrows M^{\nu_2\cdot} + (\nu_2 - \nu_1)\theta.$$

For the potential difference the following formulæ are now obtained :—

$$\Delta = -\frac{RT}{\nu_1 F} \ln \frac{K'_{M^{\nu_1\cdot}}(M_S^{\nu_1\cdot})}{(M_L^{\nu_1\cdot})}$$

$$\Delta = -\frac{RT}{\nu_2 F} \ln \frac{K'_{M^{\nu_2\cdot}}(M_S^{\nu_2\cdot})}{(M_L^{\nu_2\cdot})}$$

[1] Hydrogen is here referred to as in the "state of formation," and not in the "nascent state," since the latter term refers to the state which precedes the appearance of the hydrogen *phase*. A newly evolved phase which, however, has not yet reverted into inner equilibrium, will always be spoken of as a phase in the "state of formation."

and

$$\Delta = \frac{RT}{F} \ln \frac{K'_{\theta}(\theta_S)}{(\theta)_L}.$$

The experimental electric potential is given by

$$E = -\frac{0{\cdot}058}{\nu_1} \log \frac{L_{M^{\nu_1\cdot}}}{(M_L^{\nu_1\cdot})} - 2{\cdot}8 \quad . \quad . \quad . \quad (51)$$

and

$$E = -\frac{0{\cdot}058}{\nu_2} \log \frac{L_{M^{\nu_2\cdot}}}{(M_L^{\nu_2\cdot})} - 2{\cdot}8 \quad . \quad . \quad . \quad (52)$$

when

$$(M^{\nu_1\cdot})(\theta)^{\nu_1\cdot} = L_{M^{\nu_1\cdot}}$$

and

$$(M^{\nu_2\cdot})(\theta)^{\nu_2\cdot} = L_{M^{\nu_2\cdot}}.$$

It follows then from (51) and (52) that

$$\left[\frac{L_{M^{\nu_1\cdot}}}{(M_L^{\nu_1\cdot})}\right]^{1/\nu_1} = \left[\frac{L_{M^{\nu_2\cdot}}}{(M_L^{\nu_2\cdot})}\right]^{1/\nu_2}$$

or

$$\frac{L_{M^{\nu_1\cdot}}^{\nu_2}}{L_{M^{\nu_2\cdot}}^{\nu_1}} = \frac{(M_L^{\nu_1\cdot})^{\nu_2}}{(M_L^{\nu_2\cdot})^{\nu_1}} \quad . \quad . \quad . \quad . \quad (53)$$

If the metal is in inner equilibrium, the position of the equilibrium between the portions of the metal in the co-existing electrolyte is well defined, and hence at constant temperature and pressure the solubility products are constants. Now equation (53) indicates the connection between the ratio of the concentrations of the metallic ions of different valencies in the electrolyte and the ratio of the corresponding solubility products.

If it is assumed for a moment that the solubility product $L_{M^{\nu_1\cdot}}$ is much greater than $L_{M^{\nu_2\cdot}}$, or, in other words, that the ion $M^{\nu_1\cdot}$ behaves like the ion of a base metal, whilst $M^{\nu_2\cdot}$ functions as the ion of a much less base or of a noble metal, according to (53) the concentration ratio

$$\frac{(M_L^{\nu_1\cdot})^{\nu_2}}{(M_L^{\nu_2\cdot})^{\nu_1}}$$

is very great in the co-existing electrolyte, and consequently the electrolyte will be very rich in the baser ion.

It is at once seen from the following that when the metal is in inner equilibrium the above-mentioned ratio between the concentrations of the metallic ions in the co-existing electrolyte must be constant.

These equilibria exist in the electrolyte

$$M_L \rightleftarrows M_L^{\nu_1\cdot} + \nu_1\theta_L \quad \text{and} \quad M_L \rightleftarrows M_L^{\nu_2\cdot} + \nu_2\theta_L$$

and consequently

$$M_L^{\nu_1\cdot} \rightleftarrows M_L^{\nu_2\cdot} + (\nu_2 - \nu_1)\theta_L.$$

By eliminating (θ_L) from these equations the following expression is obtained :—

$$\nu_2 M_L^{\nu_1} \rightleftarrows \nu_1 M_L^{\nu_2} + (\nu_2 - \nu_1) M_L,$$

and from this, by applying the Law of Mass Action, we get

$$K_1 = \frac{(M_L^{\nu_2})^{\nu_1} (M_L)^{\nu_2 - \nu_1}}{(M_L^{\nu_1})^{\nu_2}}$$

or, since (M_L) is constant,

$$K_1' = \frac{(M_L^{\nu_2})^{\nu_1}}{(M_L^{\nu_1})^{\nu_2}}$$

16a. The Metal contains positive Ions of different sizes.

If the third possibility mentioned on page 115 is now considered, namely

$$M_s \rightleftarrows M_s^{\nu} + \nu\theta_s$$
$$M_{ns} \rightleftarrows M_{ns}^{n\nu} + n\nu\theta_s$$
$$M_{ns} \rightleftarrows nM_s$$

naturally corresponding equilibria are again obtained in the electrolyte, and the following formulæ are obtained for the experimental electric potential :—

$$E = -\frac{0{\cdot}058}{\nu} \log \frac{L_M}{(M_L^{\nu})} - 2{\cdot}8$$

and

$$E = -\frac{0{\cdot}058}{n\nu} \log \frac{L_{M_n}}{(M_{nL}^{n\nu})} - 2{\cdot}8$$

or

$$\frac{L_M^n}{L_{M_n}} = \frac{(M_L^{\nu})^n}{(M_{nL}^{n\nu})} = K_1.$$

Assuming these constant ratios, the following relationship also applies to the solution :

$$\frac{(M_L)^n}{(M_{n_L})} = K_2.$$

17. The Polarisation of a Metal containing Ions of different Valencies. Anodic and Cathodic Polarisation.

In the light of the foregoing remarks it is easy to understand what happens when a metal containing ions of different valencies is made the anode.

If the current density has reached a certain value, electro-ionisation in the metallic surface cannot replace the withdrawn electrons and the ions forced into the solution sufficiently quickly. Thus the metal becomes superficially poorer in electrically charged particles, electrons as

well as ions, and the consequence of this is that the potential difference becomes less negative or more strongly positive. With regard to the measurable quantities, it is, however, better to state here that in these circumstances the solubility product of the metal is diminished, and that consequently the experimental electric potential becomes less negative or more positive.

Up to this point this explanation of anodic polarisation is identical with that given in the case of metals containing only one kind of ion, for there are here two electro-ionisation equilibria, which really constitute one *large* inner equilibrium, though each can also be considered separately.

In addition to the reasons indicated here, *i.e.* in addition to the impoverishment of the metallic surface in respect of electrically charged particles, in the case of metals which give rise to ions of different valencies, polarisation is brought about by yet another circumstance when inner equilibrium is not restored sufficiently quickly, namely, the accumulation in the metallic surface of the most noble ion, which takes place under these conditions.

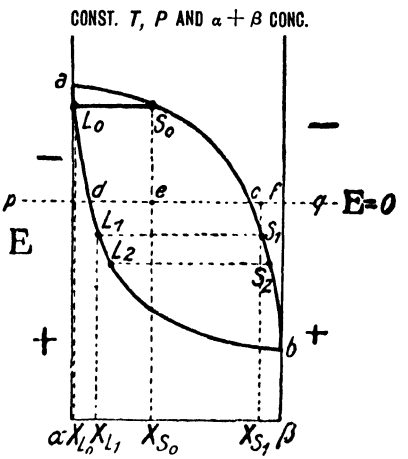


FIG. 117.

In order to demonstrate this, an EX diagram is employed, *i.e.* a diagram in which the ordinates are experimental electric potentials, while the concentrations of ions of different valencies in the electrolyte are made the abscissæ, the total concentration of these ions being kept constant. The figure holds good when the temperature and pressure are constant.

Whilst the metal previously considered contained the ions M^{ν_1} and M^{ν_2}, it is assumed in Fig. 117 that α represents a very base metal, and that it only contains the ions M^{ν_1}; β, on the other hand, denotes a metal in which the ion M^{ν_2} exclusively occurs.

The further assumption is now made that the metals α and β are miscible in all proportions in the solid state.

Every point on the line $a S_1 b$ denotes the experimental electric potential of a metal phase of definite composition.

Furthermore, if the composition of the metal phase and of the co-existing electrolyte are always indicated on the same horizontal line, and if a line is drawn through the points relating to electrolyte, the second curve $a L_1 b$ is obtained.

Now it is evident, since the signs of the electrolyte potential and the metal potential are different, that the ordinates of the liquid points on the line $a L_1 b$ and the mixed crystal points on the curve $a S_0 b$ will

likewise be of opposite sign. The signs given in the figure relate to the mixed crystal phase.

If we now suppose α and β to behave as true components, and that consequently they do not undergo mutual transformation, the result being that every metal must remain in its own inner equilibrium state, the question what will happen when a given metal phase, *e.g.* S_1, is made the anode? can be answered. It follows from the EX diagram that the anodic solution of S_1 must follow such a course that the co-existing metal and liquid phases are represented by the curves $a S_1 b$ and $a L_1 b$ respectively, and moreover that they are always situated on the same horizontal line. The metal phase and the electrolyte must therefore always change in the same direction, and hence it results that the metal phase will send α and β into solution in a proportion which is limited by S_1 and L. The metal phase and the liquid phase become richer in β as the result of this process, and so the metal phase S_2 will coexist with the electrolyte L_2. *We see, therefore, that the metal phase becomes more noble as the result of anodic solution, and that, in consequence of this, the potential of this phase always acquires a more positive value.* If the metal phase is made the *cathode*, exactly the reverse naturally takes place, and the metal phase moves upwards along the line $S_1 a$, *so that the potential becomes less positive or more strongly negative.*

The assumption has here been made that α and β each remains in inner equilibrium, *i.e.* that in the metal α the inner equilibrium

$$M_s \rightleftarrows M_s^{\nu_1} + \nu_1 \theta_s$$

and in the metal β the inner equilibrium

$$M_s \rightleftarrows M_s^{\nu_2} + \nu_2 \theta_s$$

exist; it has also been assumed that both metals behave as true components, and that they are miscible in all proportions in the solid state.

In this case an uninterrupted series of mixed crystals is obtained and in every homogeneous mixed crystal phase the equilibrium

$$M_s^{\nu_1} + \nu_1 \theta_s \rightleftarrows M_s^{\nu_2} + \nu_2 \theta_s$$

or

$$M_s^{\nu_1} \rightleftarrows M_s^{\nu_2} + (\nu_2 - \nu_1)\theta_s$$

also naturally prevails, the position of which is entirely determined by the composition of the mixed crystals.

If we now assume that the metal phase behaves as a unary substance, and that α and β undergo mutual transformation until a definite inner equilibrium position is reached, and indeed with such a velocity that inner equilibrium always prevails, a metal phase is obtained of a definite and invariable composition. If the composition of this metal phase is X_{s_0}, its experimental potential will be given in our EX figure by S_0, and that of the co-existing electrolyte by L_0. If now the metal phase S_0 is made the anode, its condition undergoes no change and the electrolyte similarly remains unaltered, for the transformation

$$\beta \rightarrow \alpha$$

keeps the composition of the metal and also the composition of the electrolyte constant, although the process of solution must result *per se* in the impoverishment of the metallic surface with respect to *a*.

In the case of cathodic deposition the co-existing phase equilibria remain at S_0 and L_0 in consequence of the reverse transformation.

It is clear that the two cases discussed here represent two extremes, and that, as has been previously pointed out, a metal can no longer exhibit unary behaviour when the velocity of solution or of deposition exceeds a given value. In the case of metals which yield ions of two different valencies our considerations lead therefore to the following result:—

If the metal is made the anode, and if a certain current density is exceeded, the potential will become less negative or more positive, firstly because the metallic surface becomes poorer in ions and electrons, and secondly because the surface becomes ennobled.

If, however, the metal is made the cathode, in consequence of the accumulation of ions and electrons on the metallic surface and because of a debasement of this surface, it will become less positive or more negative. This result again can be demonstrated by means of our E X figure.

If the metal is the anode, a decrease in the ion and electron concentration in the surface causes a depression of the points *a* and *b*, and consequently a depression of the lines $a\,S_1\,b$ and $a\,L_1\,b$; hence the metal phase S_0 is also depressed. The enrichment produces along with it a displacement of S_0 towards the right which similarly produces a depression; thus these two influences are additive and lead to a marked change of potential in the positive direction.

If the metal is made the cathode the displacement here referred to naturally takes place in the opposite direction.

The matters discussed in 16*a* are closely connected with the subject treated here.

18. The Decomposition Voltage.

Decomposition voltages must also be discussed here. If it is assumed that a non-corrodible electrode is made the cathode, the resulting processes can be explained by considering the heterogeneous equilibrium between the electrons in the metal and those in the bounding liquid.

This heterogeneous equilibrium

$$\begin{matrix}\theta_S\\ \uparrow\downarrow\\ \theta_L\end{matrix}$$

necessitates an increase in the electron concentration in the bounding surface when the electrode is made the cathode, as a result of which the potential naturally becomes less positive in accordance with the formula

$$E = -\,0{\cdot}058\,\log(\theta_L) - 2{\cdot}8,$$

This increase in the electron concentration may, however, result in the first place in the deposition of a metal (hydrogen being so considered), if the solubility product is exceeded.

If, however, the reaction

$$\nu\theta_S + M_S^{\nu\cdot} \rightarrow M_S$$

does not take place sufficiently rapidly, a metal phase in inner equilibrium will not be deposited, but a metal phase containing too many ions and electrons, in other words, a metal phase in the state of formation.

The solubility product of this metal phase is, however, greater than that of the metal in inner equilibrium, and consequently deposition can first take place at a potential which is less positive or more strongly negative than the equilibrium potential. If the non-corrodible electrode is the anode, electrons will be withdrawn from the bounding liquid, and the potential will become more positive, but in this case a non-metal can first be deposited if its solubility quotient has been exceeded. But if the reaction

$$n N_G^{\nu'} \rightarrow n\nu\theta_G + N_{nG}$$

does not proceed quickly enough, a non-metal phase is deposited, which is not in inner equilibrium and which has a greater solubility quotient, so that under these conditions deposition occurs at a potential which is more positive than the equilibrium potential. These processes may be influenced by the nature and condition of the electrode.

19. The Solution of Metals in Water or Acids.

It has been seen that anodic polarisation may be caused by a disturbance of the inner equilibrium in the electrode surface, and that cathodic polarisation is brought about by the deposition of a phase which likewise deviates from the inner equilibrium state, but in a direction contrary to that associated with anodic polarisation.

Now it can be shown that such disturbed or non-equilibrium states can also be obtained by the action of chemical reagents or as a result of chemical deposition.

In order to make this clear, it is, however, desirable more closely to consider the process of solution in the light of this theory.

(a) *The solution of metals in neutral aqueous salt solutions, hydrogen being evolved.*

The question whether a metal will liberate hydrogen from water at the ordinary temperature, the pressure being one atmosphere, may be answered from a consideration of the following equilibria

$$\begin{array}{ccc} M_S & \rightleftarrows & M_S^{\nu\cdot} + \nu\theta_S \\ \uparrow\downarrow & & \uparrow\downarrow \quad\quad \uparrow\downarrow \\ M_L & \rightleftarrows & M_L^{\nu\cdot} + \nu\theta_L \end{array} \quad . \quad . \quad . \quad . \quad (54)$$

and

$$\begin{array}{ccc} H_2 & \rightleftarrows & 2H^{\cdot}_L + 2\theta_L \\ \uparrow\downarrow & & \uparrow\downarrow \quad \uparrow\downarrow \\ H_{2G} & \rightleftarrows & 2H^{\cdot}_G + 2\theta_G \\ {\scriptstyle (1\ atm.)} & & \end{array} \quad . \quad . \quad . \quad . \quad (55)$$

The homogeneous equilibrium represented in (54) holds good for the case in which the liquid comes in contact with the metal, whilst (55) denotes the equilibrium prevailing in the liquid when this is saturated with hydrogen under a pressure of one atmosphere.

It is now immediately seen that if the electron concentration $(\theta_L)_M$ in the metallic equilibrium is greater than the electron concentration $(\theta_L)_{H_2}$ in the hydrogen equilibrium, the system Metal + Liquid cannot be in equilibrium.

The hydrogen ions which diffuse into the layer bounding the metal will there unite with electrons to form hydrogen molecules. The electrons withdrawn from the liquid in contact with the metal will be instantaneously replaced, whilst with these electrons metallic ions also go into solution.

In the above case this process will go on even though the liquid is saturated with hydrogen, and as a result hydrogen will escape.

This consideration places us in a position to indicate the conditions under which the solution of a metal is accompanied by evolution of hydrogen. For this purpose use is again made of the solubility product

$$L_M = (M^{\nu\cdot}_L)\,(\theta_L)^{\nu},$$

so that

$$(\theta_L)_M = \frac{L_M^{\frac{1}{\nu}}}{(M^{\nu\cdot}_L)^{\frac{1}{\nu}}}$$

and

$$L_{H_2} = (H^{\cdot}_L)^2(\theta_L)^2$$

or

$$(\theta_L)_{H_2} = \frac{L_{H_2}^{\frac{1}{2}}}{(H^{\cdot}_L)}.$$

The condition is

$$(\theta_L)_M > (\theta_L)_{H_2} \quad . \quad . \quad . \quad . \quad (56)$$

or

$$\frac{L_M^{\frac{1}{\nu}}}{(M^{\nu\cdot})^{\frac{1}{\nu}}} > \frac{L_{H_2}^{\frac{1}{2}}}{(H^{\cdot}_L)}$$

or

$$L_M^{\frac{1}{\nu}} > L_{H_2}^{\frac{1}{2}} \frac{(M^{\nu\cdot}_L)^{\frac{1}{\nu}}}{(H^{\cdot}_L)} \quad . \quad . \quad . \quad (57)$$

Assuming the liquid to be an aqueous salt solution in which

$$(M_L^{\nu}) = 1,$$

if no hydrolysis occurs, we can write $(H^{\bullet}) = 10^{-7}$, and the condition then becomes

$$L_M^{\frac{1}{\nu}} > L_{H_2}^{\frac{1}{2}} \cdot 10^7$$

or

$$L_M^{\frac{1}{\nu}} > 10^{-41} \quad . \quad . \quad . \quad . \quad . \quad (58)$$

If the table of solubility products is now consulted, we see that iron is the last metal, assuming unary behaviour (and the values given for the solubility products only hold good on that assumption) to liberate hydrogen under these circumstances. It is clear that when $(\theta_L)_M < (\theta_L)_{H_2}$ precipitation of the metal by hydrogen must, conversely, take place. This case will be discussed when the precipitation of metals by metals is considered.

(b) *The liberation of hydrogen from an acid solution.*

If instead of a neutral salt solution we consider an acid solution, a different result is naturally obtained.

Thus if we suppose that $(H^{\bullet}) = 1$ and $(M_L^{\nu}) = 1$, the condition for the evolution of hydrogen becomes :—

$$L_M^{\frac{1}{\nu}} > L_{H_2}^{\frac{1}{2}}.$$

or

$$L_M^{\frac{1}{\nu}} > 10^{-48} \quad . \quad . \quad . \quad . \quad . \quad (59)$$

In this case all the metals standing above hydrogen in the solubility product series go into solution.

20. The Disturbance of a Metal by an Acid.

If in the process just discussed the inner equilibria in the solid and gaseous phases are also reviewed, the homogeneous equilibria being indicated by (*a*) and (*b*), we can write

$$\left.\begin{array}{lll} M_S \rightleftarrows M_S^{\nu} + \nu\theta_S & (a) \\ \uparrow\downarrow \quad\quad \uparrow\downarrow \quad\quad \uparrow\downarrow & \\ M_L \rightleftarrows M_L^{\nu} + \nu\theta_L & (b) \end{array}\right\} \quad . \quad . \quad . \quad (60)$$

and

$$\left.\begin{array}{lll} H_{2_L} \rightleftarrows 2H^{\bullet}{}_L + 2\theta_L & (a) \\ \uparrow\downarrow \quad\quad \uparrow\downarrow \quad\quad \uparrow\downarrow & \\ H_{2_G} \rightleftarrows 2H^{\bullet}{}_G + 2\theta_G & (b) \end{array}\right\} \quad . \quad . \quad . \quad (61)$$

It is now seen, without further explanation, that the abstraction of

electrons from (*b*) in equation (60), by (*a*) in equation (61), cannot really be compensated to any extent worth mentioning by the reaction

$$M_L \rightarrow M_L^{\nu\cdot} + \nu\theta_L$$

for the concentration of (M_L) is much too small to yield electrons rapidly, and hence also the evolution of hydrogen does not take place in the liquid but only in the bounding layer. The electrons withdrawn from the bounding layer will be replenished directly from the metal with great velocity, for the heterogeneous equilibrium

$$\begin{matrix}\theta_S \\ \uparrow\downarrow \\ \theta_L\end{matrix}$$

is instantly re-established. If electrons pass from the metal to the solution, metallic ions from the metal will also go into solution, and thus we see that the true solution process consists in the direct passage of electrons and ions from the metal into the solution, thus

$$\begin{matrix}\theta_S & M_S^{\nu\cdot} \\ \downarrow & \downarrow \\ \theta_L & M_L^{\nu\cdot}\end{matrix}$$

If the behaviour of the metal is unary, the withdrawn electrons and ions will be replaced very rapidly as a result of the following process :—

$$M_S \rightarrow M_S^{\nu\cdot} + \nu\theta_S,$$

and the composition of the metal remains absolutely unchanged.

If, however, ions and electrons go into solution so rapidly that inner equilibrium can no longer be maintained, the metallic surface becomes impoverished as regards ions and electrons, just as when anodic polarisation occurs. But in the case of hydrogen special circumstances may arise. Thus it is possible that the reaction

$$2\theta_L + 2H^{\bullet}_L \rightarrow H_2$$

does not proceed sufficiently rapidly to remove the electrons so added, to the extent required by the solubility product of hydrogen. In this case, since the concentrations (θ_L) and $(H^{\bullet}_L)$ are relatively too high and (H_{2_L}) is too low, it follows from the heterogeneous equilibria

$$\begin{matrix}2\theta_L & 2H^{\bullet}_L & H_{2_L} \\ \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow \\ 2\theta_G & 2H^{\bullet}_G & H_{2_G}\end{matrix}$$

that (θ_G) and $(H^{\bullet}_G)$ will also be too high and that (H_{2_G}) will be too low; or, in other words, hydrogen containing too many ions and electrons will escape and the gas is therefore in the state of formation, a phenomenon which, as we have seen, also occurs when hydrogen is liberated electrolytically, and which may be called hydrogen over-voltage when the gas is liberated by purely chemical methods. Naturally no essential difference exists here, for whether the electrons which

unite with hydrogen ions are introduced by the metallic cathode, or whether they go into solution simultaneously with the ions of the metal, without being supplied from an external source, the evolution of hydrogen remains unaffected.

21. These Problems considered in the Light of the Phase Rule.

In studying the various heterogeneous electrolytic processes it is very important that the phase rule should also be applied, for in this way a better insight is obtained into the different relationships.

An E X diagram has already been employed when discussing the polarisation of metals which contain ions of different valencies, and this method will again be applied here; in this case the four component system metal—hydrogen—acid—water must be considered. According to the phase rule

$$F = n + 2 - r,$$

and thus we get

$$F = 6 - r.$$

If we imagine the pressure, temperature, and the sum of the concentrations of the metallic ions and the hydrogen ions to remain constant

$$F = 3 - r.$$

Consequently when *three* phases co-exist the system is invariant, and monovariant when *two* phases co-exist. Hence the co existence metal-electrolyte is monovariant, *i.e.* under the circumstances here mentioned various homogeneous equilibria are possible in our system, for in the electrolyte, in which the total concentration $(M^{\nu\cdot}) + (H^{\cdot})$ is assumed to be constant, the ratio $\frac{(M^{\nu\cdot}_L)}{(H^{\cdot}_L)}$ may be varied, and every value of this quotient corresponds to a definite value of the experimental electrolytic potential metal-electrolyte or hydrogen—electrolyte.

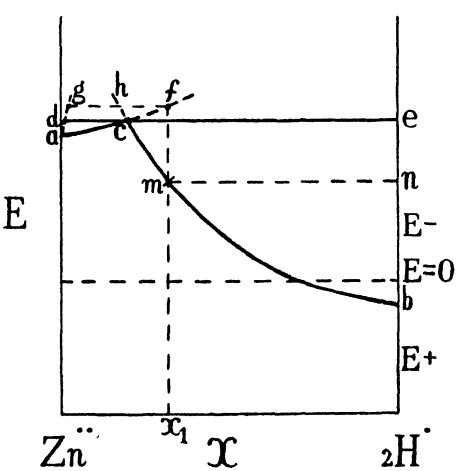


FIG. 118.

Let us now consider a concrete case, for example, the system Zn—HCl—H_2O at the ordinary temperature, under a pressure of one atmosphere and for a given total concentration $(Zn^{\cdot\cdot}_L) + (2H^{\cdot}_L)$; $2H^{\cdot}$ is written here because then the total ionic concentration remains unaltered by

substitution. In the above E X diagram the relative concentrations of the zinc and hydrogen ions are indicated on the X axis, whilst on the Y axis the experimental electrolytic potentials of the electromotive equilibria zinc—electrolyte and hydrogen electrode—electrolyte are given.

The following expression holds good for the experimental electrolytic potential of zinc

$$E_{Zn} = -\frac{0{\cdot}058}{2} \log \frac{L_{Zn}}{(Zn^{\bullet\bullet}{}_L)} - 2{\cdot}8$$

and for the hydrogen electrode we have

$$E_{H_2} = -\frac{0{\cdot}058}{2} \log \frac{L_{H_2}}{(H^{\bullet}{}_L)^2} - 2{\cdot}8.$$

Consequently if zinc is dipped into a solution of zinc chloride of known concentration, if we imagine a number of zinc ions to be replaced by an equivalent quantity of hydrogen ions, this means that $(Zn^{\bullet\bullet}{}_L)$ is diminished. The smaller $(Zn^{\bullet\bullet}{}_L)$ becomes, the greater will be the logarithm of

$$\frac{L_{Zn}}{(Zn^{\bullet\bullet}{}_L)}$$

and the smaller will be the positive value of the first term.

Hence the result is obtained that E_{Zn} becomes more negative as the concentration of the zinc ion decreases.

In Fig. 118 *a* represents the theoretical electric potential of zinc in a solution of $ZnCl_2$, containing 1 grm.-mol. per litre, which is free from hydrogen ions. It should be noticed that solutions in which $(H^{\bullet}) = 0$ are experimentally unattainable, for in such a solution (OH') would be ∞. In the above solution of a zinc salt the concentration of OH' ions must be so small that the solubility product of zinc hydroxide or of the basic zinc salts is not exceeded. Hence, experimentally, we do not start at *a*, but with a solution which already contains a certain concentration of hydrogen ions.

For diminishing values of $(Zn^{\bullet\bullet})$ increasing potentials are always obtained, indicated here by a line *a f*. Of course the same result is obtained if a hydrogen electrode under a pressure of one atmosphere, which dips into a solution of hydrochloric acid equivalent in strength to the zinc chloride solution, is made the starting point, and the hydrogen ions therein are replaced by an equivalent quantity of zinc ions.

If *b* represents the initial experimental electrolytic potential of the hydrogen electrode (this potential would be zero if $(H^{\bullet}{}_L) = 1$) as $(H^{\bullet}{}_L)$ diminishes, the quantity E_{H_2} becomes less positive or more negative, as may be seen from the line *b h*.

It should be especially emphasised that the lines *a f* and *b h* relate to liquids. Thus, for example, the line *a f* indicates those liquids which co-exist with zinc at different potentials. We know that co-existing phases are denoted by horizontal lines, and hence, to every liquid point

on the line there corresponds a second point, representing the co-existing zinc phase; this second point is connected with the first by a horizontal. If the zinc phase were absolutely free from hydrogen all these phases would lie on the Zn axis, but this is not the case; the zinc contains dissolved hydrogen, and the hydrogen content increases with increasing concentration of hydrogen ions. Consequently the hydrogen containing zinc mixed crystal phases which co-exist with liquids represented by the line af are indicated by the line ag.[1]

As regards the hydrogen phases which co-exist with electrolyte on the line bh, it can be stated that they will not contain any appreciable quantity of zinc, and consequently that they lie entirely on the hydrogen axis.

As is evident from the diagram, the lines af and bh intersect in the point c; this point therefore represents a liquid which co-exists both with the hydrogen containing zinc phase d and with the hydrogen phase e, so that $(\theta_M) = (\theta_{H_2})$.

Hence the zinc phase d and the hydrogen phase e have the same experimental electrolytic potential. This three-phase system is invariant, and it can therefore exist at only one clearly defined potential. Furthermore, it may be seen that the prolongations of these lines above c and d are metastable, *i.e.* they represent equilibria between metastable phases.

It is of interest to calculate the ratio

$$\frac{(Zn^{\bullet\bullet}{}_L)}{(2H^{\bullet}{}_L)}$$

for the electrolyte c.

In the three-phase equilibrium zinc phase—electrolyte—hydrogen phase, the experimental electrolytic potentials of the zinc and hydrogen phases are identical, and we may therefore write

$$E_{Zn} = E_{H_2}.$$

Now

$$E_{Zn} = -\frac{0{\cdot}058}{2} \log \frac{L_{Zn}}{(Zn^{\bullet\bullet}{}_L)} - 2{\cdot}8$$

and

$$E_{H_2} = -\frac{0{\cdot}058}{2} \log \frac{L_{H_2}}{(H^{\bullet}{}_L)^2} - 2{\cdot}8.$$

Hence it follows that

$$\frac{L_{Zn}^{\frac{1}{2}}}{(Zn^{\bullet\bullet}{}_L)^{\frac{1}{2}}} = \frac{L_{H_2}^{\frac{1}{2}}}{(H^{\bullet}{}_L)}$$

or

$$\frac{L_{Zn}^{\frac{1}{2}}}{L_{H_2}^{\frac{1}{2}}} = \frac{(Zn^{\bullet\bullet}{}_L)^{\frac{1}{2}}}{(H^{\bullet}{}_L)}.$$

[1] It may be noticed here that the E X diagram gives the gross composition of the electrode, so that, for example, the particular state in which the zinc and the hydrogen occur is not expressed here.

Substituting the values for the solubility products, we obtain

$$\frac{(Zn^{\bullet\bullet}_L)^{\frac{1}{2}}}{(H^{\bullet}_L)} = 10^{13}$$

and assuming that

$$(Zn^{\bullet\bullet}_L) = 1,$$
$$(2H^{\bullet}_L) = \tfrac{1}{2}10^{-13},$$

i.e. the point *c* is displaced to one side to a considerable extent.

In an aqueous solution of zinc chloride, if hydrolysis does not take place, $(H^{\bullet}_L) = 10^{-7}$, *i.e.* the composition of this solution would already lie to the right of the point *c*.

It is known that hydrogen is evolved if

$$(\theta_M) > (\theta_{H_2})$$

and since

$$E_{Zn} = -0{\cdot}058 \log (\theta_M) - 2{\cdot}8$$

and

$$E_{H_2} = -0{\cdot}058 \log (\theta_{H_2}) - 2{\cdot}8$$

hydrogen will be evolved if, by reason of the composition of the electrolyte, the potential of the metal is more strongly negative than the potential of the hydrogen electrode. As is shown by the EX diagram, the zinc must therefore be dipped into a solution which lies to the right of *c*, or into a solution the composition of which corresponds, as regards the concentration ratio

$$\frac{(Zn^{\bullet\bullet}_L)}{(2H^{\bullet}_L)}$$

with the point X_1, for example. Thus we see that zinc cannot co-exist in a stable state with this liquid, for the liquid *m*, having the composition X_1, can only exist in stable equilibrium with the hydrogen phase *n*. A metastable co-existence of zinc with a liquid having the composition X_1 would certainly be possible at a more negative potential indicated by *f* and *g*. This metastable two-phase equilibrium does not appear, however, in the case under consideration, but a condition arises in which the zinc is in equilibrium with its bounding surface. This state is reached as the result of the solution of zinc with evolution of hydrogen, because, of the electrically charged particles expelled (electrons and ions), the electrons unite with hydrogen ions, in the manner already mentioned, to form hydrogen molecules. It is assumed here that during this process the zinc and the hydrogen behave in a unary manner.

During this process of solution the liquid in the bounding layer becomes richer in zinc ions and poorer in hydrogen ions, and a bounding liquid is formed having the composition *c*.

In the bounding surface, therefore, the zinc phase *d*, the hydrogen phase *e* and the liquid phase *c* co-exist. Outside the bounding layer, however, the electrolyte has the composition X_1, and hence zinc ions diffuse from the bounding surface into the surrounding liquid; hydrogen

ions, on the other hand, pass from the electrolyte into the bounding surface, where, since the solubility product of hydrogen is exceeded, the homogeneous reaction

$$2H^{\bullet}_{L} + 2\theta_{L} \rightarrow H_{2L}$$

takes place, and also the heterogeneous processes

$$\begin{array}{ccc} H^{\bullet}_{L} & \theta_{L} & H_{2L} \\ \downarrow & \downarrow & \downarrow \\ H_{G} & \theta_{G} & H_{2G} \end{array}$$

As has already been shown, the liquid point *c* is displaced considerably to one side, whence it follows that the line *d c e*, representing the three-phase equilibrium, is situated at practically the same height as the point *a*.

A value would thus be obtained for the potential of the three-phase equilibrium, which is practically in agreement with the theoretical potential *a* of hydrogen free zinc.

It has therefore been demonstrated that, if a zinc rod is dipped into an electrolyte, the composition of which corresponds with a point lying to the right of *c*, the three-phase equilibrium *d c e* is established with evolution of hydrogen, and that consequently the escaping hydrogen has the same experimental electrolytic potential as the zinc. If now a hydrogen electrode is introduced into the liquid, the potential of the hydrogen electrode is found to be *m n*, i.e. a more positive potential. From this observation one would be inclined to conclude that under the overvoltage hydrogen would be developed on the zinc. This conclusion is not, however, justified by the observation mentioned here, for the hydrogen liberated on the zinc is derived from a solution of quite another concentration from that in which the hydrogen electrode is placed. Thus we see that the potential of the hydrogen evolved on a metal can be much more negative than the potential of the hydrogen electrode, without overvoltage occurring.[1]

22. The Inner Equilibrium in the Metallic Surface is disturbed by Chemical Action resulting in the Evolution of Hydrogen.

Hitherto it has been assumed that during the process of solution the metal behaves in a unary manner. The case will now be considered in which the metallic surface becomes impoverished as regards ions and electrons, whilst the hydrogen evolved exhibits unary behaviour.

It has already been shown that under these circumstances the potential of the metal becomes less negative, and the question now arises how this can be illustrated by means of an EX diagram. We shall again consider a liquid having the composition x_1 (Fig. 119) and,

[1] It must be pointed out here that if the hydrogen dissolved in the metal to a considerable extent, the three-phase equilibrium *d c e* could also lie between *a* and *b*. This position often occurs in cases in which two metals are concerned.

as in the previous case, a three-phase equilibrium is obtained between metal, electrolyte and hydrogen.

Since, according to our assumption the hydrogen evolved is unary in its behaviour, the electrolyte will naturally lie on the line *b c*. The disturbed metal phase, the potential of which is positive, will now be denoted by *d'*, and thus the three co-existing phases just mentioned can be represented by the points *d' c' e'*. The line *a' c'* shown here

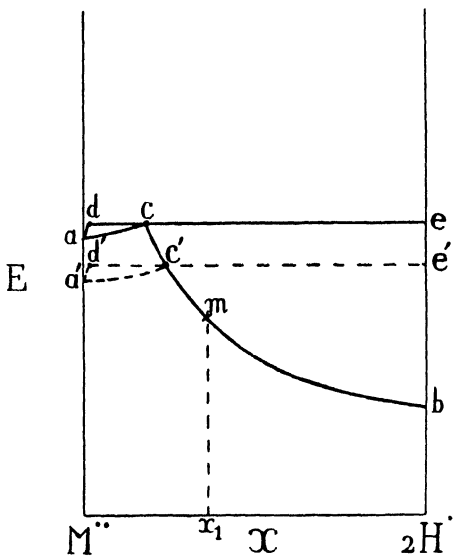


FIG. 119.

only becomes significant, however, when it is possible for the metal phase which is not in inner equilibrium to co-exist with yet another electrolyte such as *c'*.

23. The Metal Remains in Inner Equilibrium during the Evolution of Hydrogen, but the Hydrogen is in the State of Formation.

In the preceding section it was assumed that the metal phase was disturbed, whilst the hydrogen behaved in a unary manner. The converse case will now be considered; that is to say, the behaviour of the metal is unary and it is in contact with a hydrogen phase in the state of formation. The hydrogen phase contains too many ions and electrons, and hence its potential is more negative than when it is in inner equilibrium. The electrolytes of different compositions which co-exist with this hydrogen phase are situated on the line *b' c'* in Fig. 120.

Since now the liquids which co-exist with the unary metal are

represented by the line af, the three-phase co-existence indicated by the points $d'\,c'\,e'$ consequently occurs here, and thus the three-phase potential is more negative than when the hydrogen, like the metal, is in inner equilibrium (Fig. 118). The evolved hydrogen is now overstrained; still it would be incorrect to assume that the magnitude of the overvoltage is given by the difference between the potential of the hydrogen electrode and that of the hydrogen set free. The point m represents the potential of the hydrogen electrode, whilst that of the evolved hydrogen is defined by c'. The overvoltage can, however, only be correctly indicated if the potentials shown have reference to liquids of the same composition—that is to say, to the liquid c'. If this is borne in mind, it may be seen that the actual hydrogen overvoltage is represented by the line $m'\,c'$.

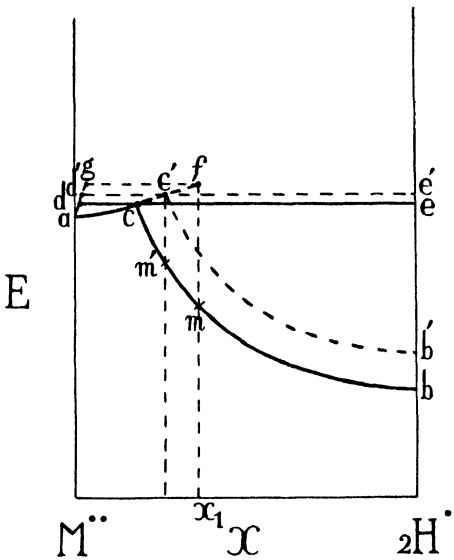


FIG. 120.

It must be pointed out here that the potential lines, and in particular the line af, are indicated very schematically. In accordance with equation (41) these lines, which originate at a and c respectively, follow for the most part a nearly horizontal course; only on approaching the axis of the other component does an ever more marked increase appear.

The line $a\,c\,c'\,f$ (Fig. 110) is therefore almost horizontal, so that even if the hydrogen reverts strongly into the state of formation, and the displacement $c\,c'$ is consequently relatively great, the line $d'\,c'\,e'$ must practically coincide with $d\,c\,e$.

24. The Inner Equilibrium in the Surface of the Metal is disturbed and the Hydrogen Phase is in the State of Formation.

The case still remains to be considered in which not only is the metal superficially disturbed by the process of solution, but at the same time the hydrogen phase in contact with the metal is not yet in inner equilibrium, *i.e.* it contains too many ions and electrons, and hence its potential is too negative.

The question now arises: What value will the three-phase potential have under these circumstances?

This case is peculiar in so far that the disturbance of the equilibrium in the metal on the one hand and the state of formation of the hydrogen on the other act in opposite directions. Consequently, whilst the left-hand portion of the EX diagram falls, the right-hand portion rises; thus, for example, the point *a* falls whilst *b* rises. If, therefore, the effect on the metal predominates, the new three-phase potential will be more positive than that which would be obtained if the metal and the hydrogen were in inner equilibrium. If, however, the state of formation of the hydrogen predominates, the three-phase potential will in consequence be more negative than when inner equilibrium exists.

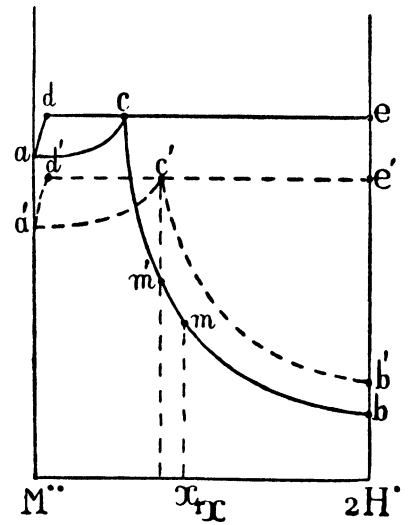


FIG. 121.

The first case has been assumed in Fig. 121. The potential of the three-phase equilibrium formed in the process of solution is indicated by *d' c' e'*. The lines *a' c'* and *b' e* would only have any meaning here if, besides existing in inner equilibrium, the metal and hydrogen phases could also exist in contact with electrolytes of composition different from *c*.

Since in this case the hydrogen phase passes into the state of formation, a hydrogen overvoltage again occurs, the magnitude of which may be found from the length of the line *m' c'*.

In Fig. 121*a* it has been assumed that the influence of the state of formation of the hydrogen predominates.

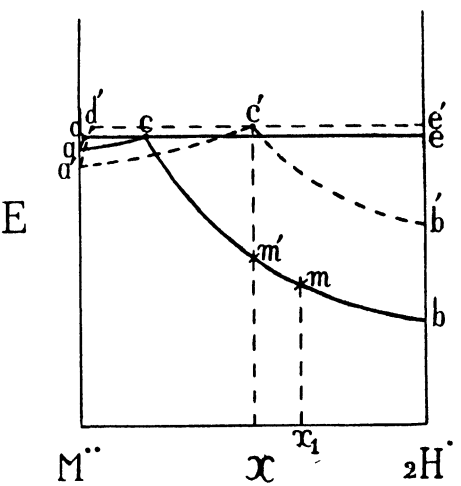


FIG. 121a.

In connection with the concluding remarks of § 23 it must be emphasised here that, on account of its smallness, the influence of the state of formation of the hydrogen on the potential

under consideration can in general be neglected. Only when the three-phase equilibrium, metal, hydrogen, electrolyte, lies between *a* and *c* will the state of formation of the hydrogen exert a great influence on the three-phase potential, but then the disturbance of the metal and the state of formation of the hydrogen would influence the potential in the same direction.

25. Very Inert Metals.

Finally a kind of limiting case must still be considered.

If the inner equilibrium in the metal is only established slowly it will be disturbed by the action of a liquid, the composition of which lies to the right of that indicated by the point *c*, and as a result the potential will be more positive.

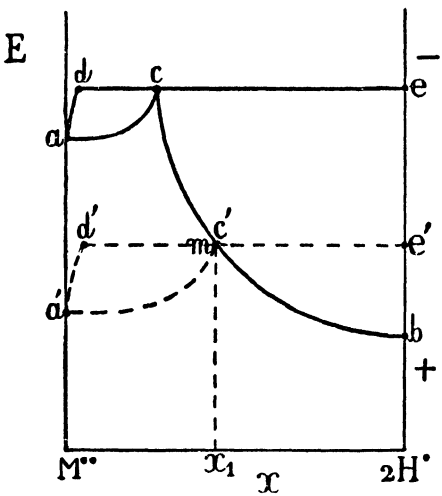


FIG. 122.

If it is assumed that the metal is extremely inert, the disturbance of the equilibrium in the surface of the metal could then proceed so far that the electron concentration in the metallic equilibrium would become equal to the electron concentration in the hydrogen equilibrium. If we call these electron concentrations $(\theta_M)_L$ and $(\theta_{H_2})_L$, it follows from the following formulæ for the potentials of the metallic and the hydrogen electrodes

$$E_M = -\frac{RT}{F} \ln (\theta_M)_L - 2{\cdot}8 \quad . \quad . \quad . \quad (64)$$

and

$$E_{H_2} = -\frac{RT}{F} \ln (\theta_{H_2})_L - 2{\cdot}8 \quad . \quad . \quad . \quad (65)$$

that in this case, since

$$(\theta_M)_L = (\theta_{H_2})_L, \quad E_M = E_{H_2},$$

or, stated in words, under these circumstances both potentials will be the same.

This result can be made clear by means of the EX diagram, Fig. 122, in the following way.

The disturbance of the equilibrium has proceeded so far that the metal phase has acquired the value *d'* instead of *d*. The liquid with which the metal phase *d'* co-exists now has the same composition as

the electrolyte outside this bounding surface. Consequently, in this limiting case, the potential of the hydrogen in the bounding surface is the same as the potential of the hydrogen electrode.

26. The Condition for the Precipitation of a Metal by Means of Hydrogen.

It has always been assumed here that the composition of the liquid lies to the right of the point *c*. But clearly cases may also occur in which the point representing the composition of the liquid is situated to the left of *c*.

In this case quite analogous phenomena may be expected if, instead of a metal, a hydrogen electrode is introduced and hydrogen is passed through the liquid.

When x_1, the composition of the liquid, lies to the left of *c*, the EX diagram (Fig. 123) shows that the potential of the hydrogen electrode, indicated by $c'e'$, is more strongly negative than the potential $g\,k$, which the metallic electrode would give if this were also introduced, disturbances being excluded.

Hence, in the equation

$$E_{H_2} = -0{\cdot}058 \log (\theta_{H_2})_L - 2{\cdot}8,$$

$(\theta_{H2})_L$ is greater than is $(\theta_M)_L$ in the following equation:—

$$E_M = -0{\cdot}058 \log (\theta_M)_L - 2{\cdot}8;$$

that is to say, if a liquid having the composition x_1 is considered.

It is evident, therefore, that the hydrogen electrode causes the solubility product of the metal to be exceeded, and that on destroying this metastable state the metal phase will be formed. Thus the processes which take place in the bounding surface of the hydrogen electrode are as follows:—

$$\begin{array}{cc} 2\theta_L & M^{\cdot\cdot}{}_L \\ \downarrow & \downarrow \\ 2\theta_S & M^{\cdot\cdot}{}_S \end{array}$$

$$2\theta_S + M^{\cdot\cdot}{}_S \rightarrow M_S$$

$$\begin{array}{cc} \theta_G & H^{\cdot}{}_G \\ \downarrow & \downarrow \\ \theta_L & H^{\cdot}{}_L \end{array}$$

$$H2_G \rightarrow 2H^{\cdot}{}_G + 2\theta_G,$$

in which it should be noticed that the heterogeneous processes take place instantaneously, and consequently the homogeneous processes proceed much more slowly. Thus, because of the smallness of $(\theta)_L$ the reaction

$$2\theta_L + M^{\cdot\cdot}{}_L \rightarrow M_L$$

may even be neglected here.

As a result of the processes mentioned above a three-phase system is

naturally formed, consisting of a metal phase, a hydrogen phase and an electrolyte. If we assume for a moment that the metal establishes itself in inner equilibrium most quickly, the position of this electrolyte in our E X diagram is at once specified.

That is to say, this electrolyte will then be indicated by *c*, for this point represents the liquid which co-exists in inner equilibrium with both the metal phase *d* and the hydrogen phase *e*. The liquid *c*, representing the bounding layer which is in contact with the metal phase and the hydrogen phase, since hydrogen ions pass into solution with the electrons and metallic ions are also deposited with electrons, has quite a different composition from that of the liquid outside the bounding surface. The latter contains more metallic ions and fewer hydrogen ions, so that metallic ions will diffuse into the bounding layer and hydrogen ions will diffuse out of it.

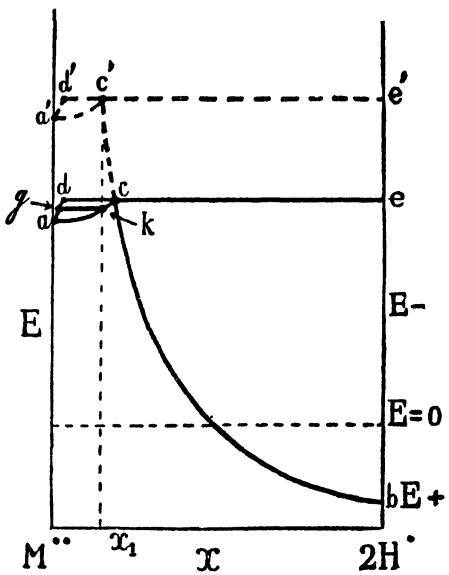


FIG. 123.

Since, generally, the potential of the three-phase equilibrium mentioned here practically coincides with the equilibrium potential,[1] the conclusion is reached that when the metal phase attains a state of equilibrium very quickly, the potential measured by means of the hydrogen electrode must correspond with the equilibrium potential of the metal.

We have here assumed that the deposited metal reaches a state of inner equilibrium very quickly. If, on the other hand, this velocity is very small, a metal phase will be deposited containing too great a concentration of ions and electrons, and the potential of this metal phase will be more negative than that of the metal phase when in inner equilibrium. It is a phase in the state of formation.

The limiting case is naturally that in which a metal phase is formed, the bounding surface of which has the same electron concentration as the hydrogen electrode.

In this case, therefore, the three-phase equilibrium *d' c' e'* will be established, the potential of which is in complete agreement with the unaltered potential of the hydrogen electrode.

[1] Naturally this would not be the case if the difference between the normal potentials of the metal and the hydrogen electrode was only very small.

27. The Precipitation of a Metal by a Baser Metal.

If a metal M_1 having a valency ν_1 is dipped into a solution of a salt of another metal M_2, it will depend on the equilibria

$$\begin{array}{c} M_{1S} \\ \uparrow\downarrow \\ M_{1L} \rightleftarrows M_{1L}^{\nu_1\cdot} + \nu_1\theta_L \end{array}$$

and

$$\begin{array}{c} M_{2S} \\ \downarrow\uparrow \\ M_{2L} \rightleftarrows M_{2L}^{\nu_2\cdot} + \nu_2\theta_L \end{array}$$

whether precipitation of M_2 will occur.[1]

From these relationships it follows that

$$L_{M_1} = (M_{1L}^{\nu_1\cdot})\,(\theta_L)^{\nu_1}_{M_1}$$

and

$$L_{M_2} = (M_{2L}^{\nu_2\cdot})\,(\theta_L)^{\nu_2}_{M_2}$$

and hence the following further equations are obtained :—

$$(\theta_{M_1}) = \left[\frac{L_{M_1}}{(M_{1L}^{\nu_1\cdot})}\right]^{\frac{1}{\nu_1}}$$

and

$$(\theta_{M_2}) = \left[\frac{L_{M_2}}{(M_{2L}^{\nu_2})}\right]^{\frac{1}{\nu_2}}.$$

Precipitation of M_2 will now occur, if

$$(\theta_{M_1}) > (\theta_{M_2})$$

or if

$$\left[\frac{L_{M_1}}{(M_{1L}^{\nu_1\cdot})}\right]^{\frac{1}{\nu_1}} > \left[\frac{L_{M_2}}{(M_{2L}^{\nu_2\cdot})}\right]^{\frac{1}{\nu_2}}$$

or if

$$L_{M_1}^{\frac{1}{\nu_1\cdot}} > L_{M_2}^{\frac{1}{\nu_2\cdot}} \cdot \frac{(M_{1L}^{\nu_1\cdot})^{\frac{1}{\nu_1}}}{(M_{2L}^{\nu_2\cdot})^{\frac{1}{\nu_2}}}.$$

If we choose a concrete example and assume that $M_1 = Zn$ and $M_2 = Cu$, the condition for the precipitation of copper by means of zinc, since $\nu_1 = 2$ and $\nu_2 = 2$, is as follows :—

$$L_{Zn} > L_{Cu} \frac{(Zn^{\cdot\cdot}{}_L)}{(Cu^{\cdot\cdot}{}_L)}.$$

[1] For the sake of simplicity the other heterogeneous equilibria are omitted here.

From the table, p. 127, we find

$$L_{Zn} = 10^{2\times-35} \text{ and } L_{Cu} = 10^{2\times-54}$$

and consequently

$$L_{Zn} \text{ is } 10^{2\times19} \text{ times as great as } L_{Cu}.$$

So long therefore as $(Zn^{\cdot\cdot})$ is less than $10^{2\times19}$ times as great as $(Cu^{\cdot\cdot})$, copper will be precipitated from a solution containing copper and zinc salts.

The discussion of this phenomenon is relevant here, because in the case of this precipitation also, retardation might naturally give rise to unstable conditions.

If hydrogen is substituted for one metal, precipitation of the metal by means of hydrogen can occur if $(\theta_{H_2})_L$ is $> (\theta_M)_L$. This will be possible, as we have already seen, in a liquid for which $E_{H_2} > E_M$, and consequently in an electrolyte the composition of which lies to the left of *c*.

28. The Dissolving (Auflösen) of Metals in Aqueous Solutions of the Halogens.

It is clear that the conditions necessary for the solution of metals in aqueous solutions of the halogens can also be deduced by a method similar to that just employed.

If we imagine a metal of valency ν to be dipped into an aqueous solution of its chloride MCl_ν at the ordinary temperature, whilst chlorine gas under atmospheric pressure is bubbled through the solution, a consideration of the following equilibria is sufficient to establish the conditions under which solution takes place:—

$$\begin{array}{l} M_S \\ \uparrow\downarrow \\ M_L \rightleftarrows M_L^{\nu\cdot} + \nu\theta_L \\ Cl_{2_L} + 2\theta_L \rightleftarrows 2Cl'_L \\ \uparrow\downarrow \\ Cl_{2_G}\ (1 \text{ atm.}) \end{array}$$

From these equations it can at once be seen that metal will go into solution when the electron concentration $(\theta_M)_L$ in the metal equilibrium exceeds the electron concentration $(\theta_{Cl_2})_L$ of the chlorine equilibrium.

In this case, that is to say, chlorine molecules will take up electrons, this reaction proceeding practically exclusively in the layer surrounding the metal.

Now

$$(\theta_L)_M = \frac{L_M^{\frac{1}{\nu}}}{(M_L^{\nu\cdot})^{\frac{1}{\nu}}}$$

and since

$$Q_{Cl_2} = \frac{(Cl'_L)^2}{(\theta_L)^2_{Cl_2}}$$

therefore

$$(\theta_L)_{Cl_2} = \frac{(Cl')_L}{Q^{\frac{1}{2}}_{Cl_2}}$$

The condition is, therefore, that

$$(\theta_L)_M > (\theta_L)_{Cl_2}$$

or

$$\frac{L^{\frac{1}{\nu}}_M}{(M^{\nu\cdot}_L)^{\frac{1}{\nu}}} > \frac{(Cl'_L)}{Q^{\frac{1}{2}}_{Cl_2}}$$

or

$$L_M \cdot Q^{\frac{\nu}{2}}_{Cl_2} > (M^{\nu\cdot}_L) \cdot (Cl'_L)^\nu \quad . \quad . \quad . \quad (66)$$

From the tables on pages 127 and 128 we now see that the product $L_M Q^{\frac{\nu}{2}}_{Cl_2}$ is in general very great. The maximum value of $(M^{\nu\cdot}_L) \cdot (Cl'_L)^\nu$ is, however, equal to the solubility product of the salt MCl_ν and hence, in nearly every case, the product $L_M \cdot Q^{\frac{\nu}{2}}_{Cl_2}$ is greater than the solubility product $(M^{\nu\cdot}_L) \cdot (Cl'_L)^\nu$.

Hence it follows that as a general rule chlorine will continue to act on the metal even though the solid chloride has begun to be deposited.

Consequently we can now write down the condition for deposition of the solid salt also. In its general form this is:—

$$L_M Q^{\frac{\nu}{2}}_{Cl_2} > L_{salt} \quad . \quad . \quad . \quad . \quad (67)$$

and for monovalent metals

$$L_M \cdot Q^{\frac{1}{2}}_{Cl_2} > L_{salt}$$

From the tables (pp. 127 and 128) it appears that for

$$AgCl\,;\ L_{Ag} Q^{\frac{1}{2}}_{Cl_2} = 10^{9\cdot6},\ \text{whilst}\ M_{AgCl} = 10^{-10}$$

for

$$AgBr\,;\ L_{Ag} Q^{\frac{1}{2}}_{Br_2} = 10^{5\cdot1},\ \text{whilst}\ L_{AgBr} = 10^{-12}$$

for

$$AgI\,;\ L_{Ag} Q^{\frac{1}{2}}_{I_2} = 10^{-4\cdot5},\ \text{whilst}\ L_{AgI} = 10^{-16}.$$

We see, therefore, that in these cases the above-mentioned condition is always fulfilled, and the fact that these salts can exist in contact with their saturated solutions is to be ascribed to this circumstance. If

$$L_M Q^{\frac{\nu}{2}}_{Cl_2} < L_{salt}$$

the action of chlorine on the metal ceases before solid salt separates out.

If, however, such a salt prepared in the dry way is put into water, it decomposes and metal is deposited. This happens in the cases of AuCl, AuBr and AuI.

29. A Disturbance of the Inner Equilibrium in the Metallic Surface takes place during Solution of the Metal in Aqueous Solutions of the Halogens.

It is clear that during the treatment of a metal with an aqueous halogen solution similar phenomena may appear to those which occur during the action of acids. If electrons and metallic ions are withdrawn from the metal so rapidly that the inner equilibrium cannot readjust itself, the potential of the metal will become more positive.

30 The Difference between Metals and Non-metals.[1]

On extending these considerations to non-metals such as chlorine, bromine, iodine, etc., the question arises how the positive charge of non-metals relative to the electrolyte is to be explained, and how it is possible for non-metals in an electrically neutral condition to possess a definite electrical conductivity, even though this is very small.

With regard to this question the author has taken up the following standpoint: If, for example, the non-metal chlorine is considered, we are forced to assume that the chlorine atom is capable of splitting off and taking up electrons, and that these processes take place side by side.

The following equations illustrate this assumption :—

$$x\mathrm{Cl}_{2G} \rightarrow 2x\mathrm{Cl}^{\bullet}{}_{G} + 2x\theta_{G} \quad . \quad . \quad . \quad . \quad (69)$$

and

$$y\mathrm{Cl}_{2G} + 2y\theta_{G} \rightarrow 2y\mathrm{Cl}'_{G} \quad . \quad . \quad . \quad . \quad (70)$$

x and y are fractions of the total number of molecules.

Since the electrons taken up according to equation (70) are produced in the dissociation process represented by equation (69) the relationship

$$y \leqq x$$

must exist. In the limiting case $y = x$, the gaseous chlorine would contain an equal number of positive and negative ions, but no electrons at all. Since chlorine is a non-metal, x, and therefore y also, must be very small. Strange to say, the chlorine phase in contact with electrolyte is now positively charged, although elementary chlorine contains more positive than negative ions. This circumstance, in conjunction with the behaviour in other respects of chlorine in the ionic condition, leads to the conclusion that, in the case of the non-metal chlorine, to all intent negative ions only go into solution; they possess, therefore, a much greater solubility than the positive ions.

[1] *Versl. Kon. Akad. v. Wet*, **27**, 1470 (1919).

Obviously these considerations do not render the calculation of the difference of potential in the slightest degree more difficult, and consequently the thermodynamical deduction previously given leads to the following formula for the negative ions :—

$$\Delta = \frac{RT}{F} \ln \frac{K'_{Cl'}(Cl'_G)}{(Cl'_L)} \quad . \quad . \quad . \quad . \quad (71)$$

and for the positive ions

$$\Delta = -\frac{RT}{F} \ln \frac{K''_{Cl^{\cdot}}(Cl^{\cdot}_G)}{(Cl^{\cdot}_L)} \quad . \quad . \quad . \quad (72)$$

If we set out from the fundamental equation

$$\Delta = \frac{RT}{F} \ln \frac{K'_{\theta}(\theta_1)}{(\theta_2)} \text{ or } \Delta = \frac{RT}{F} \ln \frac{K_{\theta}}{(\theta_2)}$$

which possesses general validity, since the electron is the common constituent of all matter, we can substitute the value of (θ_L) for (θ_2), and this can be obtained from the equilibrium

$$Cl_{2L} + 2\theta_L \rightleftarrows 2Cl'_L$$

by applying the law of mass action. The following well-known formula is then obtained :—

$$\Delta = \frac{RT}{2F} \ln \frac{K'(Cl_2)_L}{(Cl'_L)^2} \quad . \quad . \quad . \quad . \quad (73)$$

Similarly, with regard to the equilibrium

$$Cl_{2L} \rightleftarrows 2Cl^{\cdot}_L + 2\theta_L$$

we get

$$\Delta = -\frac{RT}{2F} \ln \frac{K''(Cl_2)_L}{(Cl^{\cdot}_L)^2} \quad . \quad . \quad . \quad . \quad (74)$$

If it is desired to obtain a formula in which both kinds of ions are simultaneously considered, the value of (θ_L), for example, obtained from the equilibrium

$$Cl^{\cdot}_L + 2\theta_L \rightleftarrows Cl'_L$$

is substituted. The following relationship is then obtained :—

$$\Delta = \frac{RT}{2F} \ln \frac{K(Cl^{\cdot}_L)}{(Cl'_L)} \quad . \quad . \quad . \quad . \quad (75)$$

Since practically none but negative chlorine ions go into solution, naturally only equations (71) and (73) have any practical significance.

These considerations concerning the non-metal chlorine, which are a necessary consequence of the new views with regard to electromotive equilibria, lead to a standpoint from which both metals and non-metals can be surveyed in a very satisfactory manner.

Since the metallic and the non-metallic properties in the periodic classification of the elements merge gradually into one another, the theory must accordingly allow it to be clearly seen that the difference between the metallic and the non-metallic states is quantitative only, and that therefore every possible intermediate stage may exist.

Our theory can, in fact, satisfy this requirement, since it is assumed that the atoms of *all* elements, metals and non-metals, can split off or take up electrons, and that consequently the following reactions can take place in the presence of each other:—

$$x\mathrm{E}_n \rightarrow x\frac{n}{m_1}\mathrm{E}_{m_1}^{\nu_1} + x\frac{n}{m_1}\nu_1\theta \quad . \quad . \quad . \quad . \quad (76)$$

and

$$y\mathrm{E}_n + y\frac{n}{m_2}\nu_2\theta \rightarrow y\frac{n}{m_2}\mathrm{E}_{m_2}^{\nu_2'} \quad . \quad . \quad . \quad . \quad (77)$$

in which E_n represents the molecule of the element for the time being and $\mathrm{E}_{m_1}^{\nu_1}$ and $\mathrm{E}_{m_2}^{\nu_2'}$ represent the positive and negative ions respectively.

For metals, n and likewise m_1 and m_2 will in most cases be equal to 1, and when this is not the case m_1 will often be equal to m_2. As regards ν_1 and ν_2, it may be pointed out that these quantities too, will, in all probability, often be equal to one another.

It can only be stated with certainty, however, that

$$y\frac{n}{m_2}\nu_2 \lessgtr x\frac{n}{m_1}\nu_1, \quad . \quad . \quad . \quad . \quad . \quad (78)$$

whence it follows that when $\nu_1 = \nu_2$ and $m_1 = m_2$ positive ions will predominate. The answer to the question, "How may metals be distinguished from non-metals?" is, therefore,

1. In the case of metals x is relatively large; for non-metals, however, it is very small, whilst y is probably relatively much smaller than x where metals are concerned.

2. In aqueous solutions the positive ions of metals and the negative ions in the case of non-metals have the greater solubility.[1]

The difference between the solubilities of the positive and negative ions is so great, when elements possessing exclusively metallic or exclusively non-metallic properties are considered, that as a rule only the positive or the negative ions, so far as the electromotive behaviour is concerned, need be noticed. When dealing with the intermediate or hybrid elements, however, such as iodine, sulphur, selenium, arsenic, antimony, etc., both kinds of ions must decidedly be taken into consideration.

In other respects it may be necessary, however, also to consider both kinds of metallic ions, as in the formation of compounds of different metals.[2]

31. Polarisation Phenomena in the Case of Non-Metals.

Let us now consider the polarisation of non-metals. When during electrolysis these elements are deposited on the anode, electrons are given up to this electrode. The anode consists of the element to be deposited or of a so-called non-corrodible electrode, though in this case, too, as will be more fully explained in a later section, from the electromotive point of view the electrode must be looked upon as

[1] In other solvents the behaviour may be different.

[2] That is to say, ions of opposite charge give rise to compounds, which is also possible with ions of the same element.

though it were composed of the element deposited. When the phenomena associated with the polarisation of metals were discussed only positive metallic ions and electrons were taken into consideration, and this appeared to be quite sufficient, especially in those cases in which the metallic character was very pronounced. In the case of non-metals, however, matters are somewhat different, for since, according to present-day knowledge, there is only one kind of electron, we are compelled to assume, as the author has shown, that non-metals contain positive and negative ions and electrons in addition to uncharged molecules or atoms, in order to explain the small electrical conductivity of pure non-metals and the positive charge which they are able to assume when in contact with an electrolyte. As regards elements of very pronounced non-metallic character, it is for the most part sufficient to consider the negative ions and electrons only, provided it is recognised that positive ions also are present, which, however, practically speaking, do not go into solution at all.

(a) *The polarisation of chlorine.*

The polarisation which takes place during the anodic deposition of chlorine can be explained in the following way :—

When the chlorine electrode is made the anode, electrons are withdrawn from this electrode. If now chlorine were a metal, the potential of the electrode would remain unaltered if, as a result of the electro-ionisation

$$Cl_{2_G} \rightarrow 2Cl^{\cdot}{}_G + 2\theta_G,$$

the withdrawn electrons were replaced at once, and the excess of positive ions went into solution. In consequence of the extremely small solubility of the positive ions, however, the latter process is here impossible, and hence the potential of the chlorine electrode only remains constant if negative chlorine ions from the electrolyte are deposited on the chlorine electrode, thereupon passing into molecular chlorine, electrons being split off. This chlorine naturally dissociates to an extremely small extent into positive ions and electrons. Neglecting this secondary electro-ionisation, the whole process may be represented in the following way :—

$$Cl_{2_G} + 2\theta_G \nearrow \leftarrow 2Cl'_G \uparrow 2Cl'_L.$$

As we have already emphasised, the heterogeneous equilibrium between the chlorine ions in the gaseous phase and in the electrolyte must always be instantaneously established, so that it depends on the velocity with which electrons are split off from the gas phase whether the chlorine electrode will retain its potential.

When the current density exceeds a given value, *i. e.* when electrons are withdrawn with a velocity greater than a certain fixed rate, retardations appear, for the separation of electrons can no longer keep pace with the rate at which they are withdrawn. The chlorine electrode will

then contain too few electrons and too many negative chlorine ions. From equation (71)

$$\Delta = \frac{RT}{F} \ln \frac{K'_{Cl'}(Cl'_G)}{(Cl'_L)},$$

it follows without further discussion that the potential difference becomes more positive, for (Cl'_G) has increased, whilst (Cl'_L) may be regarded as constant.

Since, however, as we have seen, the Volta effect has never been determined, and this quantity must change as a result of the phenomena associated with polarisation, it is necessary here also to make use of a formula in which the Volta effect does not occur. Hence equation (42) is employed, which for chlorine runs as follows :—

$$E = \frac{0{\cdot}058}{2} \log \frac{Q_{Cl_2}}{(Cl'_L)^2} - 2{\cdot}8 \quad . \quad . \quad . \quad (79)$$

In order to determine how the solubility quotient Q_{Cl_2} changes in consequence of polarisation, it must again be noticed that equation (71) and the electronic equation (17)

$$\Delta = \frac{RT}{F} \ln \frac{K'_{\theta}(\theta_G)}{(\theta_L)}$$

are valid, even when inner equilibrium does not exist. Now it follows from (17) and (71), that

$$\frac{(\theta_G)}{(Cl'_G)} \cdot \frac{(Cl'_L)}{(\theta_L)} = K.$$

It was found that when anodic polarisation occurred, the chlorine electrode contained too few electrons and too many negative chlorine ions. The quotient

$$\frac{(\theta_G)}{(Cl'_G)}$$

had consequently become smaller, and hence

$$\frac{(Cl'_L)}{(\theta_L{}^2)}$$

must have been increased.

The solubility quotient

$$Q_{Cl_2} = \frac{(Cl'_L)^2}{(\theta_L)^2}$$

has therefore increased as a result of anodic polarisation during the separation of chlorine, and hence E has also become more positive.

(b) *The polarisation of oxygen.*

Although it is almost superfluous, the oxygen electrode also may be briefly discussed here.

After introducing the value for (θ_L) obtained from the equation

$$O_{2_L} + 4\theta_L \rightleftarrows 2O''_L \quad . \quad . \quad . \quad . \quad (80)$$

the electron equation (17) yields the following expression :—

$$\Delta = \frac{RT}{4F} \ln k \frac{(O_{2_L})}{(O''_L)^2} \quad . \quad . \quad . \quad . \quad (81)$$

or, if (θ_L) is obtained from

$$2H_2O_L + O_{2_L} + 4\theta_L \rightleftarrows 4OH'_L \quad . \quad . \quad . \quad (82)$$

this expression results :—

$$\Delta = \frac{RT}{4F} \ln K \frac{(O_{2_L})}{(OH'_L)^4} \quad . \quad . \quad . \quad . \quad (83)$$

These formulæ cannot tell us anything concerning polarisation ; the following equations :—

$$\Delta = \frac{RT}{2F} \ln \frac{K'_{O''}(O''_G)}{(O''_L)} \quad . \quad . \quad . \quad . \quad (84)$$

and

$$\Delta = \frac{RT}{2F} \ln \frac{KK'_{O''}(O''_G)}{(OH'_L)^2} \quad . \quad . \quad . \quad (85)$$

which are analogous to (71) and which are obtained from the foregoing by substituting the value for (O''_L) from the relationship

$$H_2O + O'' \rightleftarrows 2OH'$$

are, however, quite suitable for this purpose.

Still, it is best to employ the equation for the experimental electrical potential.

From (17) and (84) we get

$$\frac{(\theta_G)^2}{(O''_G)} \cdot \frac{(O''_L)}{(\theta_L)^2} = K \quad . \quad . \quad . \quad . \quad (86)$$

In the case of anodic polarisation, which may occur during the separation of oxygen, the oxygen electrode will contain too few electrons and too many negative oxygen ions.

The quotient

$$\frac{(\theta_G)^2}{(O''_G)}$$

herefore diminishes, and in consequence

$$\frac{(O''_L)}{(\theta_L)^2}$$

increases. From equation (80) it follows that the solubility quotient for oxygen under a pressure of one atmosphere is given by the expression

$$Q' = \frac{(O''_L)^2}{(\theta_L)^4} \quad . \quad . \quad . \quad . \quad . \quad (87)$$

This quotient therefore increases as a result of anodic polarisation. The equation for the experimental electrical potential is as follows :—

$$E = \frac{0{\cdot}058}{4} \log \frac{Q'_{O_2}}{(O''_L)^2} - 2{\cdot}8 \quad . \quad . \quad . \quad (88)$$

and hence, in this case again, E will become more positive; for (OH') being constant, (O_L'') must also be constant.

It may further be pointed out here that if (17) is combined, not with (84), but with (85), which is moreover advantageous, equation (89) results.

$$\frac{(\theta_G)^2}{(O''_G)} \cdot \frac{(OH'_L)^2}{(\theta_L)^2} = K' \quad . \quad . \quad . \quad . \quad (89)$$

If we now proceed to derive a formula for the solubility quotient of oxygen from (82) we obtain

$$Q_{O_2} = \frac{(OH'_L)^4}{(\theta_L)^4} \quad . \quad . \quad . \quad . \quad (90)$$

The equation for the experimental electrical potential then assumes the form

$$E = \frac{0{\cdot}058}{4} \log \frac{Q_{O_2}}{(OH'_L)^4} - 2{\cdot}8 \quad . \quad . \quad . \quad (91)$$

Since when oxygen undergoes anodic polarisation

$$\frac{(\theta_G)^2}{(O''_G)}$$

decreases

$$\frac{(OH'_L)}{(\theta_L)^2}$$

increases, and consequently Q_{O_2} must also become greater. Hence E will be more strongly positive.

32. Amphoteric Elements.

It has already been stated that the amphoteric elements may be recognised by the fact that they can send both positive and negative ions into solution.

If therefore an amphoteric element is made the anode, it is possible not only for positive ions to go into solution, but also for negative ions from the solution to be deposited on the anode.

If, on the other hand, an amphoteric element is made the cathode, naturally the reverse process takes place, and it is not only possible for positive ions to be precipitated on the cathode, but also for negative ions to pass into solution.

The closer study of these as yet but little investigated elements must seem especially attractive in the light of these new views, and it also promises to be very profitable, the more so now that the way to experimental investigation has been prepared theoretically.

