KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday January 31, 1903.

CONTENTS.

The following papers were read:

Chemistry. — *"The velocity of transformation of Carbon monoxide."* By Dr. A. Smits and L. K. Wolff. (Communicated by Prof. H. W. Bakhuis Roozeboom).

(Communicated in the meeting of December 27, 1902).

From the researches of Boudouard[1]) on the equilibrium $2CO \leftrightarrows CO_2 + C$, where use was made of the accelerating action of the metals Ni, Co, Fe, it follows that they do not modify the equilibrium but only

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[1]) Ann. de Chimie et de Physique [7] 24, p. 5 (1901).

exercise an influence on the velocity and are, therefore, catalyzers. It was shown by BOUDOUARD that, whilst CO_2 in contact with C is practically totally converted at 1000° into CO, the amount of CO_2 in the gaseous mixture in equilibrium increases at lower temperatures in accordance with the sign of the heateffect $CO_2 + C = 2CO - 42000$ cal. until at 445° the CO ·is practically completely converted into CO_2 and C.

From this follows that below 445°, CO exists in a *metastable* condition.

<div align="center">INVESTIGATION.</div>

a. *Preparation of the catalyzer and preliminary experiments.*

1. The following research was instituted with the object of determining velocities of reaction in the metastable region in presence of a catalyzer. The apparatus employed by us was in the main the same as that used by VAN 'T HOFF in his research on the velocity of transformation of detonating gas into water. The reaction vessel, however, was filled with a catalyzer obtained in the following manner.

Pumice stone was broken up into small lumps, drenched with a solution of $Ni(NO_3)_2$ then dried, ignited and finally reduced in a current of hydrogen or carbon monoxide.

This reduction, it was observed, takes place in two stages. The greyish-black surface of NiO first turns yellow owing to the formation of a suboxide ($Ni_2 O$?)[1] and afterwards on complete reduction again becomes dark-grey. When operating at a high temperature, reduction with H_2 or CO gives apparently, the same material. If, however, the reduction takes place in a current of CO at 445° a layer of carbon is deposited on the reduced nickel.

2. The experiments with nickel-pumice obtained by reduction with either H_2 or CO at a *high* temperature gave the following result[2].

At 310° (boiling point of diphenylamine) the activity of the catalyzer did not appear constant. Successive fillings continually gave smaller diminutions of pressure in the same length of time.

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[1] MÜLLER, Bell (Chemical News 20, 258).

[2] Coating the inner wall of the reaction vessel with nickel did not appear to affect the result, probably because the surface of the glass wall was very small as compared with the surface of the catalyzer.

We found for instance:

310°.

Filling.	Diminution in mM. Hg. during 10 minutes.
1st	5,68
2nd	5,00
3rd	3,80

ect.

As we suspected that the retrogression of the activity of the catalyzer was due to the ever increasing layer of C, which deposits on the catalyzer during the experiment and fillings, we next used a nickel-pumice which had been reduced at 445° and was in consequence already coated with a layer of carbon. Although at first there was still a perceptible diminution in the activity, the differences in successive fillings become gradually smaller and finally, the activity was constant as seen from the following table:

310°

Filling.	Diminution in mM. Hg. during 10 minutes.
1st	1,88
2nd	1,80
3rd	1,78
4th	1,74
5th	1,75
6th	1,74
7th	1,74

Being satisfied with this result, we started our investigation with the catalyzer of constant activity obtained in this way.

b. Measurements concerning the order of the reaction.

For the determination of the order of the reaction the method of VAN 'T HOFF was first of all applied. It is given in this case by the equation:

$$n = \frac{log\left(\dfrac{dc_1}{dt} : \dfrac{dc_2}{dt}\right)}{log \ (c_1 : c_2)}$$

The determination was made at 310°.

In the first experiment the pressure of the CO was 786,8 mm. Hg at the commencement; after 30 minutes the pressure amounted to 739,9 mm. Hg. The diminution of pressure in 30 minutes therefore amounted to 46,9 mm. Hg.

