

THE JOURNAL  
OF THE  
American Chemical Society

with which has been incorporated the

American Chemical Journal  
(Founded by Ira Remsen)

---

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC  
COMPANY, SCHENECTADY, N. Y.]

**THE DISSOCIATION OF HYDROGEN INTO ATOMS. III. THE  
MECHANISM OF THE REACTION.**

BY IRVING LANGMUIR.

Received April 17, 1916.

In Part II of this paper<sup>1</sup> the degree of dissociation of hydrogen into atoms has been calculated from data<sup>2</sup> on the heat losses from highly heated wires in hydrogen at various pressures. In this calculation it was necessary to make certain assumptions regarding the mechanism of the processes occurring on and around the wire. The remarkable agreement between the theory thus derived and the experimental results, furnished ample justification for the assumptions, but did not necessarily indicate that the particular mechanism assumed was the only one which would lead to similar agreement.

The writer has recently developed a theory<sup>3</sup> of heterogeneous reactions which throws a great deal of light on the mechanism of such reactions. Applied to the dissociation of hydrogen around a heated wire, this theory

<sup>1</sup> THIS JOURNAL, 37, 417 (1915).

<sup>2</sup> Part I, Langmuir and Mackay, THIS JOURNAL, 36, 1708 (1914).

<sup>3</sup> This theory has, as yet, been only very briefly described (THIS JOURNAL, 38, 1139 (1915) and *J. Ind. Eng. Chem.*, 7, 348 (1915); *Phys. Rev.*, 6, 79 (1915)), but will serve as the basis of a series of papers to appear in THIS JOURNAL and in the *Physical Review*.

leads to a mechanism which may seem radically different from that previously used, but curiously enough it results in an equation identical with that obtained by the original theory.

The object of the present paper is to compare the older and the newer theories and to point out the advantages of the latter. At the same time this will serve as an illustration of the principles of the new theory and will indicate how it may be of use in the study of other heterogeneous reactions.

In the theory previously described, it was assumed that the surface of the tungsten wire contained atoms and molecules of hydrogen in chemical equilibrium with each other. The atomic and molecular hydrogen escaped from the wire at rates respectively proportional to their concentrations in the wire, while the absorption of the atoms or molecules by the wire was taken to be proportional to the corresponding pressures in the gaseous phase.

This theory led to an equation for the heat loss from the wire which proved to be in excellent agreement with experiments extending over a range of pressures from 0.01 mm. up to 760 mm. and a range of temperatures from 1000 to 3500° K. There are, however, some serious objections that may be raised against the assumption that the wire contains *concentrations* of atomic and molecular hydrogen in equilibrium with each other, and that these concentrations determine the rate at which hydrogen is dissociated by the wire. We shall see, however, that the new theory enables us to derive the same equation without making these objectionable assumptions.

The hypothesis that solid solutions of gases in metals play an important role in chemical reactions in contact with metals is a common one, and usually is not looked upon unfavorably. But it is evident that if we are to retain our ordinary conception of *concentration* the reaction must take place in a volume which contains many layers of atoms. In the experiments the range of concentrations of molecular (or atomic) hydrogen in the metal phase must have been enormous. Thus under some of the experimental conditions the concentrations were so small that the individual atoms or molecules of hydrogen were certainly separated from each other by hundreds of tungsten atoms. The rapidity of the reaction under such conditions could not possibly be very high and would be limited by the rate of diffusion of the gas through the metal.

Yet the experiments showed clearly that the velocity with which equilibrium was reached on the surface was extraordinarily high under all conditions. In fact, it was so high that practically all of the hydrogen atoms and 68% of the molecules which struck the surface reached equilibrium before leaving it again. When we consider that at atmospheric pressure and room temperature  $1.1 \times 10^{24}$  molecules of hydrogen strike

each square centimeter of surface per second, and that this number of molecules is contained in about 44 liters of gas, we realize the enormous velocity which this reaction must have. It is certainly impossible that such amounts of gas per second could diffuse *into* any kind of solid body and thus be brought to equilibrium.

These considerations compel us to assume that the reaction occurs directly on the surface of the metal and that it does not involve the diffusion through a film even as thin as that of a single layer of atoms.

A second difficulty arose in connection with the original theory.

