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

Metals used	$\dfrac{\text{litre-dose}}{\text{mol. weight}}$	salt-dose[1]) in mgr. per litre	metal-dose in mgr. per litre	total radio-activity per gramm per secunde	$\dfrac{\text{metal-dose}}{\text{atom weight met.}}=a$	$a \times$ tot. rad. in mgr. p. sec.
Potassium (as Pot.-chloride)	1.34	100	53	0.3×10^{-1} erg.	1.5	0.000045
Rubidium (as Rubidiumchloride)	1.20	150	105	0.7×10^{-1} erg.	1.2	0.000084
Uranium (mostly as uranyl-nitrate)	0.063	25	15	0.8 erg.	0.06	0.000048
Thorium (as Thoriumnitrate)	0.10	50	24	0.3 erg.	0.1	0.000020
Radium (as Radiumsalts)	1×10^{-8}	5×10^{-6}	3×10^{-6}	1.38×10^{6} erg.	1×10^{-8}	0.000019

occurs in the animal circulating-fluids and in the tissue-fluids, and that, carried along by ions, may adhere to the cells.

Utrecht, 28 September 1916.

Chemistry. — *"On the Influence of Temperature on Chemical Equilibria"*. By Dr. F. E. C. Scheffer. (Communicated by Prof. J. D. van der Waals).

(Communicated in the meeting of Sept. 30, 1916).

1. *The expression for the influence of temperature on equilibria.* When in a rarefied gas mixture or a diluted solution a chemical reaction is possible, there exists a definite relation between the concentrations of the reacting substances in the state of equilibrium. The "constant of equilibrium", the value of the product of the concentrations of the substances of one member of the reaction equation, divided by that of the concentrations of the substances of the other member, in which every concentration is raised to the power of which the exponent gives the number of molecules taking part in the conversion, is constant at a definite temperature, but

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[1]) The salt doses in Ringer's mixture give some scope for variation, also when the Calcium-content is permanent; the values given are those actually used by us.

varies at changing temperature. The dependence on the temperature is expressed by VAN 'T HOFF's well known expression:

$$\frac{d \ln K}{dT} = -\frac{E}{RT^2} \cdots \cdots \cdots (1)$$

in which K represents the constant of equilibrium, T the absolute temperature, E the energy of conversion, and R the gas constant[1]). If one wants to apply this equation to definite cases, it must be integrated; for this purpose we should know E as function of the temperature.

If one takes a constant for E, in other words if the change of energy in the reaction is independent of the temperature, if therefore, the sum of the specific heats of the substances of the first member of the reaction equation is equal to that of the substances of the second member, we get by integration of equation 1 an expression of the form:

$$\ln K = +\frac{a}{T} + b, \cdots \cdots \cdots (2)$$

in which a and b represent constants.

If we assume that the algebraic sum of the specific heats of the reacting substances is not *zero*, as was supposed in (2), but has a value that does not vary with the temperature, the change of energy is linearly dependent on T; then equation 1 gives on integration:

$$\ln K = +\frac{a}{T} - b \ln T + c, \cdots \cdots \cdots (3)$$

in which a, b, and c indicate again constants.

If the specific heats vary linearly with T, we obtain a quadratic expression for E; integration of (1) then yields:

$$\ln K = +\frac{a}{T} - b \ln T - cT + d \cdots \cdots \cdots (4)$$

I have already pointed out before that equation (2) is sufficiently in agreement with the measurements of the equilibrium for many gas reactions[2]). As was said above, this expression holds perfectly accurately only when the algebraic sum of the specific heats of the reacting substances is *zero* at all temperatures. This is certainly not the case in general; the influence of the specific heats is, however, so small for almost all equilibria that the mistake made by neglecting it, is much smaller than the inevitable errors of observation. Hence

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[1]) If in K the concentrations of the second member are in the numerator, then E is the loss of energy at the reaction.

[2]) These Proc. XV, p. 1116.

it appears in the application of equation 2 that almost all the chemical equilibria may be just as well represented by this expression as by the more complicated expressions 3,4 etc., which are pretty well universally used in the literature. This fact justifies in my opinion the preference of equation 2 to the others on account of its simplicity.

