

## THE MECHANISM OF THE CATALYTIC ACTION OF PLATINUM IN THE REACTIONS $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ and $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ .

BY IRVING LANGMUIR.

The reaction between hydrogen and oxygen in contact with a platinum surface has long served as the most typical example of catalytic action. Faraday made a detailed study<sup>1</sup> of the power of platinum to induce combination of these gases, and found that it depended upon the previous treatment of the metallic surface and upon the absence of even minute traces of certain gases.

Most chemists seem to feel that the nature of catalytic action is almost as great a mystery to-day as it was in Faraday's time. With our increasing knowledge of the structure of solid bodies and the atoms and molecules of which they are built, we should now, however, gradually begin to gain a clear insight into the mechanisms of such surface actions.

As a result of experimental and theoretical studies of thermionic emission and chemical reactions in high vacuum the writer became impressed with the remarkable stability of certain monomolecular adsorbed films even on highly heated wires or filaments and came to realise the importance of such films in determining chemical effects. To obtain a better understanding of catalytic actions, several series of experiments were carried out by heating platinum wires to various temperatures in mixtures of oxygen and hydrogen or oxygen and carbon monoxide at low pressures (below 1000 bars; 1 bar = 1 dyne per sq. cm.  $\approx 10^{-6}$  atmosphere). The products of the reaction were condensed as fast as formed in a portion of the apparatus cooled by liquid air. The rate of decrease of pressure thus served as a measure of the reaction velocity. It was hoped that the kinetics of these reactions would throw light on the mechanism of the catalytic action.

The first preliminary experiments with the platinum wire heated considerably below a red heat in mixtures of carbon monoxide and oxygen showed that the velocity of the reaction under these conditions is proportional to the pressure of the oxygen, but *inversely proportional* to the pressure of carbon monoxide. It was then found that Bodenstein and Ohlmer<sup>2</sup> in their study of the reaction between these gases on surfaces of fused quartz, had obtained these same relations at about atmospheric pressure. Subsequently, Bodenstein and Fink<sup>3</sup> suggested tentatively that the explanation of this peculiar behaviour might be that the surface of the quartz glass is covered by an adsorbed film of carbon monoxide of a *thickness* proportional to the pressure of the gas. By then assuming that the oxygen has to diffuse through the layer of carbon monoxide before coming into contact with the quartz glass where it reacts with the monoxide, it was possible to explain the fact that the rate of reaction is proportional to the pressure of oxygen and inversely proportional to the pressure of carbon monoxide.

<sup>1</sup> "Experimental Researches," Everyman's Edition, pp. 84-111.

<sup>2</sup> *Zeit. physik. Chem.*, **53**, 166 (1905).

<sup>3</sup> *Ibid.*, **60**, 46 (1907).

There were serious objections to applying this theory in the present case, for in order that the thickness of the film could be proportional to the pressure over a wide range it would be necessary to have a film many molecules deep, and this seemed improbable especially at the low pressures used in these experiments with platinum wires.

These difficulties disappear, however, if we consider that the adsorbed film of carbon monoxide is a monomolecular film which nearly but not quite completely covers the surface. Regarding the carbon monoxide molecules as chemically combined with the underlying platinum atoms, we have a logical reason for believing that the oxygen molecules striking the carbon monoxide film should be unable to react with it, for the carbon monoxide molecules would be *oriented* on the surface, the carbon atoms being directly combined with the platinum and the oxygen atoms covering the carbon atoms and protecting them from the action of the oxygen molecules which strike the surface. As the individual carbon monoxide molecules evaporate from the surface they leave vacant spaces. The oxygen molecules and carbon monoxide molecules in the surrounding gas then compete with each other in reaching these spaces. If a space becomes filled with a carbon monoxide molecule the gap in the carbon monoxide film is thus repaired, but if it becomes filled by an oxygen molecule, this molecule (or each of the resulting oxygen atoms) can react with the carbon monoxide molecules which strike it and thus form carbon dioxide which will be held by weaker chemical forces and will therefore distil off rapidly. This process leaves the space still vacant so that another oxygen molecule can be adsorbed and a carbon dioxide molecule formed. This action continues until the space becomes filled by a carbon monoxide molecule. It is almost self-evident, under these conditions, that the velocity of the reaction will be proportional to the pressure of oxygen and inversely proportional to that of the carbon monoxide. As the temperature is raised the rate of reaction increases in proportion to the rate of evaporation of carbon monoxide from the adsorbed film. The "heat of activation," of this reaction is thus merely the latent heat of evaporation of the adsorbed carbon monoxide.

On the basis of this theory, it is clear that as the temperature is raised or the pressure of carbon monoxide is lowered, the reaction velocity continues to increase until the film of monoxide no longer covers the larger part of the surface. The carbon monoxide will then cease to act as a catalytic poison. In any case, however, there must be a definite upper limit to the reaction velocity fixed by the rate at which the gas molecules strike the surface of the filament. This rate is the same as that of effusion through small openings and may be calculated according to the principles of the kinetic theory. The number of grams of any gas per square centimetre per second which strike a surface is given by

$$m = \sqrt{\frac{M}{2\pi RT}} p \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $M$  is the molecular weight of the gas,  $R$  is the gas constant ( $83.2 \times 10^6$  ergs per degree),  $p$  is the pressure in bars and  $T$  is the absolute temperature of the gas. This equation is to be applied separately to each of the gases present.

If this limit to the reaction velocity is once approached, the temperature coefficient of the reaction velocity must fall to a negligible value. A knowledge of the actual velocity under these conditions should furnish particularly good information regarding the mechanism of the reaction. When

either of the gases is present in very great excess, the phenomena should be much simplified. Let us consider each of the two limiting cases separately.

In the first case let us assume that there is a large excess of carbon monoxide, but the filament temperature is so high that only a small fraction of the surface remains covered by carbon monoxide molecules. In accordance with the results of the experiments at the lower temperatures described above, we may assume that oxygen molecules which strike carbon monoxide molecules on the surface do not react with them. When oxygen molecules strike the surface, however, a certain fraction  $\alpha$  condenses on the surface while the fraction  $1 - \alpha$  is reflected. If the temperature is not too high and if the pressure of carbon monoxide is large enough, every oxygen molecule (or the resulting atoms) which condenses will react with the carbon monoxide molecules that are continually striking the surface. The reaction velocity is thus limited solely by the number of oxygen molecules which condense and this in turn is given by the number that strike the surface (in accordance with Equation 1) multiplied by the fraction that condense.

Experiments were undertaken to measure the reaction velocity at high filament temperatures. The velocity became so high that it was necessary to employ filaments of extremely small size in bulbs of large capacity, but it was then possible to measure the velocities accurately. These experiments showed that the reaction velocity over a wide range of temperature is independent of the temperature, and that with a large excess of carbon monoxide the velocity is practically equal to the rate at which the oxygen can come into contact with the filament in accordance with Equation 1. The value of  $\alpha$  is thus found to be in the neighbourhood of unity, or in other words practically all the oxygen molecules which strike a clean platinum surface at a red heat *condense* on the surface and remain there long enough to be struck by carbon monoxide molecules. It should be kept in mind that the number of carbon monoxide molecules which could strike oxygen molecules on the surface if the oxygen molecules merely rebounded from the surface, is wholly inadequate to explain the observed reaction velocity. Thus the length of time that the oxygen molecules (or atoms) remain condensed on the surface is very great compared with the time that is required for an elastic collision with the surface.

In the second case that we wish to consider let us assume that we have a large excess of oxygen and that the temperature is so high that very little of the surface is covered by carbon monoxide molecules. Unless the temperature is too high or the pressure of carbon monoxide is too low, the oxygen which condenses on the surface remains until removed by reaction with carbon monoxide molecules that strike the surface. With a large excess of oxygen the surface thus becomes practically completely covered by a film of oxygen. The reaction velocity under these conditions is equal to the rate at which the carbon monoxide molecules strike the filament according to Equation 1, multiplied by  $\epsilon$  the fraction of the collisions between carbon monoxide and adsorbed oxygen which result in combination.

The experiments made with excess of oxygen and high filament temperature (red heat and more) showed that the reaction velocity is practically equal to the rate at which the carbon monoxide comes into contact with the filament. In other words, the value of  $\epsilon$  is approximately unity so that nearly all the carbon monoxide molecules that strike a surface covered by an oxygen film react to form carbon dioxide.

As a result of a more detailed mathematical analysis of this mechanism, we shall see that a consideration of the intermediate cases where neither

gas is present in large excess leads us to a still clearer insight into the mechanism of the reaction.

In the foregoing discussion we have dealt with conditions under which the oxygen that condenses on the surface is removed only by reaction with the monoxide. At still higher filament temperatures, however, a fraction of the oxygen which condenses must evaporate from the surface before it has opportunity to react. At extremely high temperatures even with a large excess of oxygen, only a small fraction of the surface will be covered by oxygen. The velocity of the reaction is then determined by the number of carbon monoxide molecules which strike the surface and the fraction of the surface covered by oxygen. This fraction is proportional to the pressure and inversely proportional to the rate of evaporation of the oxygen from a completely covered surface. Therefore the reaction velocity under these conditions is proportional to the product of the pressures of the oxygen and the carbon monoxide and decreases as the temperature is raised.

The experiments with the filament at a white heat have confirmed these conclusions, since the reaction velocity was found to be one-sixth as great as at a dull red heat. The results indicated that the reaction then took place only at the ends of the filament which were cooled by the leads. For this reason it was not found practicable to determine whether the reaction velocity at the hottest part of the filament was proportional to the product of the pressures of the two gases.

Similar experiments were undertaken using mixtures of hydrogen and oxygen instead of carbon monoxide and oxygen. The results showed that the mechanisms of the two reactions are essentially similar, the hydrogen in one corresponding to the carbon monoxide in the other. At a dull red heat the velocity becomes very high and independent of the temperature. The value of  $\epsilon$  was found to be approximately unity as in the reaction with carbon monoxide. At the highest temperatures, however, the velocity, in contrast with the behaviour observed with carbon monoxide and oxygen, does not decrease to any marked extent even at temperatures close to the melting point of platinum. This result suggests that the decrease observed with the monoxide is due to a decrease in  $\epsilon$  at high temperatures in the case of carbon monoxide rather than to the evaporation of oxygen, for evaporation should bring about the same decrease in the velocity of the reaction with hydrogen. This point will be discussed again in connection with the detailed experimental data.<sup>1</sup>

### MATHEMATICAL TREATMENT OF THEORY.

The theory of the mechanism of the combustion of hydrogen or carbon monoxide in contact with platinum which we have developed in the preceding pages, lends itself well to mathematical treatment. The reaction velocity depends upon the rate at which the gases can come into contact with a certain active portion of the surface of the metal and upon certain

<sup>1</sup> The experiments upon which the foregoing discussion is based (Exps. 441, 443, and 445) were carried out during the spring of 1915. A brief abstract of the general results and their theoretical interpretation was published in a paper on "Chemical Reactions at Low Pressures" (*Four. Amer. Chem. Soc.*, **37**, 1162 (1915)). A short description of the experiments and a statement of a few of the quantitative results regarding the values of  $\alpha$  and  $\epsilon$  were published in a paper on the "Evaporation, Condensation, and Reflection of Molecules and the Mechanism of Adsorption" (*Phys. Rev.*, N.S., **8**, 149 (1916)).

surface factors such as  $\alpha$  and  $\epsilon$  which are usually if not always approximately equal to unity.