At temperatures up to about 1500° K. the accommodation coefficient of hydrogen in contact with tungsten was found to be equal to 0.19. In other words, only about 19% of all the hydrogen molecules striking the filament, reached *thermal* equilibrium with it before leaving it. This figure was in good accord with the value 0.26 obtained by Knudsen with platinum at room temperature, especially when the fact was taken into account that accommodation coefficients in general appear to have slight negative temperature coefficients.

On the other hand, at high temperatures, it was found that 68% of all the hydrogen molecules striking the filament reached *chemical* equilibrium before leaving it. The original theory gave no clue to the solution of the paradox that 68% of the molecules reached chemical equilibrium, while only 19% reached thermal equilibrium. It is certainly impossible that molecules should reach chemical equilibrium while great differences in temperature still persist.

The viewpoint which has served as the basis for the new theory was gradually developed in quite other lines of work, particularly in connection with a study of the effect of gases on the electron emission from heated metals.<sup>1</sup> It was found that the electron emission was dependent on the composition of the actual surface layer of atoms. The deeper layers were apparently without effect. Subsequent work on gas reactions at very low pressures<sup>2</sup> indicated clearly that chemical reactions between a gas and a solid depend in general on the composition or structure of the outside layer of atoms of the solid, rather than on the thickness of an adsorbed film through which the gases diffuse.

This theory has now been developed much more completely than in any of the previously published work.

It is definitely known from the work of Bragg and others that the atoms of crystals are arranged according to space lattices in such a way that the identity of molecules is usually lost. The forces holding the crystal together are thus clearly chemical forces which act probably only between adjacent atoms. On the surface of a crystal the forces tend to be

<sup>1</sup> Langmuir, *Phys. Rev.*, 2, 450 (1913); *Physik. Z.*, 15, 516 (1914).

<sup>2</sup> THIS JOURNAL, 37, 1139 (1915).

chemically unsaturated, and atoms or molecules of gases can thus be held firmly by the atoms of the solid.<sup>1</sup> In general the law of multiple combining proportions will apply. Thus each metal atom of the surface will be capable of holding a definite integral number (such as one or two) of atoms of the gas, or possibly each two atoms of metal may hold one atom of gas. The atoms held on the surface in this way will form a part of the solid body, being a real continuation of the space lattice of the solid. This layer of atoms (or molecules) on the surface may be said to be adsorbed.<sup>2</sup>

The surface of the metal is thus looked upon as a sort of checkerboard containing a definite number,  $N_0$ , of spaces per square cm. Each elementary space is capable of holding an atom or a definite part of a molecule of adsorbed gas. The number of elementary spaces,  $N_0$ , is probably usually equal to the number of metal atoms on the surface. But this is not essential, for we can imagine cases in which each metal atom holds, for example, two adsorbed atoms or molecules, so that we should then have twice as many elementary spaces as metal atoms on the surface.

Let us now apply this theory to the dissociation of hydrogen in contact with a heated tungsten wire. We will first calculate the rate at which atomic hydrogen condenses on the bare surface when atomic hydrogen at a pressure  $p$  surrounds the wire.

The number of grams of gas which strikes a sq. cm. of surface per second is

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

Let  $\mu$  represent the number of gram molecules of gas striking a sq. cm. per second. Then  $\mu = m/M$  or

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

Expressing  $p$  in bars,<sup>3</sup> and placing  $R = 83.15 \times 10^6$  ergs per degree, this reduces to

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

<sup>1</sup> Haber (*J. Soc. Chem. Ind.*, **33**, 50 (1914) and *Z. Elektrochem.*, **20**, 521 (1914)) has suggested on the basis of Bragg's theory, that adsorption may be the result of unsaturated chemical forces at the surface of a solid body. Haber, however, only considers the force causing adsorption and does not take into account that the amount of adsorption depends on a kinetic equilibrium between the condensation and the evaporation of molecules.

<sup>2</sup> In a paper to appear shortly in the *Physical Review* this theory of adsorption will be developed in more detail. Preliminary accounts have already been published in THIS JOURNAL and in the *Physical Review* (*Loc. cit.*).

<sup>3</sup> The bar is the C. G. S. unit of pressure, one dyne per sq. cm. One million bars or one megabar is equal to 750 mm. of mercury, which is more nearly average atmospheric pressure than the 760 mm. usually used.

