be carried through using pure iron and following the process exactly as described.

In testing the accuracy of the method, 0.1 N solution of boron was prepared by dissolving 3.5 g. of B_2O_3 in one liter of CO_2-free water. The B_2O_3 was prepared by fusing pure boric acid in a platinum dish. When titrated in the presence of mannite, 8.68 cc. of this B_2O_3 solution required 8.75 cc. 0.1 N KOH. Known quantities of this boric acid solution were added to a solution of iron free from boron and the operations were carried out as indicated. Contrary to the experience of Wherry, when the precipitation by use of calcium carbonate was properly carried out, it was found possible to wash the iron entirely free from boric acid and recover the full amount in the filtrate. The use of the boric acid solution made up of the pure fused material as above described also served admirably as a medium for standardizing the alkali used in the titrations.

TABLE I.—DETERMINATION OF BORON IN IRON.

% Boron taken	0.038	0.188	0.424	0.850
% Boron found	0.044	0.194	0.388	0.840

URBANA, ILL.

CHEMICAL REACTIONS AT LOW PRESSURES.[1]

BY IRVING LANGMUIR.

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In the course of investigations into the causes of the blackening of tungsten lamps,[2] the effects produced by the introduction of low pressures of various gases have been studied in considerable detail.

It had been previously known[3] that the vacuum in a lighted tungsten lamp normally improves during the life of the lamp, but it was thought that this removal of the residual gases was brought about by electrical discharges in much the same way as that commonly observed in Geissler and Roentgen ray tubes. These experiments have shown, however, that a highly heated tungsten filament will cause the disappearance or clean-up of nearly any gas introduced into the bulb at low pressure, and that this action, in the great majority of cases, is purely chemical in nature.

The experimental methods that have been employed in these investigations are relatively simple. A bulb containing one or more short filaments, usually of tungsten, was sealed to an apparatus consisting essentially of a mercury Gaede pump, a sensitive McLeod gage for reading the pressures, and an apparatus for introducing small quantities of various

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[1] Paper presented before the New York Section of the American Chemical Society, March 5, 1915.

[2] *Trans. A. I. E. E.*, **32**, 1913 (1913).

[3] THIS JOURNAL, **35**, 107 (1913).

gases into the system and for analyzing the gas residues obtained in the course of the experiments.

By means of the pump, the pressure in the system could be lowered to 0.00002 mm. of mercury. The McLeod gage gave a reading of one millimeter on the scale for a pressure of 0.000007 mm. of mercury. By means of the apparatus for analyzing gas, a quantitative analysis of a single cubic mm. (at atmospheric pressure) of gas could be carried out, determining the following constituents: hydrogen, oxygen, carbon dioxide, carbon monoxide, nitrogen and the inert gases.

The apparatus by which this has been accomplished has been in almost daily use for over five years, and during that time a very large number of reactions have been studied by its aid. In a typical experiment, after having thoroughly exhausted the whole apparatus, a small quantity, usually 5–20 mm. of gas, is introduced and the filament is electrically heated to a definite temperature, while readings of the pressure are taken at regular intervals (usually one minute). By plotting the pressure readings against the time, a curve is obtained which clearly shows how the rate of clean-up varies with the pressure.

A series of such curves are prepared with different filament temperatures and with various other changes in the conditions which I shall describe later.

In this way we have studied the clean-up phenomena with many different gases and several different kinds of filaments. Most of the work has been done with tungsten filaments, but, in order to get a broader outlook over the field of low-pressure reactions, filaments of carbon, molybdenum, platinum, iron, palladium, and other metals have also been tried. The principal gases studied have been oxygen, nitrogen, hydrogen, carbon monoxide and dioxide, chlorine, bromine, iodine, methane, cyanogen, hydrochloric acid, argon, phosphine, and the vapors of many substances, such as mercury, phosphorus pentoxide, sulfur, etc.

With each of these gases, conditions can be found, under which a heated tungsten filament will cause the clean-up of the gas. The curves obtained in the course of the experiments have furnished very complete data for a study of the kinetics of the reactions involved.

It has long been generally recognized that the kinetics of gas reactions afford the best, if not the only means of studying the mechanism of reactions, and the literature of recent years shows that the velocities of many reactions have been investigated with this end in view.

Very few experimenters, however, have realized that by working with gases at extremely low pressures the experimental conditions may be enormously simplified and the velocity of the reaction is then much more intimately related to the behavior of the individual molecule than it is at higher pressures.

In fact, by working continually with gases at these low pressures, one soon acquires an entirely new view-point and sees almost daily fresh evidences of the atomic and molecular structure of matter. The kinetic theory of gases then becomes the great guiding principle. According to this view-point, the velocity of a reaction is a matter of statistics. The question becomes: Out of all the gas molecules which strike the surface of heated filament, what fraction enter into reaction with it?

This statistical view-point has become prevalent among physicists within the last few years. Without it, the tremendous advances in our knowledge of radioactivity, electric conduction through gases, applications of the quantum theory, etc., would have been impossible.

In the field of chemistry, however, only a very small beginning has been made. Chemistry was the first of the sciences to make use of the atomic theory, and, in fact, the history of chemistry in the last century shows that the great advances in both inorganic and organic chemistry were largely dependent on this theory.

The development of physical chemistry, however, took place along rather different lines. The remarkable progress which occurred from 1870 to 1900 was, in a large degree, based upon the applications of thermodynamics to chemistry. Gradually, the idea became prevalent that the atomic theory was only a working hypothesis and might perhaps profitably be dispensed with entirely. The energy relations of reactions, on the other hand, were considered to be of the most fundamental importance. Just about the time that the majority of physical chemists had been won over to this view-point the physicists began to discover absolute proofs of the existence of atoms and molecules and soon showed what remarkable results could be obtained by the applications of statistical methods.

As yet, apparently, very few chemists have awakened to the wonderful opportunities that lie open to them on all sides when they attack the problems of chemistry by the new methods which the physicists have developed. The physicist, on the other hand, is gradually beginning to extend his investigations into the field of the chemist and we may hope, if the chemist will but meet him half way, that there will result a new physical chemistry which will have an even more far-reaching effect on our ordinary chemical conceptions than has the physical chemistry of the last decades.

Perhaps the most noteworthy of the recent attempts to apply statistical methods to chemical changes is the work of J. J. Thomson on positive rays.

Strutt[1] has studied the statistics of a few gas reactions, in some of which his active modification of nitrogen (atomic nitrogen) takes part. Although his experimental methods are quite different from those we have

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[1] *Proc. Roy. Soc.*, (*A*) **87**, 302 (1912).

used in studying the clean-up of gases, his results are closely related to some of those we have obtained, and I shall therefore have occasion to refer again to this work of Strutt's.

An excellent example of the study of chemical reactions, by statistical methods, and this time by a chemist, is to be found in the work of S. C. Lind[1] on the nature of chemical action brought about by radioactive bodies.

The reactions which we are to consider this evening are for the most part reactions between gases and heated filaments; that is, they are heterogeneous reactions involving a solid and gaseous phase. The kinetics of reactions of this type have not received the attention which has been accorded to homogeneous reactions. For example, in Jellinek's recent book on the "Physical Chemistry of Gas Reactions," 34 pages are devoted to the kinetics of homogeneous reactions, but only half of one page to the kinetics of heterogeneous reactions.

It was at first thought that the law of mass action could be applied to heterogeneous reactions just as to homogeneous reactions. Experiments soon showed, however, that other factors than purely chemical ones usually determined the velocity of these reactions. Noyes and Whitney[2] studied the rate of solution of solid substances in liquids and concluded that the velocity was dependent entirely on the rate at which the dissolved substances could diffuse out through the thin layer of liquid next to the solid. Stirring the liquid had the effect of thinning this layer and so increased the rate.

Nernst extended this idea and suggested that the velocity of heterogeneous reactions in general was limited by the rate of diffusion of the reacting substances through a "diffusion layer," which he considered, under ordinary circumstances, to be of constant thickness. Thus he reasoned that the velocity of these reactions, in practically all cases, should be proportional to the concentration of the reacting substances. In other words, the reactions should follow the laws of monomolecular reactions. Nernst pointed out, however, that it was wrong to draw conclusions as to the mechanism of heterogeneous reactions from measurements of their velocity.

