Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

In this T,x-figure **L** and **S** denote the coexisting phases at the unary point of solidification of the *monoclinic* sulphur, and in the same way the points **L''** and **S''** indicate the coexisting phases at the unary point of solidification of the monoclinic *soufre nacré*, **L'** and **S'** referring to the unary point of solidification of *rhombic* sulphur, and **S₁** and **S₂** to the coexisting solid phases at the unary point of transition.

In conclusion I will *emphatically* point out that it is very well possible that in many respects the real T,x-figure of the system sulphur deviates from the diagram given here. The system sulphur may be pseudo-quaternary, or even still more complicated. Moreover it is very well possible, indeed it is even probable, that in the pseudo-binary systems no eutectic points occur etc', but, however strange this may seem, this is just now of minor importance.

At present the only end in view can be this to find a means to express the fundamental thought, that we meet here with a system that is composed of more than two kinds of molecules, and of which not only the unary vapour- and liquid phases, but also the unary solid phases are states in which these different kinds of molecules are in equilibrium. Starting from this idea the figure given here was drawn up, which will probably appear to be able for the present to account satisfactorily for the observed phenomena.

Amsterdam, Sept. 25 1912. *Anorg. chem. lab. of the University*

Chemistry. — "*The inverse occurrence of solid phases in the system iron-carbon.*" By Prof. A. Smits. (Communicated by Prof. A. F. Holleman.)

Through an investigation made by Ruff [1]) concerning the completion of the T,x-figure of the system iron-carbon I came to the conclusion some time ago that stable carbides probably occur in this system [2]). Shortly after there appeared an abstract of a preliminary investigation by Wittorf [3]), written in Russian, which seemed to confirm this surmise. When what seems very probable to me, the results of Wittorf are correct, we meet in the system iron-carbon with a pecularity, as I demonstrated before, which has been met with up to now only in the system ceriumsulphate-water. This peculiarity consists in the inverse occurrence of solid phases. One of

[1]) Metallurgie 458, 497 (1911).
[2]) Z. f. Elektr. Chem. 18, 362 (1912).
[3]) Russ. phys. chem. Ges. 43, 1613 (1911). Compt. rend 1912, 1091.

the phases which shows this phenomenon in the system iron-carbon, is *graphite*. Graphite is the second component, and when there was no deviation from the ordinary state of things the succession of the solid phases, which coexist with the saturated *solid* and *liquid* solutions, would be such that the carbon content continually increased in one direction. Starting at the ordinary temperature we find, however, this that first graphite, and then carbides are formed, which latter however will finally have to give way before the graphite again.

Now it would follow from the preliminary investigations of WITTORF, when namely the equilibria examined by him are stable, that twice such an inverse deposition takes place in the system *iron-carbon*, for with rise of temperature he found this succession:

$$C - Fe_4C - FeC - Fe_3 \quad C - Fe_2C \, ?$$
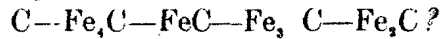
from which it appears that a solid phase with a *higher* percentage of iron succeeds not only *C*, but also *Fe C*.

This phenomenon of inverse occurrence of solid phases is still so strange to us that it is expedient theoretically to enter a little more deeply into this matter.

To throw the peculiar element into strong relief, I shall discuss the phenomenon led by the same example as I used as an illustration in the Zeitschr. f. Elektrochemie. So I shall suppose for a moment that the succession of the solid phases which coexist with saturated liquid solutions with rise of temperature, is this:

$$C - FeC - FeC_2 - C.$$

If we now suppose that the situation of the lines for the three-phase equilibrium with one of these solid phase, so for $S + L + G$, is as has been represented in fig. 1, the easiest way to find the situation of the other three-phase lines is to prolong the two three-
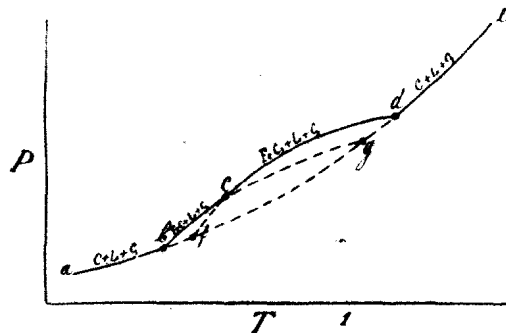

Fig. 1.

phase lines *bc* and *dc* metastable through the point of intersection *c*, till we meet the metastable middle portion of the three-phase line for $C + L + G$ in *g* resp. *f*.