By applying this equation, we can readily calculate the rate at which atomic hydrogen ( $M = 1$ ) comes into contact with each square centimeter of surface. The rate at which the gas condenses to form a layer (one atom deep) on the surface will be less than the rate at which it strikes the surface for two reasons. In the first place, only a fraction  $\alpha$  of the atoms which strike the bare surface condenses, while the fraction  $1 - \alpha$  is reflected. Secondly, as the surface becomes covered with hydrogen atoms, many atoms will strike portions of the surface already covered.<sup>1</sup> Let  $\theta$  represent the ratio of the number of vacant elementary spaces to the total number of spaces  $N_0$ . Thus  $\theta$  is the fraction of the surface which is bare. The rate at which atomic hydrogen condenses on the surface is thus equal to  $\alpha\theta\mu$ .

Consider the case of hydrogen molecules condensing on the surface. If each hydrogen molecule occupies only one elementary space, then the rate of condensation will still be given by the product<sup>2</sup>  $\alpha\theta\mu$ .

If, on the other hand, each hydrogen molecule should occupy two elementary spaces, then the rate at which molecular hydrogen would condense on the surface is equal to  $\alpha\theta^2\mu$ . The exponent 2 for the quantity  $\theta$  is due to the fact that two adjacent spaces must be vacant simultaneously, in order that the molecule may condense. The chance that a given space, towards which a gas molecule may be moving, shall be vacant, is  $\theta$ . The chance that two given spaces shall be simultaneously vacant is  $\theta^2$ .

The adsorbed atoms or molecules on the surface evaporate at a definite rate. Let the rate of evaporation in gram molecules per sq. cm. per second from a completely covered surface, be represented by  $\nu$ . If  $\theta_1$  is the fraction of the surface which is covered by the atoms or molecules in question, then the actual rate at which the hydrogen evaporates is  $\nu\theta_1$ .

In considering the mechanism of the dissociation of hydrogen in contact with a heated wire, we may make two alternative hypotheses.

**First Hypothesis.**—Hydrogen exists on the surface in the form of atoms only. Molecules, formed by the combination of adjacent atoms, leave the surface immediately.

**Second Hypothesis.**—Hydrogen can exist on the surface in either molecular or atomic condition.

#### First Hypothesis.

We assume that out of all hydrogen atoms striking a bare surface, the fraction  $\alpha_1$  condenses and that the corresponding fraction for the molecules is  $\alpha_2$ .

<sup>1</sup> There is good reason to believe that even the hydrogen atoms which strike a surface already covered condense. But the rate of evaporation of the atoms from such a surface is so much higher than that from a bare surface that the number of atoms in the second layer is probably negligible in comparison with that in the first.

<sup>2</sup> In calculating  $\mu$  in this case by (1) the value  $M = 2$  will have to be used instead of  $M = 1$ .

Let  $\omega$  be the velocity with which the dissociation of hydrogen is brought about by the heated wire. We shall express  $\omega$  in gram molecules of hydrogen ( $H_2$ ) dissociated per second per sq. cm. of surface.

The rate at which atomic hydrogen leaves the wire is  $\nu_1\theta_1$ . The rate at which it is taken up by the wire is  $\alpha_1\theta\mu_1$ . The net rate at which it is produced is the difference between these two, and this must be equal to  $2\omega$ . The coefficient 2 is due to the fact that two atoms of hydrogen are produced from each molecule. We thus obtain the equation

$$2\omega = \nu_1\theta_1 - \alpha_1\theta\mu_1. \quad (4)$$

In a similar way we may consider the role played by the molecular hydrogen. Since we have assumed that molecular hydrogen does not exist as such on the surface, each molecule condensing on the surface must fill two adjacent elementary spaces as two separate atoms. The rate at which molecular hydrogen is removed by condensation on the heated wire is thus  $\alpha_2\theta^2\mu_2$  gram molecules per sq. cm. per second. This process will be reversible. That is, adjacent hydrogen atoms on the surface may combine together to form molecular hydrogen which then escapes from the surface. The rate at which this occurs will evidently be  $\nu_2\theta_1^2$ , since the chance of two hydrogen atoms occupying adjacent positions will be proportional to  $\theta_1^2$ . The coefficient  $\nu_2$  is the rate of evaporation when the surface is wholly covered by atomic hydrogen ( $\theta_1 = 1$ ).