In perfect harmony with this appears also the fact that the observations of chemical equilibria have never been executed accurately enough to make calculations of the specific heats of the reacting substances possible.

If now the specific heats were well known through direct measurement, it would be rational to take them into account when drawing up the equation of equilibrium. For this purpose we want, however, the specific heats of *all* reacting substances, as only the algebraic sum plays a part in the equation of equilibrium. Generally, however, the specific heats of only a few substances are sufficiently known, and that at temperatures which deviate from those at which the measurements of the equilibrium have been carried out. Besides, for dissociating substances a direct measurement of the specific heat is impossible exactly in consequence of this decomposition. Generally no sufficient data are therefore available for the specific heats to justify the drawing up of an equation of equilibrium which contains more terms than equation 2.

That the influence of the specific heats is so small that equation 2 can just as well be used as 3, 4 etc., may seem astonishing at first sight. I explained the reason of this already before[1]; in the following paragraph I shall elucidate this question in a somewhat different and perhaps more intelligible way.

But it is not only for the sake of its simplicity that I prefer equation 2 to all the others. In the literature many equilibria have been described which are indicated by expressions which are more complicated than equation 2. Now there are two cases possible. Either the observations can just as well be represented by the formula with two constant quantities, or they cannot. In the latter case we have to do with very great errors of observation. The great advantage of 2 is that it draws our attention to these errors. If equation 2 cannot be used, the observations must be repeated.

I will demonstrate in the following pages by a number of examples that equation 2 is just as suitable as the more complicated equations and at the same time I shall show of some other equilibria

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[1]) These Proc. XV, p. 1114 et seq.

which cannot be represented by equation 2 that this is owing to great inaccuracies in the determinations. I shall then also have an opportunity to call attention to a few important reactions, which in my opinion have been observed little accurately, and of which a renewed examination is very desirable.

2. To begin with I will make clear why equation 2 is applicable almost without exception to the material of experimental facts, and I will illustrate this by a gas equilibrium which is one of the most accurately investigated equilibria, viz. the carbonic acid dissociation: $2 CO_2 \rightleftarrows 2 CO + O_2$. If we call E_{T_1} the change of energy on conversion of two gram-molecules of carbonic acid at the temperature T_1, it is represented at another temperature T by:

$$E_T = E_{T_1} + (c_1 - c_2)(T - T_1), \quad \ldots \quad (5)$$

in which c_1 represents the mean specific heat at constant volume of two gram-molecules of carbonic acid, and c_2 of two gram-molecules of carbonic oxide and one gram-mol. of oxygen between the temperatures T and T_1. If the true specific heats are no functions of the temperature, and the mean specific heat is none either, then equation 1 yields after substitution of E_T according to 5 on integration

$$ln K = \int \left[-\frac{E_{T_1}}{RT^2} - \frac{c_1 - c_2}{RT} + \frac{c_1 - c_2}{RT^2} T_1 \right] dT =$$

$$= \frac{E_{T_1}}{RT} - \frac{c_1 - c_2}{R} ln T - \frac{c_1 - c_2}{RT} T_1 + C_1 .$$

This equation can be transformed into:

$$ln K = \frac{E_{T_1}}{RT} + \frac{c_1 - c_2}{R} ln \frac{T_1}{T} - \frac{c_1 - c_2}{R} \frac{T_1 - T}{T} + C . \quad \ldots \quad (6)$$

If we now write $ln \frac{T_1}{T} = ln \left(1 + \frac{T_1 - T}{T} \right)$ in a series, we get:

$$ln K = \frac{E_{T_1}}{RT} + \frac{c_1 - c_2}{R} \left[\frac{T_1 - T}{T} - \frac{1}{2} \left(\frac{T_1 - T}{T} \right)^2 + \ldots \right] - \frac{c_1 - c_2}{R} \frac{T_1 - T}{T} + C . \quad (7)$$

The first term of the series disappears, so that equation 7 can be written:

$$ln K = \frac{E_{T_1}}{RT} - \frac{c_1 - c_2}{2R} \left(\frac{T_1 - T}{T} \right)^2 + \ldots + C . \quad \ldots \quad (8)$$

The term of the series which has the greatest influence, has disappeared; equation 2 is obtained from (8) by neglect of the higher terms. And these are generally small. The observations of the carbonic acid equilibrium have been carried out between 1300

and $1565°$ K. If now for T_1, $1400°$ is chosen, we shall make an error of:

$$\frac{0.003\,(c_1 - c_2)}{R} \quad resp. \quad \frac{0.006\,(c_1 - c_2)}{R}$$

on omission of the correction term of 8 at the highest and the lowest temperature.