Let us at first only consider the two three-phase lines for C+L+G and FeC + L + G, which are once more drawn separately in fig. 2. Then it is noteworthy that b and g are two quadruple points, where vapour, liquid, graphite and the carbide FeC coexist. There is,
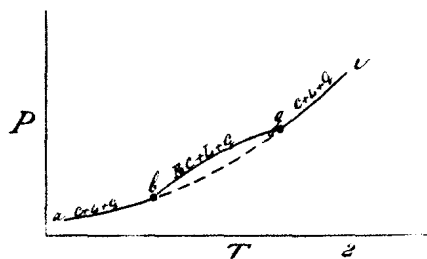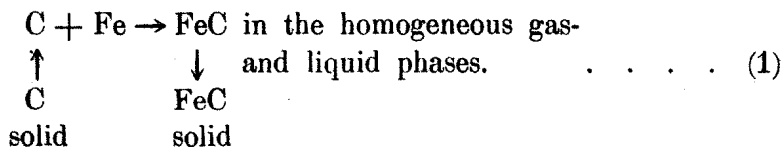

Fig. 2.

however, a difference between these two quadruple points, and the most essential difference is this that whereas in the first quadruple point b with supply of heat graphite with the vapour and the liquid phase is converted to FeC, in the second quadruple point the very reverse takes place.

If the case supposed here actually existed, we might account for it in the following way. The simplest supposition we can make is that along the three-phase line for C + L + G the concentration of FeC in the vapour and in the liquid phase continually increases from a to b, because the carbon concentration increases, and because besides we probably have here the endothermic process:

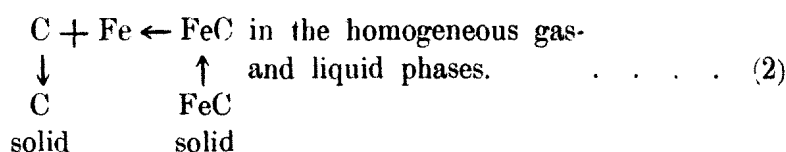$$C + Fe \rightleftarrows FeC - a \text{ cal.}$$
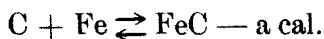
In consequence of the shifting of the above mentioned equilibrium to the right, the liquid and the vapour phases in the quadruple point b have just become saturate with FeC, and they are still just saturate with graphite. With an infinitely small rise of the temperature the two phases, which are still supposed to be in contact with graphite, become *supersaturate* with regard to FeC, and *unsaturate* with regard to graphite, from which follows that on supply of heat graphite will dissolve and FeC deposit in the quadruple point b, till all the graphite is gone.

So the symbol for the conversion, which takes place in the quadruple point b on *supply of heat* is as follows:

$$
\begin{array}{ll}
C + Fe \rightarrow FeC & \text{in the homogeneous gas-} \\
\uparrow \qquad\quad \downarrow & \text{and liquid phases.} \qquad \dots \dots \quad (1) \\
C \qquad\quad FeC & \\
\text{solid} \quad\;\; \text{solid} &
\end{array}
$$

It is clear that if the reverse happens in the quadruple point g, the *condition* must have become different in so far that the homogeneous gaseous resp. liquid phases, which were before saturate with regard to FeC and unsaturate with regard to C, must be saturate again in g with respect to both the solid phases, and infinitely little above the temperature of the quadruple point g the gaseous and liquid phases in contact with solid FeC must become unsaturate with respect to FeC, and supersaturate with respect to graphite, so that solid FeC is dissolved, and graphite is deposited, till all the carbide is gone.

