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definite boiling points of liquids which have reached their final equilibrium, which occurs after some hours at the ordinary temperature.

At the same time we get, in place of the vapour curve 2, the new vapour curve 6. As the velocity of reaction above  $40^\circ$  becomes very great, the lines 1 and 2 cannot be accurately determined above this temperature. For 1 this causes no inconvenience as its further course must be almost vertical, but the upper part of 2 becomes rather uncertain.

The final boiling-point curves 5 and 6 are situated much closer together than the first named one and have moreover an exceedingly irregular shape. It cannot as yet be decided whether this is solely attributable to the formation of  $\text{SCl}_4$  molecules in the mixtures, or whether other compound molecules are formed.

The formation of compound molecules may be noticed not only from the change of colour, but also from a diminution of the volume and will if possible, be studied quantitatively.

The important question in what manner the melting-point curve of solid  $\text{SCl}_4$  is modified by the presence of more or less compound molecules in the liquid phase is still the subject of investigation.

**Chemistry.** — “*The velocity of transformation of carbon monoxide II*”.

By DR. A. SMITS and L. K. WOLFF. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Communicated in the meeting of May 30, 1903).

In our previous paper on the above subject<sup>1)</sup> we communicated results obtained at the temperatures  $256^\circ$ ,  $310^\circ$  and  $340^\circ$ , from which we concluded that at these temperatures the transformation of CO into  $\text{CO}_2$  and C is unimolecular.

Our present paper contains the results obtained at  $445^\circ$ . This communication appears to us to be of importance for the following reasons. Three months after our first paper a communication appeared from SCHENCK and ZIMMERMANN<sup>2)</sup> from which it appeared that they had also studied the transformation of CO into  $\text{CO}_2$  and C and had arrived at the result that the reaction at temperatures from  $310^\circ$  and  $360^\circ$  was a unimolecular one, thus confirming our experiments, but that at  $445^\circ$  the reaction became bimolecular.

On continuing our investigation we found, however, that the

<sup>1)</sup> Proc. 8 Jan. 1903.

<sup>2)</sup> Ber. 36. p. 1231.

reaction at  $445^\circ$  is also a unimolecular one and that therefore the observations of SCHENCK and ZIMMERMANN must be faulty as far as the temperature  $445^\circ$  is concerned.

*Experiment.*

In order that the reaction might not take place too rapidly the reaction vessel was now filled one third with the catalyser (pumice-nickel-carbon)<sup>1)</sup>.

The object of the first experiments was to determine the order of the reaction according to the method of VAN 'T HOFF.

In the first measurement the initial pressure was 770.7 m.m. Hg. After 5 minutes the CO tension amounted to 430.5 m.m. Hg from which

$$\frac{dc_1}{dt} = 68,04$$

and for the average pressure of the carbonic oxide

$$c_1 = 600,6$$

In the second measurement the initial pressure was 442.2 m.m. Hg and after 5 minutes the CO pressure amounted to 239.0 m.m. Hg.

Here  $\frac{dc_2}{dt} = 40,64$  and  $c_2 = 340,6$ .

If from this we calculate  $n$  according to the formula of VAN 'T HOFF

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

we obtain

$$n = 0,91. ^2)$$

2. After having thus become convinced that the reaction at  $445^\circ$  is also a unimolecular one we made a series of measurements in order to calculate the reaction constant from them.

<sup>1)</sup>The result was as follows:

<sup>1)</sup> The quantity of iron present in pumice did not appear to exert any influence as no alteration in pressure was noticed in a reaction vessel containing pumice and CO when heated to  $445^\circ$ . This time, however, as in SCHENCK's experiments, the iron was removed from the pumice by reduction with hydrogen and subsequent treatment with HCl and boiling in a Soxhlet apparatus.

The  $\text{Ni}(\text{NO}_3)_2$  originally contained much iron, but was completely freed from it by leaving the solution for some time in contact with  $\text{NiCO}_3$ .

<sup>2)</sup> Also after a longer time (10--15 minutes)  $n$  was found to be practically 1.

Time in minutes	Pressure in m m. Hg.	$k = \frac{1}{t} \log \frac{P_0}{2P_t - P_0}$	$k' = \frac{1}{t} \frac{2(P_0 - P_t)}{P_0(2P_t - P_0)}$ <sup>1)</sup>
0	769 5		
4	660 1	0.03437	0 000129
6	616 6	0.03666	0.000143
8	579 1	0.03707	0 000159
10	548 7	0.03704	0 000175
15	497 8	0 03546	0 000208
20	476 7	0 03108	0.000206
30	466 3	0.02246	0 000161

The measurement was started here half a minute after the commencement of the filling. The filling lasted  $\frac{1}{4}$  minute.

