THE EVAPORATION, CONDENSATION AND REFLECTION OF MOLECULES AND THE MECHANISM OF ADSORPTION.

By Irving Langmuir.

PART I.

IN a recent paper R. W. Wood[1] describes some remarkable experiments in which a stream of mercury atoms is caused to impinge upon a plate of glass held at a definite temperature. With the plate at liquid air temperature all the mercury atoms are condensed on the plate, whereas with the plate at room temperature all the atoms appear to be diffusely reflected. Wood seems to consider that this is a real case of reflection.

There is, however, another way of interpreting the experiments, which, I think, is more in harmony with other facts than that suggested by Wood.

We may, for example, consider that all the atoms of mercury which strike the plate *condense no matter what the temperature of the plate.* When the plate is at the higher temperatures the condensed atoms may reëvaporate again so rapidly that the surface remains practically free from mercury. At first sight it might appear that there is no essential difference between this reëvaporation and a true reflection, but more careful consideration shows that the two phenomena are quite distinct. The difference would be manifest if the so-called reflection were studied at intermediate temperatures. In the case of reflection the number of atoms reflected would always be proportional to the number striking the surface, whereas, according to the reëvaporation theory, the number leaving the surface can never exceed the normal rate at which mercury evaporates into a perfect vacuum.

Wood states that he intends to undertake experiments at intermediate temperatures, and in view of this I should be loath to take up a discussion of the matter at present if it were not for the fact that much of my work during the last few years has had a very direct bearing on the question of the condensation versus the reflection of gas molecules.[2]

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[1] Phil. Mag., *30*, 300, 1915.

[2] In this connection, for the sake of historical accuracy, attention may be called to the fact that the rectilinear propagation of molecules in vacuo, which Wood and Dunoyer (Comptes Rendus, *152*, 593, 1911) have described, has long been familiar to incandescent lamp manufacturers not only in the case of tungsten lamps, but also with carbon lamps. Professor

As a result of this work, which I shall briefly describe in the following pages, I have gradually become convinced that molecules and atoms of all kinds show little or no tendency to be reflected from a solid surface against which they strike. In the case of metal vapors condensing on the corresponding metals, the evidence seems to indicate that not over one atom per thousand is reflected, if indeed, there is any reflection whatever. However, with molecules of the so-called permanent gases striking surfaces covered with adsorbed films of gas molecules, there is some evidence that a certain amount of reflection may occur. When hydrogen molecules strike a hydrogen covered surface at high temperatures it is possible that as many as 81 per cent. of the molecules are reflected. There is reason to believe that this represents the maximum possible degree of reflection and that with gases other than hydrogen and helium, the amount of reflection is always less than 50 per cent., no matter what may be the nature of the solid surface.

I. EXPERIMENTAL DATA.

Evaporation and Condensation.—In connection with an experimental determination of the rate of evaporation of tungsten filaments in a high vacuum[1] the following relation between the vapor pressure p and the rate of evaporation m (in grams per sq. cm. per second) was derived from the principles of the kinetic theory

$$m = (1 - r)\sqrt{\frac{M}{2\pi RT}}\,p. \tag{1}$$

Here M is the molecular weight of the vapor, R is the gas constant, and

W. A. Anthony, in a paper read before the American Institute of Electrical Engineers at New York in 1894, described this phenomena as follows (Trans. Amer. Inst. Elect. Eng., *11*, 142, 1894): "In the old Edison lamps the filament was copper-plated to the platinum wires. When a break in the filament occurred near the junction, the arc vaporized the copper and covered the bulb with a coating of metallic copper, except that a line of clean glass was often left on the side opposite the break, the line being the shadow of the unbroken leg of the filament. . . . The plain old-fashioned unpretentious vapor tension that bursts our steam boilers is all-sufficient to account for this rectilinear projection across the lamp bulb when there is nothing in the way." In the very active discussion which followed, Professor Elihu Thomson said "I am confident that I have seen it (this phenomenon) in series lamps when the carbon broke. In a good vacuum the carbon vapor condensing would give rise to particles which would move in rectilinear paths. The shadow effect is dependent ,on a *local* evolution of vapor, with a part of the wire or filament between the point of evolution and the opposite glass surface. I am also confident that I have seen platinum shadows." In the further discussion, J. W. Howell said, "The molecules of carbon set free by evaporation, fly from the filament as Professor Anthony says, in straight lines. They are projected from every part of the filament and . . . cast shadows on the globes. The reason why they do not cast shadows in most lamps is that the filament is not all in one plane." Mr. Howell then exhibited to those present, both carbon and platinum lamps which showed distinct shadows.

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[1] Langmuir, PHYS. REV. *2*, 329, 1913, and Phys. Zeitsch., *14*, 1273, 1913.

r is the coefficient of reflection of the vapor molecules which strike the surface of the solid (or liquid). It was stated at that time (1913) that "There are good reasons for believing that the reflection of vapor molecules from the surface takes place to a negligible degree only," and there followed a discussion of Knudsen's results on the heat conductivity of gases at low pressures which we shall consider in more detail below.

The above formula, taking $r = 0$, was then used to calculate the vapor pressure of tungsten from the experimental data on the rate of evaporation.

Subsequently[1] the vapor pressures of platinum and molybdenum were determined by the same method. At that time the question of the possible reflectivity was discussed as follows: "That the atoms of metal which evaporate from a hot wire are not reflected to any perceptible extent upon striking a surface, has been shown by many experiments in this laboratory. For example, if a single loop tungsten filament be heated in a highly exhausted bulb to such a temperature that the evaporation is fairly rapid, a dense black coating of the metal will be deposited uniformly on the glass. If, however, a screen, say of mica, be placed near the filament, that part of the bulb in the 'shadow' of the obstruction will be perfectly clear with sharp boundaries. This shows that the atoms of tungsten travel in straight lines from the incandescent wire to the bulb, and that, at least from cold tungsten surfaces, the reflection of the tungsten atoms is negligible." The other evidence referred to here will be briefly described in connection with the discussion of chemical phenomena and thermionic emission.