If we now consider that c_1 is about $6\,R$, $c_2\ 7^1/_2\,R$, and $c_1 - c_2$ amounts therefore to $-\frac{3}{2}R$, the errors in $ln\,K$ become 0.005 resp. 0.009, in K $0.5°/_0$ resp. $0.9°/_0$. At the intermediate temperatures the errors are smaller. As now errors of several percentages are not rare, the deviation keeps far within the errors of observation when the correction term in question is neglected.

On an earlier occasion I calculated the expressions of the carbonic acid equilibrium by the aid of the best known data for the specific heats for another purpose [1]). The equations used had the following form:

$$log\,K_p = -\frac{29530}{T} + 2.92\,log\,T - 0.001419\,T + 1.61\ 10^{-7}T^2 + 1.75 \quad . \quad (9a)$$

$$= -\frac{29600}{T} + 2.93\,log\,T - 0.001286\,T + 1\ 61\ 10^{-7}T^2 + 1.57 \quad . \quad (9b)$$

$$= -\frac{29570}{T} + 2.59\,log\,T - 0.001362\,T + 1.74\ 10^{-7}T^2 + 2.71 \quad . \quad (9c)$$

$$= -\frac{29600}{T} + 1.75\,log\,T - 0.00066\,T + 4.73 \quad . \quad . \quad . \quad . \quad . \quad (9d)$$

$$= -\frac{29500}{T} + 2.5\,log\,T - 3\,log\left(1 - e^{-\frac{4050}{T}}\right) +$$

$$+ 2\,log\left(1 - e^{-\frac{992}{T}}\right) + 4\,log\left(1 - e^{-\frac{2350}{T}}\right) + 2.25 \quad . \quad (9e)$$

$$= -\frac{29490}{T} + 2.5\,log\,T - \frac{3}{2}\,log\left(1 - e^{-\frac{5630}{T}}\right)\left(1 - e^{-\frac{5630}{2T}}\right) +$$

$$+ log\left(1 - e^{-\frac{1800}{T}}\right)\left(1 - e^{-\frac{1800}{2T}}\right) + 2\,log\left(1 - e^{-\frac{2920}{T}}\right)\left(1 - e^{-\frac{2920}{2T}}\right) + 2.22 \quad (9f)$$

The simple equation 2 yields, when the constant is taken in partial pressures:

$$log\,K_p = -\frac{28800}{T} + log\,T + 5.59 \quad . \quad . \quad . \quad . \quad (9g)$$

In the table on the next page I have combined the observed equilibrium values and the deviations yielded by the expressions $9a - g$.

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[1]) These Proc. XIV, p. 747 et seq.

TABLE I.

T	$\log K_p$	9a	9b	9c	9d	9e	9f	9g
1300	—13.45	0	—0.03	0	0	—0.01	—0.01	0
1395	—11.84	—0.07	—0.08	· 0.07	—0.07	—0.07	—0.07	—0.08
1400	—11.77	—0.05	—0.06	—0.06	—0.05	—0.05	—0.05	—0.06
1443	—11.11	--0.08	—0.09	—0.10	- 0.09	—0.09	--0.09	—0.10
1478	—10.79	+0.07	+0.07	+0.07	+0.06	+0.07	+0.07	+0.06
1498	—10.28	—0.18	—0.18	—0.18	—0.18	—0.17	—0.17	—0.18
1500	—10.50	+0.06	+0.08	+0.08	+0.07	+0.07	+0.07	+0 07
1565	— 9.88	+0.26	+0.28	+0.27	+0.26	+0.28	+0.28	+0 26

It will be clear from this table that the six expressions $9a$—f, which in the most accurate way take the specific heats into account, and the formula $9g$, in which the specific heats do not occur, represent the observations equally well. The sum of the deviations in absolute value is successively:

0.77, 0.87, 0.83, 0.78, 0.81, 0.81, and 0.81.

