

HIGH TEMPERATURE OXIDATION OF CARBON MONOXIDE CATALYZED BY QUARTZ SURFACE.

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The reaction between carbon monoxide and oxygen has been the subject of a great many investigations. As for the thermal reaction in a quartz vessel, there has been found an explosion peninsula in the Pressure-temperature diagram, analogous to that obtained in the hydrogen-oxygen reaction.¹⁾ The reaction above the upper explosion limit is somewhat complicated: according to Hinshelwood and his co-workers,²⁾ the dry gases react extremely slowly on the wall of the vessel; in the presence of water vapour, however, a rapid chain reaction in the gaseous phase overshadows the underlying surface reaction.

Under a suitable experimental condition, it may be possible to study the heterogeneous oxidation separately regardless of the presence of water. Our present investigation seems to present such an example, for we have obtained the results not only considerably different from those reported by the authors above-mentioned but adequately explained by a heterogeneous mechanism on the wall of the vessel.

Experimental

Carbon monoxide was prepared by dropping formic acid in hot phosphoric acid and purified by passing through the solutions of potassium hydroxide, pyrogallic acid and sulphuric acid successively. Oxygen obtained from a cylinder containing electrolytic oxygen was purified by the ordinary method. Both carbon monoxide and oxygen thus purified were stored over phosphorus pentoxide after being passed through a trap immersed in liquid air.

Carbon dioxide used for the investigation of the effect of the reaction product on the reaction rate was prepared from sodium bicarbonate.

All the experiments were carried out statically with a cylindrical quartz reaction vessel 27 mm. in diameter, the upper end of which was directly connected with a quartz Bourdon gauge. The total volume where the reaction took place was about 60 c.c. including that of the tubing leading to stop-cocks. The whole system but a portion of the tubing about 3 c.c. in volume was placed in an electric furnace.

1) Hinshelwood, *The Kinetics of Chemical Change in Gaseous Systems*, 3rd ed. (1933); Semenov, *Chemical Kinetics and Chain Reactions*, (1935); Lewis and von Elbe, *Combustion, Flames and Explosions of Gases*, (1938).

2) Hadman, Thompson and Hinshelwood, *Proc. Roy. Soc. A.*, 137, 87 (1932); *ibid.*, 138, 297 (1932).

In a series of experiments, in which the effect of water vapour on the reaction rate was examined, a Pyrex bulb containing conductivity water was attached to a Pyrex tubing connecting the reaction vessel with the gas holders and the vacuum system.

The procedure of the experiment was as follows. After the reaction vessel was evacuated, carbon monoxide and then oxygen were successively introduced.³⁾ The time required for addition of the latter was about 1 second. In the case when the effect of water vapour was examined, water vapour was first introduced and then the reactants in the order above-mentioned. The total pressure of the reactants in most cases was about 300 mm. and the temperature of the reaction was varied between 570° and 650°C.

Results

Effect of pre-treatment of the reaction vessel.—The reaction rate was found to suffer remarkable influence through the surface condition of the reaction vessel. The reaction was extremely slow in the vessel evacuated before use below 750°C., while it became much faster when the temperature of evacuation was raised above 800°C. Nevertheless, evacuation at a temperature as high as 1000°C. brought forth no more appreciable effect. The perfectness of the evacuation also influenced the reaction rate considerably. The reaction did not proceed with measurable velocity in case of incomplete evacuation even when the evacuation temperature was above 800°C. In a preliminary test, the vessel was well evacuated at 600°C. and closed; it was heated up to 820°C. and kept at the same temperature for some time. This treatment, however, gave nothing but a very slow rate of reaction.

Therefore, in all the experiments hereafter described, the reaction vessel was evacuated below 10^{-4} mm. for half an hour at 820°C. prior to the measurement, which secured readily measurable and fairly reproducible reaction rates at about 600°C.

Effect of the reaction product.—Two sets of experiments carried out at different temperatures with addition of carbon dioxide are given in Tables I and II, which show but slight effect of carbon dioxide on the reaction.

Relation between the reaction rate and the concentrations of the reacting gases.—Figs. 1 and 2 represent two series of the experiments at 600°C. in which the concentration ratio of the reactants has been widely varied, the total pressure being kept constant at about 300 mm. The results in Fig. 2 are given separately, as they have been obtained under a different surface condition of the vessel. The

3) It was found in the preliminary experiments that the reaction curve remained the same when the reactants were admitted in the reverse order.

Table I.
Effect of added carbon dioxide at 570°C.