Experiments have been made to determine the vapor pressures of silver, gold, iron, copper and nickel by this method, and the results will soon be published. The experiments with silver are of especial interest, since the vapor pressure of this metal has been determined by von Wartenburg by another method, so that the results have served as a test of the correctness of the theory.

The fact that the reflectivity of mercury atoms from a mercury surface at 100° C. cannot be very high follows from some work carried out by Hertz in 1882.[2] Hertz pointed out from theoretical considerations similar to those used above, that the rate of evaporation of mercury at 100° into a perfect vacuum could not exceed 0.016 gram per sq. cm. per second. Experimentally he found that a rate of evaporation as high as .0018 gram per sq. cm. per sec. could be realized. He considered that this result was merely a lower limit and that the true rate of evaporation

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[1] Langmuir and Mackay, Phys. Rev., *4*, 377, 1914.

[2] Ann. Phys., *17*, 177, 1882.

must lie between the two limits given. If we calculate the maximum possible rate of evaporation of mercury at 100° C. from equation (1), placing $r = 0$ and $p = 368$ bars, we obtain $m = .0117$, which is not very far from Hertz's calculated value of .016.

From Hertz's experimental result, together with the value calculated from (1), we may conclude that at least 15 per cent. of all the mercury atoms striking the surface must condense. By closer examination of Hertz's experimental conditions it is readily seen that his result must be much too low and the probability thus becomes strong that the amount of real reflection is very small.

Very recently, however, Knudsen[1] has accurately determined the rate of evaporation of mercury in a high vacuum, and by comparing this with the vapor pressure, using an equation similar to (1), he has been able to prove conclusively that, with a clean mercury surface, r does not exceed one per cent. That is, he finds that all the mercury atoms striking a mercury surface are condensed when the surface is at room temperature.

This result of Knudsen's, together with Wood's conclusion that reflection is absent when the glass plate is at the temperature of liquid air, indicates that there is little or no reflectivity of mercury atoms from either a solid or liquid surface of mercury.

Experiments on the formation of "shadows" in the evaporation of filaments in a high vacuum have proved that at least for surfaces at room temperature the same conclusion may be drawn regarding the reflectivity of atoms of tungsten, platinum, copper, gold, silver, molybdenum, carbon, iron, nickel and thorium.

In the case of thorium we have evidence that not even one atom of thorium out of millions is reflected when these strike a surface of tungsten at room temperature. This result was found in connection with experiments (as yet unpublished) on the effect of traces of thorium on the electron emission of tungsten. If a filament containing thorium is placed in a bulb close to a pure tungsten filament, the electron emission from the latter may be increased from 10,000 to 1,000,000 fold (according to the temperature) by heating the thoriated filaments so as to distill off a trace of thorium onto the tungsten filament. If, however, a screen be placed between the two filaments it becomes impossible (in very high vacuo) to raise the electron emission of the second filament by this means, although if any reflection of molecules from the surface of the bulb should occur it would result in the deposition of thorium on the tungsten filament.

These facts would seem sufficient to establish the following general rule.

The reflectivity of metal atoms striking surfaces of the same metals at room temperature (or lower) is zero.

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[1] Ann. Phys., *47*, 697, 1915.

The question remains whether the reflectivity is still zero when the surfaces are at higher temperatures and when surfaces other than that of the metal are concerned. Knudsen's work with mercury has shown that the reflectivity with this metal remains zero even at temperatures where the vapor pressure of the metal becomes fairly high.

We shall see, however, from a consideration of other cases, that the coefficient of reflectivity changes very little if at all with temperature, so that I think the above rule may safely be generalized to include metal vapors condensing on metals at any temperature.

Whether or not the same rule would apply to non-metallic substances with equal accuracy, is rather doubtful. However, we shall see from theoretical considerations that even in such cases as that of hydrogen atoms striking a surface of liquid or solid hydrogen, there is reason to believe that the amount of reflection is small.

Heat Conduction in Gases at Low Pressures.

Kundt and Warburg in 1875 predicted from the kinetic theory that there should be a discontinuity in the temperature close to the surface of a solid body which is dissipating heat by conduction into a gas at low pressure. Smoluchowski, in 1898, observed and studied this phenomenon and developed the theory of it. He found that in some gases, particularly hydrogen, the amount of heat given up to the gas by the solid was only a fraction of that which should be delivered if each molecule striking the surface reached thermal equilibrium with it before leaving.

Knudsen[1] gave the name "accommodation coefficient" to the ratio of the heat actually carried away by the gas, to that which would be carried if thermal equilibrium were reached. Knudsen measured the accommodation coefficient (α) for several gases and several different kinds of surface. The lowest value found was with hydrogen in contact with a polished platinum or glass surface, in which case Knudsen obtained $\alpha = 0.26$. With heavier gases, such as nitrogen and carbon dioxide, he found $\alpha = 0.87$.

Soddy and Berry[2] in a similar study of the heat conductivity of gases at low pressures, found that α for hydrogen in contact with platinum varied from 0.25 at $-100°$ C. to 0.15 at $+200°$. For argon they found an average value $\alpha = 0.85$, while for helium they found 0.49 at $-100°$ C. and 0.37 at $+150°$ C. The accommodation coefficients obtained with heavier gases were always close to unity.

The writer[3] has determined the accommodation coefficient of hydrogen

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[1] Ann. Phys., *34*, 593, 1911.

[2] Proc. Roy. Soc., *84*, 576, 1911.

[3] Jour. Amer. Chem. Soc., *37*, 425, 1915.

in contact with tungsten at 1500° K. and obtained $\alpha = 0.19$, while nitrogen under the same conditions gave $\alpha = 0.60$.

The evidence thus far available indicates that the accommodation coefficients of the ordinary gases range from 0.19 up to unity. Only in the cases of hydrogen and helium have accommodation coefficients less than 0.8 been found at room temperature. It is interesting to note that all observers find that the coefficient for a given gas is independent of the nature of the solid, so long as it has a polished surface. This is an indication, for which other evidence will be given below, that the surfaces under the conditions of the experiments are covered with adsorbed layers of gases.

