Chemistry. — *"On the System Iron-Oxygen"*. By Prof. A. Smits
and J. M. Bijvoet. (Communicated by Prof. S. Hoogewerff).

The equilibria to which the reactions between iron-oxides and
reducing gases as carbon oxide and hydrogen give rise, have
already repeatedly been a subject of a scientific research.

Thus of the gas phase of the three-phase equilibria $FeO + Fe + G$
and $Fe_3O_4 + FeO + G$ the ratio $\dfrac{(CO)}{(CO_2)}$ resp. $\dfrac{(H_2)}{(H_2O)}$ was studied [1]).

Three-phase systems of three components were studied, i e. systems
that were monovariant at constant pressure. In this there was, however,
no need to keep the pressure constant, because the above-mentioned
relations are independent of this. As result the researches with
CO as reducing gas yielded two equilibrium curves, which may
be called three-phase curves for the homogeneous equilibrium
in the gas phase which coexists with two solid phases, namely one
for $FeO + Fe + G$, and another for $Fe_3O_4 + FeO + G$, of which
Scheffer [2]) showed that they had to intersect in virtue of the heat-
effect of the conversions.

Researches with H_2 as substance of reduction did not only give
the situation of the three-phase line for $Fe + FeO + G$, but also
that for $Fe + Fe_3O_4 + G$. The latter was made probable by Reinders,
who also computed the situation of the three-phase line for Fe_3O_4
$+ FeO + G$ in this system from the corresponding line for the reduction
with CO by the aid of the water-gas equilibrium. When we trace
the three-phase curves for $Fe_3O_4 + FeO + G$ and for $FeO + Fe +$
G for the case $G = CO + CO_2$, we get the following figure when
log K is drawn as function of T, in which figure a third three-
phase line for $Fe + Fe_3O_4 + G$ must start from the point of inter-
section, which is here a quadruple point as Scheffer has noticed.

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[1]) A survey of the literature of these researches has been given in Reinders'
paper on: the equilibria of iron-oxide with hydrogen and water vapour. Chem-
Weekblad 15, 180 (1918).
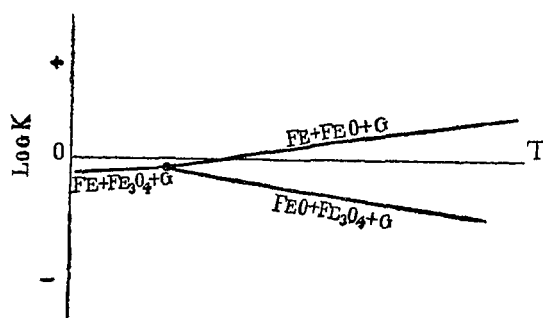
[2]) These Proc. Vol. XIX, p. 636.

Fig. 1.

On the mixture of the solid phases Fe_2O_3 and Fe_3O_4.

Now the question presents itself whether there exists also a three-phase line for $Fe_2O_3 + Fe_3O_4 + G$ [1]).

SOSMAN and HOSTETTER [2]) think that they have to derive from their determinations about the tension of dissociation and the diffraction of light of mixtures $Fe_2O_3 + Fe_3O_4$ that the oxides Fe_2O_3 and Fe_3O_4 in the solid state are miscible if not in all proportions, yet very near the concentration F_3O_4. If there really existed a continuous mixed crystal series here, there would not appear a three-phase curve for $Fe_2O_3 + Fe_3O_4 + G$, and the figure discussed here would be complete.

It is, however, the question whether on the ground of SOSMAN and HOSTETTER's researches we may conclude to a continuous mixed crystal series. When we draw up a p,x-section of the system *oxygen-iron* corresponding to the temperature $1100°$, on the assumption that Fe_2O_3 and Fe_3O_4 are only miscible to a limited degree in the solid state, we arrive at the schematic representation drawn in fig. 2.

In this p,x-section, in which it is assumed that the oxides present a certain mixture in the solid state, the line df represents the mixed crystals that are rich in Fe_2O_3, and which coexist with the vapours be, the line gh referring to mixed crystals rich in Fe_3O_4, which can coexist with the vapours eh.

A point on the line df, here p, corresponds with the concentration Fe_2O_3, and thus a point of the line gh, viz. q, corresponds with concentration Fe_3O_4.

It follows immediately from this what curve we must get, when

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[1]) These Proc. 19, 175 (1916) REINDERS has supposed the existense of such an equilibrium but the results of the experiments of SOSMAN and HOSTETTER, were unacquanted at that time.

[2]) Journal Amer. chem Soc. 38, 837 (1916).