Initial pressure	CO, 182.5 mm. O ₂ , 94.6 mm.		CO, 205.6 mm. O ₂ , 103.0 mm. CO ₂ , 52.8 mm.	
Pressure Decrease mm.	Time sec.	Reac. rate mm./sec. · 10 ²	Time sec.	Reac. rate mm./sec. · 10 ²
0	0	3.6	0	3.5
1.6	44	3.4	46	3.3
4.8	138	3.2	144	3.2
8.0	237	3.1	245	2.9
16.0	495	2.9	517	2.7
24.0	775	2.6	817	2.4
32.0	1084	2.3	1149	2.2
40.0	1435	2.0	1517	1.9
48.0	1843	1.7	1943	1.5
56.0	2327		2481	

Table II.
Effect of added carbon dioxide at 600°C.

Initial pressure	CO, 210.0 mm. O ₂ , 99.4 mm.		CO, 196.7 mm. O ₂ , 95.9 mm. CO ₂ , 94.4 mm.	
Pressure Decrease mm.	Time sec.	Reac. rate mm./sec. · 10 ²	Time sec.	Reac. rate mm./sec. · 10 ²
0	0	4.4	0	4.1
1.6	36	4.0	39	4.0
4.8	117	3.8	120	3.8
8.0	202	3.6	205	3.6
16.0	422	3.3	430	3.0
24.0	668	2.7	696	2.5
32.0	960	2.3	1021	2.1
40.0	1312	1.9	1405	1.8
48.0	1726	1.7	1851	1.5
56.0	2202	1.5	2374	1.2
64.0	2746		3028	

initial pressures of the gases in each experiment are given in Table III together with the initial rate calculated from pressure decreases in the first 200 seconds, the rates in the experiments in Fig. 2 being so corrected as to correspond to the same activity of the vessel surface as that in Fig. 1.

As seen in the table, the reaction has a maximum rate in a mixture with higher concentration of oxygen. The form of the reaction curve is related to the

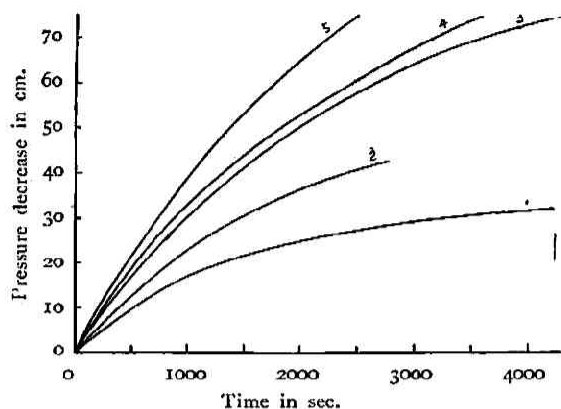


Fig. 1.—The experiments with varied concentrations of the reactants.

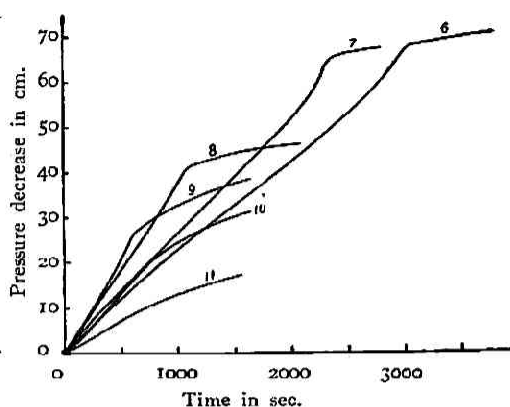


Fig. 2.—The experiments with varied concentrations of the reactants.

Table III.

Relation between the concentrations and the initial rate of reaction.

Curve number in Figs. 1 and 2	Initial pressure in mm.		Total pressure in mm.	Initial rate of the reaction in mm./sec.
	CO	O ₂		
1	258.3	43.4	301.7	0.0210
2	238.5	61.6	300.1	0.0269
3	214.1	89.0	303.1	0.0362
4	201.0	99.4	300.4	0.0383
5	180.3	120.2	300.5	0.0512
6	152.8	148.0	300.8	0.0718
7	137.7	166.8	304.5	0.0776
8	117.9	182.6	300.5	0.0833
9	103.0	200.2	303.2	0.0930
10	76.7	223.3	300.0	0.0540
11	55.0	244.9	299.9	0.0312

concentrations of the reactants in a complicated manner. Curves of autocatalytic form appear in oxygen rich experiments as seen in Fig. 2.