Let  $\mu$  represent the number of grammolecules of any gas of molecular weight  $M$  which strike each square centimetre of surface per second. Then  $\mu = m/M$  where  $m$  is given by Equation 1 in terms of  $p$ , the partial pressure of the gas. Making this substitution we obtain

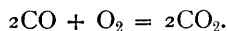
$$\mu = \frac{p}{\sqrt{2\pi MRT}} \quad (2)$$

Expressing  $p$  in bars, and placing  $R = 83.2 \times 10^6$  ergs per degree this reduces to

$$\mu = 43.75 \times 10^{-6} \frac{p}{\sqrt{MT}} \quad (3)$$

The problem of the reaction velocity is much simplified if we assume that each reacting component condenses on the surface in molecular form and that each molecule requires only one elementary space on the surface. In other words we assume that any molecule can occupy on the surface the place previously occupied by any other molecule. In view of the comparative simplicity which these assumptions bring into the problem we shall consider these conditions under "Case 1". It is more probable, however, that some or all of the components exist in the atomic form on the surface and that some of the components require two elementary spaces on the surface. The consideration of these factors introduces some mathematical difficulties and makes it more convenient to use equations which apply only to special cases. We shall consider these under the heading "Case 2".

The reaction which we wish to consider is



Let the partial pressures of the three gases be denoted by  $p_1$ ,  $p_2$  and  $p_3$  respectively, in the order in which they occur in the equation. The rates at which the gases come into contact with a given surface are then  $\mu_1$ ,  $\mu_2$  and  $\mu_3$  expressed in g. mols. per square centimetre per second, as obtained from Equation 3.

Let  $\omega$  be the reaction velocity expressed in g. mols. of oxygen which react per second per square centimetre of platinum surface. Then  $2\omega$  is the rate at which carbon monoxide disappears and also the rate at which carbon dioxide is formed.

**CASE 1.**—The problem before us may be stated mathematically in terms of the following six equations. One equation is written for each way in which each of the components may disappear, and then there is one equation to express the fact that the total surface available is the sum of all the separate kinds of surfaces that need to be considered.

**Carbon Monoxide.**—According to the mechanism we assume, the carbon monoxide which condenses on the platinum surface does not react with oxygen but leaves the surface only by evaporation. The rate of condensation on the platinum is  $\alpha_1\theta\mu_1$  where  $\theta$  is the fraction of the total surface which is bare and  $\alpha_1$  is the surface factor for condensation, that is, it represents, out of all the molecules of carbon monoxide that strike a bare surface, the fraction which condenses. The rate of evaporation of carbon monoxide from the surface is equal to  $\nu_1\theta_1$  where  $\theta_1$  is the fraction of the total surface which is covered with carbon monoxide and  $\nu_1$  is the rate at

which carbon monoxide would evaporate from a surface completely covered with an adsorbed film of this substance (expressed in g. mols. per square centimetres per second). If the reaction is proceeding at a steady rate, the amount of monoxide condensing in a given time must equal the amount evaporating, so that we obtain the equation

$$a_1\theta\mu_1 = v_1\theta_1 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The carbon monoxide, however, is also involved in another process, *viz.* the reaction with oxygen molecules and atoms on the surface. We assume that this takes place by collision between the carbon monoxide molecules and a surface already covered with an adsorbed film of oxygen. Thus if  $\theta_2$  is the fraction of the surface covered with molecular oxygen, the rate at which carbon monoxide reacts with the molecular oxygen is  $\epsilon_2\theta_2\mu_1$  where  $\epsilon_2$  is the surface factor for reaction. When a carbon monoxide molecule reacts with an oxygen *molecule*, however, it must leave an oxygen atom on the surface, and this atom, because of its strong field of force, should not evaporate easily from the surface. We may therefore assume that these atoms remain on the surface until they, in their turn, are struck by carbon monoxide molecules. The carbon monoxide thus reacts with oxygen atoms on the surface at the rate  $\epsilon_a\theta_a\mu_1$  where  $\theta_a$  is the fraction of the surface covered by atomic oxygen and  $\epsilon_a$  is the surface factor for this reaction. The total rate of disappearance of carbon monoxide ( $2\omega$ ) must thus equal the sum of the rates by the two processes, so that we obtain the equation

$$2\omega = \epsilon_2\theta_2\mu_1 + \epsilon_a\theta_a\mu_1 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The factors  $\epsilon_2$  and  $\epsilon_a$  are probably not true surface factors in the same sense as the factor  $a_1$ . It is more logical to consider that the carbon monoxide molecules condense on the oxygen covered surface and subsequently may either evaporate or react with the underlying atoms. In this case the factor  $\epsilon$  measures the fraction of the molecules which react instead of evaporating. It is very convenient, however, in most cases to look upon  $\epsilon$  merely as a surface factor.

*Oxygen Molecules.*—The rate at which oxygen disappears ( $\omega$ ) is equal to the difference between the rate of condensation and the rate of evaporation. We thus obtain

$$\omega = a_2\theta\mu_2 - v_2\theta_2 \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where  $a_2$  is the surface factor for the condensation of oxygen molecules and  $v_2$  is the rate of evaporation of molecular oxygen from a completely covered surface.

*Oxygen Atoms.*—The atomic oxygen on the surface is produced by the interaction between carbon monoxide molecules and adsorbed oxygen molecules. Thus the rate of production of atomic oxygen (g. atoms per second per square centimetre) is equal to the rate of disappearance of molecular oxygen ( $\omega$ ). The atomic oxygen is removed from the surface only by collision with carbon monoxide molecules at the rate  $\epsilon_a\theta_a\mu_1$ . Hence

$$\omega = \epsilon_a\theta_a\mu_1 \quad . \quad . \quad . \quad . \quad . \quad (7)$$

*Carbon Dioxide.*—We shall assume that the experimental conditions are such that the carbon dioxide that is produced does not accumulate in the gas phase but is removed as fast as formed so that no appreciable number of these molecules return to the platinum surface. We may therefore con-

sider  $\mu_3$  to be zero. The rate of production of carbon dioxide is  $2\omega$ , and this must be equal to the rate of evaporation of this gas from the surface. We then have

$$2\omega = \nu_3\theta_3 \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where  $\theta_3$  refers to the fraction of the surface covered by adsorbed carbon dioxide.

"*Constant Sum Condition.*"—The final equation is obtained by placing the sum of all the fractions  $\theta$ ,  $\theta_1$ , etc., equal to unity:—

$$\theta + \theta_1 + \theta_2 + \theta_a + \theta_3 = 1 \quad . \quad . \quad . \quad . \quad . \quad (9)$$

We may now eliminate the quantities  $\theta$ ,  $\theta_1$ , etc., among the last six equations. This is done most conveniently solving the equations for  $\theta$ , etc., in terms of  $\omega$  and then substituting these in (9). We thus obtain

$$\theta = \frac{\omega}{a_2\mu_2} + \frac{\nu_2\omega}{a_2\epsilon_2\mu_1\mu_2} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\theta_1 = \frac{a_1\nu_2\omega}{a_2\epsilon_2\nu_1\mu_2} + \frac{a_1\mu_1\omega}{a_2\nu_1\mu_2} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$\theta_2 = \frac{\omega}{\epsilon_2\mu_1} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$\theta_a = \frac{\omega}{\epsilon_a\mu_1} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$$\theta_3 = \frac{2\omega}{\nu_3} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Substituting these in (9), dividing by  $\omega$  and grouping the terms according to powers of  $\mu$  gives

$$\frac{1}{\omega} = \frac{a_1\mu_1}{a_2\nu_1\mu_2} + \frac{2}{\epsilon\mu_1} + \left(\frac{1}{a_2} + \frac{a_1\nu_2}{a_2\epsilon_2\nu_1}\right)\frac{1}{\mu_2} + \frac{\nu_2}{a_2\epsilon_2\mu_1\mu_2} + \frac{2}{\nu_3} \quad . \quad (15)$$

where  $\epsilon = \frac{2}{\epsilon_2} + \frac{1}{\epsilon_a} \quad . \quad . \quad . \quad . \quad . \quad (16)$

Since  $\mu_1$  and  $\mu_2$  are proportional to the partial pressures of carbon monoxide and oxygen respectively, Equation 15 shows how the reaction velocity varies with the partial pressures of the components under all conditions of temperature that are consistent with the assumptions that we have made. The equation may be simplified, however, without appreciable loss of accuracy by the omission of two terms.

Faraday showed that carbon dioxide had no appreciable effect on the velocity of the reaction between hydrogen and oxygen in contact with platinum even at temperatures as low as room temperature. This proves that the rate of evaporation of this gas,  $\nu_3$ , is so great that practically none of it remains on the surface. Special direct experiments (described below) have shown that carbon dioxide is not appreciably adsorbed by a clean platinum surface, and that under the conditions of the experiments this gas does not alter the reaction velocity. We may therefore place  $\nu_3 = \infty$  and neglect the last term in (15).

We have already discussed some of the evidence that the rate of evaporation of oxygen from the surface is very small compared to that of the carbon monoxide. Further evidence will be given below. We may therefore neglect the term  $\frac{a_1\nu_2}{a_2\epsilon_2\nu_1}$  as compared to  $\frac{1}{a_2}$ . Equation 15 thus

becomes

$$\frac{1}{\omega} = \frac{\alpha_1 \mu_1}{\alpha_2 \nu_1 \mu_2} + \frac{2}{\epsilon \mu_1} + \frac{1}{\alpha_2 \mu_2} + \frac{\nu_2}{\epsilon_2 \alpha_2 \mu_1 \mu_2} \quad (17)$$

It is readily seen that this equation gives us the limiting cases which we have obtained in connection with our preliminary discussion of the experiments. Thus at very low temperatures the rates of evaporation of the adsorbed films will be small so that the first term of the second member of (17) becomes large compared to the other terms. This gives

$$\omega = \frac{\nu_1 \alpha_2 \mu_2}{\alpha_1 \mu_1} \quad (18)$$

and by (11) we see that  $\theta_1$  must then be equal to unity.

At higher temperatures (or at lower pressures) the second and third terms in (17) will be the only ones of importance so that the reaction is given by

$$\frac{1}{\omega} = \frac{2}{\epsilon \mu_1} + \frac{1}{\alpha_2 \mu_2} \quad (19)$$

With a large excess of oxygen the last term becomes negligible and we have, by (19), (12), (13) and (16)

$$\omega = \frac{1}{2} \epsilon \mu_1, \text{ and } \theta_2 + \theta_a = 1 \quad (20)$$

while with a large excess of carbon monoxide we obtain by (19) and (10)

$$\omega = \alpha_2 \mu_2, \text{ and } \theta = 1 \quad (21)$$

Finally, at very high temperatures or at very low pressures the last term in (17) becomes the determining one, and we find by (17) and (10)

$$\omega = \frac{\epsilon_2 \alpha_2 \mu_1 \mu_2}{\nu_2}, \text{ and } \theta = 1 \quad (22)$$

**CASE 2.**—The experimental results discussed in the preceding pages indicate that oxygen evaporates from a platinum surface less readily than does carbon monoxide, but carbon dioxide evaporates extremely rapidly so that it is not appreciably adsorbed. We account for the lower rate for the monoxide as compared to the dioxide by chemical union between the carbon atom of the monoxide and the atoms of the underlying metal. It is then unreasonable to consider that oxygen is held on the surface merely by the stray field of force of the oxygen molecule. The low boiling point and the relatively small adsorption of oxygen by surfaces of glass or mica<sup>1</sup> indicate that this stray field of force is small. We are thus forced to believe that the oxygen exists on the surface in the atomic condition, that is, that the molecular structure of the oxygen is broken up and that the individual atoms are combined with the underlying platinum atoms. From this viewpoint, the statement of the problem of reaction velocity as given under Case 1 can hardly be correct. As before we shall consider one equation for each component involved in the reaction.