The difference between the two rates will be equal to  $\omega$ , the rate at which molecular hydrogen disappears. Thus we obtain

$$\omega = \alpha_2\theta^2\mu_2 - \nu_2\theta_1^2. \quad (5)$$

The fractions  $\theta$  and  $\theta_1$  must fulfill the condition<sup>1</sup>

$$\theta + \theta_1 = 1. \quad (6)$$

These three equations, 4, 5 and 6, enable us to calculate the equilibrium constant in the gas phase in terms of the quantities  $\alpha_1$ ,  $\alpha_2$ ,  $\nu_1$  and  $\nu_2$ .

There are several possible definitions of the equilibrium constant, as follows:

$$K_p = p_1^2/p_2 \quad (7)$$

$$K_c = c_1^2/c_2 \quad (8)$$

$$K_\mu = \mu_1^2/\mu_2 \quad (9)$$

Here  $p_1$  and  $p_2$  are the partial pressure of atomic and molecular hydrogen in equilibrium with each other, while  $c_1$  and  $c_2$  are the corresponding concentrations. The third equilibrium constant  $K_\mu$  as defined

<sup>1</sup> Provided the surface is perfectly clean. The presence of a gas (otherwise inert) which is strongly adsorbed on the surface will cause the larger portion of the surface to be covered with inert molecules (or atoms). Thus the Equation 6 becomes  $\theta + \theta_1 = 1 - \theta_2$  where  $\theta_2$  represents the fraction of the surface covered by the inert substance. This theory of catalytic poisons will be developed in subsequent papers.

by (9) will be found very convenient in dealing with heterogeneous reactions. Since  $p = cRT$  the relation between  $K_p$  and  $K_c$  is

$$K_p = RTK_c. \quad (10)$$

Similarly, from (2) we obtain, since  $M_2 = 2$ , and  $M_1 = 1$

$$K_\mu = K_p/\sqrt{\pi RT} = K_c\sqrt{RT/\pi}. \quad (11)$$

In order to find the value of  $K_\mu$  we place  $\omega = 0$  which is evidently the condition for equilibrium. Equations 4 and 5 then reduce to

$$\mu_1 = \frac{\nu_1\theta_1}{\alpha_1\theta}. \quad (12)$$

$$\mu_2 = \frac{\nu_2\theta_1^2}{\alpha_2\theta^2}. \quad (13)$$

Whence by (9)

$$K_\mu = \left(\frac{\nu_1}{\alpha_1}\right)^2 \cdot \frac{\alpha_2}{\nu_2}. \quad (14)$$

It should be noted that  $\theta$  and  $\theta_1$  cancel out in the derivation of this equation.

Since the factors  $\alpha$  and  $\nu$  are not functions of the pressure, Equation 14 expresses the law of mass action, which in this case follows automatically as a consequence of the mechanism we have assumed. From Equations 4 and 5 we can determine the values of the two factors in the second member of (14). Thus

$$\frac{\nu_1}{\alpha_1} = \frac{\frac{2\omega}{\alpha_1} + \theta\mu_1}{\theta_1} \quad (15)$$

$$\frac{\nu_2}{\alpha_2} = \frac{\theta^2\mu_2 - \frac{\omega}{\alpha_2}}{\theta_1^2}. \quad (16)$$

Substituting these in (14) gives

$$K_\mu = \frac{\left(\mu_1 + \frac{2\omega}{\alpha_1\theta}\right)^2}{\left(\mu_2 - \frac{\omega}{\alpha_2\theta^2}\right)}. \quad (17)$$

The value of  $\theta$  may be found by solving (4) and (6) as simultaneous equations. We thus obtain

$$\theta = \frac{\nu_1 - 2\omega}{\nu_1 + \alpha_1\mu_1} = \frac{1 - 2\omega/\nu_1}{1 + \alpha_1\mu_1/\nu_1}. \quad (18)$$

The two Equations 17 and 18 give us a complete solution of our problem. They enable us to calculate the dissociation constant  $K_\mu$  in terms of  $\alpha_1$ ,  $\alpha_2$ ,  $\nu_1$  and experimentally determined values of  $\omega$ .