So in the quadruple point g we get for the transformation on supply of heat the symbol

$$C + Fe \leftarrow FeC \text{ in the homogeneous gas-}$$
$$\downarrow \qquad \uparrow \quad \text{and liquid phases.} \qquad \qquad (2)$$
$$C \qquad FeC$$
$$\text{solid} \qquad \text{solid}$$

So the transformation given here must be endothermic in the direction of the arrows. We have to call attention to the fact that we assumed for shortness'sake that the formation of FeC in the coexisting gas and liquid phases is endothermic along the three phase line for $C + L + G$ from a to b. Now, however, we know only with certainty that the total transformation (1) is attended with absorption of heat.

When in the process of condensation resp. solidification of FeC from the coexisting phases more heat was developed than was absorbed in the process of evaporation resp. melting of graphite [1]), the process in the homogeneous phases would undoubtedly be *endothermic*, but in the opposite case the total transformation (1) could be endothermic, whereas the reaction in the homogeneous gas and liquid phases was *exothermic*. But in this case we should have to inquire how it is possible that the gas and liquid phases, which were unsaturate with respect to FeC on the three-phase lines between the points a and b, have become saturate with respect to this compound at b. This is easy to see. We must namely consider two influences here which can displace the equilibrium : in the first place the temperature, and in the second place the concentration of the reacting components. On rise of temperature in the absence of graphite the equilibrium in the homogeneous gas and liquid phases would shift to the left, but in the presence of graphite just the reverse would take place, when namely the increase of solubility of graphite predominates over

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[1]) The heat of mixing included.

the influence of the temperature on the homogeneous equilibrium on rise of temperature.

Thus we may not conclude from the circumstance that the transformation (2), which refers to the second quadruple point g is endothermic, that the conversion in the homogeneous phase proceeds endothermically in the direction of the arrow.

If we make the same supposition as we did just now, viz. this that in the process of evaporation resp. melting of FeC more heat is absorbed than is developed by the process of condensation resp. solidification of graphite, the total heat of transformation (2) might be endothermic, also when the homogeneous process in the direction of the arrow was *exothermic*.

In the opposite case, however, the reaction in the homogeneous phases in the direction of the arrow would certainly be endothermic.

Thus we come to the conclusion that the case of inverse deposition of solid phases supposed here is possible, when the conversion :

$$C + Fe \rightarrow Fe\,C$$
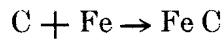
taking place in the homogeneous phases between the points g and b has become less *greatly endothermic or exothermic*.

As is known, a change in the heat-effect with the temperature is a phenomenon of general occurrence, which owes its origin to the circumstance that the specific heat is a function of the temperature. Repeatedly great changes of the heat of reaction with the temperature have been observed, so much so that a reversal of the sign of the heat took place, from which accordingly follows, that the possibility of the here supposed case was to be expected on the ground of our present knowledge.

Now we shall proceed to the discussion of the other three-phase lines, which likewise start from the two quadruple points b and g.

In the first place a three-phase line for $C + Fe\,C + G$ still starts from the point b. To determine the direction of this curve we may make use again of Van der Waals' theory of binary mixtures.

If we denote graphite by S_1 and carbide by S_2, the following relation follows from the theory mentioned for the three-phase line for $C + Fe\,C + G$:

$$T\left(\frac{dp}{dT}\right)_{S_1 S_2 G} = \frac{W_{s_1 g} - \dfrac{x_{s_1} - x_q}{x_{s_2} - x_q}\, W_{s_2 g}}{V_{s_1 g} - \dfrac{x_{s_1} - x_q}{x_{s_2} - x_q}\, V_{s_2 g}} \quad \ldots \ldots (I)$$

In the quadruple point b numerator and denominator indicate the

heat-effect and the change of volume, which attends the transformation (1). If we first consider the denominator, we see that V_{s_1g} and V_{s_2g} are both negative and differ little. And as further $x_{s_1}-$ $-x_g > x_{s_2} - x_g$, we see immediately that the denominator will be positive.