**Carbon Monoxide or Hydrogen.**—There are two hypothesis to consider in regard to the condensation of carbon monoxide. The platinum surface is to be looked upon as a kind of checker-board, each platinum atom on

<sup>1</sup> Langmuir, *Jour. Amer. Chem. Soc.*, **40**, 1361 (1918).







$$\sqrt{r\theta_2} + \theta_2 = 1 \text{ or } r = \frac{(1 - \theta_2)^2}{\theta_2} \quad (35)$$

This can be readily plotted, and from the plot and from (34) and (29) the values of  $\omega$  are conveniently found for any given values of  $\mu_1$  and  $\mu_2$ .

*CASE 3.—The Effect of a Possible Reaction between Adsorbed Carbon Monoxide and Oxygen.*—In the cases we have considered it has been assumed that no reaction occurs between carbon monoxide which has been adsorbed on the surface and oxygen molecules which strike the surface or which lie in adjacent spaces on the surface. Let us now consider what effect it would have on the reaction velocity if interaction should occur between the adsorbed carbon monoxide and the oxygen.

*A. Reaction between Carbon Monoxide and Adjacent Oxygen Atoms.*—Assuming that two spaces are required for the condensation of either carbon monoxide or oxygen molecules, the rate of condensation of the two gases is  $a_1\theta^2\mu_1$  and  $a_2\theta^2\mu_2$  respectively. The carbon monoxide which condenses either evaporates or reacts with adjacent oxygen atoms at the rate  $v_3\theta_1\theta_2$  and thus leaves the surface as dioxide. We assume that no evaporation of oxygen occurs, and therefore all the oxygen which condenses must react. Carbon dioxide is produced in two ways: by carbon monoxide molecules which strike adsorbed oxygen atoms (rate  $\epsilon\theta_2\mu_1$ ), and by reaction between adsorbed carbon monoxide, and adjacent adsorbed oxygen atoms.

We thus state the problem by the equations—

$$a_1\theta^2\mu_1 = v_1\theta_1 + v_3\theta_1\theta_2 \quad (36)$$

$$\omega = a_2\theta^2\mu_2 \quad (37)$$

$$2\omega = \epsilon\theta_2\mu_1 + v_3\theta_1\theta_2 \quad (38)$$

$$\theta + \theta_1 + \theta_2 = 1 \quad (39)$$

To solve for  $\theta_1$  and  $\theta_2$  involves inconvenient quadratic equations. Let us therefore consider special cases. At low temperatures there will be a tendency for the surface to be covered with monoxide. If we place  $\theta_1 = 1$  in (36) and (38) we can readily solve for  $\omega$  and obtain—

$$\omega = \frac{v_1}{\frac{a_1\mu_1}{a_2\mu_2} - \frac{2}{1 + \frac{\epsilon\mu_1}{v_3}}} \quad (40)$$

The fraction  $\frac{\epsilon\mu_1}{v_3}$  represents by (39) the ratio between the amounts of carbon dioxide produced by the two mechanisms. If the reaction between the monoxide and adjacent oxygen atoms is about as important as that caused by collision between monoxide molecules and oxygen, then the fraction is approximately unity and the second term in the denominator of (40) is also close to unity. Thus, according to this equation the velocity of the reaction should become indefinitely great when  $\frac{a_1\mu_1}{a_2\mu_2}$  is near unity.

Since  $a_1$  and  $a_2$  are of the order of magnitude of unity, it follows from this mechanism that the rate of reaction cannot even approximately be proportional to the pressure of the oxygen and inversely proportional to that of the monoxide, especially at low pressures of monoxide. Since this conclusion is contrary to the results of the experiments, it is evident that at low temperatures no appreciable interaction occurs between the adsorbed monoxide and the adjacent adsorbed oxygen atoms.

*B. Reaction between Adsorbed Monoxide and Impinging Oxygen Molecules.*—Let us assume that the monoxide cannot react with oxygen atoms adsorbed on the platinum in adjacent spaces, but that some monoxide reacts with oxygen molecules which strike a portion of the surface covered with monoxide just as the monoxide molecules react with oxygen atoms which they strike on the surface.

*Carbon Monoxide.*—The monoxide condenses at the rate  $\alpha_1\theta^2\mu_1$ , and leaves the surface by evaporation ( $\nu_1\theta_1$ ) and by interaction with the oxygen. When oxygen molecules strike a surface already covered with monoxide we must assume that they condense to form a second layer. Let us denote by  $\theta_2'$  the fraction of the total surface which is covered by the composite layer consisting of carbon monoxide covered in turn by oxygen molecules. Presumably the rate of evaporation of the oxygen molecules will be very high so that the molecules remain on the surface only a short time and cover only a small part of the surface. Nevertheless, the velocity of interaction with the underlying monoxide may be sufficient for a perceptible amount of reaction to occur. The rate of consumption of monoxide by this process may be taken as  $\beta\theta_2'$ , where  $\beta$  is the rate at which the interaction would occur if the whole surface were covered with the composite layer. We thus obtain the equation—

$$\alpha_1\theta^2\mu_1 = \nu_1\theta_1 + \beta\theta_2' \quad . \quad . \quad . \quad (41)$$

*Oxygen on Platinum.*—The oxygen condenses on the platinum at the rate  $\alpha_2\theta^2\mu_2$ . It leaves the platinum only by reaction with the carbon monoxide which strikes it. The carbon monoxide is consumed from this cause at the rate  $\epsilon\theta_2\mu_1$ . Since two molecules of monoxide are required to combine with one molecule of oxygen, the rate of consumption is twice that of the oxygen, so that we have—

$$2\alpha_2\theta^2\mu_2 = \epsilon\theta_2\mu_1 \quad . \quad . \quad . \quad (42)$$

*Oxygen on Carbon Monoxide Film.*—We may assume that the rate of evaporation of the oxygen which condenses on the monoxide is large compared to the rate of reaction with the underlying film. We thus obtain the equation—

$$\alpha_2'\theta_1\mu_2 = \nu_2'\theta_2' \quad . \quad . \quad . \quad (43)$$

*Carbon Dioxide.*—The rate of formation of the dioxide ( $2\omega$ ) is given by—

$$2\omega = \beta\theta_2' + \epsilon\theta_2\mu_1 \quad . \quad . \quad . \quad (44)$$

*Constant Sum Condition.*—

$$\theta + \theta_1 + \theta_2 + \theta_2' = 1 \quad . \quad . \quad . \quad (45)$$

If only a small portion of the surface is covered with monoxide it is probable that we are not justified in considering condensation of oxygen molecules on a monoxide film. In any case the amount of reaction between the oxygen and the film would be small compared to that at lower temperature and would have a negligible effect. The only case, therefore, in which we have any interest in assuming that reaction can occur in this manner, is that in which nearly the whole surface is covered with monoxide. Placing  $\theta_1 = 1$  in (41) and (43) and solving equations 41 to 44 we obtain—

$$\omega = \frac{\nu_1\alpha_2\mu_2}{\alpha_1\mu_1} + \frac{1}{2}\epsilon_2'\mu_2 + \frac{\epsilon_2'\alpha_2\mu_2^2}{\alpha_1\mu_1} \quad . \quad . \quad . \quad (46)$$

where 
$$\epsilon_2' = \frac{\alpha_2'\beta}{\nu_2'} \quad . \quad . \quad . \quad (47)$$

The factor  $\epsilon_2'$  represents, out of all the oxygen molecules which strike a surface covered with carbon monoxide, that fraction which reacts to form dioxide. Its significance is thus similar to that of other factors which we have designated by  $\epsilon$ . From the assumptions involved in (43), these equations are valid only when  $\epsilon_2'$  is small compared to unity. It is clear from (47) that this factor should vary with the temperature, but since  $\beta$  and  $\nu_2'$  are both functions of temperature it is not possible to determine in advance whether  $\epsilon_2'$  will increase or decrease with rising temperature.

It should be noted that the first term in (46) is the same as that found for corresponding conditions under Case 1, while the other two terms are of the nature of correction terms that become important only for large pressures of oxygen.

### EXPERIMENTAL PART.

In all the experiments the platinum filaments were mounted in glass bulbs sealed to a vacuum system consisting of Töpler pump, McLeod gauge, and a trap cooled in liquid air placed close to the bulb to condense mercury vapour and the carbon dioxide or water vapour produced by the reaction. The preliminary exhaustion was done by a Gaede rotary mercury pump. All joints in the apparatus were glass sealed to glass and stop-cocks were avoided entirely, mercury seals being used to separate the different parts of the system so that gases could be measured before admitting to the bulb. The McLeod gauge had a sensitiveness such that a reading of 1.0 cm. on the capillary corresponded to a pressure of 0.942 bars. The gauge had been in use several years and had been found to give very reliable readings of pressure.

The gases removed from the system by the Töpler pump were collected over mercury, and could be analysed by measuring the changes in pressure that occurred after adding oxygen or hydrogen and glowing a small platinum wire.<sup>1</sup>

Several different experiments were carried out. These will be described separately.

*Experiment 441.*—The filament in this experiment had a diameter of 0.0077 cm. and a total length of 10.4 cm. and hence a surface of 0.28 sq. cm. It was bent in the form of a single loop welded to heavy platinum leads. It consisted of extremely pure platinum having a temperature coefficient of resistance of 0.0039 between 0° and 100°. The filament was mounted in a small tubular bulb attached to the system by a tube bent in the form of a goose neck so that the bulb could be immersed in liquid air when desired. The total volume of the system including the bulb was 1080 c.c.

*Experiment 443.*—In Experiment 441, because of the small volume of the bulb compared to the rest of the system, the resistance offered by the connecting tubing to the flow of gas was a serious inconvenience and limited the accuracy of the results. To avoid this in Experiment 443, a spherical bulb 20 cm. in diameter was chosen. This was directly connected to an appendix 12 cm. long and 3 cm. diameter which was kept immersed in liquid air to remove the products of reaction as rapidly as possible. Mercury vapour was excluded from the bulb by another liquid air trap. The total volume of the system was 4.75 litres, 4.4 litres being in the bulb

<sup>1</sup> A brief description of this apparatus was published by the writer in the *Four Amer. Chem. Soc.*, **34**, 1310-3 (1912).

and its appendix. The filament was a piece of the same wire as that used in Experiment 441, its length being 11.8 cm., and its surface 0.32 sq. cm.

The temperature of the filament was determined as follows. The wire was the same as that which had been used in measuring the rate of evaporation of platinum,<sup>1</sup> and the temperature for various heating currents (in vacuum) had been determined from the intrinsic brilliancy for a range of temperatures from about 1300° to 2000° K. The change in resistance with the temperature over this range agreed well with the usual values. The total energy radiated (corrected for the cooling effect of the leads as described below) was found to vary with the 4.87 power of the absolute temperature. A table of the resistance and wattage per unit length at temperatures down to room temperature was thus prepared, and from these the current and voltage were calculated. When these were compared with the volts and amperes observed for the filament of this experiment the agreement was found to be excellent (voltage within 1 or 2 per cent. at given current) after correcting for the cooling of the leads.