### Second Hypothesis.

In this hypothesis we assume that hydrogen molecules striking the surface condense as such, each molecule occupying only one elementary

space. The atoms which strike the surface condense as atoms. Interaction between the atoms and molecules on the surface occurs.

The rate of condensation of atomic hydrogen is  $\alpha_1\theta\mu_1$  while the rate at which it evaporates from the surface is  $\nu_1\theta_1$ . Hence we have

$$2\omega = \nu_1\theta_1 - \alpha_1\theta\mu. \quad (19)$$

This is identical with Equation 4. The rate of condensation of molecular hydrogen is  $\alpha_2\theta\mu_2$  whereas the rate of evaporation is  $\nu_2\theta_2$ . This gives

$$\omega = \alpha_2\theta\mu_2 - \nu_2\theta_2. \quad (20)$$

The rate at which hydrogen atoms combine will be proportional to the square of  $\theta_1$ , since the chance that two atoms shall be in adjacent spaces is proportional to  $\theta_1^2$ . We may thus place the rate of formation of molecular hydrogen from the atoms, equal to  $\beta_1\theta_1^2$  where  $\beta_1$  is the rate of formation when the surface is wholly covered with atomic hydrogen.

The rate at which hydrogen molecules dissociate into atoms on the surface will be proportional to the product of  $\theta$  by  $\theta_2$  since a hydrogen molecule must be adjacent to a vacant space in order that it can dissociate. The chance that a hydrogen molecule and a vacant space shall be adjacent to each other is evidently proportional to  $\theta\theta_2$ . We may, therefore, place the rate of dissociation of hydrogen equal to  $\beta_2\theta\theta_2$ .

We thus obtain a third equation

$$\omega = \beta_2\theta\theta_2 - \beta_1\theta_1^2. \quad (21)$$

Finally we have the condition (in the absence of catalytic poisons)

$$\theta + \theta_1 + \theta_2 = 1. \quad (22)$$

If we substitute  $\omega = 0$  in Equations 19, 20 and 21, we obtain the values of  $\mu_1$ ,  $\mu_2$ , etc., corresponding to equilibrium conditions.

$$\mu_1 = \frac{\nu_1\theta_1}{\alpha_1\theta}, \quad (23)$$

$$\mu_2 = \frac{\nu_2\theta_2}{\alpha_2\theta}, \quad (24)$$

$$\frac{\beta_1}{\beta_2} = \frac{\theta\theta_2}{\theta_1^2}. \quad (25)$$

Substituting (23) and (24) in (9)

$$K_\mu = \left(\frac{\nu_1}{\alpha_1}\right)^2 \frac{\alpha_2\beta_2}{\nu_2\beta_1}. \quad (26)$$

From (19) we obtain

$$\frac{\nu_1}{\alpha_1} = \frac{\theta\mu_1 + 2\omega/\alpha_1}{\theta_1} \quad (27)$$

and from (20)

$$\frac{\nu_2}{\alpha_2} = \frac{\theta\mu_2 - \omega/\alpha_2}{\theta_2}, \quad (28)$$



while (21) and (25) give

$$\frac{\beta_1}{\beta_2} = \frac{\theta\theta_2}{\theta_1^2} (1 - \omega/\beta_2\theta_2) \quad (29)$$

or

$$\frac{\beta_2}{\beta_1} = \frac{\theta_1^2}{\theta\theta_2} (1 + \omega/\beta_1\theta_1^2). \quad (30)$$

From (19) we obtain

$$\theta_1 = \frac{\alpha_1\theta}{\nu_1} (\mu_1 + 2\omega/\alpha_1\theta) \quad (31)$$

and from (20)

$$\theta_2 = \frac{\alpha_2\theta}{\nu_2} (\mu_2 - \omega/\alpha_2\theta). \quad (32)$$

By combining (26), (27), (28), (30) and (31), we obtain

$$K_\mu = \frac{\left(\mu_1 + \frac{2\omega}{\alpha_1\theta}\right)^2 + \left(\frac{\nu_1}{\alpha_1\theta}\right)^2 \cdot \frac{\omega}{\beta_1}}{\left(\mu_2 - \frac{\omega}{\alpha_2\theta}\right)} \quad (33)$$

Similarly, from (26), (27), (28), (29) and (32)

$$K_\mu = \frac{\left(\mu_1 + \frac{2\omega}{\alpha_1\theta}\right)^2}{\left(\mu_2 - \frac{\omega}{\alpha_2\theta}\right) - \frac{\nu_2}{\alpha_2\theta^2} \cdot \frac{\omega}{\beta_2}} \quad (34)$$

The Equations 33 and 34 are different forms of the same fundamental equation.