Another conclusion from the experiments is that the accommodation coefficient varies only slightly with the temperature, there being a tendency for it to decrease at higher temperatures. Thus for hydrogen the coefficient seems to decrease from about 0.35 at $-190°$ to 0.19 at 1500° K. With both helium and nitrogen there is a slight tendency for α to decrease with rising temperature.

The probable relationship between the accommodation coefficient and the reflectivity of molecules from surfaces will be discussed below, together with other experimental data.

The " Slip " in Gases at Low Pressures.

The viscosity effect analogous to the temperature discontinuity at a surface has been called the " slip." This effect, first observed by Kundt and Warburg, has been the subject of much recent study. Knudsen[1] calculates the coefficient of slip on the assumption that the molecules striking any surface are emitted from it in directions which are absolutely independent of the original directions of incidence. By elaborate experimental investigations Knudsen obtains confirmation of his theoretical conclusions and thus justifies his assumptions. Smoluchowski[2] Timiriazeff,[3] Gaede,[4] and Baule,[5] however, conclude, on experimental and theoretical grounds, that the directions of the emitted molecules are not entirely independent of the directions of the incident molecules.

It is of interest to note that Gaede, as a result of extremely careful experimental work, concludes that the amount of specular reflectivity is negative. That is, he finds at pressures above .001 mm., and up to 20 mm., that the amount of gas which flows through a tube is *less* than that

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[1] Ann. Phys., *28*, 75, 1908.

[2] Phil. Mag., *46*, 199, 1898.

[3] Ann. Phys., *40*, 971, 1913.

[4] Ann. Phys., *41*, 289, 1913.

[5] Ann. Phys., *44*, 145, 1914.

calculated by Knudsen on the assumption of completely irregular reflection. Gaede draws the conclusion that a certain fraction (sometimes as large as 50 per cent.) of the incident molecules tend to return after collision in the direction from which they came. The other observers, however, all find that the amount of gas flowing through tubes is greater than that calculated by Knudsen's formula.

Knudsen, on the other hand,[1] carried out further measurements with hydrogen at low pressures and found that there cannot be a specular reflection of hydrogen molecules amounting to more than about one per cent.

Millikan[1] has calculated the coefficient of slip from his measurements on the fall of small spheres and has concluded that the slip in air is about 10 per cent. and in hydrogen about 8 per cent. greater than would be expected, according to Knudsen's assumption regarding the absence of specular reflection.

The experimental evidence on the slip of gases at low pressures does not throw much light on the reflectivity of gas molecules, but if Millikan's interpretation of his experiments is correct they would seem to indicate that a reflectivity as high as 10 per cent. occurs in some cases.

Statistics of Chemical Reactions

(*a*) *Heterogeneous Reactions.*—The rate at which the molecules of a gas come into contact with a solid surface immersed in it, may be calculated by equation (1). Suppose a heterogeneous chemical reaction occurs at the surface of the solid body. Then, if we can measure the rate at which the reaction occurs, we may be able to calculate by Equation 1 what fraction of the collisions between the gas molecules and the solid body results in a chemical reaction. Let us call this fraction ϵ.

In order to avoid complications due to the accumulation of the products of the reaction close to the surface it will be necessary either to work with very low pressures of gases or to choose reactions which take place very slowly.

The value of ϵ may in general have any value less than unity. It is evident that the reflectivity of the gas molecules striking the surface must be less than $1 - \epsilon$ and therefore, by a determination of ϵ, we obtain an upper limit for the reflectivity.

Strutt[3] has measured ϵ for two heterogeneous reactions. In the decomposition of ozone in contact with a silver surface he found ϵ equal to unity, while in the case of the conversion of atomic nitrogen into molecular

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[1] Ann. Phys., *35*, 389, 1911.

[2] Discussion before the American Phys. Soc., Chicago, Nov. 30, 1915.

[3] Proc. Roy. Soc., A, *87*, 302, 1912.

nitrogen in contact with copper oxide, he obtained $\epsilon = .002$. From this we may conclude that the reflectivity of ozone molecules from a silver surface is small. In the second case, however, it is not necessary to conclude that the reflectivity is 0.998. We shall see from the general discussion below that the small value of ϵ is probably caused by a large portion of the surface being in an inactive condition, perhaps due to its being covered with a layer of adsorbed nitrogen molecules.

In a study of the rate of attack of a heated tungsten filament by oxygen at low pressure,[1] the writer determined the values of ϵ for the reaction $2W + 3O_2 = 2WO_3$. The fraction ϵ was found to be independent of the pressure and to increase rapidly with temperature from .001 at 1270° K. to 0.15 at 2770° K.

Some recent work (as yet unpublished) has shown that at higher temperatures ϵ continues to increase so that at 3000° K. it is over 0.40. Extrapolation indicates that at still higher temperatures ϵ would reach a limiting value of about 0.7.

From these results we may conclude that the reflectivity of oxygen molecules from heated tungsten does not exceed 30 per cent. It is probable in this case also, that the small values of ϵ at low temperatures are caused by an inactive condition of the greater part of the surface, rather than by a change in the reflectivity.

Experiments on the oxidation of molybdenum filaments have led to similar conclusions in regard to the reflection of oxygen molecules.

When a wire of tungsten, or other metal capable of withstanding high temperature, is heated to 1500° K. in hydrogen at low pressure, a part of the hydrogen is converted into atomic hydrogen.[2] At very low pressures this active modification of hydrogen can diffuse long distances through glass tubing at ordinary temperatures,[3] but cannot pass even short distances through tubing cooled by liquid air.

When one considers that the pressures employed in these experiments were so low that the normal free path would be of the order of several meters, it is evident that the reflectivity of hydrogen atoms from glass surfaces cooled in liquid air must be very small, if not actually zero. With the glass at room temperature the reflectivity is probably also negligible, but the atoms then reëvaporate more rapidly and are thus able to travel considerable distances.

In connection with a quantitative study of the degree of dissociation of hydrogen at various temperatures, it has been shown[4] that *every hy-*

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[1] J. Amer. Chem. Soc., *35*, 115, 1913.