An analysis of the problem of the cooling effect of the leads<sup>2</sup> shows that the effect is to decrease the voltage drop for the whole filament by an amount which is independent of the diameter of the filament and increases nearly linearly with increase of filament temperature,<sup>3</sup> and for different metals is approximately proportional to  $\sqrt{\rho h}$  where  $\rho$  is the specific resistance and  $h$  is the heat conductivity. But according to the Wiedemann-Franz relation, the product  $\rho h$  is the same for all pure metals. Thus the cooling effect of the leads, if expressed as a voltage correction, is approximately the same for all pure metals. When the ends of the filament are cooled by large leads as in the present experiment, this voltage correction for a single loop (including the effect at the two ends) is

$$\Delta V = 0.00026 (T - 1.3 T_0) \text{ volts}$$

where  $T$  is the temperature of the central portion of the filament, and  $T_0$  is the temperature of the lead. This is accurate only when  $T$  is considerably larger than  $T_0$ . For the low temperatures of these experiments it was estimated that a more accurate expression would be

$$\Delta V = 0.00016 (T - 300) \text{ volts.} \quad . \quad . \quad . \quad (48)$$

The reaction that was studied in this experiment had a high temperature coefficient of velocity. The cooling of the ends of the filament thus decreased the observed velocity. This effect can be calculated readily as it varies only slightly with the temperature coefficient.

The correction that applies to such cases (for platinum or any other pure metal) is given by the formula

$$\Delta V_H = 0.00017 T \phi - 0.05 \text{ volts.} \quad . \quad . \quad . \quad (49)$$

Here  $\Delta V_H$  represents the voltage of a length of uncooled filament which would give the same effect as the *decrease* caused by the cooling of the leads. This equation applies to any quantity  $H$  which varies in proportion to the length of the filament. Thus  $H$  may represent candle power, electron emission, rate of evaporation or velocity of a reaction. Suppose the voltage drop along the filament is 5 volts, and  $\Delta V_H$  is calculated to be 2 volts,

<sup>1</sup> Langmuir and Mackay, *Phys. Rev.*, **4**, 377 (1914).

<sup>2</sup> Langmuir, *ibid.*, **7**, 151 (1916), abstract only.

<sup>3</sup> Langmuir, *General Electric Rev.*, **19**, 210 (1916).

while  $\Delta V$  by (48) is 1 volt. Then if there were no cooling of the ends of the filament, the voltage of the filament would be 5 + 1 or 6 volts. The decrease in the quantity  $H$  caused by the cooling corresponds to 2 volts, and thus amounts to  $\frac{2}{3}$  of the value of  $H$  for the uncooled filament. Thus the corrected value of  $H$  will be  $\frac{3}{2}$  of the observed value of  $H$  for the filaments with ends cooled.

In the above equation  $\phi$  is a number which depends upon the temperature coefficient of the quantity  $H$ . If we let  $n$  represent the exponent of the power of the temperature with which  $H$  increases, then the values of  $\phi$  depend upon  $n$  as follows:—

$n = 0.5$	1.0	2	3	5	10	20	30	50
$\phi = 0.48$	0.85	1.23	1.44	1.72	2.10	2.47	2.69	2.95

On the basis of rough preliminary estimates the temperature coefficient of the reaction velocity was taken to correspond to  $n = 40$  and therefore  $\phi = 2.8$ . The correction actually applied to the reaction velocity to take account of the cooling of the ends of the filament was thus calculated from

$$\Delta V_H = 0.00048 T - 0.05 \text{ volts.}$$

The correction usually resulted in an approximate doubling of the observed reaction velocity.

To measure the temperature of the central portion of the filament, the observed voltage used by the filament was corrected by adding  $\Delta V$  from (48); dividing this by the observed amperes gave the corrected resistance. From the table already prepared the temperature could be found.

A check on the substantial accuracy of these temperatures, even down to temperatures as low as  $450^\circ \text{K.}$ , was obtained by noting the increase in wattage required to maintain constant resistance when pressures of carbon monoxide up to about 60 bars were introduced. The heat conducted away by the gas was found to amount to  $2.4 \times 10^{-6}$  watts per bar per degree temperature difference between the filament and the bulb. This agrees reasonably well with the value  $2.2 \times 10^{-6}$  calculated from the kinetic theory.<sup>1</sup> At a temperature of  $650^\circ \text{K.}$  with 54 bars of carbon monoxide the cooling effect of the gas raised the wattage to 2.3 times its value for the best vacuum. In Experiment 441 the current through the filament was kept constant while the gases reacted in contact with the filament. The decrease in pressure thus caused a gradual increase in temperature which, however, could subsequently be determined from the changes in voltage that were recorded. In Experiment 443 this difficulty was largely avoided by maintaining constant resistance during the reaction with the gas. Because of a decrease in the correction for the cooling by the leads when gas is present, there was still a small rise of temperature amounting in some cases to  $20^\circ$ . Careful consideration shows that Equation 48 for the cooling effect of the leads, although less accurate when considerable gas is present, still gives a very fair approximation.

In Experiment 441 since the volume of the bulb was small compared to the rest of the system, the resistance which the tubing offered to the flow of the gases was often considerable although the tubing was of at least 7 mm. internal diameter. When the filament was raised to high temperature ( $600^\circ \text{K.}$  for hydrogen-oxygen or  $700^\circ$  for carbon-monoxide-oxygen mixtures) the rate of disappearance of the gases became constant, and showed no

<sup>1</sup> Langmuir, *Gen. Electric Rev.*, **19**, 210 (1916).

further increase at higher temperatures. Under these conditions the rate of decrease of pressure was accurately proportional to the pressure, the pressure giving a straight line when plotted on semi-logarithmic paper. The slope of this line corresponded to a rate of 1.18 per minute for equivalent mixtures of oxygen and hydrogen and to 1.06 per minute for carbon-monoxide and oxygen. These rates are expressed in terms of the change in the natural logarithm of the pressure per minute.

Although at lower filament temperatures the rates were less than these maximum rates, they were not so much lower that the resistance to flow of the gases could be neglected. The effect of this resistance was therefore taken into account in the following calculations.

From the pressures read by the McLeod gauge, the quantities of gas in the system (in cubic millimetres at 1 atmosphere and 20° C.) were calculated by merely multiplying the pressure in bars by the volume of the system in cubic centimetres. Let  $q_1$  and  $q_2$  be the quantities of carbon monoxide (or hydrogen) and oxygen respectively, and let  $q_0$  be the excess of one of the gases. If no impurities are present then  $q_0$  is equal to the residue left when the combustion is complete. If there is an excess of carbon monoxide (or hydrogen)

$$q_0 = q_1 - 2q_2 \quad . \quad . \quad . \quad . \quad . \quad (50)$$

while with an excess of oxygen we have

$$q_0 = q_2 - \frac{1}{2}q_1 \quad . \quad . \quad . \quad . \quad . \quad (51)$$

At the relatively low temperatures which were used in Experiment 441, the conditions were favourable for the application of Equation 18. For the present purpose we may assume that  $\alpha_1$  and  $\alpha_2$  are each equal to unity.

Substituting the values of  $\mu_1$  and  $\mu_2$  from (2) in (18) we obtain

$$\omega = v_1 \frac{\mu_2}{\mu_1} = v_1 \frac{\rho_2}{\rho_1} \sqrt{\frac{M_1}{M_2}} = v_1 \frac{q_2}{q_1} \sqrt{\frac{M_1}{M_2}} \quad . \quad . \quad . \quad (52)$$

For mixtures of carbon monoxide and oxygen this gives

$$\omega = 0.93 v_1 \frac{q_2}{q_1} \quad . \quad . \quad . \quad . \quad . \quad (53)$$

while for mixtures of hydrogen and oxygen

$$\omega = 0.25 v_1 \frac{q_2}{q_1} \quad . \quad . \quad . \quad . \quad . \quad (54)$$

When the gases are present in equivalent proportions ( $q_1 = 2q_2$ ) the reaction velocity by (54) is independent of the total pressure. It will be convenient to express the experimental results in terms of  $k$ , the number of cubic millimetres of oxygen which react per *minute* per square centimetre under these conditions. Since there are  $24.6 \times 10^6$  cubic mm. in a gram molecule of gas at room temperature and 1 atmosphere, the relation between  $\omega$  and  $k$  is

$$\omega = 6.8 \times 10^{-10} \cdot k \frac{q_2}{q_1} \text{ g. mols./cm.}^2 \text{ sec.} \quad . \quad . \quad . \quad (55)$$

In order to calculate  $k$  from the experiments we proceed as follows. If



A is the surface of the filament, then from the definition of  $k$  it is evident that

$$\frac{dq_2}{dt} = 2Ak \frac{q_2}{q_1} \quad (56)$$

This equation applies only to conditions in which the resistance to flow through the tubing is negligible. This is not the case in the present experiments. If the reaction velocity were infinite, the resistance of flow through the tube may be defined by

$$R = \frac{dt}{d\ln q} \quad (57)$$

If the filament temperature is lower so that the reaction proceeds more slowly, the filament may be regarded as offering a certain resistance to reaction which may be defined by a similar equation, it being assumed that no resistance is now offered by the tube. In case we must consider the effect of both resistances, we need merely regard them as being in series.<sup>1</sup>

When there is an excess of carbon monoxide or hydrogen we substitute the value of  $q_1$  from (50) into (56) and obtain

$$\frac{dt}{d\ln q_2} = \frac{q_2 + \frac{1}{2}q_0}{Ak} + R \quad (58)$$

Integration of this gives

$$- Ak(t - t_0) = q_2 + (AkR + \frac{1}{2}q_0)\ln q_2 \quad (59)$$

With an excess of oxygen we substitute the value of  $q_2$  from (51) into (56) and obtain

$$\frac{dt}{d\ln q_1} = \frac{q_1^2}{2AK(q_1 + 2q_0)} + R \quad (60)$$

Integration gives

$$- Ak(t - t_0) = AkR\ln q_1 + \frac{1}{2}q_1 - q_0\ln(q_1 + 2q_0) \quad (61)$$

Equations 59 and 61 show how the pressure decreases as a function of the time. In most cases the term involving  $R$  was very small, being a mere correction term. Fig. 1 shows how the pressure varied with the time in typical experiments. The curve marked "Excess of Carbon Monoxide" was calculated by placing  $Ak = 1$ ,  $R = 0$ , and  $q_0 = 1$  in (59). The values of  $q_2$  represent the quantities of oxygen. The corresponding quantities of carbon monoxide ( $q_1$ ) were then calculated by (50), and the total amount of gas was therefore  $q_1 + q_2$ . Assuming a system having a volume of one litre, the pressure in bars is numerically equal to the quantity of gas in cubic millimetres so that the ordinates in Fig. 1 are denoted pressures. In similar manner the curve marked "Excess of Oxygen" is calculated from (61) by making the same substitutions as in the preceding case. Finally the curve marked "Equivalent Proportions" is obtained by placing  $Ak = 1$ ,  $R = 0$ , and  $q_0 = 0$  in either (59) or (61).

<sup>1</sup>This and other methods of handling problems involving the flow of gases in vacuum systems is discussed at length in a paper by the writer on the condensation pump, *Gen. Electric Rev.*, 19, 1062 (1916).

At very high pressures the three curves tend to be straight and to have the same slope since the ratio of the pressures of the two gases is then nearly constant. With the gases in equivalent proportions, the curve remains straight down to low pressures. With an excess of carbon monoxide, as this gas begins to accumulate, the reaction slows up and the pressure finally approaches a horizontal asymptote, the reaction velocity becoming proportional to the residual partial pressure of oxygen. With an excess of oxygen, however, the reaction velocity increases without limit as the pressure of carbon monoxide decreases to zero. Of course actually the velocity would become limited by the factors in (15) which we have neglected in deriving (59) and (61). The curves obtained from the experimental data with carbon monoxide and oxygen were practically identical with those of Fig. 1. With an excess of oxygen, the velocity always became so great at the end of the run that it could not be measured, even with the lowest temperatures at which the reaction could be made to begin.