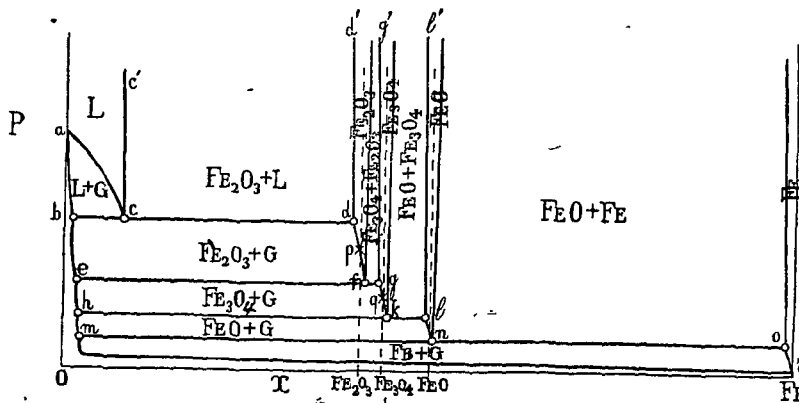we start from Fe_2O_3, and every time take away a quantity of the

Fig. 2.

vapour phase at the constant temperature of e.g. 1100°. The total concentration will then change in the direction from Fe_2O_3 to Fe_3O_4, and in this the pressure will also be subjected to a change.

First the pressure will gradually descend from p to f. During this decrease of pressure two phases coexist, viz. mixed crystals rich in Fe_2O_3 and vapours consisting almost exclusively of oxygen. When the pressure has fallen to that of the three-phase equilibrium $e f g$, a mixed crystal phase g rich in F_3O_4 will be deposited by the side of the mixed crystal phase f rich in Fe_2O_3, and a three-phase system arises of which the phase rule demands that the pressure remains constant in case of equilibrium. On continued withdrawal of a part of the gas phase, during which the total concentration continually moves to the right, the pressure therefore remains constant until the last trace of the mixed crystal phase rich in Fe_2O_3 has entirely disappeared. At this moment only the vapour and the mixed crystal phase g rich in Fe_3O_4 coexist, and on further withdrawal of the gas phase the pressure will again descend regularly, in which the solid phase moves downward along gk.

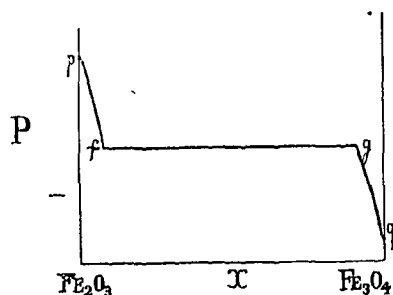When we now draw the vapour tension as function of the total

Fig. 3.

concentration, theory predicts that on partial mixing of the two oxides Fe_2O_3 and Fe_3O_4 in the solid state, a broken line as is schematically represented in fig. 3, will be found, the middle part of which runs horizontally.

This is the theoretical curve, and now it is directly to be seen,

in what the experimentally determined curve will differ from it.

In the first place it is self-evident that through all kinds of disturbing influences of these small pressures, as e.g. the presence of traces of adsorbed gases or contaminations, and the slow progress of the dissociation, there is a great chance that the middle part will not be found to be horizontal, but more or less sloping;
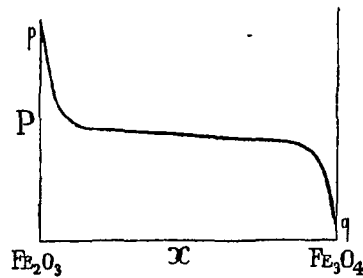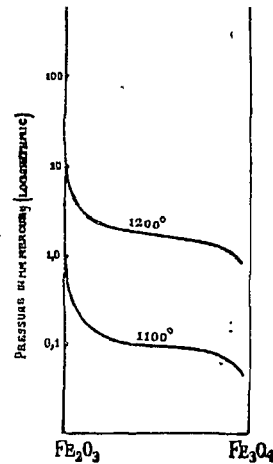

Fig. 4.   , Fig. 5.

and in the second place the transition of the two sloping parts to the horizontal part will not be found to be discontinuous, but always continuous, especially when many observations are made in the immediate neighbourhood of f and g. Instead of the above given broken line the continuous curve of fig. 4 will, therefore, be found in the most favourable case.

When with these curves we compare the lines found by SOSMAN and HOSTETTER, which have been reproduced in fig. 5, we see that the found curves closely resemble those which theory led us to expect for only *partial* mixture of Fe_2O_3 and Fe_3O_4 in the solid state.