[2] Langmuir, Jour. Amer. Chem. Soc., *34*, 1310, 1912.

[3] Freeman, Jour. Amer. Chem. Soc., *35*, 927, 1913.

[4] Langmuir, Jour. Amer. Chem. Soc., *37*, 457, 1915.

drogen atom striking a pure tungsten surface (at 2000–3500° K.) condenses and that 68 per cent. of all hydrogen molecules striking the surface condense.

When the tungsten filament was heated to a temperature over 2700° K. in hydrogen at a pressure below 200 bars, it was found that 68 per cent. of all the molecules striking the filament were dissociated and that this fraction remained unchanged even when the filament temperature was raised several hundred degrees higher.

The fact that this coefficient (0.68) is larger than the accommodation coefficient found for a tungsten wire at 1500° in hydrogen (0.19) requires some explanation. It seems at first sight paradoxical that 68 per cent. of the molecules reach chemical equilibrium and are dissociated, whereas at lower temperatures only 19 per cent. reach thermal equilibrium before leaving the surface. In a recent paper[1] the writer gives independent evidence that at lower temperatures the tungsten surface is practically completely covered with a layer of hydrogen molecules, whereas at higher temperatures only a minute fraction of the surface is so covered. Thus the coefficient 0.19 applies to hydrogen molecules striking a surface already covered with an adsorbed layer of hydrogen molecules, while the coefficient 0.68 applies to hydrogen molecules striking an absolutely clean tungsten surface.

Some interesting data on the reflectivity of molecules from a platinum surface have been obtained in connection with a study of the combustion of hydrogen and carbon monoxide at low pressures in contact with a heated platinum wire.[2] In these experiments a platinum filament was mounted in the center of a spherical bulb of four liters' capacity, provided with an appendix (10 cm. long and 3 cm. in diameter) which was cooled by liquid air. This bulb was connected through a liquid air trap to a McLeod gage and a system for the quantitative analysis of small quantities of gas (of the order of one cubic mm.). Low pressures of mixtures of oxygen with either hydrogen or carbon monoxide were introduced into the bulb and the filament heated to a definite temperature. The products of the reaction, water vapor or carbon dioxide, were condensed in the appendix and thus prevented from returning to the filament. The pressures employed ranged from 0.1 up to 30 bars, so that the mean free path of the molecules was many times greater than the diameter of the filament. The velocity of the reaction was determined by taking readings of the gage at regular intervals.

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[1] Jour. Amer. Chem. Soc., *38*, 1145, 1916.

[2] A preliminary account of these experiments, giving only qualitative results, was published in the Jour. Amer. Chem. Soc., *37*, 1162, 1915. The complete data on these experiments, together with that on several other similar reactions, will probably be published in the same journal.

With filament temperatures up to about 500–700° K., it was found that the reaction velocity increased rapidly with temperature. The rate was proportional to the partial pressure of oxygen, and *inversely proportional* to the pressure of hydrogen or carbon monoxide. Thus with an excess of oxygen the reaction started slowly, and as the proportion of combustible gas decreased, the rate increased until it became practically infinite (too rapid to measure). From this it may be concluded that hydrogen and carbon monoxide are negative catalyzers or catalytic poisons. Evidently these substances cannot prevent the reaction on the surface unless they are present on the surface. It thus follows that a surface of platinum at temperatures up to 500–700° K. in pressures of hydrogen or carbon monoxide, as low as one bar, is practically completely covered with an adsorbed film of these gases.

When the temperature of the platinum was raised, the reaction became so rapid that with a filament having a surface of 0.31 sq. cm., the pressure in the four liter bulb in some cases fell to half value in less than 6 seconds. To lower this rate a new filament (length 0.7 cm., diameter .003 cm.), having a surface of only .0067 sq. cm., was substituted for the old one. Under these conditions the velocity of the reaction could be followed up to the melting point of the filament.

With carbon monoxide the reaction velocity reaches a maximum when the filament temperature is about 900° K. and apparently becomes negligibly small in comparison, when the temperature is raised to 1300° K. or higher.

With hydrogen, the rate of reaction also reaches its maximum value at about 900° K. This rate does not decrease at higher temperatures, however, but remains practically constant up to the melting point of the filament.

From equation (1) the rate at which each gas comes into contact with the filament may be calculated. By comparing this with the actual rate at which the gas enters into reaction it is possible to determine ϵ. Out of all the hydrogen (or carbon monoxide) molecules which strike the afilment in a given time, let ϵ_1 represent the fraction which reacts with the oxygen. Similarly let ϵ_2 be the corresponding fraction for the oxygen molecules striking the surface. The following table gives the values of ϵ_1 and ϵ_2 calculated directly from the experimentally determined maximum rates of reaction.

In this table p_1 is the partial pressure of hydrogen or carbon monoxide in bars and p_2 is that of the oxygen. We see that when hydrogen is in large excess, 53 per cent. of all oxygen molecules which strike the filament react with hydrogen to form water. This may happen in either one of two ways:

Reaction $2H_2 + O_2 = 2H_2O$:

p_1	p_2	ϵ_1	ϵ_2
bars	bars		
20.0	4.2	.06	.53
1.3	11.5	.41	.09

Reaction $2CO + O_2 = 2CO_2$:

p_1	p_2	ϵ_1	ϵ_2
12.6	0.7	.02	.18
1.4	0.7	.19	.20
1.4	12.0	.31	.02

1. The oxygen may react with hydrogen already present on the surface.
2. The oxygen may condense on the surface and react with hydrogen molecules which subsequently strike the surface.

In either case the reflectivity of the oxygen molecules cannot exceed 47 per cent. (100 − 53). Similarly we may conclude that the reflectivity of hydrogen molecules is not greater than 59 per cent.