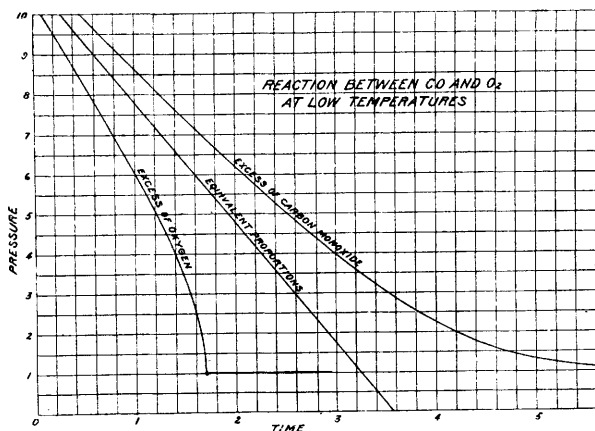


FIG. 1.

The results obtained with mixtures of carbon monoxide and oxygen in Experiments 441 and 443 are given in Table I. The second column gives the temperature of the central portion of the filament as found from the resistance corrected for the cooling effect of the leads in the manner already described. The third column gives the value of the velocity constant  $k$  expressed in cubic millimetres of oxygen which react per minute per square centimetre of filament surface with equivalent proportions of the gases, as defined by Equation (56). To determine this "constant" from the experimental data the procedure was as follows:—

The pressures of gas in the system were recorded at regular intervals of one minute. From the known composition of the gas mixture which was introduced, and also from the final residue of gas remaining when the reaction was complete, it was possible to calculate the partial pressure of each constituent at each of these periods and from these the quantities  $q_2$  and  $q_2$ . By substituting these in (59) or (61) (according to which gas was in excess), values for  $Ak(t - t_0)$  were obtained. These were plotted against the time in minutes. The points were found to lie on approximately straight lines as long as the temperature remained constant. Because of

the tendency for the filament temperature to increase even when the resistance was kept constant, resulting from the decreasing importance of the cooling effect of the leads, the curves gradually became steeper as the pressure fell. The curve was therefore usually divided into three parts and the slope and temperature recorded separately for each part. The slope thus obtained should be equal to  $Ak$ . Dividing this by the surface of the filament  $A$  yields the value of  $k$  given in Table I.

TABLE I.

VELOCITY OF REACTION BETWEEN CARBON MONOXIDE AND OXYGEN AT RELATIVELY LOW TEMPERATURES.

*Experiment 441.*

No.	Temperature ° K.	Reaction Velocity $k$ mm. <sup>2</sup> /min. cm. <sup>2</sup>	Time $t$ , in Min.	Initial Pressures. Bars.			Final Pressures. Bars.		
				CO $p_1$ .	O <sub>2</sub> $p_2$ .	Ratio $p_1:p_2$ .	CO $p_1$ .	O <sub>2</sub> $p_2$ .	Ratio $p_1:p_2$ .
1	506	0.06	7	3.40	1.94	1.79	3.34	1.90	1.76
2	569	1.6	3	3.16	1.43	2.21	2.89	1.30	2.22
3	581	2.0	5	2.89	1.30	2.22	2.26	0.99	2.28
4	592	3.5	11	2.26	0.99	2.28	0.31	0.02	15
5	572	1.7	3	3.75	1.28	2.94	3.43	1.12	3.06
6	578	2.0	4	3.43	1.12	3.06	2.98	0.89	3.35
7	585	2.2	6	2.98	0.89	3.35	2.23	0.52	4.3
8	592	2.5	32	2.23	0.52	4.3	1.20	0.006	200
9	592	3.5	3	1.67	2.33	1.39	0.03	1.51	0.02

*Experiment 443.*

1	577	0.9	4	17.6	23.3	0.75	—	—	—
2	718	123	2	3.11	4.23	0.74	0.05	2.70	0.02
3	716	96	3	3.78	4.04	0.94	0.03	2.15	0.014
4	603	1.2	1	5.25	11.43	0.46	5.15	11.40	0.45
5	606	2.4	1	5.15	11.40	0.45	4.83	11.22	0.43
6	630	12	2	4.67	11.18	0.42	0.65	9.15	0.07
7	608	7.8	7	56.8	8.64	6.58	54.4	7.95	6.83
8	644	74	14	51.9	7.74	6.71	45.3	3.41	13.3
9	648	85	21	45.3	3.41	13.3	40.1	0.80	50.3
10	725	1000	3	40.1	0.80	50.3	38.8	0.14	277
11	609	14	3	38.0	21.7	1.75	36.4	21.0	1.73
12	612	20	8.5	36.4	21.0	1.73	30.3	17.9	1.69
13	622	29	19.5	30.3	17.9	1.69	7.55	6.53	1.15

In carrying out this calculation, the value of  $R$  (the resistance of the tubing to the flow of gas) was placed equal to 0.94 minutes, this being the reciprocal of 1.06, the logarithmic rate of decrease in pressure with the filament at very high temperature, which we have already discussed. For Experiment 443 the value of  $R$  was taken to be zero. In using (59) or (61) for the data of Experiment 441 it was thus necessary to make a preliminary estimate of  $k$  to use in the correction containing  $R$ . After the new value of  $k$  was found from the slope of the line, a second approximation could be carried out if needed.

The fourth column of Table I. gives the time in minutes covered by the portion of the curve from which the value of  $k$  was calculated. In every case the points (one per minute) over this time interval gave very satisfactory agreement with a straight line.

The remaining columns give the partial pressures of the two gases in

bars at the beginning and at the end of the time interval shown in column 4, and also the ratios between the pressures of carbon monoxide and oxygen. These ratios are of interest as they are inversely proportional to the reaction velocity at any given temperature, and show the range of velocities covered by the experiments.

The values of  $k$  recorded in Table I. are plotted in Fig. 2. The points may be identified by comparing the numbers marking the points in Fig. 2 with the numbers in the first column of Table I. The data of Experiment 441 are indicated by crosses, while those of Experiment 443 are shown by circles.

From (53) and (55) we see that the reaction velocity  $k$  increases in proportion to  $v_1$  the rate of evaporation of carbon monoxide from the surface. Rates of evaporation are in general proportional to vapour pressures, and we know that the logarithm of a vapour pressure plotted against the reciprocal of the absolute temperature gives a straight line, whose slope

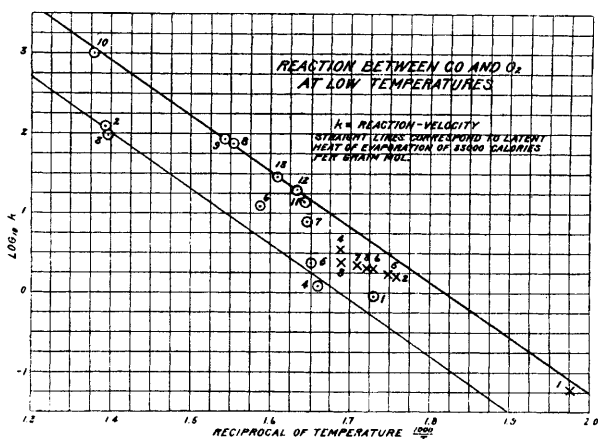


FIG. 2.

multiplied by 4.57 gives the latent heat of evaporation in calories per gram molecule. In Fig. 2 the values of  $k$  are plotted in this way so that the slope of the line should be a measure of the latent heat of evaporation of carbon monoxide adsorbed on platinum.

An examination of the points in Fig. 2 shows that although the values of  $k$  cover a range of about 17,000 fold they lie in a general way along a straight line. Closer examination shows that the values of  $k$  tended to increase steadily in the order in which the experiments were carried out, indicating that the filament was undergoing a progressive change in the direction of becoming a better catalyst or possibly that there was a change in resistance which led to the calculated temperatures being too low. Against this latter hypothesis stands the fact that the relation between the volts and the amperes, for the filament in good vacuum did not change noticeably. The extreme range of this effect, however, changed the velocity only about seven fold as compared to the 17,000 fold range covered by the experiments. In experiments with hydrogen and oxygen a similar increase of the activity with the time is observed, and is very much more marked than in experiments with carbon monoxide.

Taking the heavy straight line in Fig. 2 as representing the final values, we find that this corresponds to the equation ( $k$  in mm.<sup>3</sup> of oxygen per minute per cm.<sup>2</sup>)—

$$\log_{10} k = 12.666 - \frac{6963}{T} \quad . \quad . \quad . \quad (62)$$

The slope indicates that the latent heat of evaporation of the carbon monoxide from the platinum surface is 31,800 calories per gram molecule, which is nearly half as great as the heat of combustion of carbon monoxide. This confirms the view that there is a firm chemical union between the carbon monoxide and the platinum.

Table II. contains values of  $k$  calculated from (62) from room temperature up to 1000° K.

By eliminating  $\omega$  between (53) and (55) we find—

$$v_1 = 7.2 \times 10^{-10} k \text{ g. mols./cm.}^2 \text{ sec.} \quad . \quad . \quad . \quad (63)$$

which enables us to calculate the rate of evaporation of the carbon monoxide from the platinum into a perfect vacuum. If a substance such as a metal evaporates at a known rate, the vapour pressure can be calculated from Equation 3. The conditions are somewhat different with an adsorbed film, for condensation cannot occur at the same rate as the evaporation when the surface remains covered with the substance. However, if we apply (3) to an adsorbed film, placing  $\nu = \mu$ , the pressure that we calculate in this way is that at which about one-half of the surface is covered with adsorbed gas, for the rate of condensation is then half what it would be on a bare surface and the rate of evaporation is half of that from a completely covered surface. We cannot regard this calculated pressure as a true vapour pressure, but it has a valuable physical significance. The third column of Table II. contains the "vapour pressure" determined in this manner.

The ratio between this vapour pressure and the actual pressure of carbon monoxide in contact with the platinum at any time, is approximately equal to  $\theta$ , the fraction of the surface which is bare. Thus we may conclude that if we have a pressure of carbon monoxide as low as 0.001 bar in contact with platinum at 500° K., about 97 per cent. of the surface will be covered. These figures also show that at a temperature below 450° K. it should be impossible in any reasonable time to remove an adsorbed film of carbon monoxide merely by pumping off the gas with a good vacuum pump. At 600° or higher, however, the pressure of gas produced by evaporation from the film is high enough so that most of the gas could be pumped off in a rather short time. These conclusions are in complete accord with experiments on the adsorption of carbon monoxide by platinum.<sup>1</sup>

The fourth column of Table II. contains data on the average life  $t$  of the carbon monoxide molecules on the platinum surface. If  $N_0$  is the number of spaces in the surface checker-board, or the maximum number of molecules that can be adsorbed per unit area, and  $N$  is the Avogadro constant,  $6.06 \times 10^{23}$ , then the average life of a molecule is—

$$t = \frac{N_0}{Nv_1} \quad . \quad . \quad . \quad . \quad . \quad (64)$$

<sup>1</sup> Langmuir, *Four. Amer. Chem. Soc.*, **40**, 1398 (1918).

TABLE II.

REACTION BETWEEN CARBON MONOXIDE AND OXYGEN AT LOW TEMPERATURES.