Everything depends on this whether the non-horizontal course of the middle portion is essential or not, for if this is essential and the observed pressures correspond with the states of equilibrium, this course of the isotherm would really plead in favour of the existence of a continuous mixed crystal series. SOSMAN and HOSTETTER see a confirmation of the view that the mixing of Fe_2O_3 and Fe_3O_4 is continuous in the fact that the indices of refraction of the mixtures change far from proportionally with the quantity Fe_3O_4 between hematite ($\varepsilon = 2,78$) and magnetite ($n = 2,42$).

They give namely the following results.

Concentration of the mixture	ε for 700 $\mu\mu$
Hematite	2.74
0.58 % FeO	2.74
5.60 „ „	2.73
12.99 „ „	2.72
16.11 „ „	2.71
17.79 „ „	2.71
—	—
Magnetite (31.03 % FeO)	$n = 2.42$

It seems to us that they overlook in this that in case of unmixing it is by no means impossible that the phase rich in Fe_3O_4 of the equilibrium of unmixing would show a much stronger refraction in consequence of its content of Fe_2O_3 than the pure magnetite. This possibility is by no means improbable, because it already follows from the above determinations that independently of the fact whether or no unmixing is assumed, the refraction must diminish much more rapidly somewhere in the optically not investigated region than on the Fe_2O_3 side.

It should besides be considered that, as also Sosman[1]) remarked, if we assume a continuous series of mixing between the hexagonal hematite and the regular magnetite, this would be an instance of a continuous mixture between non-isomorphous substances, which has not yet been experimentally observed in a single case.

Now if we assume that from the p,x-figure at $1100°$ and $1200°$ we must actually conclude to a continuous mixed crystal-series between Fe_2O_3 and Fe_3O_4, the said difficulty can still be obviated by the assumption that at this temperature the two oxides are isomorphous; as Sosman and Hostetter found that the homogeneous mixed crystal phases are bi-refringent, magnetite would have to possess a point of transition below $1100°$, above which point the regular form is metastable. This not very probable change of crystal class has, however, not been observed, and can besides not render the continuous mixing plausible for temperatures below that of the point of transition.

However this may be, the existence of a continuous series of mixing of $Fe_2O_3 + Fe_3O_4$ does not seem proved to us, and we

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[1]) Journ. of the Washington Ac. of Science **7**, 10 (1917).

deem it, therefore, desirable to consider the possibility that in fig. 1 there should be added another three-phase curve, viz. that for $Fe_2O_3 + Fe_3O_4 + G$ lying under that for $FeO + Fe_3O_4 + G$.

This situation gives rise to the question, whether this new three-phase line can intersect another. If it intersected the three-phase line for $Fe + Fe_3O_4 + G$, the mutual relation would be as given in fig. 6.
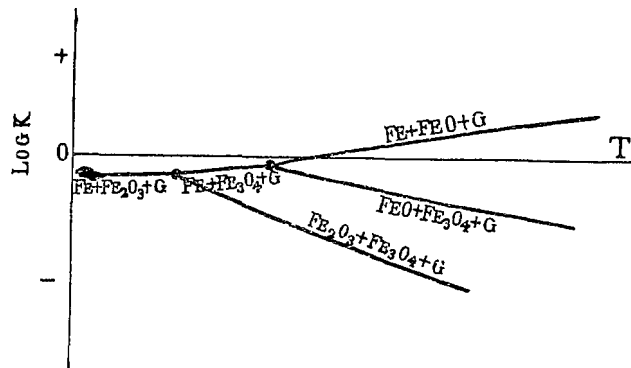

Fig. 6.

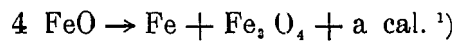The conclusion that the three-phase lines for $Fe + FeO + G$ and $Fe_3O_4 + FeO + G$ intersect, and that this point of intersection indicates, therefore, the lowest temperature at which FeO can occur stable by the side of the gas phase .G, is entirely in accordance with the sign of the conversion which must take place in this point on withdrawal of heat, viz.:

$$4 \, FeO \rightarrow Fe + Fe_3O_4 + a \text{ cal. [1]}$$

When also the three-phase lines for $Fe + Fe_3O_4 + G$ and $Fe_2O_3 + F_3O_4 + G$ intersected in the way indicated here, then the conversion:

$$3 \, Fe_3O_4 \rightarrow Fe + 4 \, Fe_2O_3$$
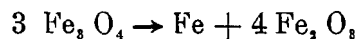
would have to take place in this point of intersection on withdrawal of heat, but this is in contradiction with the heat-effect of this reaction. It follows namely from the measurements that:

$$3Fe_3O_4 \rightarrow Fe + 4Fe_2O_3 - b \text{ cal. [2]}$$
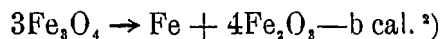
The supposition expressed in fig. 6 should, therefore, be rejected.