The third column contains the values of  $k$  calculated on the supposition that the reaction is *unimolecular* whilst the fourth column contains the values of  $k'$  assuming the reaction to be *bimolecular*, as believed by SCHENCK and ZIMMERMANN. In concordance with what has been found above, we see that the figures in the third column are much more nearly constant than those in the fourth. During the first 15 minutes the values of  $k$  (third column) agree fairly well with each other; afterwards a slow fall takes place. That the first constant would be smaller than the next was to be expected, as during the first 4 minutes a small expansion had still to take place.

Although the starting point could not be fixed with the same accuracy as before, owing to the greater velocity of the reaction, the fall of  $k$  could not be attributed to experimental errors. It therefore, made us suspect that the reaction might perhaps prove to be perceptibly reversible at  $445^\circ$ .

It is true that BOUDOUARD<sup>2)</sup> had found that CO when in contact with our catalyser was completely decomposed at  $445^\circ$  into CO<sub>2</sub> and C, but as his method was not very accurate we felt we might doubt this result<sup>3)</sup>.

In order to obtain certainty we made the following experiment. We filled the apparatus at  $445^\circ$  with CO<sub>2</sub> and observed whether an

<sup>1)</sup> SCHENCK and ZIMMERMANN have made a mistake calculating the value of  $k'$ .

<sup>2)</sup> Ann. de Chim. et de Phys. [7] T. 24. Sept. p. 5—85 (1901).

<sup>3)</sup> SABATIER and SENDERENS noticed a complete transformation between  $230^\circ$  and  $400^\circ$ . Bull. Soc. Chim. t. 29 p. 294 (1903).

increase of pressure took place which would indicate that the reaction  $\text{CO}_2 + \text{C} = 2 \text{CO}$  was proceeding.

The experiment removed all doubt as not only an increase of pressure be could very plainly demonstrated, amounting after a few hours to several c.m. of mercury, but after exhausting the apparatus a quantity of CO could be detected in the gaseous mixture which accounted for the observed increase of pressure.

Contrary to BOUDOUARD'S results we have therefore found that the reaction  $2 \text{CO} = \text{CO}_2 + \text{C}$  is *reversible* at  $445^\circ$ .

The reason why fairly concordant constants were obtained during the first 15 minutes although no notice had been taken in the calculation of the reversal of the reaction, is simply that the equation

$$\frac{dx}{dt} = k_1 (A-x) - k_2 \frac{x}{2} \quad (1)$$

differs but very little from

$$\frac{dx}{dt} = k_1 (A-x) \quad (2)$$

when  $k$  or  $x$  or both are very small.  $k_2$  is very small at  $445^\circ$  and this is the reason why at first the second equation is satisfied,  $x$  being then not yet large.

By means of the first equation we might be able to calculate  $k$  if we knew the equilibrium constant  $K = \frac{k_1}{k_2}$ .

As analysis seemed to us less accurate we have endeavoured to determine  $K$  in the following manner:

The reaction vessel was filled again with CO, while the time was noted which elapsed between the filling and the first reading so as to be able to find the starting pressure by extrapolation. The heating at  $445^\circ$  was now continued until the pressure after the lapse of some hours did not undergo any further change.

$K$  could then be calculated from the pressure at the start and at the finish.

To decide whether the final pressure corresponded with a real condition of equilibrium, the same experiment was repeated starting with  $\text{CO}_2$ . If the first final condition had been a real equilibrium, the same value ought now to be found for  $K$ .

Up to the present we found this by no means to be the case but we do not at all consider the research finished in this direction. We

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<sup>1)</sup> It is taken for granted here that the reaction  $\text{CO}_2 + \text{C} = 2 \text{CO}$  is also a unimolecular one.

only mention it to explain why the values for  $k$  in our last table have not been corrected.

3. In criticising the experiments of SCHENCK and ZIMMERMANN, it must first of all be observed that they did not reduce their NiO with CO but with H<sub>2</sub>. This is of course, wrong as during the reaction carbon is deposited and the catalytic Ni surface is changed. If, as in our experiments, we start with Ni on which previously a coating of carbon has deposited, it is evident that a further precipitation of carbon during the experiment will be of less consequence.

In our former communication it has moreover been shown that the activity of the catalyser first diminishes owing to deposition of carbon, but finally becomes practically constant.

If, therefore, we start with Ni without carbon we may expect that, on account of the deposition of carbon,  $k$  will continuously decrease. The values for  $k$  found by SCHENCK and ZIMMERMANN are not at all constants and show a decrease with an increase of the time.