This example shows clearly that the said deviations must be attributed to errors of observation, and that a change in the specific heats has not much influence on the equilibrium expression.

3. The hydrogeniodidedissociation.

On a former occasion I discussed this equilibrium at length, taking the specific heats of the substances taking part in the reaction, into account [1]. My purpose was then to test an expression derived by Prof. VAN DER WAALS JR. for the gas dissociations. I have now also examined whether the simplest expression (equation 2) can be applied to this equilibrium. If we graphically represent $\log K$ as function of T^{-1}, and if we draw a straight line through the points as well as is possible, we find:

$$\log K = -\frac{600}{T} - 0.856 \quad \ldots \quad \ldots \quad (10a)$$

In table II the values yielded by this expression, are compared with those that follow from the formula derived before:

$$\log K = -\frac{529}{T} - \log\left(1 - e^{-\frac{972}{T}}\right) - 1.079 \quad \ldots \quad (10b)$$

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and the formula proposed by NERNST:

$$log K = -\frac{540.4}{T} + 0.503 \cdot log T - 2.35. \quad \quad (10c)$$

TABLE II.

T	$log K$	$10a$	$10b$	$10c$	$\wedge 10a$	$\triangle 10b$	$\triangle 10c$
304.6	—2.925	—2.826	—2.798	—2.875	—0.099	—0.127	—0.050
328.2	—2.692	—2.684	—2.668	—2.731	—0.008	—0.024	+0.039
354.6	—2.416	—2.548	—2.542	—2.591	+0.132	+0.126	+0.175
553	—1.931	—1.941	—1.954	—1.947	+0.010	+0.023	+0.016
573	—1.905	—1.903	—1.914	—1.906	—0.002	+0.009	+0.001
593	—1.878	—1.868	—1.877	—1.866	—0.010	—0.001	—0.012
613	—1.851	—1.835	—1.842	—1.830	—0.016	—0.009	- 0.021
633	—1.823	—1.804	—1.810	—1.795	—0.019	—0.013	—0.028
653	—1.794	—1.775	—1.778	—1.762	—0.019	—0.016	—0.032
673	—1.765	—1.748	—1.748	—1.731	—0.017	—0.017	—0.034
693	—1.735	—1.722	—1.719	—1.701	—0.013	—0.016	--0.034
713	—1.705	—1.698	—1.693	—1.673	—0.007	—0.012	—0.032
733	—1.675	—1.675	—1.667	—1.646	0	-- 0.008	—0.029
753	—1.644	—1.653	- 1.642	—1.621	+0.009	—0.002	—0.023
773	—1.612	—1.632	—1.618	—1.596	+0.020	+0.006	—0.016
793	—1.580	—1.613	—1.595	—1.573	+0.033	+0.015	—0.007

The sum of the errors amounts successively to 0.414, 0,424, and 0.549. This table will in my opinion make it incontestable that pretty great experimental errors must occur in the observations and that these errors are large in comparison with those resulting from the neglecting of the specific heats. The first three observations have been made by STEGMÜLLER, the others by BODENSTEIN. Originally these latter observations were comprised by BODENSTEIN in the expression:

$$ln K = -\frac{90.48}{T} - 1.5959 \, ln T + 0.0055454 \, T + 2.6981 . \quad (10d)$$

This expression is in very good agreement with his own observations. When however, we represent the values following from this expression, in the graphical representation $log K = f(T^{-1})$, the line

exhibits an appreciable curvature. This is, indeed, also clear from table II, as Bodenstein's observations present a regularly changing deviation from expression 10a. This curvature is, however, not essential, and must be attributed to errors of observation, which appears clearly from this that expression 10d is entirely incompatible with the observations of Stegmüller. Thus —2,19, —2,17, and —2,15 follows from 10d for the first three observations, whereas Stegmüller found —2,925, —2,692, and —2,416. Here too we see therefore that the straight line 10a and the slightly curved lines 10b and 10c, represent the observations better than the more decidedly curved line 10d.