Fink,[3] as a result of his study of the kinetics of the sulfur trioxide contact process, developed a theory of the mechanism which marked a new step in our conceptions of the mechanism of heterogeneous reactions. Bodenstein and Fink[4] successfully applied this theory to a large number of other catalytic reactions.

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[1] *J. Phys. Chem.*, **16**, 564 (1912).

[2] *Z. physik. Chem.*, **23**, 689 (1897).

[3] *Dissertation*, Leipzig, 1907; see also Bodenstein and Fink, *Z. physik. Chem.*, **60**, 1 (1907).

[4] *Z. physik. Chem.*, 60, 46 (1907).

This theory differs essentially from Nernst's, in that the reaction velocity is assumed to be limited by the rate of diffusion of the reacting bodies through an *adsorbed film* of *variable thickness*. Thus, in the case of the reaction

$$2SO_2 + O_2 = 2SO_3$$

in contact with platinum is is shown that there is present on the platinum an absorbed layer of SO_3. The theory assumes that the thickness of this layer is at all times proportional to the square root of the concentration of SO_3 in the gas phase; in other words, that there is an adsorption equilibrium. The reaction is assumed to take place only at the boundary between the adsorption film and the platinum. The oxygen and sulfur dioxide must therefore diffuse through the film before being able to react. In this way the theory indicates that the velocity of the reaction should be inversely proportional to the square root of the concentration of SO_3 and should be proportional either to the concentration of oxygen or to that of the sulfur dioxide (not to both), depending upon which is in excess at the surface of the platinum.

This theory seems to have met with general favor and has been applied to the kinetics of many heterogeneous reactions.

The experiments on gas reactions at low pressures which I shall describe this evening, have shown that this theory must be modified and that we must consider the reaction velocity to be limited, not by the rate of diffusion through the adsorbed film, but rather, by the rate at which the surface of the metal becomes exposed by the evaporation of single molecules from an adsorbed layer one molecule deep. We shall see that the statistical view-point will lead us very much further in the understanding of all reactions of this type.

In interpreting the experimental results, we shall need to make use of some of the fundamental principles of the kinetic theory. I should therefore like to spend some time in discussing these and in showing their relation to the phenomena we shall have to consider.

We shall refer frequently to low gas pressures, and it will be well at the outset to say a word as to the unit of pressure which we shall use throughout. It has been customary to measure pressures in mm. of mercury, but this is really a very arbitrary and inconvenient unit for such work as this. Professor Richards, last year at Cincinnati, made a strong appeal to chemists to use the C. G. S. unit of pressure, the *bar*, or the megabar, and enumerated many good reasons for doing so. The *bar* is defined as a pressure of one dyne per sq. cm. and the megabar is a million times this. The megabar is almost exactly 750 mm. of mercury and is really more nearly average atmospheric pressure than the 760 mm. usually adopted as standard. A bar is therefore one millionth of an atmosphere, or just three-fourths of a thousandth of a mm. of mercury.

This unit is particularly convenient for our purpose, for the pressures we shall deal with are usually from 1 to 100 bars.

According to the kinetic theory, the pressure of a gas on the walls of the containing vessel is due to the impact of the rapidly moving molecules against the surface. The average velocity (Ω) of the molecules is

$$\Omega = \sqrt{8RT/\pi M} \tag{1}$$

where T is the absolute temperature, M the molecular weight, and R the gas constant (83.2×10^6 ergs/degree). If we substitute the numerical value of R in this equation we find

$$\Omega = 14550 \sqrt{T/M} \text{ cm. per sec.} \tag{2}$$

We see that the velocity is proportional to the square root of the temperature and inversely proportional to the square root of the molecular weight. For oxygen at room temperature ($T = 293$; $M = 32$), the average velocity of the molecule is 44000 cm. per second, or nearly half a kilometer per second (about 30% greater than the velocity of sound). The pressure of the gas being produced by the impact of the molecules, is proportional to the velocity of the molecules as given above and also to the total mass of all the molecules striking the surface per second. If we let m represent the number of grams of gas molecules which strike a unit surface per second, then it can be shown that the pressure p is equal to

$$p = {}^1/_2\pi m\Omega. \tag{3}$$

From this and (1), we find m to be

$$m = \sqrt{M/2\pi RT}\ p. \tag{4}$$

We shall find that this is an equation of very fundamental importance in the theory of the kinetics of heterogeneous reactions. It enables us to calculate the exact rate at which the gas can come into contact with a given surface. Substituting the numerical value of R, etc., the equation becomes

$$m = 43.74 \times 10^{-6} \sqrt{M/T}\ p. \tag{5}$$

Here m is expressed in grams per sq. cm. per second and p is in bars.

For air ($M = 29$) at atmospheric pressure (10^6 bars) and room temperature ($T = 293$), this gives $m = 13.8$ g. per sq. cm. per second. This mass of air corresponds to about twelve liters.

Let us pause a moment to consider what this means. In each second, the total number of molecules striking a single sq. cm. of surface is as great as is the number contained in twelve liters of air. Of course, under ordinary conditions, the same molecules strike the surface a vast number of times each second. As the pressure is lowered, the number of molecules striking the surface decreases, but so does the number contained in a given volume. Thus we see that no matter what the pressure, the number of molecules which strike a single square centimeter of surface in a second is the same as that contained in twelve liters.

According to Millikan's recent accurate determinations, there are 2.488×10^{19} molecules in a cubic centimeter of any gas at 20° C. and one megabar pressure. The lowest pressures that have been produced and measured are about 0.001 bar, or 10^{-9} megabars. Even in this remarkably good vacuum, there are still 2.5×10^{10} molecules per cubic centimeter. However, when we consider that the average distance between the molecules under these conditions is about 0.02 mm., a distance about equal to the diameter of the filament of a small tungsten lamp, we realize that the gas must behave very differently from a continuous medium.

For many calculations the number of molecules per g. molecule is a very convenient number. According to Millikan's data, this is 6.062×10^{23}. For example, from this figure we can calculate (by Equation 5) the number of molecules of a gas which strike a sq. cm. of surface per second. We find this number to be

$$n = 2.652 \times 10^{19}\ p/\sqrt{MT}. \qquad (6)$$

Very little is known about the diameter of molecules. The question itself probably has little meaning, for molecules are certainly not spheres, but are complex structures of electrons having no definite geometrical shape which can be adequately characterized by a single dimension. We do know, accurately, however, the distances between adjacent molecules in crystals, and in gases we know approximately how close the centers of molecules can approach during collisions. For oxygen, this distance, which, for convenience, we may call the diameter, has been found to be 2.7×10^{-8} cm. If we assume that these molecules are arranged in a single layer on a surface, much as the cells in honeycomb are arranged, it can be readily shown that the total number required to cover a square centimeter is 1.6×10^{15}.

The area covered by each molecule is the reciprocal of this, or 6×10^{-16} sq. cm. We already know, by Equation 6, how many molecules strike a sq. cm. per second, so to find how many molecules from the gas strike a given molecule on the surface we need only to multiply by 6×10^{-16}. We thus find, for the case of oxygen at room temperature and at a pressure of one bar, that an oxygen molecule on the surface would be struck by 170 molecules from the gas every second. Similarly, if the surface were originally free from oxygen and every oxygen molecule striking the surface should stick, it would take approximately only $^1/_{170}$ of a second to cover the surface with a layer one molecule deep. Even at 0.001 bar pressure, the lowest pressure that has been measured, it would require only about 6 seconds to form such a film. This explains the difficulty of preparing surfaces in vacuum which are not contaminated by gas.

A very fundamental conception is that of evaporation. By means of Equation 4 we may obtain a relation between the vapor pressure of a substance and its rate of evaporation. When a substance is in equilibrium with its saturated vapor the vapor is condensing on the substance at the same rate as the latter is evaporating. Now if we assume that every molecule of the vapor striking the surface condenses, then Equation 4 gives us the rate (*m*) at which the vapor must condense. This must be equal to the rate at which the substance evaporates.