The values for ϵ given in the above table are to be looked upon as lower limits. No correction was made for the cooling effect of the leads, which was very considerable with the short filament used. This correction would be much more important in the case of the combustion of carbon monoxide, since with this reaction the maximum velocity occurs only over a narrow range of temperature. Furthermore, traces of carbon dioxide were found to slightly poison the surface of the platinum, so that the catalyzer only slowly recovered its full activity. It may well be that minute traces of impurities have made the values of ϵ lower than they should be under ideal conditions.

From these considerations it seems probable that the values of ϵ corresponding to perfectly pure gases and a filament at uniform temperature, might approach unity as a limit in the case of each of three gases.

These experiments indicate that the reflectivity of oxygen, hydrogen, and carbon monoxide molecules is small even at temperatures of 900° K. There is every reason to believe that the reflectivity at room temperature is not greater than at higher temperatures.

A large number of other heterogeneous reactions are being studied by similar methods and the coefficients ϵ are being determined. All of this work so far seems to bear out the general conclusion that values of ϵ much less than unity occur only where the surface of the solid is largely covered by some inactive material. The velocity of the reaction is thus determined by that *fraction of the surface* which is active.

(*b*) *Homogeneous Reactions.*—Although homogeneous reactions furnish no direct evidence regarding the reflectivity of molecules from solid surfaces, yet several cases that have been studied have indicated that reactions are by no means rare in which *every* collision between unlike molecules *results in combination.* In this case we may consider that the reflectivity between the molecules is negligible, and are thus led to suspect that in many gas reactions, when two molecules collide, they stick to each other (condense), although they may subsequently separate again (evaporate).

When a tungsten filament is heated to 2800° K. in vacuum, it evaporates at the rate of 0.43×10^{-6} grams per sq. cm. per second.[1] If the filament is surrounded by nitrogen at a pressure less than 500 bars, the rate of evaporation remains unchanged, but each *atom* of tungsten vapor combines on its first collision with a nitrogen molecule to form the definite chemical compound WN_2, which collects on the bulb as a brown deposit. The nitrogen therefore disappears at the constant rate (independent of pressure) of .057 cubic mm. of nitrogen (at 1 megabar) per sec. per sq. cm. of tungsten surface. As the temperature of the filament is raised the rate of disappearance of nitrogen increases exactly in proportion to the rate of evaporation of the tungsten.

In a similar way it has been found[2] that tungsten atoms combine on the first collision with carbon monoxide molecules to form WCO, and that platinum atoms combine on the first collision with oxygen molecules to form PtO_2.

A remarkable case is that of molybdenum and nitrogen. There is definite evidence[3] that each collision between an atom of molybdenum and a molecule of nitrogen results in combination, but there are apparently two kinds of compound formed. One is a stable chemical compound which, when it deposits on the bulb, cannot be decomposed by heating to 350° C., while the other is an extremely unstable compound which decomposes spontaneously when it strikes the bulb. The stable compound tends to be formed in larger amount when the velocity of impact of the molybdenum atom and the nitrogen molecule is *small*; that is when either the bulb temperature or the filament temperature is low. On the other hand, a high velocity of impact (high temperature of bulb or filament) favors the formation of the unstable substance.

There are indications of a similar behavior when a tungsten filament is heated to a very high temperature (3000° K. or more) in hydrogen at low pressure, only in this case the compounds formed are less stable.

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[1] Langmuir, PHYS. REV., *2*, 340, 1913.

[2] Jour. Amer. Chem. Soc., *37*, 1159, 1915.

[3] Jour. Amer. Chem. Soc., *37*, 1157, 1915.

II. Theoretical Considerations.

The phenomena of condensation, evaporation and reflection of molecules are closely related to those of the viscosity, heat-conductivity and adsorption of gases at low pressures.

Various hypotheses regarding the mechanism of these phenomena have been proposed. Maxwell[1] in considering the surface conditions of a gas in contact with a moving solid, assumed that "of every unit of area a portion f, absorbs all the incident molecules, and afterwards allows them to evaporate with velocities corresponding to those in still gas at the temperature of the solid, while a portion $(1 - f)$ perfectly reflects all the molecules incident upon it."

Smoluchowski[2] used a similar hypothesis in regard to the temperature drop near a surface in a gas at low pressure. He also suggested a second hypothesis, namely: When molecules of a temperature T_1 strike a surface at a higher temperature T_2, the molecules leaving the surface have a temperature T intermediate between T_2 and T_1 such that

$$T - T_1 = \alpha(T_2 - T_1), \tag{2}$$

where α is a number less than unity which has subsequently been called "accommodation coefficient" by Knudsen.

Smoluchowski considered that the same value of f or α could be applied to the phenomena of both viscosity and heat conductivity and thus calculated a relation between the coefficient of slip and the temperature drop at the surface.

Knudsen (*l. c.*), on the other hand, considered α to be unity in the case of viscosity, although not in the case of heat conduction.

Baule[1] attempts to solve this difficulty by analyzing the probable mechanism by which heat or momentum is transferred from gas to solid. Baule assumes that the solid consists of a cubic space lattice of elastic spherical molecules or atoms which are vibrating about their equilibrium positions with a mean kinetic energy corresponding to the temperature of the solid.

The molecules of the gas strike against those of the solid and rebound from them according to the laws of elastic collision. If E_1 be the mean kinetic energy of the incident molecules, E_2 the mean energy of the molecules of the solid, and E' the mean energy of the gas molecules after one collision with the molecules of the solid, then

$$E' = \beta E_1 + (1 - \beta)E_2, \tag{3}$$

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[1] Phil. Trans., *170*, 249, 1879.

[2] Wied. Ann., *64*, 101, 1898; Wien, Sitzungsber., *108*, 5, 1899; Phil. Mag., *46*, 199, 1898.

[3] Ann. Phys., *44*, 145, 1914.

where

(4) $$\beta = \frac{m_1^2 + m_2^2}{(m_1 + m_2)^2}.$$

Here m_1 is the mass of the gas molecules and m_2 is that of the molecules of the solid.

It is evident that many of the molecules make more than one collision before leaving the solid surface. Baule assumes that, of all the molecules striking the surface, the fraction ν make only one collision, while the fraction $1 - \nu$ are absorbed and thus make such a large number of collisions that they reach complete equilibrium with the solid before leaving it again.