4. Of the gas reactions there is no example known to me for which the two-constant formula 2 expresses the observations less accurately than the more complicated formula; the influence of the specific heats is always small, and its influence is always exceeded by the errors of observation. This will no doubt be in connection with the fact that the algebraic sum of the specific heats can naturally be only small. In the two members of the reaction equation the same atoms, namely, always occur and only the different way of binding can bring about a difference in specific heat. If we imagine an equilibrium $A_2 \rightleftarrows 2A$, the specific heat of the di-atomic molecule, when there is not yet an appreciable vibration in the molecule, will amount to $5 \times \frac{1}{2} R$, corresponding with the three degrees of freedom of the translation and two of the rotation (solid of revolution). The two free atoms have a specific heat of $6 \times \frac{1}{2} R$. The algebraic sum, therefore. amounts to $\frac{1}{2} R$. If we are at temperatures at which the vibration in the molecule becomes appreciable, then a value between zero and $2 \times \frac{1}{2} R$ must be added for the vibration (for the potential and the kinetic energy). The algebraic sum will therefore vary between $+ \frac{1}{2} R$ and $-\frac{1}{2} R$. This small amount has hardly any influence on the chemical heat, and the same thing applies to the other gas equilibria in an analogous way.

A greater influence of the specific heats may be expected for the gas reactions, in which also solid substances take part. For then not only the different way of binding of the atoms, but also the difference in state of aggregation plays a part. In connection with the above I will, therefore, still discuss a few reactions with solid substances. In the literature there are described a number of equilibria, which would show a maximum or a minimum value for K at a definite temperature It is clear that if this is true, the two-constant formula 2 cannot be applicable; this, namely, excludes the appearance of

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maxima ˉand minima. I ·have examined these examples, and have
arrived at the conclusion that a maximum or minimum occurs in
none of these reactions, and the found particularities are exclusively
the result of errors in the observations.

· **5.** *The equilibria between the iron-oxides.*

These equilibria play an important part in the blast-furnace
processes. If carbon oxide is led over Fe_3O_4, it is reduced to FeO,
then to metallic iron. At a definite temperature an equilibrium can
occur between Fe_3O_4 and CO on one side, and FeO and CO_2 on
the other side. Likewise a second equilibrium is possible between
$FeO + CO$ and $Fe + CO_2$. These equilibria have been examined by
BAUR and GLÄSSNER, and they came to the conclusion that the

constant of equilibrium $K = \dfrac{cCO}{cCO_2}$ possesses a maximum for the first
equilibrium at a definite temperature, a minimum for the second
at another temperature[1]. The found values have been reproduced
in the graphical representation $log\, K = f(T^{-1})$. (See fig. 1).

The curves which according to BAUR and GLÄSSNER represent the
observations best, have not been indicated in the figure for the sake
of clearness. Between the points found for the first equilibrium,
indicated in figure 1 by triangles, a line was drawn by BAUR and
GLÄSSNER with a strongly pronounced maximum; likewise a curve
with a decided minimum through the crosses referring to the second
equilibrium. The two lines traced in this way do not intersect; the
irregular situation of the points allows of a pretty great freedom
in the tracing of these lines. The two curves mentioned divide the
field into three regions; above the line through the crosses metallic
iron is stable, between the two curves FeO is stable and below the
line through the triangles Fe_3O_4.

The curve through the crosses $(Fe + CO_2 \rightleftarrows FeO + CO)$ presents
a minimum at 680° $(10^3\, T^{-1} = 10.493)$; at this temperature the heat
of conversion is therefore zero as appears from equation 1. BAUR
and GLÄSSNER find resp. $+ 8724$ and $- 3114$ cal. at 835° and 585°
for the heat of transformation through calculation from their line.
Hence the heat of transformation changes over a range of temperature
of 250° by 11838 cal. This corresponds to an algebraic sum of
the specific heats of 47.3 cal. Such a large sum is, however,
impossible. We can make the following estimation of this sum.
If KOPP's law is valid, Fe and FeO will differ about 4 calories;