Now there remain two possibilities, namely these that the two three-phase lines for $Fe_3O_4 + FeO + G$ and $Fe_2O_3 + Fe_3O_4 + G$ intersect at higher temperature, but that melting sets in, before this intersection takes place. In this case we get a situation as' has been schematically given by fig. 7.

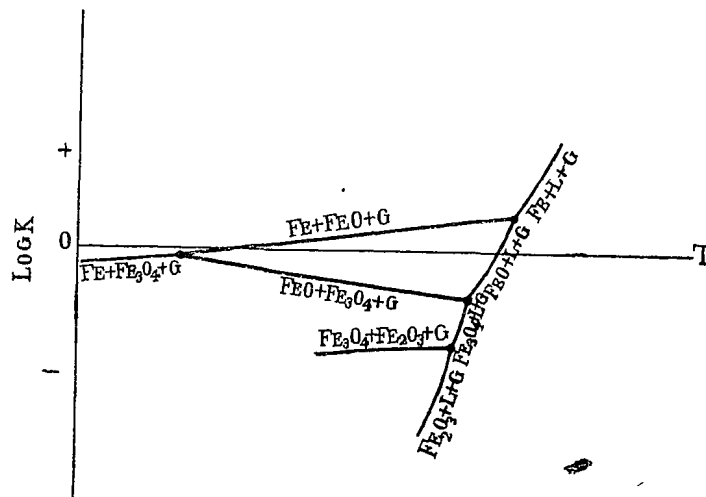---

[1] Comptes Rendus 120, 623 (1895).
[2] lóc. cit.

Fig. 7.

Another possibility is this that the just mentioned intersection does take place in the stable region, and then the situation of the lines is represented in fig. 8.[1])
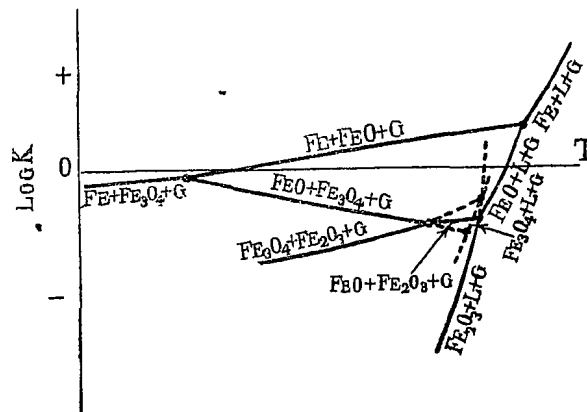

Fig. 8

It will be pretty easy to decide experimentally which of these two figures represents what really takes place. We will draw the attention on the fact that the transition point of iron is intensionally not considered here.

The Blast-Furnace Process.

What precedes gives time a survey of the three-phase lines and

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[1]) It is clear that when Fe_2O_3 and Fe_3O_4 become miscible above a definite temperature in all proportions, the line for $Fe_3O_4 + Fe_2O_3 + G$ ends abruptly.

the two-phase regions in the system Fe—CO—CO$_2$ (resp Fe—H$_2$—H$_2$O), and this has rendered it possible to elucidate the *reduction processes*, which e. g. take place in blast-furnaces, from beginning to end by means of a graphical representation [1]).

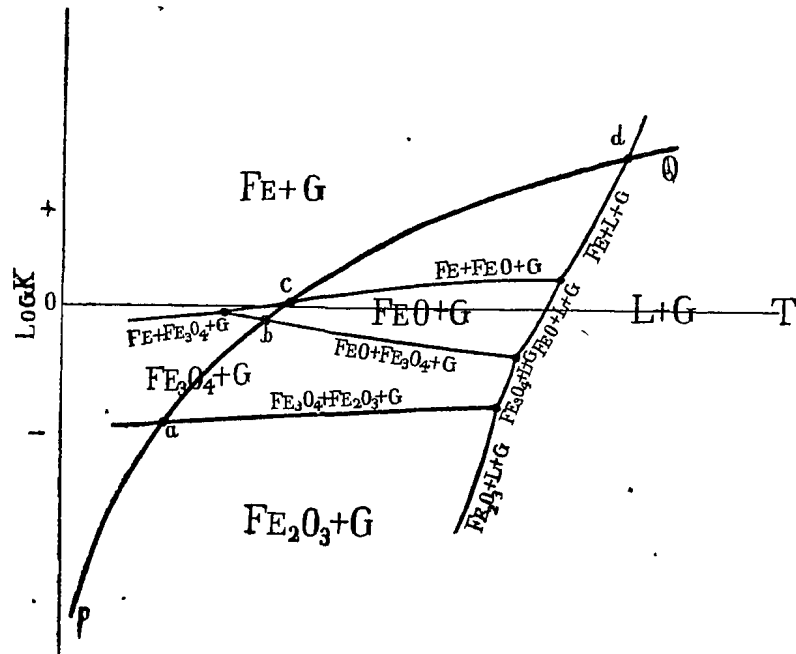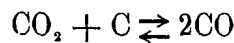For this purpose we choose one of our last two figures, e. g. the

Fig. 9.

more probable one, fig. 7, and draw in this the line pQ for the equilibrium

$$CO_2 + C \rightleftarrows 2CO$$

as this is situated in the blast-furnace.