By substituting (31) and (32) in (22), and solving for  $\theta$  we find

$$\theta = \frac{1 + \frac{\omega}{\nu_2} - \frac{2\omega}{\nu_1}}{1 + \frac{\alpha_1\mu_1}{\nu_1} + \frac{\alpha_2\mu_2}{\nu_2}} \quad (35)$$

These last three equations furnish a complete solution of our problem in the case of the second hypothesis.

### Comparison with the Older Theory.

It will be interesting to compare the results obtained by each of the above hypotheses, with those found by the theory developed in Part II of this paper. The Equations 21 and 26, of Part II (page 427), correspond to the Equations 17 and 33 derived above. However, since the nomenclature previously used differs from that employed here it will be worth while to go through the derivation of the older equation again by a method which will bring out clearly the difference between the two viewpoints.

It is assumed that out of all the atoms striking the surface, the fraction

$\alpha_1$  is absorbed by the metal, whereas for the molecules the corresponding fraction is  $\alpha_2$ . It is assumed further that the surface of the metal contains hydrogen molecules and atoms in equilibrium with each other. Let  $\nu_1$  and  $\nu_2$  be the rates at which atomic and molecular hydrogen, respectively, escape from the surface.

We may thus derive the equations

$$2\omega = \nu_1 - \alpha_1\mu_1 \quad (36)$$

$$\omega = \alpha_2\mu_2 - \nu_2, \quad (37)$$

from which we obtain

$$\nu_1 = 2\omega + \alpha_1\mu_1 \quad (38)$$

$$\nu_2 = \alpha_2\mu_2 - \omega. \quad (39)$$

It is assumed that the equilibrium inside the metal obeys the law of mass action, so that the concentration of molecular hydrogen is proportional to the square of the concentration of atomic hydrogen. It is further assumed that the rates at which each of the gases escapes from the surface, is proportional to the corresponding concentration in the metal. Thus,  $\nu_1^2/\nu_2$  is a constant proportional to the equilibrium constant in the metal. Let this constant be represented by  $A$ . Then we have by (38) and (39)

$$A = \frac{(\alpha_1\mu_1 + 2\omega)^2}{(\alpha_2\mu_2 - \omega)}. \quad (40)$$

When equilibrium exists in the gas phase, we may place  $\omega = 0$  and thus find

$$A = \frac{\alpha_1^2\mu_1^2}{\alpha_2\mu_2} = \frac{\alpha_1^2}{\alpha_2} K_\mu. \quad (41)$$

Combining (41) and (40) gives

$$K_\mu = \frac{\left(\mu_1 + \frac{2\omega}{\alpha_1}\right)^2}{\left(\mu_2 - \frac{\omega}{\alpha_2}\right)}. \quad (42)$$

This is the equation which was derived in Part II and which was found to be in excellent agreement with the results of the experiments. In fact, we may look upon this equation as having been proved correct by the experiments.

When we compare this equation with (17), which was calculated by the 1st hypothesis, we see that the two become identical if we place  $\theta = 1$ . We see by (18) that this condition will be fulfilled if  $\nu_1$  is very large, compared to  $\alpha_1\mu_1$  and  $\omega$ . We may thus conclude that the first hypothesis is entirely in agreement with the experiments if we assume that  $\nu_1$ , the rate of evaporation of hydrogen from the surface, is so high that only a small fraction of the surface remains covered.

If we compare Equation 42 with 33 and 34, we see that they become

identical if we take  $\theta = 1$  while  $\beta_1$  and  $\beta_2$  are taken to be very large. This last requirement means the velocity with which adjacent hydrogen atoms or molecules interact or dissociate must be very large compared to that at which they evaporate. This is equivalent to assuming that equilibrium exists between the atoms and molecules on the surface. Thus we see that the second hypothesis is also in accord with the experiments if the rate of evaporation is assumed to be so high that only a small fraction of the surface is covered.