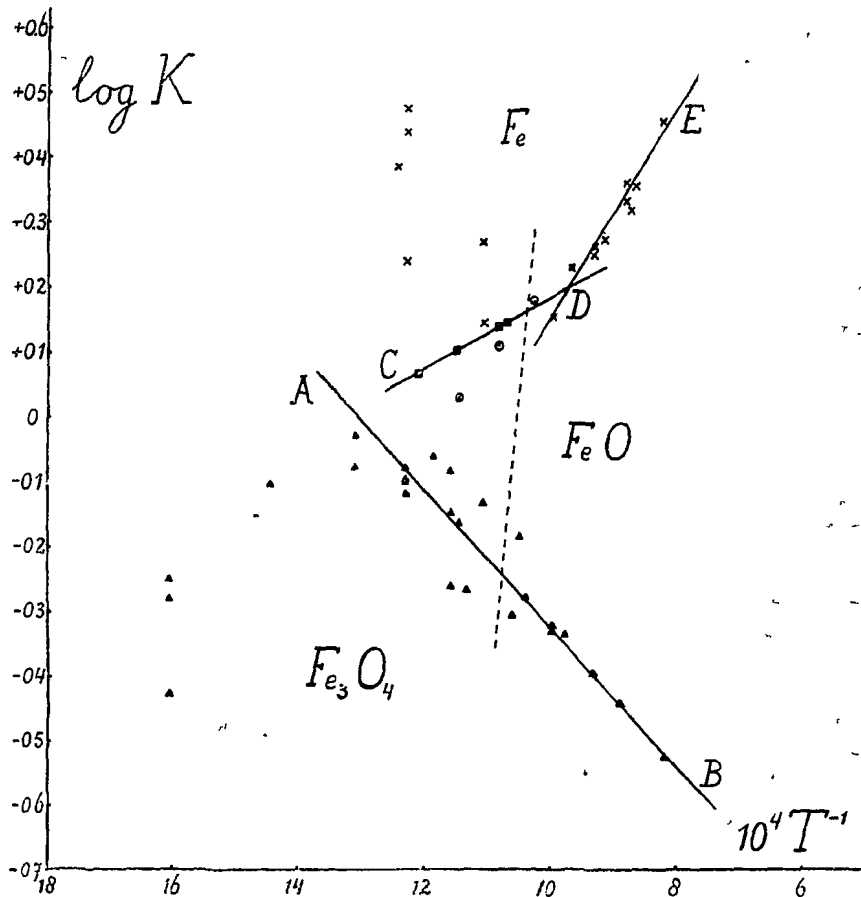[1] Zeitschr. für physik. Chem. **43**, 354, (1903).

Fig. 1.

the difference between CO_2 and CO amounts to about 2 calories, and the algebraic sum of the specific heats amounts, therefore, only to some calories. A value of 47 must certainly be considered as impossible. We find something similar for the other equilibrium. At 490° the heat of transformation is zero ($10^4 T^{-1} = 13.106$). From the observations at 765° and 400° we calculate for the heat of transformation resp. — 5176 and + 6563 cal. The heat of transformation, therefore, changes over 365° by 11739 calories, which corresponds to a sum of specific heat of 32.2 calories. Theoretically we again expect a value of some calories. Hence there is no agreement here either.

If we now examine which determinations are the most reliable it is easy to see that it is certainly the observations at the highest temperatures. At lower temperatures the said equilibria are metastable with regard to carbon. The equilibrium $2\,CO \rightleftarrows CO_2 + C$

yields a value for $\dfrac{cCO}{cCO_2}$, which is not constant at a definite tempe-