33. Non-corrodible Electrodes.

The case has already been considered in which a metal dipped into a liquid saturated with hydrogen, the composition of which in the E X diagram is determined by a point lying to the right of c, is so inert that

the electron concentration in the metal equilibrium is equal to the electron concentration in the hydrogen equilibrium. E_M is then equal to E_{H_2}, *i. e.* the experimental electrical potential of the metal and of the hydrogen electrode are equal to one another, or, in other words, the metallic electrode behaves as a hydrogen electrode. Now non-corrodible electrodes consist of metals which may be said to be *ideally inactive*, and, thanks to this circumstance, such metals may be used in the construction of gas electrodes.

Thus, if a platinum electrode is dipped into an aqueous solution of an acid, hydrogen being at the same time passed through the solution, in a short time the electron concentration of the platinum equilibrium

$$Pt_L \rightleftarrows Pt^{\cdots}{}_L + 4\theta_L$$

will become equal to the electron concentration in the hydrogen equilibrium

$$H_2 \rightleftarrows 2H^{\cdot}{}_L + \theta_L,$$

and consequently the platinum electrode must behave as a hydrogen electrode.

This result can easily be illustrated by means of an E X diagram (see Fig. 124).

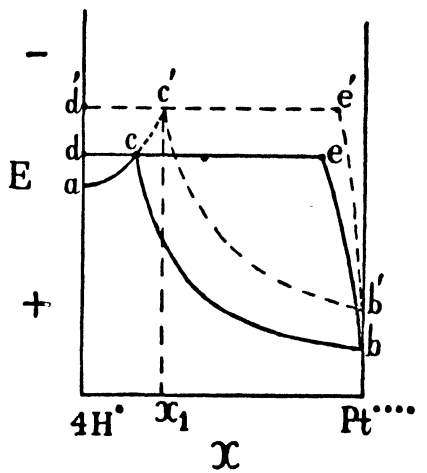


FIG. 124.

Although, in consequence of the inertness of this metal, the normal potential of platinum in a state of inner equilibrium is not accurately known, it may nevertheless be stated with certainty, that, if this equilibrium potential were measurable, it would be found to be decidedly more positive than hydrogen. Hence, in the graphic representation, the point *c*, indicating the composition of the electrolyte which is in electromotive equilibrium with both platinum and hydrogen, would be displaced so much to one side that it would almost coincide with the hydrogen axis.

For the sake of clearness, however, in the accompanying diagram it has been intentionally assumed that the point *c* is not so far displaced to one side.

The hydrogen potential for a solution having the composition x_1 is indicated by the point *c'*, which lies on the metastable prolongation of the line *a c*.

If a platinum electrode is dipped into this solution and hydrogen is simultaneously bubbled through it, after a short time the platinum electrode exhibits the same potential as the hydrogen electrode. Hence it results that the solution under consideration is in electromotive equilibrium not only with hydrogen but also with platinum.

If this platinum phase containing hydrogen is represented by *e'*,

this disturbed platinum state could still co-exist with electrolytes of different compositions; the line $c'b'$ indicates the electrolytes which would be in electromotive equilibrium with metal phases represented by the line $e'b'$.

The experimental electrical potential of the platinum electrode is, therefore, in this case, the same as the potential of the three-phase equilibrium indicated by the points $d'c'e'$.

Since, as has been stated, c coincides approximately with the hydrogen axis, and since, on applying a non-corrodible electrode as a hydrogen electrode, this electrode exists in a solution which is almost entirely free from ions of the metal constituting the electrode, x_1 likewise lies entirely on the hydrogen side, *i. e.* the point c', like c, also practically coincides with a.

This explains the fact that different non-corrodible electrodes, when used as hydrogen electrodes in the same solution, exhibit practically the same electrical potential.

It has been shown here that non-corrodible electrodes are characterised by "ideal inertness." They are unable to exhibit their own proper equilibrium potential, because the potential is entirely determined by the electron concentration prevailing in the electrolyte.

This circumstance is very convenient in experimental electro-chemical investigations, for it renders it possible to measure potentials which would otherwise have remained unknown.

Thus, we are able, by means of non-corrodible electrodes, to determine, amongst others (excluding gas potentials), the so-called and previously mentioned oxidation and reduction potentials. If, for example, a platinum electrode is immersed in a solution containing ferrous and ferric salts, the electron concentration of the platinum equilibrium adjusts itself in accordance with the electron concentration existing in the equilibrium

$$Fe^{\bullet\bullet}{}_L \rightleftarrows Fe^{\bullet\bullet\bullet}{}_L + \theta_L,$$

and hence it is possible to determine the potential difference of the platinum electrode by introducing into the electronic equation (17) a value for (θ_L) obtained from the above equilibrium. In this way we get

$$\Delta = \frac{RT}{F} \ln \frac{K_\theta}{K} \cdot \frac{(Fe_L^{\bullet\bullet\bullet})}{(Fe_L^{\bullet\bullet})}.$$

Similarly, by substituting (θ_L) in the equation

$$E = -\frac{RT}{F} \ln (\theta_L) - 2{\cdot}8$$

the following expression for the experimental electrical potential is obtained:—

$$E = \frac{RT}{F} \ln K \frac{(Fe_L^{\bullet\bullet\bullet})}{(Fe_L^{\bullet\bullet})} - 2{\cdot}8.$$

By using methods similar to that employed here for a ferro-ferri

solution, a general equation may, of course, be obtained for the potential of a non-corrodible electrode, in relation to any solution, in which an equilibrium exists between molecules, atoms, ions and electrons respectively.

If the equilibrium is represented by the equation

$$n\mathrm{A} + m\mathrm{B} \rightleftarrows p\mathrm{C} + q\mathrm{D} + r\theta,$$

then

$$\mathrm{E} = \frac{\mathrm{RT}}{r\mathrm{F}} \ln k \frac{(\mathrm{C})^p(\mathrm{D})^q}{(\mathrm{A})^n(\mathrm{B})^m} - 2{\cdot}8.$$

34. Polarisation Phenomena in the Light of the Phase Rule.

The phenomena which make their appearance during anodic and cathodic polarisation may also be very clearly illustrated by means of an E X diagram.

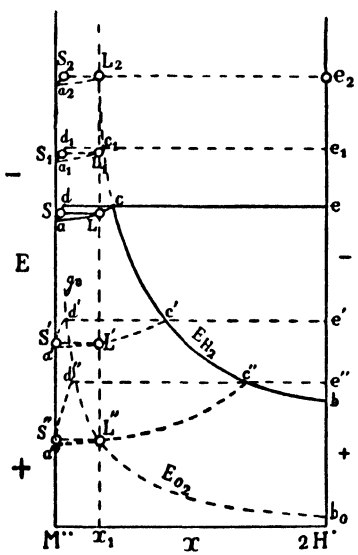


FIG. 125.

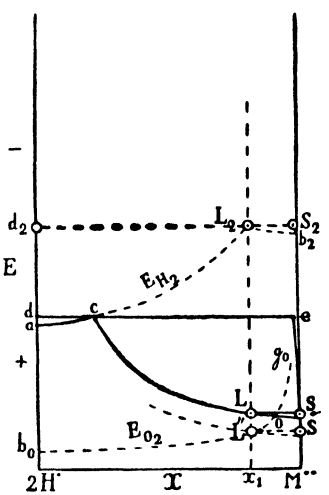


FIG. 125*a*.

Let us assume that a base metal M'' is dipped into a solution of composition x_1, lying to the left of *c*, and that this metal is made the anode. Then, if inner equilibrium is not established sufficiently quickly, its potential will be less negative, or, in other words, anodic polarisation occurs. Instead of the co-existence S—L we then get, as is shown in Fig. 125, for a given current density, co-existence between the disturbed metal phase S' and the electrolyte L'.

If now the disturbance is allowed to become very marked, either in consequence of the natural inertness of the metal or because of the action of a negative catalyst, certain peculiarities may still be noticed.

In the E X diagram solutions will be considered in which the ratio $\frac{2H}{M^{\cdot\cdot}}$ passes through every possible value. Each of these solutions contains a certain concentration of OH′ ions, and since

$$(OH'_L) = \frac{K_\omega}{(H^{\cdot}_L)}$$

(OH'_L) will increase from right to left.

If we now imagine a case in which a platinum electrode is introduced into a solution through which oxygen is passed instead of hydrogen, we shall measure the *oxygen potential* and this will become less positive as the concentration of (OH′) ions increases. A line can therefore be drawn in the E X diagram to indicate the oxygen potential. From the table on page 127 we find the normal equilibrium potential of oxygen, (OH′) therefore = 1, relative to that of hydrogen, to be + 0·41 volts. The oxygen potential in a solution in which (H·) = 2 and consequently (OH′) = $\frac{1}{2}\cdot 10^{-14}$ has, according to the equation

$$E_{O_2} = \frac{0\cdot058}{4} \log \frac{Q_{O_2}}{(OH'_L)^4} - 2\cdot8,$$

a still higher positive value, namely + 1·3 volts. This line begins, therefore, on the hydrogen axis at a point b_0, which is 1·3 volts more positive than *b*.

The line for the oxygen potential, $b_0 g_0$, thus lies, as has been schematically shown here, far below the line *b c* relating to the hydrogen potential.

Now it is clear that if the disturbance of the metal can be carried so far that it reaches S″, so that the co-existing electrolyte L″ can also co-exist with the oxygen electrode at the same potential, oxygen will be deposited on the anode, whilst this will dissolve to a greater or less extent.

Thus a three-phase equilibrium metal phase—electrolyte—oxygen phase is again obtained, the last mentioned, however, is not shown in this graphical representation for the sake of simplicity; in addition the metal phase may now contain oxygen. This, however, is no obstacle, for here we are only concerned to explain the evolution of oxygen. The main point is, that under these circumstances a three-phase equilibrium is obtained, which corresponds to a definite potential, the temperature, pressure and total ion concentration being constant.

Clearly by increasing the current density the potential may become yet more positive, especially if the disturbed metal co-exists with an oxygen phase in the state of formation. Finally it may be mentioned here that it seems possible for the disturbance of the metal to become so great that the metallic surface contains so few ions and electrons as to offer a perceptible resistance to the electric current.

If instead of a base metal a noble metal were considered, the position schematically represented in the E X diagram (Fig. 125*a*) would be obtained.

It is here of importance to determine where the point of intersection O of the oxygen potential line $b_0 g_0$ with the metal potential line $b\,c$ lies for a noble metal, *e. g.* silver.

This point of intersection would indicate the electrolyte which co-exists with silver and oxygen when both elements are in inner equilibrium. In this case the electron concentrations in the silver equilibrium and in the oxygen equilibrium in the liquid are equal to one another.

Consequently, since

$$(\theta_{Ag}) = \frac{L_{Ag}}{(Ag^{\bullet}_{L})}$$

and

$$(\theta_{O_2}) = \frac{(OH')}{Q^{\frac{1}{4}}_{O_2}}$$

we can write

$$\frac{L_{Ag}}{(Ag^{\bullet}_{L})} = \frac{(OH')}{Q^{\frac{1}{4}}_{O_2}}$$

or

$$10^{-61\cdot9} \times 10^{55} = (OH'_L)(Ag^{\bullet}_{L}).$$

If we now put

$$(Ag^{\bullet}_{L}) = 1$$

we get

$$(OH'_L) = 10^{-6\cdot9}$$

and hence

$$(H^{\bullet}_{L}) = 10^{-7\cdot1}.$$

Consequently a neutral silver sulphate solution in which $(H^{\bullet}_{L}) = 10^{-7}$ still lies to the left of the point O, *i. e.* silver dipped into a neutral aqueous solution of silver sulphate does not constitute a 1-atmosphere oxygen electrode.

As a result of these considerations, the composition x_1 of the solution is indicated in Fig. 125*a* to the left of the point O; whilst S L represents the co-existence for unary behaviour, S″ L″ indicates the co-existence for anodic polarisation up to the point at which oxygen is evolved.

(b) *Cathodic Polarisation.*

If the metal is made the cathode, the potential will be more negative if the inner metallic equilibrium is not established sufficiently quickly, and consequently, during the potential measurement, the metal still exists in the state of formation.

Hence, for a given current density, the co-existence of the metal phase with electrolyte will be indicated, as in Fig. 125, by $S_1 L_1$.

If now the distance of the deposited metal from the equilibrium state is increased still more by increasing the current density, and if S_2 has become the metal phase, at which point the co-existing electrolyte also co-exists with hydrogen at the same potential, the deposition of the metal will be accompanied by evolution of hydrogen, and a three-

phase equilibrium is again obtained which carries with it a constant potential. A further increase of the negative potential can now be brought about by increasing the current density, and then it is possible that the hydrogen phase in contact with the deposited metal is likewise unable to subside into inner equilibrium, or is converted into the state of formation.

If the metal is a noble one the form of the E X diagram is as sketched in Fig. 125*a*. If cathodic polarisation is allowed to go on to such an extent that evolution of hydrogen occurs, the two-phase co-existence S L is converted into the three-phase co-existence $S_2 L_2 d_2$, *i. e.* into a co-existence of the electrolyte with metal and hydrogen.

It is clear that in the case considered in Fig. 125 the eventual state of formation of the hydrogen can exert practically no appreciable influence on the potential. If, however, the electrolyte *c* lies markedly on the hydrogen side, as in Fig. 125*a*, *i. e.* if the metal is a noble one and if the solution under consideration is one of a pure acid or a solution having a relatively high hydrogen ion concentration, then any displacement upwards of the line *a c* results in almost exactly as marked an increase in the three-phase potential; or, in other words, the state of formation of the hydrogen then has a distinct influence.

On account of the varying catalytic influences, however, this state of formation of hydrogen will differ in different metals.

35. Small Concentrations.

Before bringing this chapter to a conclusion one more question may be discussed, which, on account of its importance, has every claim to consideration. It concerns the small concentrations with which these new views compel us to work.

These small concentrations present peculiar difficulties, which can, however, already be partially removed. These difficulties will here be treated separately.

(a) *The great velocity with which electronic reactions take place in the bounding surface, metal—electrolyte.*

The first difficulty to be mentioned arises from the great velocity with which reactions between a metal and an electrolyte can take place. According to the theory developed here the evolution of hydrogen, for example, which appears when zinc is dipped into an aqueous solution of hydrochloric acid, is due to electrons, although the electron concentration in the reacting liquid is so extremely small.

If the following zinc equilibrium is considered:—

$$\begin{array}{ccccc} Zn_S & \rightleftarrows & Zn^{\cdot\cdot}{}_S + 2\theta_S & (a) & \\ \uparrow\downarrow & & \uparrow\downarrow \quad \uparrow\downarrow & & \\ Zn_L & \rightleftarrows & Zn^{\cdot\cdot}{}_L + 2\theta_L & (b) & \end{array} \quad . \quad . \quad . \quad . \quad (1)$$

and also the hydrogen equilibrium

$$H2_L \rightleftarrows 2H^{\cdot}{}_L + 2\theta_L, \quad . \quad . \quad . \quad . \quad (2)$$

it has been emphasised that since the electron concentration in equilibrium (1*b*) is greater than in equilibrium (2), the electrons sent into solution by the zinc will unite with hydrogen ions with the formation of hydrogen molecules.

If reaction (2) were to take place extremely slowly, an electron concentration corresponding to the metal equilibrium (*b*) would prevail throughout the liquid, and naturally equilibrium (2) would not then be established.

But the reaction mentioned proceeds rapidly, much more rapidly than electrons at a great distance from the electrode can be replaced by diffusion, and thus the reaction is immediately shifted towards the bounding surface.

The heterogeneous equilibrium between the metal and the liquid bounding surface is established instantaneously, as has already been emphasised repeatedly, and therefore, at all events, much more rapidly than the homogeneous equilibrium (1*b*). Hence it may be concluded that the electrons withdrawn from the liquid bounding surface by the reaction

$$2H^{\cdot}_{L} + 2\theta_{L} \rightarrow H_{2_{L}}$$

will be replaced by the heterogeneous reaction

$$\begin{matrix} \theta_{S} \\ \downarrow \\ \theta_{L} \end{matrix}$$

and practically not at all by the homogeneous reaction (1*b*).

Now the difficulty referred to consists in this. Although the solubility product of zinc has the value $10^{2\times-35}$, the velocity of formation of hydrogen is so enormously great. In the first place, it must be pointed out most emphatically that the electron concentration calculated from the solubility product holds good for the liquid *outside the bounding layer*, whilst the reaction considered here takes place in this bounding layer. Consequently it is desirable that this bounding layer should be taken into consideration here. The theory of capillarity teaches that the so-called discontinuity between a gaseous phase and a liquid phase or between two liquid phases is really a continuity which follows an extremely steep course. This is graphically expressed in Fig. 126. In this diagram any arbitrary property is plotted as a function of the difference from a definite layer.

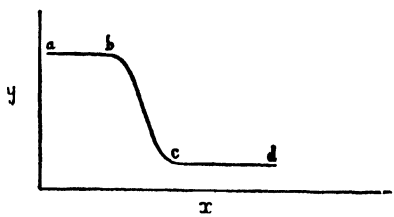


FIG. 126.

Between *b* and *c*, therefore, there lies a continually changing transition layer.

If, however, the co-existence of a metallic phase with a liquid is considered, a complication is encountered, it is true, for one phase

represents an oriented state and the other an unoriented state; but in any case the electron concentration in the liquid transition layer will increase markedly as the metallic transitional layer is approached. The hydrogen ions which diffuse into the liquid transition layer will, therefore, be converted into molecular hydrogen with so much the greater velocity the more deeply they penetrate. The amount of hydrogen evolved per second is approximately given by the formula

$$\frac{d(H_2)}{dT} = k(H^{\cdot})^2(\theta)^2,^*$$

and since the concentration of hydrogen ions in a given layer increases with the velocity of diffusion, this will be an important factor in the evolution of hydrogen. The latter is not controlled, however, by this factor alone, for this would only be the case if the reaction constant k were infinitely great. The greater the value of k, naturally so much the more closely will the velocity with which hydrogen is evolved approximate to the velocity of diffusion. For the sake of simplicity it is assumed here that this formula also holds good for the bounding layer.

From these considerations the possibility is seen of a rapid evolution of hydrogen taking place, although the electron concentration outside the liquid transition layer is extremely small.

Recapitulating, it may therefore be stated: The great velocity with which reactions between metallic phases and liquids take place presents no difficulty when the question is considered more closely.

These considerations also show how it is possible for different substances in the coexisting liquid to influence the velocities of internal changes in the metallic phase, for they lead to the view that in the metallic surface all the constituents of the coexisting liquid are dissolved to a certain extent.

(b) *The significance of the extremely small concentrations calculated from the solubility products and the solubility quotients.*

This question constitutes another difficulty.

In dealing with this matter it must be remembered that the whole question of the significance of minute concentrations has already been very thoroughly discussed. Thus, Ostwald [1] believed the small concentration of silver ions calculated for the equilibrium

$$Ag(CN)''_3 \rightleftarrows Ag^{\cdot} + 3CN'$$

must mean that many ions are indeed formed, but that they only exist for a very short time. Taking this view as his starting-point, Haber [2] then calculated the mean period of existence for ions, the concentration of which was of the order of magnitude 10^{-23}. He arrived at the result,

* In this case the second term of the right-hand side of the equation, which concerns the splitting up of the hydrogen, may be neglected on the ground of its relatively small value.

[1] *Z. f. Elektrochem.*, **10** (1904). [2] *Z. f. Elektrochem.*, **10**, 433 (1904).

however, that, in order for it to move through a path of atomic dimensions during its period of existence, the ion would have to have a velocity one million times greater than the velocity of light. This consideration led him to the conclusion that the reality of minute concentrations could not be maintained except by arbitrary means.

Bodlander[1] considered that no reason had been advanced for doubting the reality of the minute concentrations of silver ions in complex solutions. The concentrations calculated from the potential difference are found to be accurate when they can be determined analytically. On that account, in his opinion, it would be inconceivable that a limit should exist at some point or other beyond which the concentration is only a postulate and has no reality. This view, however, is incorrect, and Haber[2] pointed out that it just depends whether it is permissible to continue the extrapolation into the region of extremely small concentrations.

Abegg[3] urged another point of view. He recognised the reality of minute concentrations and pointed out that minute equilibrium concentrations could be established very rapidly, if only the ions which are present in these small concentrations could be subsequently replaced very quickly.

In this connection he pointed out that a mercury electrode in a solution in which the concentration of mercury ions is very minute, only exhibits a reproducible and correct potential when the small mercury concentration can be traced to a very slightly dissociated complex ion, which is present in greater concentration.

Danneel[4] made an attempt to save the assumption of minute concentrations, in which he adopted Ostwald's standpoint, but then assumed that an ion might be considered to be free at much smaller distances than atomic dimensions.

Finally, Haber[5] discussed these various interpretations, but remained of the same opinion as before, namely, that the minute concentrations calculated would have no reality, but would be imaginary quantities.

The difficulty discussed here is met with in various regions. It is found in the solubility products of many very slightly soluble hydroxides and salts, again in the concentrations of the very slightly volatile constituents of a gaseous phase calculated from various chemical equilibria between gases and solids, and in general in the calculated vapour pressures of all so-called non-volatile bodies and all extremely dilute gases.

Finally, the same difficulty is met with in the solution tensions calculated by Nernst and in the extremely small electron concentrations calculated from the solubility products of the metals and the solubility quotients of the non-metals.

In the author's opinion the matter must be looked at in this way. All the above-mentioned calculations of concentrations are, in reality,

[1] *Z. f. Elektrochem.*, **10**, 604 (1904).
[2] *loc. cit.*
[3] *Z. f. Elektrochem.*, **10**, 607 (1904).
[4] *Ibid.*, 609 (1904).
[5] *Ibid.*, 733 (1904).

extrapolations into a concentration region, in which ordinary thermodynamical methods of calculations are no longer really applicable.

No great value can therefore be attached to the absolute magnitudes of the calculated concentrations; it is possible, after all, that these concentrations are in reality a certain amount greater than the calculated values, and we must consequently be most cautious when these amounts are considered as arithmetical quantities.

It must be emphasised, however, that these considerations do not alter the significance of the solubility products and solubility quotients so far as this theory is concerned.

In the event of its being necessary at some future time to correct the calculated concentrations, the solubility products and quotients will still be in the same order and they will remain in the same ratio.

CHAPTER VIII

PHOTOCHEMICAL AND ELECTROCHEMICAL EQUILIBRIA

It may be mentioned at this point, that although in the theoretical considerations hitherto developed only temperature, pressure and composition have been regarded as independent variables, cases also occur in which, in addition to these variables, still others make their appearance; namely, the intensity of any kind of light or the intensity of the electrical energy.

The phase rule must then be slightly altered, and instead of $F = n + 2 - r$ we must write $F = n + 3 - r$.

If, for example, $n = 1$ and $r = 1$, *i.e.* if we have a *unary* system in a *single* phase, under ordinary circumstances $F = 2$, and consequently at a definite temperature and pressure the system is invariant, that is to say, it is completely defined. If, however, the system is sensitive to light or electrical energy, under the action of either of these, when $n = 1$ and $r = 1$, at a definite temperature and pressure it still possesses one degree of freedom, *i.e.* every value of the intensity of the light or of the electrical energy corresponds to a different state. The position of the inner equilibrium in any phase of a unary system which is sensitive to light or to electrical energy depends, therefore, at a given temperature and pressure, on the light intensity or the intensity of the electrical energy, and it can, therefore, in these cases, be illustrated by an $(I\,X)_{PT}$ diagram.

It is well known that, as a rule, the homogeneous stationary states known as photothermic or electrothermic homogeneous equilibria are established with great velocity, and they then correspond with the ordinary thermally attainable equilibria at higher temperatures, with regard to the equilibrium position, and indeed in the greater temperature stability of the substances concerned. Since the reaction velocity diminishes very rapidly as the temperature falls, it is possible, by making use of the so-called foreign energy, to cause changes to take place at the ordinary temperature and pressure which, in the absence of the influence exerted by these forms of energy, are entirely lacking, and which then are only realisable at higher temperatures when no decomposition sets in. For these reasons, too, the forms of energy in question have often falsely been compared with catalysts.

If heterogeneous equilibria are now considered and if, for example, $n = 1$ and $r = 2$, F will be equal to 2. Consequently, if a definite pressure is chosen, the temperature of the two-phase equilibrium will depend only on the intensity of the foreign energy. If a *binary* system in *two*

phases is considered, so that $n = 2$ and $r = 2$, it is seen that for a definite pressure and a definite composition the temperature of the two-phase equilibrium again depends on the intensity of the foreign energy, and so on.

Now there are doubtless many sluggish pseudo-systems which are sensitive to the foreign energies just mentioned. On the application of one of these forms of energy an internal change occurs, which will lead, at the ordinary temperature and pressure, to an end state corresponding with a purely thermal equilibrium at another temperature. To this type belong, for example, the so-called *phototropic* substances, which constitute therefore very beautiful material with which to test the theory developed here.

CHAPTER IX

THE INTERPRETATION OF THE RONTGEN SPECTRA OF CRYSTALS

THE researches of Laue[1] and of W. L. and W. H. Bragg[2] on the diffraction of X-rays by means of crystals originally gave rise to a conception of the solid state which was not in agreement with our chemical ideas.

The quintessence of this conception lay in the assumption that every atom of a crystalline substance which occupies a definite position in the lattice must be united with every neighbouring atom by forces of the same nature.

As a consequence of this, clearly, the molecular conception of the solid state must have undergone a fundamental change.

Thus, in the crystalline phase, the forces which exist between the atoms would then be of one kind only, whilst in the liquid phase, for example, the attractive force might be resolved into two different components. Of these the one component consists of forces which are universal, the action of which on any given mass is independent of the presence at the same time of other masses (physical forces of attraction), whilst the other portion consists of local forces, whose action on a given mass is dependent on whether the force is already partially saturated or not (chemical forces or valency).

As a result of the conclusion just mentioned, which is a necessary consequence of Bragg's theory, this theory was immediately disputed by Smits and Scheffer[3] from the chemical side and by Beckenkamp[4] and Niggli[5] from the crystallographic point of view. The chief argument adduced from the chemical standpoint was, that the universal homogeneous bond is at variance not only with our chemical judgment, but also with all the modern theories of the atom: Boltzmann,[6] Bohr,[7] Stark,[8] Lewis,[9] Langmuir.[10]

The question naturally arises here: Does the chemical binding

[1] *Sitzungber. d. Bayer. Akad. d. Wiss.*, June (1912).

[2] *Proc. Cambridge Phil. Soc.* **17**, I, p. 43 (1912).

[3] *Proc. Kon. Akad. v. Wet.*, Amsterdam, **19**, 432 (1916). We also gave a model, simply to illustrate our ideas. This model is inaccurate, but naturally this does not in the least weaken the objections brought against Bragg's theory.

[4] *Leitfaden der Kristallographie*, pp. 379, 410 *et seq.*

[5] *Geometrische Kristallographie des Diskontinuums*, pp. 425 *et seq.*

[6] *Vorlesungen über Gas theorie*, II, 177.

[7] *Phil. Mag.* (6), **26**, I, 476 and 857 (1913).

[8] *Prinzipien der Atomdynamik.*

[9] *Journ. Amer. Chem. Soc.*, **38**, 762 (1916).

[10] *Ibid.*, **41**, 868 (1919).

force or valency manifest itself in the same way in the crystalline phase as in the liquid and gaseous phases? This is identical with the question: "Do molecules exist in the solid state if a more comprehensive definition is given of the conception of a molecule?"

It is clear that if molecules are defined as completely independent particles, we cannot speak of molecules in the solid, the liquid, nor yet in the compressed gaseous state. Another more useful and more logical definition is obtained, however, if we agree to speak of molecules when the binding forces between a given number of atoms become so pronounced that groups of atoms or complexes can be physically distinguished. The conviction that these atomic groups or molecules, held together by valency, also exist in the solid state, formed the ground for the repudiation of Bragg's original theory.

This conviction was due in no small measure to the chemical changes which occur in crystalline phases, and to the numerous and well-known relationships which exist between the structures of molecules on the one hand and of crystals on the other.

So far as chemical changes are concerned, these indicate very clearly that chemical forces are active in the crystal also; and since in these cases exactly the same reactions occur in the solid as in the liquid or dissolved state, it is extremely probable that we are concerned with the same valency effects; *i. e.* the same molecular bond exists both in the solid and in the liquid states. A beautiful example of this is furnished by the transformation of nitro-benzaldehyde into nitroso-benzoic acid. This reaction takes place in crystalline nitro-benzaldehyde as well as in a solution of this substance, under the influence of red light. Other examples are found in the reactions between solid substances under high pressure, realised by Spring.

Fortunately this difference of opinion as regards the solid state has recently been almost completely removed, at any rate so far as the most essential point is concerned.

Thus, Debye and Scherrer [1] have shown that in crystalline lithium fluoride the valency requirements are satisfied in the same way as in the liquid or dissolved state, that is to say by the formation of ions, and consequently it is in the highest degree probable that this also holds good for all similar electrolytes.

Further, from his latest paper, Bragg [2] appears to have abandoned his original idea, and to have adopted the views of Lewis and Langmuir, which satisfy the requirements of valency. Thus, with regard to crystalline sodium nitrate, he writes:—

"In sodium nitrate the distance between the oxygen and nitrogen centres is 1·50°A, that between the oxygen and sodium centres 2·38°A. In all these atoms the nuclei are surrounded by the stable neon arrangement of electrons, and presumably these electrons are approximately the same distance from the nucleus in sodium, nitrogen and oxygen. The oxygen and nitrogen atoms have realised the same arrangement, however, by sharing electrons, and their centres are

[1] *Physik. Zeitschr.*, **19**, 474 (1918). [2] *Phil. Mag.*, **40**, 169 (1920).

correspondingly close together. The sodium atom is already surrounded by a stable shell and is isolated in the structure. In sodium nitrate there is the same arrangement of positive and negative ions as in sodium chloride, except that the negative ion in this case is the complex NO_3 group."

In another place he speaks of a crystal in which the atoms are bound together by sharing electrons.

Consequently it follows, as has already been stated above, that W. L. Bragg too has now come to the conclusion that the influence of valency manifests itself in the same way in the solid phase as in the liquid.

On applying Langmuir's theory he found, in every case investigated, that the molecule in the crystal has a form required by the above-mentioned theory.[1]

If, therefore, we review the results of investigations on X-rays in relation to the solid state, we are forced to the conclusion that these point to the fact that the forces known as valency, which give rise in the liquid state of aggregation to the existence of molecules and ions, manifest themselves in the same way in crystalline phases.

Thus, the original difference of opinion has disappeared and we can now indulge the hope that the continued investigation of the behaviour of solid substances under X-rays will yet afford an insight into the *inner equilibria* which may occur in the crystalline state.

With this object in view we are occupied, amongst other things, with the X-ray study of mercuric iodide, and it is hoped that this will give an unequivocal answer.

It may here be mentioned that Bridgman[2] is of opinion that the various phenomena associated with allotropy can be explained by attributing to the atoms a certain form, in consequence of which various equilibrium groupings are possible, corresponding to different energies and specific volumes. These different groupings then represent the different allotropic states.

In the first place it must be noticed that it appears to me impossible to explain the phenomena discussed in the experimental portion of this book equally plausibly by means of such a mechanism, and secondly it may be emphasised that it has now been well established that molecules and ions have a specific form, whilst Bridgman is compelled to assign a definite form to the atom.

[1] *Kolkmeyer, Byvoet* and *Karssen* some months previously observed analogous behaviour in the cases of $NaClO_3$ and $NaBrO_3$. *Versl. Kon. Akad. v. Wet.*, Amsterdam, **38**, 117 (1920).

[2] *Proc. Amer. Acad. of Arts & Sciences*, **52**, 91 (1916).

PART II—EXPERIMENTAL

CHAPTER I

EXAMINATION OF THE THEORY BY NON-ELECTRICAL METHODS.

1. General Considerations.

THE examination of the theory may be carried out in various ways :—

(*a*) By investigating the influence of the previous history of the substance on its melting point, solidifying point, boiling point, transition point, vapour tension, specific gravity, refractive index, viscosity, specific heat, conductivity, chemical activity or any other property whatsoever.

(*b*) By investigating the change in properties, which under certain circumstances may appear, when a unary system is subjected, relatively quickly, to any arbitrary process such as, for example, change of temperature, change of pressure, evaporation, etc., or when the system is rapidly dissolved or precipitated, either with or without the help of the electric current.

(*c*) By investigating any function whatever of the temperature, the pressure, etc. ; confirmation of the theory may result from the manner in which this function changes with the temperature or with the pressure.

In the examination, therefore, proof is sought, in the first place, that the different states of aggregation, and especially the solid phase, of a substance which exhibits the phenomenon of allotropy can, in fact, behave as a phase containing several components ; for if this is successfully established it always constitutes a confirmation of the first portion of the hypothesis on which the theory is based.

In the second place it is sought by continued study to learn something about the type of the pseudo-system and of the position of the unary system therein. This is naturally a much more difficult problem.

2. The System Benzil-*o*-Carbonic Acid.

Benzil-*o*-carbonic acid is an allotropic substance, the α and β pseudo-components of which may be obtained in a tolerably pure condition.[1]

Soch[2] first attempted to determine the melting diagram for this

[1] Grabe, *Ber. d. d. chem. Ges.*, **21**, 2003 (1888) ; **24**, 1344 (1890).
[2] *Jour. Phys. Chem.*, **2**, 364 (1890).

system. He found the melting point of the *yellow* β pseudo-component to be 141·5°, and that of the *white* α pseudo-component, in the determination of which, on account of the great velocity of transformation, the capillary method was applied, about 130°.

In order to determine the fusion line he heated small quantities of the molten acid to different temperatures and then allowed the liquid to cool until spontaneous crystallisation occurred. In this way inoculation was avoided, so that considerable supercooling might occur.

Thus he obtained the following table:—

Liquid heated to	Temp. of spontaneous crystallisation.	Temp. of total solidification.
141–142°	128°	126°
160°	120°	119°
174°	110°	112°
180°	115°	115·5°
190°	118°	118·5°

The unary melting point was determined starting from both the α and the β pseudo-components and heating very slowly. In this way the value 132° was found.

In addition, Soch still observed a transition point at about 65°, so that the phenomenon of enantiotropy occurs here. If the results

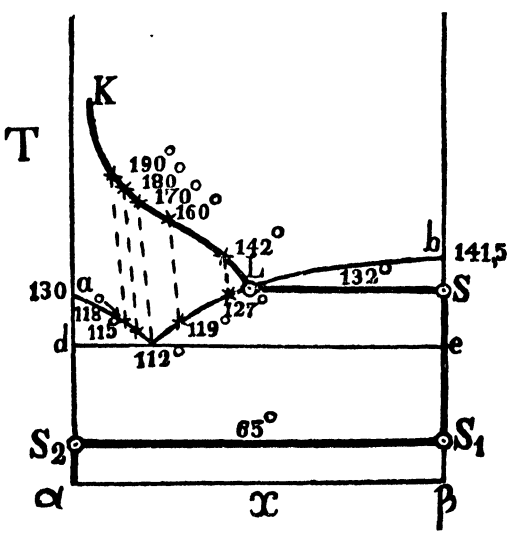


FIG. 127.

obtained by Soch are transferred to a T X diagram, Fig. 129 is obtained, in which the shape of the line for the inner equilibrium in the liquid phase is at once conspicuous; thus this line points to a very

great displacement of the inner equilibrium within a range of temperature of about 70°.

Since this is an interesting system, Vixseboxse,[1] at the instance of the author, repeated Soch's experiments.

Vixseboxse heated a sufficient quantity of the α or the β pseudo-component of benzil-*o*-carbonic acid for a quarter of an hour at 150°, 160°, 170°, 180° and 190°. He then allowed the liquid to cool down rapidly in an air bath until spontaneous crystallisation appeared; this always took place in the neighbourhood of 139°. The temperature then rose to a maximum value, remained stationary there for a short time and then fell again rapidly. The results so obtained are given in the accompanying table.

Temperature to which heated.	Initial solidifying temperature.
150°	142·2°
160°	142·1°
170°	141·7°
180°	141·5°
190°	141·3°

From this it appears, therefore, quite contrary to Soch's results, that the initial solidifying temperature falls but slightly. Soch obtained erroneous results because he worked with amounts of substance which were too small, and which were undercooled to such an extent that the heat of crystallisation could no longer raise the mass to the initial solidifying temperature.

Vixseboxse also determined the fusion diagram by the capillary method (Fig. 128).

The results varied, especially on the side of the white modification, in consequence of the velocity of transformation. Thus, the melting point of the pure white modification could only be found from the initial melting, for, after partially fusing, the mass again became solid. Each of the points shown in this diagram represents the mean of ten determinations.

In order to ascertain the position of the unary solidifying point, the yellow, or the white pseudo-component, or a mixture of the two, was heated to 150° in an oil bath; the liquid was then allowed to cool very slowly, during which process it was vigorously stirred. At 141° crystallisation commenced and the temperature rose to 142°, remaining constant at this value until the temperature of the bath had fallen to 138°. Afterwards, after the whole had been solid for about an hour, the temperature of the oil bath was raised to 144° in order to determine the unary melting point. When 142° was reached the temperature remained constant for thirty minutes, so that by means of this experiment the unary melting or solidifying point was found with great certainty to be 142°, whilst the melting point of the yellow β pseudo-component

[1] *Dissertation*, Amsterdam (1920).

amounts to 143·5°. The experiments of Soch, in which the value 132° was found, must therefore have contained a large error. The above-mentioned experiment of Vixseboxse proved that when the solidified mass is slowly heated to 142°, that is to say 1·5° below the melting point of the pseudo-component, complete fusion occurs. This experiment is very important, for it proves that the solidified mass does not consist of pure β pseudo-component, for in that case fusion would first set in at 143·5°. This experiment proves therefore that the stable unary solid phase is a *mixed crystal phase*, and this is also required by the theory.

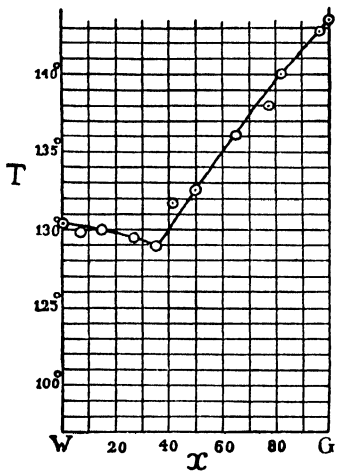


FIG. 128.

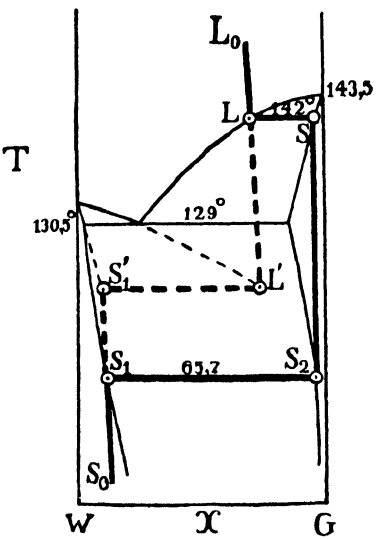


FIG. 129.

In order to determine the position of the inner equilibrium in the solid phase above the transition point, twenty capillary tubes were filled with the yellow modification and were then kept at a temperature of 130° in a wide tube for five hours. The final melting point was then determined in the case of each capillary by Soch's method.

Temperature of previous heating.	Final melting point.
130° (5 hours)	142·6°
120° (7 hours)	143·4°
100° (3 days)	143·4°
80° (7 days)	143·6°

These experiments were repeated after the benzil-*o*-carbonic acid had been heated in capillaries at 120°, 100° and 80°. In this way the results given in the preceding table were obtained.

If we set out from the assumption that inner equilibrium has in fact been established in the solid phases in the course of the periods of heating mentioned, the results obtained must lead to the conclusion that the inner equilibrium in the solid phase is only displaced to an extremely small extent within the range of temperature investigated, and, indeed, in such a way that at higher temperatures the concentration of the α pseudo-component increases.

If the table on page 184 is considered, it appears that the inner equilibrium in the unary liquid phase undergoes a similar displacement.

When the results obtained are introduced into a T X diagram, Fig. 129 is obtained, from which it is evident that the investigation of the system benzil-*o*-carbonic acid has confirmed the theory in the most beautiful way.

3. The System Monobenzoyl Camphor.

Another system investigated by Vixseboxse[1] was monobenzoyl camphor, a compound first prepared by Forster,[2] one pseudo-component of which is an enolic compound, the other having a keto-structure. Notwithstanding the rapidity with which inner equilibrium is established, he succeeded in determining the type of the pseudo-binary fusion diagram by means of the capillary method.

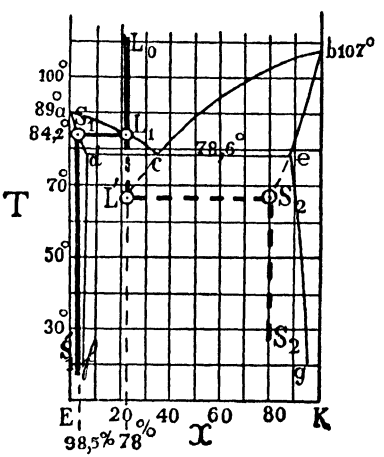


FIG. 130.

In this way it was proved, that whilst the enolic pseudo-component melts at 89° and the keto pseudo-component at 107°, the eutectic lies at 78·6°, as is shown in Fig. 130.

In order to determine the position of the unary melting point, the enolic pseudo-component was made the starting point and a trace of piperidine was introduced, since this substance exerts a powerful positive catalytic influence on the establishment of the inner equilibrium. When heat was very slowly applied fusion commenced at 84·2° and the temperature of the slowly melting substance remained at 84·2°, whilst the temperature of the heating bath rose to 86°.

The fact of fusion occurring not at 89° but at 84·2°, in itself proves the stable solid phase to be a *mixed crystal phase* in inner equilibrium, just as was found in the case of benzil-*o*-carbonic acid. The position of the unary system in the pseudo-binary system now had to be

[1] *Dissertation*, Amsterdam (1920); *Rec. d. Trav. Chim. des Pays Bas*, **1**, 1 (1921).
[2] *Jour. Chem. Soc.*, **79**, 991 (1901).

determined. The position of the inner equilibrium in the liquid phase was first of all ascertained at different temperatures. Tubes about 4 mm. in diameter and 15 cm. long were partially filled with benzoyl camphor, which was then melted. These tubes were heated for three hours to 85° or 100°, and were then suddenly cooled by plunging them into a bath containing solid carbon dioxide and alcohol, in order to fix the inner equilibrium. The amorphous mass obtained in this way was dissolved in alcohol and analysed by a method more fully explained in § 27, with the following results:—

At 100° the inner equilibrium mixture contained 79 % enol.
„ 85° „ „ „ „ „ 78·5 % enol.

Hence it may be concluded: (1) that the unary liquid line meets the fusion line of the *enol* pseudo-component, and (2) that as the temperature rises this line is displaced slightly in the direction of the enol pseudo-component.

In order to determine the position of the inner equilibrium in the unary solid phase at the unary melting point, a little piperidine was added to the benzoyl camphor, which was then melted and allowed to crystallise extremely slowly. The complete solidification, which took place at 84·2°, occupied an hour. After suddenly cooling, the amorphous mass was then ground to a fine powder under dilute hydrochloric acid, to remove the piperidine, quickly sucked dry, dissolved in alcohol and analysed.

In this way it was found that the inner equilibrium in the solid phase at the unary melting point contained 98·5 % of the enolic and 1·5 % of the keto pseudo-component.

These experiments were also repeated at temperatures between 50° and 80°, with the result that at these temperatures too the inner equilibrium contained 98·5 % of the enolic pseudo-component. Thus it appears that between 84° and 50° the inner equilibrium in the stable solid phase is not noticeably displaced.

The position of the metastable unary melting point has not so far been determined, because the metastable unary phase has not been obtained. From the T X diagram, Fig. 130, it would appear, however, that this metastable unary fusion equilibrium must lie somewhat below 70°.

From the study of the keto and enolic forms of monobenzoyl camphor in the presence of a solvent, the results of which will be communicated later, it appears that a transition equilibrium probably appears at − 83°. At this temperature, therefore, the line $S_1 S_1'$, representing the stable solid inner equilibrium, will intersect the mixed crystal line *d f* of the pseudo binary system, whilst $S_2' S_2$ representing the metastable solid inner equilibrium intersects the mixed crystal line *e g*. Thus it appears, from the results mentioned here, that the behaviour of the system monobenzoyl camphor is in accordance with the theory.

4. The Variations in the Melting Point of Trilaurin and the TX Diagram for this System.

Nearly all triglycerides exhibit the phenomenon of double melting; *i.e.* if, after the liquid fat has been caused to solidify by more or less rapid cooling heat is again supplied, the fat melts, but as the temperature is raised the liquid again becomes solid and the solid phase so obtained finally melts sharply at a higher temperature.

Bokhorst[1] first proved two modifications of the fat under investigation to be concerned here, as had already been supposed by Grün and Schacht.[2] The fats investigated by Bokhorst were *tristearin* and *trilaurin*. Both exhibit two crystalline states; up to the present, however, no transition point has been found, and it appears therefore that monotropy occurs here, at any rate under low pressures.

As a result of his researches Bokhorst has proved that tristearin and trilaurin differ from one another, amongst other things, in that the *heterogeneous* equilibrium is established with far greater velocity in the case of trilaurin than in the case of tristearin, whilst the inner homogeneous equilibrium is established much more rapidly in tristearin than in trilaurin. Consequently trilaurin is much the better adapted to the examination of the theory given here. Both modifications and the change of the metastable into the stable state were observed under the microscope. In this way both forms were proved to be crystalline.

(a) *The stable unary and the metastable melting points.*

The temperature at which the stable modification fuses, *i.e.* the stable unary melting point, was determined with great accuracy and was found to be 46·4°. The determination of the metastable unary melting point, however, presented great difficulties, because at this temperature the velocity of transformation of the metastable modification into the stable form was so great that the temperature of fusion could not be sharply observed.

Eldik Thieme[3] had already found this metastable melting point to lie in the neighbourhood of 15°. If, however, a test tube containing metastable solid fat is put into a thermostat at 18°, the temperature of the fat rises in a short time to about 30° in consequence of the heat liberated in the transformation.

From the following experiments it may be concluded, however, that the unary metastable melting point lies between 14° and 18·2°. At first, in the case of trilaurin, the velocity of transformation seems to be too great to allow of closer study. The only method which promised anything here was Soch's so-called capillary method. At the outset, however, when carried out with small quantities of substance, even this did not appear to lead to good results, for here too the transformation of the metastable into the stable form was very troublesome. Finally, however, extremely narrow and thin-walled capillaries were

[1] *Dissertation*, Amsterdam (1916). [2] *Berichte*, **40**, 1778 (1907).
[3] *Dissertation*, Delft (1911).

employed, with which it was possible to work so quickly that the observations could be completed before any noticeable transformation had taken place, so that there remained no further obstacle to the solution of the problem.

The capillary tubes used had an internal diameter of 0·33 mm., and the thickness of the wall was 0·18 mm.

These capillaries were one-third filled with fat, evacuated, and finally sealed by fusion.

For the better discussion of these experiments, it seemed desirable to draw a diagrammatic pseudo T X figure beforehand. This T X diagram, Fig. 131, contains a eutectic. The equilibrium lines for the unary system have a position such as is there schematically indicated. This may be shown in the following way.

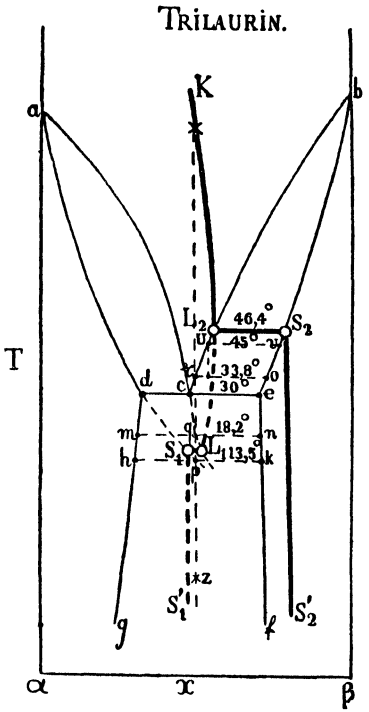


FIG. 131.

(b) *Determination of the point* q.

For this purpose we set out from the liquid K, which is in inner equilibrium. If the capillary containing this liquid is suddenly plunged into a bath of solid carbon dioxide and alcohol, a *homogeneous* solid phase Z is formed of approximately the same composition as the liquid K. The solid phase so obtained is not the metastable modification. This is a homogeneous metastable phase, which is in *inner equilibrium*. It is situated on the line $S_1 S_1'$, and has, therefore, a different composition from the solid phase obtained by sudden cooling. If this solid phase is heated it must exhibit an initial melting point at the point *p*, if the composition remains unchanged, whilst melting will first be complete at the point *q*. The determination of these two points was now attempted by working as rapidly as possible.

The point *q*, for which the value 18·2° was obtained, was fixed fairly easily; it was taken to be the lowest temperature of the bath, in which the chilled fat completely melted within a second after the introduction of the capillary. In 1·5 seconds, however, it was again quite solid. But the initial melting point *p* could not be determined in this way. By indirect methods, which will be described later, it was found to be 13·5°. Thus there is a difference of 4·7° between the initial melting point and the end melting point of the binary solid substance.

(c) *The determination of the point* r.

A capillary tube containing trilaurin was heated to 100° and then suddenly plunged into the bath of solid carbon dioxide and alcohol. The homogeneous solid phase thus obtained was then placed in a bath at a temperature of 18·2°, complete fusion resulting within a second, followed, however, within 1·5 seconds by total re-solidification. It is evident from the T X diagram that the solid phase must be a conglomerate of the two mixed crystal phases *m* and *n*. Immediately after solidification the temperature was investigated at which the mass completely melted a *second* time within one second. This was found to occur at 33·8°. Hence the point *r* lies at 33·8°, *i. e.* 12·5° *lower* than the stable unary melting point. The liquid obtained in this way only remains quite clear for a moment, and a further solidification soon takes place.

This behaviour was to be expected, because at this temperature the internal transformation takes place with great velocity. This transformation consists of the reaction $\alpha \rightarrow \beta$, and as a result of it the composition shifts from *r* in the direction of *o*, and this displacement again causes crystallisation. If it is assumed that, in consequence of this transformation, at a given moment the composition has reached the point *t* indicated here on the line *r o* (see also Fig. 132), a repetition *for the third time* of the melting experiment will result in complete fusion at the point U, again, therefore, at a higher temperature. In the actual experiment this *third* melting occurred at 45°, still 1·4° below the unary melting point. This fusion is naturally followed by solidification, etc., until finally the unary melting point is reached. *It is evident that in this way trilaurin may be completely melted and then partially solidified an indefinite number of times, but at ever-increasing temperatures.*

(d) *The indirect determination of the point* p.

It is impossible, as has already been pointed out, accurately to fix the point *p* at which fusion begins. Consequently recourse must be had to an indirect method. This was based on the fact that a co-existence of two phases which are metastable in the pseudo-system and which do not exist in the unary system, since they are not in inner equilibrium, is unstable to so great an extent that a very rapid change into a stable state results.

Two different methods of procedure were followed. A capillary containing trilaurin was heated to 100° and then suddenly cooled in solid carbon dioxide and alcohol. The tube was then kept for six seconds in a bath at 13° or at 14°. After this the capillary was taken from the bath at 13° and was placed in another bath at 18·2°; within one second complete fusion occurred. If, however, the capillary was taken from the bath at 14° and placed in the bath at 18·2°, only *partial* fusion occurred within one second. Hence it may be concluded that a transformation had taken place at this temperature which at 13° had not yet appeared. It is therefore very probable that to begin with slight fusion appeared at 14°, whereupon the pseudo-binary metastable two-

phase system solid—liquid partially changed into the pseudo-binary stable system of two mixed crystals, situated on the lines *d g* and *e f*. Hence it follows from this experiment that the point *p* probably lies very near 13·5°, and it is therefore only about 5° lower than *q*.

This conclusion is supported by the following experiment. When the capillary was first of all heated to 100° and then suddenly cooled, a mass was obtained which behaved differently at 19°, according to the temperature to which the capillary had been suddenly cooled. The following were the results obtained :—

Temperature to which suddenly cooled.	Behaviour in bath at 19°.
14·5°	Does not *melt* within 1 second.
14·0°	,, ,, ,, 1 ,,
13·5°	Partially melts within 1 ,,
13·0°	Melts completely within 1 second.
12·8°	,, ,, ,, 1 ,,
12·5°	,, ,, ,, 1 ,,

These results also point to the fact that the initial melting point of the chilled mass lies at 13·5°. The temperature of the unary metastable melting point lies therefore between 13·5° and 18·2°; on account of the great velocity of transformation, however, it cannot accurately be determined.

(e) *Determination of the eutectic temperature.*

Finally, yet another experiment was instituted with the object of determining the eutectic temperature of the pseudo-binary system.

To this end trilaurin was again heated to 100° in a number of capillary tubes and then chilled in a bath at − 80°. The capillaries were then placed in a bath at 18·2°, whereupon first of all complete fusion and afterwards complete re-solidification resulted. Immediately after this total solidification, in the course of which, according to our pseudo-binary figure, a conglomerate of the mixed crystal phases *m* and *n* is formed, by placing the tubes in baths of different temperatures, the temperature was determined at which the first signs of fusion could be observed within one second. The results were as follows :—

Temperature of bath.	Behaviour of mass after 1 sec in the bath.
33·8°	Complete fusion.
32°	Partial fusion.
31°	Very little fusion.
30°	No fusion.

From this it may be concluded that the eutectic temperature of the pseudo-binary system lies somewhat above 30°.

(f) *The position of the unary liquid line.*

From the graphical representation of the results of the experiments mentioned here, it would follow that the line relating to the inner equilibrium in the liquid phase of the unary system has a form such as is diagrammatically represented in the T X diagram (Fig. 131). This line would thus have a vertical tangent, which is very remarkable.

Now it must not be forgotten, however, that, in the determination of q and p, it has been assumed that no internal changes appear, and consequently that these points correspond in composition with the point K.

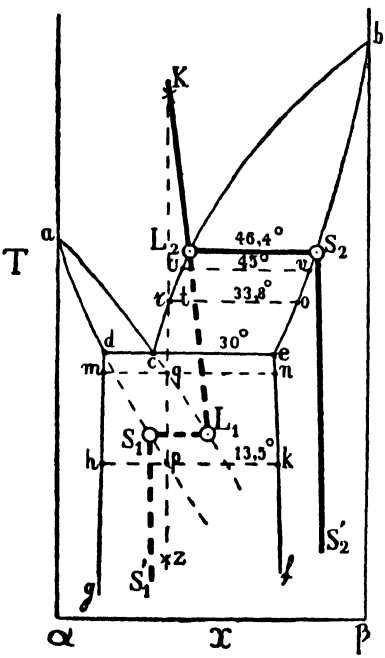


FIG 132.

Now the possibility is not by any means excluded, it is even probable, that notwithstanding the speed at which Bokhorst worked, internal changes did occur. Thus the possibility exists of the point q corresponding to a composition which contains a higher proportion of β, so that the true q, corresponding to the point K, is to be found at a higher temperature. The smallness of the distance between the points p and q also makes this assumption very probable. The T X diagram shown in Fig. 132 is based on this consideration.[1]

(g) *The inner equilibrium in the solid phase.*

Now it was also of interest to know the position of the line relating to the inner equilibrium in the solid state.

With the object of determining this line trilaurin was allowed to solidify to the stable condition in a number of capillary tubes. Of these, one half were then placed in a bath at 30° and the other half in a bath at 44°. After six hours one of the capillary tubes was taken from the bath at 44° and kept for five seconds in the bath at 30°. This capillary and another from the bath at 30° were then simultaneously introduced into a bath at 46·4°.

The result was that the contents of both these capillary tubes melted

[1] Although the observed point q differs from the true one in that the former is displaced further in the direction of the liquid point L_1 of the metastable unary equilibrium, it is still true that the temperature of this equilibrium must lie between 13·5° and 18·2°.

at the same moment. Hence it may be concluded that the line $S_2 S_2'$ relating to the inner equilibrium in the solid state follows a practically vertical course. This is also true of the line $S_1 S_1'$.

These experiments of Bokhorst's, especially those relating to the system trilaurin, thus constitute a very beautiful confirmation of the theory. They have not only shown the unary system trilaurin to be complex and therefore related to a pseudo-system, but they also made it possible approximately to ascertain the type of the pseudo-figure and even to determine several points in it. Of the allotropic substances of which until recently only the unary behaviour was known, trilaurin is the first example in which the examination of the theory could be carried so far. This is probably traceable to the fact that up to the present inorganic rather than organic substances have chiefly been investigated. In many of the latter inner equilibrium conditions are probably established more slowly, and their complexity can therefore be investigated more easily.

5. The Elevation of the Melting Point in the Case of Sulphur.

An inorganic substance, the study of which has also yielded results in support of the considerations indicated here, is the element sulphur.

Sulphur is a very complicated element, of which various solid states of aggregation have been discovered. For our knowledge of these we are deeply indebted to the work of Gernez,[1] Brauns,[2] Smith,[3] and Aten.[4]

Let us confine ourselves to two of the various pseudo-components of this system, which may be designated α and β; these components are understood to be the ones which are prominently concerned in the fusion of rhombic sulphur. The β pseudo-component was formerly called S_R and the α pseudo-component S_μ, yet the pseudo-component S_μ cannot be involved here when considering the solid substance, for Aten failed to find it in rhombic sulphur.

The pseudo-components need not, however, be further defined at this point; the results obtained by Kruyt[5] in his investigation of sulphur by Soch's method are of interest here.

It was found that if the rhombic sulphur equilibrium was established at 90° in the presence of ammonia as catalyst, when heated rapidly it melted at 110·9°—the unary melting point lies at 110·6°—but when equilibrium was established at about 65°, the melting point amounted to 111·4.

These results, which were still unapplied when the theory of allotropy was propounded, again furnish a beautiful confirmation of this theory, for they indicate very clearly that it is a question of an inner

[1] *Journ. de phys.* (2), **3**, 58 and 286 (1884); (2), **4**, 349 (1885).
[2] *N. Jahrb. Miner.-Beil.*, **13**, 39 (1900).
[3] *Zeitschr. f. physik. Chemie*, **42**, 469 (1903); **52**, 607 (1905); **54**, 257 (1906); **57**, 685 (1907); **61**, 200 (1908); **61**, 209 (1908); **77**, 661 (1911).
[4] *Ibid.*, **81**, 257 (1912); **83**, 442 (1913); **86**, 1 (1913); **88**, 321 (1914).
[5] *Ibid.*, **64**, 513 (1908); **65**, 486 (1909); **67**, 321 (1909); **81**, 726 (1913).

equilibrium in the solid rhombic phase, represented in Fig. 133 by the line S S_1.

Since this line inclines towards the left as the temperature increases, it immediately follows, provided the operation is carried out rapidly,

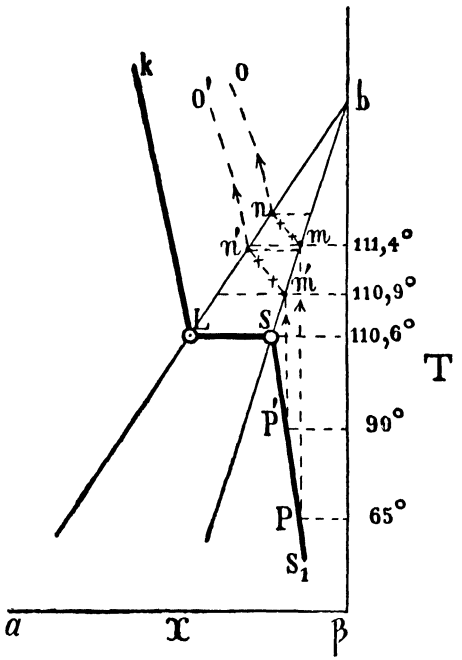


FIG. 133.

that the lower the temperature at which inner equilibrium is established to begin with, the higher will be the temperature at which the phase commences to melt, and this was also observed.[1]

6. The Variations in the Melting Point of Violet Phosphorus.

The same phenomenon is found in the case of violet phosphorus. The data given in the literature for the melting point of this substance differ considerably. Chapman [2] gives 630°, Stock [3] and Gomolka,[4] on the other hand, found 600° to 610°, whilst later Stock and Stamm found that when heated very slowly it melts at 597°.

Bokhorst and the author [5] found the melting point (triple point

[1] Smits, *Zeitschr. f. physik. Chemie*, **76**, 421 (1911); **83**, 221 (1913); de Leeuw, *Ibid.*, **83**, 245 (1913).
[2] *Journ. Chem. Soc.*, **75**, 734 (1899).
[3] *Ber. d. d. chem. Ges.*, **42**, 4510 (1910).
[4] *Ibid.*, **46**, 3497 (1913).
[5] *Zeitschr. f. physik. Chemie*, **91**, 249 (1916).

temperature) of violet phosphorus to be much lower when the temperature of the bath (nitrate bath) was raised very slowly than when the heating was carried out quickly. The highest melting point observed in the case of rapid heating was 610°, and determinations in a bath at constant temperature gave the value 589·5°, which is also the temperature obtained from a study of the vapour pressure lines. Thus, on this point our results and those obtained by Stock and Stamm are in complete agreement, that is to say, the melting point of violet phosphorus is found to be considerably lower when the substance is slowly heated than when the heating is carried out quickly.

Another phenomenon discovered by Terwen [1] belongs here. When molten violet phosphorus, a colourless liquid, is allowed to solidify, but not extraordinarily slowly, a solid is obtained which always begins to melt below 589·5°. This phenomenon again is in complete agreement with the results of Stock and Stamm, who summarise their observations in the following words.

"Our observations show quite clearly that the processes of fusion and solidification do not proceed as in single substances, but as in the case of solutions."

Thus, in agreement with the theory, violet phosphorus has been found to be complex. It is sufficient to look upon phosphorus as a pseudo-binary system, in order to explain the remarkable phenomena observed here. This is shown in Fig. 134.

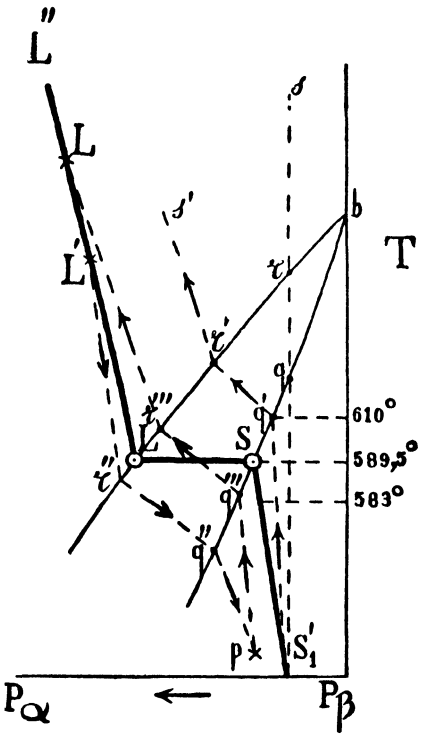


FIG. 134.

The line S_1' S indicates the inner equilibrium in the solid phase at different temperatures. From the course of this line it may be seen that if violet phosphorus is in inner equilibrium at the ordinary temperature, for example, and is then heated in such a way that the inner equilibrium is unable to follow the temperature, fusion will first commence at a higher temperature than the unary melting point. If it is now assumed for a moment that no internal change at all occurs, the solid phase moves along the line S_1' *q r s*, and whilst the phosphorus begins to melt at *q*, complete fusion is first attained at *r*. If, however,

[1] *Inaugural Dissertation* (1913), Amsterdam.

a slight change is produced by the heating, the total composition is continuously displaced towards the left and follows, for example, the dotted line $S_1'\ q'\ r'\ s'$. Consequently the substance will now begin to melt at q' and its final melting point will be reached at r'. The form of the dotted line shows that it is assumed here that the internal change is greatest during melting. This assumption is based on experience, for up to the present it has always been noticed that the appearance of a second phase exerts a powerful accelerating influence on the establishment of inner equilibrium.

Even though the establishment of inner equilibrium in the violet phosphorus has only taken place two or three degrees below the unary melting point, when heated it does not melt like a unary substance. As heat is supplied, the temperature rises and the substance exhibits an *initial* and an *end melting point*, or, in other words, it melts over a *range of temperature.*

When, however, the temperature of the violet phosphorus was kept constant at 589·5°, in half an hour the solid phase had melted completely. With the assistance of Fig. 134, Terwen's observations,[1] described above, can now also be explained. Thus, on warming, the solid mass obtained by the rapid cooling of liquid violet phosphorus begins to melt at a lower temperature than the unary melting point. That is to say, if the liquid L′ is cooled quickly, the composition follows the dotted line $L'\ r''\ q''\ p$; if it is now heated up again the composition follows another dotted line, namely $p\ q'''\ r'''$ L, and this merely expresses the fact that the initial melting point now lies below the unary melting point.

7. The Elevation of the Solidifying Point of White Phosphorus.

As in the case of violet phosphorus, the complexity of the white variety has also been established with certainty.

By using a very sensitive resistance thermometer,[2] the time temperature curve was determined for the solidification of pure white phosphorus in a vacuum.

From the curve so formed, Fig. 135, it may be seen that solidification took place practically completely in the unary manner, and indeed at 44·1°.

Since now the object was to investigate the influence of previous heating followed by sudden cooling on the solidifying point, it was desirable to investigate in the first place the extent to which the results might be influenced by the heat current which on rapid cooling must of necessity appear in the thermometer.

For this purpose an exactly similar thermometer was constructed to that in the phosphorus vessel, but without a melting vessel. After

[1] *loc. cit.*

[2] The resistance thermometer was made under the direction of de Leeuw and Zernike by my glass-blower van Deene, and was first used by de Leeuw (*Zeitschr. f. physik. Chemie*, **77**, 305 (1911)).

calibrating the thermometer the temperature recorded by it was determined when it was taken from a bath of boiling water and suddenly plunged into a thermostat at about 43·42°. The result of this experiment is shown by the line *a b c d* (Fig. 136).

The ordinates represent temperature and the abscissæ time. Zero

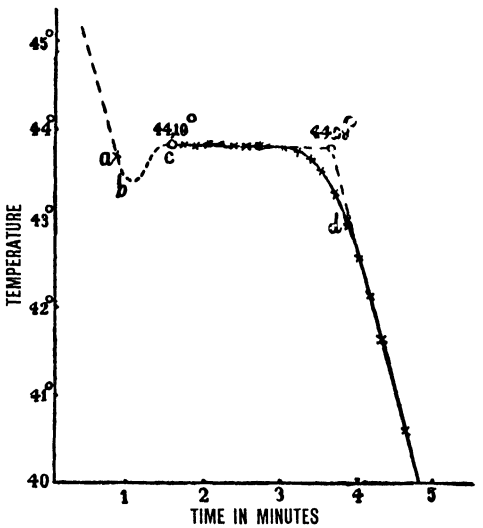


FIG. 135.

time corresponds to the moment at which the resistance thermometer was plunged into the thermostat at 43·42° from the bath at 100°. The damping of the galvanometer was insufficient for the great velocity, and

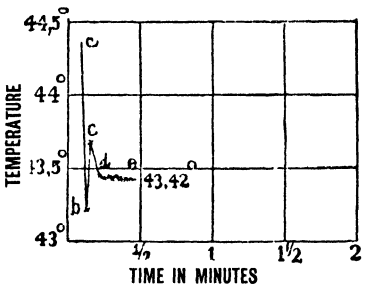


FIG. 136.

the image of the Nernst pencil consequently oscillated a little about its position of rest. It was found that after 7 seconds the throw of the mirror corresponded to 43·2°, after 9 seconds to 43·7°, after 15 seconds to 43·42° and after 24 seconds likewise to 43·42°. Hence it appears that after 15 seconds the thermometer had already assumed the same

temperature as the thermostat. This experiment proves, therefore, as was expected, that the resistance thermometer, in consequence of the flow of heat, indicates too high a temperature at the commencement, but that in 15 seconds it has actually assumed the same temperature as the thermostat. This illustrates very clearly the great rapidity with which the temperature is indicated by the resistance thermometer.

The following experiment was carried out in a vessel into which a resistance thermometer had been sealed. The same apparatus was employed as in the determination of the unary solidifying point. The vessel containing white phosphorus was placed in boiling water and two minutes later it was plunged, with vigorous shaking, into a water bath at 15°. As soon as the temperature had fallen to 44·2°, the vessel was again plunged in the same way into a thermostat at 44·75°. The course followed by the temperature in this experiment is indicated in Fig 137 by the line *a b c d*.

From this line it appears that after 10 seconds the resistance thermometer, and consequently the liquid phosphorus also, had completely assumed the temperature of the surrounding bath. The entire absence of any rise in temperature is probably explained by the fact that for some seconds the temperature of the liquid phosphorus had been below the temperature of the bath.

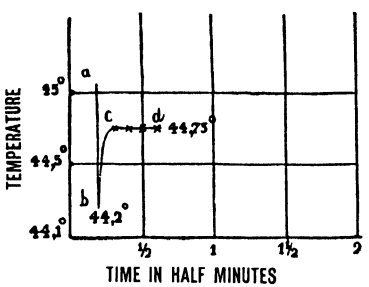


FIG. 137.

This result, which is much more favourable than was anticipated, proves that if the vessel had not been introduced into the thermostat at 44·75° *from the colder bath, and if in this case after* 10 *seconds spontaneous crystallisation had occurred, a rise of temperature above the unary solidifying point would have had to be attributed to the phosphorus.*

Let us now proceed to the real experiment with rapidly cooled phosphorus. During the sudden cooling the vessel containing the liquid phosphorus was shaken until a temperature of about 50° was reached; it was then clamped in a stand, where it was further cooled in the air without shaking. Shaking greatly promotes the establishment of inner equilibrium, and therefore in the first experiments shaking was not continued too long. But since under these circumstances temperature differences may appear between the different liquid layers, the rest of the experiments were so vigorously shaken as completely to exclude the possibility of any temperature difference in the liquid phosphorus. In this case establishment of inner equilibrium was not so much to be feared as a result of shaking, for the *magnitude* of the elevation of the solidifying point was not in question here, but rather proof of the complexity of white phosphorus.

It was found that clear effects could only be observed in this way if the cooling was carried out very rapidly, when solidification often

spontaneously appeared in 12 seconds. The result of experiments in which very unfavourable conditions were intentionally chosen should, however, be communicated here, in order to show that in these cases, too, the complexity becomes evident.

The vessel containing white phosphorus was again dipped into boiling water, and after two minutes it was suddenly plunged into a bath containing water at about 30°, as a result of which it was so cooled, being meanwhile vigorously shaken, that solidification, which under these conditions did *not* appear spontaneously, could be induced by inoculation after about 10 seconds. The inoculation was intentionally delayed until supercooling to an extent of about 1·5° had been attained. Then total solidification suddenly took place. The line *a b c d e* in Fig. 138 proves, however, that even under these unfavourable conditions, after 24 seconds a clearly perceptible elevation of the solidifying point by about 0·3° is found, and that the temperature only falls to 44·1° after 2·5 minutes.

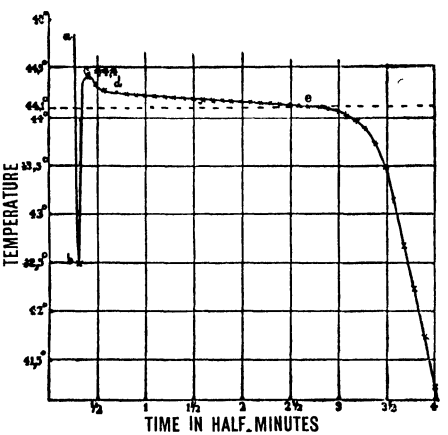


FIG. 138.

Besides this method Soch's capillary method was also employed, and the initial melting point was determined of white phosphorus obtained by the sudden cooling of liquid phosphorus to 15°. Although the initial melting point in this case could only be observed with difficulty and consequently not very accurately, the impression was gained from these experiments that solid phosphorus obtained in this way begins to melt at about 44·1°. This result, which is really in accordance with expectation, made it possible correctly to interpret the cooling curve *a b c d e*. Equilibrium in white phosphorus in the liquid state is established fairly quickly, but by rapid cooling it is still possible to carry the liquid beyond the inner equilibrium state.

As has already been mentioned, however, the metastability of a system increases to so great an extent when a phase which is itself not in equilibrium deposits a solid phase, that the establishment of inner equilibrium often takes place with great velocity.