The experiments thus do not enable us to decide between the two hypotheses. In fact, it is also possible by means of slightly different hypotheses from those described here to obtain the same equation.

But all these hypotheses have this in common: they lead to the conclusion that only a small fraction of the surface is covered with hydrogen atoms or molecules, and that the reaction is not dependent upon phenomena occurring within the surface of the metal.

This conclusion that only a small fraction of the surface is covered with hydrogen is confirmed by other facts.

We have seen that the accommodation coefficient of hydrogen in contact with tungsten at relatively low temperatures is about 19%, whereas at high temperatures 68% of the molecules which strike the filament reach chemical equilibrium. The explanation of this apparent paradox, according to the new theory, is that the surface of the tungsten is largely covered by adsorbed hydrogen at the lower temperatures, whereas at the higher temperatures it is practically bare. The 19% thus corresponds to the fraction of molecules which condenses when they strike a surface already covered with hydrogen, while the 68% represents the fraction condensing on a bare surface.

Another fact which proves nearly conclusively that the surface of a highly heated tungsten wire is not covered to an appreciable extent by hydrogen is that the electron emission from tungsten is not perceptibly influenced by the presence of pure hydrogen.<sup>1</sup> A large amount of unpublished work in this laboratory has demonstrated that the electron emission affords an extraordinarily sensitive method of detecting the presence of a film of adsorbed material, so thin that it only partly covers the surface with a layer one atom deep. Some of this evidence will soon be published.

In subsequent papers, the theory of heterogeneous reactions here outlined, will be applied to a large number of reactions. It will be shown that the equations derived by Fink, in his work on the contact sulfuric acid process, may also be derived by the new theory, and that definite proof that the mechanism postulated by Bodenstein and Fink cannot apply in this work may be adduced from the experiments themselves.

<sup>1</sup> Langmuir, *Phys. Zeit.*, 15, 523 (1914).

The work of Bodenstein and Ohlmer on the reaction between carbon monoxide and oxygen is also in quantitative agreement with the new theory. Other cases, including several studied experimentally in this laboratory, will also be discussed.

#### Summary.

1. The velocity of the reaction by which hydrogen is dissociated in contact with a heated tungsten wire is so enormous that it definitely proves that the reaction cannot depend upon a diffusion of hydrogen into the metal even if the depth of penetration should be only that of a single atom.

2. A general theory of heterogeneous chemical reactions is outlined in which the reaction is assumed to take place in the actual surface layer of atoms.

3. This theory is worked through in detail for the case of the dissociation of hydrogen. It leads to equations which become identical with that previously derived by other methods, when it is assumed the hydrogen evaporates so rapidly from the surface that only a negligible fraction of the surface is covered at any time. This equation has already been shown to be in full agreement with the experiments (Parts I and II).

4. The conclusion that very little of the surface is covered is in good accord with the fact that the accommodation coefficient of hydrogen is 0.19 at temperatures below 1500° K., while the "chemical" accommodation coefficient  $\alpha_2$  for the dissociation of hydrogen is 0.68 at high temperatures.

5. The fact that the electron emission from heated tungsten is not affected by the presence of pure hydrogen is additional evidence that the fraction of the surface covered by hydrogen atoms or molecules must be very small.

---

### ACCURACY OF COPPER VOLTAMETERS.

BY ASWINI KUMAR DATTA AND NILRATAN DHAR.

Received March 21, 1916.

When a current of moderate strength is to be measured by the copper voltameter the results given by it agree with those obtained from the silver voltameter of Rayleigh's form<sup>1</sup> improved upon by Richards<sup>2</sup> and his pupils. Richards considers that the improved silver voltameter can be relied upon to one part in ten thousand or more. The silver voltameter is therefore a very good register of current and we are quite justified in judging the accuracy of a copper voltameter by comparing its results with those of the standard silver voltameter. When very feeble currents are mea-

<sup>1</sup> *Phil. Trans.*, 175, II, 411 (1884).

<sup>2</sup> *Z. physik. Chem.*, 32, 321 (1900).