Let us now consider the essential differences between the conditions in our low pressure experiments and those that would prevail if higher pressures were used.

At pressures as high as atmospheric pressure, convection currents set up by the filament introduce very serious complications. At pressures of a tenth of a megabar or less, convection currents become negligible for most purposes, but the problem is still complicated by the sharp temperature gradients that occur in the gas around the wire. At ordinary pressures, unless the velocity of the reaction is extremely small, the rate of reaction will be determined largely, if not wholly, by the rate at which the reacting substances can diffuse to the surface and the products diffuse out. Under these circumstances, we should expect Nernst's theory to apply in general, but in this case we are really not measuring the velocity of a chemical reaction at all; we are merely measuring a diffusion coefficient in a gas.

On the other hand, at pressures as low as 10 bars, diffusion may be considered as practically infinitely rapid. At this pressure the average free path of the molecules of most gases is very close to 1 cm. This is so large, compared to the diameter of the wire, that it is evident that the molecules leaving the wire can in no way interfere with those approaching it. Under these conditions the gases don't need to diffuse through each other in the ordinary way.

At such low pressures as these we may, in fact, look upon the gas as consisting of a swarm of molecules which are independent of one another. The velocity of the molecules around the filament is then determined by the temperature of the bulb and is entirely independent of that of the filament. There is thus no temperature gradient in the gas around the filament. The average velocity of the molecules striking the filament is definitely known and, in case two or more gases are present, the relative numbers of each kind of molecules striking the filament are also known, no matter how rapid the reaction may be.

An interesting feature, possible only with reactions at very low pressures, is the fact that the temperature of the molecules striking the filament is different from that of the filament itself. At ordinary pressures, because of the heat conductivity of the gas, the molecules striking a solid body are, of course, always at the same temperature as the body itself. This opens up new possibilities in studying the kinetics of reactions. The effect of separate variation in the temperature of two reacting substances can thus be studied. If it is the impact of the gas molecules against the surface of the filament which determines the velocity of the reaction, then this velocity should depend much more on the temperature of the bulb than on that of the filament, since the impact depends on relative velocity, and the velocity of the heavy tungsten atoms, even at high temperatures, is much less than that of ordinary gas molecules at room temperature. On the other hand, if the reaction velocity is determined rather by some condition of the surface of the filament, then the effect of bulb temperature will usually be negligible.

Another result of the use of low pressures is that the molecules of the products of a reaction, when they leave the filament, do not return again until after having made many collisions with the bulb. If the substance formed is a nonvolatile solid, or can be condensed by cooling the bulb in liquid air, it is thus possible to make certain that the reaction does not take place as the result of two collisions, but necessarily occurs in one. In this way also it should be possible to produce many compounds which are very unstable at the temperature of the filament.

At sufficiently low pressures (about 1 or 2 bars) the molecules leaving the filament travel directly to the bulb without striking any other molecules on the way. Naturally, they have no chance of giving up any energy on the way to the bulb, and therefore (if we can speak of the temperature of a single molecule) reach the bulb with the same temperature as that with which they left the filament. This must produce the most sudden cooling possible, and there is then the minimum chance for the decomposition of the product formed if it happens to be unstable at some temperature between that of the filament and that of the bulb.

Another important advantage in working at low pressures is that the velocity of even the most rapid reactions in this way can be slowed down sufficiently so that they can be studied quantitatively. The heat liberated by the reaction on the filament is usually so small that it is not noticeable, or at any rate is not so large but that isothermal conditions may be maintained.

The theories of the mechanism of reactions that I will describe in connection with the experiments have been gradually developed during the last three or four years. To-night I shall discuss only the purely chemical evidence, but I should like to point out that the idea that the reaction velocity depends not upon the thickness of the adsorption layer, but upon the extent to which the surface is covered by it, was based upon experiments on the electron emission from heated tungsten wires in high vacuum. The evidence of the existence of such monomolecular layers in these experiments was very striking and the electron emission was found to depend entirely upon the extent of the uncovered part of the surface. A preliminary account of this work was published in 1913.[1] I expect later to publish the results of the more recent experiments and to show that in the measurement of the electron emission from heated wires there is opened up a powerful method of studying the properties of films so thin that they only partly cover the surface with a layer one molecule deep.

We are now in a position to consider more in detail the reactions which occur when a gas is "cleaned-up" by a heated filament. These reactions may be divided into four distinct classes, which we shall consider separately. The four types of reaction are those in which:

1. The filament is attacked by the gas.
2. The gas reacts with the vapor given off by the filament.
3. The filament acts catalytically on the gas, producing a chemical change in the gas without any permanent change in the filament.
4. The gas is chemically changed, or is made to react with the filament by means of electrical discharges through the gas.

Direct Attack of the Filament.

1. Clean-up of Oxygen by a Tungsten Filament.[2]—The action of oxygen on a tungsten filament is one of the best examples of this type of reaction. In air at atmospheric pressure tungsten begins to oxidize at about 400–500° C. and becomes coated with an iridescent film much as steel does. At higher temperatures the oxidation becomes rapid and a scale of the yellow oxide WO_3 forms on the metal. At temperatures above 1500° K. the oxide volatilizes so rapidly that it forms a dense, white smoke. Under such conditions the rate of oxidation evidently depends on the rate at which the oxygen can diffuse up to the surface of the metal through the nitrogen and through the layer of oxide on the surface. Such a large number of factors is involved that it would seem very difficult to derive much information as to the mechanism of the chemical reaction from experiments at these high pressures.

The case is quite different, however, when we study the action of a heated tungsten filament on oxygen at a pressure as low as, say, 100 bars. We then find that at temperatures above about 1200° K. the tungsten is attacked, producing the yellow oxide WO_3, but that this distils off as fast as it is formed, leaving the surface clean and bright.

The pressure of oxygen decreases in the manner shown in Fig. 1. The rate of clean-up is initially high, but gradually becomes smaller as the oxygen pressure becomes less. It is found that the slope of this curve at any point is proportional to the pressure at that point. In other words, the velocity of the reaction is proportional to the pressure. This is the law according to which a monomolecular reaction proceeds, and is also

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[1] *Phys. Rev.*, **2**, 450 (1913).

[2] THIS JOURNAL, **35**, 105 (1913).

the law which Nernst found to hold for reactions in which the velocity was limited by the rate of diffusion.

By Equation 5 we can calculate the rate at which the oxygen at a given pressure comes into contact with the filament. We can then compare this rate with the rate found experimentally for the same pressure. By dividing the two, we find what fraction of all the molecules that strike the filament react with it. Let us call this fraction ϵ. Of course this fraction must be less than unity, for the reaction cannot possibly take place more rapidly than the rate at which the molecules can come into contact with the surface. Experimentally, we have shown that the rate of clean-up is proportional to the pressure. Since the rate at which the molecules strike the filament is also proportional to the pressure by (5), it is evident that ϵ is the same at all pressures in the range covered by the experiments. Table I shows the values obtained for ϵ from experiments at different filament temperatures. We see that ϵ is always less than unity, as of course it must be, but at the highest temperatures it seems to be approaching a limit which is below unity. At the lowest temperatures ϵ has a very large temperature coefficient, much higher than if we were dealing with a reaction of the types studied by Nernst with a diffusion film of constant thickness.

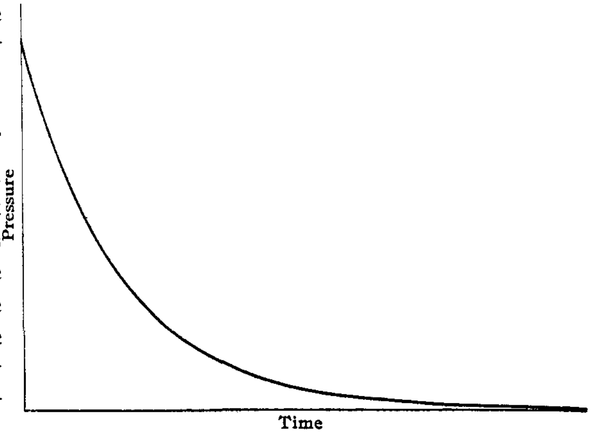

Fig. 1.—Typical curve for the clean-up of oxygen.