In connection with the already rapid establishment of equilibrium in white phosphorus, it may therefore be expected that in the separation of the solid phase from liquid phosphorus which is not in equilibrium, inner equilibrium instantaneously appears. Hence the negative results of experiments in which the capillary method was employed are explained.

It is clear that in the case described here, the elevation of the

solidifying point can only be observed by means of a thermometer which indicates every temperature change almost instantaneously; because immediately after solidification commences, in consequence of the establishment of inner equilibrium, fusion occurs to a slight extent, so that after reaching the maximum the temperature begins to fall again rapidly. Consequently the real elevation of the solidifying point can only be observed for a very short time. Hence the slow temperature fall from 44·25° (point *d*) to 44·1° (point *e*) is probably to be ascribed to the slow equalisation of temperature between the liquid layer surrounding the resistance thermometer and the solid phosphorus, and this equalisation of temperature could not be improved by shaking, for the mass was almost completely solid.

8. The Dependence of Supercooling on the Previous History.

Whilst the elevation of the solidifying point described here proves white phosphorus to be complex, this complexity is borne out by yet another phenomenon, the discussion of which is therefore relevant here.

This liquid, for example, has often been kept for days at the ordinary temperature, that is to say at about 26° below the unary solidifying point. But in this case there is this peculiarity: this property of liquid phosphorus depends to a great extent on the previous history of the substance.

If, for example, a tube filled with white phosphorus heated to 100° is *suddenly* plunged into a bath of water at room temperature, liquid phosphorus is *never* obtained. *After a few seconds spontaneous crystallisation always takes place.* Even when the *narrowest capillaries* were employed, thus completely excluding currents, this phenomenon was always observed, and hence its origin is not to be found in the existence of such currents.

From this simple but significant experiment, it follows, therefore, that rapidly cooled liquid phosphorus is much more pronouncedly metastable than the slowly cooled liquid, from which it is clear that rapidly cooled phosphorus is not in inner equilibrium. Now it is well known that the phenomenon of undercooling can always be observed most easily when the cooling is very slow, and it may therefore be concluded that we are dealing here with a general phenomenon, which is what the theory would lead us to expect.

9. The Elevation of the Solidifying Point of Cyanogen.

To the experiments described here, Terwen's[1] investigation of cyanogen may be added. The unary melting point of cyanogen, which Terwen prepared and purified with extraordinary care, was found to be − 27·92°, whilst at − 27·67° the rapidly cooled liquid had already begun to solidify.

[1] *Zeitschr. f. physik. Chemie*, **91**, 469 (1916).

10. The Elevation of the Transition Point of Mercuric Iodide.

It is well known that mercuric iodide exists in two modifications; a red tetragonal form which is stable below 127°, and a yellow rhombic variety, stable above that temperature. This behaviour, again, can be explained very simply by assuming the existence of two molecular species, which constitute the pseudo-components of the system, and which may be called αHgI_2 and βHgI_2. According to our theory the two modifications consist of mixed crystals in inner equilibrium, of which the red modification, for example, is rich in the β species, the yellow form being rich in the α species.

Now the yellow modification is peculiar in that it commences to become orange at 180°, and this change becomes still more pronounced as the temperature is increased. This colour change proceeds continuously and the crystal form remains unchanged, as von der Veen[1] proved. Just below the melting point the colour is deep orange; on melting, at 255·5°, a dark red liquid is formed. From these results it follows that the inner equilibrium line is displaced at temperatures above 150° towards the β component.

If this is expressed in our T X representation, in the same way as the fact that in the neighbourhood of the transition point the red modification becomes deeper red in colour as the temperature is raised, the following T X diagram is obtained (Fig. 139).

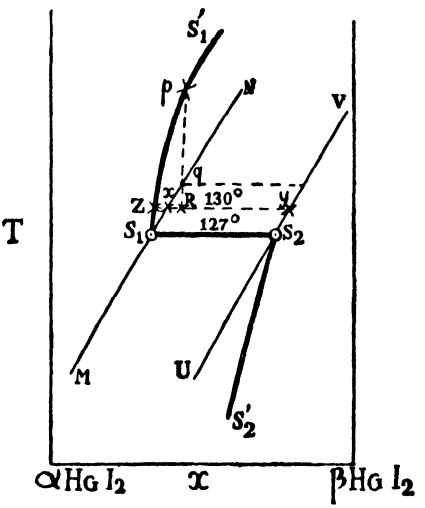


FIG. 139.

The lines M N and U V indicate the mixed crystal lines of the pseudo-binary system, whilst $S_2'S_2$ and S_1S_1' relate to the unary system. The position indicated here would lead one to expect that it might perhaps be possible, in this instance, to realise an example of the elevation of the transition point as a result of rapid cooling.

This was in fact the case. Thus, when mercuric iodide was heated to 215° in capillary tubes in an oil bath, and was then suddenly plunged into another bath at 130°, which was vigorously stirred, although 130° is above the transition point, a transient red colour appeared in various places.

Within a second the red patches had disappeared again and the whole mass was yellow. This phenomenon *only* occurred when the capillary was transferred *as rapidly as possible* from one bath to

[1] *Kon. Akad. v. Wet.*, **29**, 1557 (1916).

the other. From this it follows that it is incorrect to assume, as Tammann and Hasselblatt[1] do, that the HgI_2 is cooled in places below 127° during the manipulation described above. The observation can, however, be explained in the following way.

If we proceed from the state *p* and assume that the cooling is so rapid that the establishment of inner equilibrium cannot keep pace with the fall in temperature, and that the states indicated by the line *p q* R are passed through, we see that at 130° the mercuric iodide has reached the point R. But this point lies in a heterogeneous region of the pseudo-binary system, namely in the region in which yellow and red mixed crystals coexist; consequently the yellow phase R may break up into the yellow phase *x* and the red phase *y*. But this two-phase system is unstable in the highest degree, and consequently a rapid transformation occurs, whereby a condition of inner equilibrium is reached, corresponding to a temperature of 130°. This is situated at Z and turns out to be a yellow mixed crystal phase.

Now in mercuric iodide, however, inner equilibrium conditions are attained with great velocity, and hence this phenomenon could only be observed, as has been stated, when the cooling process was very rapid.

When the phenomenon was discovered, it could be reproduced so easily, that it was repeatedly observed by different persons.

Later, however, as is now well known, other investigators failed to reproduce it, and when the experiment was repeated with another preparation the phenomenon did not make its appearance. Thus the extremely subtile character of the experiment first became clear, and that unknown catalytic influences played a part in it became probable, so that one preparation exhibited the phenomenon and the other did not. Probably, also, the catalytic action derived from the glass walls of the tubes, or from traces of impurity, acted unequally in the different experiments; consequently it is only possible to deduce from the positive results of the first experiment, that red mercuric iodide may possibly appear at temperatures above the transition point.

Other methods of investigation.

It was therefore highly desirable to invent another and less subtile method, so that the same problem might be studied more easily. The following method of investigation was carried out by Bokhorst under the direction of the author. It offered the advantage of yielding quite reproducible results, which were the same when different preparations were used.

Very narrow capillary tubes half filled with mercuric iodide, evacuated and then sealed up, were heated to different temperatures between 192° and 257° and were then suddenly chilled in liquid air. Finally they were placed in a bath at a temperature of 18° and were thus rapidly re-heated to room temperature. In this way the following results were obtained:—

1. Temperature before chilling: 192°. Appearance of the mass at

[1] *Zeitschr. f. physik. Chemie*, **86**, 861 (1913).

the ordinary temperature: *to begin with apparently homogeneous and yellow.*

After 2 minutes the red phase appeared in some spots.

After 6 minutes these spots had noticeably increased in size.

After 10 minutes the spots had increased to large flakes. The appearance of the contents of the capillary was half red, half yellow.

After 20 minutes various fairly large yellow flakes still remained.

2. Temperature before chilling: 203°. Appearance of the mass at the ordinary temperature: *apparently homogeneous and yellow at the outset.*

After 1½ minutes some red spots could be observed.

In 6 minutes these spots had increased in number and had become much larger. The contents of the capillary were half red, half yellow.

After 9 minutes red already predominated.

After 16 minutes it was red practically throughout.

3. Temperature before chilling: 220°. Appearance of the mass at ordinary temperature: *homogeneous and yellow to begin with.*

After 1 minute a fairly large number of red spots could already be observed.

After 3 minutes the number of these spots had greatly increased so that some had grown into large red flakes.

After 6 minutes the red colour predominated.

After 10 minutes it had become almost entirely red.

4. Temperature before chilling: 231°. Appearance of the mass at the ordinary temperature: *still apparently homogeneous and yellow to begin with.*

After 20 seconds red spots were already visible.

In 1·5 to 2 minutes these had grown to large flakes.

In 3 minutes the mass consisted of red and yellow flakes in equal proportions.

In 6 minutes it was almost entirely red.

5. Temperature before chilling: 244°. Appearance of the mass at the ordinary temperature: *not homogeneous; a considerable number of red spots were present from the commencement and these rapidly extended.*

In 1 minute the mass contained red and yellow in equal proportions.

In 3 minutes it was almost entirely red.

6. Temperature before chilling: 251°. Appearance of the mass at the ordinary temperature: *not homogeneous.* A large number of red spots instantly appeared.

In one minute there was a preponderance of red in the mass.

7. Temperature before chilling: 254°. Appearance of the mass at the ordinary temperature: *not homogeneous.* A large number of red spots present.

In half a minute almost entirely red.

In 1 minute the mass was *completely* red.

8. Temperature before chilling: 255°. Appearance of the mass at the ordinary temperature: *not homogeneous,* but half yellow, half red.

In 10 seconds it was red throughout.

9. Temperature before chilling: 257°. Since this temperature lay

above the melting point (255·5°), the mass was liquid when chilled in liquid air. This liquid was dark red in colour.

At the ordinary temperature the mass was *uniformly red from the beginning*, and apparently it underwent no further change.

These results may now be explained in the following way:—

Mercuric iodide is a substance in which inner equilibrium is established very rapidly. The heterogeneous equilibrium, however, may easily be retarded.

Thus the fact is well known, that the red modification can easily be heated to a temperature several degrees above the transition point (127·5°) without transformation of the red into the yellow modification taking place. And similarly it is well known that the yellow form can exist at temperatures far below the transition temperature.

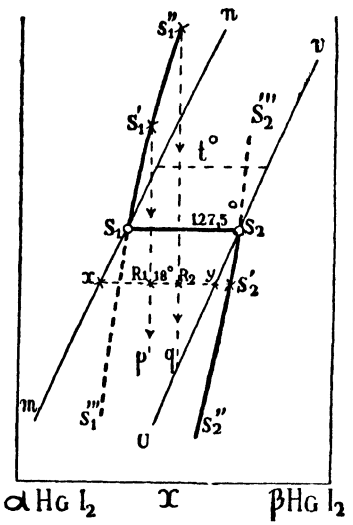


FIG. 140.

The velocity with which heterogeneous equilibrium is established increases with the temperature, and thus at about 140° the red form is rapidly converted into the yellow modification. If now the inner equilibrium state S_1' (Fig. 140) is imagined to be suddenly cooled down, naturally no division into a yellow and a red mixed crystal phase can appear unless the line $S_1'p$ meets the line mn at a temperature at which the heterogeneous transformation yellow → red takes place very rapidly. In the neighbourhood of the transition temperature, the velocities of this and of the reverse change are still fairly small. As the temperature is further increased, however, the split will markedly increase.

It might, therefore, be expected that a *directly perceptible division* into yellow and red mixed crystals would appear in the above-mentioned experiments, when the temperature of the chilled inner equilibrium state lay above a certain value.

If, however, the temperature lies below this value, only very slight division can take place; the preliminary step to the formation of a new phase, *nucleus formation*, will, however, certainly be taken. Nucleus formation will naturally take place more rapidly the higher the temperature at which the heterogeneous region in which yellow and red mixed crystals coexist is reached.

Hence it can easily be seen why the velocity with which the red phase appeared at 18° was greater the higher the temperature of the mass before chilling.

In experiments 1 to 4 the following must be supposed to occur. On suddenly cooling down the state S_1' the mass remains homogeneous, or heterogeneous to an unnoticeable extent, although the heterogeneous region for the co-existence of the yellow and the red mixed crystals of the pseudo-system has been traversed. But in any case nuclei of the red mixed crystal phase have been formed, and, indeed, their number is greater the higher the temperature at which chilling occurred. Hence it must be supposed that at 18° the mixed crystal phases x and y appear at the outset, and that this constitutes the intermediate stage of the continuous transformation into the red inner equilibrium state, S_2'.

With regard to experiments 5 to 8 the following should be noticed: In these cases the mass was suddenly cooled from higher temperatures, *e. g.* from S_1'', with the result that at $t°$, considerably above the transition temperature, therefore, where now the heterogeneous transformation takes place rapidly, a direct and easily perceptible division into yellow and red mixed crystals appears, so that at 18° the mass was distinctly heterogeneous from the commencement.

That direct division does in fact occur in these experiments was even more fully confirmed in the following way.

10. A capillary tube containing HgI_2 was suddenly cooled in liquid air from a temperature of 251°, and was then instantaneously placed in a bath at 128°, at which temperature no new formation of red mixed crystals can take place. Consequently if red flakes were observed at this temperature it would furnish proof that these red particles had been formed at the moment of cooling, and therefore at a temperature above the transition point; for if this experiment is carried out with the difference that the temperature before chilling is 130°, no red flakes are formed. The result of the experiment was as follows: At 128° the mass was clearly heterogeneous, red and yellow particles lying in juxtaposition; the whole experiment, *i. e.* the cooling down and the reheating to 128°, only lasted about 15 seconds.

Since from about 200° to its melting point yellow mercuric iodide becomes more and more deeply orange coloured, another possible explanation of these observations might perhaps be given. Indeed it might be believed that with increasing orange colour an increase takes place in the velocity with which nuclei of the red phase are formed below the transition point, in consequence of which the appearance and growth of the red phase would be accelerated.

To this it may be replied, in the first place, that in this proposition it is tacitly assumed that the orange-coloured phase is really to be looked upon as an *intermediate* state between the yellow and the red modification, and hence one is necessarily forced to adopt some such conception as is indicated here. In the second place, according to the old view, the nucleus formation referred to and the formation of the red phase would only be possible below the transition point, but experiment 10 points directly to the formation of the red phase even above the transition point.

In connection with these considerations it can be stated that the

diagram given here is in complete agreement with the colour change exhibited by both the yellow and the red forms when the temperature is reduced. That is to say, if two tubes containing yellow and red mercuric iodide respectively are cooled down in liquid air, the former becomes white whilst the latter assumes an orange-yellow colour. This probably points to the fact that the metastable prolongation of the line for the inner equilibrium in the yellow phase is displaced by a fall of temperature in the same direction as the line relating to the inner equilibrium in the red modification, and this would also follow from the diagram.

11. The Elevation of the Transition Point of Cristobalite.

Crystalline silica exists, as is well known, in various forms; amongst other modifications, α quartz is known, which changes under atmospheric pressure at 575° into β quartz; at 870° this changes into tridymite, whilst this again is converted at 1470° into β cristobalite. Furthermore, there is here the peculiarity that β cristobalite, which is therefore metastable below 1470°, undergoes transformation from this state into another α modification, at a temperature which depends on the temperature of formation of the β cristobalite.

Thus Fenner's[1] interesting and important investigations have shown that when β cristobalite was formed at about 1600° the transformation $\beta \rightarrow \alpha$ took place at about 238°. In this preparation, however, the reverse change occurred at 270°. But when the β cristobalite was prepared at about 1000° C. the temperatures of the changes $\beta \rightarrow \alpha$ and $\alpha \rightarrow \beta$ were 40°—50° lower, that is to say at 198° and 220° respectively.

These results constitute a beautiful confirmation of the theory of allotropy. They show that the temperature at which β cristobalite changes into α cristobalite, with evolution of heat, is higher, the higher the temperature at which the β cristobalite is formed. The observations were reproducible and they indicate that we are here dealing with an inner equilibrium, which, over the temperature range 1000°—1600° suffers considerable displacement as a result of change of temperature.

Since the inner transformation takes place very slowly, several days being required approximately to establish inner equilibrium at 1000° for example, on cooling, the composition remains unaltered and it may therefore be concluded that at 1600° the inner equilibrium composition corresponds with an initial transformation temperature about 50° higher than that corresponding to the inner equilibrium composition at about 1000°. This was very surprising.

Fenner's results show that the heterogeneous reaction was always retarded, otherwise it would have been possible accurately to determine the temperature range.

Since, on account of its different modifications, SiO_2 is without

[1] *Amer. Journ. of Sci.* **36**, 331 (1913); *Zeit. f. anorg. Chem.*, **85**, 173 (1914).

doubt built up from several pseudo-components, the T X diagram will be rather complicated.

If a metastable transition point makes its appearance the pseudo-system is at least ternary; a binary conception of the pseudo-system is then only successful under very definite assumptions. If the case indicated by the P T projection (Fig. 141) is imagined, it is impossible to represent the $(T X)_p$ section of the space model in the usual way, for the pseudo-system must, on account of the metastable transition point, be at least ternary. That this is so can easily be understood.

A stable transition point appears when the line for the stable inner equilibrium in the solid phase meets a mixed crystal line in the region of disintegration of the solid phase. From this it follows that a metastable transition point can only appear when the line for the metastable inner equilibrium in the solid state meets a mixed crystal line of a metastable disintegration region for the solid phase. In the

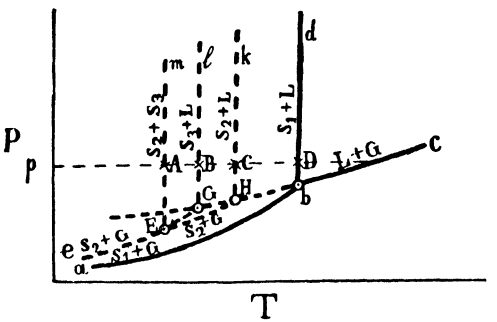


FIG. 141.

ternary representation this is certainly possible, but not in the usual binary diagram, because the line for the metastable inner equilibrium in the solid phase is situated in the disintegration region of the solid phase, where, in the usual binary conception, no metastable disintegration lines for solid phases appear.

Now, however, as a simplification, a pseudo-binary diagram can still be used instead of a ternary representation in which A, B and C are the pseudo-components, as was shown on page 62 of the theoretical part, if it is assumed, for example, that in the system A C inner equilibrium always prevails. In this case the A and C axes of the three-sided prism can be allowed to coincide, and then every noteworthy point of this double A C axis relates to a state of inner equilibrium between A and C.

If the T X diagram (Fig. 142) is considered from this standpoint, it is clear that the point *a* represents the stable unary solidifying point; *a'* the metastable unary solidifying point, and *f* the unary transition point in the pseudo-binary system A C, in which the α modification is converted into the β modification by the application of heat. In consequence of the assumption that a transition point appears in the system A C, a three-phase equilibrium between mixed crystals is formed,

indicated in our T X diagram by the points g, h, k and below this three-phase equilibrium the metastable continuation of the co-existence of the mixed crystal phases $f h$ and $f g$ extends. The existence of this metastable continuation now makes the appearance of a metastable transition point possible, as is immediately evident.

The points L_1 and S_1 indicate the stable three-component unary solidification equilibrium, corresponding to the point D in the P T figure. The points L_2 and S_2 relate to the first metastable unary solidification equilibrium, which corresponds with the point C in the P T figure.

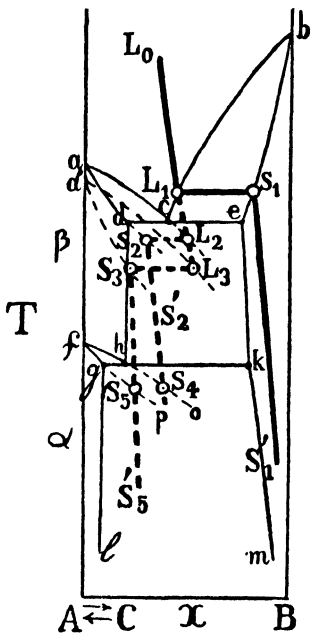


FIG. 142.

L_3 and S_3 indicate the second metastable unary solidification equilibrium, and this appears here because the first component consists of two pseudo-components which are here supposed to be in inner equilibrium with one another. This second metastable solidification equilibrium is denoted by B in the P T diagram. As is evident from our figure, the line $S_2 S_2'$ representing the metastable inner equilibrium in the solid phase meets the metastable mixed crystal line $f h o$, whence it follows that at S_4 a transition appears, in which from the one metastable inner equilibrium state S_4, another, S_5, is formed, which is likewise metastable and which continues along the line $S_5 S_5'$ in the direction of lower temperature.

This transition equilibrium corresponds to the point A in the P T diagram, which indicates the metastable transition point of the system under constant pressure.

These considerations have indicated the lines which can be followed in discussing the system SiO_2. Here also it must be assumed, if it is proposed to employ the simplification afforded by the use of a pseudo-binary representation, that the one pseudo-component is really built up from two others which exist in inner equilibrium with each other.

Figure 143 serves to illustrate these statements.[1] It indicates only one of the possibilities of the representation, which has already been fairly well developed.

From this it appears that the complete SiO_2 system will be so complicated as to compel us, in consequence of the limitations of our means of representation, to welcome methods which make it possible to represent the system in a simpler way. Such a method has already

[1] Ferguson and Mervin [*Amer. Journ. of Science*, **96**, 417 (1918)] have found the melting point of cristobalite to be 1710° ± 10°, and that of tridymite to be 1670° ± 10°.

been employed here, because the system must be at least ternary; in order that a binary diagram might be used, it has been assumed that two pseudo-components are always in inner equilibrium, so that these *two* components can be looked upon as a *single* component.

The figure given here very well illustrates the remarkable fact already communicated by Fenner,[1] namely, that the higher the temperature of formation of the β cristobalite, so much higher is the temperature at which the transformation into α cristobalite occurs.

Let us consider this phenomenon somewhat more closely with the help of a special diagram, Fig. 144, in which it is assumed that the cooling down proceeds so rapidly relatively, that internal changes are

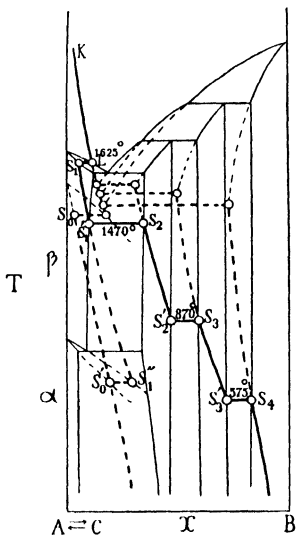


FIG. 143.

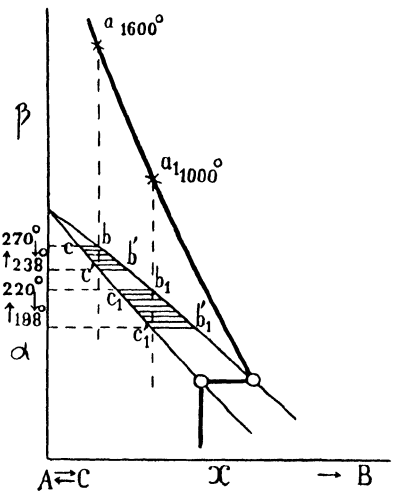


FIG. 144.

entirely excluded. In this case, therefore, the composition remains unchanged, and we move along a vertical line. If *a* represents the inner equilibrium state at 1600°, the transformation of β-mixed crystals into α-mixed crystals will commence at *b*. With the continued escape of heat this process proceeds further. During the displacement of the β-mixed crystal phase from *b* towards *b'*, theoretically the α-mixed crystal phase is displaced from *c* to *c'*, and when the α-mixed crystal phase has attained the latter composition the β-mixed crystal phase has just disappeared, having then all been converted into an α-mixed crystal phase *c'* of the same composition as the original β-mixed crystal phase. The transformation described here is of a *physical* nature only, and it has therefore taken place in the entire absence of internal change.

[1] *loc. cit.*

Taking the inner equilibrium state at 1000°, represented by the point a_1, as the starting-point, just the same phenomena appear, but at lower temperatures.

If during this physical transformation a change in the internal composition also occurs, *i.e.* if chemical change takes place, the above considerations are only altered in so far that the point c' does not then lie vertically under b, but is displaced more or less towards the right.

Whether internal change took place in Fenner's experiments it is impossible to say, and the question is without interest here. The important point is that Fenner found, using material prepared at 1600°, that the transformation $\beta \rightarrow \alpha$ had already taken place about 18° above the temperature at which the change occurred in material prepared at 1000°. Clearly, therefore, the unary transition point probably lies considerably below 198°.

It is not without interest to point out here that the mass obtained by Fenner in his experiment at 18°, for example, could not have been ordinary α cristobalite, but an α-mixed crystal phase which was not in inner equilibrium. It is clear that this phenomenon discovered by Fenner furnishes strong support for the theory of allotropy.

Now Fenner has also studied other changes in the system SiO_2 in the same way, but in these no noticeable displacement of the transition points has been found. The explanation of this must perhaps be sought in the fact that the other transition points lie several hundred degrees higher, so that the reaction velocity in the neighbourhood of these points completely prevents any retardation in the establishment of inner equilibrium. It is, however, also possible that, in consequence of the complexity of the SiO_2 system, slowly changing molecular species largely predominate in α and in β cristobalite, and that in the other modifications investigated they only occur in small quantities.

12. The Influence of Previous History on Various Properties of Selenium.

We are indebted for our knowledge of the very peculiar behaviour of selenium in great measure to Marc,[1] who investigated the influence of previous history on the electrical conductivity of the element.

Marc found that crystalline selenium can occur in two states, namely, a state A, which is non-metallic and of which the electrical conductivity is very small, and a state B, which is metallic and has a high electrical conductivity.

The non-metallic state A is formed when the supercooled amorphous mass is allowed to crystallise below 160°, *e.g.* at 110°, whilst the metallic state appears when crystallisation takes place above 160°, and preferably at 200°. By means of conductivity measurements

[1] *Zeit. f. anorg. Chem.*, **37**, 459 (1903); **48**, 393 (1906); **50**, 446 (1906); **53**, 298 (1907).

it was found that the state A changes continuously and over a great range of temperature, 20°—220°, into the state B, and that this transformation proceeds in the opposite direction when the temperature is reduced.

This led Marc to the assumption that the grey crystalline modification is an equilibrium state, consisting of two allotropic modifications Se_A and Se_B, and that this equilibrium can be displaced by change of temperature.

Incidentally it may be remarked that according to the new views it is incorrect to speak here of two modifications, for a modification is a state in inner equilibrium. We ought therefore to speak here of two different molecular species.

Thus Marc[1] assumes an inner equilibrium in the solid state, which can be represented in the following way :—

$$\alpha\,\mathrm{Se} \rightleftarrows \beta\,\mathrm{Se}.$$

This equilibrium then would lie on the α side at 20° and on the β side at 200°, and hence we can write

$$\alpha\,\mathrm{Se} \rightleftarrows \beta\,\mathrm{Se} - a \text{ cals.}$$

Kruyt[2] found the specific gravity of selenium suddenly cooled from a high temperature to be somewhat greater than the value obtained when the element was suddenly cooled from a lower temperature; for 120° it was 4·77, whilst for 220° it amounted to 4·80. Thus it may be stated that the displacement of the inner equilibrium in the direction left to right, which occurs when the temperature is increased, is accompanied by an increase in the density. On exposing the element to light, Kruyt, by a dilatometric method, found an increase of volume, which means, therefore, that on applying light energy the inner equilibrium is displaced towards the α side.

If now α selenium were a non-metallic and β selenium a metallic pseudo-component, this displacement produced by exposure to light would have to correspond with a decrease in the electrical conductivity; it is known, however, that exactly the opposite is the case.

In addition to this, Marc, on warming up the rapidly cooled metallic state, obtained conductivity temperature curves of a very peculiar form. In the absence of a catalyst he obtained a curve which always fell as the temperature rose, corresponding to a negative temperature coefficient for rising temperatures. With silver selenide as catalyst, however, a curve containing a maximum and a minimum was obtained.

Further, it was found by suddenly cooling a preparation in which inner equilibrium had been established at 200°, and then exposing it to light, that the conductivity first increased, then decreased, and finally increased again. The peculiar course of the conductivity curve for *selenium*, which reminds one of the behaviour of copper selenide,

[1] Snehamoy Datta has arrived at the same conclusion, *Phil. Mag.* **42**, 463 (1921).
[2] *Zeit. f. anorg. Chem.*, **64**, 305 (1909).

doubtless prompted Marc to assume that in selenium, too, a compound such as *selenium selenide*, Se_xSe_y, occurs, an assumption which has been further worked out by Kruyt.[1]

Gürtler's [2] investigation of the relationship between the conductivity and the constitution of binary mixtures at *constant temperature* appears to make an explanation possible. It follows from his experiments that the conductivity concentration curve at *constant temperature* in general exhibits a minimum, when a continuous series of mixtures appears.

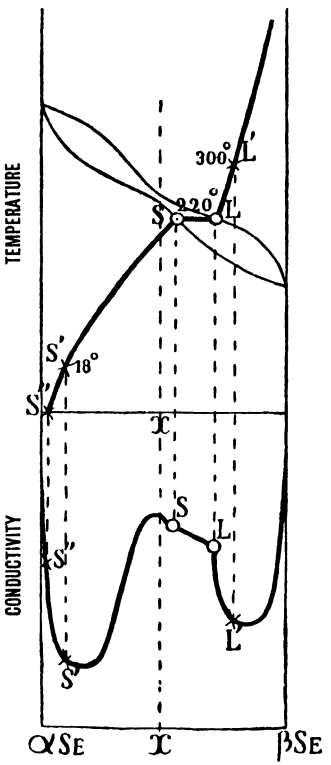


FIG. 145.

Consequently, if it is assumed that the compound is miscible in all proportions with the pseudo-components α Se and β Se, two curves might be expected, each with a minimum, covering the whole range of concentrations from α Se to β Se.

If account is taken of the facts mentioned here, the diagram here shown is obtained (Fig. 145). The upper portion consists of the fusion diagram and the lower portion indicates the conductivities of the inner equilibrium states which prevail at different temperatures, as found after suddenly cooling to the ordinary temperature. S′ relates here to the inner equilibrium state at room temperature, and S to the inner equilibrium at the melting point. Thus it may be seen, from the conductivity diagram, that by exposing to light selenium which has assumed inner equilibrium at the ordinary temperature, the inner equilibrium is displaced from S′ towards S″, and this is associated with an increase of conductivity.

Further, we see that after suddenly cooling the state S and then exposing it to light, the whole curve S S′ S″ must be traversed, whereby the conductivity first rises, then falls, and finally rises again.

The lines obtained by Marc and mentioned here may probably be explained thus: In the preparations obtained by suddenly cooling from high temperatures inner equilibrium is established during the experiment with a greater or less velocity, depending on the temperature and on the presence of catalysts.

Between S and L a straight line has been drawn in the conductivity diagram, for Gürtler found that conglomerate solid substances yield a

[1] *loc. cit.* [2] *Zeit. f. anorg. Chem.*, **51**, 397 (1906).

conductivity curve which is a straight line, and it has been assumed here that by suddenly cooling S + L a conglomerate results, consisting of two substances having the compositions of the phases S and L.

To the right of L the second conductivity curve is connected with a minimum, and this again agrees with the fact that the mass obtained by suddenly cooling from 300° has a small conductivity.[1]

It is clear that in the actual formation of a dissociating compound the pseudo-system belongs to the pseudo-ternary type; the pseudo-binary method of representation is used here, however, in order to summarise the position. The diagram given here must, however, undergo a change on yet other grounds.

In the first place, Ries[2] has shown that Kruyt's experiment, in which exposure to light produced a change of volume, was inaccurate, so that it is quite possible that the addition of light energy displaces the inner equilibrium in the same direction as does increase of temperature. In this case the explanation previously given will fall to the ground.

Secondly, it has recently been proved that elements also are complex, and phenomena have been discovered which point in the simplest case, i. e. for unary behaviour, to the establishment of an inner equilibrium between atoms, ions and electrons. Besides this, ions having opposite charges may possibly form a compound, as is assumed by Marc.

The development of these views has suddenly placed the selenium problem in quite another light. Investigations on these lines are now in progress, but the matter cannot be dealt with here.

13. The Influence of Previous History on the Specific Gravity of Tellurium.

Investigation has thus proved selenium, like sulphur, to be a very complex element. The complexity of tellurium has also been established, and indeed by examining the influence of the previous history of the element on its specific gravity.[3]

Thus it has been shown that, in contrast to selenium, the slowly cooled substance has a lower specific gravity than the value obtained when it is cooled down rapidly. Since there can be no question of a transition-point in the temperature range examined, the complexity of tellurium follows from the influence exerted by the previous history, to which reference has been made.

14. The Lowering of the Vapour Pressure of Violet Phosphorus by Expelling the more Volatile Pseudo-Components by the Process of Fractional Evaporation.

Every phase of an allotropic substance is built up from a number of pseudo-components, which differ from one another in various respects.

[1] In Kruyt's diagram no continuity is indicated in the fusion diagram.
[2] *Phys. Zeitschr.*, **12**, 480 (1911).
[3] Cohen and Kröner, *Zeitschr. f. physik. Chemie*, **32**, 331 (1913).

Since the white and the violet modifications of phosphorus differ widely in volatility, the pseudo-components of this system must therefore have different volatilities.

If now the more volatile pseudo-component can be driven off under such circumstances that inner equilibrium cannot be re-established, violet phosphorus in a non-equilibrium state will be obtained, the vapour pressure of which will be abnormally low.

In order that investigations might be instituted in this direction, it was naturally first of all necessary to determine the vapour-pressure curve for violet phosphorus as exactly as possible. With this object in view, pure violet phosphorus—in which, for determinations below 500°, inner equilibrium had been established by treating it at about 400° with iodine as catalyst—was prepared with great care by the method fully described in the paper entitled "The System Phosphorus in the Light of the Theory of Allotropy."[1] The phosphorus thus obtained was subjected to further purification.

The results obtained are set out in the following table:—

Temperature.	Observed vapour pressure in atmospheres.
290·5°	0·05
328	0·15
379·5	0·35
408·5	0·79
433·5	1·49
450·5	2·30
463·5	3·18
472·5	3·88
486·2	5·46
505·5	8·67

If these results are represented graphically, we get the line A B in Fig. 146.

After these results had been obtained, it was possible to proceed with the experiment designed to test the theory of allotropy.

It was sought, by rapid evaporation in a vacuum, to drive off the more volatile pseudo-component at a temperature at which inner equilibrium is only very slowly established, and consequently at which the formation of the more volatile pseudo-component from the less volatile one only takes place extremely slowly.

For this purpose a portion of the violet phosphorus which gave the results just mentioned was heated in a glass tube in an oven at 360° for two hours in the high vacuum of the "Gade" pump, liquid-white phosphorus condensing on the colder walls of the projecting portion of the tube. After cooling slowly, the tube was cut in the middle, so that the violet phosphorus was separated from the white variety. Without any further treatment the violet phosphorus so obtained was placed in a

[1] Smits and Bokhorst, *Zeitschr. f. physik. Chemie*, **91**, 249 (1916).

new pressure indicator and the vapour pressure was determined. The following results were obtained :—

Temperature in degrees.	Observed pressure in atmosphere.
309°	0·04
343	0·06
385·5	0·13
413·5	0 24
444	0·64
473	2·39 rising

When these vapour pressures are introduced into Fig. 146, the curve C D is obtained.

Thus it is evident that by evaporating violet phosphorus at 360°, at which temperature inner equilibrium is only established extremely

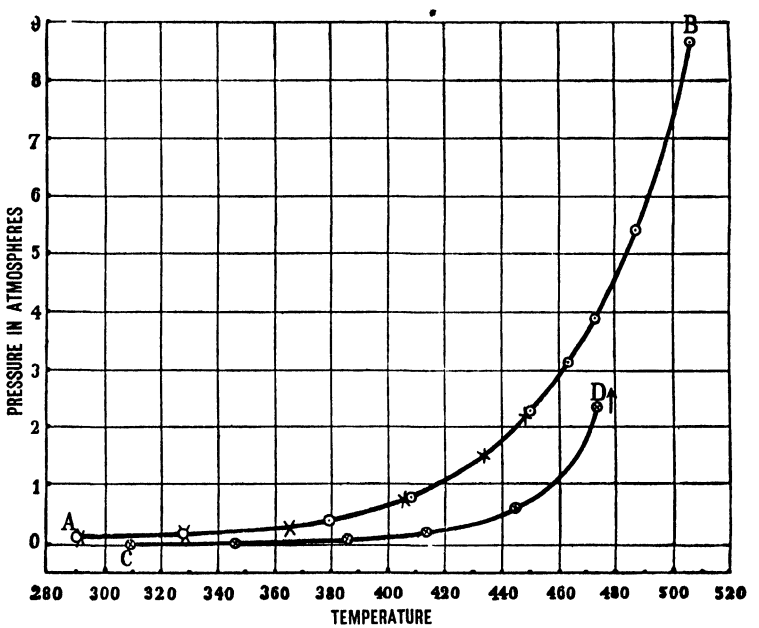


FIG. 146.

slowly, a residue is obtained which exhibits an abnormally small vapour pressure. As may be seen from the table, at 473° the pressure was rising, but this result was expected, for it had already been shown that inner equilibrium is established fairly quickly at 473°. It should, therefore, have been possible to keep the temperature at 473° until the vapour pressure curve A B was reached, but this would have necessitated

the continuation of the experiment for many hours, whereas means were found of achieving the same object much more quickly.

This method was as follows: Since iodine is a positive catalyst for the establishment of inner equilibrium in violet phosphorus, the contents of the pressure gauge were heated for five hours at 410° with 0·1% iodine; the phosphorus was then subjected to the well-known methods of re-purification.

On determining the vapour pressure of the preparation thus obtained, it yielded results which agreed very well with the curve A B, as may be seen from the accompanying table, and also from the points on the P T diagram (Fig. 146) indicated by means of crosses.

Temperature in degrees.	Observed vapour pressure in atmosphere.
291°	0·06
328·5	0·14
366	0·25
405·5	0·76
433·5	1·50
448	2·3

By treatment with the catalyst iodine the original state was therefore again reached.

The experiment described here thus shows, in the clearest possible way, that violet phosphorus is composed of at least two pseudo-components, which differ widely from one another in volatility. When the T X diagram for the phosphorus system comes to be deduced, further reference will be made to the interesting phenomena described here.

15. The Influence of Previous History on the Chemical Activity. Pyrophoric Substances.

According to the theory of allotropy every allotropic substance is complex. It is clear therefore that most, if not all, the elements and their compounds must be complex. To take a metal, for example: the complexity consists, as has already been explained in the theoretical part, in the most simple case, in the occurrence side by side of atoms, ions and electrons, the ions often being different in character, different, that is to say, as regards their charges, or their complexity, or in respect of both these properties. In less simple cases the atoms and the molecules may be different. If now a metal has combined with oxygen, and inner equilibrium has been established at a given temperature, in this compound again various oxide molecules will be present in a definite ratio. In general this ratio will not be the same as that which exists between the different ionic, atomic or molecular species in the metal at the same temperature.

Consequently, if the oxide is reduced at a temperature at which inner equilibrium in the metallic state is not re-established, a metallic phase different from the ordinary metallic state will be obtained. The

formation of some metals in the so-called pyrophoric condition may be explained in this way.

Thus it is possible, for example, that inner equilibrium is established very slowly in iron obtained from iron oxide at about 400°. When the reduction is carried out at this relatively low temperature, a form of iron results which does not correspond to ordinary iron at 400°.

By carrying out the reduction in this way, iron is obtained which perhaps contains ferrous ions exclusively. This state is so active chemically that the mass immediately ignites on exposure to air. The same is true of iron prepared by the ignition of ferrous oxalate. If this assumption is correct, pyrophoric iron will of necessity lose this remarkable property when it is heated in a vacuum to a temperature at which inner equilibrium is established at a perceptible rate. Experiments in this direction prove, as the table given below shows, that the pyrophoric property does in fact disappear when pyrophoric iron is heated above 250°, and indeed the more rapidly, the higher the temperature to which the iron is heated.[1]

Duration of heating.	Temperature.	Result.
One week	250°	Still pyrophoric.
,, ,,	290°	No longer pyrophoric.
48 hours	310°	Only very slightly pyrophoric.
24 ,,	340°	No longer pyrophoric.

This result explains at the same time why, in the preparation of pyrophoric iron, the reduction must be carried out at the lowest possible temperature. The results obtained justify the hope that the key to the explanation of this extremely interesting phenomenon will be found in the principles of the theory of allotropy.

Pyrophoric forms of many elements are already well known, and probably they can all be explained in the same way.

A new field of study is touched upon here, however, which, for the present, can only be mentioned.

16. Abnormally Large Variations of a Temperature Function as a Proof of Complexity.

When the various methods of testing the theory of allotropy were indicated, the second place was assigned to the investigation of any function whatsoever of the temperature, or of the pressure, etc., for confirmation of the theory may result from the manner in which this function varies with the temperature, etc.

Benedicks [2] has proved this for the first time in the case of silver

[1] Smits-Kettner, *Kon. Akad. v. Wet.*, **22**, 990 (1914). These experiments have been repeated with very pure hydrogen, and it was then found that the temperature at which the pyrophoric property disappears is a little higher than that indicated in the above table.

[2] *Journ. of the Iron and Steel Institute*, **2**, 242 (1912).

iodide. Thus, on investigating AgI dilatometrically, he found that, before the transition temperature was reached, the sign of the volume change with change of temperature was reversed, and the expansion changed into a contraction. The same phenomenon had been observed in the transformation β iron $\rightleftarrows$ γ iron. Both these substances therefore furnish examples of Benedicks' Type 2*a* (see p. 12).

Benedicks thought he had also discovered an example of Type 4 in iron. That is to say, experiment appeared to indicate a fairly considerable but *continuous* displacement of the inner equilibrium with rising temperature at the supposed transition point α iron $\rightleftarrows$ β iron, and indeed this could be observed in the neighbourhood of the temperature of the Curie point.

A very exact investigation of this problem has been made by

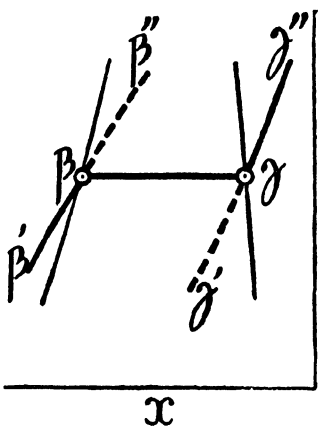


FIG. 147.

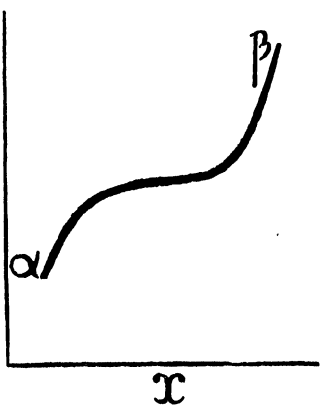


FIG. 148.

Burgess,[1] but it is not yet solved. Some very remarkable facts have emerged. Thus, it appears that a very essential difference exists between the transformations β $\rightleftarrows$ γ and α $\rightleftarrows$ β, which can be expressed in this way. The first change can be retarded, but not the reaction α $\rightleftarrows$ β.

Now this is very strong evidence in favour of the idea that the change α $\rightleftarrows$ β is not an ordinary transition phenomenon. This reaction will now be looked upon as a strong displacement of the inner equilibrium, and the change β $\rightleftarrows$ γ as a transition phenomenon between two phases. Let us then consider Figs. 147 and 148. If it is assumed that at the temperature at which these phenomena take place inner equilibrium is established with great velocity, it is very easily possible, and indeed even probable, that in the transformation β iron $\rightleftarrows$ γ iron retardation can occur. If, in Fig. 147, β′ is the starting point and the point β is ultimately reached, as a rule a portion of the metastable prolongation of the inner equilibrium line β′ β will be followed still further before the new phase γ appears.

[1] *Bulletin Bureau of Standards*, **10**, 316 (1913).

This retardation is then a retardation of the heterogeneous transformation, and this is always possible.

But the conversion of α iron into β iron cannot be retarded when inner equilibrium is rapidly established, as is illustrated in Fig. 148.

Thus far, therefore, the observed phenomena confirm Benedicks' view. The problem is, however, not yet solved, for, according to the magnetic theory of Weiss, the occurrence of the Curie point is without doubt also associated with both a thermal and a volume effect. Still it is naturally possible for the Curie point to be ultimately connected with a displacement of the inner equilibrium.

Finally, it may be noticed, as Heyn[1] has already pointed out, that the behaviour of iron can be schematically represented by means of a ternary diagram.

17. The Complexity of Mercuric Iodide and the *T X* Diagram for this System.

In the preceding sections it has been briefly shown that much experimental material, furnishing excellent confirmation of the theory of allotropy, is already in existence. Some of the substances previously mentioned will now be considered somewhat more closely. The probable connection between the various phases will be indicated, and it will be shown that the schematic diagram so obtained provides an explanation of phenomena which have long been unexplained.

In the examination of mercuric iodide it will be assumed that at the melting point of this substance the gaseous phase is colourless or light yellow, the solid phase orange, and the liquid phase dark red. From this the conclusion is drawn that in the binary diagram the composition of the solid phase is an intermediate one, and that the vapour phase occupies a very one-sided position.

This and other facts already mentioned suggest two possibilities.

Beginning with the simplest diagram, the T X figure will be considered for a pressure at which co-existence with vapour does not occur. As the first possibility a T X diagram for the pseudo-system is obtained, such as is indicated in Fig. 149 by faint lines. The pseudo-components α HgI_2 and β HgI_2 form mixed crystals, but the mixture is limited. The position of the unary system in this pseudo-figure is indicated by means of bold lines, so that the connection between the pseudo-binary and the unary systems is at once apparent. The stable inner equilibrium in the red tetragonal modification below the transition point is indicated by the line $S'_1 S_1$, whilst the line $S'_2 S_2$ represents the metastable inner equilibrium in the yellow phase below this transition point.

The inner equilibrium in the rhombic modification, which changes continuously into the orange form between 127° and 250°, is rendered by the line $S_2 S$. This line bends very markedly towards the right

[1] *Internationalen Verband für Materialprüfungen du Technik.* VI Kongress, New York, 1912. III. Berichte über die Fortschritte der Metallographie seit Beginn des Jahres 1909 bis zum ende des Jahres 1911.

just below the melting point, thus expressing the fact that the unary mixed crystal phase becomes richer in the β pseudo-component as the temperature rises.

When mercuric iodide melts its composition lies between those of the yellow and the red modifications. The corresponding liquid, on the other hand, contains a great deal of the β pseudo-component. This again agrees with the dark red colour of the liquid. The inner equilibrium in the liquid phase above the melting point is denoted by the line $L L_1$.

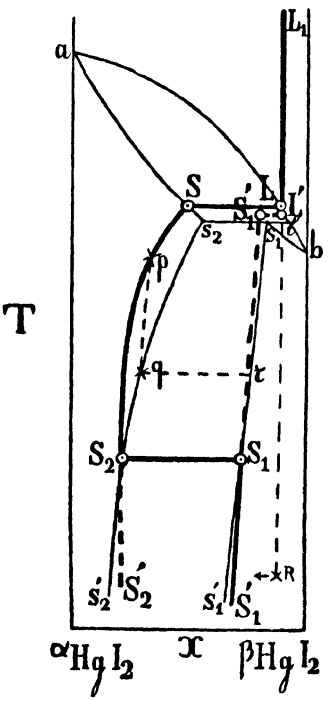


FIG. 149.

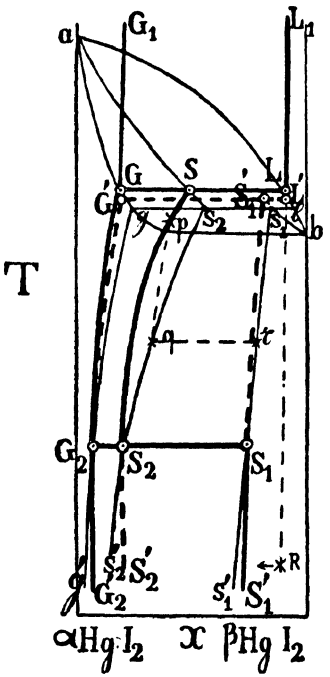


FIG. 150.

Confirmation of the correctness of the position assigned to the liquid phase L was obtained from a special experiment. A capillary tube containing the liquid phase was suddenly cooled in liquid air and then quickly brought to room temperature. The solid substance obtained in this way was homogeneous and red from the commencement. If no internal change appears during the cooling down and the subsequent heating to room temperature, according to the TX diagram the resulting solid mass will then be a red mixed crystal phase R, which soon passes, in consequence of internal change, into a state of inner equilibrium situated on the line $S'_1 S_1$.

It is almost superfluous to point out that, as a result of the rapid

cooling of mercuric iodide, from 200° or 250°, for example, the possibility of red mixed crystals being formed above the transition point also follows from this diagram. This is sufficient to show that the figure given here takes full account of the observed phenomena.

One of the two possibilities has been outlined here. Now the second possibility only differs from the first in that the pseudo fusion-diagram contains a eutectic.

In order to explain those phenomena which appear in the presence of the vapour phase, the T X projection of the three-phase area of the pseudo-system must be given, and also the position of the unary system in this projection. In this diagram the unusual character of the system HgI_2 becomes clearly evident. The vapour which co-exists at the triple point simultaneously with the orange-coloured solid phase and the dark red liquid, is colourless or faintly yellow. Thus the vapour contains the α pseudo-component almost exclusively, whilst the liquid is very rich in the β pseudo-component and the composition of the solid phase lies between the compositions of the other phases, as shown in Fig. 150.

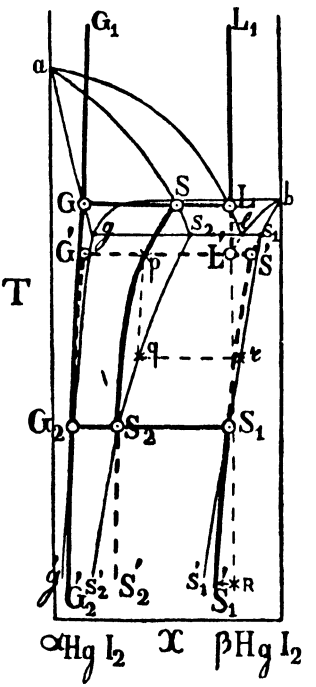


FIG. 151.

This is indeed an unusual position, but it is certainly a frequent one. The vapour lines of the unary system are indicated by means of heavy lines, in the same way as the lines relating to the unary solid phases and the unary liquid phase. The direction of the vapour lines and of the liquid lines in the unary system is, however, still uncertain. If β HgI_2 were a polymer of α HgI_2, rise of temperature would probably displace the inner equilibrium in the vapour towards the left. That this happens here is, however, improbable, for at the triple-point temperature the liquid is richer in the β pseudo-component than is the co-existing solid phase. It appears, therefore, that a species of isomerism occurs here. This, however, is a problem which can only be solved in the future.

Fig. 151 gives the T X projection of the three-phase areas of the pseudo-system with the two-phase areas of the unary system contained therein, when the pseudo-system has a eutectic.

These diagrams, which are at once intelligible, represent a case which up to the present has not been considered. In one or both of the three-phase areas for S + L + G in the pseudo-binary system the solid phase lies between the other two phases.

18. Mercuric Iodide and the Law of Successive Transformations.

When mercuric iodide vapour is cooled from a temperature above the transition point to the ordinary temperature, it is well known that the metastable yellow modification is always obtained, which then changes into the stable red form, so that under these circumstances the Law of Successive Transformations holds good.

Now the diagram sketched for the pseudo-system immediately furnishes a very simple explanation. Here we have an example of a liquid differing markedly in composition from the vapour. Hence the rule previously deduced holds good, viz., *the supersaturated vapour will first deposit that modification which most closely approaches the vapour in composition.*

The vapour and the yellow modification show much similarity as regards composition both below and above the transition point. This circumstance explains the order in which the phases appear. Both below and above the transition point the yellow phase is first deposited from the vapour. This is in complete agreement with our rule, but it is *entirely opposed* to the Law of Successive Transformations, for according to it the metastable modification should appear first above the transition point also. The incorrectness of the Law of Successive Transformations, as formulated by Ostwald, is clearly demonstrated here.

Finally, it may be pointed out that by suddenly cooling the vapour a white or very pale yellow substance can be obtained, of approximately the same composition as the vapour.

19. Mercuric Iodide in Presence of a Solvent.

We now come to the investigation of the behaviour of mercuric iodide in various solvents. Bancroft observed, as has already been pointed out in the theoretical portion, that on adding water to a solution of HgI_2 in methyl alcohol at the ordinary temperature, the metastable modification first of all separates out, and this subsequently passes into the stable red form. In agreement with the considerations put forward in Chap. VI (*c*), an explanation of this singular phenomenon is easily found by assuming that the system solvent—HgI_2 is pseudo-ternary.

Fig. 152 can therefore be employed, in which it is supposed that α HgI_2 is the light yellow and β HgI_2 the dark red pseudo-component. The saturated solution co-existing with the stable red modification below 127° is just as yellow in colour as the solution which co-exists at the same temperature with the metastable yellow modification. Hence it follows that the points L_2 and L_1 lie markedly on the side of the O—α HgI_2 axis. The points L_2 and L_1 therefore, just like the point S_1, must be supposed to lie very much to one side, even more than is assumed here. Now supposing the unsaturated methyl alcohol solution L to be poured into water in which HgI_2 is extremely slightly soluble, a solid phase will be deposited in which α HgI_2 and β HgI_2 molecules will occur, and indeed in the same proportion in which these molecular

species existed in the solution L. This solid phase will be represented by S, and consequently it will be a yellow metastable phase.

It must be noticed, however, that this phase, too, is a binary non-equilibrium state, for it lies in the heterogeneous region between *e* and *d*. If, now, under the given conditions, this state can rapidly pass into inner equilibrium, provided the velocity of transformation into the stable state is not too great, this solid phase S will first be transformed, in consequence of internal change, into the nearest metastable inner equilibrium state S_1. The phenomenon discussed here provided a beautiful example of fixation, of which a second example will now be given. If a solution of potassium iodide is added to a solution of mercuric chloride and the solutions are not too concentrated, yellow

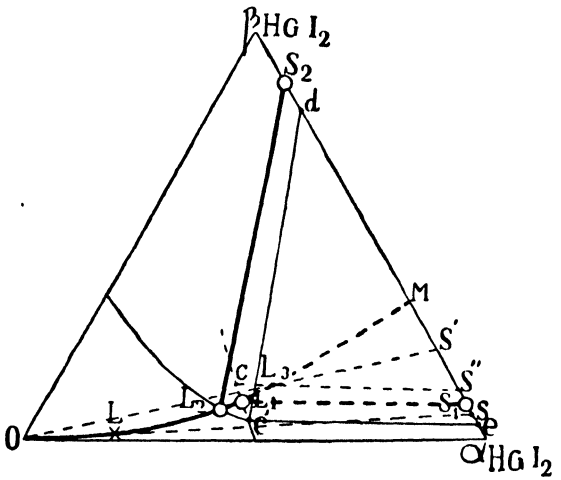


FIG. 152.

mercuric iodide is first of all thrown down, which, after some seconds, passes into the red modification.

If it is now assumed that before precipitation the mercuric iodide was present in the supersaturated condition and in inner equilibrium, an assumption which is undoubtedly correct, the sudden separation of the yellow form can again be easily explained in a similar way.

A similar solubility diagram to the one sketched here holds good for the system H_2O—HgI_2. The points L_1 and L_2 in this case, however, lie in the immediate vicinity of O. The supersaturated solution referred to naturally lies on the curve O M, *i. e.* at L_3. If now crystallisation suddenly occurs, the inner equilibrium between α HgI_2 and β HgI_2 which prevails in the solution is fixed by the precipitation,[1] and the resulting yellow solid phase S', situated hard by

[1] Strictly speaking, it should be noticed here that the markedly one-sided position of the inner equilibrium hinders the formation of red nuclei.

S_1, will pass into inner equilibrium, becoming thereby transformed into S_1.

The fact of S′ lying between *d* and *e* indicates that in its binary behaviour the phase S′ is split up into the red phase *d* and the yellow phase *e*. The red phase, which changes into the stable inner equilibrium S_2, will then inoculate the yellow phase, and in a few seconds the whole solid mass will become red. The further S′ is removed from S_1 the greater is the prospect of a splitting up into *d* and *e*. Therein lies the explanation of the fact that when concentrated solutions are used red HgI_2 always separates out almost instantaneously.

The phenomena discussed here are to be considered as a fixation of the dissolved state. If, on the other hand, the question is one of rather slow spontaneous crystallisation, such as may be observed from supersaturated solutions of HgI_2, just as in the case of solidification phenomena, the concentration of the pseudo-associations will exert great influence on the spontaneous appearance of the phases. As a rule, in this crystallisation too, the yellow modification first appears, because of the markedly one-sided position of the line relating to the equilibrium between $\alpha\,HgI_2$ and $\beta\,HgI_2$ in the solution. Consequently, below the transition point the metastable solid phase first appears, but above this point the stable phase appears first. In the latter case, therefore, Ostwald's formulation of the Law of Successive Transformations is not in agreement with experience.

To bring this discussion of mercuric iodide to a conclusion, it may be mentioned that Bridgman has investigated the transition curve at high pressures. He found that the tangent to this curve is vertical, and this must be due to the vanishing of the difference $V_{S\ \text{yellow}} - V_{S\ \text{red}}$ in Clapeyron's equation:—

$$T\frac{dp}{dT} = \frac{Q_{S\ \text{red} \rightarrow \text{yellow}}}{V_{S\ \text{yellow}} - V_{S\ \text{red}}}.$$

20. The Complexity of Phosphorus and the *T X* Diagram for this System.

(a) *The vapour-pressure curves for liquid violet and liquid white phosphorus.*

When the theory of allotropy was advanced, and an attempt was made to apply this theory to the phosphorus system, many difficulties were encountered, which could be ascribed to insufficient knowledge of the system. As has already been mentioned, Chapman [1] found that red phosphorus fuses to a colourless liquid very closely resembling liquid white phosphorus, but it was quite uncertain whether there were *one* or *two* varieties of liquid phosphorus. Similarly our knowledge of solid phosphorus was also extremely slight.

Various experimenters had, indeed, devoted themselves to the study of phosphorus, as, for example, Hittorf,[2] Lemoine,[3] Troost and Haute-

[1] *Journ. Chem. Soc.*, **75**, 734 (1899). [2] *Pogg. Ann.*, **81**, 276 (1845).
[3] *Ann. chim. Phys.*, (4), **24**, 129 (1871), and (4) **27**, 289 (1872).

feuille,[1] Schenck,[2] Stock,[3] Jolibois[4] and others. As a result many important facts had been discovered, but the real problem, the interpretation of the various phases which had been observed, and their inter-connection, still remained entirely unsolved.

As is well known, Bakhuis Roozeboom[5] had already indicated the possibility of liquid white phosphorus having to be considered as undercooled liquid violet phosphorus.

The P T diagram would then have the form indicated in the following diagram, Fig. 153.

It was, however, very doubtful whether this schematic figure correctly indicated the position. From Aston and Ramsay's[6] determinations of the surface tension of white phosphorus it may be deduced, as Schenck pointed out,[7] that the liquid phase attains its critical temperature at about 422° and therefore below the triple point temperature of violet phosphorus. In this case, as will be seen later, the phosphorus system would be completely analogous to the cyanogen system. In discussing cyanogen Bakhuis Roozeboom had already touched upon this second possibility.

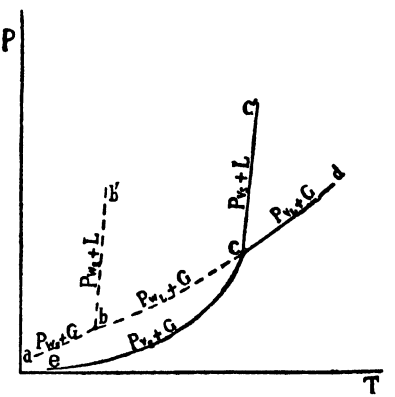


FIG. 153.

He states: "Cyanogen further differs from phosphorus in that no melting point is known for the polymeric form (paracyanogen). It is practically impossible to reach such a point, for above 600° paracyanogen rapidly decomposes.

"The interesting question is raised, however, whether a melting point could be obtained if this decomposition were avoided. The conversion of paracyanogen into the ordinary liquid is naturally impossible, for its critical point lies at 124°."

But transformation into a polymeric liquid might easily be "conceivable" above 640°, and consequently under a pressure greater than one atmosphere. "In such cases there is no continuous transition between the two liquids. For that reason the relationship of the different solid phases to one another is really no longer a monotropic one, but the polymeric form behaves as a separate compound." And in a note on the same page he writes: "It is even questionable whether

[1] *Ibid.* (5), **2**, 153 (1874).
[2] *Zeitschr. f. elektro. Chem.*, **11**, 117 (1905).
[3] *Ber. d. d. chem. Ges.*, **41**, 250 and 1593 (1908); **42**, 4510 (1910); **45**, 1514 and 3527 (1912); **46**, 3497 (1913).
[4] *Compt. rend.*, **149**, 287 (1909); **151**, 382 (1910).
[5] *Lehrb. Heterog. Gleichgewichte*, p. 176.
[6] *Journ. Chem. Soc.*, **65**, 173 (1894).
[7] Abegg's *Handb. d. anorg. Chem.*, **3**, 3, 374.

phosphorus does not also belong to this category, for a continuous transition has not been established between ordinary liquid phosphorus and molten red phosphorus."[1] These expressions of opinion by Bakhuis Roozeboom show that the phosphorus problem was quite unsolved at that time. It could not indeed be otherwise, in the first place on account of the apparently insuperable experimental difficulties presented by the phosphorus system, and secondly because of the lack of a new conception with the aid of which it might be possible to survey and to explain the various and enigmatical phenomena from a single point of view.

A particularly thorough investigation of the phosphorus system was therefore undertaken, involving, in the first instance, the exact determination of the vapour-pressure curve for this element.[2] In spite of the experimental difficulties, the vapour-pressure curves for liquid violet and for liquid white phosphorus were finally successfully determined with the desired accuracy, partly by Smith's dynamic method and partly by means of a pressure indicator of hard glass based on Jackson's[3] principle. The vapour-pressure curve of liquid violet phosphorus was investigated from 504° to 634°, the pressure rising from 23·2 atmospheres to 58·6 atmospheres. The vapour-pressure curve of liquid white phosphorus was obtained from 169° to 409·3°, between which points the pressure rose from 0·04 atmospheres to 7·36 atmospheres. This curve could not be determined for higher temperatures, because above 400° liquid white phosphorus changes into solid violet phosphorus so rapidly that in a short time the liquid phase disappears and the pressure indicated is no longer the vapour pressure of liquid phosphorus. In order to establish with complete certainty whether the vapour-pressure curves for liquid violet and liquid white phosphorus are really portions of one and the same curve, the following procedure was adopted.

If the heat of evaporation is not a temperature function, by integrating the relationship

$$\frac{d \ln p}{dT} = \frac{Q}{RT^2}$$

it follows that

$$\ln p = -\frac{Q}{RT} + C$$

or

$$T \ln p = -\frac{Q}{R} + CT.$$

Hence it follows that on plotting $T \ln p$ as a function of T, a straight line would be obtained.

Graphic representation gave a practically straight line for liquid violet phosphorus; for liquid white phosphorus, however, a curve was

[1] *Lehrb. Heterog. Gleichgewichte*, pp. 176 and 177.
[2] Smits, Bokhorst, *Zeitschr. f. physik. Chemie*, **91**, 248 (1916).
[3] *Journ. Chem. Soc.*, **99**, 1066 (1911).

obtained which was extremely slightly concave with respect to the temperature axis, but which, as a first approximation, could be considered to be a straight line. In Fig. 154 these curves are indicated by *c d* and *a b*. If the curve *c d* were really straight, for two points on this line

$$T_1 \ln p_1 = -\frac{Q}{R} + CT_1$$

and

$$T_2 \ln p_2 = -\frac{Q}{R} + CT_2,$$

so that

$$C = \frac{T_2 \ln p_2 - T_1 \ln p_1}{T_2 - T_1} = \text{tang } \alpha,$$

or

$$C = \frac{2{\cdot}3025\ (T_2 \log p_2 - T_1 \log p_1)}{T_2 - T_1} = \text{tang } \alpha,$$

i. e. the tangent of the angle which the straight line makes with the temperature axis gives the integration constant C.

In this way the value

$$C = 9{\cdot}6$$

was found for the integration constant, so that we can write:—

$$T \ln p = -\frac{Q}{R} + 9{\cdot}6\ T.$$

By means of this relationship the quantity $\frac{Q}{R}$ can now be calculated from every determination, and the mean value of this quantity can thus be found. The mean value obtained from numbers differing but slightly from one another was

$$\frac{Q}{R} = 50 \times 10^2,$$

so that

$$Q_{Ig} = 1{\cdot}98 \times 50 \times 10^2 = 99 \times 10^2 \text{ cals.}$$

Similarly in the case of white phosphorus, when $T \ln p$ was plotted as a function of T an approximately straight line was obtained, and hence it was possible to apply the same method to the vapour-pressure curve of liquid white phosphorus *a b* as has already been employed in the case of *c d*.

In this way the integration constant

$$C = 11{\cdot}1$$

was obtained. This line therefore makes a somewhat greater angle with the T axis.

Thus we can now write

$$\ln p = -\frac{Q}{R} + 11{\cdot}1\ T.$$

The mean value obtained in this case was

$$\frac{Q}{R} = 61 \times 10^2,$$

or

$$Q_{L_g} = 121 \times 10^2 \text{ cals.}$$

As Fig. 154 shows, the line *c d* is not exactly a prolongation of *a b*, and this also finds expression in the difference between the values obtained for Q_{L_g}. The deviation is, however, so slight that it cannot

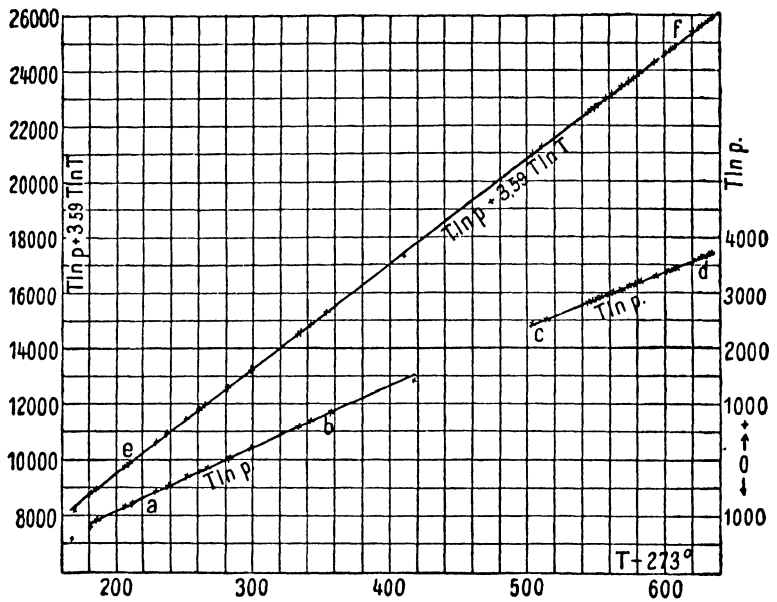


FIG. 154.

be doubted for a moment that the vapour-pressure curves belong to one another.

The vapour-pressure curve for liquid violet phosphorus yields a somewhat smaller value for the molecular heat of evaporation than does the vapour-pressure curve for liquid white phosphorus. Consequently, our assumption that the heat of evaporation is not a temperature function is not in agreement with the actual facts; it will, indeed, diminish as the temperature is increased.

Now it is worth while finding this temperature function. In calculating the integration constant for the vapour-pressure curve of liquid violet phosphorus, 160° and 360° were the temperatures chosen for T_1 and T_2; hence the mean molecular heat of evaporation

$$Q_{L_g} = 121 \times 10^2 \text{ cals.}$$

might be considered to be the value corresponding to the mean temperature, *i.e.* 260°. In the same way 512° and 630° were the temperatures chosen for the calculation of the integration constant of the vapour-pressure curve for liquid violet phosphorus, and hence the value $Q_{Lg} = 99 \times 10^2$ cals. could be looked upon here as the heat of evaporation at the mean temperature 571°.

Thus the conclusion was arrived at, that between 260° and 571° the molecular heat of evaporation diminishes by about 2200 cals., so that as a rough approximation we can write :—

$$\frac{d\,Q}{d\,T} = -\,7{\cdot}1.$$

Returning now to the equation

$$\frac{d\,\ln p}{d\,T} = \frac{Q}{RT^2}$$

and writing

$$Q_T = Q_0 + a\,T$$

on integration

$$\ln p = -\,\frac{Q_0}{RT} + \frac{a}{R}\ln T + C,$$

and since

$$\frac{d\,Q_T}{d\,T} = a = -\,7{\cdot}1,$$

we obtain

$$\ln p = -\,\frac{Q}{RT} - 3{\cdot}6\,\ln T + C.$$

The equation obtained here should naturally serve equally well for both the experimentally determined portions.

In order to investigate this, the graphical method was again applied. For this purpose the last relationship was written in the following way : —

$$T\,\ln p + 3{\cdot}6\,T\,\ln T = -\,\frac{Q_0}{R} + CT.$$

If this equation is to meet the requirements indicated above, the value $T\,\ln p + 3{\cdot}6\,T\,\ln T$ when plotted against T must yield a straight line. From the curve *ef*, Fig. 154, it may be seen that the points arrange themselves very beautifully on one and the same straight line, which proves that the relationship just derived represents with sufficient accuracy the dependence of the heat of evaporation on the temperature.

From the position of this line the value of the constant C naturally follows at once, for this is given by the tangent of the angle between the straight line itself and the temperature axis.

p in Atm.	t.	$T \ln p$.	$T \ln p + 3{\cdot}59\, T \ln T$.	$\frac{Q_0}{R}$.	$\Delta \frac{Q_0}{R}$.	Calc. p in Atm.	Δp.
0·04	169·0	− 1423	8242	8386	+ 129	0·05	+ 0·01
0·07	181·3	− 1208	8771	8320	+ 63	0·08	+ 0·01
0·09	185·5	− 1104	8982	8267	+ 10	0·09	0·00
0·18	206·9	− 823	9814	8240	− 17	0·17	− 0·01
0·20	210·0	− 777	9939	8232	− 25	0·19	− 0·01
0·32	229·8	− 573	10655	8261	+ 4	0·32	0·00
0·42	237·9	− 443	10995	8225	− 32	0·40	− 0·02
0·54	252·0	− 323	11482	8268	+ 11	0·55	+ 0·01
0·96	261·4	− 198	11852	8252	− 5	0·68	− 0·01
0·74	265·5	− 162	11995	8263	+ 6	0·75	+ 0·01
1·00	280·5	0	12554	8269	+ 12	1·22	+ 0·02
1·38	298·6	+ 185	13212	8288	+ 31	1·46	+ 0·08
2·47	331·8	+ 547	14453	8300	+ 43	2·65	+ 0·18
2·61	332·9	+ 582	14518	8276	+ 19	2·70	+ 0·09
2·95	342·0	+ 665	14943	8294	+ 37	3·13	+ 0·18
3·88	355 7	+ 852	15395	8257	0	3·88	0·00
(7·36	409·3	1362	17346	8322	65	8·10	0·74)
23·2	504	2443	21007	8224	− 33	22·20	− 1·0
24·3	512	2504	21288	8244	− 13	23·90	− 0·4
31·9	545·5	2834	22543	8247	− 10	31·6	− 0·3
32·4	548	2855	22633	8253	− 4	32·2	− 0·2
33·0	550	2878	22712	8249	− 8	32·7	− 0·3
33·6	553	2903	22820	8254	− 3	33·5	− 0·1
34·5	555·5	2934	22920	8248	− 9	34·2	− 0·3
35·4	559	2967	23050	8250	− 7	35·1	− 0·3
35·5	560	2973	23083	8254	− 3	35·4	− 0 1
35·9	562	2990	23156	8357	0	35·9	0·0
37·6	569	3054	23414	8268	+ 5	37·8	+ 0·2
38·8	574	3099	23598	8266	+ 9	39·2	+ 0·4
40·3	578	3146	23756	8259	+ 2	40·4	+ 0·1
41·1	581	3173	23867	8261	+ 4	41·3	+ 0·2
44·2	593	3281	24309	8270	+ 13	44·9	+ 0·7
47·0	602	3369	24648	8270	+ 13	47·7	+ 0·7
48·6	606·5	3416	24821	8266	+ 9	49·1	+ 0·5
49·0	608	3429	24876	8268	+ 11	49·6	+ 0·6
53·9	621	3564	25374	8258	+ 1	53·9	0·0
55·6	625·5	3610	25546	8256	− 1	55·5	− 0·1
56·5	627·5	3633	25625	8252	− 5	56·2	− 0·3
57·7	632	3670	25788	8258	+ 1	57·8	+ 0·1
58·6	634	3692	25866	8256	− 1	58·5	− 0·1

In the original tables, pp. 230 and 236, the numbers in columns 3 to 7 are given in units, although no value can be placed on the last two figures.