To find out what can be the cause of the *bimolecular* course at 445° as found by SCHENCK and ZIMMERMANN we have repeated the experiment with pumice-nickel in which the NiO had been reduced with very pure hydrogen. <sup>1)</sup>

Our first work was again the determination of the order of the reaction.

1<sup>st</sup> measurement. Initial pressure = 756,0 m.m. Hg

CO pressure after 3 min. = 528,6 " "

$$\frac{dc_1}{dt} = 75,8 \quad c_1 = 642,3$$

2<sup>nd</sup> measurement. Initial pressure = 275,1 m.m. Hg

CO pressure after 2 min. = 210,9 " "

$$\frac{dc_2}{dt} = 32,1 \quad c_2 = 243,0$$

therefore  $n = 0,9$  <sup>2)</sup>.

Having found that, contrary to the statement of SCHENCK and ZIMMERMANN, the reaction with this catalyser is also *unimolecular* we made a further series of measurements in order to calculate  $k$ .

The results were as follows:

<sup>1)</sup> By electrolysis of a NaOH solution, using nickel electrodes.

<sup>2)</sup> After a longer time (5—10 minutes)  $n$  was found to be practically 1.

Time in minutes.	Pressure in m.m. Hg.	$k = \frac{1}{t} \log \frac{P_0}{2P_t - P_0}$
0	762.1	
2	671.7	0.0580
4	606.3	0.05708
6	560.5	0.05451
8	528.8	0.05143
10	508.6	0.04753

The larger values of  $k$  and their regular change are due to the absence of a layer of carbon at the commencement of the experiment.

If we compare this table with the one given by SCHENCK and ZIMMERMANN for 445°

Time in minutes.	Pressure in m.m. Hg.	$k = \frac{1}{t} \log \frac{P_0}{2P_t - P_0}$
0	759	
2	626	0.09369
4	548	0.08815
6	522	0.07090
10	510	0.04636

we notice that the very considerable change of  $k$  cannot be fully explained by the absence of a layer of carbon but that there must have been another disturbing factor.

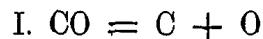
From SCHENCK and ZIMMERMANN'S description it is evident that it cannot be the absorbed hydrogen<sup>1)</sup>, for this was introduced into their apparatus only in the *first* series of experiments and the second series shows a still greater change.

For want of further particulars as to the research of SCHENCK and ZIMMERMANN we cannot make any further suggestions as to the nature of this second disturbing factor.

<sup>1)</sup> We found that H<sub>2</sub> is very strongly absorbed by finely divided Ni but gradually expelled in vacuum. According to SABATIER and SENDERENS [C.r. 134 p. 514—516 (1902)] CO and H<sub>2</sub> react with each other above 200° in contact with finely divided nickel according the equation: CO + 3 H<sub>2</sub> = CH<sub>4</sub> + H<sub>2</sub>O.

We must say a few words about their plausible explanation of the change from a *unimolecular* to a *bimolecular* course, which they thought they had discovered.

After having made the same supposition as we did for the unimolecular course namely



they say:

„Der Dissociation des Kohlenoxydes in seine Elemente würde dann ein Oxydationsvorgang folgen. Spielt sich der letztere, wie bei dem Sauerstoff im *status nascens* zu erwarten ist, mit sehr grosser Geschwindigkeit ab, welche die Dissociationsgeschwindigkeit übertrifft, so findet man eine monomolekulare Reaction. Steigt bei höherer Temperatur die Geschwindigkeit des Dissociationsvorganges verhältnissmässig mehr an als die des Oxydationsprocesses, so fallen schliesslich die Vorgänge zeitlich zusammen, und wir erhalten den Eindruck einer bimolecularen „gekoppelten“ Reaction.

Auf diese Weise lässt sich für die auffällige Erscheinung eine plausible Erklärung geben.“

But what has been overlooked here is that in order that the reactions I and II shall give the impression of a unimolecular reaction, the second must take place with immeasurable velocity. If this is true at a low temperature it is certainly so at higher temperatures and even if the velocity of the first reaction has increased this will be the only one which will be observed so long as it proceeds with measurable velocity.

We are, therefore, inclined to contend that it is plausible to assume that if the reaction is a unimolecular one at a low temperature it cannot be expected that the order of the reaction will increase at a higher temperature.

Summary of our conclusions:

1. The transformation of CO into CO<sub>2</sub> and C is unimolecular for all the temperatures at which we have experimented: 256°, 310°, 340° and 445°.

2. Contrary to the result obtained by BOUDOUARD the reaction is reversible at 445°.

3. The equilibrium constant could not be determined, as up to the present, we have found that the same condition of equilibrium is not attained starting from CO and from CO<sub>2</sub> + C.

*Amsterdam*, Chem. Lab. University, May 1903.