Effects of water vapour and temperature.—These effects were examined at 578°, 600°, 620° and 647°C. and under the water vapour pressures 0.2–5 mm. with equivalent mixtures of both reactants. The reaction was found to suffer marked retardation by water vapour. The kinetics, however, remained nearly the same, as a greater part of the reaction, regardless of the presence of water, could be represented by a first order relation with respect to oxygen pressure as seen in Fig. 3. Fig. 4 shows the falling off of the velocity constant caused by water vapour. The reaction between the dried gases has a small temperature coefficient giving about 7200 cal. per mole as the activation energy, while, in the presence of water vapour,

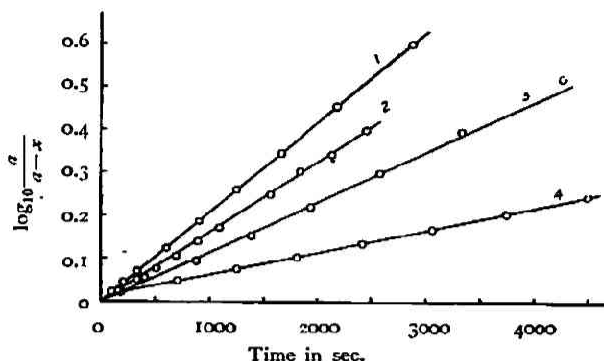


Fig. 3.—The experiments with addition of water vapour at 647°C.; a , initial pressure of O_2 ; x , pressure of O_2 reacted: Curve 1, without water vapour; Curve 2, 0.2 mm. H_2O ; Curve 3, 0.6 mm. H_2O ; Curve 4, 3.2 mm. H_2O .

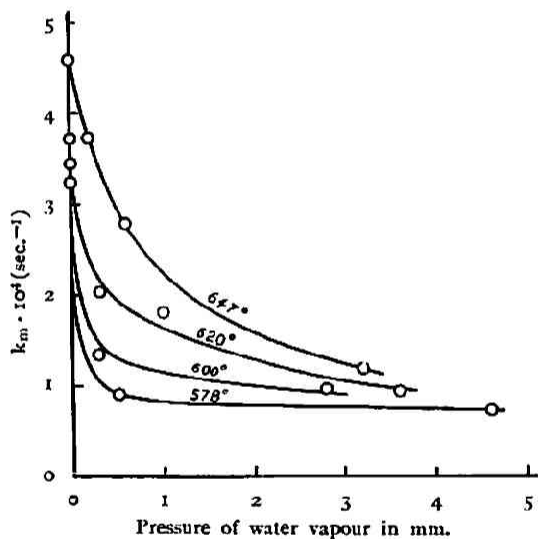


Fig. 4.—Effect of water vapour on the velocity constant.

the temperature coefficient of the rate rises to a greater value and falls off again as the pressure of water vapour increases. The corresponding values of the activation energy are 26,600, 22,400, 15,500 and 11,500 cal. at the pressures of water vapour 0.5, 1, 2 and 3 mm. respectively.

Discussion

The most striking feature of the results obtained in the present investigation is the marked retarding effect of water vapour. Hinshelwood and his co-workers (loc. cit.) reported that the reaction rate increased in proportion to the pressure of water under much the same experimental condition as in the present work, a

result which is evidently opposite to the present results. The 'dry' reaction was also investigated by the same authors with the result that the measurable rate was not obtained below about 700°C., while we have carried out measurements at about 600°C. Moreover, there exists additional difference in the kinetics of the reaction: according to Hinshelwood, the rate of the 'dry' reaction increases less than in linear proportion to the concentration of each reactant and the rate of the 'wet' reaction is proportional to the product of the pressures of both carbon monoxide and water, and inversely to oxygen pressure. In our case, on the contrary, it is rather carbon monoxide and not oxygen that exhibits a retarding effect, though the kinetics is somewhat complicated. In addition, it makes a sharp contrast to the results obtained by Hinshelwood that the presence of water vapour altered the rate only and not the kinetics.

Hinshelwood drew a conclusion from his results that the 'dry' reaction took place on the wall of the reaction vessel, while the 'wet' reaction had a chain mechanism in the gaseous phase. Though in what the difference between the results of Hinshelwood and ours originated is not clear, yet it must be concluded that the 'wet' reaction in the present investigation has an entirely different mechanism from such as given by Hinshelwood and that both the 'dry' and 'wet' reactions should have essentially the same mechanism in our case since no abrupt change in the kinetics has been observed between both kinds of reactions.