For two different temperatures it is again true that

$$T_1 \ln p_1 + 3{\cdot}6\, T_1 \ln T_1 = -\frac{Q_0}{R} + CT_1$$

and

$$T_2 \ln p_2 + 3{\cdot}6\, T_2 \ln T_2 = -\frac{Q_0}{R} + CT_2,$$

so that

$$C = \frac{(T_2 \ln p_2 + 3{\cdot}6\, T_2 \ln T_2) - (T_1 \ln p_1 + 3{\cdot}6\, T_1 \ln T_1)}{T_2 - T_1} = \text{tang } \alpha.$$

In this way the following value is obtained :—

$$C = 37{\cdot}6.$$

If this value is substituted in the equation, we get

$$T \ln p + 3{\cdot}6\, T \ln T = -\frac{Q_0}{R} + 37{\cdot}6\, T.$$

If now the value of $\frac{Q_0}{R}$ is calculated by means of this relationship from the various measurements, it is found that

$$\frac{Q_0}{R} \text{ (mean value)} = 82 \times 10^2.$$

In criticising the results obtained it is of great importance that the foregoing table should be taken into consideration.

In column 6 the deviation of the various values of $\frac{Q_0}{R}$ from the mean value 82×10^2 is given; it may be seen that these deviations are relatively small and that they are sometimes positive and sometimes negative. If the mean value of $\frac{Q_0}{R}$ is substituted in the last equation, the following expression is obtained :—

$$T \ln p + 3{\cdot}6\, T \ln T = 37{\cdot}6\, T - 82 \times 10^2,$$

from which the pressures corresponding to the various temperatures at which observations were made can be calculated.

The results of these calculations are given in column 7. By comparing this column with column 1, the last column is obtained, in which the difference between the observed and the calculated pressure is indicated. These differences are so small that, considering the difficulties encountered in making the measurements, no better result could be expected. Further, from the mean value of $\frac{Q_0}{R}$ a value for Q_0 can be calculated

$$Q_0 = 164 \times 10^2 \text{ cals.}$$

In the following diagram, Fig. 155, *abcdef* is the vapour-pressure curve for liquid phosphorus calculated from the equation just derived. The observed pressures are indicated by means of crosses.

Finally, it may be mentioned here that Jolibois[1] has also determined the vapour pressure of liquid white phosphorus, but, owing to experimental difficulties, his measurements came to an end just where the

[1] Compt rend. **149**, 387 (1909); **151**, 382 (1910).

results would have been most interesting. The highest temperature at which he obtained a reading was 321°. The pressures observed by him

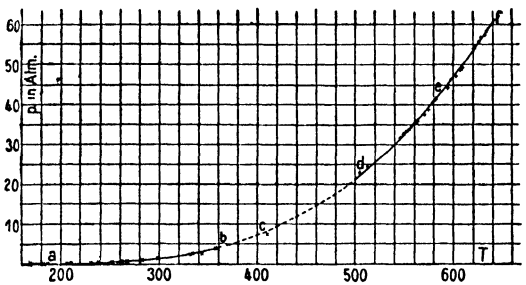


FIG. 155.

fit in very well, however, with the more recent measurements discussed above, as the following table shows :—

Temperature.	Pressure in atmospheres.	Temperature.	Pressure in atmospheres.
145°	0·017	259°	0·675
173°	0·064	262°	0·705
184°	0·093	268°	0·797
192°	0·124	273°	0·850
200°	0·157	275°	0·925
205°	0·178	279°	0·990
219°	0·253	281°	1·034
235°	0·366	283°	1·071
239°	0·418	285°	1·122
244°	0·464	295°	1·329
247°	0·499	299°	1·437
250°	0·543	307°	1·650
254°	0·591	312°	1·817
257°	0·633		

At the commencement of this investigation it was quite doubtful whether liquid white phosphorus should be considered to be super-cooled liquid violet phosphorus or not. Eötvös' rule, applied to the determinations of Aston and Ramsay, seems to indicate that white phosphorus has a critical point at about 420°, and this appears to contradict the above-mentioned assumption.

As a result of our recent work on phosphorus this question has now been unequivocally disposed of. It has been established with absolute certainty that liquid white phosphorus is under-cooled liquid violet phosphorus.

Aston and Ramsay's determinations of the surface tension, of which only two were carried out, do not justify a calculation of the critical temperature. From the experimentally determined vapour-pressure curve it appears that the vapour pressure of liquid phosphorus in the

neighbourhood of 420°, where the critical point should appear, only amounts to about nine atmospheres.

Thus phosphorus does not belong to the same type of system as cyanogen, and the very remarkable fact emerges here, that at 44°, although under-cooled to an extent of about 545°, the viscosity of liquid white phosphorus is still only very small, and inner equilibrium conditions are assumed with great velocity.

(b) *The critical point of phosphorus and the size of the phosphorus molecule.*

The vapour-pressure curve of liquid phosphorus, the position of which has now been fixed, ends in a critical point. Wahl[1] has determined the temperature at which this point appears, obtaining the value 695°.

The more recent vapour-pressure determinations have been continued up to 634°, and therefore to a temperature fairly nearly the critical temperature. It was therefore allowable to obtain the critical pressure by graphical extrapolation, and in this way the value 88·2 atmospheres was found.[2]

With the help of the critical data for phosphorus now available the calculation of the molecular magnitude is of interest. For this purpose the value of b in van der Waals' equation is obtained:—

$$b = \frac{1}{8 \times 273} \cdot \frac{T_C}{P_C} = \frac{1}{8 \times 273} \cdot \frac{968}{88{\cdot}2}$$
$$= 0{\cdot}00539.$$

If b is considered to be an additive quantity, it should be possible to find its value for a phosphorus atom from the value of b for PH_3, for example. Then, by dividing the value of b for a phosphorus molecule by the value obtained for the phosphorus atom, the number of atoms in the phosphorus molecule is obtained.

Leduc and Sacerdote[3] for the critical data of PH_3 found

$$P_C = 64 \text{ atmospheres}$$
$$T_C = 52{\cdot}8° + 273° = 325{\cdot}8°.$$

If b is calculated from these figures we get

$$b = 0{\cdot}00233.$$

According to more recent investigations of van der Waals, entitled "Das Volumen der Molekule und das Volumen der Zusammenstellungen von Atome,"[4] hydrogen exhibits the peculiarity that the value of b for the hydrogen atom in a compound is much less than its value for the hydrogen molecule. Instead of 0·000825 it only amounts to

[1] *Meddelan den Fran Finska Kemistamfundet* (1913).

[2] Van Laar, *Kon. Akad. v. Wet.*, **25**, 1498 (1917), calculated $t_c = 675$ and $P_c = 80$.

[3] *Compt. rend.*, **125**, 397 (1897).

[4] *Versl. Kon. Akad. v. Wet.*, **22**, 782 (1914).

0·000362, from which it appears that for the three hydrogen atoms in PH_3 the figure 0·001086 must be adopted. Thus the calculation of b for an atom of phosphorus yields the following result:—

$$b = 0{\cdot}00233 - 0{\cdot}001086 = 0{\cdot}00124.$$

The magnitude of the phosphorus molecule at the critical temperature and pressure is therefore

$$\frac{0{\cdot}00539}{0{\cdot}00124} = 4{\cdot}33.$$

This result would indicate slight association, but the method is not sufficiently accurate to permit of this conclusion being definitely drawn.

(c) *The vapour pressure curve for violet phosphorus.*

A portion of the results obtained in the determination of the vapour pressure of violet phosphorus have already been communicated in a previous section. The complete vapour-pressure curve up to the triple point will now be subjected to a thorough examination. It has already been mentioned that these determinations were very tedious, particularly below 500°, since below this temperature the phosphorus had always to be brought into equilibrium by heating it with iodine as a catalyst. After this process it was always necessary to re-purify it in order to remove white phosphorus and phosphoric acid. If this re-purification is dispensed with, below 500° inaccurate results are always obtained. The vapour pressure of the preparation, which unless re-purified always contains a little white phosphorus, will thus be found to have too high an initial value. Above 450°, however, the error is easily noticed by continued observation, for the vapour pressure soon falls. As has been seen, this circumstance may lead to deception as regards discontinuity in the vapour pressure, etc. In this connection it may be mentioned that Jolibois observed a discontinuity in the heating curve at about 450°, but this corresponded with an evolution of heat. The discontinuity in the vapour pressure curve does not appear when a re-purified phosphorus preparation is employed, so that the discontinuity observed by Jolibois must be attributed to the presence of white phosphorus.

In discussing the results obtained when the purest possible preparations of violet phosphorus were used, the formula

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

can again be applied, and it may be assumed that Q is not a temperature function. Just as in the case of liquid phosphorus the relationship

$$T \ln p = -\frac{Q}{R} + CT$$

is used.

On plotting T ln p as a function of T a straight line was in fact obtained, as in Fig. 156.

The heat of sublimation of violet phosphorus is therefore not perceptibly a temperature function in the range of temperature investigated.

Here again the constant C can easily be found graphically from the tangent of the angle which the curve makes with the temperature axis, for in this case too

$$C = \frac{T_2 \ln p_2 - T_1 \ln p_1}{T_2 - T_1}.$$

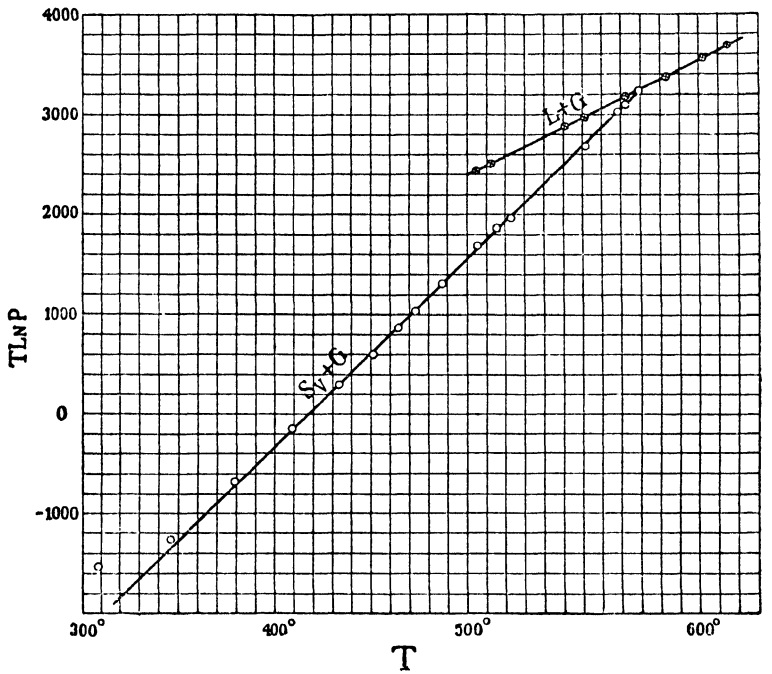


FIG. 156.

In this expression

$$T_1 = 343{\cdot}5 + 273, \quad T_1 \ln p_1 = -1400$$

and

$$T_2 = 589{\cdot}5 + 273, \quad T_2 \ln p_2 = -3246{\cdot}6,$$

so that

$$C = 18{\cdot}9.$$

By means of this value the quantity $\frac{Q}{R}$ was calculated from the different measurements; as a mean value the figure 13050 was obtained.

We can therefore write

$$T \ln p = 18{\cdot}9\ T - 13050,$$

and thus the vapour pressures at the different temperatures at which observations were made can now be calculated.

In the following table will be found, amongst other things, the calculated and the observed values for the vapour pressure:—

Temperature in degrees.	P in atmospheres.	T ln P.	$\frac{Q}{R}$.	P (calculated) in atmospheres.
308·5	0·07	− 1543·1	12527	0·03
346	0·13	− 1263·1	12958	0·11
379·5	0·35	− 685·13	13010	0·33
408·5	0·79	− 160·67	13034	0·77
433·5	1·49	281·79	13065	1·52
450·5	2·30	587·64	13079	2·34
463·5	3·18	852·20	13060	3·22
472·5	3·88	1011·0	13071	3·99
486·4	5·46	1289·5	13057	5·51
505	8·67	1680·4	13006	8·29
515	10·43	1847·6	13037	10·26
522·5	11·61	1950·4	13076	11·98
(561)	(24·30)	(2661·3)	(13092)	(25·50)
578	34·35	3009·6	13065	34·95
581	36·49	3071·8	13060	36·90
587·5	41·77	3211·5	13043	41·38
588	42·10	3220·1	13044	41·77
589	42·5	3232·1	13051	42·5
589·5	43·1	3246·6	13046	42·9
			mean = 13050	

In the calculation of the average value of $\frac{Q}{R}$, the two first values and also that obtained at 561° were not taken into account, for, as the graph shows, these measurements undoubtedly contain a much greater accidental error than do the remainder.

Since $\frac{Q}{R} = 130 \times 10^2$ cals. it follows that $Q_{S_v G} = 258 \times 10^2$ cals.

(d) *The determination of the position of the triple-point* S + L + G *for violet phosphorus.*

The curve obtained by plotting T ln p against T yields a straight line in the case of violet phosphorus, but, as has been seen, on plotting T ln p as a function of T in the case of liquid phosphorus the curve obtained is not a straight line. It has been established, however, that between 504° and 634° the curve is practically a straight line, and therefore if both these lines are graphed and the point of intersection

ascertained, the position of the triple point is simply and with certainty fixed. This has been done in Fig. 156. The point of intersection is found to be at **589·5°**, the value of T ln p being **3246·6**, whence it follows that P = **42·9** atmospheres.

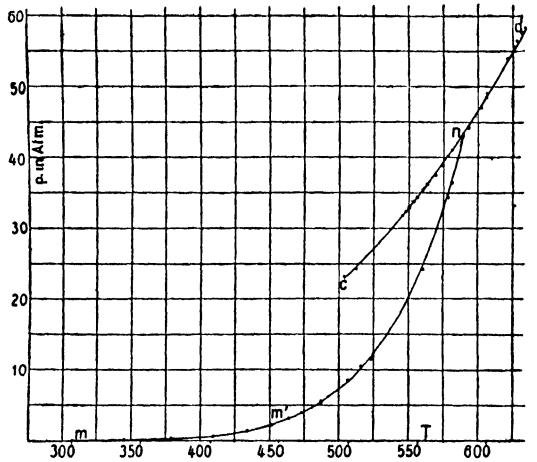


FIG. 157.

The temperature so obtained is in good agreement with the result of direct observation and with the melting point under the vapour pressure, for which the value **589·5°** was also found.

If, therefore, the vapour-pressure curve and the sublimation curve are represented on the same graph, Fig. 157 is obtained.

(e) *The heats of sublimation, evaporation and fusion in the light of the theory of allotropy.*

The results of the study of phosphorus which have just been under discussion will now be considered from the point of view of the theory of allotropy, and the quantities of heat involved will then be discussed; from these many valuable conclusions may be drawn.

From the vapour-pressure curve for violet phosphorus the value of $\frac{Q}{R}$ was found to be

$$130 \times 10^2,$$

consequently for violet phosphorus the extremely high value

$$Q_{s_v G} = 258 \times 10^2 \text{ cals.}$$

is obtained for the molecular heat of sublimation.

This value does not vary perceptibly with the temperature, so that it also holds good at the temperature of the triple point.

The molecular heat of evaporation of liquid phosphorus which will

now be calculated is, as has already been mentioned, affected to a slight extent by the temperature, so that in calculating this quantity at the triple point temperature the equation

$$Q_T = Q_0 + aT$$

must be employed, where

$$Q_0 = 164 \times 10^2 \text{ cals.} \quad \text{and} \quad a = -7{\cdot}1.$$

Then

$$(Q_{LG})_{T = 862\,5} = 102 \times 10^2 \text{ cals.}$$

From these two figures we get for the molecular heat of fusion

$$Q_{S_vL} = 156 \times 10^2 \text{ cals.}$$

It has already been pointed out above that the molecular heat of sublimation of violet phosphorus has an extremely high value, whilst the heat of evaporation of liquid phosphorus is quite normal.

This becomes very clearly evident if Trouton's rule is applied. According to this the molecular heat of evaporation at the boiling point under atmospheric pressure, divided by the absolute temperature, is approximately constant and equal to about 22.

The boiling point of liquid phosphorus is 280°, and T_S is therefore equal to 553°.

To obtain the heat of evaporation at this temperature, it must be supposed that

$$Q_T = Q_0 + aT \quad \text{and that} \quad a = -7{\cdot}1$$

whilst

$$Q_0 = 164 \times 10^2 \text{ cals.}$$

Hence it follows that

$$Q_T = 164 \times 10^2 - 39 \times 10^2 = 125 \times 10^2 \text{ cals.},$$

so that

$$\frac{(Q_{LG})_{T_S}}{T_S} = \frac{125 \times 10^2}{553} = 22$$

Thus the normal value is obtained here.

Now Le Chatelier has shown that Trouton's equation can also be applied to the heat of sublimation, and that if this quantity is divided by the sublimation temperature on the absolute scale the quotient is always approximately 30.

Thus

$$\frac{Q_{SG}}{T_{Subl}} = 30.$$

The molecular heat of sublimation of violet phosphorus is 25859 cals., and the sublimation temperature may easily be calculated from the equation

$$T \ln p = -\frac{Q_{SG}}{R} + C\,T$$

if the value $p = 1$ is introduced.

Then

$$T_{subl.} = \frac{\frac{Q_{sg}}{R}}{C} = \frac{130 \times 10^2}{18{\cdot}9} = 688°$$

and

$$\frac{Q_{sg}}{T_{subl.}} = \frac{258 \times 10^2}{688} = 37{\cdot}5.$$

In this case therefore Trouton's formula yields an abnormally high value, and this is to be ascribed to the abnormally high heat of sublimation of violet phosphorus.

The results obtained here are very significant, for they confirm our deductions from the Theory of Allotropy in the clearest possible way.

This theory leads to the conclusion that evaporation and fusion are associated with chemical reaction between the pseudo-components, and the more the co-existing phases differ from one another in composition, the greater will be the chemical change as one phase passes into the other. The heat of sublimation, the heat of evaporation of the liquid and the heat of fusion will therefore consist of chemical heat to a greater extent the greater the difference between the co-existing phases as regards composition. From its colour one would expect violet phosphorus to differ widely in composition from the colourless vapour, and the high heat of sublimation entirely confirms this view. The fusion of violet phosphorus should also be associated with a distinct chemical change, for liquid phosphorus is colourless. This conjecture again is confirmed by the high heat of fusion. Conversely, the fact that the heat of evaporation of liquid phosphorus is not abnormal is explained by the slight difference in composition between the colourless liquid and the colourless vapour.

In the derivation of the various diagrams for the pseudo-system, and for the unary system situated therein, account must naturally be taken of these results.

Before turning to the diagrams the energy difference between white and violet phosphorus must be dealt with. The conversion of white into violet phosphorus is accompanied by a fairly large evolution of heat; thus Giron [1] found

$$P_{white} \rightarrow P_{violet} + 44 \times 10^2 \text{ cals.}$$

This heat doubtless consists for the most part of chemical heat. If it is assumed for a moment that this evolution of heat is due exclusively to chemical change, and that the two phases mentioned differ from one another in composition to almost as great an extent as violet phosphorus differs from its vapour, the molecular heat of sublimation should contain a chemical heat of $4 \times 44 \times 10^2$ cals. $= 176 \times 10^2$ cals. The molecular heat of sublimation is 258×10^2 cals., so that $258 \times 10^2 - 176 \times 10^2$ cals $= 82 \times 10^2$ cals. would remain as the physical heat. This figure is fairly near the heats of sublimation of other substances into which chemical heat also enters, though probably to a much smaller extent.

[1] *Ann. Chem. Phys.*, **7**, 30, 203 (1903).

(f) *The name assigned to the unary stable solid state of phosphorus and the nature of red-coloured phosphorus.*

An explanation must be given why the name "red phosphorus" has never been employed in this book, but "violet phosphorus" has always been spoken of instead. Various experimenters have determined the vapour pressure of red phosphorus, with the result that this has always been found to be higher than the vapour pressure of violet phosphorus. More recent investigations have now proved this higher pressure to be due either to the presence of white phosphorus or to the mass not being in inner equilibrium. It appears that only one stable solid modification of phosphorus exists under the vapour pressure of the system.

When not in the form of very small crystals this stable modification has a violet colour. If, however, this substance is powdered, its colour becomes dark red, and the greater the degree of fineness the lighter the colour becomes. The colour of the preparation may vary even when the same method of preparation is employed, but this difference in colour is to be attributed mainly to a difference in size of the particles, for in spite of the difference in colour these preparations always exhibited the same vapour pressure and approximately the same specific gravity.

For these reasons the stable solid modification of phosphorus has been called *violet phosphorus.*

As will presently be seen, the so-called red phosphorus is an intermediate state; that is to say, it is a mixture of various mixed crystals, and consequently is not a modification of phosphorus; *for a modification is a state of aggregation which can exist in inner equilibrium, and which is able, therefore, to behave in a unary manner.* In other words, red phosphorus does not belong to the unary phosphorus system, but to the pseudo-system, as will be seen later.

(g) *The* T X *diagram for the phosphorus system.*

The pseudo-system in the case of phosphorus probably contains four or five different molecular species; P_2 and P_1, however, only appear at high temperatures, and so it is understandable that the phenomena observed at temperatures which are not too high can, as a rule, be rationally explained by assuming the existence of two components.

It is now assumed that the first pseudo-component, consisting exclusively of α molecules, is white, and that it has the lower melting point, whilst the second pseudo-component, consisting of β molecules, is dark violet in colour and only melts at a very high temperature, *i. e.* above 590°. Further, the second pseudo-component β is much less volatile than the first, and it is also much less reactive at the same temperature.

The difference between white and violet phosphorus in volatility, and also in the position of their melting points, most probably points to the fact that we are concerned here with molecular species which differ from one another in magnitude.

Presumably, therefore, the question here is one of association, and the main difference between violet phosphorus and the white modifica-

tion is that the former contains a much greater number of associated molecules.

As has already been emphasised in Chapter II, page 60, in this case the P T X diagram for the pseudo-system will contain no eutectic line. The T X diagram of the system under its own vapour pressure, with that for the unary system contained therein, can then be schematically drawn, as in Fig. 158.

On the other hand, if β were an isomer of α, Fig. 159 would also be possible.

The faint lines relate to the pseudo-system, whilst the heavy lines and the dotted lines have reference to the unary system.

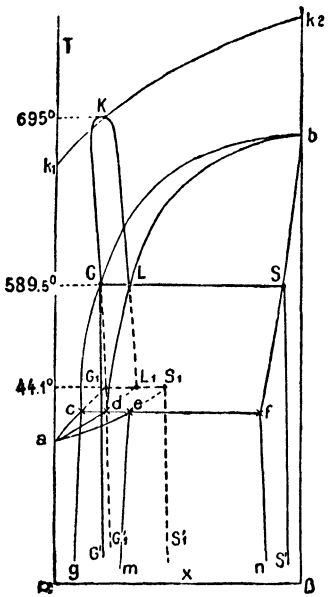


FIG. 158.

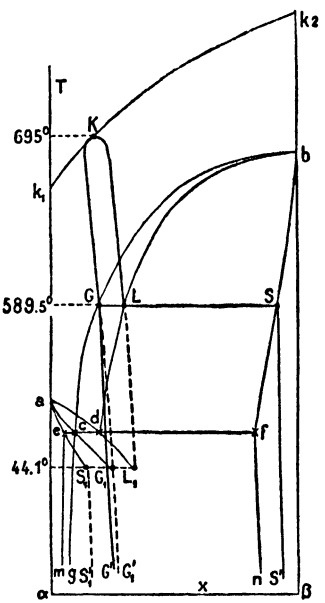


FIG. 159.

The points *a* and *b* indicate the melting points of α and β under the vapour pressure, whilst the critical temperatures of α and β are situated at the points k_1 and k_2. Two three-phase areas proceed from *a* and *b*. Thus the lines *a e* S_1, *a d* L_1 and *a c* G_1 relate to the three-phase area for white mixed crystals liquid and vapour, whilst the lines *b* S *f*, *b* L *d* and *b* G *c* indicate the three-phase area for violet mixed crystals, liquid and vapour. At the intersection of these two three-phase areas a four-phase equilibrium appears, in which violet mixed crystals *f*, white mixed crystals *e*, liquid *d* and vapour *c* co-exist.

In this four-phase equilibrium there are still two other three-phase areas which are intersected, namely, a third relating to the co-existence between violet mixed crystals, white mixed crystals, and vapour,

represented in the diagram by the lines fn, em and cg, and a fourth for the co-existence between violet mixed crystals, white mixed crystals and liquid, which owing to an oversight has not been indicated in the figure.

The T X diagram of the unary system under the vapour pressure is contained in the T X figure for the pseudo-system given here. Commencing with the critical point of the unary system, *i.e.* with the critical point of the phase in which the molecular species α and β are in inner equilibrium with one another, this point must be situated on the plait point or critical curve $k_1 k_2$. This point is represented in our diagram by K, and according to van der Waals' investigations it lies at 695°.

Two lines proceed from this point K, indicating the co-existence between liquid phosphorus and its vapour when inner equilibrium prevails in both phases. These equilibrium lines are heavily drawn, and at K they pass without discontinuity the one into the other. At the intersection of this two-phase area with the three-phase area of the pseudo-system a new phase appears, namely violet phosphorus. This occurs at the triple point temperature of violet phosphorus, and consequently at 589·5°.

The points L and G represent the liquid phase and the co-existing vapour phase, which are in inner equilibrium, and these two phases are at the same time situated in the three-phase area relating to violet mixed crystals, liquid and vapour; *i.e.* the two phases L and G can co-exist with the violet mixed crystal phase S, which is then likewise in inner equilibrium.

From this the conclusion may be drawn that if heat is withdrawn from the two-phase equilibrium L + G, in the case of inner equilibrium and when retardation of the heterogeneous process does not occur, the violet phase will be deposited.

At lower temperatures a two-phase area relating to violet mixed crystals and vapour proceeds from the solidifying or fusion equilibrium represented by the points S L G, and both phases are therefore in inner equilibrium. They are indicated by the two heavy lines S S′ and G G′.

Accordingly, if the withdrawal of heat at the triple point has continued so long that the liquid L has completely disappeared, on withdrawing still more heat, the inner equilibrium in the violet phosphorus is displaced along the line S S′, whilst the inner equilibrium in the vapour which co-exists with violet phosphorus continues along the line G G′.

If, however, solidification does not make its appearance at the triple-point temperature, and there is also no spontaneous formation of violet phosphorus at lower temperatures, it must be possible to follow the two-phase area for liquid and vapour, indicated here by the dotted lines L L_1 and G G_1, until it meets the three-phase area white mixed crystals, liquid, vapour at 44·10.° This would occur at G_1 and L_1. At these points, which are situated at the triple-point temperature of white phosphorus, on heat being withdrawn, the white mixed crystal phase S_1 or the white modification of phosphorus will be deposited, and this

also reverts into inner equilibrium, assuming always that the heterogeneous process is not retarded.

But now it is known that the lines $L L_1$ and $G G_1$ cannot be realised to their full extent. There is a range of temperature between 400° and 500° where the velocity of crystallisation of the undercooled liquid phosphorus is so great that crystallisation takes place with explosive violence.

The maximum velocity with which the spontaneous crystallisation of violet phosphorus occurs must therefore lie between 400° and 500°. Below the triple-point temperature of white phosphorus a two-phase area again appears, relating now to the unary equilibrium between white phosphorus and vapour, and indicated by the lines $S_1 S_1'$ and $G_1 G'$. It is assumed here that the pseudo-component β is a polymer of α. If, on the other hand, β is an isomer of α, besides Fig. 158, Fig. 159 would also be possible.

The first-mentioned diagram will always be employed unless the contrary is expressly indicated. It may be pointed out that the behaviour of phosphorus has not been completely represented here.

Thus Bridgman found that white phosphorus has a transition point at − 80°, probably connected with the appearance of several different molecular species.

Furthermore, Bridgman has also obtained phosphorus in yet another state by heating white phosphorus to 200° under a pressure of 13000 kilograms per square centimetre. This form was black in colour, and will be discussed in a separate section.

(h) *The properties of phases as functions of the composition.*

The accompanying T X diagram gives a rational explanation of many of the phenomena observed in the phosphorus system. It is capable of explaining not only the difference between the various phosphorus phases as regards colour, position of the melting point, specific gravity, etc., but, by means of it, the extremely high heat of sublimation of violet phosphorus, and with it the high heat of fusion of this modification, can also be explained. These explanations are entirely based on the difference in composition. As has already been stated, the α pseudo-component is assumed to be colourless and fairly volatile, besides having a low melting point, whilst the β pseudo-component is dark violet, only slightly volatile, and has a high melting point. The violet modification is very rich in β, whilst the white modification, the liquid and the vapour are always very rich in α. The last-mentioned phases must in reality lie very much more to one side than has been shown in the diagram; they are all colourless. The passage of white phosphorus into the liquid or into the vapour phase will therefore be accompanied by very little chemical change, but the evaporation of violet phosphorus, and also the fusion of this modification, must be attended by marked chemical transformation.

In addition, the diagram illustrates the connection between the two modifications, that is to say, between white and violet phosphorus.

In this way the phenomenon of monotropy between these two modifications is explained, and an insight is obtained into the order in which the phases appear.

(i) *The order in which phases appear.*

If it is assumed, for example, that violet phosphorus has been sublimed and the vapour cooled down to about room temperature, liquid phosphorus is obtained, which afterwards passes into metastable white phosphorus. This phenomenon may be at once explained by means of the P X section. This relates to a temperature below the unary melting point of white phosphorus; the form of this section depends indeed on the temperature chosen, but for our purpose this is immaterial, inasmuch as every section leads to the same result provided only that it relates to a temperature below 44·1°.

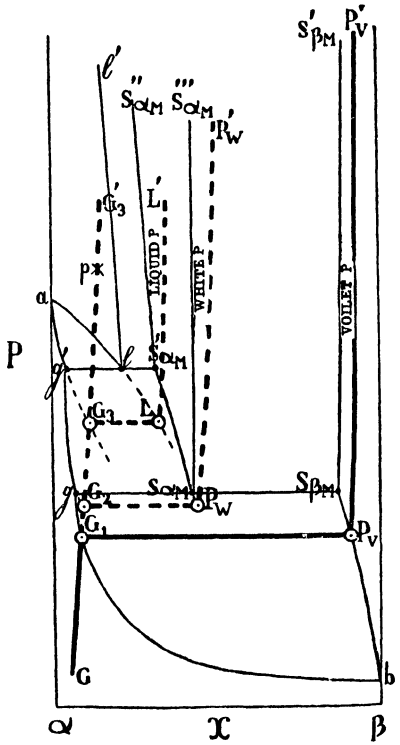


FIG. 160.

In Fig. 160 a P X section of the space model is given for a temperature lying between that of the quadruple equilibrium *c d e f* and the triple point temperature *a* of the *α* component. (See Fig. 158.) It will now be assumed that the supersaturated vapour obtained by cooling down the vapour of violet phosphorus is represented by the point *p*. It is then immediately seen that this vapour, which must be supersaturated not only in respect to violet phosphorus, but in respect to white and liquid phosphorus also, can condense in three ways.

But since liquid is the phase most closely approaching it, a metastable liquid will first of all be precipitated from the vapour.

The changes which will subsequently take place may also easily be deduced from the diagram. The two solid phases, white and violet phosphorus, lie on the same side of the liquid obtained; of these, white phosphorus is by far the nearer, so that crystallisation of the metastable white modification may be expected here.

This conclusion is further supported by the great difference between the solidifying points of the stable and the metastable modifications,

amounting in fact to about 545°. Thus the *f* value of the metastable modification (see page 105) is almost certainly the greater.

An explanation has therefore been found of the interesting fact that it is possible by an indirect method to pass from the stable violet modification to the metastable white form by way of the vapour. This phenomenon occurs in many allotropic substances; its explanation is always to be found in the fact that, as regards its composition, the metastable modification approximates most closely to the vapour.

(k) *The lowering of the vapour pressure of violet phosphorus.*

A knowledge of the T X diagram for phosphorus also enables us to investigate other phenomena more thoroughly. One of these is the lowering of the vapour pressure of violet phosphorus already mentioned, which can be brought about by driving off the more volatile pseudo-component by fractional evaporation. This phenomenon will now be once more considered with the assistance of a P X section. The fractional evaporation referred to took place at 360°, and our T X diagram now shows the form of the P X section at this temperature. This diagram is very simple, and is given in Fig. 161.

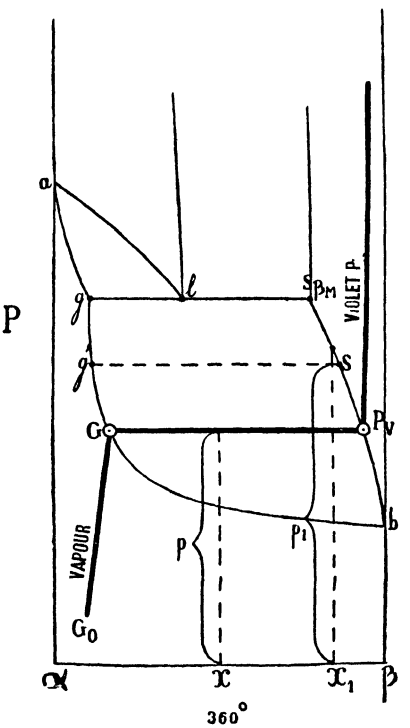


FIG. 161.

If it is assumed that the violet phosphorus was initially in inner equilibrium, the co-existing solid and gaseous phases at 360° will be indicated by the points P_v and G.

But if vapour is now imagined to be removed so rapidly that inner equilibrium in the violet phosphorus cannot adjust itself to the withdrawal of the vapour, the violet form must grow continually poorer in that component which predominates in the vapour. Consequently violet phosphorus becomes poorer in the α component, and it will move from P_v along the line $P_v b$ towards *b*, as a result of which the vapour pressure decreases.

This phenomenon which so irrefutably proves the complexity of violet phosphorus was actually observed, for inner equilibrium is only very slowly re-established at 360°.

(l) *The retrogression of the vapour pressure according to Lemoine.*

Another phenomenon, first observed by Lemoine, and which will be called the retrogression of the vapour tension of violet phosphorus when rapidly heated, can likewise be immediately explained by means of the diagram given here, Fig. 161.

Lemoine[1] found that on heating violet phosphorus as rapidly as possible to a really high temperature in a vacuum, after some time its vapour tension diminished.

The above PX diagram might correspond to Lemoine's rapidly attained temperature, and the mass might then be expected to contain too much of the volatile component, for it is in the highest degree probable that Lemoine's violet phosphorus was not in inner equilibrium. If x_1 represents the composition of Lemoine's violet phosphorus, it is clear without further explanation that if the volume of vapour were relatively small, violet phosphorus would only undergo a slight change in composition during the evaporation. The co-existing phases could therefore be represented by the points S and g'. This co-existence corresponds to a pressure p_1 greater than the pressure p of unary violet phosphorus. Finally, therefore, inner equilibrium in the violet phosphorus is re-established, and thus the pressure must diminish, as Lemoine observed.

For very large volumes of vapour the amount of α pseudo-component in the solid phase will greatly diminish during the heating, assuming that at the temperature concerned inner equilibrium is re-established but slowly or not at all. In this case the composition of the violet phosphorus may undergo so great a change that the vapour tension falls below the unary vapour pressure, and then, finally, a rise of the vapour pressure would be observed. From the fact that Lemoine obtained a decrease of pressure, it follows that he worked with a relatively small volume.

(m) *The formation of red-coloured phosphorus by rapidly cooling superheated phosphorus vapour.*

We owe our knowledge of the peculiar behaviour of phosphorus vapour, when heated to a high temperature and then rapidly cooled, to the interesting researches of Stock, Schröder and Stamm.[2] The results of their investigations will now be briefly considered.

White phosphorus, in such amount that on heating to 200° all the liquid was converted into vapour, was sealed up in a quartz tube. If after heating to 700° the tube was allowed to cool down in the air, white phosphorus condensed. But if the tube was suddenly chilled by plunging one end into cold water, a dark red precipitate was formed. On repeating the experiment at temperatures between 400° and 1175° the condensed mass was found to contain so much the more red-coloured phosphorus the higher the temperature to which the phosphorus vapour had previously been heated. The investigators

[1] *Ann. Chim. Phys.* (4), **24**, 129 (1871). Lemoine speaks of red phosphorus, but we have called this preparation violet phosphorus.

[2] *Ber. d. d. chem. Ges.*, **42**, 4510 (1910); **46**, 3497 (1913).

mentioned write: "After previously heating to 400° the phosphorus condensed in the form of colourless drops; on cooling down from higher temperatures the condensed drops agreed with the following descriptions: 450°—just perceptibly yellow in colour; 550°—very distinctly yellow; 600°—a few purple-coloured flakes; 700°—a heavy brownish-red precipitate which at 900° increased to such an extent that the liquid was opaque, and which at 1000°, 1100° and 1175° became still heavier."

The peculiarity of this phenomenon finds still clearer expression in a further experiment of Stock and Stamm, in which phosphorus vapour under a pressure of 5 mm. of mercury was led through a tube heated to 1200° and then suddenly cooled down. *Nearly pure red phosphorus* was thus precipitated, the maximum amount of colourless phosphorus contained therein being 1 %.

On calculating from the vapour-pressure curve of violet phosphorus the temperature at which phosphorus vapour under a pressure of 5 mm. mercury or 0·0066 atmosphere is supersaturated with respect to violet phosphorus, the value 273·6° is obtained. It is known that the velocity of crystallisation of violet phosphorus from the vapour is so small at this temperature that when the vapour is slowly cooled down in the air violet phosphorus never separates out, and consequently it is really remarkable that in these experiments involving sudden cooling, nearly pure red phosphorus was deposited.

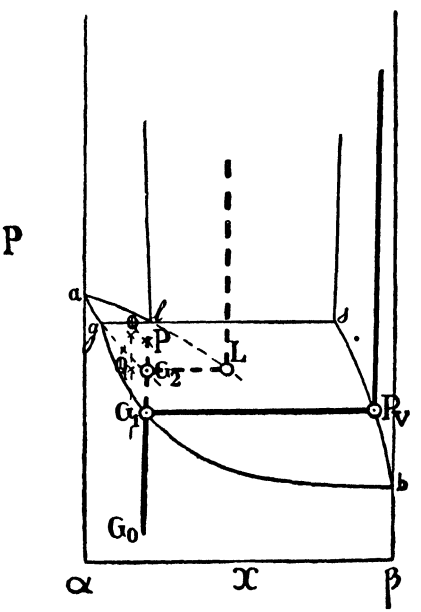


FIG. 162.

The explanation, however, is easy to give.

Since the separation of red-coloured phosphorus doubtless takes place above the solidifying temperature of white phosphorus, the P X diagram, Fig. 162, which can be applied to any temperature between 44·1° and 589·5°, will be used.

On slowly cooling the vapour, Stock and his collaborators always obtained a deposit of liquid white phosphorus. When the cooling was slow the phosphorus vapour remained in inner equilibrium, so that before condensation the supersaturated vapour was to be found on the metastable prolongation of the line G_0 G_1, relating to the inner equilibrium in the vapour phase, at the point P, for example. In this case, therefore,

the nearest metastable liquid phase is deposited and the unary metastable two-phase equilibrium $G_2 + L$ is established.

When the cooling is brought about suddenly, the result is quite different. Liquid white and solid red-coloured phosphorus are formed side by side, and of the latter so much the more, the higher the temperature to which the vapour was heated and the lower its pressure. This phenomenon also points to the complexity of phosphorus, for phosphorus vapour does not possess this property, so that the velocity of cooling could exert no influence on the mode of condensation.

From their results the experimenters mentioned conclude that at higher temperatures a chemical change makes its appearance, which on rapid cooling cannot be completely reversed. They connect this with the dissociation of P_4 and P_2 molecules at high temperatures, and assume that on chilling the following reaction takes place—

$$x\ P_2 + y\ P_4 \rightarrow P_{2x+4y}$$

This reaction should explain the formation of red-coloured phosphorus. This assumption lacks a rational basis, however. Four different solid states of phosphorus are known, and it is in the highest degree probable that at least three molecular species, α_1, α_2 and β, must be taken into consideration here. The existence of three molecular species, namely P_4, P_2 and P_1* at high temperatures has, however, been experimentally confirmed with more or less certainty, whilst the existence of a much less reactive and probably still more complicated molecular species has not as yet been established, because it probably only occurs in any great concentration in solid violet and in black phosphorus.

The molecular species P_2 and P_1, which are formed only at high temperatures, cannot be present except in extremely small amount in the solid phases of phosphorus, and hence there must be still another simple molecular species α_2, which, together with P_4 or α_1 and the complicated molecular species β, *mainly* constitutes the solid modifications of phosphorus.

Stock's experiments and those of other investigators will now be considered in the light of the Theory of Allotropy.

The experiments mentioned indicate that on rapid cooling, phosphorus vapour which is not in inner equilibrium is obtained, and thus at low temperatures a vapour results which corresponds to an inner equilibrium state at a higher temperature. If dissociation is increased by rise of temperature, as has been assumed here, the state of the chilled vapour at a given temperature will lie to the left of the inner equilibrium line for the vapour, and as a result this will exert a higher pressure than would be the case after slow cooling.

Now investigations undertaken with the object of testing the Theory of Allotropy have shown that a phase always possesses a certain stability if it reverts into inner equilibrium, even if it is metastable. If, however, an unstable phase is not in inner equilibrium the stability becomes so greatly diminished that an instantaneous transformation

* Preuner and Brochmöller, *Zeitschr. f. physik. Chemie*, **81**, 129 (1912).

often results, for the system then behaves like the pseudo-system concerned. If, in order to explain this phenomenon, it is assumed that, on sudden cooling, the state of the vapour at a given temperature is indicated by the point Q in Fig. 162, there are two possibilities :—

1. The vapour can only behave in a metastable pseudo-binary manner, and breaks down into vapour and liquid, the gaseous phase lying on the line *g* G_2 and the liquid phase on the line *l* L.

2. The vapour may behave in a stable pseudo-binary manner, as a result of which it dissociates into a gaseous phase situated on the line *b g* and a solid phase lying on the line *b s*.

Now we know that the initial state at the higher temperature lay in the vapour region, and therefore below the vapour line *b g* in the corresponding P X figure. During the cooling process, this state has overstepped the line *b g*, and consequently the region for the co-existence of violet mixed crystals and vapour has been entered; only later and at a lower temperature does it enter the metastable region in which vapour and liquid co-exist. The first-mentioned state might therefore be indicated by Q′ and the second by Q if it is borne in mind that the temperatures in the two cases were different, and consequently that these two states really belong to two different P X sections. For the sake of simplicity, however, both states are indicated here in the same P X diagram. Thus it follows from these considerations that on rapidly cooling phosphorus vapour a splitting up into a gaseous phase and violet phosphorus first appears. But if this dissociation is not instantaneously completed, at a lower temperature yet another dissociation will make its appearance, namely into a gaseous phase and liquid white phosphorus, so that a condensate is then obtained which contains both liquid white phosphorus and also solid violet phosphorus.

It is clear that in the event of slight deviation of the rapidly-cooled vapour from the inner equilibrium state, the smallest retardation in the cooling, which may be caused by a slight deposition of violet phosphorus, suffices to allow the vapour again to revert into inner equilibrium. The separation of violet phosphorus thus comes to an end. From these considerations it follows that deposition of violet phosphorus will increase with increasing deviation from inner equilibrium conditions, and consequently the quantity of phosphorus deposited will be so much the greater the higher the temperature from which the vapour is chilled and the smaller the partial pressure of the phosphorus. Stock found this to be the case.

Further, it is self-evident that the quantity of violet phosphorus deposited will increase, the greater the temperature range between the commencement of sublimation of violet phosphorus and the condensation of liquid white phosphorus. For, the greater this range is, the longer will the sublimation of violet phosphorus continue before condensation of liquid phosphorus can begin. This range of temperature increases with decrease of pressure, so that a reduction of the partial pressure will result in an increase in the amount of violet phosphorus in the precipitate, as Stock proved by means of experiments which will be described later.

(n) *The position of red-coloured phosphorus in the pseudo-binary system.*

It is well known that red-coloured phosphorus is prepared technically by heating white phosphorus for a short time to from 250° to 400°, the product so obtained being treated, after cooling, with carbon disulphide or caustic soda. Basing our considerations on Fig. 158, the starting-point is thus a liquid on the line L_1 L, co-existing with a vapour situated on the line G_1 G. This two-phase equilibrium is very metastable and cannot be maintained. On the stable unary equilibrium being attained the end product would be violet phosphorus, situated on the line S S′, and a co-existing vapour phase which lies on the line G G′.

But the two-phase system liquid phosphorus—vapour at the temperature mentioned here, 250°—300°, lies in the two-phase region of the pseudo-binary system relating to the co-existence of violet mixed crystals and vapour.

The deposition of a solid phase may be explained by the great metastability of the co-existence of the liquid and gaseous phases, as a result of which a sudden change occurs into a solid phase and the vapour co-existing with it, which at the temperature under consideration belongs to the pseudo-system. The transformation resulting in the establishment of inner equilibrium immediately follows, but at the temperature under consideration this can only take place slowly in the solid phase. The solid phase deposited, lying to commence with on the line *b f*, and indeed between S and *f*, will therefore slowly change in the direction of inner equilibrium, and this lies on the line S S′.

Technically the heating period is but short, so that when the process is interrupted, the solid phase still consists of mixed crystals, lying between the lines S *f* and S S′, the compositions of which vary. Thus the heated mass consists of a number of different states, firstly those which approximate very closely to the stable solid equilibrium state, and in addition those which are rather far removed from this state. The red-coloured phosphorus of commerce, therefore, even after treatment with carbon disulphide, is never quite homogeneous; its vapour pressure is too high, but this diminishes when the preparation is kept at constant temperature until the vapour-pressure curve of violet phosphorus is reached.

(o) *A second modification of white phosphorus.*

In the course of his investigation of the behaviour of white phosphorus under different pressures, Bridgman[1] found that under a pressure of 12000 kilograms per square centimetre at 64·4°, under the atmospheric pressure at − 72·9°, and under its own vapour pressure at − 80°, white phosphorus reaches a transition point, at which, on withdrawing heat, the ordinary regular modification changes into a hexagonal form. Phosphorus belongs therefore to that type of

[1] *Journ. Amer. Chem. Soc.*, **36**, 1244 (1914).

substance in which a metastable transition point appears below the stable melting point. This phenomenon is always associated with the existence of at least three molecular species.

The elevation of the solidifying point of ordinary white phosphorus, observed when the liquid phase is suddenly cooled, is now probably to be ascribed to retardation of the inner equilibrium between those molecular species which are most prominent in these two white modifications.

(p) *Black phosphorus.*

Bridgman's researches on white phosphorus not only resulted in the discovery of a second modification of white phosphorus, they also led to the discovery of a still more interesting form, namely *black* phosphorus. This last modification he obtained by subjecting white phosphorus at 200° to a pressure of from 12000 to 13000 kilograms per square centimetre. The black phosphorus obtained in this way must at once be recognised as a new modification, firstly on account of its high specific gravity, 2·69, the value for violet phosphorus varying between 2·21 and 2·34, and secondly because black phosphorus exhibits a much greater electrical conductivity than that of violet phosphorus.

In order to establish the relationship between black phosphorus and the violet form, Bridgman determined the vapour pressure at definite temperatures by Hittorf's method.[1] A small quantity of phosphorus was heated at a definite temperature in an evacuated and sealed vessel, the volume of which was known, until the vessel was filled with the saturated vapour. The vessel was then quickly removed from the constant-temperature bath and cooled down in the air. In this way the vapour was condensed to white phosphorus. Now on treating the contents of the vessel with carbon disulphide the weight of the white phosphorus dissolved could be determined by weighing. The vapour pressure can then be calculated after the size of the phosphorus molecules in the gaseous phase has been determined at the temperature of the experiment and under the pressure of its saturated vapour. From the investigations of Stock, Gibson and Stamm,[2] Bridgman assumed the molecular magnitude to be P_4.

Determinations of the vapour pressures of violet and black phosphorus, carried out in this way, yielded the following results :—

Temperature.	Vapour tension of *black* phosphorus in cms. Hg.	Vapour tension of *violet* phosphorus in cms. Hg.
357·1°	2·3	5·2
443·7°	—	73·2
445·2°	58·5	—

From these few figures it follows that the vapour pressure of black phosphorus under the conditions prevailing in Bridgman's experiments,

[1] *Pogg. Ann.* **126**, 193 (1865). [2] *Ber.* **45**, 3527 (1912).

is undoubtedly lower than that of violet phosphorus. As Bridgman has pointed out, according to these results black phosphorus should be looked upon as the stable modification under the vapour pressure. But he found it impossible to confirm this conclusion in any other way, for he did not succeed in converting violet into black phosphorus. Bridgman's results are very remarkable, for when studying the vapour pressure of violet phosphorus, it was found that after evaporating this modification in a vacuum at 360° a mass remained which at **445°** had a vapour pressure of about **0·64** atmosphere, whilst Bridgman found the vapour pressure of black phosphorus at the same temperature to be 58·5 cms. or **0·77** atmosphere, higher therefore than that exhibited by violet phosphorus when subjected to rapid evaporation.

Now it has been shown that this form of violet phosphorus is a very disturbed state of the violet modification, and that on heating to 410° in contact with 1 per cent. iodine, inner equilibrium was re-established; the vapour pressure had therefore again become normal and amounted at 445° to 2·2 atmospheres.

(q) *Exact determinations of the vapour pressure of black phosphorus.*

Since it follows from these data that Bridgman's black phosphorus cannot be stable under the pressure of its vapour, the vapour pressure of black phosphorus was studied at various temperatures, the methods employed being the same as those employed in the case of violet phosphorus.[1]

As the black phosphorus contained carbon, efforts were first of all made to remove this by grinding and then washing with water. After this treatment the mass was extracted in a Soxhlet apparatus with carbon disulphide, washed, first with alcohol and then with aqueous ammonia, and finally dried over phosphorus pentoxide in a vacuum.

This method of purification, however, proved to be quite insufficient, for the substance obtained in this way always contained kerosene. The presence of this was due to the fact that Bridgman used it as the compressing liquid. After this impurity had been removed by heating the mass in sealed and evacuated tubes to 550° in a bath of molten potassium nitrate and sodium nitrite, followed by the usual re-purification, the following vapour pressures were obtained:—

Temperature.	Vapour pressure in atmospheres.	
	Black phosphorus.	Violet phosphorus.
515°	8·5 (rising)	10·5
553°	19·3 ,,	21·5
567°	28 6	28 5
578°	38·7	35

[1] *Proc. Akad. v. Wet.*, Smits, Meyer and Beck, **18**, 992 (1915).

From these figures it follows that at temperatures above 560° the vapour pressure of black phosphorus obtained in this way undoubtedly exceeds the vapour pressure of violet phosphorus. From the results obtained it is impossible to say what the position is at lower temperatures, for even after standing half an hour at constant temperature the pressure was always still slowly rising. In order to ascertain whether or not black phosphorus is stable below 560°, equal amounts of the violet and black forms, together with 1 per cent. iodine, were heated in a tube of very hard glass to about 480° in a vacuum for thirteen days without interruption. At the end of this heating period the contents were extracted with carbon disulphide, etc., and the specific gravity was then determined by the suspension method. The result was that practically the whole had been converted into a substance of specific gravity 2·3, though isolated particles still had a specific gravity of 2·7. On repeating this experiment at 380°, especially when violet phosphorus was present in great excess, a distinct transformation of black into violet phosphorus could still be detected.

Consequently although below 560° black phosphorus exhibits a lower vapour pressure than the violet form, which however gradually increases, it follows that even at 380° violet phosphorus must be acknowledged to be the stable modification.

(r) *The behaviour of black phosphorus in the light of the Theory of Allotropy.*

The fact that black phosphorus, in spite of its metastability, under certain circumstances still has the lower vapour pressure, cannot be explained by means of the older view. The Theory of Allotropy, however, enables this to be done in a very simple way. Accepting the older theory, it would be absurd to state that an unstable form of an element or a compound may possess a lower vapour pressure than the stable state. But if it is assumed that the element or the compound is complex, *i. e.* that it consists of various molecular species, quite another result is obtained. In this case the same phenomenon is, in fact, in question as has already been observed in the case of violet phosphorus. The possibility of converting an element simply by rapid evaporation into a state having a smaller vapour pressure would have been flatly denied by the former theory, whilst the Theory of Allotropy points to the possibility of this, thus suggesting experiment. In the case of black phosphorus the theory did not, it is true, lead to the experiment, nevertheless it did point to the possibility of the phenomenon discovered by Bridgman.

This may easily be shown. In order that black phosphorus may be included in the pseudo-binary figure, a discontinuity in the mixed crystal curve can be assumed, as has been done in the following T X diagram.

From this diagram it is at once evident that, in agreement with its higher specific gravity, black phosphorus contains the β pseudo-component in greatest amount, and that under the pressure supposed to prevail this modification is metastable. On the other hand, experiment

indicates, as we have seen, that under very high pressure black phosphorus is stable. Hence it follows that whilst the T X diagram for pressures greater than the vapour pressure has the form schematically indicated in Fig. 163, at much greater pressures the curve relating to the inner equilibrium in the liquid phase does not meet the fusion curve *l d*, but the fusion curve *b l*, as shown in Fig. 164.

Under this pressure, therefore, black phosphorus is the stable modification at high temperatures; at lower temperatures, however, violet phosphorus is the stable form.

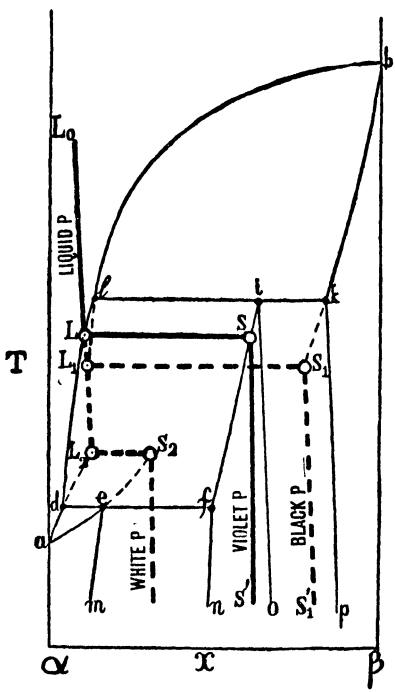


FIG. 163.

The transition equilibrium indicated here by the points $S'S'_1$ is thus displaced by increase of pressure in the direction of lower temperatures.

If a P X section corresponding to a temperature of 200° is now considered, a diagram is obtained such as that indicated in Fig. 165.

The pseudo P X diagram is immediately intelligible, and it is in accord with the assumption that a discontinuity appears in the mixed crystal series. The unary figure may be briefly discussed here. The inner equilibria in the vapour phase at different pressures are indicated by the line $G_{u_0} G_u$. At G_u this line meets the curve G G' of the pseudo-binary system, *i.e.* the curve relating to the vapour which can co-exist with the mixed crystal phases represented by the line $S_{\alpha_M} S'_{\alpha_M}$.

Thus, so far as unary behaviour is concerned, at G_u solid violet phosphorus will be deposited from the vapour, and this process will continue as the volume is decreased, until all the vapour has been converted into solid violet phosphorus. If now the compression is continued, the inner equilibrium in the solid violet phosphorus will be displaced along the line $S_{u_1} S'_{u_1}$. At S'_{u_1} this line enters the disintegration region for the mixed crystals, in which the violet mixed crystal phase S_{α_M} and the black mixed crystal phase S_{β_M} co-exist. If no retardation occurs, on reducing the volume, the violet mixed crystal phase S'_{u_1} will change into the black phase S'_{u_2}, the pressure remaining constant. If the violet phase S'_{u_1} has been completely converted into the black phase S'_{u_2}, continued diminution of volume will result in an increase of pressure, and the inner equilibrium

in the solid phase will be displaced along the line S'_{u_2}, S''_{u_2}. This line has its origin in the point S_{u_2}, where metastable black phosphorus co-exists with a vapour G'_u.

Let us now suppose the point P to correspond to a very high pressure, more than 13000 kilograms per square centimetre, and that the black phosphorus which exists under this pressure is fixed by reducing the pressure so rapidly that the inner equilibrium cannot readjust itself to the pressure. If it is then assumed, for the sake of simplicity, that this condition becomes really fixed, a vertical line will be followed downwards.

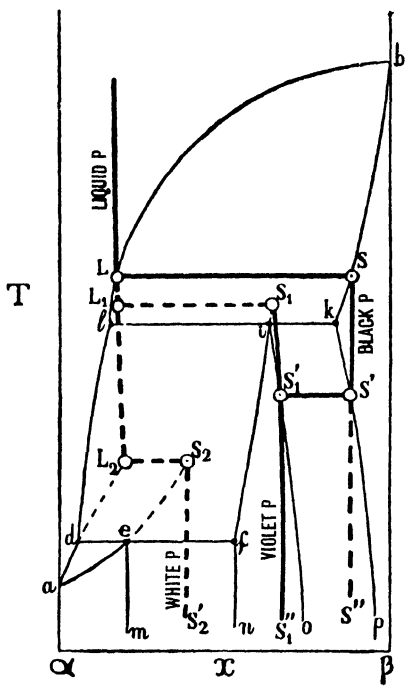


FIG. 164.

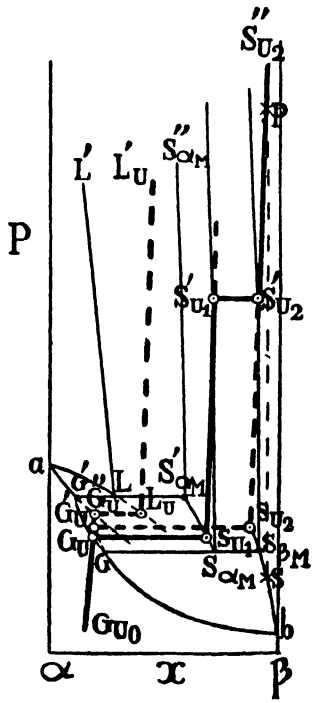


FIG. 165.

In this case, therefore, a solid substance is obtained which contains more of the α pseudo-component than would be present in inner equilibrium. This state has, as the diagram shows, a vapour pressure represented by the point S, and this is *smaller* than the vapour pressure of *stable violet* phosphorus.

But if the mass is heated to temperatures at which inner equilibrium is re-established with appreciable velocity, the vapour pressure will rise above that of violet phosphorus. Thus, although the mass is unstable, at the outset it had a lower vapour pressure than the stable modification.

From these considerations an explanation is obtained of the abnormally low vapour pressures found by Bridgman for black phosphorus.

It must be assumed that a state which was in inner equilibrium at a high pressure has been fixed. This phenomenon exhibited by black phosphorus has thus given powerful support to the Theory of Allotropy.

(s) *The determination of the triple-point temperature for black phosphorus.*

Since black phosphorus is metastable under its own vapour pressure, its melting point must be lower than the melting point of violet phosphorus. The black phosphorus obtained by Bridgman's method of preparation is not, however, the true black modification, but a fixed equilibrium state corresponding to a higher pressure. This fixed state has a lower vapour pressure than that of violet phosphorus and consequently it might be expected to have a higher melting point. But, since at these high temperatures inner equilibrium is doubtless established after some time, there is still the prospect of the melting point soon falling below the melting point of violet phosphorus, and also that the correct melting point would appear most rapidly in those preparations to which a minute quantity of iodine had been added.

An experiment was now carried out in the following manner: Three thick-walled tubes of very hard glass were filled, each with different material. The tube *a* was two-thirds filled with the purest black phosphorus; the tube *b* contained a certain quantity of the same preparation of black phosphorus to which 1 per cent. iodine had been added, and in *c* violet phosphorus with 1 per cent. iodine was placed. These three tubes were bound together with copper wire and hung in such a way that a swinging motion could be imparted to them. Finally a copper rod was fastened beneath the hanging contrivance. This system of tubes was then placed in a bath composed of a fused mixture of potassium nitrate and sodium nitrite at about 200°. The temperature of the bath was kept uniform by means of a stirrer, and it was measured by means of a calibrated thermo-element inserted in the usual way in one of the branches of a Wheatstone Bridge.

Preliminary experiments had already indicated with certainty that when it is slowly heated black phosphorus melts at a temperature 5°–10° higher than does violet phosphorus, which of course might be expected from the results of the vapour-pressure measurements.

Since this phenomenon must be due to the heating being too rapid to permit of inner equilibrium being established, in the definitive experiment the bath was first kept for half an hour at 580° and then heated up extremely slowly.

In this way it was observed that in the tube *b* containing black phosphorus and iodine fusion first appeared, namely at about 588°, whilst in tube *c*, containing violet phosphorus and iodine, fusion was first observed at 589·5°. In tube *a*, which contained black phosphorus without the addition of iodine, fusion first occurred at 598°. When this had been established the bath was brought back to 588° as quickly as possible. At this instant only about one quarter of the black phosphorus in tube

a was molten. Attempts were now made to ascertain whether on long-continued heating without the addition of iodine black phosphorus would melt completely at the same temperature as that observed when a trace of iodine had been added. Experiment proved this to be the case; thus after heating for half an hour at 588° the black phosphorus fused completely to a colourless liquid.

From this it follows, therefore, that black phosphorus obtained by the fixation of the state existing at high pressures melts at a higher temperature than the violet modification. Furthermore, it follows that when black phosphorus has attained a state of inner equilibrium the melting point is lowered to such an extent that, its behaviour being unary, the melting point of black phosphorus under its own vapour pressure lies about 1·5° below the melting point of violet phosphorus, thus again proving that under the vapour pressure black phosphorus is the metastable modification.

From the foregoing considerations it may be seen how easily and rationally the peculiar behaviour of black phosphorus can be explained from the standpoint of the Theory of Allotropy.

(t) *The position of the black phosphorus region in the* P T *diagram.*

In order that the position of the black phosphorus region may be indicated with some probability, it is necessary to examine the results of some further investigations by Bridgman, undertaken as the result of correspondence between him and the author. His original experiments had already shown that at 200° white phosphorus is converted into black phosphorus by a pressure of 12000 kilograms per square centimetre, whilst under the same pressure but at a temperature of 175° violet phosphorus results. When a pressure of 4000 kilograms per square centimetre was applied and a small quantity of *sodium*, which acts as a catalyst, was added to the white phosphorus, violet phosphorus was likewise produced. From these facts one would be inclined to the conclusion that at 200° the transition point between violet and black phosphorus lies between 4000 and 12000 kilograms. A peculiar difficulty must present itself here, however, for all Bridgman's efforts to convert violet phosphorus into black phosphorus at 200° and under a pressure of 13000 kilograms per square centimetre yielded negative results.

Even when he submitted a mixture of violet phosphorus and white phosphorus to a pressure of 12500 kilograms at 200° the white phosphorus was converted into the black form but the violet phosphorus remained entirely unchanged. At first sight these results are very surprising, but on closer consideration they become quite intelligible.

The study of violet phosphorus has proved that the internal change into solid violet phosphorus first takes place with appreciable velocity at temperatures over 400°, so that it is not surprising if at 200° and under a pressure of 12500 kilograms there is no perceptible transormation of violet into black phosphorus, although increase of pressure

increases the reaction velocity. But this is not contradictory to the result quoted, *i.e.* that under the same conditions of temperature and pressure white phosphorus is rapidly converted into the black form, for in the transformation of white into black phosphorus it is only a question of nucleus formation in a highly metastable liquid. This process, which precedes chemical reaction, can be brought about very rapidly, whilst the conversion of solid violet phosphorus into solid black phosphorus, which necessitates a reaction in a *solid* phase, does not proceed to any perceptible extent. If violet phosphorus were compressed at a temperature between 400° and 500°, probably the conversion into black phosphorus would easily be realised, but the difficulties attending such an experiment are too great.

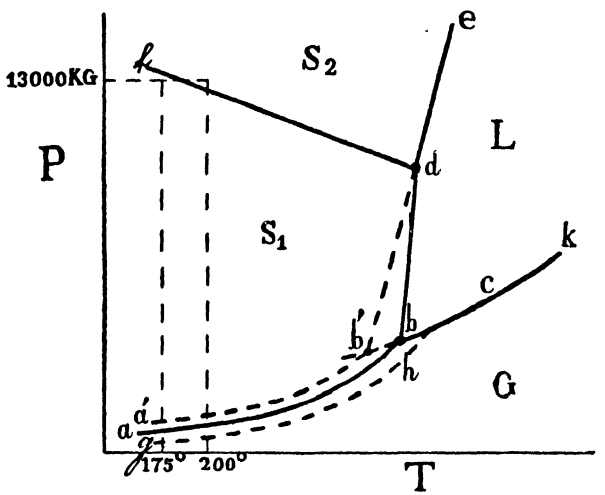


FIG. 166.

The P T diagram shown in Fig. 166 has now been built up from the collected results of the investigation of black phosphorus.

The line *df* is the transition curve for violet and black phosphorus. Concerning this line the following remarks may be made: Bridgman did not succeed in converting white phosphorus into the black modification at 175°; even when a pressure of 13000 kilograms per square centimetre was employed no formation of black phosphorus occurred. This circumstance points to the fact that at 175° the transition pressure is *higher* than 13000 kilograms. On the other hand, at 200°, and under a pressure of 13000 kilograms, the formation of black phosphorus takes place rapidly. It follows from these observations that the transition pressure at this temperature is *less* than 13000 kilograms. On this experimental result the position in the diagram of the transition line *fd* is based. The point relating to a temperature of 175° and a pressure of 13000 kilograms lies in the violet phosphorus region,

whilst the point representing the state of affairs at 200° and the same pressure, 13000 kilograms, lies in the region relating to black phosphorus.

Further, it may also be pointed out that the point *b'* denotes the melting point of black phosphorus under its own vapour pressure. This point lies at 588°.

(u) *The representation of the entire phosphorus system.*

If the complete P T diagram is now schematically represented, Fig. 167 is obtained.

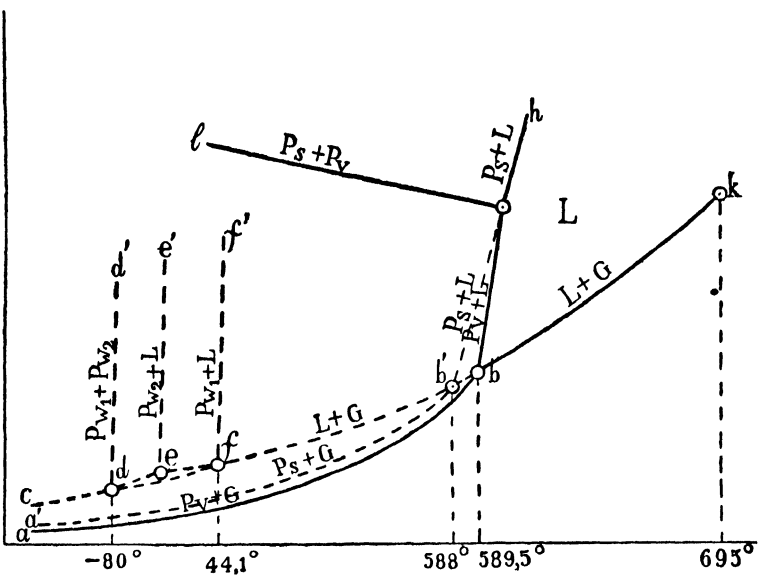


FIG. 167.

In conclusion, reference may be made to the following points. If the pseudo-binary conception of the metastable transition point of white phosphorus is accepted for our T X diagram, a method must be employed which has already been discussed. This method depends on the supposition that a certain number of the pseudo-components are always in inner equilibrium, so that this inner equilibrium system can be looked upon as a *single* pseudo-component.

Thus, it may be assumed that the molecular species α_1 P and α_2 P constitute a pseudo-system in which a transition equilibrium, *i. e.* an equilibrium between two solid modifications, appears. If it is supposed that the inner equilibrium between α_1 P and α_2 P is established very rapidly, the system can be looked upon as a single pseudo-component α P, which, however, then has a transition point.

Fig. 168 is then obtained.

In this way a pseudo-binary representation is obtained for the phosphorus system, which summarises the properties and the com-

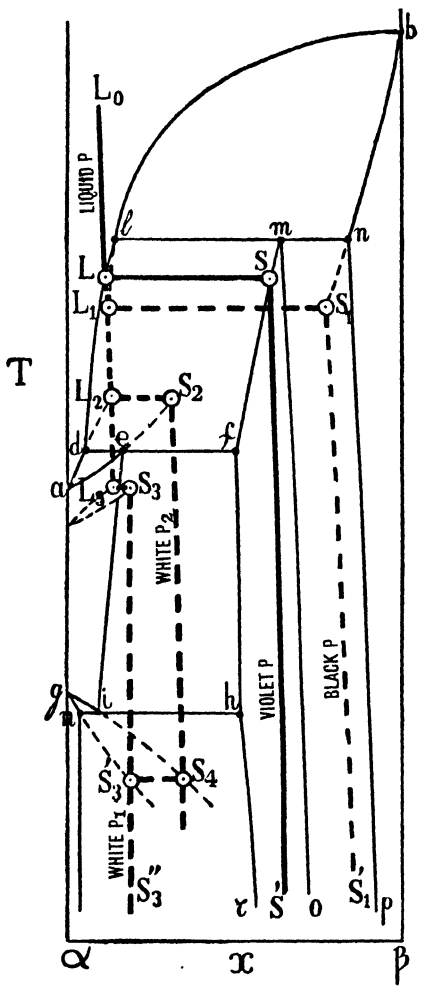


FIG. 168.

positions of the various states of aggregation. Naturally, on account of the large number of pseudo-components, this system is very intricate; so far as can be seen, however, the representation given here is provisionally sufficient.

Finally it may be specially mentioned here that the investigation of

the phosphorus system has led, amongst other things, to the important conclusion that the phases investigated are all complex.

But what the origin of the complexity is has not as yet been definitely decided. It may consist in the existence in juxtaposition of simple and associated molecules; it may be due to isomeric molecules, or to the presence in juxtaposition of the different species of ions and electrons arising therefrom.

It should also be noticed that black phosphorus conducts electricity fairly well, whilst the violet form is a bad and white phosphorus a very bad conductor. Hence it follows that in black phosphorus we have to do with a distinct electro-ionisation, which in the other phases may be neglected.

21. The Cyanogen System.

Two modifications of cyanogen are known: a very volatile easily fusible form to which the name cyanogen is given, and a very slightly volatile modification only known in the solid state—paracyanogen.

In 1815 Gay Lussac obtained cyanogen by heating dry mercuric cyanide or silver cyanide. Paracyanogen was discovered in 1829 by Johnston [1] in the brownish-black residue from the preparation of cyanogen by Gay Lussac's method.

According to Troost and Hautefeuille [2] paracyanogen is formed when gaseous cyanogen is heated above 500° for a long time, or when electric sparks are passed through the gas. Conversely, paracyanogen is easily converted into cyanogen, according to Troost and Hautefeuille, by heating paracyanogen to 860° and condensing the vapour. Thus both modifications of cyanogen can be converted the one into the other, and there must therefore be a certain relationship between them. The problem with which we are faced can best be surveyed with the help of the P T diagram, and this, thanks to Terwen's exact measurements,[3] has already been determined with certainty, at any rate so far as cyanogen is concerned. In the first place, Terwen prepared cyanogen in a state of purity such as has been attained in the case of but few substances. With this preparation he determined the vapour-pressure curve for solid and for liquid cyanogen, in addition to the melting point of the substance under its own vapour pressure.

From his investigations it appears that the triple point of cyanogen under its own vapour pressure lies at $-27{\cdot}92°$, the pressure being 55·50 cms. Hg. The boiling point is $-21{\cdot}35°$ and the critical point occurs at 126·55 and 58·2 atmospheres.