Thus, if E is the mean energy of all the molecules leaving the surface we have

(5) $$E = \nu E' + (1 - \nu)E_2,$$

whence from (3)

(6) $$E = \beta\nu E_1 + (1 - \beta\nu)E_2.$$

Since the mean energy of molecules is proportional to their temperature Equation 6 may be written

(7) $$T = \beta\nu T_1 + (1 - \beta\nu)T_2,$$

or

(8) $$(T - T_1) = (1 - \beta\nu)(T_2 - T_1).$$

By comparing this equation with (2) it is seen that they are of the same form and that $(1 - \beta\nu)$ has the same significance as Knudsen's accommodation coefficient.

In a similar manner Baule calculates the coefficient of slip. Let v_1 be the average velocity component, parallel to the surface, of the incident molecules; v_2 the tangential velocity of the surface in the same direction, and v' be the average velocity (parallel to the surface) of the gas molecules which rebound from the surface after one collision. Baule shows that

(9) $$v' = \gamma v_1 + (1 - \gamma)v_2,$$

where

(10) $$\gamma = \frac{m_1}{m_1 + m_2}.$$

Of all the molecules striking the surface, the fraction ν make only one collision and are thus reflected with the velocity component given by (9), whereas the fraction $(1 - \nu)$ are absorbed and thus finally leave the surface with the average velocity component v_2. If v be the average velocity component parallel to the surface of *all* the molecules leaving it, then

(11) $$v = \nu v' + (1 - \nu)v_2,$$

whence from (9)

$$v = \gamma\nu v_1 + (1 - \gamma\nu)v_2 \tag{12}$$

or

$$(v - v_1) = (1 - \gamma\nu)(v_2 - v_1). \tag{13}$$

The accommodation coefficient for viscosity is thus $(1 - \gamma\nu)$ instead of the $(1 - \beta\nu)$ which applies to heat conductivity. Thus Baule shows that there is no theoretical justification for Smoluchowski's assumption that the coefficients for heat conduction and viscosity are the same.

In the case of hydrogen in contact with a platinum surface we have $m_1 = 2$ and $m_2 = 195$, whence by (4) and (10), $\beta = 0.98$ and $\gamma = .01$. If we take Knudsen's value $\alpha = 0.26$ for the accommodation coefficient (heat conduction), we find $1 - \beta\nu = 0.26$, whence $\nu = 0.76$. From this we obtain $(1 - \gamma\nu) = 0.992$, which should be the accommodation coefficient for viscosity. This is in good agreement with Knudsen's experiments from which he concludes that the directions of the reflected molecules are independent of those of the incident molecules; in other words, that $\alpha = (1 - \gamma\nu) = 1.00$.

If we consider the case of argon in contact with platinum, for which Soddy and Berry found $\alpha = 0.85$, we obtain:

$$\begin{aligned} m_1 &= 40, \\ m_2 &= 195, \\ \alpha &= 0.85, \\ \beta &= 0.72, \\ \gamma &= 0.17, \\ 1 - \beta\nu &= 0.85, \\ 1 - \gamma\nu &= 0.965. \end{aligned}$$

The accommodation coefficient for viscosity thus decreases with increasing density of the gas, but remains nearly equal to unity.

The experimental work on slip has shown that the accommodation coefficient for viscosity is nearly unity, but the accuracy of the results has not yet been sufficient to determine whether the values calculated by Baule's theory are correct.

Baule attempts to calculate the coefficient ν by making various assumptions as to the manner in which the molecules on the surface are "shadowed" by others, but the validity of the assumptions seems so doubtful that the resulting equations have little more value than empirical equations.

On the whole, Baule's theory marks a distinct advance in our understanding of the mechanism of the exchange of energy between a gas and a solid, but closer consideration of the assumptions underlying Baule's theory shows that they cannot correspond to the facts.

Baule fails to take into account the attractive forces between the atoms, although it is evident that such forces must be of prime importance in determining the amount of condensation and reflection. The phenomena of cohesion, condensation and adsorption are all manifestations of these attractive forces, and Sutherland[1] has shown that even in the gaseous state the attraction between molecules considerably decreases their mean free path.

We know from the work of Bragg and others that the atoms of crystals are arranged according to a space lattice structure in which the identity of molecules usually disappears.

In a crystal of sodium chloride the forces holding the crystal together evidently act between adjacent sodium and chlorine atoms; in other words, they are of the nature of what we have usually called chemical forces. In a diamond crystal the carbon atoms form an endless chain of benzol rings, and the stability of this chemical group is probably the cause of the hardness, high melting-point and low vapor pressure of solid carbon. There is every reason to assume that all forces acting between the atoms of solid bodies are qualitatively of the same nature. The inert gases crystallize at low temperatures, so that even with these substances the atoms are surrounded by force fields which are only quantitatively different from those of more chemically active substances.

In the case of the diamond the arrangement of the atoms corresponds to the tetravalent character of the carbon atom, but in most crystals the valency of the atoms appears to be *divided* between several other atoms. Thus in the sodium chloride crystal the single valency of the sodium is divided between six chlorine atoms.

The principal characteristics of chemical forces are that they act only through very short distances and that they show in a marked degree the phenomena of saturation. Thus chemical forces act only between *adjacent* atoms, and even then only when the distances between the atoms are of the order of magnitude of the diameter of the atoms. When an atom of oxygen has taken up two hydrogen atoms it loses its attraction for other hydrogen atoms: it becomes chemically saturated. However, from the fact that water molecules become associated $(H_2O)_n$ and readily combine with substances as water of crystallization, we may conclude that the presence of two hydrogen atoms around an oxygen atom does not entirely saturated the chemical forces. Werner's theory of valence recognizes the existence of residual valences.

In a crystal the forces of attraction must be balanced by repulsive forces. We cannot assume that the repulsive forces are exerted only

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[1] Phil. Mag., *36*, 507, 1893.

during collisions between adjacent atoms but, because of the work of Einstein,[1] Lindemann[2] and others, must assume that the atoms oscillate about positions of equilibrium in which the attractive and repulsive forces balance.