About the numerator we know that it is negative in b, so that it follows from the sign of numerator and denominator, that $T \dfrac{dp}{dT}$ is negative, and that the three-phase pressure will descend with rise of temperature, at least in the neighbourhood of b.

With a view to the further discussion it is desirable to examine the numerator somewhat more closely. W_{s_1g} and W_{s_2g} are the quantities of heat which are developed when a gr. mol. of S_1 resp. S_2 evaporates in an infinitely large quantity of the coexisting vapour phase. We can divide both quantities into two others, viz. into a molecular heat of evaporation and a molecular differential heat of mixing e.g.

$$W_{S_1g} = (W_{S_1g})_x + W_{g_{x_1}g}$$

The heat of evaporation $(W_{S_1g})_x$ is negative. If now we further assume that the formation of FeC is endothermic at b, so
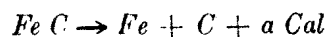
$$C + Fe \rightarrow FC - a\ Cal,$$

which is more probable, the heat of mixing $W_{g_{x_1}g}$ will also be negative, so that W_{S_1g} is also negative then.

For W_{S_2g} we may write:

$$W_{S_2g} = (W_{S_2g})_x + W_{g_{x_2}g}.$$

The molecular heat of evaporation $(W_{S_2g})_x$ is again negative. The differential heat of mixing $W_{g_{x_2}g}$ will consist almost exclusively in the heat effect of the conversion:

$$Fe\ C \rightarrow Fe + C + a\ Cal$$

which as has been indicated here, is positive at b, so that $W_{g_{x}g}$ can be also positive, and W_{S_2g} negative or even positive. So we see from this how it is possible here that notwithstanding the fraction $\dfrac{x_{S_1}-x_g}{x_{S_2}-x_g} > 1$ the quantity W_{S_1g} predominates in equation (I), so that the numerator is negative.

It is now clear that when on rise of temperature the heat of formation of FeC becomes smaller negative in the gas phase, and finally passing through zero, assumes a positive value, the negative

value of W_{s_1g} will continually decrease, and that of W_{s_2g} will increase. From this it follows that the numerator which is at first negative, will likewise pass through zero and become positive. This happens before the second quadruple point g has been reached, for in that point the numerator must be positive already. So we arrive at the conclusion that $T\dfrac{dp}{dT}$ for the three-phase line $S_1 + S_2 + G$ starting from b is negative, then passes through zero, and has a positive value in g, so that the said three-phase line, which joins the two quadruple points b and g, possesses a minimum pressure, as is indicated in fig. 3.
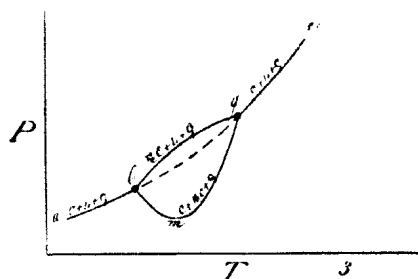

Fig. 3.

The considerations given here may be directly applied to the fourth three-phase line of the mentioned two quadruple points, viz. to that for $S_1 + S_2 + L$. The equation, which we want in this case, is quite analogous with equation (1), and we need only substitute the letter l for g to obtain the true relation, so:

$$T\left(\frac{dp}{dT}\right)_{S_1 S_2 L} = \frac{W_{s_1 l} - \dfrac{x_{s_1} - x_l}{x_{s_2} - x} W_{s_2 l}}{V_{s_1 l} - \dfrac{x_{s_1} - x_l}{x_{s_2} - x_l} V_{s_2 l}} \quad \ldots \quad (II)$$

The discussion of the numerator is perfectly identical with that just given, but now the denominator requires further consideration.