Temperature T.	Reaction Velocity $k$ mm. <sup>3</sup> /min. cm. <sup>2</sup>	Pressure $p$ bars.	Average Life $t$ Seconds.
300°K	$2.86 \times 10^{-11}$	$4.31 \times 10^{-14}$	$1.2 \times 10^{11}$
350	$5.92 \times 10^{-8}$	$9.60 \times 10^{-11}$	$5.8 \times 10^7$
400	$1.81 \times 10^{-5}$	$3.14 \times 10^{-8}$	$1.9 \times 10^5$
450	0.0016	$2.87 \times 10^{-6}$	2200
500	0.055	$1.06 \times 10^{-4}$	63
550	1.01	0.00207	3.3
600	11.5	0.0244	0.30
650	81.4	0.197	0.038
700	523	1.20	0.0066
750	2410	5.75	0.0014
800	9200	22.4	0.00038
900	85000	222	0.00004
1000	505000	1390	0.00001

Placing  $N_0 = 1.5 \times 10^{15}$  molecules per square centimetre, and substituting the value of  $v_1$  from (63), we obtain—

$$t = \frac{3.46}{k} \text{ seconds}$$

from which the data of Table II. were prepared. This average life represents the time that would be required for the amount of carbon monoxide on the surface to fall to one  $e$ th of its original value when the platinum is in a perfect vacuum. Again we see that 450° is about the lower limit at which we can expect the carbon monoxide to leave the surface spontaneously. Although this result is in accord with the experiments which showed that carbon monoxide cannot be pumped off below 500° K., it does not seem to agree with Faraday's observation that this gas has only a temporary effect in stopping catalytic action. Faraday found that traces of monoxide prevented the combination of oxygen and hydrogen on platinum, but the reaction started as soon as the platinum was transferred to pure hydrogen-oxygen mixtures. The foregoing calculations and experimental results prove that the spontaneous recovery of activity cannot be due to evaporation of carbon monoxide from the platinum. The removal of the monoxide under these conditions must result from reaction between the monoxide and the impinging oxygen molecules, as was considered under Case 3. This conclusion is also in accord with direct experiments, for when a monoxide film on platinum at room temperature is brought into contact with oxygen at low pressure, the monoxide is removed, carbon dioxide is formed, and the surface becomes covered by adsorbed oxygen (*loc. cit.*, p. 1396.)

Some later experiments on the velocity of reaction between carbon monoxide and oxygen (Experiment 482 carried out in 1916) gave a measure of the velocity with which adsorbed monoxide is capable of reacting with oxygen.<sup>1</sup>

<sup>1</sup> Experiment 482 includes work with many mixtures of carbon monoxide and oxygen at several temperatures. The writer has not yet found an opportunity to calculate the detailed results of these Experiments as he has for Experiments 441 to 445. The results confirm those of Experiments 441 and 443. The detailed results of Experiment 482 will probably be considered in a subsequent paper.

The catalyst consisted of a cylinder of platinum foil 1.3 cm. diameter and 4.0 cm. length, closed at one end while the other end was sealed to a short but large diameter glass tube connecting to a bulb of about 4.5 litres capacity. The platinum surface of 17.1 sq. cm. was maintained at a constant temperature of 200° C. by an electrically heated oven. A pressure of 160 bars of a mixture of carbon monoxide and oxygen in exactly equivalent proportions was admitted to the system. According to Equation 18, since the ratio of the partial pressures of the two gases remains constant, the rate of reaction should be constant so that the pressure should vary linearly with the time. Actually, however, the plot of pressure against time gives a distinctly curved line. Expressing the velocity in terms of the number of cubic millimetres of oxygen reacting per minute per square centimetre of catalyst surface we find

$$K = 0.052 + 0.00132 p_2 \quad . \quad . \quad . \quad (66)$$

$p_2$  being the partial pressure of oxygen in bars.

For the case of equivalent proportions of carbon monoxide and oxygen, the last two terms of Equation 46 can be combined into one so that the equation takes the same form as (66). Substituting the numerical values  $\mu_1$ ,  $\mu_2$  and  $\omega$  from (3) and (55) into (46), and by comparing with (66), we find

$$\begin{aligned} k_0 &= 0.052 \text{ mm.}^3 \text{ of O}_2 \text{ per cm.}^2 \text{ per min.} \\ \text{and } \epsilon'_2 &= 2.1 \times 10^{-12}. \end{aligned}$$

The value of  $k_0$  agrees with that given for 500° K (227° C.) in Table II.

Thus the removal of the carbon monoxide from the surface occurs in two ways: (1) By collision of monoxide molecules from the gas phase with adsorbed oxygen atoms on the surface. We shall see that nearly every such collision results in combination; (2) By reaction between oxygen molecules from the gas phase with adsorbed monoxide molecules. Only one out of  $5 \times 10^{11}$  molecules of oxygen which strike the surface at 200° C. react with the monoxide. This low rate of reaction indicates that the reaction does not occur as a result of the collision of a molecule with the surface, but may occur at any time during the very short interval that elapses between the condensation and the evaporation of an oxygen molecule on the surface.

From the above data the life of a monoxide molecule on the surface at 200° C. is 1360 seconds, with a pressure of oxygen of one bar, assuming for the present that no evaporation of monoxide occurs. This life is inversely proportional to the pressure of oxygen. Thus, with a pressure of oxygen of fifty bars, the carbon monoxide film should be removed in about half a minute, with the platinum at 200°. The experiments on adsorption by platinum have shown that even at room temperature most of the adsorbed monoxide film is removed in a few minutes by such pressures of oxygen. This indicates that  $\epsilon'_2$  changes very little with the temperature. At low temperatures we should therefore expect the last two terms of (46) to become relatively more important.

*Reaction between Hydrogen and Oxygen.*—In Experiments 441, 443 and 482 the data obtained with hydrogen and oxygen were very erratic compared to those obtained with carbon monoxide and oxygen. The reaction velocity was always greater than with the monoxide, but seemed to depend to a large extent upon the past history of the platinum surface. When the previous treatment of the platinum was alike in two cases it was found that

the reaction was much higher with an excess of oxygen than with excess of hydrogen. In a few of the runs (in Experiment 443) in which an excess of oxygen was present, the pressure decreased at an accelerating rate just as in the corresponding runs with carbon monoxide. In these cases the activity of the platinum was not high, so that the velocity was only a little greater than with the monoxide. This result showed that the reaction took place principally between adsorbed oxygen atoms and hydrogen molecules which strike against them. Adsorbed hydrogen then acts as a catalytic poison.

With the platinum in a more active condition, especially in Experiment 482 where the reaction often occurred rapidly at room temperature, the reaction always took place most rapidly at the highest pressures. It seems, therefore, that the activation of the platinum is caused by some condition which favours interaction between adsorbed hydrogen atoms and oxygen which strikes the surface. The variability of the reaction velocity, however, makes it difficult to obtain reliable data.

*Experiment 445.—Reaction Velocity at Higher Filament Temperature.*—With the filaments and bulbs used in Experiments 441 and 443, the reaction velocity became too great to measure when the filament temperature was raised above about 725° K. In order to determine the velocity at higher temperatures, the length of the filament was decreased as much as possible. In Experiment 444 the filament consisted of a piece 4 mm. long of the same platinum wire that was used in Experiment 443 (diameter 0.0077 cm.). This was welded to moderately heavy platinum leads. It was found that the temperature of this filament, as indicated by its resistance, continued to rise for several minutes after the current was turned on. This was due to the gradual heating up of the leads. The data on the reaction velocity obtained in this experiment were therefore unreliable and are not worth recording here. To avoid this difficulty, another bulb was made up (Exp. 445) with a filament of much smaller diameter, only 0.00305 cm., and a length of 0.72 cm. The leads were of very heavy platinum wire, 0.056 cm. diameter, doubled back and twisted so as to form a small loop, into which the ends of the filament were clamped. These leads were so heavy compared to the filament that they did not become perceptibly heated. The total energy input into the filament at 1300° K. was only about 0.07 watt. Because of the small diameter of the filament and the relatively large extent to which it was cooled by the leads, it reached its maximum temperature almost immediately after turning on the current. The total surface of the filament was 0.0069 sq. cm., but because of the cooler ends the effective area was considerably less.

Because of the short length of the filament, the cooling by the leads was so great that the current needed to heat the filament to a bright red heat was two or three times that which would have been needed to melt the filament if a long piece had been used. The heat radiated was thus negligible compared with that conducted to the leads. Under these conditions the temperature distribution along the filament can be readily calculated. Assuming a constant heat conductivity for platinum equal to that at room temperature, and taking the electric resistance proportional to the absolute temperature, it can be readily shown that the temperature  $T$  at a point at a distance  $x$  from the centre of the filament is

$$T = T_1 \cos (1680Lx) \quad . \quad . \quad . \quad (67)$$

the angle being expressed in degrees, and  $x$  in cm., while  $T_1$  is the tempera-



ture at the centre of the filament, and  $I$  is the heating current in amperes. The uncertainty as to the thermal contact at the leads makes it impractical to calculate the maximum temperature  $T_1$  in this way. The temperatures were therefore estimated by the brilliancy of the light from the filament. A current of 0.08 amperes gave a temperature estimated to be  $1000^\circ\text{K}$  while 0.13 amperes gave  $1500^\circ$ . The filament finally melted at the end of the experiment, with a current of 0.17 amperes. Allowing for probable volatilization before melting we may assume a temperature of  $1900^\circ$  corresponding to 0.17 amperes. These temperatures and currents give a straight line plot on double logarithmic paper, and this plot was therefore used for determining intermediate temperatures. It is evident that this temperature scale is only rough.

The filament was mounted in a large spherical bulb of 4.2 litres capacity, as in Experiment 443, the total volume of the system being 4.75 litres.

In carrying out the experiments, mixtures of carbon monoxide and oxygen or hydrogen and oxygen were introduced into the system, the pressure was read on the gauge, and the filament was heated to a given temperature, while gauge readings were taken every minute.

Filament temperatures ranging from  $900^\circ\text{K}$  to  $1500^\circ$  were employed in the experiments with carbon monoxide, while temperatures from  $900^\circ$  to  $1900^\circ$  were used with hydrogen. With a large excess of any gas present, the velocity was found to be proportional to the amount of combustible mixture still present. Thus if  $q$  is the quantity of mixture in the system at any time  $t$  and  $q_0$  is the residue of gas remaining after the combustion is complete, it was found that  $q - q_0$  plotted against  $t$  on semi-logarithmic paper, gave a straight line when either oxygen or carbon monoxide (or hydrogen) was present in large excess. The same relation also held when the gases were present in equivalent proportions. But if one of the gases was present in only moderate excess, the plot on semi-logarithmic paper was very distinctly curved.

These results are just what our theory has taught us to expect. With a large excess of oxygen the velocity of the reaction according to either Case 1 or 2 (Equations 19 or 33) is proportional to the partial pressure of carbon monoxide, while with an excess of monoxide the velocity is proportional to the pressure of oxygen. With equivalent proportions the ratio of the partial pressures remains constant and it is then readily seen from the theory that the velocity is proportional to the partial pressure of either gas. A quantitative study of the experimental results enables us not only to determine the numerical values of the coefficients  $\epsilon$  and  $\alpha_2$  but allows us to choose between the two theories treated under Cases 1 and 2.

Tables 3 and 4 contain the data furnished by two typical runs with mixtures of carbon monoxide and oxygen.

In preparing these tables, the experimentally determined values of  $q - q_0$  were plotted on semi-logarithmic paper. A smooth curve was drawn through the points, and tangents were drawn at several points which corresponded to certain evenly spaced values of  $q$  such as 150, 90, 60, 45, etc. The slopes of the tangents at these points are recorded in the tables under the heading  $s$  in the fifth column. The slopes are expressed in terms of the change in the natural logarithm of  $q - q_0$  per minute. The second and third columns give the quantities of carbon monoxide and oxygen in the system at the times  $t$  given in the first column.

In order to compare the results of the experiments with the theory which led to the derivation of (19) and (33) we need to calculate the quantity  $r$ ,

TABLE III.

REACTION BETWEEN CARBON MONOXIDE AND OXYGEN WITH HIGH FILAMENT TEMPERATURE (1110° K.) AND EXCESS OF OXYGEN.