If we take for $\dfrac{dc}{dt}$ the diminution of pressure per minute then $\dfrac{dc_1}{dt}$ becomes 1,56.

In the second experiment the pressure of the CO was 535,3 mm. Hg at the commencement and after 30 minutes the pressure had come down to 501,7 mm. Hg. Here, the diminution of pressure in 30 minutes amounted, therefore, to 33,6 mm. Hg or $\dfrac{dc_2}{dt} = 1,12$.

C_1=aver. of press. at beginn. and end at the 1st experim.=763,35mm.Hg.
C_2= „ „ „ „ „ „ „ „ „ 2nd „ = 518,5 „ „

If from this we calculate n, we find
$$n = 0,86,$$
from which it is apparent that the reaction is a monomolecular one. In order to make more certain of this, the order of the reaction was also determined at two other temperatures according to the method given by NOYES. In this case n is calculated from the following formula:

$$n = 1 + \frac{log\dfrac{t_1}{t_2}}{log\dfrac{c_2}{c_1}}.$$

in which t_1 and t_2 are the times during which the same part of the original quantity is converted when starting from different concentrations c_1 and c_2.

At 256° we obtained the following result:

$$n = 1 + \frac{log\dfrac{192}{200}}{log\dfrac{525,1}{770,9}} = 1,1.$$

The experiment at 340° gave

$$n = 1 + \frac{log\dfrac{60}{58}}{log\dfrac{519,0}{792,8}} = 0,92.$$

The observations at the three temperatures 256°, 310° and 340°, therefore lead to the conclusion that we are really dealing here with a *monomolecular* reaction.

c. Determination of the reaction-constant at 256°, 310°, 340°.

These determinations were conducted with the same reaction vessel and the same catalyzer.

256° (boiling point of amyl benzoate).

Time in minutes.		Pressure in m.m. Hg	$k = \dfrac{1}{t} log \dfrac{P_0}{2P_t - P_0}$
1	2		
0		761 0	—
5	0	758 9	0 000464
10		757.6	0 000381
	10	756.4	0.000287
	20	754 1	0.000276
	30	751.7	0.000277
	40	749.3	0 000278

average 0.000279

The following may serve to elucidate this table:

At 256° the catalyzer seemed to still perceptibly absorb the CO, which caused the diminution of pressure during the first 5 minutes to be excessive. The values for k are, therefore, not constant when we start from the pressure corresponding with the time 0, but they gradually diminish which may be seen from the first two figures in the last column of the table. To eliminate the error caused by absorption, we have, when calculating k, started from the pressure corresponding with the time 5 minutes (column 2) and, therefore, have called this pressure P_0. As the CO concentration had diminished very little in 5 minutes the error thus introduced could be disregarded. The values obtained for k are found in the last column beneath the dotted line. The following table relates to the temperature 310°.

310° (boiling point of diphenylamine)

Time in minutes	Pressure in m.m. Hg	$k = \dfrac{1}{t} \, log \dfrac{P_0}{2P_t - P_0}$
0	786 8	
10	769.8	0.00192
20	754.8	0.00184
30	739 9	0 00184
40	725.6	0.00184

average 0.00186

· As was to be expected, the absorption at this high temperature was scarcely perceptible and in the following table, which shows the results obtained at 340°, no absorption whatever was noticed.

340° (boiling point of phenantrene)

Time in minutes	Pressure in m.m. Hg	$k = \dfrac{1}{t} \, log \dfrac{P_0}{2P_t - P_0}$
0	791.1	
10	746.1	0.00524
20	705.9	0.00527
30	668 7	0.00536
50	612.7	0.00521

average 0.00527

In order to make sure that the activity of the catalyzer had not diminished during these three series, a series of experiments was finally taken at 310° with the following result.