TABLE I.—RATE OF CLEAN-UP OF OXYGEN.

Temp.	1070° K.	1270	1470	1570	1770	2020	2290	2520	2770
ϵ	0.00033	0.0011	0.0053	0.0094	0.0255	0.049	0.095	0.12	0.15

Experiments were made with the bulb cooled by liquid air and also heated to 300° in an oven. The rate of reaction was found to be independent of the bulb temperature.

Let us now examine these experimental data and see what conclusions can be drawn as to the mechanism of the reaction.

Since the oxide formed is WO_3, it is evident that at least two molecules of oxygen must react with each atom of tungsten.

There are two possibilities to consider. Either both the oxygen molecules simultaneously strike a single tungsten atom or else an oxygen atom or molecule must already be present on the surface at the point where the second molecule strikes.

We have already seen that the number of oxygen molecules striking the surface per second within an area of molecular dimensions is $170 \times p$. The velocity of the molecule is 44,000 cm. per sec. If we consider a molecule which strikes the surface and rebounds, the length of time it remains within molecular dimensions of the surface is the time taken to travel twice the diameter of the molecule, or 5.4×10^{-8} cm. In other words, the duration of a collision is only 1.2×10^{-12} seconds. Since there are $170 \times p$ collisions per second, the total time in each second during which molecules are present at a given point is $170 \times 1.2 \times 10^{-12} p$ or $2.1 \times 10^{-10} p$. This gives us directly the probability that a molecule striking a given point on the surface will find a molecule of oxygen already present. Thus, if we had to depend on simultaneous collisions we see that ϵ could not exceed $2.1 \times 10^{-10} p$. This is vastly less than the values of ϵ actually observed. At a pressure of 10 bars this would give for ϵ a value of only 2×10^{-8}, whereas at the higher temperatures we have found values as high as 0.15. A further objection to the hypothesis of simultaneous collisions is that it would lead to values of ϵ which are not independent of the pressure. With this hypothesis, the reaction velocity would be proportional to the square of the pressure (bi-molecular reaction).

We must therefore conclude that the oxygen molecule striking the surface reacts with those already present. There is thus definite proof that some sort of film containing oxygen is present on the surface.

This film, however, cannot be in equilibrium with the space around it, as was assumed in Bodenstein and Fink's theory. Since the oxide formed travels directly to the bulb and condenses, there is no possibility that any appreciable number of molecules of oxide return to the filament.

On the other hand, it is not possible to assume that each molecule of oxygen striking the filament remains there a short but indefinite time before distilling off. In this way it would be possible to account for any given value of ϵ, but the velocity of the reaction would then be proportional to the square of the pressure rather than the first power.

From another point of view, we also must conclude that there is a film on the surface which determines the velocity of the reaction. We have seen that at the lower temperatures only a small fraction of the molecules which strike the filament react. According to the ordinary conception of a reaction in a homogeneous system, it is the relative velocity of two molecules with respect to each other at the moment of contact which largely determines whether or not they will react. The higher the relative velocity, the greater the chance of reaction is supposed to be. The experiments in the present case have shown that the rate of reaction does not depend on the relative velocity of the molecules, since changing the temperature of the bulb had no effect. What is it, then, that determines whether a given oxygen molecule shall react or not? It must be something that depends solely on the condition of the surface of the filament.

We have just seen that the older theory, which supposes that it is the thickness of an adsorption film which determines the velocity, leads us into difficulties. Let us now look upon the problem from the point of view of the new theory, according to which the adsorption film is only one molecule thick.

Since the experiments have shown that ϵ is independent of the pressure, it is natural to assume that the condition of the surface responsible for determining the reaction velocity, is also independent of the pressure. This requirement would be met if we assume that the surface film covers the surface nearly completely and consists of two kinds of molecules in thermal equilibrium with each other. One of the kinds of molecules is to be regarded as capable of reacting directly with the oxygen striking the surface, while the other is incapable of so doing. The conclusion that the surface must be nearly completely covered with an adsorption film of oxide is based largely on experiments on the electron emission, where it is found that a pressure of oxygen even as low as 0.01 bar cuts the electron emission from tungsten at 1900° K., down to less than 1% of its value in the absence of oxygen.

In formulating the above theory more precisely we may proceed as follows:

Let us assume that of all the oxygen molecules striking the bare surface of tungsten, the fraction α is absorbed or sticks to the surface, the fraction $1 - \alpha$ being reflected or rebounding from the surface. Only a very small fraction of the surface, however, is bare and we may assume that the oxygen molecules striking a surface already covered, are not absorbed in this way. If we let θ represent the fraction which is bare, then of all the oxygen molecules striking the whole surface only the fraction $\alpha\theta$ is absorbed. Now the rate at which the oxygen molecules strike the surface is given by Equation 5 and we see that it is proportional to the pressure. We thus see that the rate at which oxygen is absorbed by the surface is

$$\alpha \, \theta \, p$$

if we neglect for convenience the constant factor in Equation 5.

To form a more concrete picture of the mechanism of the reaction, let us assume that the oxygen on the surface is at first in the form of the compound WO_2, but that this reacts with the tungsten in contact with it to form $2WO$, and that this reaction is reversible and that equilibrium prevails between the two compounds.[1] According to the law of mass action, the surfaces covered by the two compounds will have to fulfill the relation

$$\theta_1 = K\theta_2$$

where K is the equilibrium constant and θ_1 is the fraction of the surface covered by WO_2 and θ_2 is the surface covered by WO.

It is now natural to assume that if oxygen striking the surface collides with a WO_2 molecule, no reaction takes place, but that when the oxygen strikes a WO molecule it reacts to form WO_3, which distills off. Of all the O_2 molecules striking the WO we may, for the sake of generality, assume that only the fraction ϵ_2 reacts.

From these considerations it is easy to state the problem mathematically as follows:

$$\alpha\,\theta p = {}^1/_2\theta_2\epsilon_2 p \tag{7}$$

$$\theta_1 = K\theta_2 \tag{8}$$

$$\theta + \theta_1 + \theta_2 = 1 \tag{9}$$

The first equation states simply that the rate at which the oxygen is adsorbed is equal to the rate at which it is removed by the reaction. The coefficient $^1/_2$ is necessary because each molecule of oxygen striking the filament only removes one atom ($^1/_2$ molecule) of oxygen from it in forming WO_3. The second equation merely expresses that equilibrium exists between the WO_2 and the 2 WO, and the third equation states that the bare surface is equal to that which is not covered by the WO_2 and the WO. For a more general solution of the problem we may also take into account the fact that the WO_2 and the WO are probably evaporating or dissociating to some extent and that the WO_3 that is formed requires some time before it evaporates. The equations obtained in this way are more complicated than those above, but can easily be worked out. The results in the present case are not essentially different from those we obtain by the above equations.

From the three equations above we may eliminate θ, θ_1 and thus obtain

$$\theta_2 = \frac{2\alpha}{\epsilon_2 + 2\alpha(K + 1)} \tag{10}$$

The rate R at which the oxygen is converted into WO_3 is

$$\frac{3}{2}\epsilon_2\theta_2 p$$

or

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[1] This assumption of the existence of the compounds WO and WO_2 on the surface is made only to form a picture of a possible mechanism. It is much more probable that the oxygen atoms are chemically combined with tungsten atoms which form the surface of the filament and which are part of the "space lattice" of the tungsten crystals.

$$R = \frac{3\alpha\epsilon_2 p}{\epsilon_2 + 2\alpha(K + 1)} \qquad (11)$$

This shows that the rate of clean-up by this theory is proportional to the pressure, in agreement with the experiments. If every oxygen molecule which struck the filament reacted, the rate of clean-up would be p (neglecting the same constant factor as before) and hence the value of ϵ which we determined from the experiments and have given in Table I, would be

$$\epsilon = \frac{3\alpha\epsilon_2}{\epsilon_2 + 2\alpha(K + 1)} \qquad (12)$$

This is independent of the pressure. It is probable that ϵ_2 and α are nearly independent of the temperature and that the large temperature coefficient of ϵ is due to that of K. Thus, at low temperatures, K must be very large, which means that the amount of WO in equilibrium with the WO_2 is very small. As the temperature rises, K decreases and ϵ therefore increases, but finally reaches a limiting value,

$$\epsilon_{\text{max.}} = \frac{3\alpha\epsilon_2}{\epsilon_2 + 2\alpha} \qquad (13)$$

which is always less than unity. This is in splendid agreement with the experiments. In order that $\epsilon_{\text{max.}}$ may be as large as 0.2, the value estimated from Table I, it is necessary that ϵ_2 shall be greater than 0.2 and that α shall be greater than 0.1. That is, at least 0.2 of the O_2 molecules, colliding with WO molecules must react and at least 0.1 of the oxygen molecules striking the bare surfaces must be absorbed or react to form WO_2.