Time <i>t</i> Min.	<i>q</i> <sub>1</sub> mm. <sup>3</sup> of CO.	<i>q</i> <sub>2</sub> mm. <sup>3</sup> of O <sub>2</sub> .	<i>r</i> by (34)	<i>s</i> per Min.	Case 1.		Case 2.	
					<i>θ</i> <sub>2</sub> .	<i>s</i> <sub>1</sub> .	<i>θ</i> <sub>2</sub> .	<i>s</i> <sub>1</sub>
0.9	96	102	0.500	0.153	0.80	0.192	0.50	0.31
3.4	60	84	0.384	0.210	0.84	0.25	0.54	0.39
6.3	30	69	0.232	0.252	0.90	0.28	0.62	0.41
8.6	16	62	0.136	0.281	0.94	0.30	0.69	0.41
10.1	8	58	0.074	0.292	0.96	0.31	0.76	0.38
13.4	4	56	0.038	0.316	0.98	0.32	0.82	0.39

TABLE IV.

REACTION BETWEEN CARBON MONOXIDE AND OXYGEN WITH HIGH FILAMENT TEMPERATURE (1110° K.) AND EXCESS OF MONOXIDE.

Time <i>t</i> Min.	<i>q</i> <sub>1</sub> mm. <sup>3</sup> of CO.	<i>q</i> <sub>2</sub> mm. <sup>3</sup> of O <sub>2</sub> .	<i>r</i> by (34).	<i>s</i> per Min.	Case 1.		Case 2.	
					<i>rθ</i> <sub>2</sub> .	<i>s</i> <sub>2</sub> .	<i>rθ</i> <sub>2</sub> .	<i>s</i> <sub>2</sub> .
0.3	153	50	3.06	0.135	0.755	0.179	0.628	0.215
3.9	113	30	3.76	0.145	0.790	0.184	0.676	0.214
6.6	93	20	4.65	0.153	0.823	0.186	0.718	0.213
11.1	73	10	7.3	0.165	0.879	0.188	0.792	0.208
15.2	63	5	12.6	0.172	0.926	0.186	0.867	0.198
17.9	59	3	19.6	0.181	0.952	0.190	0.911	0.199
21.6	56	1.5	37	0.194	0.975	0.199	0.948	0.204
24.5	54.6	0.8	68	0.205	0.986	0.208	0.970	0.211

defined by (34). Substituting the numerical values for *M* and placing *T* = 300° K. and *q* = 4.75 *p* in (3) gives

$$\mu_1 = 1.005 \times 10^{-7} q_1 \text{ for CO} \quad . \quad . \quad . \quad (68)$$

$$\mu_2 = 0.941 \times 10^{-7} q_2 \text{ for O}_2 \quad . \quad . \quad . \quad (69)$$

Equation (34) thus gives

$$r = 0.535 \frac{\epsilon q_1}{a_2 q_2} \quad . \quad . \quad . \quad (70)$$

The values of *r* in the fourth column of Table III. were calculated from this equation by placing  $\epsilon$  and *a*<sub>2</sub> each equal to unity, while those in Table IV. were obtained by placing  $\epsilon$  = 1 and *a*<sub>2</sub> = 0.535 which gives *r* equal to the ratio of *q*<sub>1</sub> to *q*<sub>2</sub>. The reason for choosing these values will be explained later.

As we have already seen, the theory indicates that with a very large excess of either oxygen or monoxide, the value of *s* should remain constant as the total pressure decreases. The excess of oxygen shown in Table III. and the excess of monoxide in Table IV. are not sufficient to give strictly constant values of *s*. It is seen in each case that *s* increases at first rather rapidly and then more slowly and approaches a limiting value as the gas present in smaller amount tends to disappear. In order to calculate these



two spaces upon the surface, the carbon atom being presumably attached to two platinum atoms by its two bonds.

The data in Tables III. and IV. represents only those taken at a particular filament temperature. The results obtained at other temperatures were plotted and calculated in the same manner. The limiting values  $s_1$  and  $s_2$  calculated according to Case 2 were in every instance more nearly constant than those found by the equations for Case 1. The results given by all these experiments is summarised in Tables V., VI., and VII.

TABLE V.  
REACTION AT HIGH TEMPERATURES WITH AN EXCESS OF OXYGEN.

Run No.	Fil. Temp. ° K.	Limiting Velocity $s_1$ .	$\lambda\epsilon$ .	$\lambda_{cal}$ .
6	900	0.84	0.82	0.75
5	1110	0.40	0.39	0.50
1	1260	0.35	0.34	0.32
3	1350	0.215	0.21	0.28
4	1500	0.16	0.16	0.15

TABLE VI.  
REACTION AT HIGH TEMPERATURES WITH AN EXCESS OF CARBON MONOXIDE.

Run No.	Filament Temperature. °K.	Limiting Velocity. $s_2$ .	$\lambda a_2$ .	$a_2$ .
10	900	0.26	0.274	0.33
8	1110	0.210	0.221	0.56
7	1260	0.143	0.150	0.71
9	1500	0.110	0.116	0.73

TABLE VII.  
REACTION AT HIGH TEMPERATURES WITH EQUIVALENT PROPORTIONS OF OXYGEN  
AND MONOXIDE.

Run No.	Filament Temperature. °K.	Observed Velocity. $s$ .	Calculated Velocity.					
			From $s_1$ $a_2 = 1$ .			From $s_2$ $a_2$ variable.		
			$r$ .	$\theta_2$ .	$s_c$ .	$r$ .	$r\theta_2$ .	$s_c$ .
13	900	0.17	1.07	0.372	0.32	3.25	0.64	0.166
11	1110	0.14	1.07	0.372	0.15	1.91	0.52	0.110
2	1260	0.104	1.07	0.372	0.13	1.51	0.47	0.067
12	1500	0.051	1.07	0.372	0.06	1.46	0.46	0.051

From the limiting velocities  $s_1$  and  $s_2$  we may now determine approximate values for the coefficients  $\epsilon$  and  $a_2$ . Equations 20 or 32 enable us to calculate  $\epsilon$  from  $s_1$  while we may obtain  $a_2$  from  $s_2$  by means of (21) or (31). Expressing  $q_2$  in cubic millimetres and  $t$  in minutes, while  $\omega$  is in g. mols. per square cm. per second, we find

$$-\omega = \frac{1}{24.6 \times 10^6 \times 60 \text{ A}} \frac{dq_2}{dt}$$

since there are  $24.6 \times 10^6$  cubic mm. per g. mol. of gas. In this equation A represents the effective surface of the filament. The total filament surface was 0.0069 sq. cm., but because of the cooled ends, only a certain fraction  $\lambda$  was effective in causing reaction. Taking the effective area as 0.0069  $\lambda$ , the above equation becomes

$$-\omega = \frac{9.84 \times 10^{-8}}{\lambda} \frac{dq_2}{dt} \quad . \quad . \quad . \quad (76)$$

Substituting this value of  $\omega$  and the value of  $\mu_1$  from (68) in (20) or (32), and remembering that  $s_1$  is equal to  $\frac{1}{q_1} \frac{dq_1}{dt}$  and that  $dq_1 = 2dq_2$  we find

$$s_1 = 1.020 \lambda \epsilon \quad . \quad . \quad . \quad . \quad (77)$$

Similarly by substituting (76) and (69) into (21) or (31), and remembering that  $s_2$  is equal to  $\frac{1}{q_2} \frac{dq_2}{dt}$  we obtain

$$s_2 = 0.955 \lambda a_2 \quad . \quad . \quad . \quad . \quad (78)$$

The values of  $\lambda \epsilon$  in Table V. and  $\lambda a_2$  in Table VI. were calculated from the corresponding limiting velocities by means of these equations. Since  $\lambda$  must be less than unity, it is evident from the values of  $\lambda \epsilon$  in Table V. that  $\epsilon$  must be very close to unity. In other words, nearly every carbon monoxide molecule which strikes an adsorbed film of oxygen atoms on a platinum surface at about 1000° K. reacts to form carbon dioxide.

The decrease in  $\lambda \epsilon$  at higher temperatures is of particular interest. Because of the cooling by the leads, and the negative temperature coefficient, most of the reaction must occur near the ends of the filament when the filament temperature is high. By means of (67), the temperature distribution along the filament can be calculated. Assuming that the reaction occurs only at those parts of the filament where the temperature lies between 750° and 1050° K., the values of  $\lambda$  for each filament temperature have been calculated and are recorded in the last column of Table V. It is seen that  $\lambda$  calculated in this way is approximately equal to the value of  $\lambda \epsilon$  for the same temperature. At any rate the agreement seems to justify, within the probable experimental error, the conclusion that over a range of temperatures from 800° to 1000° K., and with a sufficiently large excess of oxygen, the surface of the filament is covered by atomic oxygen which reacts with every molecule of carbon monoxide which strikes it. At lower temperatures the reaction velocity decreases rapidly because the surface becomes covered with monoxide, while at higher temperatures the velocity also decreases rapidly and becomes negligible at temperatures much above 1100° K.

The data of Table VI. show that  $\lambda a_2$  is also of the order of magnitude of unity. Assuming that  $\epsilon$  is equal to unity, we may take the data in the fourth column of Table V. as giving the values of  $\lambda$ . Dividing these into  $\lambda a_2$  given in the fourth column of Table VI., we obtain  $a_2$  as recorded in the last column. These values are not very far from unity, and show a distinct tendency to become unity at the higher temperatures. It seems

improbable that  $a_2$  should be inherently variable. We should rather look for some secondary cause for the variation. An explanation in accord with all the facts is obtained by assuming that the surface of the platinum is not perfectly homogeneous, but that certain of the elementary spaces hold carbon monoxide much more firmly than other spaces do, so that from a portion of the surface the monoxide evaporates more slowly. Thus when there is an excess of monoxide a part of the surface is more or less permanently covered with a film of monoxide while the rest of the surface remains bare and allows the reaction to proceed in accord with the theory already developed. With an excess of oxygen instead of monoxide, the monoxide film would tend to disappear owing to the interaction with the oxygen such as that observed with in Experiment 482 and in the experiments on adsorption by platinum surfaces.

According to this explanation, the values of  $a_2$  in Table VI. give the fraction of the surface which is not poisoned by the semi-permanent film of monoxide. As the temperature is raised it is therefore natural that the value of  $a_2$  should increase, for less of the surface is covered by this film. When there is an excess of oxygen, the value of  $a_2$  should increase to unity according to this theory. In Table III.  $r$  was calculated by taking  $a_2 = 1$ . If, however, the value  $a_2 = 0.53$  is taken as in Table IV.,  $s_1$  does not come out nearly so constant. This result seems then to confirm the conclusion that  $a_2$  differs appreciably from unity only when a considerable pressure of monoxide is present.

Table VII. contains the results of some experiments with equivalent proportions of carbon monoxide and oxygen. In these runs the observed values of  $s$ , in accord with the theory, remained practically constant as the pressure decreased. The sixth and ninth columns contain values of  $s$  calculated from the data of Tables V. and VI. for the case of equivalent proportions. Because of the uncertainty regarding the value of  $a_2$ , two methods were employed in calculating  $s$ .

In the first method  $a_2$  and  $\epsilon$  were assumed equal to unity as they were in the calculations of Table III., and  $r$  was found from (70), placing  $q_1 = 2q_2$ . From this,  $\theta_2$  was obtained by (35), and  $s$  was then calculated by (72) from the values of  $s_1$  given in Table V.

By the second method  $\epsilon$  was taken equal to unity, but the values of  $a_2$  used in calculating  $r$  were taken from Table VI., and  $s$  was then obtained by (74) from  $s_2$  in Table VI.

The observed values of  $s$  in Table VII. lie between those calculated by the two different methods. This indicates that with equivalent proportions of the two gases the values of  $a_2$  approach unity a little more closely than those corresponding to a large excess of monoxide. This is quite in accord with explanation offered.