We were convinced that $V_{S_1 g}$ and $V_{S_2 g}$ are negative, but about the quantities $V_{S_1 l}$ and $V_{S_2 l}$ we must make the following remarks. The known increase of volume, which takes place in iron-carbon mixtures on solidification leads us to expect that this property is to be attributed to the presence of the component carbon, which behaves probably in the same way as the substance water. In consequence of this not only carbon, but also carbon-compounds will exhibit increase of volume on solidification, specially when the compound

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contains comparatively much carbon, whereas compounds with a smaller percentage of carbon will probably behave like iron.

If we now assume that $V_{S_1 l}$ and $V_{S_2 l}$ are both positive, then it is possible that the denominator of equation (II) is negative, and the numerator also having a negative value at b, $T\left(\dfrac{dp}{dT}\right)_{S_1 S_2 L}$ will begin in this case in b with a positive value. In the second quadruple point g the numerator is positive, as I showed before, and consequently $T\left(\dfrac{dp}{dT}\right)_{S_1 S_2 L}$ will be negative.

Reasoning in the same strain as before in the discussion of the three-phase line for $S_1 + S_2 + G$ it follows that the three-phase line for $S_1 + S_2 + L$ will possess a pressure maximum, as has been schematically represented in fig. 4.
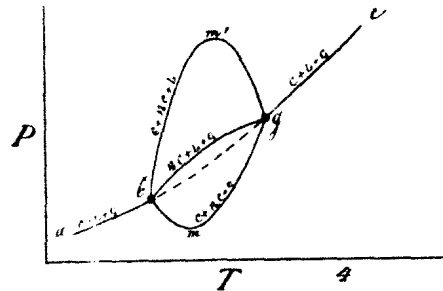

Fig. 4.

When on the other hand $V_{S_1 l}$ is positive and $V_{S_2 l}$ negative, the denominator has a positive value, and $T\left(\dfrac{dp}{dT}\right)_{S_1 S_2 L}$ will consequently be negative at b and positive at g, in consequence of which the P,T-figure becomes as it has been drawn in fig. 5.
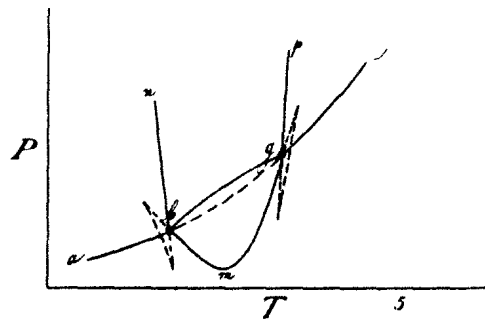

Fig. 5.

A metastable minimum cannot occur here, because the three-phase lines for $C + FeC + G$ and for $C + FeC + L$ pass continuously

into each other by means of two cusps in the way indicated in fig. 5'). Finally it may still be pointed out that it is possible that in the last case the denominator passes through zero, which would bring about a combination of the figures 4 and 5.

If we now apply the results obtained here to our original case indicated in fig. 1, we arrive easily at the correct result, when we omit in our thoughts first the three-phase line for $FeC_2 + L + G$, and then that for $FeC + L + G$. We then get two intersecting figures, in which we can easily distinguish the stable equilibria from the metastable ones.