The most plausible mechanism which is compatible with these conclusions and also explains all the characteristics of the reaction investigated is the heterogeneous interaction of the both reactants on the wall of the quartz vessel. According to the heterogeneous mechanism, the retarding effect of water is simply attributed to its preferential adsorption on the active surface and it is, therefore, a matter of course that no discontinuity exists between the 'dry' and 'wet' reactions. It is also comprehensible, on the other hand, that the reaction is highly sensitive to the surface condition of the vessel.

The kinetics of the heterogeneous oxidation of carbon monoxide on the surface of quartz was studied by Bodenstein and Ohlmer⁴⁾ and by Benton and Williams⁵⁾ at lower temperatures. Although these investigators could not give any detailed mechanism on the surface, their results may be interpreted to indicate that the reaction rate was determined by a bimolecular process on the quartz surface. Since the termolecular interaction $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ on the surface is less probable,

4) *Z. physik. Chem.*, 53, 166 (1905).

5) *J. Phys. Chem.*, 30, 1487 (1926).

a bimolecular process should be considered in our case too, that is,



The oxygen atom thus liberated will immediately combine with another carbon monoxide molecule, so that the over-all reaction rate will be determined by the primary process (1).⁷⁾

Whether the bimolecular process (1) takes place between the two species of gases adsorbed on the surface or between one of the reactants adsorbed and the other impinging on it from the gaseous phase may be decided by the consideration on the experimental results: the appearance of the curves of autocatalytic form in the experiments with excess of oxygen (Fig. 2) indicates that the reaction is accelerated with a pressure decrease of carbon monoxide which hinders the adsorption of oxygen owing to its stronger adsorption.⁸⁾ Therefore it may be concluded that not only carbon monoxide but also oxygen must be adsorbed. Little effect of the addition of carbon dioxide (Table I) shows that the adsorption of the product is but slight.

According to the picture of the reaction given above, the appearance of a maximum rate in the oxygen rich experiment in Table III are explained as follows. Oxygen being weakly adsorbed, its adsorbed amount does not attain to a value comparable with that of carbon monoxide unless its presence is in excess. Therefore the product of the adsorbed amounts of both reactants and consequently the rate of the reaction which is proportional to this product has a maximum value in an oxygen rich mixture.

It may be of interest to see to what extent the ordinary theory of the kinetics in the heterogeneous catalysis can represent the experimental results given in Figs. 1 and 2 and Table III.

According to the theory, the velocity formula for the bimolecular reaction (1) between the adsorbed molecules is given by

$$\frac{d[\text{CO}_2]}{dt} = k \frac{[\text{CO}][\text{O}_2]}{(1 + a[\text{CO}])^2}, \quad (2)$$

6) The same heterogeneous reaction was assumed by Hinshelwood (loc. cit.) and Semenov (loc. cit.) as a chain initiating process.

7) The adsorption process will be rapid enough at such high temperatures as in the present case, and any disturbance due to a diffusion process may be neglected, for the reaction rate has remained nearly unaltered when a mixture of the reactants has been diluted with such a foreign gas as carbon dioxide (Tables I and II).

8) A similar relation was dealt with in a study of the hydrogenation of ethylene on nickel catalyst (*This Journal*, 11, 153 (1937)).

provided that the adsorption of oxygen as well as carbon monoxide is small and further diminished by the stronger adsorption of carbon monoxide. a is the adsorption coefficient for carbon monoxide.

The expression for the initial rate of the reaction is obtained by substituting the initial pressures in formula (2), i.e.,

$$v_0 = k \frac{ab}{(1+ua)^2},$$

where v_0 is the initial rate and a and b are the initial pressures of carbon monoxide and oxygen respectively. Since the initial total pressure was kept constant at 300 mm. in the experiments given in Table III, b may be replaced by $300-a$. Putting $\frac{dv_0}{da} = 0$, we have

$$a = \frac{300}{2 + 300a}.$$

This indicates that a maximum initial rate appears in an oxygen rich mixture as actually observed. Formula (2) fails, however, to represent exactly such a sharp maximum as given in Table III.

The curves in Figs. 1 and 2 are similarly explained by formula (2) in the qualitative aspects. Formula (2) may be rewritten as follows:

$$v = k \frac{(a-2x)(b-x)}{\{1+u(a-2x)\}^2},$$

where v is the rate of the reaction and x the pressure decrease due to the reaction. Putting $\frac{dv}{dx} = 0$, we have

$$x = \frac{a + 2b + ua(a-2b)}{4 + 2u(a-2b)}. \quad (3)$$

x thus obtained has a possibility to have a reasonable value when $a < 2b$. Hence the pressure-time curve may take an autocatalytic form in the presence of excessive oxygen as really found experimentally (Figs. 1 and 2).