By this theory it may be predicted that with still higher filament temperatures ϵ will begin to decrease when a point is reached at which the WO_2 and WO evaporate or dissociate so rapidly that only a small fraction of the surface is covered. For similar reasons it may be predicted that ϵ cannot remain independent of the pressure down to the lowest pressures. There is excellent experimental evidence that the last prediction is in accord with the facts. It is found that an extremely low pressure, probably less than 0.001 bar, of oxygen in a tungsten lamp not only does not perceptibly attack the filament, but actually prevents the tungsten which evaporates from discoloring the bulb. This action is probably due to the dissociation of the WO on the filament producing atomic oxygen which, traveling to the bulb, reacts with the deposited tungsten even at room temperature, to form WO_3. In a later paper I hope to take up this point in more detail and consider the phenomena quantitatively from the view-point of the theory I have outlined this evening.

I have spent much more time on this reaction between tungsten and oxygen than its experimental importance warrants, but I wished to illustrate by it in some detail the application of the theory of molecular films.

2. Reactions between Chlorine and Tungsten.—Chlorine at low pressures attacks tungsten, forming WCl_6. The velocity of the reaction reaches a maximum at about 1500° K. and becomes extremely small at higher temperatures. This is undoubtedly to be explained by the dissociation of some of the intermediate products which are necessary steps in the formation of WCl_6. The chlorine leaving the filament is largely dissociated into atoms under these conditions and produces some extremely interesting effects which I shall discuss more in detail a little later.

3. Reactions between Carbon and Oxygen.—It has long been a disputed question whether carbon monoxide is a direct product of the oxidation of carbon or whether it is formed only by the interaction of carbon with carbon dioxide produced as a primary product.

By heating a carbon filament in oxygen at very low pressures in a bulb immersed in liquid air, a definite answer to this question is readily obtained. If carbon dioxide is produced and leaves the filament, it must travel directly to the bulb and there be condensed at the low temperature of liquid air where the vapor pressure of carbon dioxide is barely measurable. The filament therefore never comes in contact with carbon dioxide.

The first experiments showed that the phenomena involved in the oxidation of carbon are very complex as compared with those of the oxidation of tungsten. With tungsten the results were always accurately reproducible, but with the carbon filaments the rate of clean-up depended entirely upon the previous history of the filament.

In the experiments metalized carbon filaments were used. These consist of a highly graphitized carbon of the highest attainable purity (ash about 0.01%). After mounting in the lamp the filament was heated in a high vacuum for several hours until it ceased giving off measurable quantities of gas. Small quantities of oxygen at a pressure about 5–10 bars, were admitted and the rate of clean-up with different filament temperatures was noted.

With the filament at 1220° K. the oxygen began to disappear very rapidly, but soon slowed down to a rather uniform slow rate. At this temperature the whole of the oxygen gradually disappeared and CO_2, without a trace of CO, was formed. The amount of CO_2, however, was considerably less than the equivalent of the oxygen which disappeared. On adding a second supply of oxygen the rate of clean-up was very much slower than the first time. After three or four treatments the rate of clean-up finally became reproducible. On raising the filament temperature to 1700° K. the rate of clean-up increased again, but gradually decreased as before. In the first treatment, at 1700° K., all the oxygen disappeared and no CO was formed, but in subsequent treatments at the same temperature there began to be formed increasing amounts of CO. After five or six runs in oxygen, pumping out the residues of CO each time, the pressure would decrease only 10 or 20% when the filament was lighted in a fresh supply of oxygen, and would then increase until finally a residue of pure CO would remain, having a volume usually about 30% greater than that of the oxygen used.

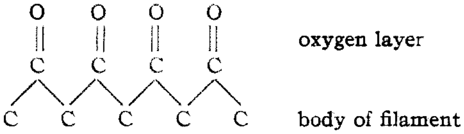
If the filament was now heated in vacuum, it gave up CO extremely slowly at 1700° K., but at 2200° K. the evolution was much more rapid, although even at this temperature from half an hour to an hour was required before the evolution ceased. The total amount of CO so obtained usually amounted to 3–5 cu. mm. After having thus heated the filament in vacuum, the first run in oxygen with the filament at 1700° K. gave nothing but carbon dioxide, but the runs following this gave, as before, an increasing amount of carbon monoxide.

With the filament at 2100° K. in oxygen, there was always a large quantity of carbon monoxide produced, even in the first run.

These experiments seem to show that when oxygen acts on carbon at, say, 1200° K., part of the oxygen reacts to form CO_2, but another part forms an adsorption layer of some sort on the surface which retards the velocity of the reaction. This adsorption layer is probably chemically combined with the carbon, presumably as an extremely stable solid oxide of carbon.

At higher temperatures the rate of formation of this adsorption layer increases rapidly. When a sufficient quantity has accumulated this compound begins to decompose, forming carbon monoxide, the higher the temperature the more rapid being the formation of this gas.

Judging from the great stability of this adsorption layer, which enables it to be heated for half an hour at 2200° K. in the highest vacuum without being completely decomposed, a plausible guess as to its constitution is that it consists of oxygen atoms chemically combined with the carbon atoms which form the surface of the filament. According to our recent knowledge of the structure of solid bodies, we have the best of reasons for believing that the atoms of solid bodies are held together directly by chemical forces and that a crystal must be looked upon as a single molecule. The carbon atoms in the filament must thus be considered as forming endless carbon chains with each other. It is probably due to the great stability of these carbon chains that carbon has such a low vapor pressure and such a high melting point. In the present case, if we consider the oxygen atom to be chemically combined with one of the outer carbon atoms, we have a structure that could be represented by the formula



This hypothesis would seem to afford an unforced explanation of the extraordinary difficulty of removing oxygen and hydrogen from carbon.

Experiments were also made to study the action of the heated carbon filament on carbon dioxide and monoxide.

With carbon dioxide at 1220° K. no change occurred, but at 1700° K. carbon monoxide was formed at first slowly, and then gradually more rapidly. The total volume, however, usually remained nearly constant, showing that the reaction was not

$$CO_2 + C = 2CO,$$

but was rather

$$CO_2 + C = \underset{\text{(gas)}}{CO} + \underset{\text{(adsorbed on carbon)}}{CO}.$$

On the other hand, at temperatures up to 2400°, there was never any perceptible change in volume when the filament was heated in carbon monoxide, showing that the adsorbed compound is not formed by adsorption of carbon monoxide.

These results should be looked upon merely as preliminary results, and I hope to be able to present further details of the experiments with carbon and oxygen at a later date.

II. Reactions with Vapor from Filament.

Clean-up of Nitrogen by a Tungsten Filament.[1]—When a tungsten filament is heated to 2700 or 2800° K. in nitrogen at low pressure, the nitrogen slowly disappears at a rate which is independent of the pressure. Fig. 2 gives a good example of the way the pressure decreases in a typical experiment. At the high temperatures employed in these experiments it has been found that the filament evaporates fairly rapidly. A comparison of the amount of nitrogen cleaned up with the loss of weight of the filament, showed that the ratio was the same as

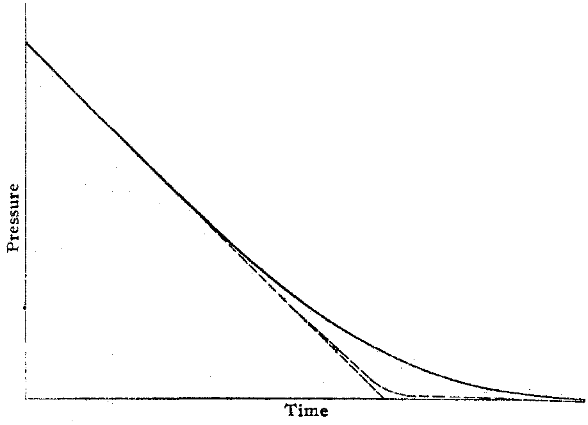


Fig. 2.—Typical curve for the clean-up of nitrogen.