rature, but still depends on the total pressure; consequently in the graphical representation of fig. 1 not one line, but a series of lines, which each hold for a definite total pressure, are obtained for this equilibrium. If we now determine the situation of the line of equilibrium for one atmosphere total pressure in the graphical representation, it appears that it ascends very rapidly, and intersects the two lines of BAUR and GLÄSSNER. It is indicated dotted in figure 1. The equilibria on the left of the minimum and on the left of the maximum of BAUR and GLÄSSNER are metastable with respect to carbon; in this region carbon can be deposited; this can account for the branch of the Fe_3O_4—FeO equilibrium that ascends towards the right, the more so as the setting in of the generatoɪ gas equilibrium is accelerated by iron oxides. Of the branch of the Fe—FeO-equilibrium descending towards the right no sufficient explanation is to be given in my opinion. The equilibrium $FeO + CO \rightleftarrows Fe + CO_2$ has been later examined by SCHENCK; the minimum was not found back by him, his observations are indicated in fig. 1 by squares [1]. Through his points the line CD has been drawn. Also FALCKE's determinations [2] yield a line without minimum (in fig. 1 three points are indicated by circles), which, however, ascends more abruptly than CD and is in better agreement with the determinations at higher temperatures (line DE through BAUR and GLÄSSNER's points).

No other data of the equilibrium $Fe_3O_4 + CO \rightleftarrows 3 FeO + CO_2$ are known to me than those mentioned by BAUR and GLÄSSNER. The line AB has been drawn as well as possible through the observations at the highest temperatures.

The remarkable conclusion to which these considerations lead, is *that the lines for the two equilibria intersect*. And this must be the case both when for the equilibrium $FeO + CO \rightleftarrows Fe + CO_2$ we consider the observations of SCHENCK (CD) as accurate, and when we consider those of FALCKE (circles in fig. 1) and those of BAUR and GLÄSSNER at the highest temperatures (DE) as valid.

If this intersection occurs, it follows from this that *below the temperature of the point of intersection FeO must be a metastable compound*. This is easy to see, as in this point of intersection Fe, FeO, and Fe_3O_4 occur in equilibrium by the side of the gasphase, and there also exists, therefore, equilibrium between the three solid phases without gas. Hence at lower temperatures FeO will continue to be either metastable, or break up into $Fe + Fe_3O_4$.

Below the temperature of the point of intersection the equilibrium

[1] SCHENCK, Ber. **40**, 1704 (1907).

[2] FALCKE, Zeitschr. f. Elektroch. **22**, 121, (1916).

$Fe_3O_4 + 4CO \rightleftarrows 3Fe + 4CO_2$ will then be stable. It would. be desirable, in my opinion to test this conclusion experimentally.

If, therefore, the situation of the equilibria of the iron oxides with carbonic acid and carbon oxide is still insufficiently known, these equilibria are even quite in conflict with the determinations of DEVILLE and PREUNFR [1]) concerning the reaction $3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2$, which was studied between 200° and 1600°. It is clear that when the above interpretation is correct, this equilibrium must be metastable with respect to FeO at the higher temperatures; FeO may have been present in these determinations, and the observations may have been wrongly interpreted.

In conclusion it may still be said that v. JUPTNER's calculations lead to the entirely divergent conclusion that FeO should be always metastable in the range from 600° abs. to 2400° abs. In these calculations use has, however, been made of uncertain data and uncertain hypotheses. [2])

In his paper (These Proc. XIX, p. 175) Prof. REINDERS pointed out that the separation of iron carbide will give rise to new equilibria; this formation, can however in my opinion not affect the above conclusion. This will be clear on a consideration of fig. 10 of Prof. REINDERS's paper.

6. The dissociation of ammonium bromide.

In his researches on the homogeneous dissociation of the ammonium-halides Prof. SMITH found a maximum at about 320° for the equilibrium constant of the ammonium bromide [3]) : above this temperature the dissociation constant diminishes at rising temperature. This decrease is very peculiar, as evidently no heat is required here for the splitting up of NH_4Br into NH_3 and HBr but heat is liberated. At the splitting up of a molecule into two it might be expected that energy was required to neutralise the chemical attraction.

At 320° the heat of transformation is zero as appears from equation 1. When the value of E is calculated from SMITH's line at the highest temperatures, 43000 cal. are found at the mean temperature of 384° C. Accordingly the heat of transformation varies over the range of 64° C. by 43000 cal., hence the algebraic sum of the specific heats is about 670 cal. A value is expected for this sum which will not be higher than about 10 calories and with the opposite sign, as it is the difference between the specific heat of a

1) PREUNER. Zeitschr f. physik. Chem. **47**. 416 (1904).