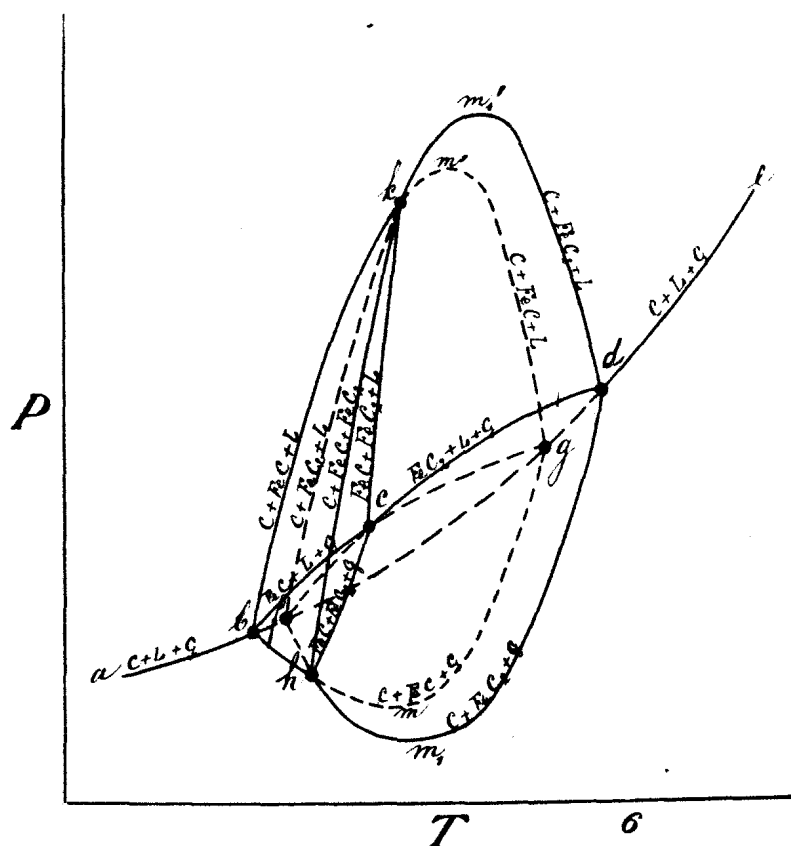Fig. 6 gives the P,T-projection for the case that we have twice the same type as fig. 4.

Fig. 6.

The three-phase lines for $C + FeC + G$ and $C + FeC_2 + G$ intersect in h, where a new quadruple point is formed, from which two more three-phase lines start, viz. hk for $C + FeC + FeC_2$ and hc for $FeC + FeC_2 + G$. The point k is the point of intersection for the three-phase line $hm'g$ for $C + FeC + L$, and of the three-

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1) Comp. the paper of Dr. SCHEFFER, These Proc. p. 389.

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phase line $fm_1'd$ for $C + FeC_2 + L$, and so this latter three-phase line, which starts from the metastable quadruple point f, becomes stable at k, and then after having reached a maximum, it runs to the quadruple point d. So the point k is also a quadruple point, where besides the two mentioned three-phase lines, two others meet viz. the three-phase line for $FeC + FeC_2 + L$ and that for $C + FeC + FeC_2$. It is clear that the situation could also have been such that the three-phase line for $C + FeC + L$ possessed a stable maximum, but this does not give rise to essential modifications. If we examine a combination of twice the type of fig. 5, the case is less remarkable.

Anorganic Chemical Laboratory

Amsterdam, September 8, 1912. *of the University.*

Physics. — *"On the system ether-water."* By Dr. F. E. C. SCHEFFER.

(Communicated by Prof. J. D. VAN DER WAALS).

1. In his Thesis for the doctorate (1912) Dr. REEDERS described a number of experiments which were undertaken with a view to the experimental realisation of the phenomenon of double retrograde condensation, which had been predicted by Prof. VAN DER WAALS. Both the systems which were used for this investigation, carbonic acid and urethane, resp. carbonic acid and nitrobenzene exhibited three-phase pressures, which at the same temperature, were lower than the vapour pressures of the carbonic acid. In neither of the systems the direct observation of the said phenomenon has been possible. In my opinion Dr. REEDERS justly ascribes the failure of this observation to the fact that the difference in volatility of the components of both systems is so great that the vapour phase under three-phase pressure practically consists of pure carbonic acid, and consequently the quantity of the liquid layer, poor in carbonic acid, which is formed during the retrograde condensation, is so small that it escapes observation. The critical points of the upper layer lie for both systems at concentrations which are smaller than 2 mol. percentages of the least volatile substance, and hence the concentration which is to present the double retrograde condensation contains still less of the second component.

When Dr. REEDERS told me his results a long time before the publication of his Thesis for the Doctorate, it did not seem impossible to me that a system, in which the volatility of the components