Thus arises fig. 9, and the processes that take place in the blast-furnace are read from the graphical representation bearing in mind that then the course of this line of equilibrium should be followed through the different regions given here. We then start from point P and end in point Q.

In this way we see that theoretically the reduction from Fe$_2$O$_3$ to Fe$_3$O$_4$ takes place for the first time in the point a. then in b the reduction from Fe$_2$O$_3$ to FeO, in c that from FeO to Fe, and finally in d melting of the iron. Hence we shall remain in each of these
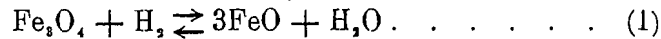
[1]) The Figure can easely be completed considering the formation ot cementit hut this is omitted here intensionally. REINDERS (Proceedings **19**, 175 (1916) has already indicated partly the equilibriums with cementit.

points of intersection which represent four-phase equilibria on addition of heat, until one of the phases has been completely converted.
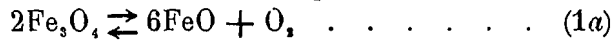
It is known that especially the equilibria with carbon are comparatively slowly established below 800°, which is the reason that in experiments with flowing gas, the just mentioned stage-wise reactions are found at temperatures above those corresponding with the points a, b, and c.

Derivation of the P,T-Figure of the System $O-Fe$ from the Equilibria of the Iron-Oxides with Reducing resp. Oxidising Gases.
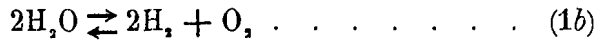
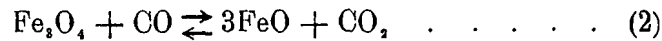When it is borne in mind that an equilibrium as the following

$$Fe_3O_4 + H_2 \rightleftarrows 3FeO + H_2O \qquad (1)$$

may be conceived as consisting of the two equilibria:

$$2Fe_3O_4 \rightleftarrows 6FeO + O_2 \qquad (1a)$$

and

$$2H_2O \rightleftarrows 2H_2 + O_2 \qquad (1b)$$

and likewise

$$Fe_3O_4 + CO \rightleftarrows 3FeO + CO_2 \qquad (2)$$

as consisting of the equilibria:

$$2Fe_3O_4 \rightleftarrows 6FeO + O_2 \qquad (2a)$$

and

$$2CO_2 \rightleftarrows 2CO + O_2 \qquad (2b)$$
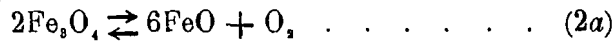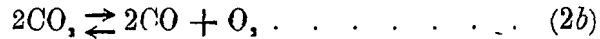
it is clear that from the equilibria (1) and (1b) resp. (2) and (2b) the situation of (1a) can be derived, and the same thing may be said in reference to the other equilibria that are considered here.

It also follows from this that where the three-phase line for $FeO + Fe_3O_4 + (CO + CO_2)$ was studied, also $FeO + Fe_3O_4 + O_2$ were in equilibrium with each other. Hence the shape of part of the P,T-projection of the system $O + Fe$ can be derived from the situation of the determined lines of equilibrium.

Thus it is immediately seen that, the three-phase lines for $Fe + FeO + (CO + CO_2)$ and for $FeO + Fe_3O_4 + (CO + CO_2)$ intersecting this must also be the case with the three-phase lines of $Fe + FeO + G$ and of $FeO + Fe_3O_4 + G$ in the system $O-Fe$.