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[1] This Journal, **35**, 931 (1913).

that in a compound of the formula WN_2. This ratio still held if the temperature of the filament was raised several hundred degrees, where the rate of clean-up was over four hundred times more rapid. Measurements showed that the rate of loss in weight of the filament in low pressure nitrogen was the same as in vacuum, so it was evident that the nitrogen did not attack the filament.

In these experiments the tungsten does not collect on the bulb as the usual black deposit, but was of a clear, brown color. On opening the bulb and admitting moist air the brown color disappeared and a strong smell of ammonia was observed.

It is evident that the nitrogen in this case combined with the tungsten vapor as fast as it is given off. By working at such low pressures that only a few of the tungsten atoms collided with nitrogen molecules on the way to the bulb it was proved that practically every collision between the nitrogen molecules and tungsten atoms resulted in the formation of the compound. In other words, the coefficient ϵ is unity. We are here dealing then in reality with a bimolecular homogeneous reaction of maximum possible velocity.

The true reaction velocity is independent of the temperature. What is measured in the experiment is only the rate at which the tungsten evaporates.

Recent experiments have shown that the rate of clean-up of the nitrogen at higher pressures is the same whether the bulb is heated to 300° C. or is cooled in liquid air. But at lower pressures an interesting difference occurs, which is shown by the dotted curve in Fig. 2. With the bulb at room temperature the curve departs from the straight line at the lower pressures because the nitrogen molecules become so scarce that a large fraction of the tungsten atoms strike the bulb without colliding with nitrogen molecules. From the agreement between the calculated and observed curves at the lowest pressures, it was reasoned (in the paper on the nitrogen clean-up) that the tungsten atoms striking the glass deposit as such, do not combine with nitrogen. This suggested that few, if any, nitrogen molecules are present on the glass at room temperature. The more recent experiments now prove that when the bulb is cooled in liquid air the tungsten atoms do combine with nitrogen even if the pressure is so low that they do not strike them on the way to the bulb. The shape of these curves at low pressures proves that the glass surface, or rather that of the tungsten nitride layer on the glass, at liquid air temperature is covered by an adsorbed film of nitrogen, but at room temperature it is not. This method can even be used to calculate quantitatively the fraction of the surface that is covered by the nitrogen at any given temperature.

Clean-up of Nitrogen by a Molybdenum Filament.—Molybdenum evaporates much more readily than tungsten, and it was thought that nitrogen would therefore be cleaned up more easily by a molybdenum than by a tungsten filament. This was not found to be the case. On further investigation it was found that the molybdenum lost weight at the same rate as in vacuum and that the rate of clean-up was independent of the pressure, as in the case of tungsten, but that the amount of gas cleaned up was only about one-tenth of that which would have been observed if every molybdenum atom combined with a nitrogen molecule.

Under these conditions we should expect that the rate of clean-up would vary with the pressure, for the higher the pressure the more collisions the molybdenum atoms must make with the nitrogen molecules before striking the bulb. In order to account for the fact that the rate of clean-up is independent of the pressure, it is necessary to assume that if combination does not take place during the first collision it does not take place at all. The question arises: What is the difference between the first and the subsequent collisions which can account for the different behavior in the two cases? Since the nitrogen molecules are the same in both cases, the difference must lie in the molybdenum atoms. Now, according to our ordinary conceptions, atoms can differ from each other only in respect to their translational velocity.[1] Since the velocities of the molybdenum atoms leaving the filament are higher than those after collision with nitrogen molecules, it would seem that this could readily explain the fact that combination can occur only on the first collision.

If this were the case, then raising the temperature of the filament should increase ϵ; that is, the percentage of successful collisions. Actually, however, the reverse was found. By lowering the filament temperature 100°, ϵ increased from 0.11 to 0.33, and by raising it 100°, ϵ decreased to 0.05. The effects of varying the bulb temperature were still more striking. With the bulb in liquid air, ϵ became about 0.4 and by heating the bulb to 270° C. ϵ became 0.01.

In other words, the reaction velocity has a very marked negative temperature coefficient; there is thus a much larger fraction of successful collisions if the relative velocities of the nitrogen molecules and molybdenum atoms are small at the moment of collision.

This, however, makes it still more difficult to explain why the reaction can occur only at the first collision, for it would seem that if the first collision were unsuccessful the subsequent collisions would be more likely to result in combination because the velocities would then be lower.

I think the solution of this difficulty is to assume that the first collision always results in a union of the nitrogen and molybdenum so that they travel together to the bulb, but that this union may occur in one of two ways, depending upon the relative velocity of the molecule and atom at

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[1] Experiments show that neither the nitrogen nor the molybdenum is electrically charged.

the moment of their collision. If the relative velocity is high, the union is so weak that the two components fall apart when the unstable molecule strikes the bulb. On the other hand, if the relative velocity at the moment of contact is small enough, actual chemical combination occurs.

This may seem a rather far-fetched theory, but there is a very large amount of experimental evidence in its favor which I have not time to go into this evening. A paper describing these results in more detail is now nearly ready for publication.

The striking fact that the velocity of the actual chemical reaction has a large negative temperature coefficient will be considered again in connection with other experiments. It must be pointed out, however, that this effect is only noticed because of our analysis of the reaction into its separate partial reactions. If the temperature of the gas and filament varied together and if the function of the molybdenum vapor were not known, the effect would never be noticed, for the large positive temperature coefficient of the rate of evaporation of molybdenum would completely mask that of the true chemical reaction.

In these experiments the molybdenum deposit which collected on the bulb had very remarkable properties. It adsorbed large quantities of nitrogen, but not hydrogen, if cooled by liquid air. But, at room temperature and above, it could slowly dissolve large quantities of hydrogen which it would slowly give up again at 300° C. Although it contained a large amount of nitrogen, none of this gas could be driven off by heating it at 360°; but if it was heated in nitrogen at 250° C. it apparently combined with the nitrogen, for this gas was absorbed and was not liberated by heating at 360° C. in a vacuum.

Another characteristic of this deposit was that it reacted rapidly at room temperature with water vapor, producing hydrogen, most of which remained dissolved and was liberated on heating.

Molybdenum deposited on the bulb in high vacuum does not exhibit any of these characteristics. It seems that the molybdenum described above, is in an atomic state of division as a result of being deposited atom by atom by the decomposition of the unstable compound formed in the "unsuccessful collisions."

Clean-up of Carbon Monoxide by Tungsten.—With the bulb at room temperature this gas behaved exactly like nitrogen. In fact, with the filament at a given temperature, the curves obtained first with nitrogen and then with carbon monoxide proved to be identical. This proved that each atom of tungsten combined with one molecule of CO, presumably to form a compound WCO. The coefficient ϵ must have been unity as in the case of nitrogen.

Since with nitrogen and molybdenum ϵ was found to vary with the temperature, it was of interest to see if ϵ with carbon monoxide and tungsten might not vary also.

Raising the bulb temperature to 300° gave a value of ϵ distinctly less than at room temperature, so that the expected effect was present and in the same direction as with the Mo-N_2 reaction.

When a similar experiment was tried with the bulb in liquid air, the surprising result was obtained that on lighting the filament the gas cleaned up about five times as fast as with the bulb at room temperature. Further experiments showed that the filament under these conditions lost weight about five times as fast as in a vacuum, so that the filament was clearly being attacked by the carbon monoxide. The rate of clean-up, however, was still linear; in other words, was independent of the pressure. Evidently, the compound formed was of approximately the same composition as that formed by interaction with the vapor, namely WCO.