The vapour-pressure curve of paracyanogen is as yet entirely unknown, although Troost and Hautefeuille carried out determinations of the vapour pressure of this substance up to 641°. The determination of this curve fails because below 500° the equilibrium is established too slowly, whilst above this temperature decomposition of para-

[1] *Ann. d. Chem. u. Pharm.*, **22**, 280 (1835).
[2] *Compt. rend.*, **66**, 735 and 795 (1868).
[3] *Zeitschr. f. physik Chemie*, **91**, 469 (1916).

cyanogen into carbon and nitrogen occurs. In spite of our ignorance of the exact position of the vapour-pressure curve for paracyanogen, it is nevertheless known that paracyanogen is still solid far above the critical temperature of cyanogen. This circumstance places us in a peculiar difficulty. If it is supposed for a moment that the decomposition of the paracyanogen does not take place, the substance will attain its melting point at a temperature far above 600°, and the question then is, what will be the connection between the liquid so obtained and that produced by melting cyanogen, the critical point of which is situated at 126·55°?

Reference will once more be made to the views of Bakhuis Roozeboom on this question. He writes: "The interesting question is raised, however, whether, if this decomposition were prevented, a melting point could be reached. Transformation of paracyanogen into the ordinary liquid is naturally impossible, for its critical point lies at 124°.

"But a transformation into a polymeric liquid might well be 'imagined' at temperatures above 640°, and consequently under pressures greater than one atmosphere.

"In such cases there is no continuous transition between the two liquids.

"Consequently, the various solid phases are no longer really monotropic, but the polymeric form behaves as a distinct and separate substance."

If the P T curves for cyanogen are shown in a P T diagram in which the P T curves for paracyanogen are also schematically indicated, assuming the absence of decomposition at high temperatures, and that therefore the melting point under the vapour pressure can be reached, the diagram shown in Fig. 169 is obtained.

The peculiarity is now sharply defined. The critical point K′ of cyanogen lies below the melting point of paracyanogen under its own vapour pressure, and thus the P T diagram for paracyanogen cannot be brought into contact with the cyanogen P T diagram by prolonging the vapour-pressure curve for liquid paracyanogen into the metastable region, and hence it would be concluded in fact that the two forms of cyanogen are in no way connected with each other.

But this conclusion cannot be correct, for it is known that each state can be converted into the other. This example again most clearly shows that something was lacking in the older view, and here again the Theory of Allotropy furnishes a solution of this interesting problem.

The P T diagrams for pseudo-binary systems, Figs. 24 and 41, which up to the present have been considered, correspond with the usual case: The plait-point curve runs through the region of unsaturated solutions, and the critical phenomena will therefore be observed in unsaturated solutions. As the author showed in 1903,[1] this is not true generally, and indeed a deviation might be expected if component A were very volatile and component B but slightly volatile, if the triple

[1] *Zeitschr. f. Electrochem.*, 663 (1903). *Zeitschr. f. physik. Chemie*, **51**, 193 (1905); **52**, 587 (1905).

point of component B were rather far above the critical point of component A, and if the solubility of solid B in liquid A is small, right up to the critical temperature of A. The three-phase line for $S_B + L + G$ will, as has been fully discussed elsewhere, twice meet the plait-point curve, and each such meeting denotes the appearance of the critical phenomena in a saturated solution.

The P T diagram represented in Fig. 170 by means of faint lines relates to the case under discussion here.

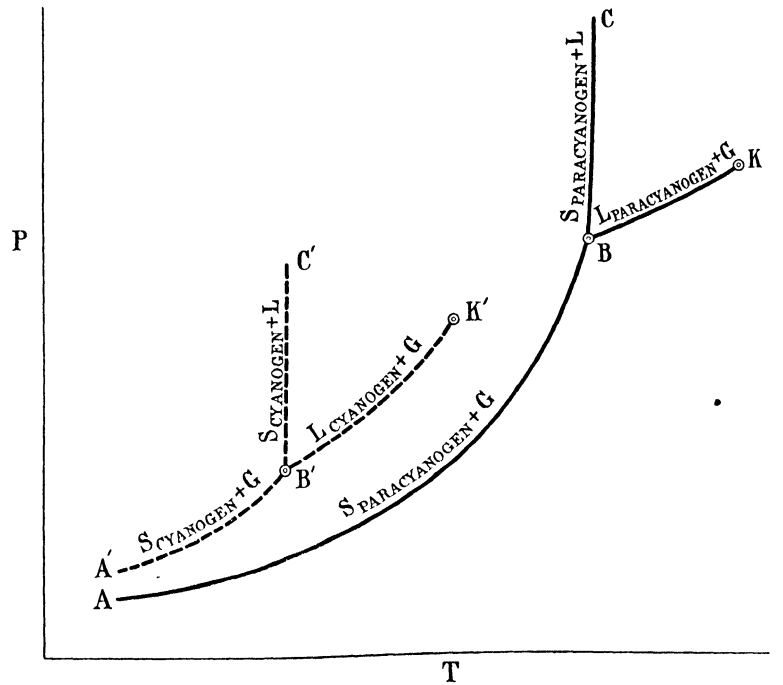


FIG. 169.

In Figs. 24 and 41 the three-phase line

$$S_{\beta M} + L + G$$

lies entirely *below* the plait-point curve, that is to say, critical phenomena can only appear in the case of unsaturated solutions. Now Fig. 170 only differs from Fig. 41 in that the three-phase line meets the plait-point curve in the so-called critical end-points p and q. According to Fig. 170 critical phenomena in unsaturated solutions appear from k_1 to p; at p the critical phenomenon occurs in a saturated solution; from p to q, however, these phenomena can only be observed in supersaturated solutions. At q a critical phenomenon in a saturated solution occurs and from q to k again in unsaturated solutions. Thus from p to q the plait-point curve is metastable.

These phenomena were first observed by the author in the system ether—anthraquinone, which was therefore subjected to a thorough investigation. The circumstance that the two modifications, cyanogen and paracyanogen, differ so markedly from one another in volatility, and that the melting point of paracyanogen under the vapour pressure, if realisable, would lie very much above the critical point of cyanogen, gave rise to the prediction that most probably the pseudo-components of cyanogen constitute a system belonging to the ether—anthraquinone type. Herein lies the solution of the cyanogen problem.

The P T diagram given here, Fig. 170, thus corresponds with the pseudo-binary cyanogen system, and in it the P T diagram relating to

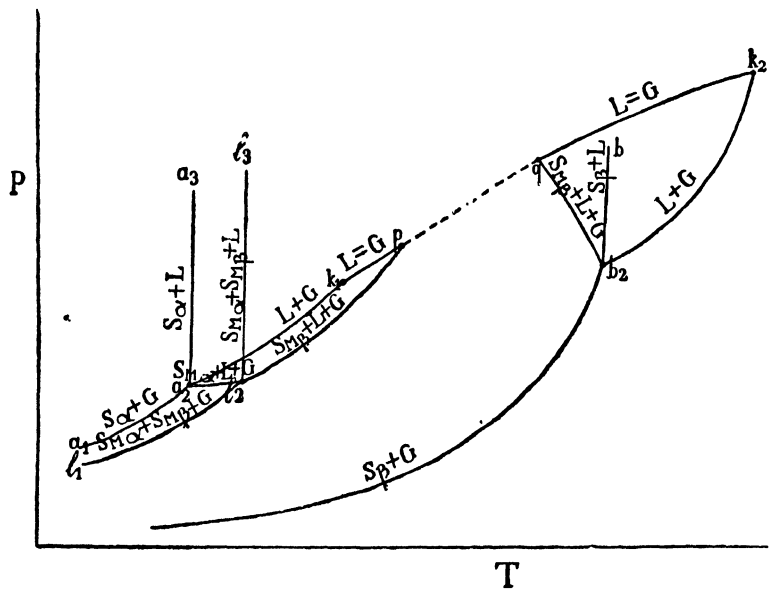


FIG. 170.

the unary behaviour of cyanogen is easily indicated. This has been done in Fig. 171.

If K_3 is the critical point of unary liquid paracyanogen, K_3B will be the vapour-pressure curve for liquid paracyanogen. B is the melting point of paracyanogen under the vapour pressure, and from this point two other two-phase lines proceed, namely the sublimation line A B and the fusion line B C. In the usual case the melting point of the metastable modification lies on the metastable prolongation of the vapour-pressure line for the liquid phase in the direction of lower temperatures; but this is not so here. To show this, the metastable modification, cyanogen, will now be considered. As is well known, the unary melting point of the metastable modification under the vapour pressure always lies on the metastable prolongation of a three-phase line

of the pseudo-system relating to solid, liquid and vapour. The triple point S + L + G for cyanogen lies on the metastable prolongation of the three-phase line S_{M_α} + L + G, at B′, for example, where the sublimation line A′ B′, the fusion line C′ B′ and the vapour-pressure curve for the liquid phase all meet together. Now we know that this vapour-pressure curve reaches its critical point below the triple point of paracyanogen, *i. e.* the vapour-pressure curve for liquid cyanogen ends in the plait-point curve between *p* and *q*. Consequently this curve has a position such as is indicated by the line B′ K_1. It is clear that this behaviour has become possible through the appearance in the pseudo-

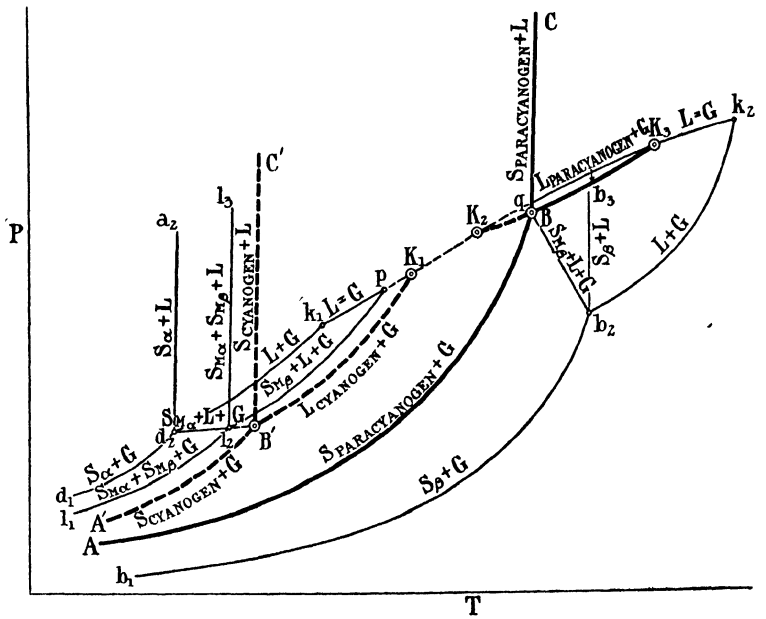


FIG. 171.

binary system of the critical end-points *p* and *q*. As regards the metastable prolongation of the vapour-pressure line for liquid paracyanogen, it should be noticed that it might be possible to continue this to lower temperatures, but then, at the ordinary temperature, for example, two different liquid phases would exist, each of which singly must be in inner equilibrium. But since this is not the case, there only remains one possibility, namely, that the metastable prolongation referred to likewise meets the plait-point curve, *e. g.* in K_2, where it comes to an end. Liquid paracyanogen would then have an upper critical point K_3 and a lower critical point K_2. Such a phenomenon has never been established in a unary system; on account of the decomposition of paracyanogen it cannot be realised here. In all probability it can only

appear when, as is the case here, the critical point of the metastable modification lies far below the melting point of the stable form.

On sketching the T X diagram (Fig. 172) a connection is obtained which only differs from Fig. 158 in that the liquid and vapour lines of the three-phase area $S_{\beta_M} + L + G$ in the pseudo-binary figure merge into each other without discontinuity at two points p and q. Consequently at these points the critical phenomenon appears side by side with the β mixed crystals S_3' and S_2' respectively, and the plait-point curve passes therefore through these points p and q.

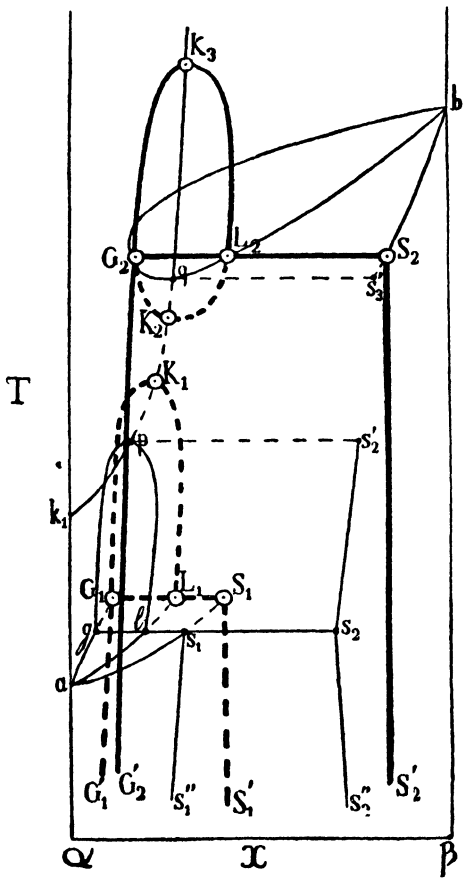


FIG. 172.

K_3 is also here again the unary critical point of paracyanogen. At this point, therefore, the liquid curve in the unary system passes without discontinuity into the vapour line of the two-phase area. These curves, which relate to the co-existence between liquid and gaseous paracyanogen, are indicated here by $K_3 G_2$ and $K_3 L_2$.

At the points G_2 and L_2 the two-phase area for liquid and vapour in the unary system meets the three-phase area of the pseudo-binary system relating to the co-existence of mixed crystals $b S_3'$, liquid $b L_2 q$ and vapour $b G_2 q$; the two lines last mentioned merge without discontinuity in the point q. This meeting indicates that at the appropriate temperature the liquid phase of the invariant unary system will change when heat is withdrawn into the solid unary phase S_2 and the vapour phase G_2 until all the liquid has disappeared; thus:—

$$L_2 \rightarrow S_2 + G_2.$$

When the liquid has been completely converted, the system has become monovariant, and now on withdrawing still more heat, the

temperature of the two-phase system will fall, whilst the inner equilibrium in the solid paracyanogen phase moves along the line $S_2 S_2'$ and the inner equilibrium in the co-existing gaseous phase moves along the line $G_2 G_2'$. But if deposition of the solid phase S_2 does not take place, at lower temperatures a further movement into the two-phase area occurs, which comes to an end, however, at K_2, since there it meets the plait-point curve a second time, and the vapour and liquid lines of the unary system again pass continuously the one into the other. At this point, therefore, paracyanogen would reach its lower metastable critical point. If we now set out from the unary equilibrium between solid cyanogen and vapour, this equilibrium will be indicated in the figure by the two-phase area $S_1 S_1'$, $G_1' G_1$. At $S_1 L_1 G_1$ this two-phase area meets the three-phase area for the co-existence of mixed crystals $a s_1 S_1$, liquid $a l L_1$, and vapour $a g G_1$, *i. e.* at the temperature of this meeting, and for unary behaviour the following reaction will take place with absorption of heat:—

$$G_1 + S_1 \rightarrow L_1.$$

So long as the invariant three-phase equilibrium exists the temperature remains constant.

If the solid phase disappears, this case will now be considered here, the monovariant two-phase system $L_1 + G_1$ is obtained, and by continued addition of heat we now move along the two-phase area relating to liquid cyanogen and vapour. But this two-phase area meets the plait-point curve of the pseudo-binary system at K_1, so that at this point the liquid line $L_1 K_1$ passes continuously into the vapour line $G_1 K_1$; in other words, the critical point of metastable cyanogen is reached.

Whilst according to the older view it was quite impossible to show the connection between cyanogen and paracyanogen, the new theory brings out this relationship perfectly clearly. Formerly this was impossible, for it can only be brought about by a consideration of the pseudo-system.

As has already been stated, the portion of the plait-point curve between p and q can only be realised in supersaturated solutions. The critical point of cyanogen, the point K_1, is therefore the critical point of a solution which must be looked upon as supersaturated with respect to paracyanogen. If, therefore, this liquid is brought into contact with paracyanogen, at best paracyanogen might separate out. But since the liquid consists almost exclusively of cyanogen molecules, this separation would necessitate a conversion of cyanogen into paracyanogen, and at the critical temperature of cyanogen this does not take place to a perceptible extent, not even in contact with paracyanogen. Hence it follows that the presence of paracyanogen will not influence the position of the critical point, and this has been confirmed by Terwen.

22. Inert Organic Allotropic Substances.

As has been shown, the Theory of Allotropy maintains that phase allotropy is due to molecular allotropy.

The existence of molecular allotropy is most easily established in

the domain of organic chemistry. This is really due to the fact that the reaction velocity between different molecular species which exhibit the phenomenon of isomerism or of polymerism is generally much smaller than in the case of inorganic substances; in many organic substances it seems to be imperceptible.

But the substances in which this is the case and which are known as tautomers are at the present time rather few in number, but this number will doubtless increase as experiments become more refined.

In the investigation of systems composed of organic substances which can appear in two different forms, Bancroft[1] first took into account the influence of time. As a result of this consideration he distinguished three cases.

1. The time element does not enter, because equilibrium is established practically instantaneously.

2. The establishment of equilibrium takes place so slowly that so-called "false equilibria" appear; for this case Bakhuis Roozeboom[2] has derived various T X diagrams.

3. Equilibrium is established with such a velocity that, working rapidly, the system behaves as a binary one, but when the work is carried out slowly it behaves in a unary manner.

The substances belonging to the last-mentioned group, the number of which, especially in the organic region, is doubtless enormously great, form excellent material for investigation.

Bancroft first discovered a pseudo-binary system in the di-chlor-stilbene investigated by Zincke[3] and succeeded in explaining its behaviour. Zincke had established the fact that the solidifying point is lowered from 192° to 160° when the form having the higher melting point is kept in the fused state (200°) for a long time. This depression of the melting point is explained, according to Bancroft, by the fact that at 200° the substance established itself in (inner) equilibrium, as a result of which the molecules of one form were partially converted into the other.

Many examples of organic substances which can appear in various isomeric forms and which in many cases exhibit a change of melting point appear in the literature; these phenomena are to be ascribed to reactions which tend to establish inner equilibrium, or also to a retardation of the establishment of inner equilibrium.

The oxime group especially furnishes various examples of this.

In the first place, acetaldoxime may be mentioned, investigated by Dunstan and Dymond,[4] and later and more thoroughly by Carveth.[5] Benzaldoxime may also be noticed. The first statements with regard to this substance were made by Beckmann,[6] the discoverer of the isomeric change in this type of compound. This substance was more

[1] *Journ. Phys. Chem.*, **2**, 143 (1898).
[2] *Zeitschr. f. physik Chemie*, **28**, 298 (1899).
[3] *Lieb. Ann.*, **198**, 115 (1879).
[4] *Journ. Chem. Soc.*, **61**, 470 (1892); **65**, 206 (1894).
[5] *Journ. Phys. Chem.*, **2**, 159 (1898).
[6] *Ber. d. d. chem. Ges.*, **20**, 2768 (1887); **37**, 3042 (1902).

closely investigated by Cameron,[1] whose results were afterwards confirmed and improved as a result of the work of Schoevers.[2]

Carveth[3] also investigated still another oxime, namely, *p*-anisaldoxime, of which Beckmann[4] had also found two isomers.

Another interesting substance is benzil-orthocarbonic-acid, two clearly different crystalline modifications of which were discovered by Graebe and Juillard;[5] of these one appeared to be white, the other yellow. Whilst enantiotropy frequently occurs in inorganic chemistry, it is found to be extremely rarely mentioned in the literature of organic chemistry. But it would be quite wrong to conclude from this that in the region of organic chemistry this phenomenon should really only be looked upon as a great exception. This idea, certainly a false one, must be ascribed in the first place to the fact that, on account of the low reaction velocity between the different molecular species in organic substances, enantiotropy is much less easily revealed, and secondly a reason for this assumption may be found in the fact that no accurate and systematic investigation has yet been carried out in this region.

As regards benzil-orthocarbonic-acid, however, it is well known that this substance is enantiotropic. Soch[6] has established this with certainty, and he has also attempted to extend Graebe's[7] researches.

Then the extremely interesting system to which the aldehyde of acetic acid gives rise may be mentioned; this has been investigated by Holman[8] and by Smits and de Leeuw.[9] Then again we have a large and very important group of allotropic substances, exhibiting very distinct transformations, in the keto and enol compounds. Wolf[10] carried out an investigation of formyl-phenyl-acetic ester, of which, two years previously, Wislicenus[11] had discovered two modifications, a solid keto and a liquid enolic compound. Since then a number of researches on other substances exhibiting intramolecular changes have been published by Dimroth.[12] These very interesting papers deal with the investigation of derivatives of triazol, chiefly in different solvents.

One of these isomers is always an acid, which may be determined by titration, and this, of course, is a great advantage in the investigation of the phenomenon of transformation.

Another substance which by reason of its peculiar behaviour had already attracted various investigators is the hydrazone of acetaldehyde, of which Fischer[13] discovered two modifications.

Bamberger and Pemsel[14] carried out a more thorough investigation

[1] *Journ. Phys. Chem.*, **2**, 409 (1898).
[2] *Dissertation*, Amsterdam, 1907, p. 43.
[3] *Journ. Phys. Chem.*, **3**, 437 (1899).
[4] *Ber. d. d. chem. Ges.*, **23**, 2103 (1890).
[5] *Ibid.*, **21**, 2003 (1888).
[6] *Journ. Phys. Chem.*, **2**, 364 (1898).
[7] *Ber. d. d. chem. Ges.*, **23**, 1344 (1890).
[8] *Zeitschr. f. physik. Chemie*, **43**, 157 (1903).
[9] *Ibid.*, **77**, 269 (1911).
[10] *Journ. Phys. Chem.*, **4**, 123 (1900).
[11] *Ber. d. d. chem. Ges.*, **20**, 2933 (1887); **28**, 767 (1895).
[12] *Ibid.*, **35**, 4041 (1902); *Lieb. Ann.* **335**, 1 (1904); **338**, 243 (1905); **364**, 183 (1909); **373**, 336 (1910); **373**, 127 (1910).
[13] *Ibid.*, **29**, 793 (1896).
[14] *Ibid.*, **36**, 85 (1903).

of this substance, as also did Lockmann and Liesche[1] two years later, and Laws and Sidgwick[2] six years afterwards, but none of these workers was able to unravel the behaviour of these singular substances. Another hydrazone directly connected with the last is *p*-nitrobenzal-phenyl-methyl hydrazone investigated by Backer.[3] Of this substance two modifications exist, a yellow and a red form, but the relationship in which these two forms stand to one another is as yet unknown.

The system urea—ammonium cyanate (Walker and Hambly)[4]—the names of the investigators who have thoroughly and successfully investigated the substances mentioned are placed in brackets—just like the system thiourea—ammonium thiocyanate (Reynolds),[5] (Volhard),[6] (Waddell),[7] (Reynolds and Werner),[8] (Findlay),[9] (Atkin and Werner)[10] and (Smits and Kettner)[11] belong to the organic pseudo-systems, just as does cyanogen-paracyanogen (Terwen),[12] which on account of its great similarity to phosphorus has already been discussed, and finally hydrocyanic acid, cyanuric acid and cyamelid (Troost and Hautefeuille).[13]

Amongst the organic nitro-compounds there are some which belong to the pseudo-acid group, as Hantsch[14] and Hollemann[15] found in their researches on brom-phenyl-nitromethane and phenyl-nitromethane. These substances too must be reckoned amongst the pseudo-systems.

The same is true of dimethyl ketol (Pechmann and Dahl),[16] similarly of benzene-azo-cyanacetic ester (F. Krukeberg),[17] and again of benzilidene hydrindone (Kipping)[18] and of tolane dibromide (Limpricht and Schwanert).[19]

In the region of structural isomerism, too, tautomerism or internal change has been observed. Of this Polak[20] found a beautiful example in the para- and meta-benzene disulphonic acids, and Smits and Vixseboxse[21] another in methyl thiocyanate and methyl mustard oil, in which yet a third pseudo-component, namely the tri-polymer, appears, as Gillis[22] has shown. In this connection Terwen[23] has already expressed the opinion that structural isomers are perhaps tautomers which pass, the one into the other, very slowly.

Finally milk sugar may be mentioned, the behaviour of which points

[1] *Lieb. Ann.*, **342**, 14 (1905).
[2] *Journ. Chem. Soc.*, **99**, 2085 (1911).
[3] *Dissertation*, Leyden (1911).
[4] *Journ. Chem. Soc.*, **67**, 746 (1895).
[5] *Ibid.*, new series, **7**, 1 (1869).
[6] *Ber. d. d. chem. Ges.*, **7**, 92 (1874).
[7] *Journ. Phys. Chem.*, **2**, 525 (1898).
[8] *Journ. Chem. Soc.*, **83**, 1 (1903).
[9] *Ibid.*, **85**, 403 (1904).
[10] *Ibid.*, **101**, 1167 (1912).
[11] *Versl. Kon. Akad. v. Wet.*, **21**, 669 (1912).
[12] *loc. cit.*
[13] *Compt rendu*, **66**, 795 (1868); **67**, 1345 (1868).
[14] *Ber. d. d chem. Ges.*, **29**, 669, 2251 and 2253 (1896).
[15] *Rec. Tr. chim.*, **14**, 121 (1895).
[16] *Ber. d. d. chem. Ges.*, **23**, 2421 (1890).
[17] *Journ. f. prakt. Chem.*, **46**, 579 (1892); **47**, 591 (1893).
[18] *Journ. Chem. Soc.*, **65**, 499 (1893).
[19] *Lieb. Ann.*, **145**, 348 (1868).
[20] *Dissertation*, Amsterdam (1908).
[21] *Versl. Kon. Akad. v. Wet.*, **22**, 46 (1913).
[22] *Rec. Trav. chim. des Pays-Bas*, **1**, 330 (1920).
[23] *Zeitschr. f. phys. Chem.*, **91**, 443 (1916).

most clearly to the existence of two molecular species (Smits and Gillis).[1]

This survey of the organic substances which undoubtedly belong to pseudo-systems makes no claim to completeness; no attempt was made to accomplish this. Its only purpose was to show, by the bare enumeration of a few facts, how enormously great, in organic chemistry, the region available for testing the Theory of Allotropy is. Here and there investigators have taken the trouble to find the connection between the pseudo-binary and the unary fusion diagrams, but in no case have these investigations been brought to a conclusion.

Bancroft and his pupils have gone furthest in this direction, but, as has been shown, from the point of view of the Theory of Allotropy, more is wanted.

The study of organic allotropic substances is so interesting, because there are amongst these substances systems, the pseudo-components of which change so slowly in the dissolved state in the absence of catalysts, that the two pseudo-components with the solvent behave as a ternary system. This phenomenon very seldom occurs in inorganic substances, which generally pass into inner equilibrium with great velocity.

After the introduction of a catalyst or after longer standing, the two pseudo-components do settle into inner equilibrium, however, and then the behaviour of the system is binary.

In this case the position of the binary system within the pseudo-ternary system may be determined with great certainty.

Thus by the study of certain organic allotropic substances in the presence of a solvent, a complete picture is obtained of the general behaviour of allotropic systems in the presence of solvents, but in the rapidly occurring changes in inorganic allotropic substances this is for the most part hidden.

The study of allotropic substances in the presence of a solvent often offers yet another practical advantage. It may happen that the fusion diagram of a pseudo-system cannot be determined, because the pseudo-components decompose even below their melting points, or change the one into the other very rapidly at this temperature, whilst at lower temperatures they do not decompose and only undergo mutual transformation very slowly, and this is also true of the dissolved state.

It is clear that in this case the study of the allotropic system in the presence of a solvent is the method by which the character of the system can be most thoroughly explored.

23. The Unary Bimolecular System Ammonium Thiocyanate—Thiourea.

Before passing on to the treatment of an ideal system, two other cases will be considered, simply to show how the investigation of an allotropic system in the presence of a solvent may lead to interesting results.

[1] *Versl. Kon. Akad. v. Wet.*, **26**, 280, 540 (1917).

In the first place the system *ammonium thiocyanate—thiourea* may be mentioned. After Reynolds,[1] Volhard,[2] Waddell,[3] Reynolds and Werner,[4] had examined this system, it was thoroughly investigated by Findlay.[5] He determined the fusion diagram, by means of cooling curves, from 100 per cent. NH_4CNS to 48 per cent. NH_4CNS.

He obtained the following results:—

Thiourea per cent.	Solidifying point.	Thiourea per cent.	Solidifying point.
9·1	135·5°	30·4	106·2°
12·8	131·0°	32·9	105·9°
16·6	127·4°	35·7	110·5°
17·4	124·0°	40·2	117·5°
22·3	118·2°	51·9	131·3°
25·9	113·4°		

But we are dealing here with two pseudo-components which at about 140° undergo marked change the one into the other in a short time. The position of the inner equilibrium in the liquid phase at various temperatures was found to be 75 per cent. ammonium thiocyanate and 25 per cent. thiourea. In agreement with this Findlay gives a temperature of about 114° for the stable unary solidifying point.

At the suggestion of the author the system mentioned was further investigated by Kettner.

Findlay was unable to determine the fusion curve for thiourea beyond 131° on account of the conversion of this pseudo-component into thiourea.

Kettner,[6] on the other hand, applied Soch's method as soon as the change in the course of the experiment became so marked as to detract from the accuracy of the results obtained, and in this way he succeeded in determining the fusion diagram for the whole system.

The results of Kettner's work are collected in the table on p. 273.

The last four initial solidifying points could only be determined by Soch's method, whilst the others were obtained by means of cooling curves; those corresponding to a high thiourea content were also controlled by Soch's method. The end solidifying points, however, were all obtained with the help of cooling curves.

If now a T X diagram is constructed from these results, Fig. 173 is obtained.

Since mixtures containing more than 80 per cent. thiourea exhibit an end solidifying point at 146·3° instead of at 105°, it was suspected that the compound $NH_4CNS,4CS(NH_2)_2$ appears at this point, and this was confirmed in another way. Before dealing with this, the peculiarity of the system may be pointed out. We have here an example of the case, already discussed in the theoretical portion, of *a pseudo-system containing a compound,* and, indeed, this is the only

[1] *loc. cit.* [2] *loc. cit.* [3] *loc. cit.* [4] *loc. cit.*
[5] *loc. cit.* [6] *loc. cit.*

example which up to the present has been obtained. Moreover, both ammonium thiocyanate and thiourea are known in two modifications.

Thiourea per cent.	Initial solidifying point.	End solidifying point.
0	148·6°	
5·3	142·3°	
10·4	136·0°	
13·8	131·0°	
16·3	127·5°	
20·0	122·1°	
26·6	113·0°	
30·2	107·7°	105·0°
31·8	106·0°	
33·7	108·9°	
38·4	115·8°	
45·9	124·5°	
57·7	135·7°	
57·8	135·3°	
71·6	146·0°	
74·0	146·0°	
78·0	148·0°	
85·3	157·0°	146·3°
91·5	168·0°	
100·0	182·0°	

Whilst in the case of ammonium thiocyanate these are enantiotropic, the modifications of thiourea appear to be monotropic.

Hence the result is obtained that the pseudo-system is at least

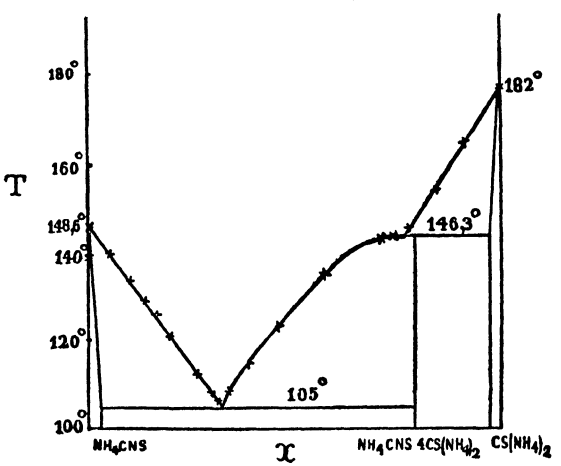


FIG. 173.

quaternary, for each of the two substances, ammonium thiocyanate and thiourea, is built up from two different molecular species. But if, for

the sake of simplicity, it is assumed that both in the case of ammonium thiocyanate and of thiourea these different kinds of molecules revert into inner equilibrium with great velocity, the pseudo-system can be looked upon as binary.

In this way Fig. 174 is obtained, which, as regards the portion

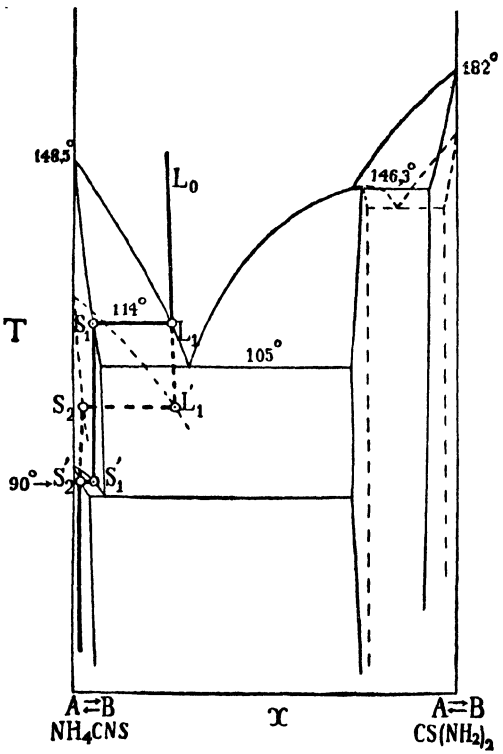


FIG. 174.

below 105°, and also so far as the dotted lines are concerned, is only diagrammatic in character.

Unfortunately the position of the inner equilibrium in the solid phase is as yet unknown.

24. The Binary Trimolecular System Ammonium Thiocyanate—Thiourea—Water.

Since ammonium thiocyanate and thiourea in aqueous solution are also very inert as regards their mutual transformation, the system built up from these two substances with the addition of water could be studied as a pseudo-ternary system.

This was desirable in order that the position of the compound

might be established with certainty. The following diagram, Fig. 175, corresponding to a temperature of 25°, gives the position of the solubility isotherms.

The figure contains three isotherms: *a b* for solutions which co-exist with mixed crystals B *m* rich in NH_4CNS, *d c* for solutions that co-exist with mixed crystals C *n* rich in $CS(NH_2)_2$ and *b c* for solutions

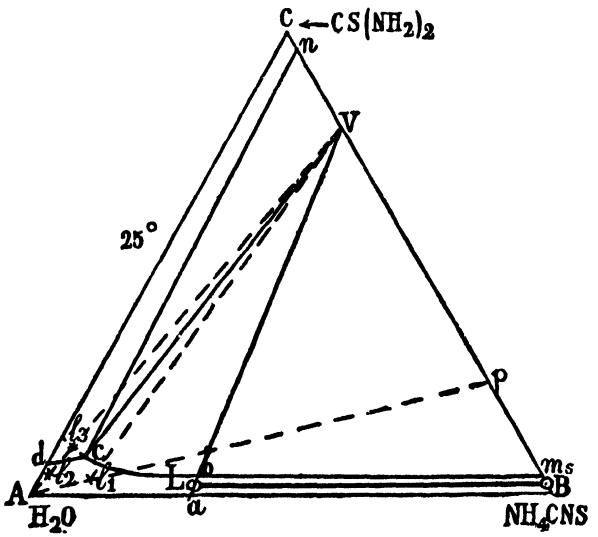


FIG. 175.

that co-exist with the compound. On applying the remainder method the composition of the compound V was found to be

$$NH_4CNS,4CS(NH_2)_2,$$

whilst Atkins and Werner[1] were of opinion that the compound

$$NH_4CNS,3CS(NH_2)_2$$

appears. If the conversion of NH_4CNS and $CS(NH_2)_2$ into the equilibrium state in solution at 25° had been successfully accomplished, naturally only the co-existence of the saturated solution L with the solid phase S would have been observed. This diagram permits of a reasonable explanation being given of the preparation of the pseudo-component $CS(NH_2)_2$ from the pseudo-component NH_4CNS.

According to Reynolds and Werner,[2] thiourea is prepared by heating ammonium thiocyanate to 160° for some time; the liquid is then poured into cold water and the solid substance obtained by concentrating this solution is then separated from the solution, dissolved in pure water and again allowed to crystallise. Now how is this method of preparation to be explained?

[1] *loc. cit.* [2] *loc. cit.*

The inner equilibrium in the liquid phase at 160° contains 75 per cent. NH_4CNS and 25 per cent. $CS(NH_2)_2$.

When the liquid is poured into cold water this inner equilibrium is fixed. Let us assume that at 25° the substance is completely dissolved, then the unsaturated solution obtained will lie on the line joining the point P, which corresponds to 75 per cent. NH_4CNS and 25 per cent. $CS(NH_2)_2$, with A, it will in fact lie in the unsaturated region, for example at l_1. If now this solution is concentrated, the equilibrium will move along the line A l_1 P, from l_1 in the direction of P, and as a result the solubility isotherm of the compound will be over-stepped, *i. e.* the region in which the compound V is supersaturated is entered and this will crystallise out. If the solid phase is now separated from the mother-liquid and the solid compound V is dissolved in pure water, the solution obtained will again lie in the unsaturated region, but now on the line joining the point V with the point A, *e. g.* at l_2. Now it may chance that this line does not intersect the solubility isotherm for the compound V, but that of thiourea. Therefore, if the solution l_2 is concentrated, the solution is naturally displaced along the line passing through the points A and l_2, and, indeed, it is displaced in such a way that it is always moving further from A; thus the compound V does not separate out, but thiourea.

It is clearly sufficient to bring the compound V into contact with water, for the pure saturated solution of V, lying at l_3, is metastable and thiourea will be deposited. This change continues until the solid compound completely disappears.

25. Milk Sugar.

Introduction.—The second inert organic allotropic substance to be discussed here is *milk sugar*.

When Schmoeger[1] and Erdmann[2] commenced their researches on milk sugar in 1880, in addition to the hydrated form, an anhydride could also be obtained by heating the hydrate to 125° in a drying oven. Later, in order to distinguish it from another anhydride, this modification became known as the α form. The other modification of the anhydride, the β form, was obtained by evaporating a saturated solution of milk sugar at its boiling point, 108°.

That this form is in fact a different modification of the anhydride from the α form follows from its behaviour towards water. Whilst the α modification is extremely hygroscopic and causes a distinct *evolution of heat* when placed in water, giving rise to a solution the rotation of which *decreases* on standing, the β modification, on the other hand, is not hygroscopic; it dissolves with *absorption of heat* and yields a solution, the rotation of which *increases* with time.

Hudson,[3] in the year 1903, first considered the milk-sugar problem from the physico chemical point of view. He showed that, no matter

[1] *Ber. d. d. Chem. Ges.*, **13**, 1915 (1880). [2] *Ibid.*, **13**, 2180 (1880).
[3] *Zeitschr. f. physik. Chemie*, **44**, 487 (1903).

which form of milk sugar was dissolved in water, the final stage was always the same, and that it corresponded with a condition of equilibrium.

He was of opinion that this equilibrium was:—

$$C_{12}H_{24}O_{12} \rightleftarrows C_{12}H_{22}O_{11} + H_2O,$$

so that

$$K = \frac{(\text{anhydride}) \cdot (\text{water})}{(\text{hydrate})}$$

or

$$K' = \frac{(\text{anhydride})}{(\text{hydrate})}.$$

Hudson assumed the hydrate to possess a very high rotatory power, but that the rotation of the β anhydride was very low. He further showed that mutarotation proceeds as a monomolecular reaction. On the one hand, he determined $k_1 + k_2$, on the other, k_2, and thus he obtained k_1 indirectly. In this way, for the equilibrium constant, he obtained

$$K' = \frac{k_1}{k_2} = 1{\cdot}6 \text{ at } 10{\cdot}2°.$$

In consequence of the slowness with which inner equilibrium is established in the solution, the hydrate of milk sugar exhibits this remarkable phenomenon: the *initial solubility* is much smaller than the *final solubility*.

Now if the total concentration is not too great, it can doubtless be assumed that the concentration of the hydrate in a solution which co-exists with solid hydrate remains constant. The equilibrium constant then likewise follows from the initial and the final solubilities, for

$$\frac{\text{final solubility} - \text{initial solubility}}{\text{initial solubility}} = \frac{[\text{anhydride}]}{[\text{hydrate}]} = K'.$$

In this way K′ was found to be 1·44 at 15°. It is clear that this equilibrium constant is also obtained from the initial and final rotations of hydrate and β-anhydride.

For the initial rotation of the hydrate Hudson found

$$[\alpha]^{D}_{20°} = 86{\cdot}5°$$

and for the β-anhydride

$$[\alpha]^{D}_{20°} = 33{\cdot}4°,$$

whilst for the final rotation Schmoegers had already obtained 55·3°.

It follows, therefore, that at 20°

$$K' = \frac{86{\cdot}0 - 55{\cdot}3}{55{\cdot}3 - 35{\cdot}4} = 1{\cdot}54.$$

This value lies between the other two.[1]

[1] *Journ. Amer. Chem. Soc.*, **30**, 1381 (1908).

Since the establishment of inner equilibrium in the solution is so sluggish, it became possible to determine the initial heats of solution of the different modifications, and likewise the heat pressure for the conversion of hydrate and α-anhydride into β-anhydride in the dissolved state.

This was carried out by Hudson and Brown,[1] who employed a method devised by Brown and Pickering.[2]

The following results relate to 1 gram of anhydrous milk sugar at 20°.

$$\left.\begin{array}{c}\text{Hydrate (solid)} \rightarrow \text{hydrate (dissolved)} - 12{\cdot}6 \text{ cals.} \\ \text{(Initial heat of solution)}\end{array}\right\} \quad . \quad (1)$$

$$\left.\begin{array}{c}\beta \text{ (solid)} \rightarrow \beta \text{ (dissolved)} - 2{\cdot}3 \text{ cals.} \\ \text{(Initial heat of solution)}\end{array}\right\} \quad . \quad . \quad (2)$$

$$\left.\begin{array}{c}\alpha \text{ (solid)} \rightarrow \text{hydrate (dissolved)} - 7{\cdot}3 \text{ cals.} \\ \text{(Heat of hydration} + \text{initial heat of solution)}\end{array}\right\} \quad . \quad . \quad (3)$$

$$\left.\begin{array}{c}\text{Hydrate (dissolved)} \rightarrow \beta \text{ (dissolved)} + 1{\cdot}05 \text{ cals.} \\ \text{(Heat of transformation in solution)}*\end{array}\right\} \quad . \quad (4)$$

From these figures the following calculations can be made:—

From (1), (2) and (4)

$$\text{Hydrate (solid)} \rightarrow \beta \text{ (solid)} + H_2O - 9{\cdot}25 \text{ cals.} \quad . \quad . \quad (5)$$

From (1) and (3)

$$\alpha \text{ (solid)} + H_2O \rightarrow \text{hydrate (solid)} + 19{\cdot}9 \text{ cals.} \quad . \quad . \quad (6)$$

From (5) and (6)

$$\alpha \text{ (solid)} \rightarrow \beta \text{ (solid)} + 10{\cdot}75 \text{ cals.} \quad . \quad . \quad . \quad (7)$$

In the course of these determinations Hudson found that the difference between the initial and the end solubilities of both the α-anhydride and the hydrate had exactly the same value. From this it follows that α-anhydride in contact with water is *instantaneously* hydrated, and that the following slow reaction afterwards take place:—

$$\text{Hydrate} \rightarrow \beta\text{-anhydride} + H_2O.$$

Observations of the rotation lead to the same conclusion; the initial rotation is exactly the same for both α-anhydride and hydrate.

Hudson has extended his researches still further and has also determined the temperature of the dehydration point, at which the co-existence solid hydrate (S_H) + solid β-anhydride (S_β) + liquid (L) makes its appearance.

From determinations of the final solubility of the hydrate between 0° and 89°, and from two measurements of the final solubility of the β-anhydride at 0° and 100° he found the temperature of this point to be 92°.[3]

[1] *Journ. Amer. Chem. Soc.*, **30**, 960 (1908).
[2] *Journ. Chem. Soc.*, **71**, 782 (1897).
* The position of the equilibrium at 20° is here taken into account.
[3] *Journ. Amer. Chem. Soc.*, **30**, 1775 (1908).

In addition he determined this point from the intersection of the three-phase lines for $S_H + L + G$ and $S_H + S_\beta + G$. In this way the quadruple point

$$S_H + S_\beta + L + G$$

was found to lie at 94°.

The experiments by means of which it was sought to determine this dehydration point by thermal or dilatometric methods were, however, without result, owing to the extremely small velocity of the change.

In 1910 Hudson put forward a general Theory of Mutarotation[1] based on the results communicated here, which, when represented in the following way, can be applied to every kind of sugar.

$$\underset{\text{high rotation}}{\alpha \text{ sugar}} + H_2O \overset{1}{\rightleftarrows} \text{hydrate} \overset{2}{\rightleftarrows} \underset{\text{small rotation}}{\beta\text{-sugar}} + H_2O$$

Equilibrium 1 is established very rapidly, whilst equilibrium 2 is only very slowly reached, consequently the phenomenon of mutarotation must be associated with the second process.

(a) *The investigation of the stability of the solid phases which appear, and the determination of the transformation point hydrate → β-anhydride + solution.*

Ideas regarding the milk-sugar problem had assumed the form set forth in the foregoing introduction when Gillis,[2] at the author's suggestion, commenced the investigation of milk sugar from the point of view of the Theory of Allotropy. The problem indicated was a suitable one, for inner equilibrium in the solutions was established very slowly. Consequently there was the possibility of learning something regarding the connection between the pseudo-system and the binary system, in which the various molecular species of milk sugar revert into inner equilibrium.

First of all the stability of the solid phases hydrate, β-anhydride and α-anhydride had to be investigated. From the method of preparation and from Hudson's work it appears that the hydrate is stable below 93°. Thus the β-anhydride, just like the α-anhydride, always yields the hydrate when brought into contact with water.

The further conclusion may also be drawn from the method of preparation and from Hudson's experiments that above 93° β-anhydride is the stable solid phase. Above this temperature hydrate when brought in contact with saturated solution always produces β-anhydride, and under these circumstances α-anhydride also always changes into the β-modification.

Thus it appeared that the α-modification of milk sugar is metastable above 93°, yet it was possible that a transition point existed below the

[1] *Journ. Amer. Chem. Soc.*, **32**, 889 (1910).

[2] *Versl. Kon. Akad. v. Wet.*, **26**, 280 (1917); 540 (1917). *Rec. d. Trav. chim. des Pays-Bas*, **1**, 87 (1920).

melting point of the α- and β modifications. In order to investigate this possibility Gillis determined the final solubility both of the α- and of the β-modifications between 93° and 200°.

He found that the α-form always obviously changed into the β-form and the point at which this occurred was always and without exception found to lie on the solubility curve of the β-modification. Combining these results with those of Hudson for the hydrate, the T X diagram shown in Fig. 176 is obtained.

For the exact determination of the temperature of the transformation equilibrium

$$S_H \rightarrow S_\beta + L$$

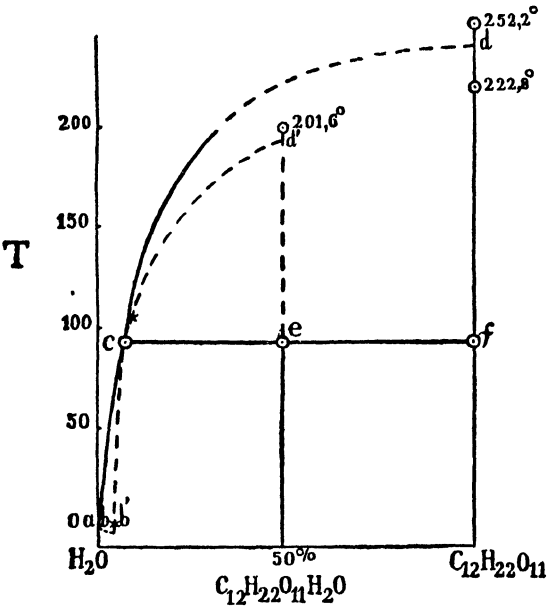


FIG. 176.

if log x is represented as a function of $\frac{1}{T} \cdot 10^3$, the diagram shown in Fig. 177 is obtained, from which it follows that the temperature just mentioned is 93·5°.

Now, owing to decomposition of the milk sugar, it was not possible to continue solubility determinations beyond 200°. Up to this temperature β-anhydride was the stable modification. It was, however, still possible that a transition point would appear at a higher temperature.

In order to decide this point the melting points of both modifications were determined by Soch's method in extremely narrow and thin-walled capillary tubes. This method yielded quite convincing

results; the α-modification melted in two seconds in a bath at 222·8°, whilst the β-modification fused in the same time when placed in a bath at 252·2°. Thus the β-modification melts at a temperature 29·4° higher than the melting point of the α-modification; and consequently the α-modification is metastable right up to its melting point.

On this occasion an attempt was also made to determine the melting point of the hydrate by Soch's method. The experiment was successful, and 201·6° was obtained for this melting point.

There is quite striking proof of the small velocity of transformation in the solid substance in the fact that it is here possible to realise the melting point of a hydrate, though it lies more than 100° above its transformation point.

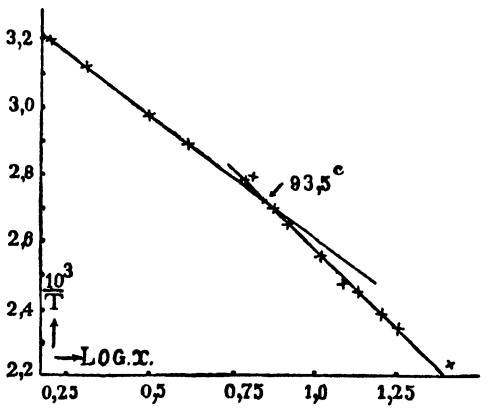


FIG. 177.

(b) *The hydrate is a hydrate of the α-modification.*

These results were far from sufficient to solve the milk-sugar problem. For example, amongst other things, an extremely remarkable phenomenon was observed in the case of the hydrate, which, so far as our knowledge goes, has never been established in the case of a hydrate, although it probably occurs in many. That is to say, when heated in the dry state to 125°, the hydrate appeared to yield the α-modification, whilst in contact with saturated solution at the same temperature the β-modification was always formed.

To examine this phenomenon more closely, the solid hydrate was kept over concentrated sulphuric acid in a vacuum at temperatures between 65° and 200°. In all these experiments it was found that the hydrate yielded the α-modification exclusively, and indeed both below and above 93·5°.

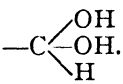
It will at once be seen that this observation enables us to consider the milk-sugar problem from another point of view, as a result of which all the phenomena hitherto observed in the system water—milk sugar can very simply be explained.

Hudson had already assumed that the following transformation takes place:—

$$S_H \rightarrow S_\beta + L.$$

Here expression is naturally given to the idea that a hydrate of the β-modification is in question.

Hudson further assumed that the water in the hydrate is combined in the following manner:—



But from this it follows that the hydrate might, with equal justification, have been called a hydrate of the α- as of the β-modification, for the stereochemical difference which is assumed between the α-modification and the β-modification in regard to the end carbon atom,[1] namely

$$\underset{\wedge}{H \cdot C \cdot OH} \text{ and } \underset{\wedge}{HO \cdot C \cdot H}$$

completely disappears in the structural formula of the hydrate.

If this should really be the case, the hydrate would be neither an α- nor a β-hydrate, and it would then be absolutely incomprehensible why the dry hydrate always yields α-anhydride even above 93°, whilst the moist hydrate at temperatures above 93° is converted into β-anhydride.

Hudson's assumption must therefore fall to the ground. The hydrate is undoubtedly a hydrate of either the α- or the β-anhydrous modification.

The experiments carried out by Gillis, according to which the hydrate in the dry state always yielded α-anhydride both below and also above 93°, point to the fact that milk-sugar hydrate is a hydrate of the α-modification.

(c) *The hydrate exhibits a transition-dehydration point.*

The above conclusion, in fact, places the problem in another light. The transformation point at 93·5° is not an ordinary transition point, for the following change take place there:—

$$\alpha\text{-hydrate} \rightarrow \beta\text{-anhydride} + L.$$

If we were dealing with an ordinary transformation point the reaction would be

$$\alpha\text{-hydrate} \rightarrow \alpha\text{-anhydride} + L.$$

Thus, in the case of milk sugar, dehydration is combined with a change of the α-modification into the β-modification.

Proof is thus given here of a change which hitherto has never been observed. To distinguish this peculiarity we shall here speak of a *transition-dehydration point.*

[1] *Journ. Amer. Chem. Soc.*, **31**, 66 (1909).

(d) *The system water—milk sugar must be resolved into a pseudo-ternary one. The derivation of the isothermal diagram.*

The above-mentioned result must find expression in our representation of the system under consideration here. Data were collected for the construction of the solubility isotherms of the system H_2O—α milk sugar—β milk sugar for a temperature below 93·5°.

The points *a* and *b* in Fig. 178 indicate the initial solubilities of α-hydrate and β-anhydride at a definite temperature which was lower than 93·5°. These were determined by Hudson.[1]

The three-phase equilibrium

$$\alpha_{aq_M} + \beta + L,^*$$

however, was not determined; it was ascertained by Gillis, who set out from these three phases and heated them for an hour in a bath at the required temperature, shaking them violently during the heating process. A portion of the liquid was then filtered at the same temperature and analysed. The total concentration, *i.e.* the total quantity of milk sugar, was found by evaporating to dryness and weighing the residue. In this way, therefore, the line parallel to the axis α β on which the point D lies was found. Now, in order that the position of the point D on this line might be indicated, a second quantity was filtered and then passed through a glass tube, bent twice at right angles, and surrounded throughout its length by a cooling jacket through which flowed water at the same temperature as the bath. Immediately after leaving this tube the solution was collected in ice in order to fix the inner equilibrium. By determining the initial and the end rotation of this solution the ratio $\frac{\beta}{\alpha}$ was found.[2]

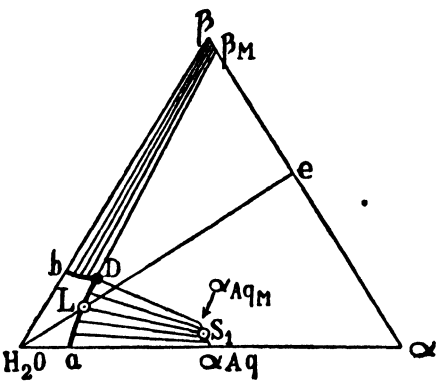


FIG. 178.

In the determination of the end rotation a little solid sodium

[1] *Journ. Amer. Chem. Soc.* **30**, 1767 (1908).

* The letter M indicates that the solid is a mixed crystal phase.

[2] The relationship between the initial rotation r_0 and the end rotation r_∞ was determined, at a given temperature, for mixtures of hydrate and β-anhydride of different compositions. Graphic representation yielded a straight line, thus permitting the calculation from $\frac{r_0}{r_\infty}$ not only of the ratio $\frac{\beta}{\alpha}$, but also of the equilibrium constant.

carbonate was added, since this substance has a strong positive catalytic influence on the establishment of inner equilibrium.

It is clear that in specifying the ratio $\frac{\beta}{\alpha}$ it should not be stated that the molecules of the pseudo-components actually occur in the solution in an entirely unhydrated condition. This fraction merely indicates how great the ratio between the concentrations of α and β is, apart from the extent to which the molecules are hydrated.

Thus the point D, the point of intersection of the hydrate isotherm with the isotherm of the β-modification, was determined.

The question whether the position of the equilibrium between α and β in solutions of different total concentrations varied with the

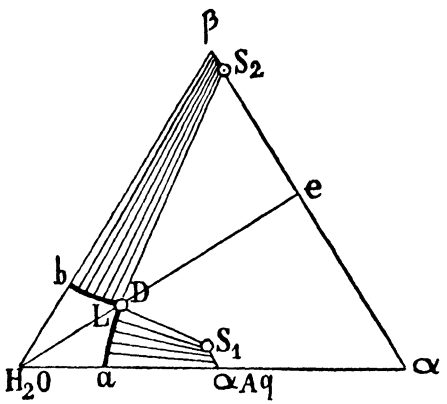


FIG. 179.

concentration had already been investigated by Hudson. It appeared that the inner equilibrium

$$\alpha \rightleftarrows \beta$$

does not change on dilution, as might be expected, for we are concerned here with isomers. This inner equilibrium in the liquid can therefore be indicated in our triangle by a straight line having its origin at the point H_2O.

Since α_{aq} has been proved to be the stable solid phase in the system water—milk-sugar below 93·5°, the line for the inner equilibrium in the solution will cut the α_{aq}-isotherm. This point of intersection was determined by shaking the hydrate for two or three days with a saturated solution, at the constant temperature chosen. By analysing the solution—this was carried out in the same way as in the case of the solution D—the point L on the isotherm of α_{aq} was found. The phases S_1 and L and the inner equilibrium line H_2O—L then indicate the binary trimolecular system at the temperature chosen. From Fig. 178 it is clear that the assumption has here been made that the hydrate, just like the β pseudo-component, forms mixed crystals. This must

also be assumed for the α pseudo-component, and from this it follows that the α- and the β-*modifications*, as well as the hydrate of the α-modification, are mixed crystals in inner equilibrium.

Temperatures lower than 93·5° are under consideration here. If the exact transformation temperature is now chosen, it is clear, without further explanation, that at this temperature the inner equilibrium line $H_2O - e$ must pass through the point of intersection D, as indicated in Fig. 179, so that in the binary system S_1, S_2 and L co-exist with one another.

Similarly, it is clearly evident that at any temperature above 93·5°

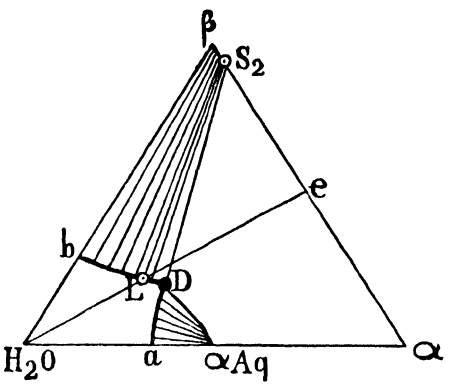


FIG. 180.

the inner equilibrium line will occupy a different position, and indeed this line will now intersect the β_M isotherm and not that for α_{aq_M}; this is shown in Fig. 180.

(e) *The experimental confirmation of the pseudo-ternary conception.*

In order to test the considerations here put forward, Gillis determined the positions of the points D and L at different temperatures with great accuracy. The investigation of the position of L for different temperatures presented no difficulties, and the heavy line in Fig. 181, which may be called the L line, indicates the position of the inner equilibrium

$$\alpha \rightleftarrows \beta$$

in the solution at various temperatures. It is seen that on raising the temperature this equilibrium is slightly displaced in the direction of the α side.

From this alone the conclusion may be drawn, that on increasing the temperature the point D will also be displaced towards the α side, and indeed this must occur to a much greater extent.

The determination of the position of the point D at temperatures below 50° was very easily carried out, because at these temperatures

the transformation of β-anhydride into α_{aq} is very slow. By adding β-anhydride from time to time it was possible to ensure that besides α_{aq}, β-anhydride was always present.

But at higher temperatures the velocity of transformation rises so rapidly, as a result of the increase in the velocity with which inner equilibrium is established, that 50° was the maximum temperature at which direct and yet accurate observations could be carried out. As Fig. 181 shows, the point D was determined at 0°, 25°, and 50°.

The diagram illustrates the displacement of this point towards the α side as the temperature is increased. This result was indeed expected. If a line is drawn through the three points obtained for D, it appears that this D line does in fact intersect the L line approximately at 93°. Thus this experiment completely confirms the assumption made.

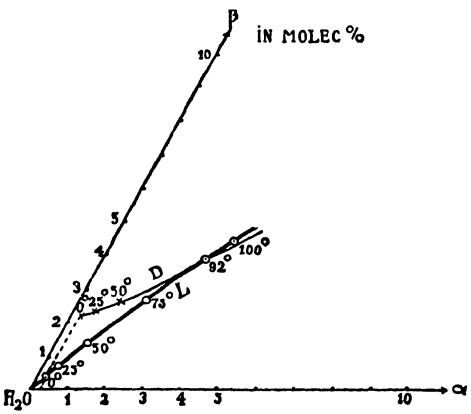


FIG. 181.

Above 93·5°, therefore, the relationship schematically indicated in Fig. 180 would exist.

After this confirmation of our conclusions we may go a little further, and employ the ternary isothermal diagram in order to make some predictions regarding the stability of the α- and β-modifications.

It is known that in the ternary system H_2O—α—β, α_M never appears as the solid phase, but always α_{aq_M}; this merely signifies that the solubility of α_M is always greater than that of α_{aq_M} and thus the solubility isotherm of α_M lies in the region in which α_{aq_M} is supersaturated.

If now the corresponding solubility isotherm for α_M at 25° is drawn in the isothermal diagram, two possibilities arise, which are represented in Figs. 182 and 183.

The line *a* D is the solubility isotherm of the α-hydrate and *a'* D' that of the α-anhydride. The point D' therefore indicates the solution which would co-exist in the metastable state with the solid phase α_M and β_M.

Let us first consider Fig. 182. Here the L-line, *i.e.* the line

H_2O—*e*, relating to the inner equilibrium in the solution, intersects the α_M isotherm in L′, and therefore below D′. Whilst α_{aq_M} is the stable solid phase in the binary system, in consequence of the non-appearance

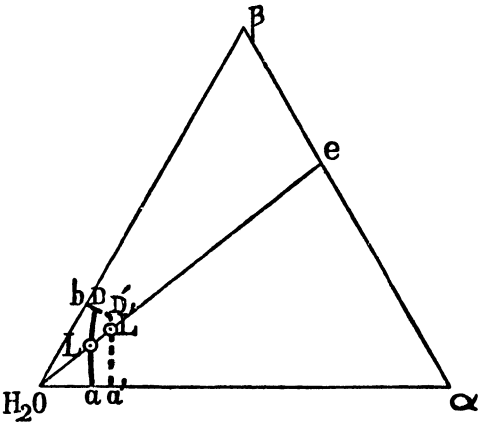


FIG. 182.

of this solid hydrate, the anhydride α_M would be the stable solid phase, β_M being the metastable phase.

We have seen that as the temperature is increased, the point D approaches ever nearer to the line H_2O—*e*, reaching it at 93·5° and passing beyond it at higher temperatures. It is clear that the point D′

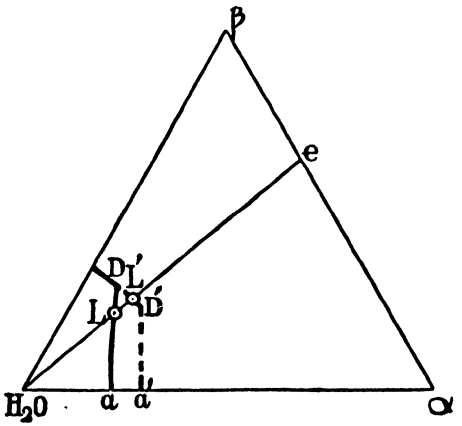


FIG. 183.

will move in a similar way. Furthermore, since in comparison with D this point corresponds to a higher value of $\frac{(\alpha)}{(\beta)}$, it will reach the line

H_2O—*e* when D still lies above this line, or, in other words: In the system in which solid hydrate is not formed the transition

$$\alpha_M \rightarrow \beta_M$$

will appear at a temperature *below* that of the transformation

$$\alpha_{aq_M} \rightarrow \beta_M + L.$$

Above the temperature of the transition equilibrium

$$\alpha_M \rightleftarrows \beta_M$$

the position of the isotherm would be as indicated in Fig. 183. In systems in which solid α-hydrate is not formed, β_M will then be the stable modification.

From these considerations it follows therefore that in order that a transition equilibrium between α_M and β_M may appear, the temperature must be below 93·5°.

To ascertain whether this is actually the case, the investigation of milk sugar in the presence of a solvent with which it does not combine is necessary.

(f) *The pseudo-ternary* T X *diagram.*

Fig. 184 is obtained as the pseudo-ternary T X diagram. In the plane relating to α-anhydride—H_2O the initial solubility from 0° to 25° is known as a result of Hudson's work; in addition, the eutectic *d* is known to lie at −0·3°, it contains 0·27 mols. per cent. α.

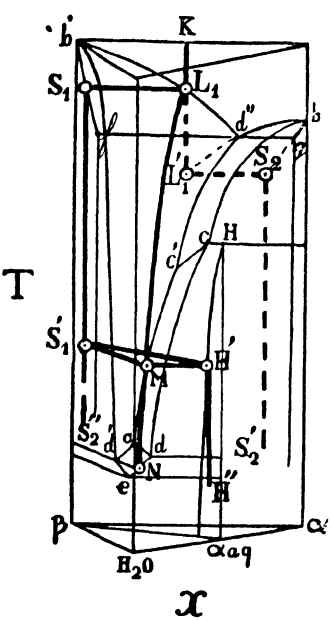


FIG. 184.

Gillis found the melting point of α to be 222·8° and that of α_{aq} to be 201·6°. As regards the *real* transformation point of α_{aq}, *i.e.*, the point at which the transformation

$$\alpha_{aq} \rightarrow \alpha + L$$

takes place under a pressure of one atmosphere, it may be stated that this lies above 100°, for when Gillis placed α-anhydride in a saturated solution of milk sugar at 100° a distinct evolution of heat occurred, thus proving that hydration of solid α-anhydride still takes place even at this temperature.

If instead of a saturated milk-sugar solution pure water at 100° is taken, this evolution of heat is no longer observed, because under these circumstances the rate of solution is very great and the negative heat of solution completely masks the smaller positive heat of hydration.

In the plane relating to β-anhydride—water the initial solubility at 0° is known, the eutectic *d'* lies at 2·3° and contains 2·2 mols. per cent. β, the melting point of water, *a*, is known, and *b'*, the melting point of the β-anhydride, is situated at 252·2°.

In the α-anhydride—β-anhydride plane only the melting points *b* and *b'* are known, but it is assumed that this binary system contains a eutectic.

The fusion surfaces of the space diagram are clearly recognisable. As a result of the intersection of the fusion or solubility surfaces a line of the three-phase equilibrium appears, a so-called ternary fusion line, and at the points where such lines again meet one another, three lines always simultaneously coming together, the liquid phase of a four-phase equilibrium is situated.

In this space diagram there are two such four-phase equilibria. The liquid phase of one lies at C'; this belongs to the four-phase equilibrium

$$S_{\alpha_{aq}} + S_{\alpha} + S_{\beta} + L,$$

situated at 93·5°, and the liquid of the other, that is to say the liquid *e* of the ternary eutectic

$$S_{\alpha_{aq}} + S_{\beta} + S_{H_2O} + L$$

which was found to be situated at — 2·6°.

(g) *The* T X *diagram for the binary system.*

From the pseudo-ternary diagram discussed here, that of the binary system is obtained by causing the inner equilibrium plane to pass through the axis of the component H_2O. This plane intersects the fusion surface of the β-anhydride in the line L_1 M. From this it follows that in the binary system water—milk sugar (in inner equilibrium) saturated solutions co-exist in stable equilibrium with β-anhydride mixed crystals situated on $S_1 S_1'$. But at the point M a change appears; below this point the inner equilibrium plane referred to does not intersect the fusion surface of the β-anhydride mixed crystals, but the fusion surface for α_{aq_M}. But from this it appears that this point represents the liquid of the remarkable dehydration transition equilibrium previously noticed, which lies at 93·5° and at which the transformation

$$S_{\beta} + L \rightarrow S_{\alpha_{aq}}$$

takes place with absorption of heat. The three-phase equilibrium prevailing here is denoted by the points S'_1 M H'.

Besides intersecting the fusion surface for S_{β_M} and $S_{\alpha_{aq_M}}$ the equilibrium surface under discussion also intersects the fusion surface relating to ice, and thus the line of intersection *a* N indicates the fusion line of ice in the binary system. This fusion line and that of the hydrate intersect one another in the binary system at N, which corresponds to —0·65° and to about 0·6 mols. per cent. milk sugar. This intersection takes place, of course, at the point where the inner equilibrium surface meets the eutectic line *d e* of the pseudo-binary

system. This point of intersection N thus corresponds to the eutectic liquid of the binary system.

It may be pointed out here that the final solubility curves for $S_{\alpha_{aq_M}}$ and S_{β_M} from 0° to 70°, and the projections of these curves on the bottom plane over a range of temperature from 0° to 100°, makes clear the form of the surface relating to the inner equilibrium.

(h) *The determination of the inner equilibrium in the solid state.*

We have not as yet dealt with the internal condition of the solid phases.

If it had been possible to determine the fusion diagram for the pseudo-binary system α- — β-milk sugar it would have been less difficult to learn something about the nature of the solid phases. Since, however, decomposition gives rise to considerable disturbance at high temperatures, another method had to be adopted.

The β-modification was heated for a long time to various temperatures between 93·5° and 200°, and was then suddenly plunged into ice water, after which the initial and end rotations were determined.

This attempt to learn something concerning the change in composition of the β-modification with increase of temperature had no result, however, for here also decomposition gave rise to considerable disturbance.

(i) *Theory of Mutarotation.*

The discussion of the system water—milk sugar cannot be concluded without reference being made to the fact that the results which have been obtained lead to a Theory of Mutarotation which is essentially different from Hudson's theory.

According to the explanation given here of the system water—milk sugar, this system must be looked upon as pseudo-ternary, water being one component and the α- and β-modifications of milk sugar the two pseudo-components. From this it immediately follows that these different molecular species will occur side by side in the liquid phase, in which the phenomenon of mutarotation must take place. Further, it is known that the solid hydrate, namely α_{aq}, also appears.

But, as has already been shown, other phenomena point to the existence of this hydrate in solution.

Now, from the possibility of the combination of α-anhydride with water, forming a hydrate, it is but a step to assume that this is also true of the β-modification. The fact that this hydrate is not known in the solid state is not evidence against the correctness of this assumption, such a non-existence in the solid state merely indicates that the solubility of the hydrate β_{aq} must be greater than that of the β-anhydride, whilst in the case of the other pseudo-component the position is just the reverse.

In the case of maltose,[1] a substance which also exhibits mutarota-

[1] *Journ. Amer. Chem. Soc.*, **31**, 76 (1909); **32**, 894 (1910).

tion, β_{aq} is known in the solid state, but α_{aq} is not. Here, therefore, we have just the reverse of that which probably occurs in the case of milk sugar.

It is assumed, therefore, that in the aqueous solution the following equilibrium occurs:—

$$\begin{array}{l} \alpha + H_2O \rightleftarrows \alpha_{aq} \\ \uparrow\downarrow \\ \beta + H_2O \rightleftarrows \beta_{aq} \end{array}$$

Of the changes indicated here, it would appear from the experiments which have been described that the equilibrium

$$\alpha + H_2O \rightleftarrows \alpha_{aq}$$

is established with great velocity. Since now the α and β pseudo-components, apart from optical rotation, differ from one another but slightly, the equilibrium

$$\beta + H_2O \rightleftarrows \beta_{aq}$$

will also most probably be established rapidly, as in the case of maltose.

Thus the conclusion is reached that the hydration equilibria for the pseudo-components are established rapidly, and since mutarotation cannot be caused by rapid transformation, the origin of this phenomenon must be sought in the internal changes

$$\begin{array}{c} \alpha \\ \uparrow\downarrow \\ \beta \end{array} \quad \text{and} \quad \begin{array}{c} \alpha_{aq} \\ \uparrow\downarrow \\ \beta_{aq} \end{array}$$

These reactions, which are intramolecular, must therefore take place *slowly*.

26. The Investigation of the Binary Pseudo-ternary System Monobenzoyl Camphor in the Presence of a Solvent.

Although, as we have seen, the enol- and keto-pseudo-components of monobenzoyl camphor pass the one into the other with great velocity at temperatures above 80°, yet, fortunately, the transformation velocity at ordinary temperatures is so small, that in the absence of positive catalysts these pseudo-components, even in the dissolved state, undergo no marked change in the course of several hours.

This is especially fortunate, as it places us in a position to look upon the system monobenzoyl camphor as a ternary system, and as such to study it.

In addition, it was well known, as has also already been mentioned, that piperidine exerts a powerful positive catalytic influence on the establishment of inner equilibrium between the enol- and keto-pseudo-components, so that there was also the possibility of investigating the binary system, and of defining its position in the pseudo-ternary system.