More quantitative analysis of the reaction curves on the basis of formula (2) is, however, difficult, for it has been found necessary for that purpose to use the values of k and u increasing with the progress of the reaction.

For example, the values of u determined by equation (3) from the positions of maximum rates in the curves shown in Fig. 2 are given in Table IV together with pressures of carbon monoxide corresponding to the maximum rates. As seen in the table, greater value of u corresponds to lower pressure of carbon monoxide.

Such variations in the values of the constants seem to result from the inhomogeneity of the quartz surface in the following way. At the initial stage of

Table IV.
Relation between α and carbon
monoxide pressure.

Curve number in Fig. 2	α mm. ⁻¹	Pressure of CO mm.
6	0.058	22.8
7	0.113	9.7
8	0.033	39.9
9	0.026	51.8
10	0.023	57.5
11	0.026	47.0

the reaction, the highly active parts of the surface will be mostly covered with carbon monoxide, which will be adsorbed more strongly the more active the surface is. Consequently, the reaction will proceed at the remaining less active parts of the surface. As carbon monoxide, however, is used up, its poisoning action is exhausted and the highly active parts will come into play, giving rise to increases in the values of k and α .

An evidence of the inhomogeneity of the quartz surface is given in the results of the experiments with addition of water vapour. As already described, the activation heat rose from a small value, 7200 cal. to a greater one, 26,600 cal. when 0.2 mm. of water vapour was added. This sudden rise is yet explainable since the heat of adsorption of water is now included in the apparent heat of activation. But if the surface were homogeneous, the activation heat would not change any more when the pressure of water vapour was further increased. The observed falling off in the value of the activation heat, therefore, must be ascribed to the inhomogeneity of the quartz surface.

The results obtained by Bodenstein and Ohlmer (loc. cit.) was approximately represented by the following empirical formula:

$$\frac{d[\text{CO}_2]}{dt} = k' \frac{[\text{O}_2]}{[\text{CO}]} \quad (4)$$

Comparison between formulae (2) and (4) shows that formula (4) is derived from formula (2) in case $\alpha[\text{CO}] \gg 1$, that is, formula (2) obtained in the present investigation represents a more general form of formula (4). Hence the mechanism of the reaction seems to be identical in both cases.⁹⁾ The retarding action of carbon monoxide was much stronger in the investigation by Bodenstein and Ohlmer perhaps because they carried out experiments at about 300°C., a far lower temperature.

Benton and Williams (loc. cit.) studied the kinetics at about 500°C., using silica powder as a catalyst. Although their results are quite complicated, the general characteristics of the reaction, on the whole, does not differ much from ours, for the retarding action of carbon monoxide is noticeable in their results

9) The same interpretation of formula (4) was given by Hinshelwood in his book (loc. cit).

too. Therefore formula (2) explains the results of these investigators more adequately than the following expression given by them:

$$\frac{d[\text{CO}_2]}{dt} = k''[\text{CO}]^{\frac{1}{2}}[\text{O}_2].$$

Summary

The kinetics of the reaction between carbon monoxide and oxygen has been investigated statically in the region above the upper explosion limit with a quartz vessel. The rate of the reaction is markedly influenced by the pre-treatment of the vessel. Addition of carbon dioxide to a mixture of the reactants has little effect on the rate. Carbon monoxide exerts a retarding effect unless its pressure is low, while oxygen favours the reaction even in its large excess. Water vapour acts as a powerful inhibitor. The inhibiting power, however, falls off as the pressure of water vapour increases. The activation energy of the reaction in the absence of water vapour is about 7000 cal. per mole.

The results are considerably different from those obtained by Hinshelwood and his co-workers, who explained the reaction between the wet gases by a chain mechanism in the gaseous phase. Our results are best interpreted by a heterogeneous mechanism: the rate-determining process seems to be a bimolecular interaction of both reactants adsorbed on the wall of the vessel. The retarding effects of both water vapour and carbon monoxide are simply attributed to their strong adsorption, the effect of the former being greater because of its stronger adsorption. Application of the ordinary theory of the kinetics in the heterogeneous catalysis is successful in the qualitative aspects. Some complications arise, however, most likely due to the inhomogeneity of the quartz surface.

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