The atoms on the surface of a crystal must also be held by attractive and repulsive forces, so that they oscillate about equilibrium positions, but these atoms must be looked upon as being in an unsaturated state. There is every reason, therefore, for the existence of very strong attractive forces within a short distance of the surface of solid bodies. The phenomena of adsorption may be looked upon as a result of these unsaturated chemical forces. This will be discussed in more detail in Part II. of this paper.

By the aid of the viewpoint developed above, let us analyze more closely the probable mechanism of condensation, reflection and evaporation of atoms or molecules.

If an atom (or molecule) A approaches the surface of a solid body, it will be subjected to an attractive force as soon as it comes within a certain distance of the surface. This force will increase in intensity as A approaches nearer the surface, will pass through a maximum and will then decrease to zero when A reaches the equilibrium position. The work done by the attractive forces will have been converted into kinetic energy, part of which is possessed by the atom and the remainder of which is divided among atoms forming the surface.

The kinetic energy of A will carry it past the equilibrium position into a region in which it is subjected to a repulsive force. The component of its velocity toward the surface will thus decrease to zero. It will then be driven back through the equilibrium position, and if its outward velocity is sufficient it may escape from the region of attractive forces and travel indefinitely away from the surface. On the other hand, if its velocity is not great enough to enable it to escape, it will describe a complex orbit and, by loss of energy to adjacent atoms, will finally oscillate about its equilibrium position with a mean kinetic energy corresponding to the temperature of the surface.

The amount of work done by the attractive forces upon an atom A while it moves to an equilibrium position is measured by the heat of evaporation or adsorption and is equal to λ/N, where λ is the internal heat of evaporation per gram molecule and N is equal to 6.062×10^{23}. In the case of adsorption of a gas by a solid λ represents the heat of adsorption.

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[1] Ann. Phys., *34*, 170, 1911, and *35*, 679, 1911.

[2] Phys. Ztschr., *11*, 609, 1910.

If the attractive and the repulsive forces were both exerted by a single atom of the solid, and if this atom could move freely towards the incident atom, then we should be justified in treating the problem as if attractive forces were absent and elastic collisions occured. In this case we could apply Baule's results directly.

But it is almost certain that the attractive forces are exerted by several atoms. Bragg has found that among metals the face centered cubic lattice structure is the most common. In this lattice each atom is surrounded by twelve others equally spaced from it. An atom on the surface must then usually have from four to eight other atoms exerting force on it. On the other hand, it is very probable that an atom which passes through the equilibrium position with high velocity would be subjected to repulsive forces exerted principally by *one* atom of the solid. This would naturally follow from the fact that the repulsive force must increase with the proximity to an atom much more rapidly than the attractive force decreases on receding from the equilibrium position.

In order to be able to estimate the magnitude of the effects produced by this difference in the origin of the attractive and repulsive forces, let us consider the case of the following model:

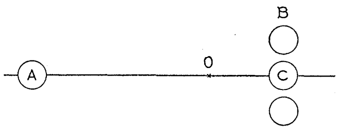

Fig. 1.

In Fig. 1, let A be an atom of mass m_1 which is attracted by a group of atoms B, each of mass m_2. Consider that all the atoms are elastic spheres initially at rest. Let O be the common center of gravity of all the atoms. Then the atoms will all move towards O. If we consider the one dimensional problem only, then we may assume that A will collide with *one* of the atoms B (say C) at the point O, and those two atoms will continue to move along the line AO. Let n be the number of atoms in the group B, excluding C, the one which collides with A. If V_1 and V_2 are the velocities (all measured from left to right) of A and C respectively just before their collision, and V_1' and V_2' are the velocities just after their collision, then we have by the principles of the conservation of energy and momentum:

$$m_1V_1^2 + m_2V_2^2 = m_1(V_1')^2 + m_2(V_2')^2, \tag{14}$$

$$m_1V_1 + m_2(1 + n)V_2 = 0, \tag{15}$$

$$m_1V_1 + m_2V_2 = m_1V_1' + m_2V_2'. \tag{16}$$

Let the ratio of the velocity of A before and after the collision be β, thus

$$\beta = \frac{V_1'}{V_1} \tag{17}$$

and let

$$\gamma = \frac{m_1}{m_2}. \tag{18}$$

If we substitute these in equations (14), (15) and (16) and solve for β, nd

$$\beta = \frac{\gamma n \pm (\gamma + n + 1)}{(n + 1)(\gamma + 1)}.$$

For the case in hand it can be readily seen that we should take the negative sign. Equation (19) thus becomes:

$$\beta = -\frac{1 + \gamma\left(\dfrac{1 - n}{1 + n}\right)}{1 + \gamma}. \tag{20}$$

If $n = 0$, this gives $\beta = -1$, so that the atom A has its velocity reversed. Thus when $n = 0$ the existence of attractive forces between the atoms does not change the conditions from those of elastic collisions. If, however, $n = 1$ we find

$$\beta = -\frac{1}{1 + \gamma},$$

so that the velocity after collision is much less than we would calculate according to the laws of elastic collision.

This loss in velocity, which Baule has failed to take into account, would result in a very great decrease in the number of atoms reflected from the surface. In order to estimate the effect on the reflectvity we need to consider the initial velocity of the atom A, due to its thermal energy.

We may calculate this effect approximately by considering two atoms A and C having given initial velocities, but without attractive force between them. Let the initial velocities of A and C be v_1 and v_2 respectively. Let v_0 be the velocity of the common center of gravity of A and C and let v_1' be the velocity of A after collision.