Consequently we should thus be in a position to test the conclusions developed in the theoretical part with regard to this case; this is either not at all or only partially possible where systems composed of inorganic

allotropic substances in the presence of solvents are concerned, because of the rapidity with which inner equilibrium is established in such systems.

Further, it should be possible to submit to examination both van't Hoff's formula[1] and the general formula developed by the present author.[2]

Finally, the author's hypothesis concerning the influence of the solvent on the equilibrium position could now also be investigated.

Vixseboxse[3] has undertaken this important work. He has investigated the behaviour of monobenzoyl camphor in the solvents alcohol, acetone and toluene at three temperatures, namely 5°, 10° and 17°. For this purpose a new method of analysis had first of all

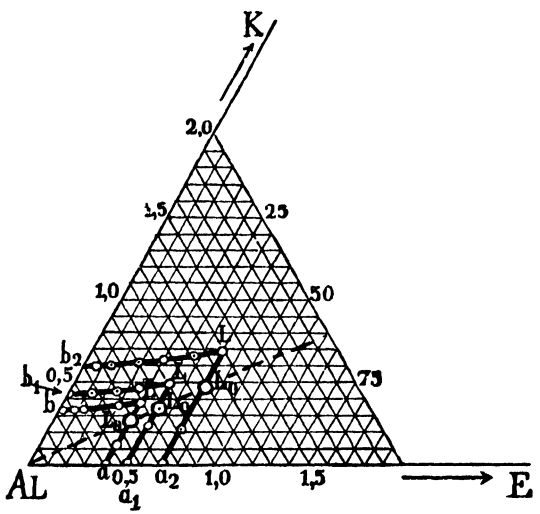


FIG. 185.

to be worked out, for the titration method of Kurt H. Meyer[4] proved to be much too inaccurate. On examination this method was found to be subject to an error of 3 per cent.

Since the pseudo-components of monobenzol camphor are optically active and exhibit a great difference in specific rotation, a method of analysis based on this optical behaviour naturally suggested itself.

In working out such a method the following points had obviously to be ascertained :—

1. The influence of the concentration of the dissolved substance on the rotation of the plane of polarisation.

2. The variation of the rotation of a solution of given total concentration with the ratio enol/keto.

On investigation, the answer to the first question was found to

[1] *Vorlesungen*, 1, 219. [2] *Zeitschr. f. physik. Chemie*, **92**, 35 (1916).
[3] *Dissertation*, Amsterdam (1919). [4] *Lieb. Ann.*, **380**, 227 (1911).

be, that for all three solvents, when the rotation is regarded as a function of the concentration of the dissolved active pseudo-component, it is represented graphically by a straight line.

The answer to the second question was also quite simple; it was found that the rotation of a solution of enol- + keto- is exactly the sum of the two rotations which these two substances would separately exert in solutions of corresponding concentrations. Hence it follows, therefore, that as regards rotation of the plane of polarisation, the two pseudo-components are without influence on one another.

The influence of temperature on the rotation was proved to be extremely slight; in general the rotation decreases with rise of temperature; this effect, however, is always very small.

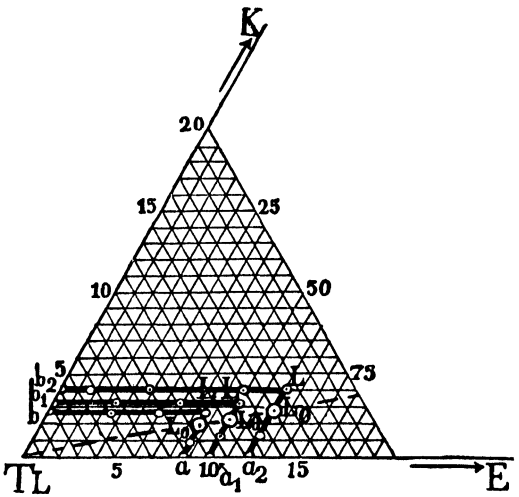


FIG. 186.

In order that the position of the binary system, *i.e.* monobenzoyl camphor in inner equilibrium and solvent, might be determined, the rotations of solutions of different concentrations up to saturation were determined at the three temperatures mentioned, after the enol- and keto-pseudo-components had become established in inner equilibrium. When the rotation was expressed as a function of the total concentration, naturally a straight line was again obtained, and since the temperature effect is so small, for the same solvent the lines corresponding to 5°, 10° and 17° practically coincide.

After this method of exact analysis had been developed, the solubility isotherms of the enol- and keto-pseudo-components were next determined at 5°, 10° and 17° in the three solvents mentioned, and then, at each of these three temperatures the position of the inner equilibrium in each of the three solvents was determined for different total concentrations.

The result is shown in Figs. 185, 186 and 187. Thus it was proved

that the connection between the pseudo-ternary and the binary isothermal diagrams was entirely in agreement with expectation, and that the inner equilibrium line intersected the solubility isotherm of the enol- mixed crystals. This was found to hold good at each of the three temperatures 5°, 10° and 17°, at which, consequently, the enolic form is the stable phase. The position of the inner equilibrium between the isomeric molecular species in the various solvents was, as has already been mentioned, found to be independent of the concentration right up to the saturation point, and it was also found that within the temperature range 5°–17° change of temperature did not appreciably affect it. The heat effect of the chemical reaction is therefore very small.

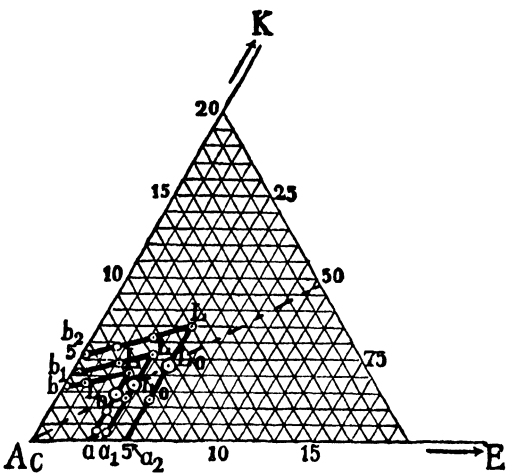


FIG. 187.

Further, the solubility isotherm for the solvent toluene is shown to occupy an ideal position. This is no longer true of the alcohol isotherm, at any rate so far as the solubility isotherm of the keto-phase is concerned, for a clear deviation from the ideal position has been established here. Similar relationships to those found in the case of alcohol hold good for acetone; here, however, the deviation of the solubility isotherm from the ideal position is such as to suggest that a reaction occurs between the keto-pseudo-component and the solvent.

(a) *Examination of van't Hoff's formula.*

If van't Hoff's formula

$$\frac{C_E}{C_K} = \frac{L_E}{L_K} \cdot G$$

is now examined, we get

Solvent.	$\left(\frac{L_E}{L_K}\right)_{5°}$.	$\left(\frac{L_E}{L_K}\right)_{10°}$.	$\left(\frac{L_E}{L_K}\right)_{17°}$.	$\frac{C_E}{C_K}$.	$G_{5°}$.	$G_{10°}$.	$G_{17°}$.
Alcohol . .	1·242	1·238	1·241	1·56	1·25	1·26	1·26
Acetone . .	0·882	0·878	0·942	1·08	1·22	1·23	1·15
Toluene . .	3·185	3·185	2·988	4·56	1·43	1·46	1·53

This table shows that the quantity G is not constant, as according to van't Hoff's formula it should be. This, however, is not surprising, for the solubility isotherm only occupies an ideal position in the case of toluene.

(b) *Examination of the general formula.*[1]

Turning now to the formula

$$\frac{x_E}{x_K} = \frac{X_E}{X_K} f_1$$

we obtain

Solvent.	$\left(\frac{X_E}{X_K}\right)_{5°}$.	$\left(\frac{X_E}{X_K}\right)_{10°}$.	$\left(\frac{X_E}{X_K}\right)_{17°}$.	$\frac{x_E}{x_K}$.	$(f_1)_{5°}$.	$(f_1)_{10°}$.	$(f_1)_{17°}$.
Alcohol . .	1·08	1·06	1·04	1·56	1·44	1·47	1·50
Acetone . .	0·754	0·74	0·724	1·08	1·44	1·46	1·50
Toluene . .	3·17	3·08	4·00	4·56	1·44	1·48	1·52

It is now evident that the factor f_1, for the same temperature, is a constant quantity for the three different solvents.

It has already been pointed out in the theoretical portion of this volume that the temperature at which $f_1 = 1$ is the transition temperature.

The last table shows that f_1 diminishes as the temperature falls, and the temperature at which $f_1 = 1$ may now be approximately determined. Since f_1 diminishes by 0·06 during a fall of temperature at 12°, it may be concluded that if the temperature were reduced 100° f_1 would fall to 1. The transition temperature would thus be − 83°, assuming this extrapolation to be permissible. But since this seems very debatable, the only conclusion that will be drawn from this consideration is that the transition temperature is at least very low.

27. Examination of the Hypothesis: The Influence of the Solvent on the Position of the Inner Equilibrium in the Solution depends on the Difference in the Heats of Solution of the Reacting Constituents in the Various Solvents.[2]

Monobenzoyl camphor is a very suitable substance with which to test experimentally the hypothesis developed on page 82 *et seq.* of the

[1] Smits, *Versl. Kon. Akad. v. Wet.*, Amsterdam, **24**, 283 and 300 (1915); *Zeitschr. f. physik. Chemie*, **92**, 34 (1916).

[2] *Ibid.*, Amsterdam, **25**, 641 (1916).

theoretical part, to account for the displacement of inner equilibrium by the solvent, since the positions of the inner equilibrium in the three solvents alcohol, acetone and toluene differ rather widely.

As has been pointed out, before the hypothesis referred to can be tested, the heats of solution of the enol- and the keto- form must be determined in the various solvents. Vixseboxse obtained the following results :—

Solvent.	Mol. heat of solution of the keto- form.	Mol. heat of solution of the enol- form.
Alcohol . . .	− 5770 cal. − 5740 ,,	− 6190 cal. − 6140 ,,
Toluene . . .	− 4890 ,, − 4850 ,, − 4870 ,,	− 4680 ,, − 4680 ,,
Acetone . . .	− 4920 ,, − 4900 ,, − 4930 ,,	− 5480 ,, − 5460 ,,

From these the following mean values are obtained :—

(Q_K) alcohol $= -5750$ cals.; (Q_E) alcohol $= -6170$ cals.
(Q_K) toluene $= -4870$ cals.; (Q_E) toulene $= -4680$ cals.
(Q_K) acetone $= -4920$ cals.; (Q_E) acetone $= -5470$ cals.

With the help of these experimental data we can now ascertain whether the altered position of the inner equilibrium in the various solvents is in fact explained by the different heats of solution of the reacting constituents in these different solvents.

In the three solvents investigated the following values were found for the equilibrium constant :—

$$K_{\text{alcohol}} = \frac{(\text{enol})}{(\text{keto})} = \frac{61}{39}$$

$$K_{\text{toluene}} = \text{,,} = \frac{82}{18}$$

$$K_{\text{acetone}} = \text{,,} = \frac{52}{48}.$$

Writing now

$$K_{\text{alcohol}} = K_1,\ K_{\text{toluene}} = K_2 \text{ and } K_{\text{acetone}} = K_3,$$

and denoting the heat of mixture of liquid keto with the solvent alcohol by Q_{K_1} and the heat of solution by $Q_{K_{1_0}}$, etc., we may write :—

$$\ln K_1 = \frac{Q}{RT} + C_1 \quad . \quad . \quad . \quad . \quad (1)$$

and

$$Q = -Q_{K_1} + Q_R + Q_{E_1}$$

where Q_R is the pure heat of reaction.

Since now from the relationships

$$Q_{K_{1_0}} = Q_{K_s} + Q_{K_1}$$

and

$$Q_{E_{1_0}} = Q_{E_s} + Q_{E_1}$$

where Q_{K_s} and Q_{E_s} are heats of fusion, we obtain

$$- Q_{K_1} + Q_{E_1} = - Q_{K_{1_0}} + Q_{E_{1_0}} + Q_R,$$

so that

$$Q = - Q_{K_{1_0}} + 2Q_R + Q_{E_{1_0}}$$

and

$$\ln K_1 = \frac{- Q_{K_{1_0}} + Q_{E_{1_0}}}{RT} + \frac{2Q_R}{RT} + C_I \quad . \quad . \quad (2)$$

According to the hypothesis which has been put forward, C_I is independent of the solvent, and consequently this is also true for the term

$$\left(\frac{2Q_R}{RT} + C_I\right)$$

since this only contains quantities which are independent of the solvent. At constant temperature, therefore, this term is a constant. This constant will be designated by C_T.

We can then write

$$\ln K_I = \frac{- Q_{K_{I_0}} + Q_{E_{I_0}}}{RT} + C_T \quad . \quad . \quad . \quad (3)$$

Introducing into this equation the values found for the heats of solution, and likewise the values for the inner equilibrium constant, we obtain

$$\ln \frac{61}{39} = \frac{5750 - 6170}{1{\cdot}985 \times 290} + C_T.$$

This equation then leads to the determination of the value of C_T.

For the solvent alcohol this is

$$C_T = 1{\cdot}176.$$

Similar calculations for the two other solvents toluene and acetone give

$$\ln \frac{82}{18} = \frac{4870 - 4680}{1{\cdot}985 \times 295} + C_T;$$

consequently for toluene

$$C_T = 1{\cdot}186$$

and

$$\ln \frac{52}{48} = \frac{4920 - 5470}{1{\cdot}985 \times 290} + C_T,$$

whence for acetone

$$C_T = 1{\cdot}035.$$

These results completely confirm the hypothesis in regard to the constant value of C_T for alcohol and toluene, whilst in the case of acetone a deviation is found to occur. This deviation was to be expected; the position of the isotherm of the keto- form in this solvent has already led to the conclusion that in this solvent a chemical reaction very probably occurs between the keto- form and the solvent.

The fact that no compound appears as the solid phase naturally does not constitute evidence against this view.

The value of C_T has now been calculated from the heats of solution, and also from the position of the homogeneous equilibrium in the solution. To determine how far it is possible, on the ground of this hypothesis, to calculate the position of the inner equilibrium in the solution from the heats of solution we can now proceed in the reverse direction.

For this purpose the mean value of C_T obtained for the solvents alcohol and toluene is taken, namely 1·181.

In this way the following values are then calculated :—

$$K_{\text{alcohol}} = \frac{81{\cdot}9}{18{\cdot}1}, \text{ whilst the value found was } \frac{82}{18},$$

and

$$K_{\text{toluene}} = \frac{61{\cdot}1}{38{\cdot}9}, \text{ whilst the value found was } \frac{61}{39}.$$

If we suppose the position of the inner equilibrium in toluene to have been determined with an accuracy of $\pm$ 0·5 per cent. and in alcohol $\pm$ 0·8 per cent., the agreement between the calculated and the observed values of the equilibrium constant can, according to the results obtained, be regarded as complete.

These results show, therefore, that the difference in position of the inner equilibrium in various solvents is, in fact, due to the difference between the total heat effects, or, in other words, it is to be ascribed to the difference in the heats of solution of the reacting constituents in the various solvents. Consequently in this case entropy plays no part at all.

These considerations are naturally applicable not only to inner equilibria in different solvents, but quite generally to every homogeneous equilibrium in different solvents. It is highly desirable, therefore, that the examination of this hypothesis, which has been carried out here, should also be undertaken for other cases. But in doing so it must always be borne in mind that the hypothesis excludes those cases in which the dissolved substance enters into chemical reaction with the solvent.

The appearance of a chemical reaction was the probable cause, as has already repeatedly been stated, of the deviation observed in Vixseboxse's experiments with acetone. Although we know that no agreement is obtained with acetone as solvent, it is nevertheless interesting to carry out with this solvent calculations similar to those already made for alcohol and toluene.

In this case we obtain

$$K_{\text{acetone}} \frac{55{\cdot}6}{44{\cdot}4}, \text{ whilst the value found was } \frac{52}{48}.$$

Consequently, although chemical influence is here very clearly noticeable, the equilibrium constant can still be determined to 86·4 per cent. by means of the energy term.

28. The Unary Trimolecular System Formed by the Aldehyde of Acetic Acid.

(a) *The bimolecular or pseudo-binary conception.*

The classical example of a unary trimolecular system will now be discussed; that is to say, the system to which the aldehyde of acetic acid gives rise.

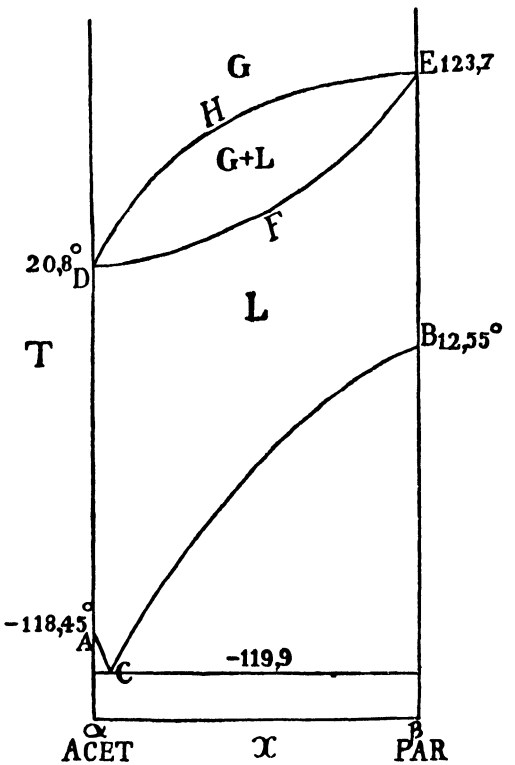


FIG. 188.

Although the three pseudo-components, acetaldehyde, paraldehyde and metaldehyde had long been known, Hollmann,[1] in his interesting

[1] *Zeitschr. f. physik. Chemie*, **43**, 157 (1903).

investigation, adopted the standpoint that the pseudo-system is a binary one.

In his opinion it is permissible to proceed from acetaldehyde and paraldehyde only, since in most phases of the unary system metaldehyde only occurs in small quantities.

As it has always been found expedient here to present the historical development of the problem, in the first place Hollmann's researches will be dealt with, and his results discussed.

It is well known that in the absence of catalysts and at temperatures which are not too high acetaldehyde and paraldehyde cannot be converted the one into the other, consequently the pseudo-system may easily be defined. Hollmann first of all studied the T X diagram at a pressure of about one atmosphere (Fig. 118).

He obtained for

D — the boiling point of acetaldehyde, 20·8°,

and for

E — the boiling point of paraldehyde, 123·7°.

Acetaldehyde is much more volatile than paraldehyde; this is in harmony with the fact that the vapour line D H E is far removed from the liquid line D F E. The boiling-point diagram determined by Hollman holds good for a pressure of 756 mms. Hg.

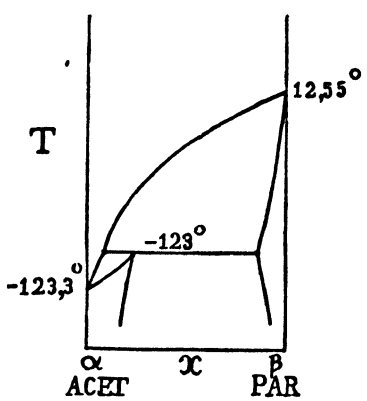


FIG. 189.

In addition, the solidifying temperature of acetaldehyde was found to be — 118·45° and that of paraldehyde 12·55°.

Furthermore, Hollmann found—this is also shown in Fig. 188—that the fusion diagram contains a eutectic. It may, however, easily be understood that the appearance of a eutectic is extremely improbable here, for if the solidifying point of acetaldehyde were really lowered by addition of paraldehyde, the outcome would be that the liquid phase co-existing with solid acetaldehyde or mixed crystals could contain more complicated molecules than the solid phase.

The probability of this occurring is very small, and it has indeed been shown that on this point Hollmann was mistaken,[1] and that the fusion line has no eutectic (see Fig. 189). The solidifying point of acetaldehyde was found to be — 123·3° and the temperature of the three-phase equilibrium — 123°.

At the same time this result naturally proved the solid phases to be mixed crystals.

[1] Smits, *de Leeuw, Zeitschr. f. physik. Chemie*, 77, 269 (1911).

Although at higher temperatures and in the absence of catalysts a slow change takes place, Hollmann succeeded, by working rapidly, in determining the plait-point curve. After observing the critical temperature the composition was found by determining the boiling point, the state having been fixed by sudden cooling. The critical temperature of acetaldehyde was found to be 188° and that of paraldehyde 290°, whilst the critical temperatures of mixtures lay in between these values.

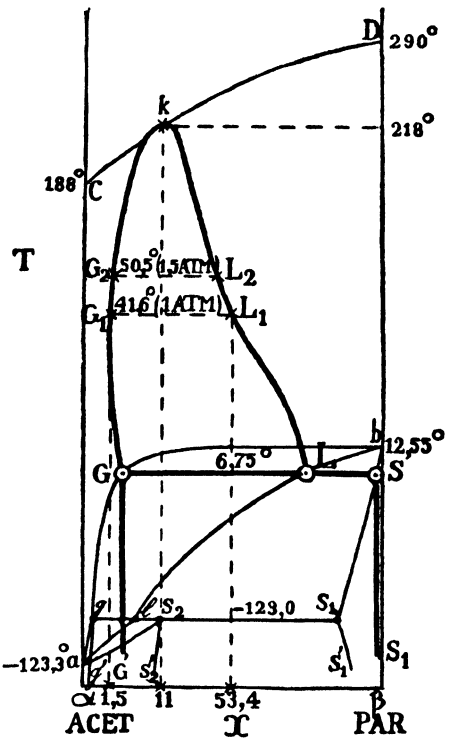


FIG. 190.

The projection of the three-phase areas and of the plait-point curve on the T X plane yields a diagram such as is shown in Fig. 190.

In this figure the position of the unary system may now be indicated, always assuming, naturally, that the system contains only two molecular species. The position of the unary system was found by Hollmann in this way: a little sulphuric acid was added to paraldehyde at the ordinary temperature, whereupon a vigorous endothermic change

paraldehyde → acetaldehyde — *a* cals.

immediately took place, as a result of which so much heat was absorbed that the liquid was cooled to its solidifying point. Solidification did not,

however, take place at 12·55°, but at a lower temperature depending on the quantity of acetaldehyde formed. As paraldehyde separated out the solidifying temperature fell to 6·75° and then remained constant. This is the unary solidifying temperature, for if the tube containing the solidifying mass is placed in a bath having a temperature of 0°, the temperature falls no further, but remains unchanged until the whole has become solid and has therefore been converted into paraldehyde. During the solidification at 6·75°, therefore, the following reaction :—

$$\text{acetaldehyde} \rightarrow \text{paraldehyde} + a \text{ cals.}$$

has taken place in the liquid, whereby the paraldehyde which was removed in the above-mentioned reaction has been reproduced. In order to check the position of the unary solidifying point the following method of procedure was adopted.

The paraldehyde produced in the preceding experiment, and containing therefore a trace of H_2SO_4, was fused and then rapidly cooled to 6°. At this temperature, therefore, the liquid was under-cooled. Crystallisation now suddenly occurred and the temperature rose again to 6·75°, where it remained throughout the crystallisation.

Naturally the same unary melting point must be found when acetaldehyde is made the starting point. The vessel used in the previous experiment was emptied, placed in melting ice, and then filled with acetaldehyde. Sufficient H_2SO_4 from the previous experiment remained by accident on the rim of the vessel to bring about the rapid transformation of the acetaldehyde. Indeed the reaction proceeded so vigorously that the temperature rose to 30° in one minute. On cooling rapidly, the inner equilibrium was unable to follow the temperature and solidification of paraldehyde began at 2·8°; during this separation, however, the temperature rose to 6·75° and then remained constant.

The position of the unary solidifying point was thus fixed with certainty at 6·75°, and this corresponds to a composition of 88·3 mols. per cent. paraldehyde. In order to ascertain the shape of the line relating to the inner equilibrium in the liquid phase the unary boiling point under a pressure of 761 mms. Hg. and the unary critical point were also determined.

The boiling point was found to be 41·6°; from the pseudo-binary boiling-point diagram the point L_1 thus corresponds to 53·4 mols. per cent. paraldehyde.

By condensing the vapour, and determining the boiling point of the liquid so obtained, the composition of the co-existing vapour G_1 was found to be 1·5 mols. per cent. paraldehyde.

This result provides the wished-for explanation of a long-known, interesting, but hitherto unexplained phenomenon.

If a trace of H_2SO_4 is added to paraldehyde, or to any mixture whatever of paraldehyde and acetaldehyde, the liquid will boil under a pressure of 716 mms. Hg. at 41·6°; in so doing liquid containing 53·4 mols. per cent. paraldehyde yields a vapour which only contains 1·5 mols. per cent. paraldehyde. Thus a distillate is obtained which

is almost pure acetaldehyde, a fact which has been known for many years.

The result of one of Turbaba's [1] experiments will now also be utilised to determine an additional point on the unary liquid line. According to this experiment the unary boiling point under a pressure of 1·5 atmospheres amounts to 50·5°. This temperature corresponds to a content of 39·4 mols. per cent. paraldehyde. This observation yields a third point on the unary liquid line, denoted by L_2.

Finally, Hollmann found the unary critical point to lie at 218°, the composition being 11 mols. per cent. paraldehyde. This critical point is naturally situated on the plait-point curve for the pseudo-system and it furnishes a fourth point on the unary liquid line. At this critical point *k* the vapour line and the liquid line pass continuously the one into the other. The vapour line thus runs from G through G_1 towards *k*. Below the unary solidifying point mixed crystals rich in paraldehyde and vapour naturally co-exist, both being in inner equilibrium. These phases are indicated in the diagram by the lines $S S_1$ and $G G'$. These lines are displaced by rise of temperature towards the acetaldehyde side.

(b) *The trimolecular or pseudo-ternary view.*

The problem of the connection between the various modifications of aldehyde, *i. e.* acet-, para- and metaldehyde, was not solved, however, by this method of treatment.

In the foregoing investigations the system was always looked upon as pseudo-binary, although three different molecular species were known, according to which the system must be pseudo-ternary. This was the position of the aldehyde problem when the author suggested to de Leeuw [2] that he should undertake a special study of the system acetaldehyde—alcohol.

In the course of this investigation, on cooling one of the mixtures, a large quantity of metaldehyde separated in the form of fine needles. This occurred without our having for the moment any clear idea as to the cause of the phenomenon.

The appearance of metaldehyde at this juncture added yet another to the many contradictory observations recorded in the literature with regard to the formation of metaldehyde. It suggested the investigation presently to be described,[3] as a result of which the relationship between acet-, para- and metaldehyde has been explained.

Kekulé and Zincke [4] in 1872 found that, just as in the case of paraldehyde, the formation of metaldehyde from acetaldehyde is promoted by the presence of certain substances, and they further observed that paraldehyde is produced at the ordinary and higher temperatures, whilst metaldehyde usually appears at low temperatures.

The publication of Kekulé and Zincke quoted here is distinguished

[1] Tomsk, *Verlag. d. Tech. Hochschule* (1901).
[2] *Zeitschr. f. physik. Chemie*, **77**, 284 (1911).
[3] Smits and de Leeuw, *loc. cit.*
[4] *Lieb. Ann.*, **162**, 125 (1872).

by the great accuracy with which the observed phenomena are described, and it contains several sentences the importance of which has apparently been overlooked by other workers, and which indicate very clearly the direction in which the explanation of the problem must be sought.

The sentences to which reference has been made are the following :—

"If a small quantity of hydrochloric acid gas, carbonyl chloride, sulphurous acid or dilute sulphuric acid is added to pure aldehyde and the mixture is at once cooled, preferably in a freezing mixture, fine long needles of metaldehyde separate out, which sometimes spread like a fine network through the entire liquid. Always only a small portion of the aldehyde is transformed into metaldehyde and the amount of the latter is not increased on long standing; *rather can it diminish and the metaldehyde may entirely disappear, particularly if an energetic ferment is present in fairly considerable amount, and if the temperature is not kept sufficiently low.*

"*Besides metaldehyde paraldehyde is always formed in greater or less amount.*" [1]

In addition to these observations of Kekulé and Zincke in 1872 there are a number of others which, taken together, lead to the conclusion that we are dealing here with a pseudo-ternary system, which passes when in inner equilibrium into a unary trimolecular system.

Let us once more review these observations. First in importance comes the one mentioned above, namely that metaldehyde is formed from acetaldehyde in the presence of a catalyst, paraldehyde being simultaneously produced. Connected with this is the fact that this metaldehyde may disappear again if a very active catalyst is present in sufficient quantity. Advantage has not been taken of this very remarkable result until the present day. In addition to these phenomena Tröger,[2] Friedel,[3] Orndorff and White [4] have now proved that metaldehyde passes after some time at the ordinary temperature into paraldehyde and a little acetaldehyde; we have succeeded in confirming this result. Kekulé and Zincke also observed that at 120° conversion into acetaldehyde almost exclusively occurs.

These observations may therefore be summarised as follows: At low temperatures metaldehyde can be formed from acetaldehyde, whilst the reverse reaction proceeds at higher temperatures.

The following reversible reaction has therefore been established :—

$$\text{acetaldehyde} \rightleftarrows \text{metaldehyde}.$$

Secondly, metaldehyde is known to change into paraldehyde, but the reverse action has also been observed. As a second reversible reaction we have therefore :—

$$\text{metaldehyde} \rightleftarrows \text{paraldehyde}.$$

Thirdly, it has been established that acetaldehyde can easily be

[1] The italics are ours. In a still earlier communication, Fehling, *Lieb. Ann.*, **27**, 319 (1838), likewise mentions that metaldehyde on keeping again disappears.

[2] *Ber. d. d. Chem. Ges.*, **25**, 3316 (1892).

[3] *Bull.*, **9**, 208 (1893).

[4] *Journ. Amer. Chem. Soc.*, **16**, 43 (1894).

converted into paraldehyde, and also, conversely, paraldehyde into acetaldehyde, so that the following equilibrium can also be assumed :—

$$\text{acetaldehyde} \rightleftarrows \text{paraldehyde}.$$

These three reversible reactions thus constitute one great equilibrium, which may be expressed in the following way :—

$$\begin{array}{ccc} & (1) & \\ \text{acetaldehyde} & \rightleftarrows & \text{paraldehyde} \\ & {}_{(2)}\nwarrow\searrow \quad \nearrow\swarrow_{(3)} & \\ & \text{metaldehyde} & \end{array} \qquad \ldots \quad (a)$$

It must, however, be emphasised that only two equilibria need always be assumed, namely (2) and (3), although this assumption has not much probability *per se*.

There still remains the possibility, as will be shown below, that equilibrium (1) never arises directly; that is to say, the conversion of acetaldehyde into paraldehyde takes place through metaldehyde. On this assumption the complete equilibrium would be represented thus :—

$$\underset{}{\text{acetaldehyde}} \underset{(2)}{\rightleftarrows} \underset{}{\text{metaldehyde}} \underset{(3)}{\rightleftarrows} \underset{}{\text{paraldehyde}} \quad \ldots \quad (b)$$

This also expresses the fact that acetaldehyde and paraldehyde can be in equilibrium with one another; direct transformation is, however, excluded.

But fortunately the manner in which the complete equilibrium is formed, *linear* or *triangular*, is of no importance to the further explanation; the ternary equilibrium is completely defined by two binary equilibria.

It is clear that, in general, one and the same catalyst can influence the various equilibrium reactions in different ways, from which the impression may be gained that one reaction exclusively, or at any rate mainly occurs.

This will be made clear by reference to an experiment carried out by us in the same way as those of Kekulé and Zincke.

If acetaldehyde is cooled in ice and to it very dilute H_2SO_4 is added, *e.g.* 1 mgrm. to 1000 grms. acetaldehyde, after slight shaking the formation of solid metaldehyde is observed, which does change instantaneously at room temperature, but in reality disappears again very slowly.

This disappearance can now be accelerated by the addition of more sulphuric acid.

Now this suggests that H_2SO_4 has a much more powerful catalytic action on the equilibrium reaction : acetaldehyde $\rightleftarrows$ metaldehyde than on the other two reactions, so that at 0° a very small amount of H_2SO_4 gives rise to the formation of metaldehyde.

Since metaldehyde separates here in the solid state, in the system acetaldehyde — metaldehyde the inner equilibrium must lie in the supersaturated metaldehyde region. If the two other reactions were

entirely uninfluenced by this small amount of sulphuric acid, naturally the whole would pass into solid metaldehyde, but this is not the case. An approximation to their equilibrium states is produced, though with much smaller velocity, in the other two equilibrium reactions by addition of a small quantity of H_2SO_4, and thus the formation of paraldehyde, observed by Kekulé and Zincke, which always accompanies that of metaldehyde, is explained.

It is clear without further discussion that, by means of an extremely small quantity of sulphuric acid, the establishment of inner equilibrium can be attained, but only after a *very* long time. If, however, more sulphuric acid is introduced, each equilibrium will appear more rapidly, and if the amount of sulphuric acid is infinitely large this velocity becomes so great that each of the three equilibria is instantaneously established; the three aldehydes would then always be in equilibrium with one another. Inner equilibrium will therefore prevail, and the trimolecular system will behave as a unary system. Attention will now be directed to the fact that solid metaldehyde, which is formed from acetaldehyde at 0° by the addition of a little sulphuric acid, disappears again at the same temperature on the addition of more sulphuric acid. This signifies that the unary liquid phase cannot be in equilibrium with solid metaldehyde, or, in other words, this liquid is unsaturated in respect to metaldehyde.

If a trace of H_2SO_4 is added to acetaldehyde at the *ordinary* temperature, metaldehyde does not separate out. One might surmise that inner equilibrium in the pseudo-binary system acetaldehyde—metaldehyde already exists at the ordinary temperatures in the region unsaturated with metaldehyde. This, however, is definitely not the case. In one of Fehling's[1] experiments which we have repeated, when acetaldehyde was brought into contact at ordinary temperatures with a few pieces of $CaCl_2$, after several hours crystals of metaldehyde were deposited on the calcium chloride, a very small amount of paraldehyde being simultaneously formed. This experiment does not succeed when sulphuric acid is used, for at ordinary temperatures sulphuric acid accelerates the conversion of metaldehyde and acetaldehyde into paraldehyde too strongly, whilst the influence of calcium chloride on these transformations at the ordinary temperature is extremely small, as appears from the very slight formation of paraldehyde.

When paraldehyde is left in contact with calcium chloride at ordinary temperatures, after some days a deposition of metaldehyde crystals is also observed, which, however, soon disappears. From this it appears, therefore, that the inner equilibrium in the pseudo-binary system paraldehyde—metaldehyde also lies in the region supersaturated with metaldehyde. Whilst, therefore, the inner equilibria in the two pseudo-binary systems acetaldehyde—metaldehyde and paraldehyde—metaldehyde lie in the region supersaturated with metaldehyde, it can now be demonstrated that the mixture corresponding to the complete trimolecular inner equilibrium may quite possibly be unsaturated as regards metaldehyde.

[1] *Lieb. Ann.*, **27**, 319 (1838).

The above diagram, Fig. 191, holds good for constant temperature and constant pressure. If the ordinary temperature is selected, metaldehyde alone appears as the mixed crystal phase, and *p q* then denotes the solubility isotherm of this mixed crystal phase. The points *a*, *b*, and *c* indicate the inner equilibria in the pseudo-binary systems. According to Turbaba,[1] the point *b* corresponds approximately to 16 mols. per cent. acetaldehyde and 84 mols. per cent. paraldehyde.

The points *a* and *c* lie in the region supersaturated with metaldehyde; this has also been observed. These two points will now be assumed to be fixed. To the supersaturated solution, represented by the first starting-point *a*, and which is in inner equilibrium, paraldehyde will now be added. If the inner equilibrium is not disturbed and the paraldehyde remains unchanged, the composition will move along the line *a* P, the

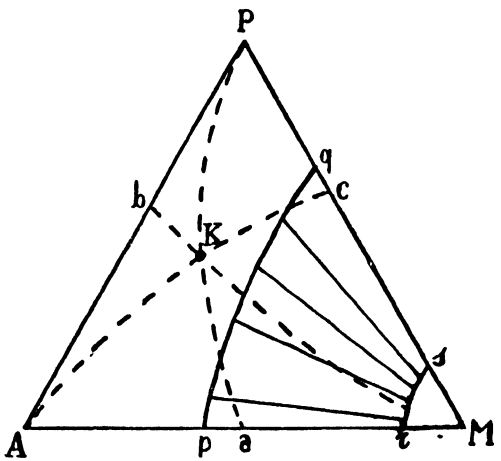


FIG. 191.

law of chemical mass-action also being supposed to remain valid. Since dilution with paraldehyde causes an increase in the amount of acetaldehyde, the line *a* P will touch the P axis at P.

If *c* is then chosen as the starting-point and the same assumptions are made, on the addition of acetaldehyde the composition makes its way along the line *c* A.

The two lines *a* P and *c* A intersect in the point K, and we shall now endeavour to ascertain the significance of this intersection. At K we have a liquid in which inner equilibrium prevails, not only between acet- and metaldehyde but between para- and metaldehyde also. The consequence of this is, that in this liquid equilibrium also prevails between acet- and paraldehyde, and the line *b* M must likewise pass through the point K.

Thus the assumption is justified that the great inner equilibrium K

[1] Tomsk, *Verlag der Techn. Hochschule* (1901): "Aus dem Gebiete der Katalyse."

lies in the unsaturated region, whilst *a* and *c* are found in the regions which are supersaturated with metaldehyde.

In this way, therefore, the observations of Kekulé and Zincke are explained in a simple manner. From these considerations it also follows immediately that any other assumption, such as those on which equations (*a*) or (*c*) rest, leads to contradiction. If, for example, the transformation is considered to be linear, and if instead of the idea actually employed the following view is adopted:—

$$\text{metaldehyde} \rightleftarrows \text{acetaldehyde} \rightleftarrows \text{paraldehyde} \quad . \quad . \quad (c)$$

the formation of solid metaldehyde from paraldehyde by means of calcium chloride cannot be explained. If the intermediate formation of acetaldehyde is necessary to the production of metaldehyde we remain in the triangle P *b* K, for the equilibrium lines may not be overstepped, and consequently the region in which metaldehyde is supersaturated is never reached.

On analogous grounds the linear transformation

$$\text{acetaldehyde} \rightleftarrows \text{paraldehyde} \rightleftarrows \text{metaldehyde} \quad . \quad . \quad (d)$$

leads to a contradiction of the observed facts. In this case the formation of solid metaldehyde from acetaldehyde by the action of a catalyst would be impossible, for only points within the triangle A *b* K could be traversed, until finally the ternary inner equilibrium was reached. A linear transformation which would not lead to such contradictions would only be possible if based on equation (*b*), but the triangular arrangement—the one subject to least constraint—is certainly more probable *per se*. It can scarcely be assumed that the most complicated substance must always appear as an intermediate state.

Since it may now be stated with certainty that the large inner equilibrium K at ordinary temperatures contains dissolved metaldehyde, it may also safely be assumed that at temperatures about 20° higher, at which according to Hollmann[1] the unary boiling point (41·6°) lies, metaldehyde is still present in appreciable amount.

In order to test this assumption, the boiling liquid was suddenly shaken into water at 18°; as a result of this treatment, metaldehyde, if it were present at all in the boiling liquid, must have been deposited in the solid state, on account of its small solubility in aqueous mixtures.

A small yet very distinct deposition of metaldehyde was, in fact, obtained in this way, thus proving, therefore, that the system under consideration here is a unary trimolecular one.

The question of the change in position of K when the temperature is raised will now be investigated. Paraldehyde exists in the state of vapour and also, when dissolved in phenol, as the molecule $(CH_3CHO)_3$, and metaldehyde, when dissolved in the same solvent, as the molecule $(CH_3CHO)_4$,* so that of the three aldehydes metaldehyde is therefore the most complicated.

Assuming for the sake of simplicity that the molecular magnitudes

[1] *Zeitschr. f. physik. Chemie*, **43**, 157 (1903).

* W. Burstyn, *Sitzungsber. d. Wiener Akad.*, 511 (1902).

of the various aldehydes when dissolved in one another do not differ from their molecular magnitudes in phenol solution, the inner equilibrium will be represented by :—

$$12CH_3.CHO \overset{(1)}{\rightleftarrows} 4(CH_3.CHO)_3$$
$$(2) \quad (3)$$
$$3(CH_3.CHO)_4$$

Now, on increasing the temperature, each of the three unary bimolecular equilibria will be displaced in the endothermic direction, or, in other words, in these three inner equilibria dissociation will occur to an increased extent.

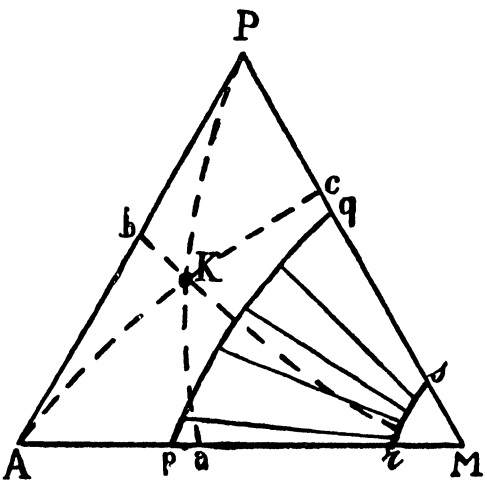


FIG. 192.

From Lougunine's[1] determination of the heats of combustion it might be expected that, on raising the temperature, equilibrium (2) would be displaced to a greater extent than equilibrium (1), whilst in all probability (3) would not be very sensitive to change of temperature, at least in comparison with the other equilibria (2) and (1). If the temperature rises the point *b* will be displaced downwards, *a* towards the acetaldehyde side and *c* slightly towards the paraldehyde side.

Now, having regard to the fact that on raising the temperature the solubility isotherm inclines back, *a* and *c* will certainly soon be found in the unsaturated region, *vide* Figs. 192 and 193. No single catalyst will then be able to cause the deposition of solid metaldehyde from acetaldehyde or paraldehyde. This result is in agreement with our observations in respect to calcium chloride, which, when the temperature exceeds from 30° to 40°, actually does not cause the deposition of solid metaldehyde from the other two aldehydes. Furthermore, it

[1] *Compt. rend.*, **108**, 620 (1889).

would appear from this, that on increasing the temperature the great inner equilibrium mixture K becomes richer and richer in acetaldehyde, just as Hollmann has found.

A representation of the results of the investigations discussed here is given in Fig. 194, which depicts an equilateral prism, on the surfaces of which the T X sections at constant pressure, *e.g.* one atmosphere, have been indicated.

On the A P T surface is shown the T X section for the pseudo-binary system acetaldehyde—paraldehyde, as determined by Hollmann, but with the difference that no eutectic has been indicated, since it has been found that the three-phase equilibrium, liquid + acetaldehyde mixed crystals + paraldehyde mixed crystals lies at −123°, whilst the melting point of acetaldehyde lies somewhat lower, at −123·3°. This

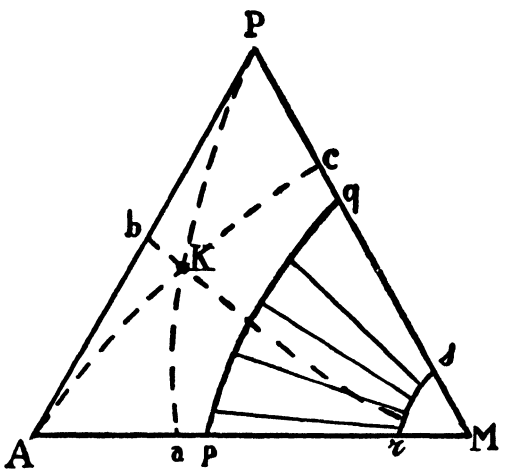


FIG. 193.

T X section is indicated by the fusion diagram *a c b e g d f* and by the two lines *k l* constituting the boiling-point diagram. The temperatures of the most important points are given in the diagram, so that this section needs no more detailed explanation.

On the paraldehyde—metaldehyde plane, the surface P M T, a complicated diagram has been developed, because metaldehyde sublimes under a pressure of one atmosphere. At what height this sublimation point lies cannot be determined because of the decomposition of metaldehyde into acet- and paraldehyde. Soch's method, which was employed in the determination of the triple point, for which the figure 246·2° was obtained, cannot be used here. It may be stated provisionally that the sublimation point probably lies only a little below the temperature of the triple point, for the triple-point pressure probably does not much exceed one atmosphere. Whilst the melting-point of paraldehyde lies at 12·55°, the somewhat higher temperature 12·9° was obtained for the three-phase equilibrium paraldehyde mixed crystals +

liquid + metaldehyde mixed crystals. Thus in this case again no eutectic appears. The T X section of this system is indicated by $b\, c_2\, n_2\, l\, m_2\, o\, p_2\, g_2\, e_2\, d_2 f_2$.

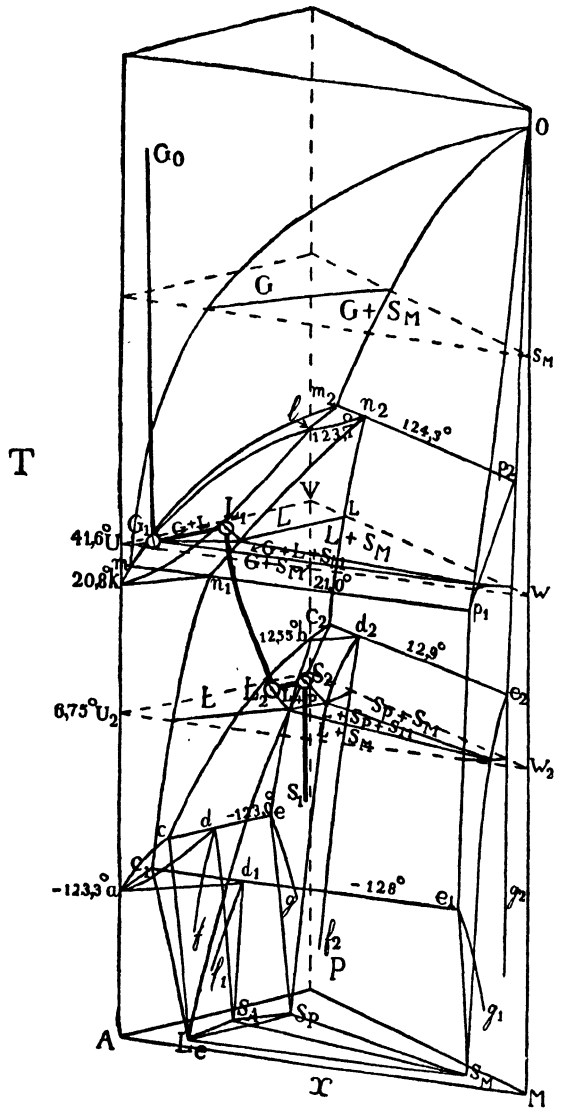


FIG. 194.

The temperature of the three-phase equilibrium $S_m + L + G$ indicated by the line $p_2\, n_2\, m_2$, was determined by working very rapidly, and

found to be 124·3°; thus the boiling solution, saturated with metaldehyde mixed crystals, contains relatively but little metaldehyde, for paraldehyde boils at 123·7°.

On the front face—the plane relating to acetaldehyde—metaldehyde—the T X section of this system is indicated by $a\, c_1\, n_1\, k\, m\, o\, p_1\, e_1\, g_1\, d_1 f_1$. In character this system closely resembles the paraldehyde system. For the temperature of the three-phase equilibrium $S_m + L + G$, or, in other words, for the boiling point of the solution saturated with metaldehyde mixed crystals, the value 21° was obtained, and this is only about 0·2° higher than the boiling point of acetaldehyde. At 21°, therefore, the solubility of this solid phase in acetaldehyde is extremely small. The value − 122·8° was found for the temperature of the three-phase equilibrium, acetaldehyde mixed crystals + metaldehyde mixed crystals + liquid, and consequently this system also does not contain a eutectic. The most important portions of the space diagram are made intelligible by means of sections.

(c) *The position of the unary system.*

The only point requiring fuller discussion is the position of the unary system in the trimolecular pseudo-ternary system. Hollmann found the boiling point of the unary system to be 41·6°, and it will

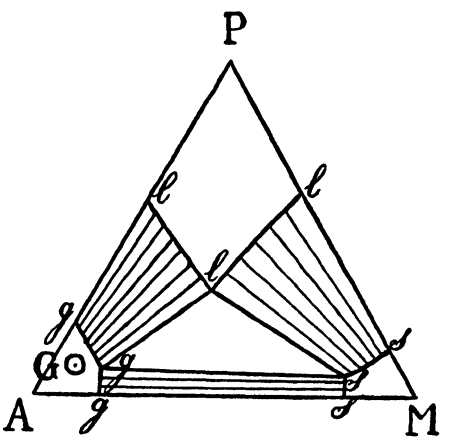


FIG. 195.

now be assumed that the section U V W holds good for just this temperature.

Unfortunately, however, the points of the three-phase triangle are displaced towards the front plane to so great an extent that the section can no longer be clearly indicated. Several sections have therefore been specially represented here.

Fig. 195 relates to a temperature somewhat above the boiling point. The regions in the pseudo-ternary system are at once recognisable,

and the regions in which two phases co-exist are shaded. The letters *s*, *l* and *g* indicate the solid, liquid and gaseous phases respectively. So long as the behaviour is unary only the gaseous phase G exists, and this is situated in the vapour region. At the boiling point (41·6°) the

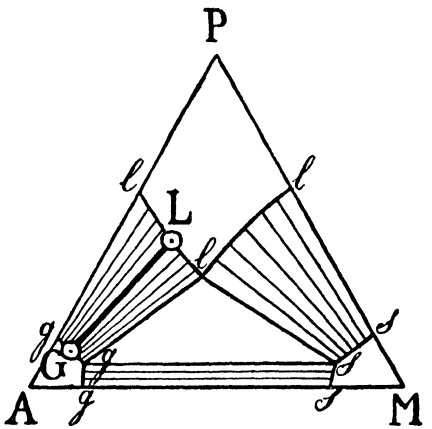


FIG. 196.

vapour phase G of the unary system lies on the vapour line *g g*. Consequently a liquid phase L co-exists with the vapour phase G, and this also reverts into inner equilibrium; thus it, too, belongs to the unary

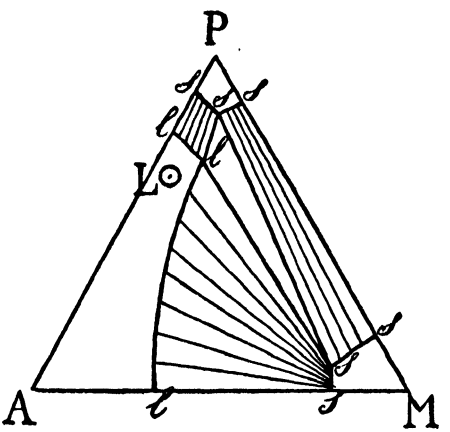


FIG. 197.

system (see Fig. 196). Hollman gave 53·4 mol. per cent. paraldehyde and 46·6 mol. per cent. acetaldehyde as the composition of this liquid, but our experiments have shown that it contains metaldehyde also, even though in very small quantity; this is also true of the vapour phase G.

At a somewhat lower temperature G wanders into the two-phase region between *g g* and *l l*, and is therefore metastable, whilst L moves into the liquid region within the quadrilateral *l l l* P, and is therefore stable.

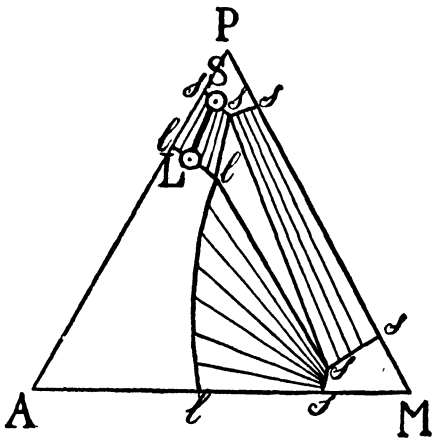


FIG. 198.

Fig. 197 illustrates the position at a temperature a little above the unary melting point. The liquid phase L is the only stable unary phase. At the temperature of the stable unary melting point, 6·72°, the unary liquid phase L has reached the solubility isotherm of the paralde-

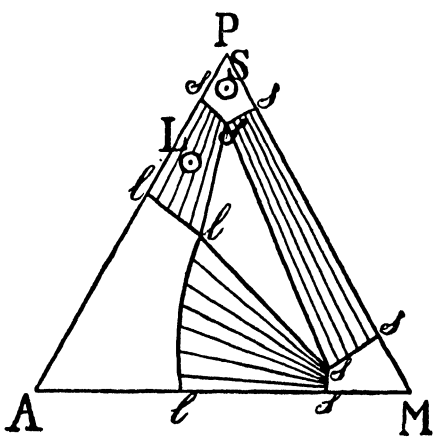


FIG. 199.

hyde mixed crystals. Consequently, in addition to this liquid phase, the solid phase S can now appear, containing, besides paraldehyde, both acetaldehyde and metaldehyde, and which, like L, reverts into inner equilibrium.

The unary system, therefore, consists at this temperature of the two phases L + S, as shown in Fig. 198.

Below the temperature of the stable unary melting point the position is as indicated in Fig. 199. The unary liquid L now lies in the heterogeneous region for solid + liquid, and is therefore metastable, whilst the unary solid phase S has moved into the region of homogeneous paraldehyde mixed crystals; *i. e.* below the stable unary melting point the solid phase S is the stable phase of the unary system. In this way, so far as the most important points are concerned, the ternary space diagram, which is, of course, less easily understood, is made quite intelligible. The inner equilibrium surfaces, through the intersection of which the unary inner equilibrium lines are formed, are, for the sake of simplicity, omitted here.

In the space diagram the heavy line $G_0\ G_1$ indicates the vapour phase, the line $L_1\ L_2$ the liquid phase, and the line $S_1\ S_2$ the solid phase of the unary system.

At the points where the metastable prolongation of the line $L_1\ L_2$ meets the metastable portion of the fusion surface for acetaldehyde or metaldehyde, the metastable unary melting points of the two other modifications are situated; these modifications are rich in acetaldehyde and metaldehyde respectively.

If the line $S_2\ S_1$ relating to the inner equilibrium in the solid phase meets the ternary surface for the co-existence $S_P + S_M$ or $S_P + S_A$, a transition equilibrium will appear in the unary system.

(d) *The paraldehyde of the unary system is a mixed crystal phase in inner equilibrium.*

Proof of this statement is easily obtained. The same method was followed as in the treatment of other allotropic substances. To the liquid phase a trace of sulphuric acid was added and the liquid was then allowed to solidify completely; as is well known, this occurs under these conditions at 6·75°. The solid mass was then filtered at −10° as rapidly and completely as possible by means of a pump. The mass so obtained was quickly placed in a tube 2 cm. wide which was then immersed in a bath at a temperature of 0°.

The temperature of the bath was now slowly raised and the time temperature curve determined, readings being taken at equal intervals of time (minutes) of a thermometer placed in the tube and surrounded by the aldehyde. This curve exhibited a horizontal portion which corresponded exactly with a temperature of 6·75°.

If the solid mass obtained in this way were the pure pseudo-component, fusion would first occur at 12·55°. But this phenomenon actually occurred at 6·75° exactly. No better proof than that furnished by this observation could be given in support of the view that we are dealing here with a mixed crystal in inner equilibrium, which exhibits a lower melting point than pure paraldehyde because it still contains the other pseudo-components.

29. The Experiments of H. Brereton Baker.[1]

Baker's experiments, with a discussion of which this chapter will be brought to a conclusion, are of especial interest here.

After Baker in his classical experiments had discovered the enormous influence of intensive drying on the chemical reactivity of gases, he applied his method of drying to liquids also, and in 1912 the results of his experiments with N_2O_3 and N_2O_4 were published. These results are very remarkable; thus, it was found that whilst N_2O_3 dried in the ordinary way boiled at $-2°$, nitrogen trioxide which had been intensively dried for three years over pure P_2O_5 commenced to boil at $+43°$. Baker had already formed the opinion that this large elevation of the boiling point must be ascribed to a change in the complexity of the liquid, because a vapour density determination yielded results which corresponded with a composition of three molecules N_4O_6 to one molecule N_2O_3. Further, he succeeded in showing that traces of moisture were sufficient to re-convert the intensively dried liquid with great velocity into its original state.

In the case of the tetroxide a similar phenomenon was observed, for, whilst the liquid when dried in the usual way boiled at 22°, on heating a small quantity of the liquid, which had been intensively dried for three years, above 22°, evaporation certainly occurred, but even at 69° liquid which had not yet boiled was still present.

Baker's experiments with the trioxide and tetroxide of nitrogen marked the commencement of a series of extremely interesting investigations. The publication of the results of the above-mentioned experiments concluded with the following sentence: "Further experiments are in progress to determine the boiling points of dried liquids in order to see if the dissociability of the vapours is an essential condition for the raising of the boiling points."

Liquids of widely differing natures and also solid substances were sealed up by Baker in 1912 and 1913 in glass vessels containing pure P_2O_5, but on account of the war it was not until a year ago that the study of the influence of intensive drying could be begun.[2]

It was found, as may be seen from the Table on p. 317, that when the boiling point came to be determined, every liquid which had been intensively dried exhibited a large elevation of the boiling point.[3]

The results quoted here are of the utmost importance and they furnish as convincing proof as could be wished of the complexity of the liquid phases of these systems, hitherto looked upon as being of a simple unary character. The temperatures given in this Table were registered by a mercury thermometer, the bulb of which was immersed in the boiling liquid. Now Baker points out that a second thermometer, the

[1] *Trans. Chem. Soc.*, **51**, 2339 (1912).

[2] It is therefore quite possible that the effects obtained could have been observed much earlier. In any case it is not improbable that means will be found to dry substances more rapidly.

[3] *Trans. Chem. Soc.*, **121**, 568 (1922).

bulb of which was 3 cms. above the liquid surface gave readings which were only about 2° higher than the ordinary boiling points.[1]

Liquid.	Duration of drying in years.	Usual boiling point.	Boiling point of the dried liquid.	Rise.
Bromine . .	8	63°	118°	55°
Mercury . .	9	358°	420° — 425°	62°
Hexane . . .	8·5	68·4°	82°	14°
Benzene . .	8·5	80°	106°	26°
Carbon bisulphide .	27	49·5°	80°	30°
Carbon tetrachloride	9	78°	112°	34°
Ethyl ether . .	9	35°	83°	48°
Methyl alcohol .	9	66°	120°	54°
Ethyl alcohol . .	9	78·5°	138°	60°
Propyl alcohol .	9	95°	134°	39°

At first sight the conclusion might be drawn that this behaviour proves the intensively dried liquid to be a system of at least two components, the volatilities of which differ widely. After distilling off a portion, the vapour was still very rich in the more volatile pseudo-component. This vapour condensed to such an extent on the long stem of the thermometer under discussion that as a result it could only indicate the temperature of this condensed liquid, and this could only differ slightly from the ordinary boiling point.

It is obvious that after the distillation has been in progress some little time the temperature recorded by the thermometer in the vapour phase must rise, at first slowly, but finally more and more rapidly, in the same way as the temperature indicated by the thermometer in the liquid. Thus the temperatures given by Baker are probably to be looked upon as initial boiling points, and it might be concluded that, on further distillation, they would, therefore, rise still further. This, however, is not in agreement with Baker's statement that "when the condensed liquid from the distillation was again heated it did not enter into a state of ebullition until the abnormally high temperature had been reached," for this would prove the vapour and the liquid to have nearly the same composition. This point requires further investigation.

Some very interesting peculiarities noticed in the cases of benzene, ether and the alcohols may be mentioned. A portion of the intensively dried benzene, boiling at 106°, was left in contact with dry air for a day; its boiling point was then re-determined, and the value 105° was then obtained. This benzene was thereupon poured into water and the system of two layers thus formed was heated with the following result. When the water had reached its boiling point and water vapour was escaping through the benzene layer the latter evaporated but slowly. Under these circumstances therefore the high boiling benzene underwent no noticeable change.

[1] At first sight it might be thought that the phenomenon observed here is a simple superheating of the liquid, but the changes in the vapour tension and the surface tension prove that the composition of the liquid has changed.

If this high boiling benzene had been permanent, from the theoretical point of view a serious difficulty would have arisen. Fortunately, however, Baker succeeded in proving that this was not the case. He allowed the vessel in which the value 106° had been obtained for the boiling point to cool and then he replaced the extremely dry air with air which had been passed first through concentrated sulphuric acid and then over phosphorus pentoxide. The apparatus was then sealed up and set aside for a month. When, at the expiration of this period, the boiling point was again determined, the value 81° was obtained. During this time, therefore, the benzene, under the influence of extremely small traces of water, had changed back into its original state. Thus this experiment proves that the velocity with which inner equilibrium is re-established under the catalytic influence of traces of moisture is here very small.

In the case of ethyl ether, however, this velocity was found to be much greater; for when Baker distilled off a portion of the intensively dried liquid, which boiled at 83°, in a flask which had only been dried by heating it in dry air, this liquid immediately exhibited a much lower boiling point, namely 47°, and by the next day this had fallen to 36°. Here, therefore, inner equilibrium was established much more rapidly. At this point it should be mentioned that Baker also determined the vapour pressure of intensively dried ether at 20° and found it to be 374 mm. Hg, whilst the vapour pressure of moist ether at the same temperature amounted to 442 mm. Hg, *i. e.* 68 mms. higher. The three alcohols investigated closely resembled ethyl ether in this respect, for the high boiling non-equilibrium state was again converted into inner equilibrium after very brief contact with moist air.

In order to arrive at some conclusion regarding the mean molecular state, Baker determined the surface tension of some of the liquids mentioned here by the method of Ramsay and Shields, both moist and also in the intensively dried condition. The following results were obtained.

Liquid.	Mean molecular weight.	
	Moist.	Intensively dried.
Bromine . . .	1·34 × 80	1·99 × 80
Benzene . . .	1·29 × 78	3·39 × 78
Hexane . . .	0·92 × 86	3·16 × 86

From this Table it follows that the complexity consists in this case in the existence of molecular species of different magnitudes (association or polymerisation) and that the intensively dried liquids investigated are much more strongly associated, or contain a much higher concentration of the polymeric molecular species than do the moist liquids.

Baker's extension of these investigations to crystalline substance is also of very great importance. In 1912 rhombic sulphur and iodine

were sealed up in glass vessels containing pure P_2O_5. The melting point of the rhombic sulphur was then 112° and that of the iodine 114°. When the melting points were re-determined in 1921 both were found to be higher; the sulphur now melted at 117·5°, an increase of 5·5°, and the iodine at 116° or 2° higher. From both these results it follows that the fusing crystalline substance which had been intensively dried had a different composition from that of the moist crystalline phase when melting.

It must be especially emphasised that it is clearly probable that the intensively dried solid substances behave here as mixtures, so that fusion does not take place at one definite temperature but over a considerable temperature range. In this case the temperatures mentioned by Baker may represent initial melting points.

It is, however, also possible that by the drying process the inner equilibrium is displaced completely to the side of the pseudo-component having the highest melting-point, and that fusion then takes place at one definite temperature.

The important question still remains, what really happens in the drying process? It might at first sight appear permissible to explain the results obtained by assuming that in the reversible change $\alpha \rightleftarrows \beta$ the reaction $\leftarrow$ becomes stationary sooner than the reverse change $\rightarrow$, as a result of which a phase arises containing an *excess* of the β type of molecule or this molecular species *exclusively*; but it is then tacitly assumed that a trace of moisture can displace the inner equilibrium to a very considerable extent, the thermodynamical significance of which is that a very large amount of work is necessary in order to withdraw the last traces of water from the substance, and this is not improbable.

One might, however, be inclined to assume that by subjecting substances to intensive drying Baker simply fixed the internal conditions existing at the temperature at which the drying was carried out, and that the boiling point obtained related to liquids which partially evaporated whilst being heated to the boiling point, and consequently before this temperature was reached; a certain amount of fractionation had, therefore, already taken place.

It is clear that a small elevation of the boiling point could have been explained from the circumstance that the fixation temperature was generally considerably lower than the boiling point. If, for example, in the case of unary behaviour, the concentration of the polymeric molecules decreases with rising temperature, the intensively dried liquid, in which the composition does not change with the temperature, may, on that account, already exhibit a somewhat higher boiling point. Here, however, the observed changes are of such a kind that they must undoubtedly be attributed to the operation of entirely different causes.

In the case of the elevation of the melting point of sulphur or of iodine, it might rather be expected that these *much smaller* temperature increases are perhaps to be explained by the displacement which the inner equilibrium in the solid phase undergoes with change of temperature. The question what actually happens during intensive drying, whether it is merely a fixation or whether displacement of the inner equilibrium

first occurs, followed by fixation, has not yet been answered with certainty from the results of Baker's experiments. It can, however, easily be answered. If the vapour pressure of the liquid phase changes *solely* as a result of intensive drying, this change must take place before any portion of the liquid is distilled off, and thus it is certain that during the drying process the inner equilibrium has been displaced. If, however, the vapour pressure remains constant and a decrease in the vapour pressure first appears after a portion of the liquid has been removed by distillation, intensive drying then acts merely by fixing the inner equilibrium state. The same question can also be answered by determining the boiling point, if the boiling point is observed when the intensively dried liquid is boiled under a reflux condenser and the volume of the vapour is kept small. If fixation only occurs, the boiling point will not change; but if a portion of the liquid is distilled off, the boiling point will then rise immediately. If, however, the inner equilibrium is also displaced, the boiling point will change before any liquid is distilled off. My impression is that this actually occurs.

The influence of the temperature at which drying took place on the elevation of the melting points of crystalline substances ought to be determined, for from this it will probably be possible to decide whether we have to do in such cases simply with a fixation of the inner equilibrium or whether a displacement also occurs. The answer to this question, however, must be patiently awaited. As has already been stated, in the author's opinion the inner equilibrium is displaced by drying, often completely to the side of the least volatile pseudo-component.

It can already be asserted that Baker's discovery is of extraordinary importance, inasmuch as it proves in a very convincing way that in the case of no less than ten substances, differing widely from one another, the unary phase is complex, as had already been assumed in the Theory of Allotropy. At the same time it becomes evident that intensive drying will probably become one of the most beautiful, if not the most beautiful, means of establishing the complex nature of the unary phase.

The number of problems, the solution of which now appears to be possible, is very great, and so it may be claimed that Baker's discovery has added an extremely important and interesting method to those available for the thorough study of unary phases. The application of this method will doubtless yield beautiful and valuable results.

CHAPTER II

THE EXAMINATION OF THE THEORY OF ALLOTROPY IN THE DOMAIN OF ELECTRO-CHEMISTRY

1. The Electromotive Behaviour of Metals when they are Attacked by Acids.

(a) *Statement of the problem.*

WHEN a metal, which when placed in an acid liberates hydrogen, is dipped into an aqueous solution of one of its salts and acid is added thereto with continued and vigorous shaking, it will depend on the velocity with which inner equilibrium is established, both in the metallic surface and also in the hydrogen phase, whether the electrical potential will undergo any change.

It has been shown in the theoretical portion that the potential measured after the addition of the acid from which hydrogen is evolved is not only the potential of the metal but of the evolved hydrogen also; for the potential measured corresponds to the three-phase equilibrium metal phase—hydrogen phase—electrolyte in the bounding surface (Fig. 118). If now the metal is superficially disturbed, whilst inner equilibrium in the hydrogen is established very rapidly, the potential will always be less negative.

In the converse case, *i. e.* if a state of inner equilibrium is maintained in the metal and the hydrogen cannot settle into inner equilibrium, so that the hydrogen phase reverts into the state of formation, the potential must become somewhat more negative; still, the amount of this change, for the reasons given, must always be extremely small, so that this influence can be neglected here.

If, therefore, on dissolving a metal in a dilute acid solution of one of its salts the potential exhibits a relatively large change in the direction of greater positivity, this points to a disturbance of the metal surface.

But if in a solution of a salt in a solution of 0·1 N. acid, for example, the potential shows a distinct change in a more negative direction, this behaviour certainly cannot be ascribed to the state of formation of the hydrogen.[1] The cause of this phenomenon may be, firstly, that before the addition of acid the metal was disturbed to some extent in the

[1] Metals less noble than zinc are here excluded, for these metals can only coexist in inner equilibrium with a liquid bounding layer and hydrogen, when the hydrogen is in the state of formation. See *Rec. d. trav. Chim.* (1922).

direction of greater nobility, and that after the introduction of the acid, this disturbance, notwithstanding the greater velocity of solution, has become smaller.

Naturally this is only possible when the acid is able to eliminate any negative catalyst. As we have already pointed out, it is very probable that when a metal co-exists with a liquid, the bounding layer of the metal will contain every part of the coexisting liquid in concentrations which vary with the depth. When a metal placed in a pure aqueous solution of one of its salts liberates hydrogen, the co-existing liquid layer will certainly contain dissolved metal hydroxide. Amongst other things the metallic bounding layer will then, in consequence of this, also contain the metal hydroxide in solid solution and experiment seems now to indicate, that this hydroxide dissolved in the metal is a negative catalyst for the inner transformations in the metal.

As a result of increasing the hydrogen-ion concentration the hydroxide concentration in the metallic bounding surface will be greatly diminished, and so it becomes possible, although on increasing the acid concentration the metal is more vigorously attacked, for the accompanying diminution in the hydroxide concentration to cause the disturbance of the metal to become smaller, and consequently the potential will approximate more closely to the equilibrium potential.

In the second place the potential may become more negative as a result of the formation of complex ions. It is clearly advisable to carry out these corrosion experiments in an atmosphere of nitrogen. If, however, the metal gives rise to considerable evolution of hydrogen even before the addition of acid, when the work is conducted in an atmosphere of nitrogen, the potential will be found to be only slightly more negative than in air.

(b) *Experiments with zinc.*

Zinc was dipped into a zinc chloride solution which was vigorously stirred, and the potential of the metal relative to a normal calomel electrode was then determined. According to the calculations made in the theoretical part, zinc must liberate hydrogen from aqueous solutions of its salts when $(Zn^{\cdot\cdot}) = 1$, or, in other words, if the relative concentrations of metallic and hydrogen ions are considered, the composition of the solution certainly lies to the right of the point c in the E X diagram. Consequently, at the very outset, the potential measured is that of a three-phase equilibrium, whilst the metal will be attacked, and it is therefore possible that it is already disturbed even before the addition of acid.

Experiments in which zinc was dipped into a solution of zinc sulphate containing 0·5 grm.-mols. of the salt per litre yielded the following results:—

Experiments in an Atmosphere of Nitrogen.

The potential of zinc at 18°, relative to a normal calomel

electrode, when dipped into zinc sulphate solutions of the following compositions :—

0·5 grm.-mol. dissolved in 1 litre of pure water.	0·5 grm.-mol. dissolved in 1 litre of 0·05 N.H_2SO_4.	0·5 grm.-mol. dissolved in 1 litre of 0·1 N.H_2SO_4.	0·5 grm.-mol. dissolved in 1 litre of 0·5 N.H_2SO_4.	0·5 grm.-mol. dissolved in 1 litre of N.H_2SO_4.	0·5 grm.-mol. dissolved in 1 litre of N.K_2SO_4.
— 1·077 V.	— 1·077 V.	— 1·077 V.	— 1·079 V.	— 1·081 V.	— 1·078 V.

These results, which are easily reproducible if a carefully etched zinc electrode is employed, show, therefore, that when zinc is attacked by sulphuric acid of strength less than 0·5 N. the potential of the metal is quite unaffected, and that stronger acid exerts only an extremely weak influence on this potential, rendering it a couple of millivolts more negative.

Corrosion experiments in hydrochloric acid solutions of zinc chloride yielded the following results :—

Experiments in an Atmosphere of Nitrogen.

The potential of zinc at 18°, relative to a normal calomel electrode, when dipped into solutions of zinc chloride of the following compositions :—

0·5 grm.-mol. dissolved in 1 litre of pure water.	0·5 grm.-mol. dissolved in 1 litre of 0·05 N.HCl.	0·5 grm.-mol. dissolved in 1 litre of 0·1 N.HCl.	0·5 grm.-mol. dissolved in 1 litre of 0·5 N.HCl.	0·5 grm.-mol. dissolved in 1 litre of N.HCl.	0·5 grm.-mol. dissolved in 1 litre of N.KCl.
— 1·060 V.	— 1·060 V.	— 1·062 V.	— 1·081 V.	— 1·098 V.	— 1·062 V.

This table shows an acid concentration up to 0·1 N.HCl to be without influence on the potential, but that 0·5 N.HCl and 1 N.HCl displace the potential 0·021 volts. and 0·038 volts. respectively in the negative direction.