310°

| Time in minutes	Pressure in m.m. Hg	$k = \dfrac{1}{t} \log \dfrac{P_0}{2P_t - P_0}$
0	805.5	.
10	788.3	0.00189
20	773.0	0.00183
30	757.8	0.00182
40	742.8	0.00184

average 0.00184

The activity of the catalyzer had, therefore, undergone no change during these measurements, so that we were justified in calculating the temperature-coefficient from the results obtained. The result was as follows:

| Temperature.	$k.$	$\dfrac{k_{t+10}}{k_t}$
256°	0.000279	
310°	0.00186	$>1,4$
340°	0.00527	$>1,4$

d. Mechanism of the reaction.

What idea are we to form about the mechanism of the reaction if this takes a monomolecular course?

If we assume the formation of $Ni(CO)_4$ with an immeasurably large velocity and the subsequent breaking up of this compound according to the equation

$$Ni(CO)_4 = Ni + 2\,CO_2 + 2\,C$$
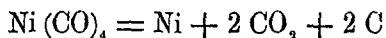
we must also accept the equilibrium

$$Ni(CO)_4 \leftrightarrows Ni + 4\,CO$$
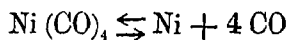
of which the constant is given by the equation:

$$K = \frac{C_{co}{}^4}{C_{Ni(co)_4}}$$

This would then necessarily lead to the conclusion, that the velocity

of reaction should be proportional to the 4th power of the CO-concentration whereas it appears to be proportional to the 1st power of the CO-concentration. Rejecting this hypothesis two further suppositions remain.

Firstly:

      I. $CO = C + O$ (with measurable velocity)

      II. $CO + O = CO_2$ (with unmeasurable velocity).

Secondly:

      I. $CO + Ni = C + Ni O$

      II. $CO + Ni O = CO_2 + Ni.$

In the last case it need not be assumed that one of these reactions takes place with unmeasurable velocity, but only that the second one proceeds more rapidly than the first.

As regards the nature of the catalyzer we think we may conclude from the result of several experiments, that it is not the carbon but the finely divided nickel which possesses the catalytic action.

Amsterdam, Chem. Lab. University. Dec. 1902.

Chemistry. — Professor Bakhuis Roozeboom presents a communication from Dr. J. J. van Laar on: "*The course of the melting-point-lines of solid alloys or amalgams.*" (First Communication).
(Communicated in the meeting of December 27, 1902).

1. In the researches of van Heteren [1] on Tinamalgams a meltingpoint-line occurs [2] of a kind, which has not as yet been studied over such an extended course (from 0 to nearly 100 atom % of mercury). This is chiefly due to the fact, that the temperatures of fusion of the two metals are so very different; tin 231°, mercury —38.6°. In consequence the meltingpoint-line of th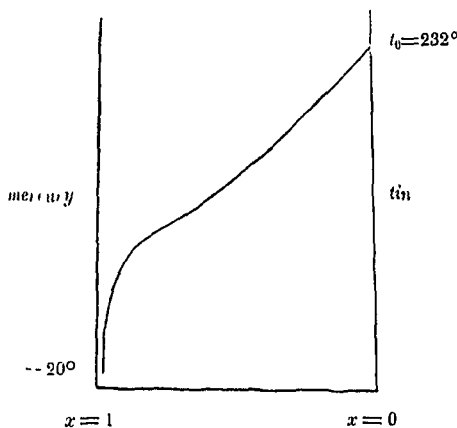e tin meets that of the mercury practically at 100 atom % mercury, so that the meltingpoint-line of the mercury has not even been observed. We therefore see for the first time a meltingpoint-line in its full course, and the question arises whether the course, found by van Heteren, may be predicted theoretically.

The answer to this is in the affirmative. Let us, to start with, take the most simple view as regards the molecular poten-

Fig. 1.

[1] Dissertation 1902. (also Report Meeting 29 Nov. 1902).
[2] l. c. pg. 18.