There is apparently no escape from the conclusion that the attack of the filament by CO is a reaction which takes place more rapidly when the velocity (or at least kinetic energy) of the CO molecules is small. We thus again have a case of negative temperature coefficient.

The simplest explanation of the fact that the rate of attack is independent of the pressure, seems to be that the velocity of the reaction is so great that the rate of evaporation of the compound formed determines the rate of reaction.

Thus we assume that the surface is practically completely covered with a film (1 molecule deep) of WCO. As fast as molecules of this distil off, the surface of tungsten is exposed to the attack of the CO.

If this explanation is correct, then as long as the bulb temperature is low enough to cause the formation of a film of WCO, it is evident that a further lowering of the bulb temperature should cause no further increase in rate. Another conclusion may be drawn. At a bulb temperature so high that the supply of WCO is barely sufficient to keep the surface covered, we should expect that the rate of clean-up at the lower pressures would be less than at higher. In other words, there should be certain intermediate temperatures at which the rate of clean-up is no longer linear.

The experiments made to test these points have yielded results in quantitative agreement with the theory. Thus it was found that the rate of clean-up at —78° C. (solid CO_2) was the same as at —190° C., and on the other hand the rate at —20° was the same as at +20°. But at —40° the rate was intermediate between that at —78° and that at —20°, and, furthermore, the curve was no longer straight, but was in splendid agreement with a calculated curve which was based on the assumption that the rate of formation of WCO on the *exposed surface* of tungsten was proportional to the pressure of CO.

I think this case is an excellent illustration of the general applicability of what I might call the molecular film theory of heterogeneous reactions. In this case also I hope soon to publish quantitative data with a more completely developed theory.

Clean-up of Oxygen by Platinum.—A platinum filament at temperatures above about 1600° K. gradually causes the clean-up of low pressures of oxygen. With pressures less than 100 or 200 bars the rate is independent of the pressure. The filament loses weight at the same rate as in vacuum. Quantitative measurements show that the oxygen combines with the platinum atoms as fast as they evaporate from the filament and form the compound PtO_2 which collects on the bulb as a brown deposit. At higher pressures the oxygen also begins to attack the platinum at a rate dependent on the pressure.

III. Catalytic Reactions.

Dissociation of Hydrogen into Atoms.[1]—It has been shown that when a wire of tungsten, platinum, or palladium is heated to a temperature above 1300° K., in hydrogen at very low pressure (1–20 bars), a portion of the hydrogen molecules which strike the filament is dissociated into atoms. This atomic hydrogen has remarkable properties. It is readily adsorbed by glass surfaces at room temperature, although more strongly at liquid air temperatures; but only a very small amount (a few cu. mm.) can be so retained because the atoms evidently react together to form molecular hydrogen as soon as they come in contact, even at liquid air temperatures. The atomic hydrogen reacts instantly at room temperature with oxygen, phosphorus and many reducible substances such as WO_3, PtO_2, etc.

When a tungsten wire is heated to very high temperatures (above 2000°) in hydrogen, the dissociation of the gas in contact with the wire causes the absorption of a very large quantity of heat. The atomic hydrogen produced diffuses out from the wire and as soon as it reaches a cooler region recombines to form molecules and liberates the heat of the reaction. The result is that the heat conductivity of hydrogen, at temperatures where dissociation occurs, is several times larger than it would otherwise be.

Recently, Mr. Mackay and I have made a series of measurements on the heat losses from tungsten wires at pressures ranging all the way from 10 bars up to atmospheric pressure and at temperatures up to the melting point of tungsten. From these data I have been able to show that the dissociation of the hydrogen does not occur in the space around the wire, but takes place only among the hydrogen molecules which have been absorbed or dissolved by the metal. The mechanism is as follows:

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[1] *Trans. Am. Electrochem. Soc.*, 20, 225 (1911); THIS JOURNAL, 34, 860 (1912); 34, 1310 (1912); 35, 927 (1913); 36, 1708 (1914); 37, 417, (1915); *Z. Elektrochem.*, 20, 498 (1914).

All the hydrogen atoms striking the surface of the wire and about 70% of all the molecules striking the wire are absorbed by it. The velocity of the reaction between the molecules and atoms of hydrogen absorbed is so great that equilibrium prevails among them at all times. The rate of dissociation of the hydrogen by the wire can thus be calculated from the dissociation constant of the hydrogen and from Equation 5, which gives us the rate at which the gas comes into contact with the wire. By reversing this process it has been possible to determine the degree of dissociation of hydrogen at all temperatures and pressures and to calculate the heat of dissociation. At 2000° K., hydrogen is 0.33% and at 3000° K., 13% dissociated at atmospheric pressure.

Dissociation of Chlorine into Atoms.—By heating a tungsten filament for a short time to 3000° K. in a high vacuum a sufficient quantity volatilizes to form a black deposit on the bulb. If, now, a low pressure of chlorine be admitted to the bulb, this does not perceptibly attack the deposit on the bulb nor the filament, even if the bulb is heated to 200° C. However, if the filament is now heated to a high temperature, while the bulb is kept cool, the tungsten deposit on the bulb soon disappears. The chlorine has evidently been activated or dissociated by the filament and the atoms formed travel at these low pressures directly from the filament to the bulb without having any chance to recombine on the way.

The experiment is more striking if two filaments be placed side by side in the same bulb containing a very low pressure of chlorine. If one of the filaments be heated to a high temperature it is found that the other one, which remains cold, is gradually eaten away on the side facing the hot filament until it finally disappears completely. The hot one does not lose at all in weight, but may even become heavier, by having tungsten deposited on it by the decomposition of the chloride formed by the attack of the cold filament.

Dissociation of Oxygen into Atoms.—In connection with the clean-up of oxygen by a tungsten filament I have already spoken of some of the evidence for the dissociation of oxygen into atoms at extremely low pressures. Still better evidence has been obtained in some experiments on thermionic currents in which the bulb containing the filaments is immersed in liquid air. Under these conditions an active form of oxygen can be collected on the glass which is slowly given off and reacts even at liquid air temperatures with tungsten. The phenomena are in many ways similar to those observed with hydrogen. A further quantitative study of the formation of this active oxygen is being undertaken.

Reaction between Carbon Monoxide and Oxygen in Contact with Platinum.—In all the reactions I have spoken of, thus far, there has been only one gas in contact with the filament. The case where the filament acts catalytically on a reaction between two gases is an important one and warranted special study. For this purpose a short filament of fine platinum wire was mounted in the center of a four-liter bulb. Pressures of carbon monoxide and oxygen up to a total of about 30 bars were admitted and the filament was heated to such a temperature that the reaction proceeded at a convenient rate. A large tube extended from the lower part of the bulb and was kept immersed in liquid air, so that the molecules of carbon dioxide produced in the reaction were condensed before they had any opportunity of striking the filament.

The results were very striking. The rate of clean-up was found to be directly proportional to the pressure of oxygen, but *inversely proportional* to the pressure of carbon monoxide. Reference to the literature showed that Bodenstein and Ohlmer,[1] in their study of the reaction between these gases on quartz glass surfaces, had found these same relations at about atmospheric pressure. Subsequently, Bodenstein and Fink[2] suggested tentatively that the explanation of this peculiar behavior might be that the surface of the quartz is covered with an adsorbed film of carbon monoxide of a thickness proportional to the pressure of this gas. If it was further assumed that the oxygen had to diffuse through the layer of carbon monoxide and come into contact with the platinum before it could react with the monoxide, then the reason for the reaction being directly proportional to the oxygen pressure and inversely proportional to that of the carbon monoxide was apparent.

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

If, on the other hand, we apply the "theory of molecular layers," these difficulties disappear. Let us assume that, of all the CO molecules striking the surface, a certain fraction α, are condensed and that the CO layer thus formed distils off at a certain rate. Let us assume further that the reaction occurs when CO molecules strike oxygen on the surface, but does not occur when O_2 molecules strike CO molecules. We might picture the cause of this as being due to the carbon monoxide molecules on the surface arranging themselves with the carbon atoms in contact with the platinum, while the oxygen atoms cover these and thus protect the carbon from attack by the oxygen.