In order to investigate the influence exerted separately by sulphate ions and chlorine ions, the same quantities of zinc sulphate and zinc chloride were dissolved in a litre of 1 N. potassium sulphate and 1 N. potassium chloride respectively, and the zinc potential was thereupon measured. In this way the values — 1·078 volts and — 1·062 volts were obtained, from which it is evident that the influence of sulphate and chlorine ions is not appreciable. The above-mentioned displacement can therefore be ascribed solely to the influence of hydrogen ions. As regards the nature of the action of hydrogen ions, I have expressed the opinion, however, that these experiments are to be considered as preliminary experiments only; the results to be obtained by continuing them with other metals will prove the correctness of this view.

2. The Peculiarity of Very Inert Metals.

When the inert metal nickel was dipped into a solution of nickel sulphate, to which sulphuric acid had been added in order that the

composition might lie to the right of *c* in the E X diagram, a very interesting result was obtained.

From the considerations developed in the theoretical portion of this book the condition for the liberation of hydrogen by nickel is :—

$$L_{Ni} > L_{H_2} \frac{[Ni^{\cdot\cdot}]}{[H^{\cdot}]^2},$$

so that, if $[Ni^{\cdot\cdot}] = 1$

$$L_{Ni} > \frac{L_{H_2}}{[H^{\cdot}]^2}$$

or

$$[H^{\cdot}]^2 > \frac{L_{H_2}}{L_{Ni}}.$$

Since now

$$L_{H_2} = 10^{2x-48} \quad \text{and} \quad L_{Ni} = 10^{2x-45}$$

the condition is

$$[H^{\cdot}] > 10^{-3}.$$

In this case, therefore, the composition of the solution lies to the right of the point *c* in the E X diagram.

In order to make certain that the composition of the solution did lie to the right of *c*, sulphuric acid was added as has already been mentioned.

The potential measurements were carried out in an atmosphere of pure hydrogen in order to prevent any disturbances to which the presence of oxygen might give rise, and which are particularly liable to occur in the case of inert metals. When the composition of the solution lies to the right of that represented by the point *c* the introduction of nickel must cause hydrogen to be evolved, but this effect is not measurable; the potential of the nickel becomes continuously less negative, thus proving that the metal has become disturbed.

The processes taking place here are :—

$$\begin{array}{cc} 0_S & Ni^{\cdot\cdot}{}_S \\ \downarrow & \downarrow \\ 0_L & Ni^{\cdot\cdot}{}_L \end{array}$$

and

$$2H^{\cdot}{}_L + 2O_L \rightarrow H_{2_L},$$

i. e. electrons and nickel ions pass from the electrode into the solution, the electrons uniting with hydrogen ions to form hydrogen molecules.

The inner metallic equilibrium

$$Ni_S \rightleftarrows Ni^{\cdot\cdot}{}_S + 2O_S$$

is only established extremely slowly, for we are dealing here with an inert metal, the inertness of which has been still further increased by the amount of hydrogen absorbed.

Thus the metal becomes poorer as regards electrons and ions and the potential became less negative.

It was therefore expected that the disturbance of the nickel would continue to such an extent that the limiting case would be reached, *i.e.* until

$$[\theta_{Ni}]_L = [\theta_{H_2}]_L$$

or

$$E_{Ni} = E_{H_2}.$$

In this experiment, therefore, it was expected that the nickel electrode would be disturbed in the direction of greater nobility until the nickel potential became equal to the potential of the hydrogen.

The results of the experiment completely justified this view. The potential of the nickel finally reached −0·350 volts, and when the hydrogen electrode was now introduced, and hydrogen bubbled through, its potential was found to be − 0·348 volts.

The interesting result thus obtained in the case of nickel, which can be very readily explained on the basis of the Theory of Allotropy, has the following significance: When an inert metal is placed in a solution from which, theoretically, it should liberate hydrogen, a disturbance of the metal in the direction of greater nobility occurs, which in particular cases may proceed until the hydrogen potential is reached. This phenomenon, observed here in the case of nickel, is doubtless exhibited by other very inert metals also. The same behaviour has already been observed by Beck[1] in the case of cobalt.

3. Disturbances in the Supposed Measurement of the Equilibrium Potentials of Inert Metals.

Peculiar difficulties are encountered in the measurement of the equilibrium potentials of inert metals, to which many of the inaccurate statements appearing in the literature with regard to equilibrium potentials are to be ascribed.

In order that these difficulties may be clearly demonstrated, the inert metal nickel will again be taken as an example.

Let us assume that a solution of a nickel salt is taken, in which $[Ni^{\cdot\cdot}] = 1$ and the hydrogen-ion concentration is less than 10^{-3}, so that the composition of the solution will lie to the left of the point *c*, and therefore, on dipping into it a nickel electrode, hydrogen will not be liberated. It might be thought that in this case the equilibrium potential would always be measured, *i. e.* the potential of nickel which is in inner equilibrium with regard to the solution under discussion here. This potential is indicated in Fig. 123 by the line *g k*, which, owing to the very one-sided position of *c*, lies very little above *a*. In the case of inert metals, however, the equilibrium potential is only established under very definite conditions. If the solution is in contact with air the metal is attacked; electrons are removed by oxygen in accordance with the equation

$$O_2 + 2H_2O + 4\theta \rightarrow 4OH'$$

[1] These investigations are not yet published.

and these are replaced by the metal, since it sends metallic ions and electrons into solution.

In the case of inert metals this corrodibility leads to a disturbance in the direction of greater nobility, so much the more since oxygen, as we have previously seen, exerts a negative catalytic influence on the establishment of inner equilibrium.

Various experimenters have consequently thought it necessary to work in an atmosphere of hydrogen in order to obtain the equilibrium potential.

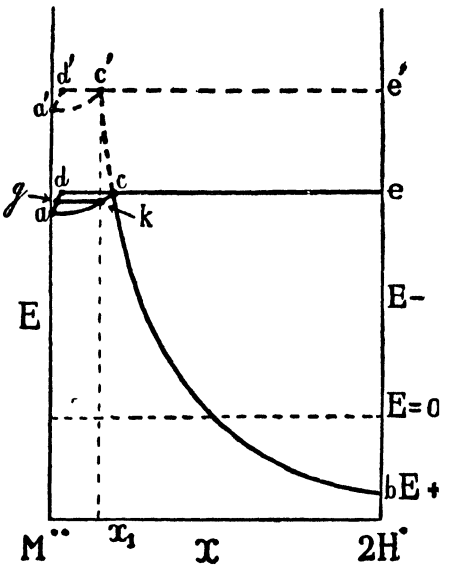


FIG. 123.

The error in this method of procedure may be demonstrated in the following way.[1] A faint turbidity was produced in a 1 N. solution of nickel sulphate by the addition of sodium hydroxide, with the object of diminishing the hydrogen-ion concentration as far as possible. A nickel electrode and a hydrogen electrode were then placed in this solution, and finally very pure hydrogen was passed through it, air being rigidly excluded.

Now, in the theoretical part it was shown quite generally that this case could be treated in an exactly similar way to the case in which two metals are dipped into an electrolyte containing ions of both metals. Here one of the two metals is replaced by hydrogen.

The potential of the hydrogen electrode in relation to the bounding liquid is given by the formula:—

$$E_{H_2} = -0{\cdot}058 \log (\theta_{H_2})_{B.L.} - 2{\cdot}8,$$

whilst the potential of the metal in relation to its bounding liquid is

$$E_M = -0{\cdot}058 \log (\theta_M)_{B.L.} - 2{\cdot}8.$$

If the composition of the liquid lies to the left of the point c, the E X diagram shows the potential of the hydrogen electrode, indicated by the line $e'c'$, to be more negative than that of the metal electrode. Thus it follows that, expressed in terms of the above equation,

$$(\theta_{H_2})_{B.L.} > (\theta_M)_{B.L.}$$

and consequently electrons and ions pass from the hydrogen electrode

[1] Smits and Lobry de Bruyn. *loc. cit.*

and from the hydrogen gas into the solution, whilst electrons, with metallic ions, will be deposited on the metal.[1]

When inner equilibrium is established in the metal very rapidly, the above-mentioned process, as has already been noticed, will exert no influence on the potential of the metal. If, however, the metal is inert, a displacement of the potential in the direction of less nobility will result, and if the inertness is very pronounced the limiting case may eventually be reached, in which

$$(\theta_{H_2})_{B.L.} = (\theta_M)_{B.L.}$$

i. e. the potential of the metal has become equal to the potential of the hydrogen.

Nickel is an inert metal and consequently a considerable disturbance of the nickel electrode in the direction of decreased nobility was to be expected; though it was doubtful whether the limiting case just referred to would be realised.

Although at the commencement of this experiment the nickel potential was much less negative than that of the hydrogen electrode, it grew steadily more negative as the experiment proceeded, approaching that of the hydrogen electrode, until finally both electrodes exhibited exactly the same potential. This may be seen from the table given below.

Electrode.	Potential of the electrode in normal $NiSO_4$, relative to the normal calomel electrode.
Nickel .	− 0·527 V.; − 0·550 V.; − 0·590 V.; − 0·610 V.; − 0·640 V.
Hydrogen .	− 0·623 V.; − 0·640 V.; − 0·641 V.; − 0·640 V.; − 0·640 V.

In a normal solution of $NiSO_4$, as will presently be seen, the equilibrium potential of nickel is − 0·480 volts; consequently in the above experiment the nickel was disturbed by hydrogen, in the direction of less nobility, to the extent of 0·160 volts.

In the case of nickel, therefore, the limiting case can be realised which, according to the deductions made in the theoretical portion, applies to electrodes which do not corrode or which are ideally inert. The appearance of this phenomenon is due to the fact that the inert metal nickel becomes ideally inert in consequence of the small amount of hydrogen absorbed. That is to say, it has been established that hydrogen, like oxygen, exerts a negative catalytic influence on the establishment of inner equilibrium in metals.

To summarise the result of this experiment: If the nickel potential is measured in a solution which, from its composition, actually lies to the left of *c*, and through which hydrogen is simultaneously passed, the equilibrium potential is not obtained, but the potential of nickel in the state of formation. After some time the deviation from

[1] Hydrogen ions will also be precipitated on the metal, but to a very small extent.

the inner equilibrium state becomes so great that the nickel potential acquires the same value as the potential of the hydrogen electrode.

Schweitzer,[1] who carried out his measurements in an atmosphere of hydrogen in order to eliminate the influence of oxygen, in this way obtained the value — 0·616 V for the nickel potential. He was therefore far from measuring the equilibrium potential.

It is clear that the only certain method of determining the equilibrium potential of inert metals in general, and of nickel in particular, is to carry out the measurement in solutions which are as free as possible from both oxygen and hydrogen. This condition was attained by means of the apparatus depicted in Fig. 200.

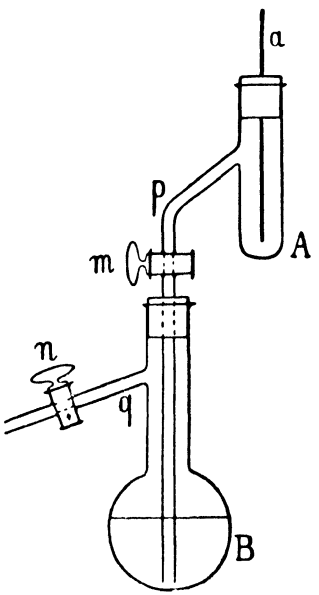


FIG. 200.

The upper portion of the apparatus consisted of the vessel A with the nickel electrode *a* and the bent side tube *p* which could be closed by means of the tap *m*. A was connected in the manner indicated with the fractionating flask B, which contained the nickel sulphate solution. The apparatus was then evacuated, being placed for this purpose in a sloping position, so that the end of the tube *p* no longer dipped into the solution. Connection with the air pump was made by means of the tube *q*. During the evacuation the solution was boiled. After cooling and arresting the evacuation—this was done by means of the tap *n*—the apparatus was again placed in a vertical position. Solution was then forced into the electrode vessel by opening the taps *m* and *n*. After closing the tap *m* the fractionating flask could be removed and the measurement of the potential commenced. These measurements yielded the following results:—

Time interval.	Potential of the nickel in relation to a normal calomel electrode.
4 hours	— 0·453 volts.
47 ,,	— 0·477 ,,
52 ,,	— 0·480 ,,
70 ,,	— 0·480 ,,

In 52 hours, therefore, the final potential, 0·480 volts., was reached, corresponding to the equilibrium potential of nickel.

[1] *Zeit. f. Elektrochemie*, **15**, 602 (1909).

Schoch[1] and Schildbach[2] likewise worked in a vacuum, without however, finding the correct explanation of the disturbing influence of oxygen and hydrogen. They also found the equilibrium potential of nickel to be — 0·480 volts.[3]

After the equilibrium potential of nickel had been determined in the manner described, a hydrogen electrode was introduced in addition to the nickel electrode, and hydrogen was bubbled through the solution. In complete agreement with the values already obtained, after 48 hours the potential of the nickel electrode was found to be —0·638 volts, and the potential of the hydrogen electrode to be — 0 640 volts.

It is clear, however, that the composition of the solution in which the equilibrium potential of nickel was determined had to lie to the left of *c*. The experiment described in the section entitled: "The peculiarity of very inert metals" (p. 323), points to the fact that when the composition lies to the right of *c*, the final potential of nickel, no hydrogen being passed, would also be equal to the hydrogen potential.

This case would therefore be met if a $NiSO_4$ solution acidified with H_2SO_4 and boiled in a vacuum were employed. This experiment also was performed and the nickel potential, which was established fairly rapidly, now amounted to — 0·317 volts.

To determine the hydrogen potential of this solution the hydrogen electrode was now introduced and hydrogen led through. In this way the value — 0·315 volts was obtained.

Now, therefore, as a result of changing the composition of the solution in a manner corresponding to a movement from left to right with reference to the point *c*, the equilibrium potential of nickel was not measured, but, by means of the disturbed nickel, the hydrogen potential was obtained.

Since chlorine ions in general exert a positive catalytic influence on the establishment of inner equilibrium, an attempt was finally made to determine whether this influence was sufficient to compensate the negative catalytic influence of the oxygen and the hydrogen. The negative catalytic influences of these substances proved, however, to be so powerful that precisely the same results were obtained when solutions of nickel chloride were used instead of nickel sulphate.

The difficulties encountered in the case of nickel are also met with in the investigation of other less inert metals, though to a smaller extent, so that when dealing with metals which are somewhat inert it is always advisable to repeat the measurement of the equilibrium potential in the manner indicated above, using a solution which has been boiled in a vacuum.

[1] *Journ. Amer. Chem. Soc.*, **41**, 208 (1909).

[2] *Zeit. f. Electrochemie*, **22**, 977 (1910).

[3] Equilibrium potentials can often be measured in an atmosphere of nitrogen. In this way also Schoch obtained the figures—0·48 for nickel. The method mentioned above is, however, safer.

4. Powerful Disturbances, brought about by Purely Chemical Methods, which may lead to So-called Passivity.

In the case of metals it happens that when they are rapidly dissolved a state results which is violently disturbed in the direction of greater nobility, and which, under the influence of negative catalysts for the establishment of inner equilibrium, may last, under certain circumstances, for a considerable time.

This state, which differs from the inner equilibrium state in potential, and also therefore in chemical activity, is called the *passive* state, and the phenomenon is known as *passivity*. Various metals exhibit this phenomenon, but perhaps the most interesting in this respect is iron, in which it was discovered.

Thus in 1790 Bergmann[1] discovered that iron when dipped into strong nitric acid containing silver nitrate was converted into a state in which it was no longer able to precipitate silver.

Independently of Bergmann, Keir[2] found in the same year that iron, after being dipped into strong nitric acid, passed into a form which no longer dissolved in acids, but that this condition could be destroyed by scratching, contact with a piece of ordinary iron or a light blow.

This phenomenon, interesting though it was, attracted but little attention and it was soon quite forgotten. In 1827, thirty-seven years later, the phenomena just described were rediscovered by Wetzlar.[3] Soon afterwards dissertations appeared on the same subject by Herschel,[4] Fechner[5] and Braconnet,[6] and in 1836 Schönbein[7] commenced his important investigations, as a result of which the rather unfortunately chosen term *passive* came into use to describe the state into which iron passes as the result of contact with strong nitric acid. Since then *active* and *passive* iron and the phenomenon of *passivity* are commonly spoken of.

Schönbein was the first thoroughly to investigate the transformation of active into passive iron through contact with nitric acid. He found, amongst other things, that contact between the iron and platinum or Fe_3O_4 favoured the appearance of the passive state, and that iron rendered passive by concentrated nitric acid retained its passivity unimpaired in dilute nitric acid.

Since then the phenomenon of passivity has been studied by a large number of chemists and physicists, and many theories have been advanced to account for it, none of which, however, has found general acceptance.

Some of these theories will be referred to later; the simplest form

[1] Dissertat. divers, philogist. quantit. metals.
[2] *Phil. Trans.*, **80**, 374 (1790).
[3] *Schweiggers, Journ. f. Chem. u. Phys.*, **49**, 470 (1827); **56**, 206 (1827).
[4] *Ann. de Chem. et de Phys.* (2), **54**, 87 (1833).
[5] *Schweiggers, Journ. f. Chem. u. Phys.*, **53**, 61, 129, 151, 470 (1828).
[6] *Ann. de Chem. et de Phys.* (2), **52**, 288 (1831).
[7] *Phil. Mag.* (3), **9**, 53, 59 (1836); **10**, 113, 172, 267, 425, 428 (1837); **11**, 544 (1837).

in which the passive state appears will, however, first be considered somewhat more closely.

If a piece of bright iron (pure iron exhibits the same phenomenon) to which a piece of platinum wire is attached is dipped into a solution of copper sulphate, the base iron passes into solution and copper is precipitated on the iron. This process was well known to the ancients. ["Mars lays aside his armour and puts on the dress of Venus."]

If this experiment is repeated in a somewhat altered form, thus if the iron is first dipped into strong nitric acid, and is then placed in a solution of copper sulphate, deposition of copper no longer occurs.

The surface of the iron has now become passive, and in this state iron is more noble than the silver. This condition, which is highly unstable, can immediately be reconverted into the active form, as Keir found, by a light blow, by scratching, or by contact with ordinary iron. The activity proceeds from the point of contact, and from this point it spreads uniformly over the whole surface.

If Bergmann's experiment is repeated and iron is placed in silver nitrate containing strong nitric acid, it is observed that at the outset the iron is less noble than the silver, for during the first moments silver is deposited on the iron in a black, finely-divided state. But the silver soon redissolves, whence it follows that the iron has now become more noble than the silver.

It has already been mentioned that the passive state can be destroyed by various mechanical influences, but there are in addition other activating influences, of which the halogen ions are the most interesting. This also was first discovered by Schönbein. More extended investigations have shown that other metals besides iron, *e.g.* nickel, cobalt and chromium, can similarly be rendered passive, and that not only nitric acid, but other solvents also can be used for that purpose, for example, concentrated aqueous solutions of H_2CrO_4, $HClO_3$, H_3AsO_4, etc.

Although the phenomenon can easily be explained by means of the theory developed in the theoretical part, this explanation will not yet be given. The powerful disturbances produced by the application of an electric current must first of all be more closely considered.

5. The Disturbance produced by Dissolving the Metal by means of an Electric Current. Anodic Polarisation.

The solution of metals in acids consists in the withdrawal of electrons to the metallic equilibrium in the bounding liquid, as a result of which electrons and ions instantaneously pass into solution. Throughout the process of electrolytic solution electrons are withdrawn by the metal, the result being that ions immediately go into solution. It is at once recognised that the two processes are not fundamentally different. When the solution process is accompanied by the simultaneous corrosion of the metal, electrons and ions pass into solution

together, whilst in electrolytic solution electrons and ions move in opposite directions.

The difference in the direction in which the ions and electrons move has, however, no significance as regards the solution process. From these considerations the same phenomena might be expected to appear during electrolytic solution as occur when the metal is corroded. Moreover, electrolytic solution offers further advantages in that by varying the current density, or, in other words, by changing the velocity with which electrons are carried off, the velocity of the solution process can be varied at will. Since the heterogeneous equilibrium between the metal and the bounding layer is, as we have seen, instantaneously established, it will depend on the velocity with which electrons are withdrawn, and on the speed with which the inner equilibrium

$$M_S \rightleftarrows M_S^{\nu\cdot} + \nu\theta_S$$

is established, whether the potential[1] of the metal remains constant as it dissolves. For metals in which inner equilibrium is established with great velocity, if potentials are made the abscissæ of a system of right-angled co-ordinates, current densities being the ordinates, one would expect the potential–current density curve to be a horizontal line.

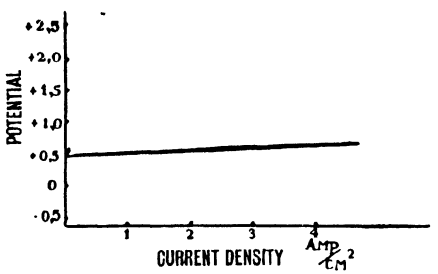


FIG. 201.

Silver, when dipped into a vigorously stirred solution of silver nitrate, gave Fig. 201.

This curve is, in fact, nearly horizontal, and thus it illustrates the great velocity with which inner equilibrium is established in silver.

Naturally, in spite of vigorous stirring, as the current density increases the concentration in the bounding liquid will increase; yet, as has already frequently been noticed, the formula

$$E = -\frac{0{\cdot}058}{\nu}\log.\frac{L_M}{(M_L^{\nu\cdot})} - 2{\cdot}8$$

shows that the potential only becomes $\frac{0{\cdot}058}{\nu}$ volts. more positive when the concentration of the metallic ions is increased tenfold, and consequently the increase in concentration which occurs will only produce an extremely small increase of potential.

If in the process of electrolytic solution, the metal being made the anode, the potential of the metal rises, *anodic polarisation* is said to occur. Consequently the conclusion may be drawn from the experi-

[1] When not otherwise indicated the term "potential" will mean the potential relative to the normal calomel electrode.

ment with silver that in the case of this metal the anodic polarisation is very slight.

Of the remaining metals, some, such as zinc, iron and copper in solutions of their *chlorides*, yield potential–current density curves which do indeed deviate somewhat further from the horizontal, thus pointing to slight polarisation; nevertheless they closely resemble the curve obtained for silver in silver nitrate.

In solutions of their sulphates the polarisation is always greater; when the chlorides are used the positive catalytic action of the chlorine ions must also be borne in mind.

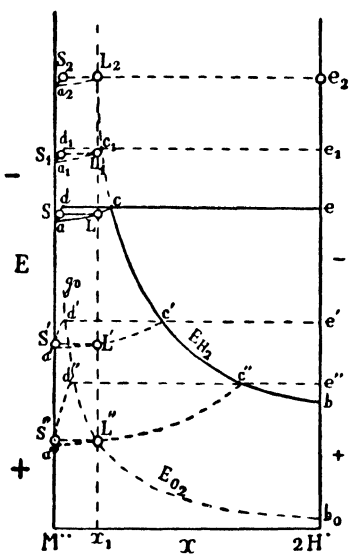


FIG. 125.

When an inert metal undergoes anodic solution, according to the considerations developed in the theoretical part, Chapter VII, § 32, the following phenomena may be expected. With increasing current density the potential will become less negative or more positive and a rising potential–current density curve will be obtained. If the disturbance of the metal proceeds so

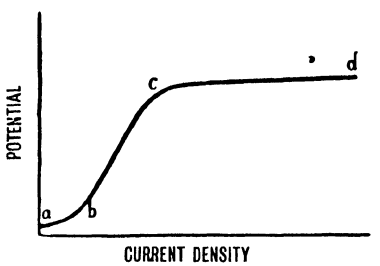


FIG. 202.

far that the deposition potential of oxygen is reached, a three-phase equilibrium will be established between the metal phase, the oxygen phase and the electrolyte. If the system behaves as a four-component system, this three-phase equilibrium will correspond, at constant temperature, constant pressure and constant total concentration, to a very definite potential. But with increasing current density the potential will become more positive. This would also be possible if the co-existing oxygen phase were always in inner equilibrium, but only in cases in which the metal may be still further disturbed by increasing the current density. Under these circumstances, therefore, the point L″ in Fig. 125, which is reproduced here, would be displaced along the line L″ b_0.

If, however, as is usually the case, the oxygen formed at higher current densities is no longer able to establish itself in inner equilibrium, not only will the line $a''\,c''$ in the diagram fall, but the line $b_0\,g_0$ also,

the result being, therefore, that a marked change of potential occurs in the positive direction.

It may be noticed here, that whilst before the separation of oxygen the withdrawal of electrons only caused metallic ions to go into solution, when oxygen is liberated the anions in the solution will also be deprived of their electrons, so that the influence of the electric current then distributes itself over both metal and oxygen.

It should further be noticed that the velocity of the internal change, both in the metal and in the oxygen, greatly increases the more widely these phases deviate from the inner equilibrium state, so that as the current density is increased the increase in the disturbance may be expected constantly to diminish, finally to become very small.

From these considerations, therefore, the potential–current density curve should have the form indicated in Fig. 202.

The potential–current density curve for metals which are not active has in fact a form similar to this. In the case of very inert metals, such as nickel, cobalt, chromium, aluminium, etc., a very large value is obtained for $\frac{dV}{dS}$ [1] even though the current density is very small, so that the portion of the curve $a\,b$ then appears to be lacking. Naturally this is not really the case, for however inert a metal may be, there must always be a minimum current density which will disturb the metal to only a slight extent.

6. The Appearance of the State of Formation during Electrolytic Deposition. Cathodic Polarisation.

In the electrolytic deposition of a metal, electrons are conducted to the cathode, with the result that metallic ions are immediately deposited on the cathode. It will now again depend on the velocity with which electrons are deposited, and on the velocity with which the inner equilibrium

$$M_S^{\nu\cdot} + \nu\theta_S \rightleftarrows M_S$$

is established, whether the potential of the metal will remain steady during the deposition. If the last-named velocity is too small, the newly formed metallic surface will contain too many ions and electrons, and the potential will be much too negative. This case is known as cathodic polarisation.

It is natural, of course, that active metals which exhibit slight anodic polarisation should also undergo cathodic polarisation to only a small extent, whilst in the case of inert metals where pronounced anodic polarisation occurs, a large cathodic polarisation would also be expected, which, as Fig. 125*a* shows, may lead to the evolution of hydrogen. If this point is reached, and therefore the phases S_2L_2 and d_2 co-exist, the potential will become still more negative as the current density increases. Consequently the three-phase equilibrium $S_2L_2d_2$ moves

[1] Here V represents the potential and S the current density.

upwards ; but since the instability, and with it the velocity of the internal change, will thus finally become very great, the cathodic polarisation curve may be expected to have the same general form as that shown for anodic polarisation ; if, that is to say, the negative potential is now numbered upwards.

It will be seen, however, that in reality the polarisation curve often has a form which deviates from that expected to a greater or less extent, in consequence of the negative catalytic influence exerted by oxygen or hydrogen.

It is noteworthy that the powerful positive catalytic influence which chlorine ions have been proved to exert on the processes of non-electrolytic solution and anodic polarisation is absent in the case of cathodic polarisation.

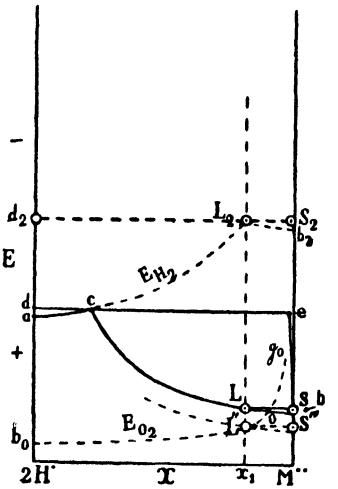


FIG. 125*a*.

This phenomenon can, however, be very easily explained. When cathodic polarisation occurs, the chlorine ions are conducted away from the metal, so that there is much less contact between metal and chlorine ions than in the case of anodic polarisation.

7. Strong Disturbances, resulting from Electrolytic Solution, which lead to Anodic Passivity.

Since between the solution of a metal, accompanied by corrosion, in the purely chemical way and electrolytic solution no essential difference exists, wherever the first-mentioned process can give rise to passivity, this phenomenon may also be expected when electrolytic solution takes place.

Schönbein succeeded in proving that iron, for example, can be converted into the passive state not only by dipping it into strong nitric acid, but also when it is made the anode in a solution of ferrous sulphate and is therefore electrolytically dissolved.

When this experiment is performed and the potential of the iron and the current density are simultaneously observed, the graph shown in Fig. 203 is obtained.

This curve shows that at a current density of approximately 0·4 amperes per sq. centimetre, the potential of the iron always changes in a remarkable way as the current density is further increased. It passes from negative values through 0, becomes positive, and between the points *b* and *c* it exceeds the deposition potential of oxygen.

Consequently oxygen is evolved, whilst the iron electrode entirely retains its lustre. From this point the potential rises still further as the

current density is increased, and indeed very rapidly at the outset; finally, however, as the curve *c d* shows, the rise of potential with increasing current density becomes very slight. Unfortunately the portion *b c* cannot be determined accurately, because the iron electrode never becomes passive over the whole surface at the same moment.

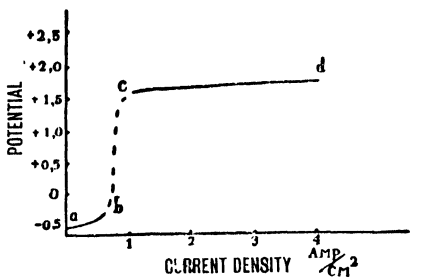


FIG. 203.

The upper half of the polarisation curve, of which only the approximately horizontal portion can be determined, refers therefore to the polarisation of the passive iron and the oxygen.

The polarisation curve discussed here appears, not only when electrolytic iron is used, but also for every variety of iron containing carbon.

8. The Activation Curve.

The peculiar behaviour of iron appears most clearly when the potential of the passive iron is measured after interrupting the current.

When the current is interrupted during the anodic polarisation of silver a rapid fall of potential to the normal value is observed, as was to be expected. This is shown in Fig. 204.

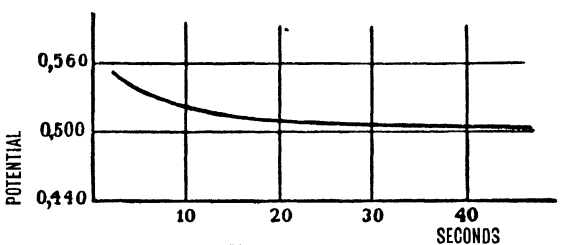


FIG. 204.

But iron, in a solution of ferrous sulphate, was found to behave in an entirely different way, as Fig. 205 shows. Immediately after the interruption of the current causing the anodic polarisation, the potential of the iron is still strongly positive in relation to a normal calomel electrode, but it diminishes rapidly at first, then for some time only extremely slowly, and finally it falls very rapidly to the value it had before polarisation. This curve is called the activation curve.

Over the whole of the portion of the curve which is very nearly horizontal the iron is still passive; if during this period it is dipped into a solution of copper sulphate, no copper is deposited on the surface of the iron.

The behaviour of iron which has been converted into the passive state by means of nitric acid agrees completely with that of the passive iron formed by anodic polarisation, hence it follows that the former,

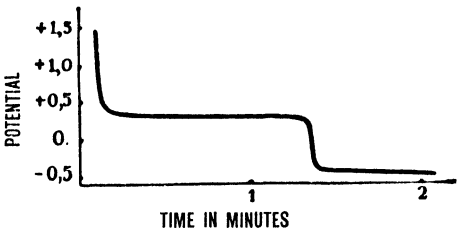


FIG. 205.

when dipped into the same ferrous sulphate solution, will exhibit a potential which lies on the horizontal portion of the activation curve.[1]

9. Historical.

Now that the experimental facts necessary to the statement of the problem have been given, the question will be considered from the historical side. As has already been pointed out, attempts to explain the remarkable phenomenon known as passivity have not been lacking. Faraday[2] was of opinion that the surface of the passive iron was either oxidised or that the particles of iron held the oxygen bound in some other way. He expressed his views as follows: "The phenomena are due to a relation of the superficial particles of the oxygen," and further, "My strong opinion is, that the surface of the iron is oxidised or that the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation, and that, having thus their affinity for oxygen satisfied and not being dissolved by the acid under the circumstances, there is no renewal of the metallic surface."

Notwithstanding some scepticism, led by Schönbein, the oxidation theory was for a long time considered to furnish a correct explanation of the phenomena, until Hittorf[3] sharply criticised it. By means of experiments on iron and chromium he showed that according to the oxidation theory the existence of as yet unknown and very unstable oxides must be assumed, having properties surpassing those of the known oxides. These oxides would not be soluble in acids and on increasing the temperature they would decompose, for passivity disappears at high temperatures.

Hittorf showed that chromium can go into solution in the di-, tri- or hexa-valent condition. He investigated the solution process accompany-

[1] Smits, Aten. *loc. cit.*

[2] *Phil. Mag.* (3), **9**, 122 (1836).

[3] *Zeitschr. f. physik. Chemie*, **25**, 729 (1898); **30**, 481 (1899); **34**, 385 (1900). *Zeitschr. f. Elektrochem.* **4**, 482 (1898); **6**, 6 (1899); **7**, 168 (1900).

ing anodic polarisation, and found that when the chromium had become passive chromic acid was formed on the anode. Naturally this might have been produced by a secondary process, but in any case it proved that chromium dissolves even though it is in the passive state, and this cannot be explained by means of the oxidation theory. He states: "In den drei Zustanden (Chrom in Lösung gehend als $Cr^{\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$ and als Chromat) zeigt unser Metall so verschiedene Eigenschaften, wie sie sonst nur verschiedene Metalle besitzen. Im inaktiven Zustande ist es ein edles Metall, reduziert kein anderes Metall aus der Lösung seiner Salze und steht am Ende der Spannungsreihe beim elektronegativen Platin. Befindet es sich dagegen in dem Zustande, welches es bei der Bildung seiner elektrolytischen niedrigsten Verbindungsstufe hat, so nimmt es unmittelbar hinter dem Zink in der Spannungsreihe Stellung und verdrängt die Metalle, welche elektronegativer sind als ihre Salze."[1] He further states: "Ware das elektrochemische Verhalten des Chroms vor demjenigen des Eisens bekannt gewesen, so hatte die Erklarung des Passivitat des letzteren aus der Anwesenheit eines Oxydhautchens nicht leicht Annahme gefunden."[2]

The statements of Hittorf himself concerning the cause of passivity are very indefinite. Thus he says: "In der Passivitat oder Inaktivitat, welche die vier Metalle Chrom, Eisen, Nickel, Kobalt annehmen, liegt offenbar ein Zwangszustand in ihren Molekulen vor, der unter bestimmten Bedingungen entsteht und mit dem Aufhören derselben schneller oder langsamer, aber stetig sich verliert. Die Teilchen kehren von selbst in den normalen aktiven Zustand zuruck, bei welchem sie ihre niedrigsten Verbindungstufen bilden."

Besides Hittorf, Leblanc[3] and Fredenhagen[4] have also expressed themselves against the oxidation theory, and Müller and Königsberger[5] have shown, by observation of the reflective power of active and passive iron, that this property is exactly the same both for the active and the passive states.

Films of oxide, even when very thin, would strongly affect the reflective power of metals. They proved this by depositing an extremely thin film of PbO_2 (0·8 $\mu\mu$) on a platinum mirror the reflective power of which was known. This property was then re-determined. They found the reflective power of the mirror to be greatly impaired by this extremely thin film of oxide, and since the optical constants of the known oxides and hydroxides of iron differ but little from those of PbO_2, they concluded that passive iron cannot be coated with a film of oxide. Micheli[6] arrived at the same result.[7] Haber and Goldschmidt,[8] Haber

[1] *Zeitschr. f. physik. Chemie*, **25**, 748 (1898).
[2] *Ibid.*, **34**, 386 (1900).
[3] *Boltzmann-Festschrift*, 183 (1904). *Zeitschr. f. Elektrochem.* **11**, 9 (1905).
[4] *Zeitschr. f. physik. Chemie*, **63**, 5 (1908).
[5] *Physik. Zeitschr.* **5**, 415, 797 (1904); **6**, 847 (1905); **7**, 797 (1906); **13**, 659 (1907).
[6] *Arch. Sci. phys. Geneve*, **115**, 122 (1900).
[7] Bennet and Burnham, *Zeitschr. f. Elektrochem.* **22**, 377 (1916), again assume the existence of oxides which are dissolved or absorbed in the solid metal.
[8] *Zeitschr. f. Elektrochem.* **12**, 49 (1906).

and Maitland,[1] and Krassa [2] have disputed this inference. They are of opinion, that is to say, that both active and passive iron are coated with a porous film of iron oxide and that there merely exists a difference in the number of the pores. According to their conception these pores are continually being formed and closed up again, and in this way they seek to explain the conduction of electricity by the film of oxide and also the distinct solubility of the metal even when in the passive state. The existence of a series of different passive states they explain by assuming differences in the number and size of the pores. Apart from the arbitrary nature of Haber and Goldschmidt's view, the possibility of explaining the great positive catalytic influence of halogen ions by means of this theory is just as remote as in the case of the old oxide theory, and further it is clear that their conception can never serve to explain cathodic polarisation.

If anodic polarisation is supposed to continue until oxygen is evolved, as a result of which the iron is converted into the passive state, it is easy to recognise that the whole question whether or not iron in the passive state is covered with a film of oxide is of secondary importance. The *main point* is always the great displacement of the iron potential in the direction of greater nobility, until it may even attain the deposition potential of oxygen. This phenomenon of passivity, the primary phenomenon, first needs explaining. The theory developed in the theoretical part is capable of furnishing such an explanation, and at the same time it enables us to prove that passive iron can be something different from iron which is coated with a film of oxide.

A few other theories will also be briefly discussed here; they represent advances on the old oxide theory, since they show that the phenomena of polarisation and the appearance of passivity must find their explanation in retarded reactions.

Thus, Leblanc [3] supposed the *heterogeneous* process, the solution of the metal, to be retarded. Jordis [4] and Fredenhagen,[5] whilst following the method indicated by Leblanc, formulated a theory in which an oxygen charge is assumed, on the ground that the *heterogeneous* process of solution in metals is retarded by oxygen. Muthmann and Frauenberger [6] differ from Fredenhagen, in that, instead of an oxygen charge, they speak of a metal–oxygen alloy. In addition to this, they assume that the most negative value of the metal potential during cathodic deposition or cathodic polarisation is the equilibrium potential.

Flade [7] again goes somewhat further, in that he maintains the possibility of the formation of an oxide from the oxygen alloy.[8]

[1] *Zeitschr. f. Elektrochem.* **13**, 309 (1907).
[2] *Ibid.*, **15**, 490 (1909).
[3] *Zeitschr. f. physik. Chemie*, **6**, 472 (1900).
[4] *Zeitschr. f. Elektrochem.* **11**, 787 (1905).
[5] *Zeitschr. f. physik. Chemie*, **43**, 1 (1903); **63**, 1 (1908). *Zeitschr. f. Elektrochem.* **11**, 857 (1905); **12**, 797 (1906).
[6] *Zeitschr. f. Elektrochem.* **10**, 929 (1904); *Sitz-Ber. der. Kgl. Bayr. Akad.*, **34**, 210 (1914).
[7] *Zeitschr. f. physik. Chemie*, **76**, 513 (1911).
[8] See also Bennet and Burnham.

The hydrogen theory of Grave,[1] Adler[2] and Rathert[3] is opposed to these oxygen theories. According to this view metals in the active state contain dissolved hydrogen, which exerts a positive catalytic influence on the heterogeneous solution process. The passivating action of oxidising agents and of anodic polarisation consists, according to their theory, in the removal of hydrogen ions from the metal.

Much more comprehensive than the one-sided oxygen charge or hydrogen charge theories is the hydrogen–oxygen theory advocated by Foerster[4] in 1909.

Foerster originally adopted the point of view expressed in the hydrogen activation theory; he thought that the *heterogeneous* solution process

$$M_S \rightarrow M_L^{\nu\cdot} + \nu 0_S$$

could be retarded, but that hydrogen was instrumental in determining the potential.

Under certain circumstances he was willing to combine this conception with the theory of the existence of a film of oxide, in order to include all the phenomena associated with passivity and activity. Since the above-mentioned process can also be retarded in the reverse direction, this conception also makes it possible to explain cathodic polarisation.

In his magnificent work *Elektrochemie wäffriger Losungen,* however, Foerster in 1915 developed an idea which differs from that mentioned above, in that the oxygen charge theory is combined with the hydrogen theory. In this theory Foerster considers hydrogen to be a positive, *i. e.* an activating catalyst. In a later publication he returns to this idea.[5] He shows, however, on the ground of the retardation of the cathodic deposition of the metal, that hydrogen, just like oxygen in the process of anodic solution, must have a negative catalytic influence ascribed to it. Hydrogen and oxygen are therefore negative catalysts and the activating influence of hydrogen consists in the elimination of the oxygen by the formation of water. This theory is more general than either of Foerster's earlier theories, and consequently it is in better agreement than the others with the observed phenomena. Yet one serious objection can be raised against this view. In this combined theory, as in each of those from which it is built up, it is assumed that the primary cause of passivity is a retardation of the *heterogeneous* solution process.

It must therefore be imagined that no heterogeneous equilibrium exists, in polarised and passive states, between the metal and the liquid bounding layer. But this assumption cannot be correct, because, for the same reasons as Nernst has already shown to apply to ordinary

[1] *Zeitschr. f. physik. Chemie*, **77**, 513 (1911).
[2] *Ibid.*, **80**, 835 (1912). [3] *Ibid.*, **86**, 567 (1914).
[4] "Beitrage zur Kenntnis des elektrochemischen Verhaltens des Eisens." *Abh. der Deutschen Bunsengesellschaft*, No. 2.
[5] *Zeitschr. f. Elektrochem.* **22**, 95 (1916).

solution processes, heterogeneous equilibrium must always exist between a metal and its bounding liquid.

The solution of the problem must therefore be sought in another direction.

Apart from the attempts at explanation already mentioned, Leblanc[1] has published another, to which the objections previously raised cannot validly be made. In this he assumes that the equilibrium between anhydrous ions, water and hydrated ions is established slowly. Since the potential is determined by the non-hydrated ions, and the concentration of these ions increases during anodic solution and decreases during the cathodic deposition of the metal, on the basis of this assumption polarisation phenomena might be expected.

From this idea Leblanc came to the conclusion that the cause of passivity is to be found in the solution, and that it is therefore really a concentration polarisation.

Kuessner[2] and Schildbach[3] are of the same opinion. Although a small fraction of the effects observed during polarisation can be produced in this way, this theory cannot be accepted as adequate to the phenomena of passivity. It may easily be shown that the cause of passivity cannot lie in the liquid. Thus passivity can remain in existence when the metal is transferred to another liquid, even when the latter is vigorously stirred. Further, it has even been proved that passive iron can be kept for many hours in the dry state.

The valency theory put forward by Finkelstein in 1901[4] represented an advance. He assumed that the metals which can be rendered passive are alloys of metals of different valencies, and that in the active state metal of the lower valency is mainly present; in the passive state, however, the higher valency predominates. The fundamental idea in this theory is that the origin of the passivity of the metal is to be explained by a displacement of the proportions in which the constituents of different valencies are present. At a given temperature and pressure naturally only *one* distribution of the two constituents in the metal can be stable. Thus, according to Finkelstein, active iron is ferrous iron, and passive iron is iron which is superficially in the ferric condition. This theory, although somewhat indefinite, yet seemed more comprehensive than Hittorf's, the most worthy of consideration amongst the older theories. It will be seen later, however, that this theory too, even when more carefully worded, can have no general significance.

A rather different idea was put forward by Müller.[5] He looked upon the difference in the electron density as the cause of activity and passivity. Further, he was of opinion that states of different valency formed different phases, whence a homogeneous equilibrium such as

[1] *Zeitschr. f. Elektrochem.* **9**, 636 (1903); **11**, 705 (1905). *Zeitschr. f. physik. Chemie*, **46**, 213 (1903). *Boltzmann-Festschrift*, 183 (1904); *Chem. News*, **109**, 63 (1914).

[2] *Zeitschr. f. Elektrochem.* **16**, 754, 967 (1910). [3] *Ibid.*

[4] *Zeitschr. f. physik. Chemie*, **39**, 91 (1902).

[5] *Ibid.*, **48**, 577 (1904); *Zeitschr. f. Elektrochem.*, **15**, 696 (1909).

Finkelstein assumed between ions of different valencies becomes impossible.

This point of view too has found no following. The general opinion was well expressed by Beyers [1] when he wrote: "The valency hypotheses of Finkelstein and of Müller are not yet demonstrated to be true or false, but in their present forms are unsatisfactory."

This was the position with regard to the problem of passivity and polarisation, when by applying the principles of the Theory of Allotropy to electromotive equilibria I was led to a general theory of the phenomena in question.

Since a heterogeneous equilibrium must always be assumed to exist between a metal and its bounding liquid, according to our results polarisation must be considered to be a disturbance of the inner equilibrium in the metal, *i.e.* in the most simple case, the equilibrium between metal atoms, metallic ions and electrons.

If a marked disturbance occurs, so that superficially the metal is converted into a less active state, which under the influence of a negative catalyst may persist for some time, the term passivity is usually employed.

The theory showed that the phenomena of anodic and cathodic polarisation, and therefore passivity also, can even appear when *one* species of ion exists besides metallic atoms and electrons, and that the existence of ions of *different species, i.e.* of different *sizes* or *different valencies*, in the metal leads to special cases.

The charges of gas which in other theories were considered to be the primary phenomena, are in this theory of a secondary nature only.

Some of the more important metals will now be considered somewhat more thoroughly in the light of this theory.

10. Iron.

(a) *The equilibrium potential of iron.*

Because of the considerations dealt with in a previous paragraph, it is advisable to employ a solution of an iron salt in which the relative hydrogen ion concentration is as small as possible for the determination of the equilibrium potential of iron. Thus the point in the E X diagram corresponding to the composition lies as far as possible to the left of *c*. To avoid the disturbing influence of oxygen or of hydrogen, it is then advantageous to carry out the measurements with solutions which have been boiled in a vacuum in the manner already described.

With regard to this mode of procedure, Lobry de Bruyn, using a pure 0·1 N. solution of ferrous sulphate, obtained the value − 0·720 V relative to the normal calomel electrode or $E_H = -0{\cdot}434$ V.[2] In a second experiment in which the hydrogen-ion concentration had been

[1] *Journ. Amer. Chem. Soc.*, **30**, 1718 (1908).

[2] *Dissertation*, Amsterdam (1920); *Rec. d. Trav. Chem. des Pays-Bas*, **11**, 30 (1921).

reduced as much as possible by the addition of several c.cs. of a solution of sodium hydroxide, the value $E_H = -0{\cdot}436$ V was found.

In the case of iron, which is much less inert than nickel, it was found less dangerous to carry out measurements in an atmosphere of hydrogen. Thus Richards and Behr,[1] working in hydrogen, found the potential of iron in normal ferrous sulphate solution to be between $-0{\cdot}46$ and $-0{\cdot}43$ volts.

Believing that iron can only attain its equilibrium potential when hydrogen is present, Muthmann and Frauenberger[2] measured the most negative potential exhibited by electrolytic iron after cathodic polarisation. In this way they obtained the value $-0{\cdot}946$ V or $E_H = -0{\cdot}66$ volts. This potential, however, is not the potential of iron in a state of inner equilibrium, but that of iron which is still in a state of formation.

(b) *The influence of ferric ions in the electrolyte on the potential of iron.*

In the determination of the equilibrium potential of iron, if the electrolyte contains ferric ions the disturbing influence it may exert must be borne in mind. It has already been shown that when ferric ions are present in the electrolyte the potential of the iron is less negative.[3] This behaviour may easily be explained.

When a solution of an iron salt is left in contact with iron for a long time in a closed vessel, this solution, which originally contained ferric ions, finally contains ferrous ions practically exclusively. This fact proves that iron can only exist in inner equilibrium with a solution containing, for practical purposes, ferrous ions only.

If, therefore, iron is dipped into a solution containing ferric ions in addition to ferrous ions, the consequence can easily be indicated.

In the solution the following equilibria exist:—

$$Fe_L \rightleftarrows Fe^{\bullet\bullet}{}_L + 2\theta_L$$

$$Fe_L \rightleftarrows Fe^{\bullet\bullet\bullet}{}_L + 3\theta_L$$

And therefore also the equilibrium

$$Fe^{\bullet\bullet}{}_L \rightleftarrows Fe^{\bullet\bullet\bullet}{}_L + \theta_L.$$

Iron cannot co-exist in equilibrium with this solution, since it contains an appreciable quantity of ferric ions; in other words, because the electron concentration is too small. At higher electron concentrations the ferric ions would be reduced to ferrous ions. It is clear, therefore, that iron is able, by expelling electrons, to convert this solution into one with which it can co-exist in inner equilibrium.

If, now, the inner equilibrium

$$Fe_S \rightleftarrows Fe^{\bullet\bullet}{}_S + 2\theta_S$$

originally prevails in the iron, on dipping it into the solution the metal

[1] *Zeitschr. f. physik Chemie*, **58**, 301 (1907).
[2] *Sitzungsber. der Kgl. Bayr. Akad. d. Wiss.*, **34**, 206 (1904).
[3] Finkelstein, *loc. cit.*

will send electrons, and with them naturally ferrous ions also, into the solution. This process is indicated by the symbols

$$\begin{array}{cc} 2\theta_S & Fe^{\cdot\cdot}{}_S \\ \downarrow & \downarrow \\ 2\theta_L & Fe^{\cdot\cdot}{}_L \end{array}$$

If inner equilibrium were instantaneously established in the iron, the ferrous ions and the electrons expelled would be replaced by the homogeneous reaction

$$Fe_S \rightarrow Fe^{\cdot\cdot}{}_S + 2\theta_S ;$$

but if this electro-ionisation does not take place so rapidly, the iron will become poorer in electrically charged particles, the solubility product will be smaller and the potential will become less negative.

On the basis of the simple assumption that iron only contains iron atoms, ferrous ions and electrons, the disturbance, or polarisation of iron in the direction of greater nobility, by an electrolyte containing ferric ions, can thus be explained in a simple manner.

Since, however, ferrous and ferric ions are known to be present in the solution, ferrous and ferric ions may be supposed to occur in metallic iron also; thus the method of consideration employed must be somewhat more general.

In the unary metal the equilibrium

$$Fe_S \rightleftarrows Fe^{\cdot\cdot\cdot}{}_S + 3\theta_S$$

prevails, and therefore the equilibrium

$$Fe^{\cdot\cdot}{}_S \rightleftarrows Fe^{\cdot\cdot\cdot}{}_S + \theta_S \text{ also.}$$

If the iron sends electrons and ferrous ions into solution, as a result of which inner equilibrium is established less rapidly in the metal, it is evident from the last equation that a diminution of the ratio $\left(\frac{Fe^{\cdot\cdot}{}_S}{Fe^{\cdot\cdot\cdot}{}_S}\right)$ is associated with a decrease in the concentration of electrons and ferrous ions. This also leads, as has already been shown in the theoretical part, to a change of potential in the direction of greater nobility.

If the influence of ferric ions in the electrolyte on the potential of the iron is experimentally investigated, this potential will obviously depend on the vigour with which the liquid is stirred. It has already been pointed out that iron sends electrons and ferrous ions into solution, and therefore the liquid bounding layer is much poorer in ferric ions than the liquid outside the bounding layer. The presence of ferric ions in the bounding layer is traceable to the fact that the velocity with which electrons are formed in the metal is too small to allow of the ferric ions which have diffused into the liquid bounding layer being converted immediately and completely into ferrous ions. For a given concentration of ferric ions in the electrolyte, at constant temperature, the thickness of the layer in which the decrease in the concentration of ferric ions takes place will naturally depend on the velocity with which the liquid is stirred. The greater this velocity, the smaller will the diffusion

layer be, and the greater will be the number of ferric ions per second to reach the liquid surface immediately touching the iron. Hence it follows, therefore, that the disturbance of the iron will increase with the speed with which the liquid is stirred.

In addition, it has been established that the potential always fluctuates to a greater or less extent when the velocity of stirring is very great, for then the iron is not uniformly corroded, so that the disturbance does not remain the same over the whole surface, but continually changes. The figures given below, representing the disturbance produced in active iron by vigorously stirred solutions containing ferric ions, are therefore only mean values.

THE POTENTIAL OF ACTIVE IRON IN 1 N. SOLUTIONS OF FERROUS-FERRIC SULPHATE VIGOROUSLY STIRRED.

Per cent. ferrous sulphate.	Per cent. ferric sulphate.	Potential.		
		Hard steel.	Mild steel.	Platinum.
100	0	— 0·600	— 0·605	0·220
86·2	13·8	— 0·470	— 0·440	0·320
60·1	39·9	— 0·404	— 0·430	0·361
49·5	50·5	— 0·390	— 0·410	0·372
30·0	70·0	— 0·370	— 0·397	0·394
16·1	83·9	— 0·370	— 0·386	0·416
4·0	96·0	— 0·370	— 0·150	0·457
1·9	98·1	considerable fluctuation		0·506

Both kinds of iron thus become more disturbed as the concentration of the ferric ions increases. In the case of mild steel the disturbance could be pushed further, the result, probably, of more uniform corrosion.

(c) *The passivation of iron.*

(1) *Passivation by means of strong nitric acid of Sp. Gr.* 1·4.

The interesting phenomenon of the passivation of iron by means of strong nitric acid of Sp. Gr. 1·4 will now be considered more fully.

When iron is dipped into strong nitric acid the metal is violently attacked. The electron concentration of the iron equilibrium in the liquid is much greater than the electron concentration of the hydrogen equilibrium in strong nitric acid. The hydrogen ions which therefore diffuse into the bounding surface of the iron will combine with electrons to form hydrogen molecules, and this molecular hydrogen will in turn diffuse into the nitric acid and be oxidised away. This corrosion of the iron by strong nitric acid proceeds very rapidly, and in consequence the metal becomes poorer in ions and electrons.

That the disturbance can in this case be forced to such an extreme is due to the fact that the electron concentration in strong nitric acid is much smaller than in other acids, so that the solution process also takes place extremely rapidly.

This extremely small electron concentration is connected with the powerful oxidising action of strong nitric acid. In this acid, therefore, the concentration of molecular hydrogen is extraordinarily small—very much smaller than in strong hydrochloric acid, for example. As regards the concentration of molecular oxygen, the reverse is the case; in strong nitric acid there is a relatively high concentration of molecular oxygen. The following equations express this fact:—

$$H_{2L} \rightleftarrows 2H^{\cdot}_{L} + 2\theta_{L}$$

and

$$2H_2O_L + O_{2_L} + 4\theta_L \rightleftarrows 4OH'_L.$$

Since $(H_2)_L$ is so extremely small in strong nitric acid, according to the first equation (θ_L) must also be very small, compared with strong hydrochloric acid, in which we will assume for a moment, the concentration of hydrogen ions to be the same. Consequently, according to the second equation, in the same way (O_2) is relatively great in strong nitric acid as compared with strong hydrochloric acid.

Thus strong nitric acid contains a relatively large concentration of molecular oxygen, and in consequence iron, if it is so violently disturbed in strong nitric acid that it only dissolves extremely slowly, will dissolve oxygen. Now since oxygen is a strong negative catalyst for the establishment of inner equilibrium in the metal, the disturbance will still further increase, and for some time the superficially dissolved oxygen will be able to prevent activation of the passive iron even when it is transferred to other solutions.

(2) *Passivation by means of solutions containing a high concentration of ferric ions.*

From the above considerations it follows that the violent disturbance of the iron known as passivation can be caused by any electrolyte in which the electron concentration is extremely small, if only no activating constituents such as halogens are present. Now, since it is known that the equilibrium

$$Fe^{\cdot\cdot}_{L} \rightarrow Fe^{\cdot\cdot\cdot}_{L} + \theta_{L}$$

in the solution with which unary iron can co-exist lies practically completely towards the left, and a displacement of this equilibrium towards the right takes place when electrons are withdrawn, and therefore, conversely, with increasing concentrations of ferric ions the electron concentration becomes smaller, very concentrated solutions of ferric salts might be expected to be good passivating agents; if, that is to say, the anions present exert no activating influence. In fact, Lobry de Bruyn[1] succeeded in converting iron into the passive condition by dipping it into a concentrated solution of ferric sulphate, though in this he was only once successful, and while these investigations were being continued, a private communication was received from Ornstein and Moll, to the effect that they had succeeded in transforming active into passive iron by dipping it into a solution of ferric nitrate. On this,

[1] *loc. cit.*

experiments were carried out with concentrated solutions of ferric nitrate, as a result of which not only the influence of concentration, but also that of temperature, was studied. The results obtained are given in the table below.

From this table it is clear that passivation by means of ferric nitrate solutions is promoted both by increase of concentration and also by reducing the temperature, as was indeed to be expected. It may be pointed out here that in this passivation of iron, the metal can naturally also superficially dissolve a little oxygen.

Temperature of the solution.	Concentration of the solution.	State of the iron on dipping it into the solution.	Temperature limits for passivation.
35°	0·14 g. mol. $Fe(NO_3)_3$ per litre	active	31° – 34°
34°		active	
31°		passive	
30°		passive	
20°		passive	
23°	0·11 g. mol. $Fe(NO_3)_3$ per litre	active	20·5° – 22°
22°		active	
20·5°		passive	
20°		passive	
10°		passive	
10°	0·06 g. mol. $Fe(NO_3)_3$ per litre	active	8° – 9°
9°		active	
8°		passive	
5°		passive	

Although the activating influence of halogen ions will again be discussed, this influence may also clearly be indicated here. When an extremely concentrated solution of ferric chloride was employed, which only commenced to solidify at – 40°, Lobry de Bruyn never succeeded in passivating active iron, not even at – 40°, by means of this solution. A marked disturbance was indeed observed at this temperature, on one occasion to the extent of + 0·180 volts., but this disturbed condition was still far removed from the passive state.

(d) *The anodic polarisation and passivity of iron.*

(1) *The retarding influence of dissolved oxygen on the establishment of inner equilibrium in iron.*

Although the anodic polarisation and passivation of iron have already briefly been mentioned, in some particulars they will be more thoroughly discussed here.

In the absence of activating influences, as we have seen, iron may easily be disturbed during anodic solution to such an extent that the deposition potential of oxygen is reached. As was shown in the theoretical portion of this work, the positive value of the potential may then still increase slightly with increasing current density, especially if

the oxygen phase can co-exist in the state of formation, or, in other words, if oxygen over-voltage can occur. Now the strongly positive value of the potential in the case of anodic polarisation points to the oxygen overvoltage being considerable, for indeed evolution of oxygen commences, in Fig. 203, approximately half-way between *b* and *c*.

If the iron anode contains no cavities, scratches or other irregularities, on the anodic evolution of oxygen, the iron becomes passive over its entire surface. If now the current density is allowed to diminish a

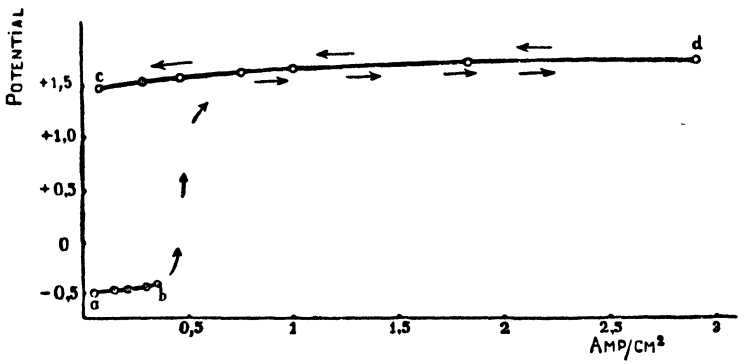


FIG. 206.

peculiar behaviour is established. It then appears, as is indicated in Fig. 206 by the arrows pointing backwards, that the iron remains passive even when the current density is very small, and that therefore the establishment of inner equilibrium in the iron surface is now very much retarded. This retardation may be explained thus: On passivation the iron absorbed a little oxygen, and this acted as a powerful check on the activation process.

(2) *The current efficiency in the anodic solution of iron.*

Since, in the anodic solution of iron, the behaviour of the current efficiency with increasing current densities was very encouraging, at my suggestion Lobry de Bruyn made some experiments in this direction.

With fairly pure commercial iron (carbon content 0·1 per cent.) in the active state the following figures were obtained:—

Current density, amps. per sq. cm.	Current efficiency per cent [1]
0·013	99·9
0·020	99·6
0·027	99·4
0·034	99·1

[1] The electrolyte was, to begin with, a solution of Na_2SO_4.

Thus, from these numbers, which relate to experiments carried out with such current densities that the iron still remained active, it appears that the current efficiency diminishes slightly as the disturbance of the iron increases, and with increase of the potential. This result could naturally be explained by assuming that with increasing potential, besides ferrous ions the iron sends an increasing number of ferric ions into solution. As was shown in the theoretical part, this would be a necessary consequence of the assumption that iron contains both ferrous and ferric ions. But it is also possible that although the iron electrode exhibits an active potential there are already single spots which are more highly disturbed, so that, locally, electrons may be carried away from the liquid.

In the determination of the current efficiency during the anodic solution of passive iron, various kinds of iron were used, indicated here by the numerals I to VI. These six varieties of iron were:—

I. Technical iron containing 0·1 per cent. carbon.
II. Iron with 0·4 per cent. carbon.
III. Iron containing phosphorus but of low carbon content.
IV. Tool steel containing 1·1 per cent. carbon.
V. Cast-iron containing 3·5 per cent. carbon.
VI. Electrolytic iron.

The following table gives the results obtained with these different kinds of iron.

Kind of iron.	Current density, amps. per sq. cm.	Current efficiency per cent.
I	0·0005	1·09
II	0·0005	1·21
III	0·0005	1·23
IV	0·0005	1·24
V	0·0005	4·75
VI	0·0005	The iron was active.

These figures show that even when the metal is in the passive condition iron undergoes anodic solution. Varieties I to IV exhibited but slight differences, the current efficiency amounting to about 1 per cent. Cast-iron, however, dissolves much more rapidly in the passive state, this behaviour being connected with its higher carbon content and its coarser structure. As Centnerzwer's[1] investigations on the rate of solution in acids of zinc containing carbon showed, carbon exerts an accelerating influence on the process of solution, and the coarse structure of cast-iron makes it perhaps impossible to convert every point of the surface into the passive condition.

The behaviour of electrolytic iron is very remarkable. This variety of iron is difficult to render passive, and it is still more difficult to keep

[1] *Zeitschr. f. physik. Chemie*, **87**, 692 (1914).

it in the passive state. As we shall see presently, these facts may easily be explained; for this reason no results could be obtained for this variety of iron in the passive state.

The results obtained with other kinds of iron are of importance because they show that passive iron does not constitute a non-corrodible electrode.

The phenomenon of the withdrawal of electrons to the passive iron anode gives rise not only to a discharge of anions with the separation of an oxygen phase, but also to the passage of metallic ions into solution, though only to the extent of about 1 per cent. This behaviour is in complete agreement with the new theory.

During the anodic polarisation of passive iron a three-phase equilibrium prevails, since oxygen has now made its appearance as a third phase. In connection with the well-established retarding influence of oxygen dissolved in the iron on the establishment of the inner metal equilibrium, it might be expected that electro-ionisation, in the passive iron, would take place very slowly. If this should be the case the electrons withdrawn to the metal must be furnished, for the most part, by the electrolyte, since otherwise the potential would rise very considerably. An efficiency of only 1 per cent. was therefore not surprisingly small.

(e) *The potential of passive iron in* 0·1 N. *solutions of ferrous—ferric sulphate.*

Since passive iron, though it is only slightly attacked, does not constitute a non-corrodible electrode, it became of interest to compare the potential of passive iron with that of the non-corrodible platinum electrode. The results are combined in the following table.

THE POTENTIALS OF PASSIVE IRON AND OF PLATINUM IN 0·1 N. SOLUTIONS OF FERROUS—FERRIC SULPHATE.

Per cent ferrous.	Per cent. ferric.	Platinum potential.	Passive iron potential.
69	31	+0·345	+0·335
55	45	+0·362	+0·352
48·5	51·5	+0·369	+0·358
39	61	+0·382	+0·369
30	70	+0·394	+0·384
5	95	+0·450	+0·442

From these data, which are graphically represented in Fig. 207, it appears that the potential of passive iron is always somewhat lower than that of platinum, as was to be expected from the fact that it is slightly corrodible.

(f) *The activation curve for passive iron.*

If, after anodically passivating iron in a solution of ferrous sulphate,

the current is interrupted and the potential is then read at definite intervals of time, a peculiar result is obtained, which becomes evident by reference to the table given on the next page.

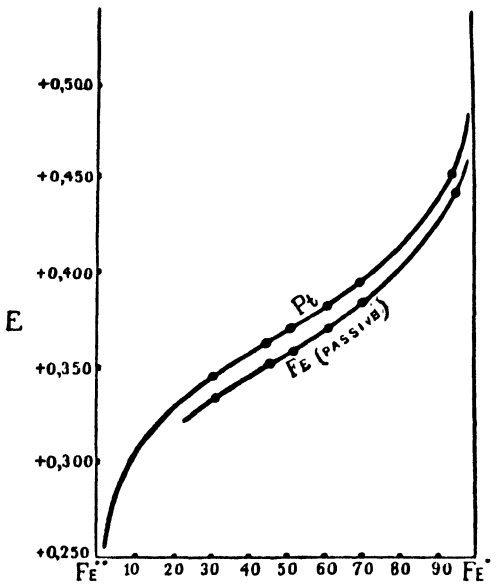


FIG. 207.

By recording the results photographically, using Moll's excellent galvanometer, the curve shown in Fig. 208 was obtained.

Thus it is seen that the potential first of all falls rapidly, then for

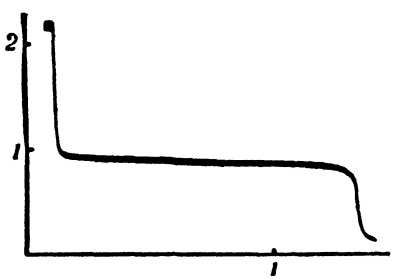


FIG. 208.

some time it decreases very slowly, and finally for the second time it falls rapidly. Until this second rapid decrease of potential occurs the iron is passive. The question now arises, What is the explanation of

this behaviour? In conjunction with the foregoing considerations the answer to this question can easily be given.

THE ACTIVATION CURVE OF AN IRON ELECTRODE IN SOLUTION OF FERROUS SULPHATE.

Time after the interruption of the current (seconds).	Potential relative to 1 N. calomel electrode.
3	+ 0·300 V.
12	+ 0·265 V.
21	+ 0·254 V.
32	+ 0·238 V.
40	+ 0·220 V.
49	+ 0·202 V.
55	+ 0·180 V.
64	+ 0·130 V.
69	− 0·420 V.
75	− 0·550 V.

During anodic polarisation the electron concentration in the bounding liquid diminishes in consequence of the increasing positive value of the iron potential and as a result the concentrations of the hydrogen ions and of the ferric ions increase.

When the current is now interrupted, the three-phase equilibrium, consisting of iron phase, oxygen phase and electrolyte, immediately comes to an end, for the disturbance caused by the withdrawal of electrons at once diminishes and the composition of the bounding liquid layer immediately changes as a result of diffusion with the surrounding liquid. Still, regard must be had to the fact that during passivation the iron has dissolved some oxygen, and thus a retarding influence will be exerted on the establishment of inner equilibrium in the metal. The marked decline in the potential immediately after the interruption of the current shows, however, that this retarding influence is not sufficiently great for the maximum disturbance to be at once attained. But, since the velocity of the internal change diminishes as equilibrium is more nearly approached, the retarding influence of the dissolved oxygen steadily increases, and if the concentration of oxygen in the metal were to undergo no change, at a given moment the internal change would come to a stop before the inner equilibrium state was reached. In reality the rapid fall of potential changes into a slow decrease, which finally again resolves itself into a rapid fall.

For this two reasons may be given. First, that iron always contains some hydrogen. During anodic polarisation hydrogen is removed from the metallic surface and in its place oxygen appears. After the interruption of the current, however, this superficially absorbed oxygen is gradually destroyed by hydrogen diffusing back, and thus the concentration of the retarding oxygen decreases. The activation curve

cannot therefore contain a horizontal portion; there must be a section, however, in which a gradual fall occurs. If the concentration of the oxygen in the metallic surface has become sufficiently small, a rapid change into the active state—activation—occurs, and the surface of the iron is again found to contain hydrogen. The second reason for the peculiar form of the activation curve depends on the nature of the solution. There are liquids in which the electron concentration is so extremely small that even passive iron is still slightly corroded, and in which the equilibrium

$$2H_2O + O_2 + 4\theta \rightleftarrows 4OH'$$

gives rise to a distinct oxygen concentration, corresponding to a similar one in the iron, which under these circumstances is sufficient for a definite passive state to be maintained. To this class of liquids belong, amongst others, nitric acid of Sp. Gr. 1·4 and solutions of ferric sulphate and ferric nitrate, in which the concentration of ferric ions is sufficiently high. In this connection it may also be pointed out that, after long use, solutions of ferrous sulphate, instead of activating a given passive state, may preserve it, in consequence of their having become richer in ferric ions.

If the degree of acidity of the electrolyte is not altered, it follows from the last equation that an increase in the electron concentration, corresponding in accordance with

$$Fe^{\cdot\cdot} \rightleftarrows Fe^{\cdot\cdot\cdot} + \theta,$$

to an increase in the concentration of the ferrous ions, will lead to a diminution in the oxygen concentration.

If therefore the liquid contains more ferrous ions, not only will the passive metal be less corroded, but owing to the smaller concentration of oxygen in the liquid, the oxygen concentration in the surface of the iron will also diminish. On investigating solutions having increasing values for the concentration ratio $\frac{Fe^{\cdot\cdot}}{Fe^{\cdot\cdot\cdot}}$, solutions will be obtained in which no single passive state will be stable, both because the corrosion is less and also on account of the smaller oxygen concentration.

If, therefore, after interrupting the current, passive iron finds itself in such a solution, which in the usual experiments is always the case, which process will occur? It should be noticed that the solution contains too little oxygen for it to remain unchanged in heterogeneous equilibrium with the passive iron.

Naturally the passive iron will still instantaneously establish itself in heterogeneous equilibrium with its bounding liquid, while oxygen passes from the iron into the bounding liquid. Since now the bounding surface so formed contains more oxygen than the surrounding solution, oxygen will continuously diffuse from the bounding surface into the liquid, and oxygen will pass from the passive iron, the result being that at a given moment activation occurs.

In the case here mentioned, therefore, two influences are at work in removing absorbed oxygen from the surface of the passive iron, thereby leading to its activation.

As has already been stated, it is also possible, if the experiment is carried out very carefully, to keep passive iron in the dry state; it is first of all washed with pure water, then with alcohol and ether, and finally it is allowed to dry in the air.

From this fact it might perhaps be concluded that the partial pressure of oxygen in the air was sufficient to maintain the oxygen concentration in the surface of the passive iron. Anyhow in the absence of air this experiment is unsuccessful; passive iron becomes active in a vacuum, and in the absence of air active iron cannot be rendered passive.

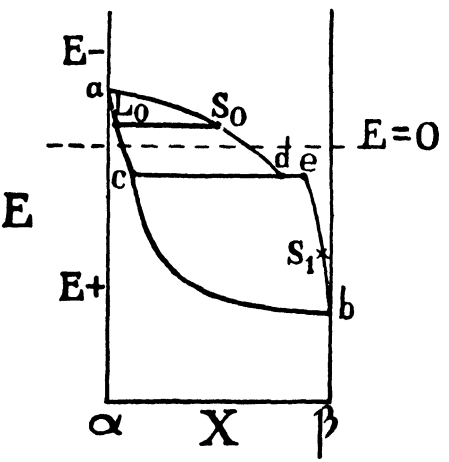


FIG. 209.

The statements made here with regard to the activation curve hold good for most of the different kinds of iron except cast-iron. Electrolytic iron also behaves in a completely analogous manner, although in consequence of its high hydrogen content the passivation of this variety of iron is very difficult.

To explain the peculiar form of the activation curve still another method of procedure was employed by me. There, the starting-point was the assumption that both ferrous and ferric ions occur in iron. An indication has already been given in the theoretical part of the explanation of the phenomenon of polarisation in metals containing ions of two different valencies. If in these considerations the assumption is now made that the pseudo-component α, containing only iron atoms, ferrous ions and electrons, is not miscible in all proportions in the solid state with the β pseudo-component, which consists

only of iron atoms, ferric ions and electrons, the pseudo E X diagram will have the form indicated in Fig. 209.