When we express this in a diagram, and when we also assume the existence of the three-phase line $Fe_2O_3 + Fe_3O_4 + G$, we arrive at the following P,T-projection (Fig. 10) on the assumption, as was also supposed in fig. 7, that the three-phase lines $FeO + Fe_4O_4 + G$ and $Fe_3O_4—Fe_2O_3 + G$ do not intersect in stable points. '

Accordingly this projection presents the peculiarity, which up to now has never yet been observed in a case like this, that

namely two three-phase lines for two solid phases and vapour, intersect, without inverse melting taking place in the system. In case of inverse melting such an intersection must take place, as was before demonstrated by one of us [1]); the case of such an
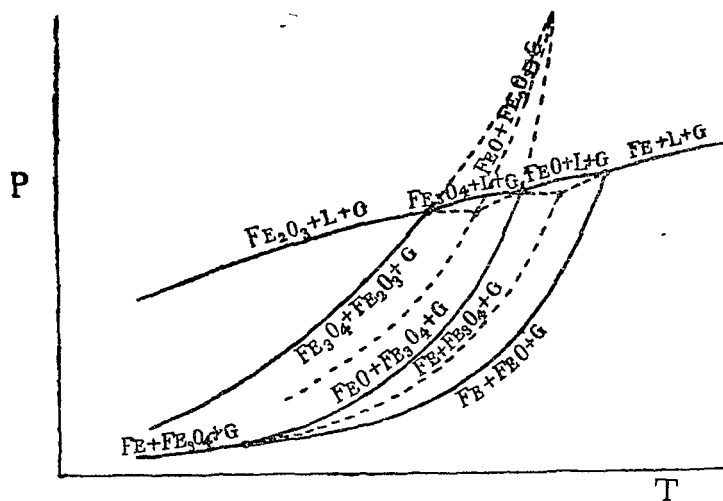

Fig. 10.

intersection without inverse melting, had however not yet been considered, so that the system O—Fe teaches us something new here.

When we now consider the possibility of a stable intersection of the two three-phase lines for $FeO + Fe_3O_4 + G$ and $Fe_3O_4 + Fe_2O_3 + G$,
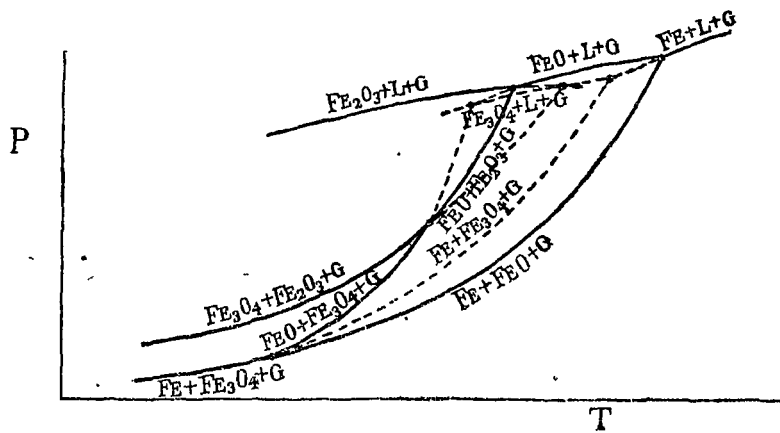

Fig. 11.

according to the supposition in fig. 8, we get a shape for the P, T-projection of the system O — Fe as indicated in fig. 11. In this case the three-phase line for $Fe_3 O_4 + L + G$ would, therefore, be metastable.
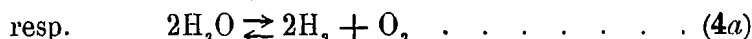
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[1]) A. SMITS. Zeitschr. f. Elektr. Chem. 18, 1081 (1912).

Calculation of the Oxygen-Pressure of the Dissociation-Equilibria.

When we know the constant of equilibrium of an equilibrium like

$$M + CO_2 \rightleftarrows MO + CO \quad \ldots \ldots \ldots (3)$$

$$\text{resp.} \quad M + H_2O \rightleftarrows MO + H_2 \quad \ldots \ldots \ldots (3a)$$
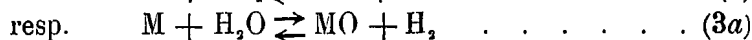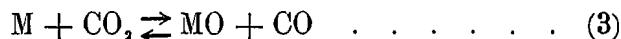
and likewise the constant of equilibrium of the equilibrium:

$$2CO_2 \rightleftarrows 2CO + O_2 \quad \ldots \ldots \ldots (4)$$

$$\text{resp.} \quad 2H_2O \rightleftarrows 2H_2 + O_2 \quad \ldots \ldots \ldots (4a)$$

at the same temperature, the oxygen pressure follows immediately from these data.