2) v. JÜPTNER. Theorie der Eisenhüttenprozesse (1907).

3) SMITH Journ. Amer. Chem Soc. **37**, 38. (1915).

hexatomic molecule and two tri-atomic ones. It can be directly derived from the number of degrees of freedom that a value of 67.0 cal. must be impossible. I think the conclusion must be drawn from this that in spite of the care devoted by Prof. SMITH to these measurements, the observations cannot be right or that they have been wrongly interpreted. The researches are very difficult, and an error in the observation passes into the value of the equilibrium constant greatly enlarged. The observations with ammonium chloride yield a normal behaviour in contrast with the just mentioned observations.

To prevent misunderstanding it may be pointed out that great specific heats can certainly occur, but that it must then be derived from that value that then a chemical reaction plays a part. Thus the specific heat of nitrogen-tetroxide is for instance very great; it can even amount to 100 cal. and more. This, however, is to be attributed to the decomposition of N_2O_4 into $2NO_2$. The specific heat of the equilibrium mixture, 'the composition of which varies with the temperature, is then e.g. 100 cal., but by far the greater part of this is caused by the shifting of the equilibrium with change of temperature and the great reaction energy attending it. If, however, we calculate the constant of equilibrium of the dissociation, we have no longer to do with the specific heat of the mixture, but with the algebraic sum of the specific heats, which is very small, also here. This also tallies with the fact that the dissociation constant of N_2O_4 in its dependence on the temperature can be represented by the two-constant formula 2, in which this sum is put zero.

If SMITH's experiments are correct, we should expect a second reaction, which has not been taken into account.

7. *The water gas equilibrium.*

The water gas equilibrium is also sometimes found mentioned as an example of a reaction with a maximum value of K. This conclusion, however, is not derived from direct observation, but rests on great extrapolation of data which are partly still little accurate. The observations have been carried out between 700° C. and 1400° C.; calculated is a reversal of sign of $\dfrac{d\log K}{dT}$ at about 2800° C.[1]). No straight line can be drawn through the observations in the graphical representation $\log K = f(T^{-1})$; only the points which are given as little accurate, however, deviate appreciably from the straight line through the other points. Besides, at the temperature where this equilibrium would present this peculiarity,

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[1]) HABER. Thermodyn. techn. Gasreakt.

the reacting substances themselves would be subjected to, new decompositions, and the realization of the phenomenon would be excluded.

8. *Conclusions.*

At the present state of our knowledge of the gas equilibria every gas reaction may be represented by the two-constant formula

$log\ K = \dfrac{a}{T} + b.$ There are no reasons to add more terms with T

to this expression in the second member, as the experimental errors are always greater than the change that can be effected by these T-terms in the formula. If the addition of these terms is necessary, and if they, therefore, bring about an appreciable modification in the curve, we have to do either with a wrong interpretation or with errors of observation.

In contradiction with what is recorded in the literature, the transition case of $\dfrac{d\ l\hat{o}g\ K}{dT} = 0$ has not been found with any certainty for a single reaction, and it will not be easy to realize either in my opinion. This case might be found for a reaction that has a very small heat of conversion over a very great range of temperature; an example of this is, however, not known.

Physics. — *"Comparison of the Utrecht Pressure Balance of the* van 't Hoff *Laboratory with those of the* van der Waals *Fund at Amsterdam."* By Mrs. E. I. Hoogenboom—Smid. Van der Waals fund researches N°. 9. (Communicated by Prof. P. Zeeman).

(Communicated in the meeting of Sept. 30 1916).

Introduction. In the former half of 1915 a comparison was made of the small Amsterdam pressure balance with the open standard manometer at Leiden from 20 to 100 atmospheres [1]). The result of this was that the effective area appeared to be not equal to the real area; a constant value was not even found, but a value dependent on the pressure.

To be able to make accurate determinations of the pressure in spite of this it is required to study the theory of the instrument.

[1]) See C. A. Crommelin and Miss E. I. Smid, Comparison of the pressure balance of S. and B. etc. These Proceedings XVIII, p. 472.