It is easy to state these assumptions mathematically and thus derive an equation giving the rate of the reaction in terms of the partial pressures of the gases. This relation is of the form:

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[1] *Z. physik. Chem.*, **53**, 166 (1905).

[2] *Ibid.*, 60, 46 (1907).

$$R = \frac{1}{\dfrac{ap_1}{p_1} + \dfrac{b}{p_1} + \dfrac{c}{p_2} + \dfrac{d}{p_1p_2}} \qquad (14)$$

where p_1 is the partial pressure of CO and p_2 is that of the oxygen. The coefficients a, b, c and d all have a definite physical significance in this theory, but I will not go into this at present.

It is readily seen that at higher pressures the terms involving b, c and d become negligible compared to that involving a. The p_2 in this term goes into the numerator and we have

$$R = p_2/ap_1 \qquad (15)$$

which is the law observed in the experiments I have described.

On the other hand, at lower pressures or at higher temperatures, the first term in the denominator becomes negligible and the fourth term still remains so and the relation becomes

$$R = \frac{1}{\dfrac{b}{p_1} + \dfrac{c}{p_2}} \qquad (16)$$

At still lower pressures or higher temperatures the last term in the denominator would become the important one and the equation would reduce to

$$R = p_1p_2/d. \qquad (17)$$

This theory thus suggested that if higher filament temperatures were used in the experiments the rate would no longer be in accord with Equation 15 but would follow Equation 16. Furthermore, the term containing d involved the rate of evaporation of the CO and O_2 from the surface in such a way that it must increase with the temperature. The velocity of the reaction would therefore decrease at higher filament temperatures.

To test this prediction it was necessary to use a filament of extremely short length (1 cm.) and very small diameter (0.003 cm.), so that the rate of clean-up would not be too rapid to measure. Under these conditions it was found that the rate of clean-up actually reached a maximum at a temperature below a red heat, and at a bright red heat the rate was only about one-tenth of that at the lower temperature.

By studying these data in the light of this theory, I am confident that it will be possible to calculate in detail the statistics of this reaction; for example, the rate of evaporation of each constituent, the proportion of the collisions between the CO and the oxygen which result in combination, etc.

Reaction between Hydrogen and Oxygen in Contact with Platinum.—This reaction proves at low pressures in absence of water vapor to be essentially similar to that between carbon monoxide and oxygen. At low temperatures the rate of reaction is directly proportional to the pressure of oxygen and *inversely proportional to that of the hydrogen.* At higher temperatures the rate varies with the pressure as indicated by Equation 16, but in contrast to the behavior of oxygen and carbon monoxide, the velocity does not decrease when the temperature is raised even to the melting point of the filament.

Other Catalytic Reactions.—The theory here outlined would seem to be generally applicable to all heterogeneous reactions, even at atmospheric pressure. The many reactions studied by Bodenstein lend themselves admirably to testing out this theory.

There is every indication that the experimental results of Fink will be in at least as good agreement with equations derived by this theory as with those derived from the theory that involves diffusion through a film of variable thickness. For a given concentration of SO_3 the equations take the form

$$R = \frac{1}{\frac{b}{p_1} + \frac{c}{p_2}}. \qquad (18)$$

When one constituent is in excess the reaction velocity is thus proportional to the concentration of the other. When there are equivalent proportions, then the velocity is proportional to the total pressure. These are the relations found by Fink, but here one equation fits all the results, whereas by Fink's theory two equations are necessary.

Theory of Adsorption.—The "theory of molecular layers" leads to a simple but quantitative theory of adsorption.

In every reaction we have studied we have found that of all the molecules striking a surface, a large proportion are absorbed. If the rate of evaporation is high the molecules will leave the surface very soon, while if the rate of evaporation is low they may remain a long time. The adsorption is due to the fact that a certain time must elapse between the condensation and the evaporation of a molecule.

In the case of strongly adsorbed bodies, or in all cases where the vapor is nearly saturated, we must take into account the condensation and evaporation in the second and subsequent layers. If we assume that the rate of evaporation in the first layer is different from that for the others, this theory, stated mathematically, leads to an equation of the form

$$Q = \frac{1}{\frac{a}{p} + b - cp} \qquad (19)$$

where Q is the amount adsorbed at the pressure p.

This theory will be developed in detail in a subsequent paper.

IV. Reactions Caused by Electrical Discharges.

If a positive potential of a hundred volts or so is applied to an auxiliary electrode in a bulb containing a heated filament, electrons are given off from the heated filament and these, in passing through the gas, may produce ionization. The positive ions then are attracted to the hot filament and strike it with high velocity. Under these conditions reactions often occur which otherwise would not take place. For example, if the gas is nitrogen, these positive ions will combine with the tungsten filament to form the nitride WN_2 even at temperatures where there is normally no appreciable volatilization of the tungsten.

Similar effects are observed with hydrogen and carbon monoxide.

The effects are in general more complicated than those observed in the purely thermal reactions, and largely for that reason I shall not consider them further at present. The phenomena, however, are of very great interest and will probably be the subject of many further investigations.

General Considerations.

This evening I have attempted to present to you a rather new view-point by which we may regard heterogeneous chemical reactions. By working at very low pressures it has been possible to learn much about the mechanism of these reactions.

In each case we have seen that the velocity of the reaction has been limited by the rate at which the reacting molecules come into contact with each other.

With reactions occurring on the surface of the wire, only a small fraction of the surface was in condition suitable for the reaction. The rate of reaction in these cases was limited by the rate at which the gas molecules could strike that part of the surface where the reaction could occur. In no case was there any evidence that the reaction was limited by any diffusion process in the ordinary sense.

In the case of reactions where the gas combined with vapor from the filament, the rate was again limited by the rate at which the molecules came in contact. All those that made contact reacted.

Only in two cases was it possible to measure a velocity which was not limited by such purely physical factors. These cases were the combination of nitrogen with molybdenum vapor and the attack of tungsten filament by carbon monoxide with low bulb temperatures. It is remarkable that in both these cases the temperature coefficient of the reaction velocity was strongly negative. In all the other reactions the large positive temperature coefficient was due to the fact that the rate of evaporation of the filaments or of adsorbed materials on them increases so rapidly with temperature.

I do not mean to imply that all the truly chemical reactions must have negative temperature coefficients, but the results strongly suggest that such chemical reactions are very common, and that their effects are masked by other physical factors having large positive temperature coefficients.

The number of chemical reactions previously known which have negative temperature coefficients is extremely small. Bodenstein cites one case, that of the reaction: $2NO + O_2 = 2NO_2$.

Strutt found that atomic nitrogen recombines to form molecules much more rapidly at low temperatures than at high, and he reasons that a high translational velocity of the molecule should in general hinder rather than hasten the reaction. He considers that rotational velocity of the molecules, on the other hand, favors the reaction and that this factor in the majority of reactions greatly outweighs that of the translational velocity. Thus reactions between atoms should always have negative temperature coefficients, since atoms cannot have rotational energy. The present work lends further support to Strutt's views.

The view-point developed as a result of this work with low pressure reactions is undoubtedly applicable to reactions at high pressures and also to reactions between solids and liquids. It is hoped that further work will lead in a similar way to a better understanding of the mechanism of homogeneous reactions.

In conclusion, the writer wishes to express his appreciation of the valuable assistance of Mr. S. P. Sweetser, who has carried out most of the experimental part of this work.

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CUPROUS SALTS OF OXYGEN ACIDS AND A NEW METHOD FOR PREPARING CUPROUS SALTS.

[PRELIMINARY PAPER.]

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The number of cuprous salts of oxygen acids is so small, and those that are known are so unfamiliar, that it is not surprising that the misstatement is often made in text-books, even in the larger number of the more modern ones, that such compounds do not exist.

The longest known and most familiar member of this class of compounds is red cuprous sulfite, $Cu_2SO_3.H_2O$, first prepared by Rojoski.[1] Bourson[2] gives, as the best method for its preparation, the addition of a concentrated solution of sodium bisulfite to a solution of cupric sulfate, filtration from the slight precipitate, and gentle warming of the filtrate. Sulfur

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[1] *Jahresber.*, **1851**, 366.

[2] *J. prakt. Chem.*, **25**, 399 (1842).