From (3) follows namely ·

$$K = \frac{P_{CO}}{P_{CO_2}}$$

and from (4)

$$K_{P_{CO_2}} = \frac{P^2_{CO} P_{O_2}}{P^2_{CO_2}}$$
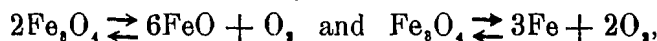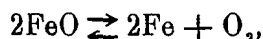
so that

$$K_{P_{CO_2}} = K^2 P_{O_2}$$

or

$$P_{O_2} = \frac{K_{P_{CO_2}}}{K^2}$$

hence

$$\log P_{O_2} = \log K_{P_{CO_2}} - 2 \log K \quad \ldots \ldots \ldots (5)$$

In this way the oxygen pressures for the equilibria of dissociation:

$$2FeO \rightleftarrows 2Fe + O_2,$$

$$2Fe_3O_4 \rightleftarrows 6FeO + O_2 \quad \text{and} \quad Fe_3O_4 \rightleftarrows 3Fe + 2O_2,$$

have been calculated by us between $400°$ C. and $1000°$ C.

We had to use for this an equation of $\log K_P$ for the CO_2 dissociation equilibrium. Wishing to apply this equation for temperatures between $\pm 500°$ and $\pm 1000°$, we have substituted the heat-effect corresponding to the temperature of about $800°$, viz. $- 133000$ cal. for E in the equation:

$$\frac{d\ln K_c}{dT} = -\frac{E}{RT^2}$$

and put $\Sigma_i c_v = 0$, so on integration we got:

$$\log K_c = -\frac{133000}{4{,}571\,T} + C \quad \ldots \ldots \ldots (6)$$

or:

$$\log K_p = -\frac{133000}{4{,}571\,T} + \log T + C' \quad \ldots \ldots (7)$$

Then C' is chosen so that agreement is obtained with the experimental data[1]. Thus was found e. g. when p is indicated in atmospheres:

$$\log K_{p_{(T=1300°)}} = -13,45.$$

When we substitute this value in our equation for $\log K_p$, we find:

$$C' = 5,8$$

and then equation (7) becomes:

$$\log K_p = -\frac{133000}{4,571\,T} + \log T + 5,8 \quad . \quad . \quad . \quad (8)$$

or

$$\log K_p = -\frac{29100}{T} + \log T + 5,8 \quad . \quad . \quad . \quad (9)$$

When we now calculate $\log K_p$, by means of this equation for temperatures between 400° C. and 1000° C., we find what follows:

TABLE I.

t	$\log K_{p_{CO_2}}$ (p in Atmospheres)
400	— 34.6
450	— 31.5
500	— 28.9
550	— 26.7
600	— 24.6
650	— 22.8
700	— 21.1
750	— 19.6
800	— 18.3
850	— 17.1
900	— 15.9

When at the same temperatures and pressure we now also know the values of $\log K$ for the equilibrium in the gas phase of the different three-phase equilibria in the system $Fe — CO — CO_2$, then follow from equation (5) the values for the oxygen tensions at the different temperatures.

The values of $\log K$ for the equilibria $Fe + CO_2 \rightleftarrows FeO + CO$, $3 FeO + CO_2 \rightleftarrows Fe_3O_4 + CO$ and $3Fe + 4 CO_2 \rightleftarrows Fe_3O_4 + 4CO$, have

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[1] ABEGG, Handbuch III, 2. 183.

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TABLE II.

|	$\log K_{p_{CO_2}}$	Fe + CO$_2$ $\rightleftarrows$ FeO + CO		3 FeO + CO$_2$ $\rightleftarrows$ Fe$_3$O$_4$ + CO		3 Fe + 4 CO$_2$ $\rightleftarrows$ Fe$_3$O$_4$ + 4 CO	
		$\log K_3$	$\log K_{p_{CO_2}} - 2\log K_3 = \log P_{O_2}$	$\log K_2$	$\log K_{p_{CO_2}} - 2\log K_2 = \log P_{O_2}$	$\log K'_3$	$\log K_{p_{CO_2}} - 2\log K'_3 = \log P_{O_2}$
400	— 34.6					— 0.16	— 34.3
450	— 31.5					— 0.10	— 31.3
500	— 28.9					— 0.05	— 28.8
550	— 26.7	— 0.01	— 26.7	— 0.11	— 26.5		
600	— 24.6	+ 0.06	— 24.7	— 0.17	— 24.3		
650	— 22.8	+ 0.12	— 23.0	— 0.23	— 22.3		
700	— 21.1	+ 0.18	— 21.5	— 0.29	— 20.5		
750	— 19.6	+ 0.22	— 20.0	— 0.34	— 18.9		
800	— 18.3	+ 0.27	— 18.8	— 0.39	— 17.5		
850	— 17.1	+ 0.31	— 17.7	— 0.44	— 16.2		
900	— 15.9	+ 0.34	— 16.6	— 0.49	— 14.9		
			$\log P_{Fe + FeO + O_2}$ (in atmospheres)		$\log P_{FeO + Fe_3O_4 + O_2}$ (in atmospheres)		$\log P_{Fe + Fe_3O_4 + O_2}$ (in atmospheres)

been borrowed from REINDERS 's paper on· "The Equilibria of Iron and Iron Oxides with Watervapour and Hydrogen" [1]).