It is of interest to note that with equivalent proportions  $s$  is smaller than if either one of the gases is present in excess. It is readily seen by (33) that this is in accord with the theory.

The actual reaction velocities observed in Experiment 445 were very much higher than those of Experiments 441 and 443. Thus according to the data of Table VII., at a temperature of  $900^\circ \text{K}$ ., and a total pressure of 60 bars of mixture in equivalent proportions, the rate of reaction corresponds to 3300 cubic mm. of oxygen per minute per square cm. of effective filament surface. By comparison with the values of  $k$  given in Table II., we see that such a high velocity could be attained by the low temperature type of reaction only at temperatures a little above  $750^\circ \text{K}$ . It is evident that at about this temperature the temperature coefficient of the

reaction velocity must become negligible. This deduction checks well with the conclusion already reached that the effective surface of the filament is that portion which has a temperature between  $750^\circ$  and  $1050^\circ$  K.

*Reaction between Hydrogen and Oxygen.*—With mixtures of hydrogen and oxygen in contact with platinum at high temperature the results were very similar to those found with carbon monoxide and oxygen. Tables VIII. and IX. give typical experimental data, the arrangement being the same as in Tables III. and IV.

TABLE VIII.

REACTION BETWEEN HYDROGEN AND OXYGEN WITH HIGH FILAMENT TEMPERATURE ( $1110^\circ$  K.) AND EXCESS OF OXYGEN.

Time <i>t</i> Min.	$q_1$ mm. <sup>3</sup> of H <sub>2</sub> .	$q_2$ mm. <sup>3</sup> of O <sub>2</sub> .	$r$ by (34).	$s$ (per Min.).	$\theta_2$ .	$s_1$ .
0.25	60	92	1.31	0.575	0.338	1.70
0.90	40	82	0.98	0.75	0.385	1.94
1.60	20	72	0.56	1.05	0.481	2.19
2.25	10	67	0.30	1.22	0.582	2.10
2.95	4	64	0.12	1.34	0.702	1.94

TABLE IX.

REACTION BETWEEN HYDROGEN AND OXYGEN WITH HIGH FILAMENT TEMPERATURE ( $1110^\circ$  K.) AND EXCESS OF HYDROGEN.

Time <i>t</i> Min.	$q_1$ mm. <sup>3</sup> of H <sub>2</sub> .	$q_2$ mm. <sup>3</sup> of O <sub>2</sub> .	$r$ by (34).	$s$ (per Min.).	$r\theta_2$ .	$s_2$ .
1.5	105	25	8.4	0.49	0.815	0.60
2.7	83	14	10.8	0.51	0.860	0.59
4.6	65	5	26	0.54	0.930	0.58
6.3	59	2	59	0.56	0.965	0.58

In calculating  $r$  by (34), the value of  $\mu_2$  is given by (69) but  $\mu_1$  for hydrogen is obtained from

$$\mu_1 = 3.76 \times 10^{-7} q_1 \quad (79)$$

This gives

$$r = 2.00 \frac{\epsilon q_1}{a_2 q_2} \quad (80)$$

in place of Equation (70).

Substituting  $\omega$  from (76) and  $\mu_1$  from (79) in (20) we find in place of (77):—

$$s_1 = 3.81 \lambda \epsilon \quad (81)$$

while the value of  $s_2$  is given as before by (78).

In calculating  $r$ ,  $\epsilon$  was placed equal to  $a_2$  in (80), for rough preliminary calculations showed this to be justified. In Tables VIII. and IX.  $\theta_2$  was calculated from  $r$  by (35), corresponding to Case 2. The values of  $s_1$  thus obtained, are much more nearly constant than if the formulas of Case 1 are employed.

The agreement between experiment and theory shown by the data of Tables VIII. and IX. is very satisfactory. Thus with an excess of oxygen,  $s$  increases 2.3 fold as the partial pressure of hydrogen falls, but as the relative constancy of the values of  $s_1$  shows, this increase is just about that required by the theory. With an excess of hydrogen, on the other hand,  $s$  increases only very slightly (1.14 fold) as the oxygen disappears, but this again is in full accord with the theory.

Table X. gives a summary of the limiting values of  $s$  obtained at various temperatures with mixtures of hydrogen and oxygen, together with  $\lambda\epsilon$  and  $\lambda a_2$  calculated from them by (81) and (78). The data for the temperature 1110° are those given in more detail in Tables VIII. and IX. It is seen that  $\lambda\epsilon$  and  $\lambda a_2$  do not decrease at the higher temperatures to the same extent as they did with mixtures of carbon monoxide and oxygen (see Tables V. and VI.). This indicates that the oxygen film is not removed from the surface to any great extent by distillation even at 1500°. Therefore, the decrease in the velocity of the reaction with the monoxide at the high temperatures cannot be due to evaporation of the oxygen film but must be due to a decrease in the value of  $\epsilon$ . This may best be interpreted as an indication that the rate of evaporation of monoxide molecules from a surface covered with adsorbed oxygen atoms, increases with the temperature more rapidly than the velocity of interaction between the monoxide and the underlying oxygen atoms.

TABLE X.

REACTION BETWEEN HYDROGEN AND OXYGEN AT HIGH TEMPERATURES.

Filament Temperature.	Excess of Oxygen.		Excess of Hydrogen. $a_2 = \epsilon$ .	
	$s_1$ .	$\lambda\epsilon$ .	$s_2$ .	$\lambda a_2$ .
900° K	1.5	0.39	0.55	0.58
1110	2.1	0.55	0.59	0.62
1260	2.3	0.60	0.44	0.46
1500	1.6	0.42	0.41	0.44

The values of  $\lambda\epsilon$  and  $\lambda a_2$  are so nearly equal that we are justified in placing  $\epsilon = a_2$  in calculating  $r$  by (80). When we take into account that  $\lambda$  must be materially less than unity, it is evident that  $\epsilon$  and  $a_2$  must be nearly if not actually unity.

A large number of experiments were carried out with hydrogen-oxygen mixtures with filament temperatures ranging from 1500° to 1900° K. Even at the highest temperatures the velocity of the reaction was about the same as at 1500°. Reliable quantitative measurements, however, were impossible owing to a gradual disappearance of oxygen without corresponding disappearance of hydrogen. Thus in a typical case, the filament was heated to 1650° K. for 15 minutes in a mixture originally consisting of 36.1 mm.<sup>3</sup> of oxygen and 56.2 mm.<sup>3</sup> of hydrogen. There remained 7.2 mm.<sup>3</sup> of gas which analysis showed to be practically pure hydrogen, although from the original composition we should have expected a residue of oxygen. Assuming that the 49.0 mm.<sup>3</sup> of hydrogen combine with 24.5 of oxygen to form water, we find that 11.6 mm.<sup>3</sup> of oxygen must have disappeared in some other way. About 8 runs at temperatures above 1500° were made, and in these the total amount of oxygen which remained unaccounted for was 66 mm.<sup>3</sup>.



Previous work with platinum filaments heated to very high temperature in pure oxygen had shown that the platinum vapour combines with oxygen to form  $\text{PtO}_2$  which deposits on the bulb.<sup>1</sup> This, however, cannot be the cause of the disappearance of oxygen in the present experiments, for even if the whole of the platinum filament (0.00012 grams) were to combine with oxygen this would cause the disappearance of only 15 mm.<sup>3</sup>, while the observed amount was 66.

It seems then that the disappearance must be caused by the evaporation of oxygen *atoms* from the surface and their subsequent combination with oxygen to form ozone which condenses in the appendix cooled by liquid air or combines with water vapour on the bulb to form hydrogen peroxide. A more detailed experimental and theoretical study of this effect should make it possible to measure the degree of dissociation of oxygen into atoms in much the same way that the writer has measured the dissociation of hydrogen.

#### SUMMARY.

*Carbon Monoxide and Oxygen.*—When mixtures of carbon monoxide and oxygen at pressures up to a few hundred bars (0.1 mm.) are brought into contact with a smooth platinum surface at 500° to 700° K., they react at a rate proportional to the partial pressure of oxygen and inversely proportional to the pressure of monoxide. The reaction velocity increases rapidly with the temperature, about 1.6 fold for 10° at 600°.

With the platinum at 750° to 1050° K. the velocity is practically independent of the temperature, being limited largely by the rate at which the gases can come into contact with the surface. With an excess of oxygen, the velocity is proportional to the pressure of monoxide, while with an excess of monoxide the rate is proportional to the pressure of the oxygen.

A theoretical quantitative analysis of the experimental results leads to the following conception of the mechanism of the reaction. Every oxygen molecule which strikes a *clean* platinum surface condenses on the surface in the form of single atoms combined with separate platinum atoms. This chemical union is so firm that there is no appreciable evaporation of the oxygen atoms from the surface even with the platinum at 1500° K. These adsorbed oxygen atoms are in a very active condition in regard to their ability to react with monoxide, for *every* molecule of carbon monoxide which strikes an adsorbed oxygen atom reacts with it to form dioxide. When monoxide molecules strike a clean platinum surface, every one condenses on the surface, being held by chemical union between the carbon atom and two platinum atoms. An adsorbed film of monoxide thus consists of a monomolecular layer of oriented molecules. These adsorbed molecules are not as firmly held to the surface as oxygen atoms for they evaporate at an appreciable rate at temperatures as low as 500° K. Because of their orientation the monoxide molecules are very inert chemically towards oxygen. At 500° K. only about one oxygen molecule out of  $10^{12}$  which strike a surface covered with adsorbed monoxide reacts with the monoxide. The heat of evaporation of adsorbed monoxide is 31,800 calories per gram molecule.; and at 700° K. with a pressure of one bar of monoxide, at least half of the platinum surface is covered with adsorbed monoxide.

In the low temperature range the surface is nearly completely covered by a monoxide film, and the reaction occurs only when monoxide molecules

<sup>1</sup> Langmuir, *Four. Amer. Chem. Soc.*, **37**, 1161 (1915).

strike oxygen atoms which have become adsorbed in the spaces left vacant by the evaporation of monoxide molecules.

In the high temperature range the surface is nearly covered with oxygen when there is an excess of oxygen, and the reaction velocity is then limited by the rate at which the monoxide strikes the surface. With an excess of monoxide the surface is largely bare. The reaction velocity is limited by the rate at which the oxygen strikes the surface, for every oxygen molecule remains on the surface (in atomic condition) until struck by a monoxide molecule.

*Hydrogen and Oxygen.*—At low temperatures ( $300^{\circ}$  to  $600^{\circ}$  K.) rather erratic results are obtained for the reaction velocity with mixtures of hydrogen and oxygen, for the velocity depends upon the previous treatment of the platinum. When the platinum is in a relatively inactive condition, the results are similar to those obtained with carbon monoxide and oxygen, the velocity being roughly proportional to the pressure of oxygen and inversely to that of the hydrogen.

At high temperatures ( $700^{\circ}$  to  $1900^{\circ}$  K.) the results correspond closely with those obtained with monoxide, the hydrogen having the same function as the monoxide. At these temperatures, the reaction is not sensitive to the previous treatment of the platinum.

These results indicate that the adsorbed oxygen atoms are very reactive towards hydrogen, every collision between a hydrogen molecule and an adsorbed oxygen atom resulting in combination. Under certain conditions adsorbed hydrogen atoms are relatively inactive towards oxygen molecules, but the platinum can be brought into a condition which enables the adsorbed hydrogen to react with oxygen molecules or with the oxygen adsorbed in adjacent spaces on the surface.

*Research Laboratory,  
General Electric Company,  
Schenectady, N. Y.*