Since the mixed crystal series is interrupted, a three-phase equilibrium is formed between the two mixed crystal phases *d* and *e* and the electrolyte *c*, and at constant temperature and constant pressure this requires a perfectly definite potential.

If now active iron lies at S_0, and if under powerful anodic polarisation it reaches the point S_1, on interrupting the current, if it is left in contact with the electrolyte, it must always pass the three-phase equilibrium *c d e*, or, in other words, the potential must remain constant for some time. This method of explanation, in conjunction with the considerations mentioned in Chapter VII. § 17 of the Theoretical Part, cannot be rejected, for, though it has not yet been proved, it is very probable that passive iron is richer in ferric ions than the active form.

It may be pointed out here that Allen's[1] study of the photoelectric effect has yielded results which are in excellent agreement with my views, for he says:—

"When the iron is chemically active it exhibits large photoelectric activity, while in the passive state this activity is greatly diminished."

(g) *Directions for the maintenance of moist iron in the passive condition for some time, and instructions for the proper treatment of the iron electrode in order accurately to investigate passive iron.*

In this section some instructions will be given which are of value in the experimental treatment of the problem. Formerly it seems to have been customary to suspend the iron to be rendered passive from a platinum wire. This method is favourable to the preparation and the preservation of the passive state, since contact with platinum alone has a certain passivating influence on iron, as Schonbein had already found. This phenomenon is explained by the fact that passive iron does not constitute an absolutely non-corrodible electrode. If a galvanic element is constructed in which electrodes of passive iron and platinum are immersed in an electrolyte, the passive iron is found to be negatively charged with respect to the platinum. In this case, therefore, the passive iron is the anode, and on closing the circuit it will become anodically polarised.

If therefore during anodic polarisation iron is suspended from a platinum wire, and if after interrupting the current the passive iron is taken out from the electrolyte by means of the platinum wire, it can easily be kept passive for some time, because, as a result of contact with the platinum, the iron will be permanently polarised anodically, though very weakly.

If it is desired more accurately to investigate the passive state of iron, contact with platinum must be avoided. This can easily be done by boring a hole in the iron, and after it has been anodically polarised lifting the passive iron out of the electrolyte by means of a small hook on the end of a glass rod. In the passivation of iron by means of

[1] *Proc. Roy. Soc. London*, **88**, 70 (1913).

strong nitric acid and solutions of ferric salts also (sulphate and nitrate) the metal can be hung from a glass hook. If it is intended to carry out potential measurements, the iron electrode may be cemented into a glass tube with a mixture of sealing wax and shellac. This treatment, however, must be carried out extremely carefully, for if the boundary between the iron and the wax is unsymmetrical, points may easily be produced on which bubbles of gas will remain behind, thus preventing passivation on these spots.

If the current is then interrupted, and if the passivation is being effected by means of a corrosive liquid, the iron electrode is then withdrawn from the electrolyte, activation will immediately set in at these points and will spread with great velocity over the entire surface. If, then, on repeated passivation, no improvement appears, the iron electrode must be cemented in afresh.

It may also be that the error is to be found in the iron electrode itself. If, for example, there are cavities or sharp edges on the iron, on passivation gas bubbles will again form in the small depressions, and as these cannot escape the iron situated under them remains active.

It is also advisable, therefore, previously to dress the surface of the iron with a fine file.

All the experiments which have been carried out in the Amsterdam laboratories in the field of polarisation and passivity, have been performed with cemented-in electrodes. These were previously worked, chemically and mechanically, sufficiently long for the passive state to be preserved successfully for several minutes after the removal of the passivating influence. It may also be mentioned here that iron was successfully fused into glass with the assistance of enamel; this is not recommended, however, for by this treatment a border of Fe_3O_4 is produced, and this oxide, just like platinum, has a more positive potential than passive iron.

(h) *The removal of the passive state.*

(1) *By mechanical treatment.*

It has already been mentioned briefly that the passive state can be suddenly destroyed in various ways. By a light blow, by scratching, by bending, even by contact, activation can be induced. This reminds one of the commencement of the break-up of a highly unstable state, such as nitrogen iodide, for example; in this case also the change may be brought about simply by contact. Activation by means of a powerful and rapidly alternating magnetic field is worthy of notice. The transmission of activity over the whole surface of the passive iron is probably to be explained by the fact that, as soon as a spot has once become active a galvanic element is formed at that point, and as a result hydrogen is deposited on the passive iron in the neighbourhood; the effect of this is to remove the negative catalyst, and consequently the passive iron eventually passes into the active condition.

(2) *By a momentary reversal of the current (the iron becoming the cathode).*

This extension of the problem of activation leads to another possible method of destroying the passive state; this consists in making the passive iron the cathode for a moment.

In this way an explanation is obtained of the phenomenon, that though passive iron can often endure a very light touch, activation immediately occurs if the slightest contact is made with a baser metal such as zinc, magnesium or active iron.

(3) *By contact with a solution containing halogen ions.*

Passive iron is extremely sensitive to halogen ions. This phenomenon, which has also long been known, may be beautifully illustrated in various ways. For example, an iron plate can be used, from which an arm A projects, as shown in Fig. 210. If this plate is rendered passive by means of strong nitric acid, and is thereupon washed with a saturated solution of copper sulphate, the plate remains passive. If now the end of the arm A is brought into contact with a solution of KCl, KBr or KI, activation sets in at that point and naturally spreads rapidly over the whole plate. Thus, the arm is first of all seen to become coated with copper, this process being propagated from the point of contact with the inoculating solution. It may be demonstrated that halogen ions, and not molecules, actually exert the activating influence, on repeating the experiment, but inoculating with a solution of corrosive sublimate which is almost undissociated, activation is *not* induced.

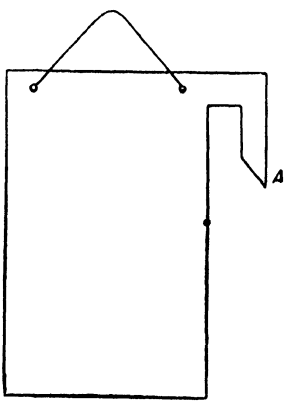


FIG. 210.

The remarkable activating action of halogen ions may also be demonstrated in yet another way. With the help of Moll's sensitive galvanometer and a photographic recording arrangement, the activation curves were obtained for iron which had been anodically polarised in a pure solution of ferrous sulphate, and also after polarisation in exactly similar solutions to which small quantities of a solution of ferrous chloride had been added. The resulting curves are shown in the following line reproduction of the photograph. The passive iron, after the interruption of the passivating current, was connected to active iron placed in the same solution, so that the potential indicated was the potential relative to that of active iron. The photographs obtained, *a*, *b*, *c* and *d*, are here placed one behind the other. The intervals marked on the X axis represent periods of one minute. It is evident that extremely small concentrations of chlorine ions are sufficient

strongly to accelerate the activation. At the highest concentration of chlorine ions, namely 0·00048 grm.-mols. $FeCl_2$, the portion of the curve which is almost horizontal could no longer be detected in the photograph, whilst at the somewhat lower chlorine ion concentration, 0·00036 grm.-mol. $FeCl_2$, only a slight thickening could be observed.

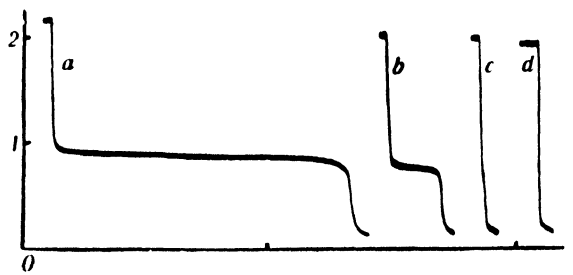


FIG. 211.

(*a*) The activation curve for iron after anodic polarisation in a solution of $FeSO_4$ containing 0·473 grm.-mol. per litre.
(*b*) The activation curve for iron after anodic polarisation in a solution of $FeSO_4$ containing 0·473 grm.-mol. per litre + 0·00024 grm. mol. $FeCl_2$.
(*c*) In this case the same concentration of $FeSO_4$ was used with the addition of 0·00036 grm -mol. $FeCl_2$.
(*d*) In this case 0·00048 grm.-mol. $FeCl_2$ was added.

Chlorine ions and the other halogen ions likewise are therefore powerful positive catalysts for the establishment of inner equilibrium in iron; as regards the mode of action of these catalysts, however, as in the case of most catalytic effects, it is to be regretted that even to-day no definite statement can be made.

(i) *The activation of passive iron by increase of temperature.*

As was to be expected, the activation of passive iron was found to take place more readily the higher the temperature. The temperature influence was even suspected to be very powerful, for the velocity of the internal change and of diffusion increase greatly with the temperature.

We shall commence by showing that the influence of temperature is already evident in the potential exhibited during anodic polarisation. If an iron electrode is anodically polarised at different temperatures, the current density being the same in each case, as the temperature is increased the potential very clearly diminishes. This is shown in the following table.

The current density employed, 10 milliamperes per square centimetre, has a powerful stabilising influence on passive iron; nevertheless, on heating from 15° to 90°, the potential decreases by about 200 millivolts.

Temperature.	Potential of passive iron, the current density being 10 mil. amps. per sq. centimetre.
15°	+ 1·603 volts.
20°	+ 1·590 ,,
30°	+ 1·560 ,,
40°	+ 1·540 ,,
50°	+ 1·520 ,,
60°	+ 1·496 ,,
70°	+ 1·458 ,,
80°	+ 1·426 ,,
90°	+ 1·390 ,,

Clearly, within this temperature range, activation will only occur when much smaller current densities are employed. Using the same electrode as in the above experiments, the temperature was now determined at which activation appeared, for different very low current densities. For this purpose Moll's sensitive galvanometer was again employed. In the galvanometer circuit (shunt) a very high resistance was placed, so that the current passing through the galvonometer could be completely neglected as against the current used for polarisation. On raising the temperature a slow fall of potential was again first of all observed, which continued until a sudden decrease showed that activation had occurred.

The following are the results obtained in this way:—

Polarising current in mil amps. per sq. centimetre.	Temperature at which activation took place.
1·0	93°
0·6	79°
0·3	64°

It is obvious that in the absence of the polarising current activation would appear if the increase of temperature were still less. In the case of the electrode used here the temperature at which activation appeared under such conditions was found to be in the neighbourhood of 40°; this temperature now depends to a much greater extent on the composition of the electrolyte and on chance circumstances than when the electrode is feebly polarised anodically.

(k) *The periodic passivity of iron.*

It has already been seen that the passive condition of iron can be removed by bringing the metal into contact with solutions containing halogen ions. The question now arises whether it would not be possible to set up periodic phenomena, which would make their appearance if halogen ions were added to the electrolyte during anodic polarisation. When iron is anodically polarised in a solution of ferrous

sulphate, and a solution of ferrous chloride is added thereto, the catalytic influence of the chlorine ions manifests itself in a fall of the potential. If the addition of ferrous chloride is continued, at a given moment a fairly rapid and considerable fall of potential occurs, and simultaneously the iron passes from the passive into the active condition.

Now it is clear that for a given velocity of solution of the iron, which is determined by the current density, there must exist a chlorine ion concentration, at which, at any given moment, the chance of the iron remaining passive is equal to the chance of its becoming active. If it be granted that at this moment activation appears, the following considerations arise: Whilst the iron anode only dissolves extremely

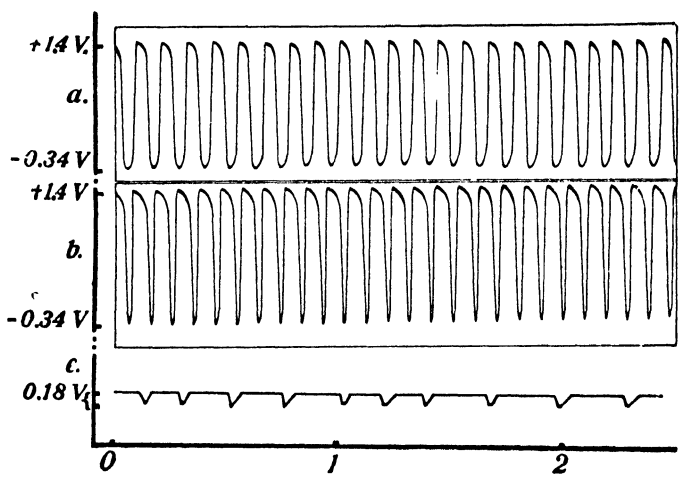


FIG. 212.

slowly when in the passive state, now that it has become active it passes into solution at a rate corresponding to the strength of the current. The influence of chlorine ions on the anode has now changed, for the extent to which chlorine ions dissolve in the metal must depend on the rate at which metallic ions and electrons pass into solution. If this velocity is great fewer chlorine ions can be dissolved in the metallic surface than when the velocity of solution is small. Because of this slighter solution of chlorine ions, once the iron has become active it can again be strongly disturbed. If, however, it becomes passive, the solution of chlorine ions again becomes greater and at a definite moment activation will again occur. This consideration led me, in conjunction with Lobry de Bruyn,[1] to carry out experiments in this direction.

The photographic recorder was again employed in conjunction with Moll's galvanometer.

[1] *Versl. Kon. Akad. v. Wet.*, Amsterdam, **24**, 745 (1915); **27**, 159 (1918).

The conjecture previously mentioned was completely confirmed, as may be seen from the photograph reproduced in line in Fig. 212.

For any given concentration of chlorine ions the current density could be so chosen that the period of existence of the strongly passive state was approximately equal to that of the most strongly active condition. This is shown in curve *a*. When the current density was increased somewhat the passive state remained in existence longer than the active, as is clear from curve *b*. In these curves the iron is passive at the maxima and active at minima. The oscillations are very large; the maxima and the minima lie 1·74 volts apart. The periods amount to 6·54 and 5 8 seconds. Mention should not be withheld here of the fact that various experimenters have previously observed periodic phenomena in the solution of passive metals, but none of these workers has succeeded in producing a periodic phenomenon in which the oscillations are so large and regular as those photographically depicted here.

Thus, in Adler's[1] experiments with iron, the potential exhibited periodic oscillations; in these experiments hydrogen was evolved behind an iron septum the front of which functioned as the anode. This hydrogen diffused through the iron and, by removing dissolved oxygen from the side acting as the anode, it could then bring about activation. The re-occurrence of the passive state is not, however, easy to explain intelligibly here, because in this case the substance which brings about the activation was introduced through the metal from behind.

In Adler's experiments the iron remained passive for a long time and only became active for brief periods; the potential difference amounted to 180 millivolts only, and thus the phenomenon was less regular. The curve obtained by him is marked *c*, and is drawn to the same scale as the other curves.

(1) *New experiments with cemented-in iron electrodes.*

On continuing our experiments an improvement was introduced, in that, with the help of a time signal apparatus, we were able to include time lines in the photograph, so that the regularity of the phenomenon could be still better judged.

Fig. 213 shows the periodic passivity phenomenon, time lines being indicated and thus bringing out the great regularity very clearly. The potential was determined in relation to that of the normal calomel electrode, the end of the electrode being placed half-way up the iron electrode.

The experimental details are briefly summarised below the diagram. In this case the iron remains rather a long time passive and only a short time active. The information regarding the current density is to be interpreted in this way. When the iron was passive the current density amounted to 28 milliamperes per square centimetre and when it was active to 33 milliamperes per square centimetre.

[1] *Zeitschr. f. physik. Chemie*, **60**, 385 (1912).

The photograph reproduced in line in Fig. 214 refers to an experiment with the same electrode, but with a slightly smaller current density, in which longer periods were obtained and the durations of the active and the passive states were approximately equal.

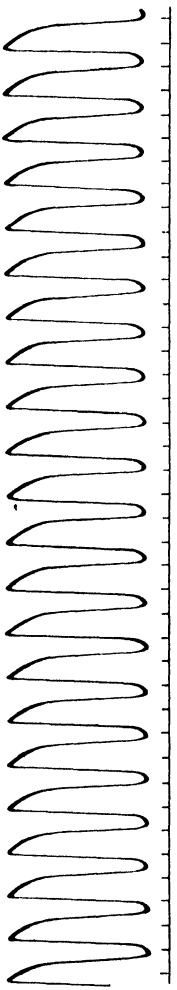


FIG. 213.

Cemented in iron electrode, 1·5 cm. long, diameter 3 mm. Solution contained 0·72 grm.-mol. $FeSO_4$ + 0·014 grm.-mol. $FeCl_2$ per litre. The potential was measured half-way up. Current density 28–33 milliamperes per square centimetre. One period = 6·15 seconds. The potential difference between the extreme values was about 1·7 volts.

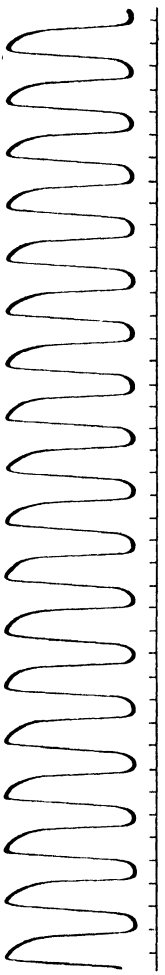


FIG. 214.

The cemented-in electrode, the solution and the position of the standard electrode were the same in this case as in the preceding experiment. The current density, however, was here 25–30 milliamperes per square centimetre and the period 7·8 seconds.

(2) *Experiments with uncemented iron electrodes.*

Uncemented electrodes were then used, and for purposes of comparison with the preceding experiments these were simply dipped 1·5 cms. deep into the electrolyte, the tip of the standard electrode being thus situated at the lower part of the iron electrode. In this case, naturally,

an activating influence continually existed, proceeding from the particles of iron situated up above in the liquid surface; still, preliminary experiments showed that this activating influence could not prevent the lower portion of the electrode from exhibiting regularly periodic activity.

The photograph reproduced in Fig. 215 illustrates the periodic passivity observed in this way.

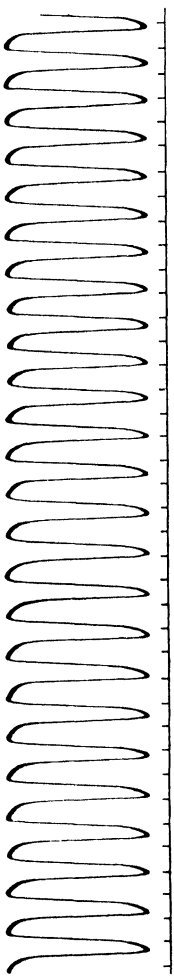


FIG. 215.

Uncemented electrode immersed 1·4 cm. deep, diameter 3 mm. Solution as in previous experiments. The potential was measured below the electrode. Current density 32·36 milliamperes per square centimetre. Period = 5·25 seconds.

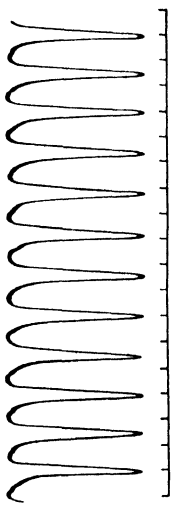


FIG. 216.

Uncemented electrode 5·1 cm. deep, diameter 3 mm. Solution the same as in previous experiments. The potential was measured 1 mm. below. Current density 24·33 milliamperes per square centimetre. Period = 5·1 seconds.

(3) *The periodic passivity of an uncemented electrode placed at various distances below the liquid surface.*

The behaviour of an uncemented electrode at different depths below the liquid surface was next investigated. For this purpose an

electrode was employed which dipped much deeper, *i.e.* a good 5 cms. into the liquid.

The tip of the standard electrode was again brought to the lowest part of the iron electrode, and, just as when the position of the iron

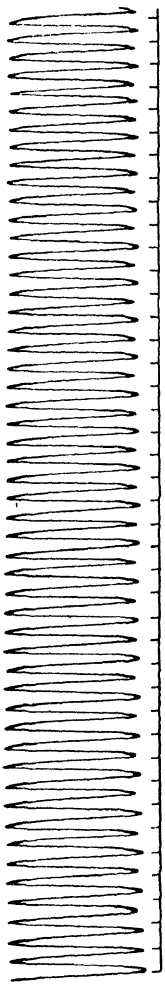


FIG. 217.

Uncemented electrode immersed to a depth of 5·3 cms. Diameter 3 mm. Solution as in the previous experiment. The potential was measured 15 mm. from the bottom. Current density 38·43 milliamperes per square centimetre. Period 2·7 seconds.

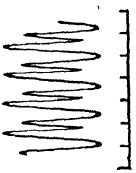


FIG. 219.

Conditions the same as in the previous experiment. The potential was measured in the middle. Current density 28·32 milliamperes per square centimetre.

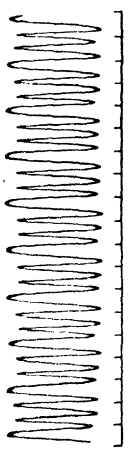


FIG. 218.

Uncemented electrode immersed 5·3 cms. deep. Diameter 3 mm. Potential measured in the middle. Current density 30·34 milliamperes per square centimetre. Period 2·2 seconds.

electrode was not so deep, a fairly regular periodic passivity was observed; this is clear from the photograph reproduced in Fig. 216.

When, however, the tip of the standard electrode was not quite below, but was placed 15 mm. above the bottom of the iron electrode, the activating influence having its origin above was already very noticeable, as Fig. 217 shows. For, although the phenomenon was still quite

regular, the character of the curve had changed considerably. The periods had become much smaller, the active period being somewhat longer than the passive. Especially on the lower or active side of the curve it may be noticed that the oscillations are not all equally great, but that the deeper ones and those which are less deep alternate regularly, from which it is clearly evident that the phenomenon has become complicated by the activating influence from above.

In the middle of the immersed portion of the electrode the periodic phenomenon becomes still more complicated, as is clearly shown in Fig. 218. This phenomenon changes at a given moment into another, which is represented in Fig. 219.

This last diagram shows to what an extraordinary extent the activating influence from above increases as the liquid surface is approached, and it was therefore to be expected that immediately below the liquid surface the periodic passivity would be very greatly disturbed. In order to verify this the potential was now determined at a point 1 mm. below the liquid surface. The result is shown in Fig. 220.

The only remaining regularity consists simply in the fairly regular recurrence of the active state.

(4) *The influence of the area of the iron surface on the periodic passivity.*

It has already been pointed out that with increasing iron surface passivation of the metal becomes more difficult. The greater the iron surface is, the smaller will be the chance of the iron being passive over the whole surface at the same moment.

From this the disturbance of the periodic passivity might therefore be expected to be much greater when electrodes exposing a greater surface were used.

One experiment was made with a spiral electrode, of which 5 turns, having a total length of 60 cms., were immersed in the electrolyte. The cathode was placed within the spiral and the potential was measured at the second turn. Whilst the current strength again altered regularly, the variation of the potential appeared to be quite irregular. Fig. 221 illustrates this. The irregularity was so great that even the state of maximum activity no longer returned regularly. The experiment with the spiral electrode clearly proved that passivity never appears at the same moment over the whole surface. Different portions become passive at different moments.

(l) *The phenomenon which occurs after anodic polarisation.*

A new phenomenon was discovered in 1917 by the author and his assistant, Lobry de Bruyn, as a result of the application of Le Blanc's rotating commutator to the study of anodic polarisation. This commutator is constructed in such a way that the potential is measured immediately after the current is interrupted.

On making the measurement in this way a remarkable phenomenon appeared. When the current density was not so great as to cause the iron to become passive, instead of being less negative the iron proved

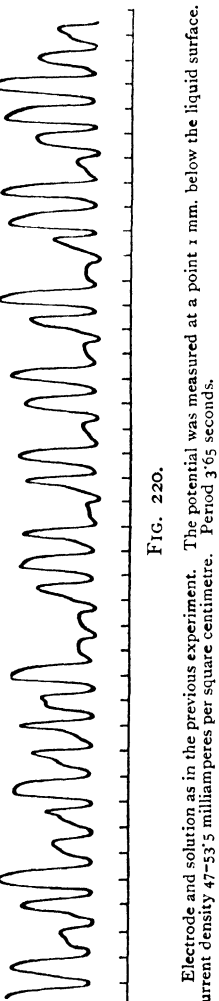


FIG. 220.

Electrode and solution as in the previous experiment. The potential was measured at a point 1 mm. below the liquid surface. Current density 47–53·5 milliamperes per square centimetre. Period 3·65 seconds.

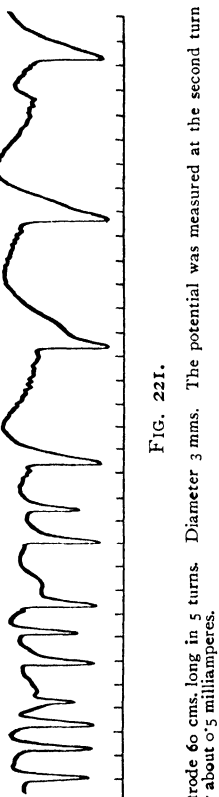


FIG. 221.

Spiral electrode 60 cms. long in 5 turns. Diameter 3 mms. The potential was measured at the second turn from above. Current density about 0·5 milliamperes.

to be more strongly negative. Thus *after* anodic polarisation iron exhibited a change of potential in the opposite direction to that observed during the passage of the current.

At first this phenomenon was thought to be due to some mistake in setting up the experiment, but this proved not to be the case. The

same phenomenon occurs in the case of nickel, and, as Aten[1] found later, of chromium also.

Working without the commutator mentioned above, and observing the course of the iron potential immediately *after* anodic polarisation, this potential appeared, strange to say, to pass through a minimum and then rapidly to rise again to its original value.

(1) *The method of recording the phenomenon.*

In order to define the phenomenon, in the experiments carried out by me in conjunction with La Bastide, van den Andel and de Crauw,[2] the photographic method was again employed. The potential of an iron electrode I in relation to another standard iron electrode II was measured, a platinum electrode being used as the cathode. The electrolyte consisted of a 0·5 N. solution of ferrous sulphate. The iron

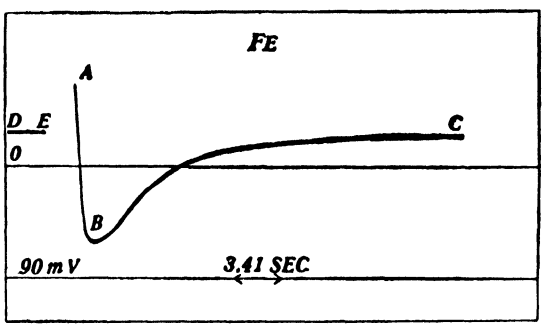


FIG. 222.

electrode I, the surface of which had an area of about 25 sq mm., was made the anode for a short time, the current density being so chosen (about 0·360 amp. per sq. cm.) that on passing the current for some time the iron would become passive.

Immediately after anodic polarisation the galvonometer was switched into the circuit iron I—electrolyte—iron II, so that the course followed by the potential of the iron *after* anodic polarisation could be accurately recorded. The following data were recorded on the film: (1) The potential of iron I in relation to iron II *before* the experiment, indicated by the line D E. (2) The curve showing the course of the phenomenon under discussion, marked A B C. (3) The zero line denoted by O. (4) A line corresponding to a definite difference of potential. (5) Time-lines from the time-signal apparatus.[3]

In our experiments with iron in a 0·5 normal ferrous sulphate solution the following photographic diagrams were thus obtained:—

Fig. 222 shows that, after anodic polarisation, iron electrode I was

[1] *Versl. Kon. Akad. v. Wet.*, **26**, 1187 (1918).
[2] *Ibid.*, Amsterdam, **27**, 1253 (1919); **27**, 1260 (1919); **28**, 141 (1919).
[3] These lines are not reproduced here.

first disturbed in the direction of greater nobility, but that this disturbance very rapidly decreased. It is, however, remarkable that the potential should fall so far as to become nearly 90 millivolts more negative than it was before anodic polarisation. This most negative potential, however, is only retained for a short time and the potential almost immediately rises again, first with increasing and then with diminishing velocity, asymptotically to approach the value it had before anodic polarisation.

Fig. 223 depicts the phenomenon which occurs when, instead of a ferrous sulphate solution, a 0·1 N. solution of ferrous chloride was used.

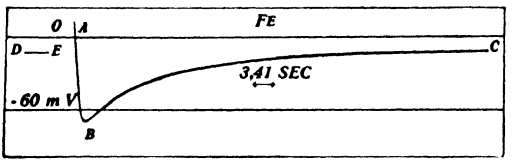


FIG. 223.

It may be briefly recalled here that, in consequence of the period during which anodic solution takes place, which is, however, short, the increase of concentration in the bounding layer causes a slight change of potential in a positive direction, so that the phenomenon under discussion here is diminished to a slight extent.

Since the same phenomenon had been observed in the case of nickel, a similar experiment was made with nickel in a solution of nickel chloride, and, as Fig. 224 shows, the curve obtained, A B C, also contained a minimum, but in this case the phenomenon occurs more slowly, as was indeed to be expected of the inert metal nickel.

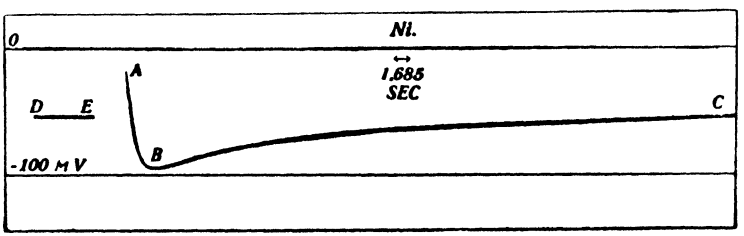


FIG. 224.

(2) *The explanation of this "phenomenon."*

The phenomenon observed in the case of iron occurred when the metal was anodically polarised in a solution of ferrous sulphate or ferrous chloride, which had been freshly prepared, it is true, but which had not previously been heated with iron powder.

It has already been shown that iron can only exist in inner equilibrium with solutions which do not contain ferric ions in detectable

amount.[1] Further, solutions containing ferric ions have been proved to disturb the iron, and, indeed, this disturbance is the greater, the greater the concentration of ferric ions.

In a solution containing ferric ions, therefore, the iron potential is less negative than it is in a solution which co-exists with unary iron and which is practically free from ferric ions.

Thus, in solutions with which this phenomenon had been observed, and which contained ferric ions, the potential of the iron was not the true equilibrium potential, but a less negative value.

If now iron is anodically dissolved in such a solution, the electrolyte in the neighbourhood will undergo a change, for, so long as it is not passive, the iron sends ferrous ions almost exclusively into solution.

During this solution process the iron becomes disturbed, as is shown by the less negative iron potential obtained whilst the current is passing.

In this connection, however, it is deserving of notice that during the solution process the neighbourhood of the iron becomes poorer in ferric ions, so that the bounding layer contains fewer ferric ions than the solution outside this layer.

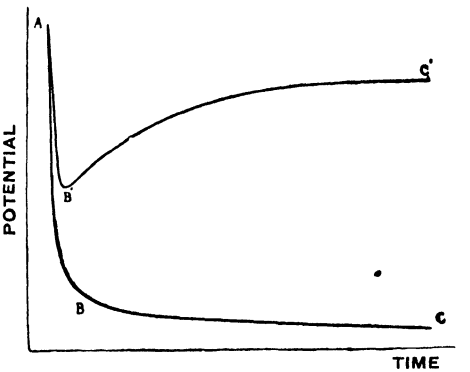


FIG. 225.

After the interruption of the current the iron surface changes very rapidly in the direction of inner equilibrium. Since now the iron is surrounded by a liquid layer containing fewer ferric ions than the liquid outside this layer, its potential will be more negative than it was before anodic polarisation.

But this condition can only last for a very short time, for ferric ions diffuse into the bounding layer from outside, so that the potential again becomes less negative; it gradually rises again to its original value. Fig. 225 helps to elucidate the process.

The line A B C indicates the course followed by the potential of iron after anodic polarisation when it is immersed in a solution of a ferrous salt which is practically free from ferric ions.

Immediately after anodic polarisation the iron is rather violently disturbed, yet this disturbance diminishes, first of all rapidly and afterwards more slowly. The curve A′ B′ C′ likewise indicates the course followed by the iron potential after anodic polarisation, but in this case a small quantity of a ferric salt was added to the solution previously

[1] The solution must indeed contain ferric ions, but they are not detectable by any direct method.

used. Here, again, the potential first sinks rapidly, and, indeed, to a point below its final value.

If the liquid in the bounding layer were, and remained, practically free from ferric ions the potential would follow the curve A B C, but its course is now different; for, in this experiment, the iron does indeed lie within a liquid bounding layer which is poorer in ferric ions than the liquid outside this layer, but owing to the influence of the ferric ions present it cannot settle down into inner equilibrium, and the potential cannot therefore attain so negative a value as it has in the absence of ferric ions. But, in addition to this, more ferric ions continually diffuse into the bounding layer, so that the disturbance of the iron again increases and the potential again becomes less negative.

The correctness of this explanation has now been established in the following way. A solution of a ferrous salt was continually heated with iron powder in the vessel used for the potential measurement, pure hydrogen being meanwhile passed over it. The results obtained with solutions prepared in this way do not admit of argument. Now, as the photograph reproduced in Fig. 226 shows, after anodic polarisation a

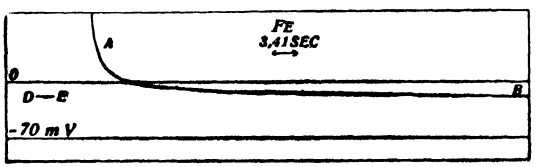


FIG. 226.

curve having no minimum was obtained. By heating it with powdered iron in an atmosphere of hydrogen, the whole solution acquired such a composition that iron in which inner equilibrium had been established could co-exist with it. In this case, according to the considerations which have been advanced, after anodic polarisation the curve can have no minimum.

Now since this phenomenon was also observed in nickel after this metal had been anodically polarised, it was natural to suppose the same cause to be operative, and to assume, therefore, that the solution of the nickel salt used contained ions of different valencies, *e. g.* $Ni^{\cdot\cdot}$ and $Ni^{\cdot\cdot\cdot}$, where the concentration of the $Ni^{\cdot\cdot\cdot}$ ions might be extremely small. If this were so, on heating the solution of a nickel salt with freshly prepared nickel powder in an atmosphere of hydrogen, the minimum in the curve obtained after anodic polarisation should again disappear. This conjecture was in fact shown by experiment to be justified. The photograph obtained, Fig. 227, exhibits a curve in which no minimum appears. As the result of this experiment, therefore, we are faced with the interesting question of the existence of a second nickel ion. The investigation of this problem has only just been begun, so that no results can as yet be communicated.

It may, however, already be predicted that, in all probability, this

phenomenon will furnish us with a very sensitive method of investigating whether a solution contains different kinds of ions of the same element or not.

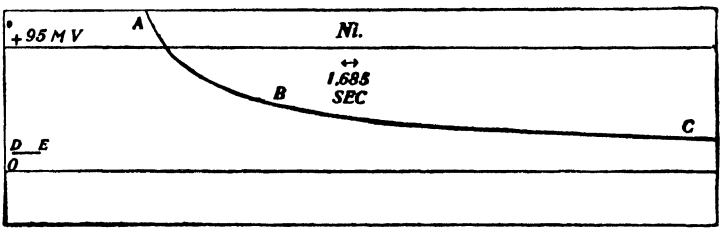


FIG. 227.

(m) *The phenomenon after cathodic polarisation.*

Since an explanation has been found for the phenomenon observed after anodic polarisation, it seemed possible that after cathodic polarisation the mirror image of this phenomenon, so to speak, would appear. The grounds for this belief are as follows: If an iron electrode is dipped into a solution containing both ferrous and ferric ions, the ratio $\left(\frac{Fe^{\bullet\bullet}}{Fe^{\bullet\bullet\bullet}}\right)$, which will be denoted by H, will be greatest at the surface of the iron, for, by emitting ferrous ions, the iron tends to change the bounding liquid in such a way as to make it possible for it to co-exist

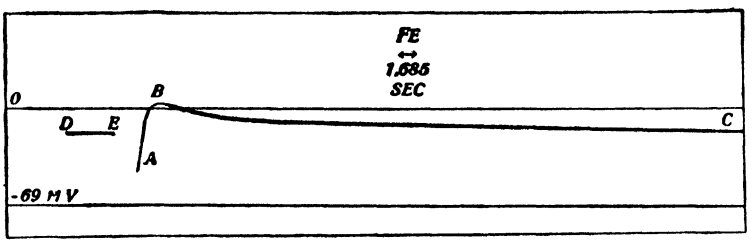


FIG. 228.

with this liquid in a state of inner equilibrium. The further any given liquid layer is removed from the iron surface, therefore, the smaller will be the ratio H.

If, therefore, iron is made the cathode in the supposed solution, and after some seconds the current is interrupted, during the passage of the current iron will be precipitated from the bounding layer and ions from the succeeding layers will now diffuse into the bounding layer. Since the ratio H is smaller in each succeeding layer, it follows that after cathodic polarisation iron comes into contact with a liquid surface in which the ratio H is smaller than it was before cathodic polarisation. Consequently a disturbance, and therefore a displacement, of the potential will occur in the direction of less negative values, and this is also shown in the photograph reproduced in Fig. 228.

Thus the conjecture was confirmed; after cathodic polarisation a curve was obtained in which a maximum potential appeared, which was approximately 30 millivolts more positive than the initial potential D E.

(n) *The cathodic polarisation of iron.*

It has already been shown in the theoretical part, Chapter VII, § 19, that, from the condition for evolution of hydrogen

$$L_M^{\frac{1}{\nu}} > L_{H_2}^{\frac{1}{2}} \frac{(M_L^{\nu})^{\frac{1}{\nu}}}{H_L^{\bullet}},$$

it follows that supposing in pure neutral aqueous solutions containing 1 grm. mol. per litre, $(M_L^{\nu}) = 1$, iron is the last metal which must liberate hydrogen from such a solution.

In reality, in consequence of hydrolysis, solutions of iron salts always react acid, and thus the circumstances are still more favourable

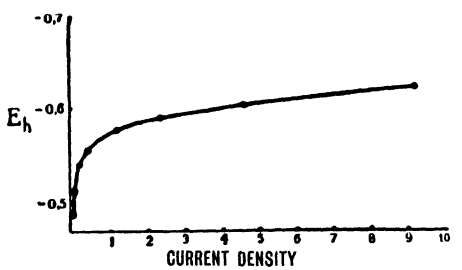


FIG. 229.

to the evolution of hydrogen. A decrease in the ferrous ion concentration acts in the same direction, and it is therefore certain that an iron electrode, if its behaviour is unary, must liberate hydrogen when it is placed in a normal solution of ferrous sulphate. If therefore under these circumstances the iron electrode is made the cathode, at the outset a three-phase equilibrium exists between an iron phase, a hydrogen phase and the electrolyte. On increasing the current density the negative value of the potential also increases, because the iron phase, like the hydrogen phase, cannot settle down into inner equilibrium sufficiently quickly, and consequently they both exist in the state of formation.

The question whether a metal already liberates hydrogen from the electrolyte before cathodic polarisation or not, is not without importance in connection with this phenomenon.

When hydrogen is evolved from the commencement, it might certainly be expected that the current density chosen could be so small as to produce no appreciable increase in the cathodic potential, and consequently, from a superficial consideration, the existence of any phenomenon of particular interest might not be suspected.

The results obtained by Foerster[1] using a normal solution of $FeSO_4$ containing 0·5 per cent. H_3PO_3 at 50° were as follows :—

Current density in mil. amps. per sq. centimetre.	E_h in volts.
0·057	— 0·490
0·076	— 0·514
0·113	— 0·542
0·227	— 0·556
0·45	— 0·566
1·13	— 0·576
2·27	— 0·589
4·55	— 0·607
9·1	— 0·620

so that the cathodic polarisation curve has the form shown in Fig. 229.

Now from this curve, the first approximately horizontal portion, with which, theoretically, every polarisation curve should begin, is apparently lacking; for even at extremely low current densities the potential is already fairly strongly negative. This points to the fact of iron being very inert under these circumstances, and we are compelled to look upon hydrogen dissolved in the iron, and which was present from the outset, as the cause of the inertness of this metal in the case of cathodic polarisation.

Foerster[2] first recognised this; he came to the conclusion, from the polarisation phenomena which accompany the cathodic deposition of metals, that in this process hydrogen exerts an influence similar to that exerted by oxygen on the anodic solution of metals, namely a retarding influence. He further concluded that in those cases in which hydrogen apparently acts as a positive catalyst, as, for example, in the conversion of passive into active iron, the hydrogen removes the other negative catalyst.

Foerster is of opinion that oxygen and hydrogen have a negative catalytic action on the *heterogeneous* electrolytic processes of solution and deposition, whilst we have emphasised here that the heterogeneous processes are always instantaneously produced, and that the retarding influence of the gases mentioned must be exerted on the internal changes in the metallic surface.

The cathodic polarisation of iron has been investigated by Foerster in various directions; amongst other things he found it to decrease with rising temperature; this must be connected with the increase in the reaction velocity in the iron surface.

In addition, he also investigated the influence of acidity on the cathodic potential and found that, at 50° for example, on addition of sulphuric acid (up to 0·03 grm. equivalents) to a ferrous sulphate

[1] *Abh. d. Deutschen Bunsen-Gesellschaft*, No. 2 (1909).
[2] *Zeitschr. f. Elektrochem.*, **22**, 85 (1916).

solution containing 2·6 grm. equivalents per litre, the current density being kept constant at 18·2 milliamps per sq. centimetre, the potential rose from — 0·612 to — 0·666 volts., whilst the current efficiency fell from 99·3 per cent. to 38 per cent. This decrease in the current efficiency proves that, as was to be expected, the addition of electrons brings about the deposition of hydrogen to a greater extent, the greater the increase in concentration of the hydrogen ions.

It might be thought that the smaller the amount of iron deposited, so much the more slowly has the deposition taken place and the greater has been the opportunity for the iron deposited to undergo change in the direction of inner equilibrium; a less negative potential might therefore be expected. But the fact is then lost sight of that the observed potential is the potential corresponding to a three-phase equilibrium and that the iron and the hydrogen have the same potential. In this case the current efficiency for iron must be diminished because iron is deposited in a higher degree of formation.

The fact that in the experiment quoted here the potential became more strongly negative on increasing the acidity, proves that iron and hydrogen occur to a greater extent in the state of formation with increasing acidity.

It must be emphasised here that the investigation of cathodic polarisation is generally less simple than the investigation of anodic polarisation, for it is often very difficult to obtain good pure metallic precipitates, and this is necessary if reproducible results are to be obtained.

(o) *The cathodic passivity of iron.*

In conclusion, still another phenomenon must be discussed; this was first observed by von Escher[1] in Foerster's laboratory and called cathodic passivity.

In the electrolysis at 75° of a 0·01 N. acid solution of $FeSO_4$ + $ZnSO_4$ containing 9 grm. equivalents of iron to 1 grm. equivalent of zinc, von Escher found that so long as the current density remained below 5 milliamperes per sq. centimetre the cathodic polarisation was very slight.

Under these circumstances the metal deposited contained about 90 per cent. Fe. On increasing the current density, however, the polarisation rather suddenly increased, and at a current density of 10 milliamps. per sq. centimetre the metal deposited contained only about 40 per cent. iron.

When the current density reached 20 milliamperes per sq. centimetre the composition of the metal deposited had again greatly changed, namely to 21·5 per cent. Fe and 78·5 per cent. Zn. If now the current density was increased still further, the composition appeared to undergo no further change. When these results are represented graphically Fig. 230 is obtained.

[1] *Zeitschr. f. Elektrochem.*, **22**, 85 (1916).

At the same time the cathodic potential altered considerably. When the current density was increased from 5 to 10 milliamperes per sq. centimetre this potential rather suddenly acquired a much greater negative value, *i. e.* cathodic polarisation became much more marked. The value of the current density with which the polarisation is associated, throughout the marked change just referred to, proved to depend on the degree of acidity and the zinc content of the solution. In

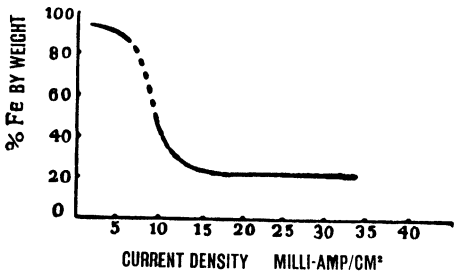


FIG. 230.

the experiment discussed above the curve shown in Fig. 231 was obtained.

From this result Foerster concluded that small quantities of zinc, like hydrogen, exert a retarding influence, and since the cathodic polarisation varies here with the current density in a manner similar to anodic polarisation, Foerster speaks here of *cathodic passivity*.

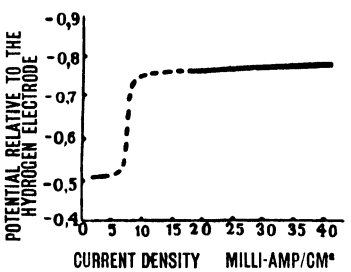


FIG. 231.

The system investigated here is a system of five components, namely, $Fe^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $H^{\cdot}$, SO''_4, H_2O, and therefore if the temperature, the pressure and the total concentration are assumed to be constant, when three phases co-exist the system is univariant. A co-existence of three phases is obtained when the current density is very small; namely, an iron phase containing zinc, a hydrogen phase and the electrolyte. The fact that with increasing current density the iron content of the

precipitate becomes smaller proves the zinc to exert a strongly negative catalytic influence on the establishment of inner equilibrium in the iron, and this is in agreement with the more negative value of the potential. The constant value of the potential when the current density exceeds 20 milliamperes per sq. centimetre, while the deposited mass also has a constant composition in which 21·5 per cent. Fe is present, points to the possibility that at this potential the compound $FeZn_3$ separates out from the electrolyte.

(p) *The allotropy of iron.*

If, in the simplest case, it is assumed that the solid phase of iron contains only one kind of ions, namely ferrous ions, and is therefore composed of iron atoms, ferrous ions and electrons, the iron atom should be looked upon as one and the dissociated iron atom, $Fe^{\cdot\cdot} +$

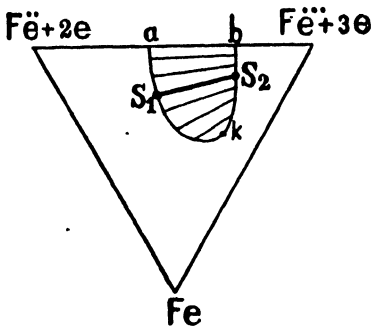


FIG. 232.

2θ, as the other pseudo-component. If it is then supposed that in the solid state these two pseudo-components are miscible to only a limited extent, the phenomenon of allotropy may again be explained, in the usual way, with the help of a binary method of representation.

If, however, the possibility of the iron containing both ferrous and ferric ions is considered, there are three pseudo-components, namely, iron atoms, $Fe^{\cdot\cdot} + 2\theta$ and $Fe^{\cdot\cdot\cdot} + 3\theta$, between which, for unary behaviour, inner equilibrium must prevail.

As is well known, it is assumed that the pseudo-components $Fe^{\cdot\cdot} + 2\theta$ and $Fe^{\cdot\cdot\cdot} + 3\theta$ are only partially miscible in the solid state. If the further assumption is made, to choose the simplest case, that Fe is miscible in all proportions with both $Fe^{\cdot\cdot} + 2\theta$ and with $Fe^{\cdot\cdot\cdot} + 3\theta$, the isothermal diagram corresponding to a temperature and pressure at which all are solid will have a form such as that shown in Fig. 232.

The inner equilibrium between the three pseudo-components at constant pressure will naturally be indicated as a function of the temperature by a curve within the ternary space figure, so that in a

constant temperature section the inner equilibrium will be represented by a point.

Now it is possible for the inner equilibrium curve to meet the region of immiscibility, and when this meeting takes place at the exact temperature corresponding to the section represented in Fig. 232, at this temperature the unary solid phase S_1 is transformed into the unary solid phase S_2, or conversely S_2 changes into S_1.

11. Nickel.

(a) *The equilibrium potential.*

In Chapter II, §§ 2 and 3, it has already been shown that nickel is a very inert metal, and that in consequence too high a concentration of hydrogen ions, and also of molecular hydrogen, can disturb a nickel electrode so profoundly that its potential becomes the same as the potential of the hydrogen electrode. Under these circumstances the equilibrium potential of nickel could only be obtained by using a solution, the composition of which lies to the left of the point *c* in the E X diagram for the system $Ni^{\cdot\cdot} - 2H^{\cdot}$, *i. e.* a solution in which the hydrogen-ion concentration is smaller than 10^{-3}. Further, hydrogen must not be led through or over the solution, as is often done, but nitrogen; or, safer and more convenient still, the electrode vessel should be completely filled with a nickel solution which has been boiled in a vacuum in an apparatus such as that described on page 328. In this way the equilibrium potential of nickel relative to the normal calomel electrode was found to be $-0{\cdot}480$ volts., and therefore $E_h = 0{\cdot}194$.

(b) *The disturbance of nickel by strong nitric acid.*

Just as in the case of iron, nickel can be at once converted into the passive state by dipping it into strong nitric acid of Sp. Gr. 1·4.

This phenomenon may naturally be explained in the same way as in the case of iron.

That is to say, the equilibrium

$$\begin{array}{ccccc} Ni_S & \rightleftarrows & Ni^{\cdot\cdot}{}_S + 2\theta_S & (a) \\ \uparrow\downarrow & & \uparrow\downarrow \quad \uparrow\downarrow & \\ Ni_L & \rightleftarrows & Ni^{\cdot\cdot}{}_L + 2\theta_L & (b) \end{array} \quad . \quad . \quad . \quad . \quad (1)$$

shows, that when the electron concentration in equilibrium (1*b*) is greater than the concentration of electrons in strong nitric acid, electrons and nickel ions pass from the metal into the solution.

The inner equilibrium in the nickel surface will thus be disturbed, and this disturbance, under the influence of negative catalysts, proceeds so far that, as in the case of iron, a passive condition makes its appearance.

But, as in the case of iron, the passivation of nickel by means of

strong nitric acid is only possible below a certain limiting temperature. In the case of nickel this limiting temperature has been shown to be about 80°.

(c) *The disturbance of nickel by means of bromine water and the catalytic influence of bromine ions.*

It had already been noticed [1] that nickel could be easily disturbed by means of bromine water, and consequently at my suggestion Lobry de Bruyn made a close study of this phenomenon.

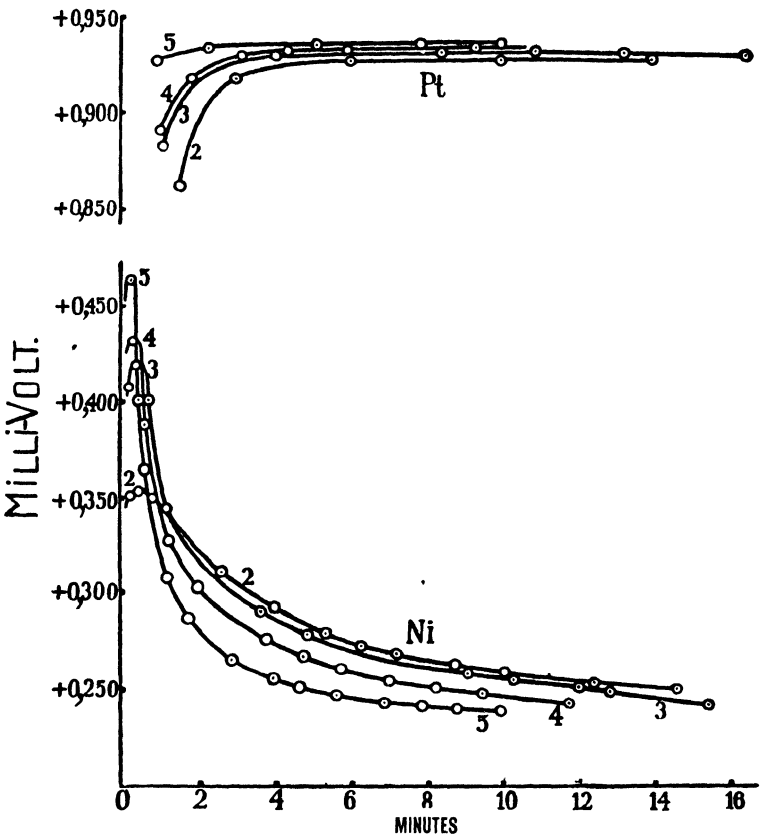


FIG. 233.

The explanation of this disturbance must naturally again be that in the bromine equilibrium (2)

$$Br_2 + 2\theta \rightleftarrows 2Br', \quad . \quad . \quad . \quad . \quad (2)$$

[1] Smits and Aten, *Versl. Kon. Akad. van Wet.*, **23**, 677 (1914).

the electron concentration is smaller than the electron concentration in the nickel equilibrium (1*b*), so that electrons and nickel ions pass from the metal into the solution. If, under these circumstances also, nickel behaved as a very inert metal, it might be disturbed to such an extent that the potential of the nickel would become equal to the bromine potential. But, in consequence of the activating influence of the bromine ions formed, the disturbance cannot reach this limiting value. This was proved experimentally to be the case.

In Fig. 233 the lower curves 2, 3, 4, and 5 indicate the course of the nickel potentials observed when to 140 c.cs. of a 0·1 N. solution of $Ni(NO_3)_2$, in which the nickel electrode was immersed, 0·4, 0·6, 0·8 and 1 c.c. respectively of a 3 per cent. solution of bromine water were added. The upper curves 2, 3, 4 and 5 show the course followed by the bromine potential in the same solutions.

As this diagram shows, the potential of the nickel electrode immediately rises after the addition of bromine water to the electrolyte to much more positive values. This was also to be expected. The nickel potential, however, does not become equal to the bromine potential, but reaches a maximum at a lower value and thereupon sinks rapidly.

The potential of the platinum electrode also rises at the outset, for in about two minutes the bromine potential is established; when this value is reached, as may easily be understood, an extremely slow fall of potential occurs, as a result of the increase in concentration of the bromine ions produced by the corrosion of the nickel by bromine. The course which the nickel potential curve is seen to follow suggests that to begin with the metal is greatly disturbed by the corrosive action of the bromine, but that this disturbance is soon neutralised by the activating influence of the bromine ions thus formed.

That bromine ions do really exert a positive catalytic influence on the establishment of inner equilibrium in the nickel surface follows from the fact that, on replacing the 0·1 N. nickel nitrate solution by a 0·1 N. solution of $NiBr_2$, the maximum nickel potential observed after the addition of 1 c.c. of bromine water lies approximately 100 millivolts lower.

(d) *The disturbance of nickel by a solution of hypobromous acid.*

The corrosive action of bromine water can be traced to the extremely small electron concentration in this solution. If a solution of hypobromous acid is taken, a compound which also occurs in solutions of bromine, a solution is employed in which the electron concentration is likewise extremely small. It might therefore be expected to cause deep disturbance in the nickel. The disturbance was found to be greatest when the following procedure was adopted.

The nickel electrode was allowed to stand for about ten minutes in a dilute solution of HBrO; it was then sprayed with distilled water and introduced into a 0·1 N. solution of $Ni(NO_3)_2$ and the potential was then immediately determined.

The variation of the potential with the time was found to be as follows :—

Time in seconds after the introduction of the Ni electrode into the $Ni(NO_3)_2$ solution.	Potential of the nickel in relation to the normal calomel electrode.
9	+ 0·888
14	+ 0·690
23	+ 0·540
39	+ 0·378
57	+ 0·322
128	+ 0·263
340	+ 0·206
516	+ 0·191

From these results it appears, therefore, that the disturbance, especially at the commencement, rapidly decreases.

A rather less marked disturbance was obtained when a solution of $KMnO_4$ was employed.

(e) *The disturbance of nickel by anodic polarisation.*

When nickel is anodically polarised rather different qualitative results are obtained from those observed in the case of iron. When the experiment is carried out in air, a state which has been disturbed by oxygen in a positive direction is naturally present to commence with.

If now the anodic potential is measured at increasing current densities, using a nickel sulphate solution, the potential, as Schoch[1] found, rises considerably though the current density is still very small, and as a result the nickel changes into the passive condition. On diminishing the current density, just as in the case of iron, the metal remains passive at current densities at which to begin with it was still active.

In every instance Schoch determined the potential when the current had been constant for about two minutes, and the current was then again increased. The results were as follows :—

Current density milliamps per 100 sq. cms.	Potential relative to the normal calomel electrode, in volts.	
0	− 0·475	
0·04	− 0·463	
0·2	− 0·445	
2	− 0·39	The nickel electrode
4	− 0·36	is active.
22	− 0·27	
24	− 0·123	
32	− 0·05	
24	+ 1·06	The nickel electrode
185	+ 1·131	is passive.

[1] *Amer. Chem. Journ.*, **42**, 323 (1909).

The nickel electrode becomes passive rather suddenly, wherefore the current recedes.

When these results are represented graphically Fig. 234 is obtained.

If nickel is anodically dissolved, not in a solution of nickel sulphate but in a nickel nitrate solution, under the catalytic influence of the nitrate ions, the metal, as Lobry de Bruyn discovered, becomes passive when the current density is quite small, so that the impression is conveyed that, in this case, the active portion of the polarisation curve is missing. This is, of course, not really the case; under these circumstances the metal is extremely inert and hence this portion of the curve is much shorter and occurs at extremely small current densities.

That nickel is much more inert than iron also follows from the behaviour of this metal when it is anodically dissolved in a solution of any nickel halide.

As we have already stated, when iron is immersed in a solution of

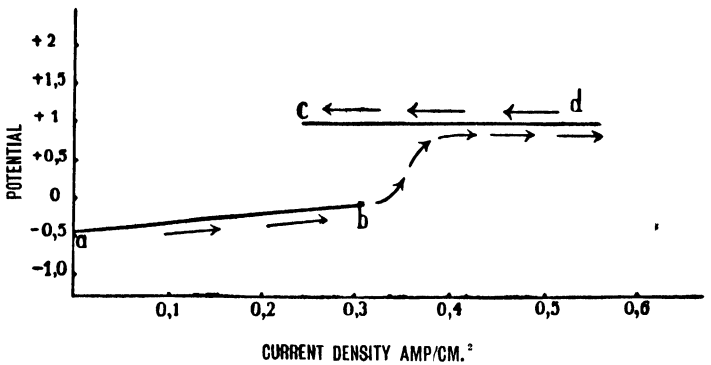


FIG. 234.

one of its halogen salts, it can only be disturbed to a very slight extent, because of the catalytic influence of the halogen ions.

In the case of nickel, however, the disturbance under these circumstances is very considerable, whence it follows that nickel is much more inert. The strong positive catalytic action of halogen ions, which, however, also exists here, ensures that under these circumstances nickel can never be changed into the passive state.

(f) *The activation curve for nickel.*

The activation curve for nickel, after the metal has been anodically polarised in a solution of $NiSO_4$ or $Ni(NO_3)_2$, depends in great measure on the atmosphere in which the experiment is carried out. Let us first consider the nickel activation curve when the experiment is carried out in air. Nickel is, as we have seen, very inert and is already disturbed to a considerable extent by the oxygen present in the air and in the solutions referred to, so that its potential is consequently much less negative than the equilibrium potential.

It might therefore be predicted that the activation curve for nickel in the air would be very different from that of iron.

As Lobry de Bruyn found, this curve, shown in Fig. 235, has two distinct points of inflection, but nowhere does an almost horizontal portion appear, such as was observed in the case of iron, although the fall took place so very slowly that only after several hours was an approximately constant end value reached.

If, in addition to the explanation of the form of the activation curve of iron, the much greater inertness of nickel is taken into consideration, an activation curve might be expected such as has been found here.

As has already been fully discussed, the inertness of nickel[1] leads to the very interesting phenomenon that the metal can become so inert through the action of hydrogen or acids under the negative catalytic influence of this gas, that the nickel potential becomes equal to the potential of the hydrogen electrode. It is therefore very clear here that

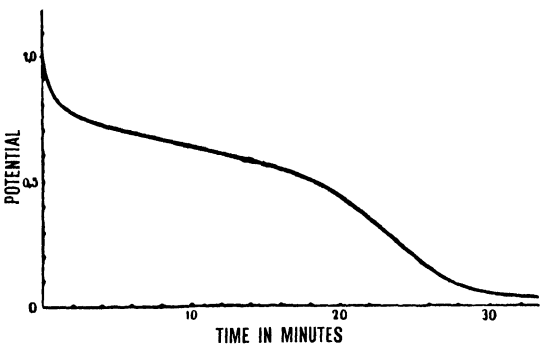


FIG. 235.

oxygen and hydrogen negatively catalyse the establishment of inner equilibrium in nickel. If, therefore, nickel is anodically polarised, hydrogen being at the same time passed through the solution, if the experiment is continued after the interruption of the current the following changes will take place. The oxygen taken up by the nickel surface during anodic polarisation will be gradually removed by the hydrogen and finally, instead of containing oxygen, the nickel surface will contain hydrogen.

Thus an interval of time will elapse, during which the surface of the nickel electrode will contain only extremely small quantities of oxygen or hydrogen, *i. e.* it will be almost free from negative catalysts. In this period the surface will attain inner equilibrium conditions more quickly, with the result that the potential will fall rapidly in the direction of less positive values. But since the hydrogen content of the nickel surface steadily increases and hydrogen is here a negative catalyst, this initial rapid activation does not lead to inner equilibrium, but to a disturbed state, which in this case has the same potential as the

[1] Cobalt behaves in a similar manner.

hydrogen electrode. The activation curve might be expected, therefore, to fall very slowly to commence with, then fairly rapidly, and finally again very slowly. In agreement with this, the activation curve shown

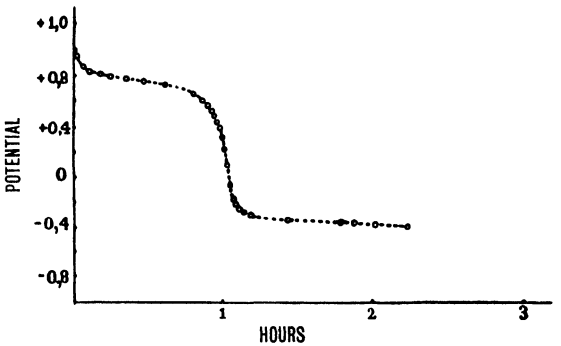


FIG. 236.

in Fig. 236 was obtained for nickel in a solution of $Ni(NO_3)_2$ through which hydrogen was passed.

In solutions of nickel halogen salts activation followed the same course, but somewhat more rapidly.

(g) *The cathodic polarisation of nickel.*

In the case of all metals which are violently disturbed by solutions containing oxygen, it is possible, by carrying out the deposition of the metal on the cathode in air, to obtain potentials for very small current densities which are still always somewhat less negative than the equilibrium potential. This will naturally be the case so long as the velocity of the cathodic deposition is so small that corrosion can bring about an appreciable disturbance of the deposited metal. Nickel, which can be very strongly disturbed by dissolved oxygen, exhibits this phenomenon particularly clearly. For very small current densities, the potential during cathodic deposition remains less negative than the equilibrium potential; only at higher current densities does the potential become more negative than the equilibrium potential, and only then is the deposited metal in the state of formation. In a 0·1 N. solution of $Ni(NO_3)_2$ the curve shown in Fig. 237 was obtained.

The equilibrium potential is — 0·48; thus it may be seen here, that even when the current density amounted to about 200×10^{-6} amperes per sq. cm. the potential was still less negative than the equilibrium potential.

Finally it may be mentioned that on employing a solution of a halogen salt of nickel instead of a nickel nitrate or nickel sulphate, the potential of the nickel passed much sooner through the value of the equilibrium potential, as was also to be expected. So long as the rate of deposition is so small that the nickel can be appreciably

disturbed by dissolved oxygen, so long will halogen ions exert a marked catalytic influence tending to annul the disturbance.

At greater current densities the disturbing influence of the dissolved oxygen will become relatively smaller and the positive catalytic influence

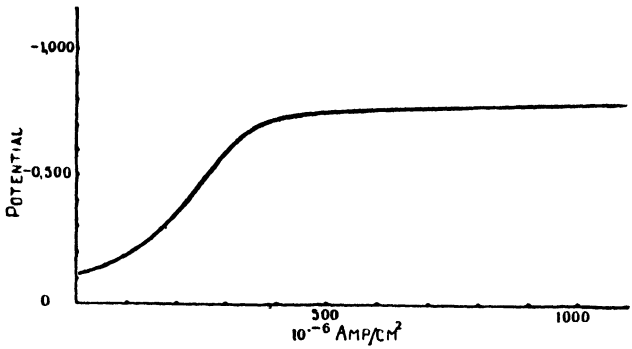


FIG. 237.

will also relatively decrease. If, therefore, the current density is allowed to increase, it follows from the circumstances mentioned that the nickel potential must soon pass through the equilibrium potential, and it will then exhibit cathodic polarisation which increases strongly at the outset and afterwards more slowly.

12. Aluminium.[1]

Since the theory of electromotive equilibria developed here has proved to be a reliable guide in the investigation of the electromotive relationships of metals and non-metals, the experimental study of the most important elements will now be carried out in my laboratory.

It has already been established that, in the main, the behaviour of cobalt is similar to that of nickel. Aten [2] has begun the investigation of chromium, but the work is not as yet complete.

Aluminium has proved to be a most interesting metal, and although its study has only just been commenced, this book will conclude with a few remarks concerning this element.

Aluminium is a most remarkable metal, especially as regards its electromotive behaviour. It is not usually included in the voltage series, because its position is still uncertain. In alkaline solutions zinc is precipitated by aluminium; in neutral or acid solutions, however, this is not the case. Here the remarkable fact should be mentioned that amalgamated aluminium also precipitates zinc from neutral solutions

[1] Smits and Aten, *Versl. Kon. Akad. v. Wet*, **22**, 1133 (1914); Smits, same journal, **28**, 930 (1920). Smits and de Gruyter, same journal, **29**, 747 (1920).

[2] *Ibid.*, **26**, 800, (1917); 1185 (1918); 1385 (1918).

and decomposes water vigorously; in the air it oxidises rapidly and exhibits such chemical characteristics that from them it might be

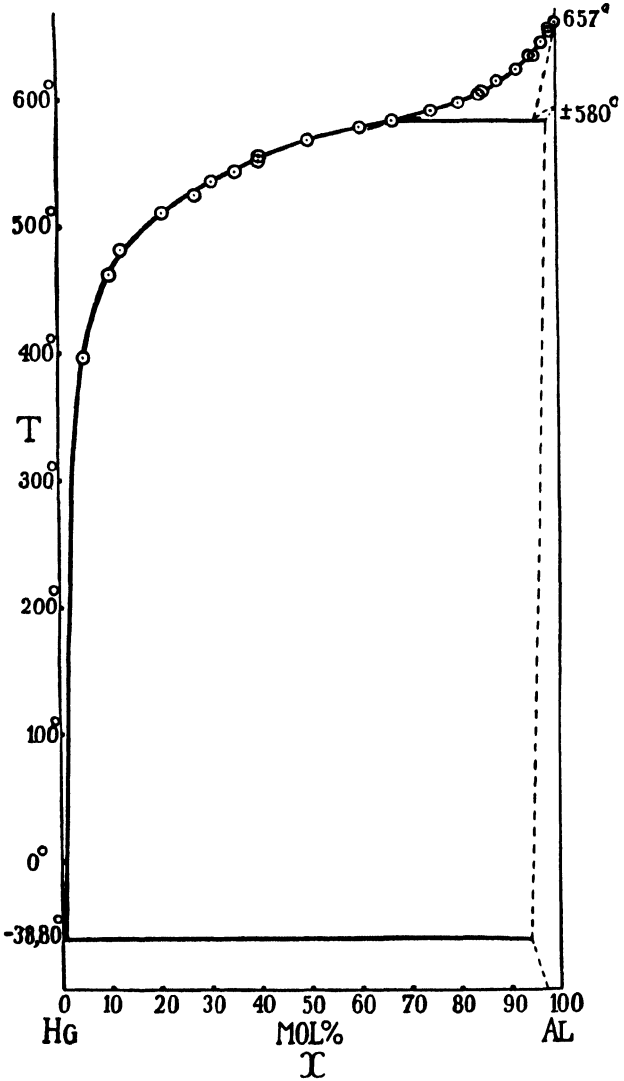


FIG. 238.

deduced that aluminium in this condition should be placed immediately after the alkaline earth metals, thus: Ca, Mg, Al, Mn, Zn.

From this behaviour the conclusion might be drawn that the pure

aluminium of commerce exists in a passive condition. Günther Schulze[1] is of opinion that polished lustrous pure commercial aluminium is always coated with a non-porous insulating film of oxide of molecular thickness, and that therein lies the cause of this passivity. Our investigations have yielded results, however, which tend to show that the assumption of the existence of such a film is incorrect, and on this account new experiments have been instituted with the object of determining the equilibrium potential and the influences to which it is subject, and of investigating the phenomena of polarisation. The results of these experiments, however, cannot yet be communicated.

The study of the activation of aluminium by means of mercury has now proceeded sufficiently far for some of the results obtained to be given here.

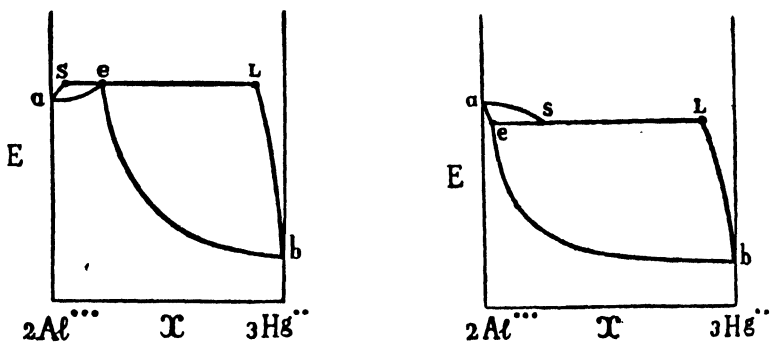


FIG. 239.

In the first place the melting-point diagram was determined for the rapid orientation of the system mercury-aluminium. As Fig. 238 shows, this diagram proved to be a very simple one; no compound appears, the only peculiarity being that the fusion line for aluminium consists of two portions, for at about 580° this metal has a transition point.

When this fusion diagram had been obtained, it could naturally at once be concluded whether the E X diagram, at the ordinary temperature for example, belongs to type 1 or type 2 in Fig. 239.

Assuming Gibb's *Paradoxon* to be also applicable to the constituents of a mixed crystal phase present in a dilute condition, the formula

$$E = -\frac{0{\cdot}058}{\nu F} \log \frac{L_M}{(M^{\nu}_{L})} - 2{\cdot}8$$

was obtained. This formula now holds good also for the potential of aluminium–mercury mixed crystals if the mercury content is very small, in the sense that the quantity L_M is no longer constant, even when the

[1] *Ann. der Phys.*, **28**, 787 (1909).

metal is in inner equilibrium, but decreases as the mercury content increases.

If, therefore, the potential of aluminium is first determined in a non-aqueous solution of one of its salts, and then in an equivalent non-aqueous solution of a mixture of mercury and aluminium salts, according to the formula the direction of the change of potential will depend on which of these values has decreased to the greater extent.

If the decrease in ($Al_L^{\cdot\cdot\cdot}$) is the greater, the potential will be more negative; if, on the other hand, (L_{Al}) has suffered the greater decrease the potential will become less negative. It is clear that the question can also be treated in the converse manner; that is to say, if electrodes of varying mercury content are previously prepared, and these are then dipped into a solution of an aluminium salt, the potential can also be determined in this way.

Without going into the question of the experimental details more closely, some results may be briefly mentioned here. It was found that the co-existing electrolyte was always relatively much richer in aluminium than the mixed crystals, so that from this the conclusion may safely be drawn that the E X diagram for the system Al—Hg belongs to the second type. Whilst, therefore, it might be expected, from the composition of the co-existing phases, that the potential of aluminium in a solution of an aluminium salt would become less negative as the result of addition of a small quantity of a mercury salt, the remarkable fact emerges, on the other hand, that just the reverse takes place, and, indeed, to an extraordinarily great extent.

This behaviour proves that when mercury is dissolved in aluminium it catalyses the establishment of inner equilibrium, as was indeed already anticipated. Pure aluminium is always disturbed in the direction of greater nobility, and the continuation of our investigation of the electromotive behaviour of the system Al—Hg will doubtless enable us to find the potential of pure aluminium in inner equilibrium. These investigations are in full swing.

This book must therefore be concluded at this point and the communication of further results must be postponed. The first step in a new direction has been taken, as a result of which so many interesting researches will suggest themselves that many years' work will be necessary for the carrying out of the most important of them.

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