The results of these calculations of the oxygen tensions have been expressed in the following table 2. (See table 2 pag. 398).

In this table we find, therefore, the oxygen-dissociation tensions of the equilibria:

$$2FeO \rightleftarrows 2Fe + O_2$$

$$2Fe_3O_4 \rightleftarrows 6FeO + O_2$$

and

$$Fe_3O_4 \rightleftarrows 3Fe + 2O_2$$
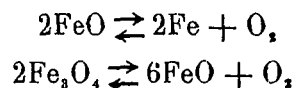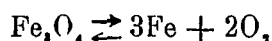
and we see from this that these expressions are very small, as was to be expected.

No importance is, of course, to be attached to the absolute values of these pressures, from which we should have to conclude to the presence of one gas-molecule in many litres, when we continue to consider the ordinary gas-laws as valid, because the formulae which we used in our calculation rest on the supposition that we have to do with a great number of molecules. Yet at the lower T the real oxygen pressures corresponding to these calculated numerical quantities will be so exceedingly small that the question suggests itself whether the oxidation of the reducing gas, which in this case proceeds with pretty great velocity, can still be considered as a homogeneous gas reaction. [2])

P,T-Projection of the System O—Fe.

By the aid of these data we are now able to indicate part of the P,T-projection of the system O — Fe, when we put the found oxygen-pressure equal to the total pressure.

When in this projection we also indicate the points p and q which would follow from SOSMAN and HOSTETTER's observations for the vapour pressure of the equilibrium $Fe_2O_3 + Fe_3O_4 + G$, corresponding to the temperatures 1100° and 1200°, starting from the supposition that the almost horizontal part of the isotherms of disso-

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[1]) l. c

[2]) Entirely analogous questions suggest themselves in the study of the mechanism of the reactions between e.g. solutions and salts, or between metals with very small solubility-product and electrolytes Especially in the latter case the numerical values, which denote the electron concentration, in solution, can be exceedingly small, as one of us showed already. *)

*) Zeitschr. für physik. Chemie **92**, 1 (1916).

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ciation found by them actually refers to this three-phase equilibrium, we get the P, T figure (12).
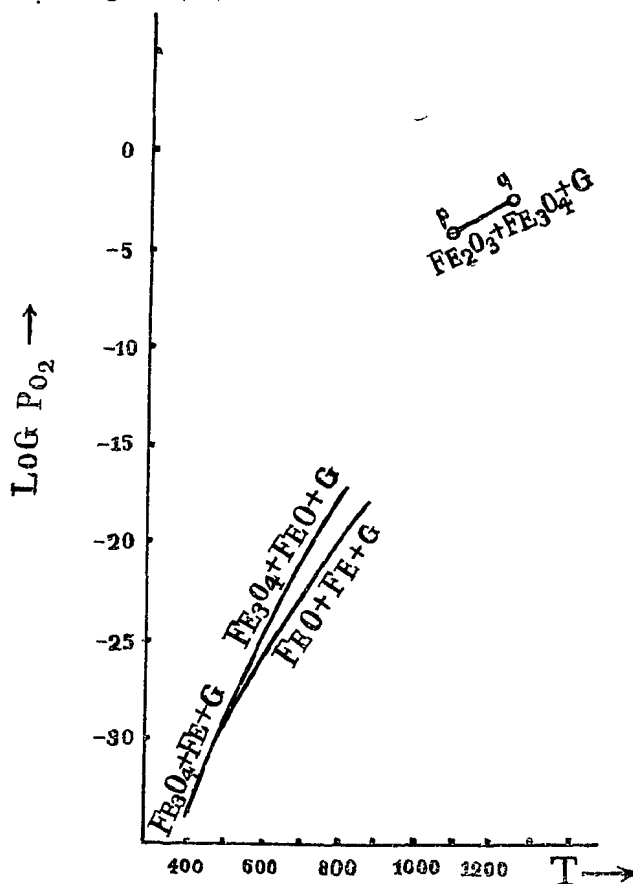

Fig. 12.

Of course these two last mentioned isotherms are perfectly inadequate to determine the direction of the three-phase line for $Fe_2O_3 + Fe_3O_4$ + G with any certainty; we will, therefore, only point out that the situation of this three-phase line, as it would follow from these two data, with respect to other three-phase lines, would be in good agreement with the expectation expressed schematically in fig. 10 or fig. 11.

General and Anorganic Chemical
Laboratory of the University.

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