Then

$$v_0 = \frac{m_1 v_1 + m_2 v_2}{m_1 + m_2} = \frac{\gamma v_1 + v_2}{\gamma + 1} \tag{21}$$

The velocity of A towards the center of gravity is $v_1 - v_0$ before collision. After collision this velocity is reversed. The actual velocity of A after collision v_1' is thus equal to $-(v_1 - v_0) + v_0$. This gives, with (21)

$$v_1' = \frac{\gamma v_1 + 2v_2 - v_1}{1 + \gamma} \tag{22}$$

Let us now return to the consideration of an atom striking a surface toward which it is attracted. We have seen that the work done by the attractive forces in bringing the atom to an equilibrium position is λ/N. This appears as kinetic energy of the atom $\frac{1}{2}m_1V_1^2$. If M_1 is the molecular weight of the atom or molecule A, then since $M_1 = Nm_1$

$$V_1 = \sqrt{\frac{2\lambda}{M_1}}. \tag{23}$$

After collision with the atom C the velocity of A will be

$$V_1' = \beta\sqrt{\frac{2\lambda}{M_1}}.$$

But because of the initial velocities of A and C the velocity V_1' should be increased (approximately) by v_1', so that the velocity of A, upon returning to the equilibrium position, will be

$$\beta\sqrt{\frac{2\lambda}{M_1}} + v_1'.$$

The condition that the atom may just be able to escape from the surface is that this velocity shall be equal to $-\sqrt{2\lambda/M_1}$, in other words, the condition is

$$v_1' = -(1+\beta)\sqrt{\frac{2\lambda}{M_1}}. \tag{24}$$

Now let α_1 and α_2 be the ratios between the initial velocities of A and C respectively, and the mean velocities due to thermal agitation. Thus,

$$\alpha_1 = \frac{v_1}{\bar{v}_1} \quad \text{and} \quad \alpha_2 = \frac{v_2}{\bar{v}_2}, \tag{25}$$

where the mean velocities of thermal agitation $\bar{v}_1$ and $\bar{v}_2$ are given by

$$\bar{v}_1 = \sqrt{\frac{3RT_1}{M_1}} \quad \text{and} \quad \bar{v}_2 = \sqrt{\frac{3RT_2}{M_2}}. \tag{26}$$

Substitute (25) and (26) in (22), and the resulting value of v_1' in (24). Then substitute the value of β from (20), and remembering that $M_1/M_2 = \gamma$ we obtain our final equation:

$$\tfrac{1}{2}\alpha_1(\gamma - 1) + \alpha_2\sqrt{\frac{\gamma T_2}{T_1}} = -\frac{\gamma n}{n+1}\sqrt{\frac{2\lambda}{3RT_1}}. \tag{27}$$

This equation furnishes us an approximate method of estimating the effect of various factors upon the reflection of atoms from a surface. This will best be illustrated by a few examples.

First Case: $m_1 = m_2$.

In the first place, let us consider the case of a substance in equilibrium with its own saturated vapor. We then have $T_1 = T_2$ and $m_1 = m_2$, so that $\gamma = 1$.

If we express λ and R in calories ($R = 2$). then equation (27) reduces to

$$\alpha_2 = -\frac{n}{n+1}\sqrt{\frac{\lambda}{3T}}. \tag{28}$$

This equation tells us how large α_2 must be in order that the atoms of vapor may be reflected. In the case of tungsten at 3000° K., $\lambda = 206{,}000$ calories, so that we have

$$\alpha_2 = -4.8\frac{n}{n+1}. \tag{29}$$

The following table gives the values of α_2 corresponding to different values of n.

Table I.

n	α_2	P
0	0	0.50
0.1	−0.435	0.23
0.2	−0.80	0.08
0.3	−1.10	0.028
0.4	−1.37	0.0087
0.5	−1.60	0.0028
0.6	−1.80	0.00093
0.7	−1.97	0.00032
1.0	−2.40	$17\text{x}10^{-6}$
2.0	−3.20	$14.0\text{x}10^{-9}$
3.0	−3.60	$1.0\text{x}10^{-9}$

In this table n gives the effective number of atoms which attract but do not subsequently repel the incident atom. We have seen that there is good reason to believe that the attraction is exerted by three, four, or even more atoms, while the repulsion is exerted principally by one or two. We may therefore expect the value of n to be of the order of 2 or 3. The above table shows, however, that even if n should be as small as 0.1, reflection of the incident atom can occur only if it collides with an atom for which $\alpha_2 = -0.445$; that is, an atom which is already moving by its thermal agitation with a velocity component away from the surface equal to 44 per cent. of the mean thermal velocity. The column headed P gives the probability, according to Maxwell's distribution law, that any given atom on a surface should have a velocity in a given direction exceeding $\alpha_2\bar{v}_2$. Thus, according to the table, only 23 per cent. of the atoms on the surface have an outward velocity component greater than

44 per cent. of the mean velocity. The probability P is calculated by the equation

$$P = \frac{1}{\sqrt{\pi}} \int_{\alpha_2\sqrt{3/2}}^{\infty} e^{-x^2}\, dx. \tag{30}$$

With values of n as large as 2 or 3, the probability is negligibly small that an atom on the surface will have a sufficient velocity to cause the reflection of an incident atom.

The above calculations lead to the conclusion, which is in good accord with experimental facts, that the reflection of tungsten atoms from a tungsten surface takes place to a negligible degree only.

By equation (28) we see that the reflectivity of atoms from a surface will depend on the coefficient n and the ratio λ/T. It seems probable that n is of the same order of magnitude for all substances and has a value somewhere between 1 and 3. According to Trouton's rule the latent heats of evaporation of different substances are proportional to the absolute boiling points. Nernst finds that this rule is only approximate, and modifies it by placing the ratio λ/T proportional to log T. If we consider a series of different substances at "corresponding" temperatures the values of λ/T will not differ very greatly, but according to Nernst will be smaller the lower the absolute boiling point of the substance.

TABLE II.

Substance.	T_0	λ	λ/T	α_2	P
H_2	20.4	205	10.1	0.92	.055
O_2	90.	1,680	18.7	1.25	.015
H_2O	373.	9,000	24.1	1.42	.0069
Hg	631.	12,300	19.5	1.28	.013
Pt	4200.	109,000	26.0	1.47	.0054
Mo	3900.	160,000	41.0	1.85	.0007
W	5100.	200,000	39.0	1.82	.00085

Table II. contains data for a few substances. The absolute boiling point T_0 is given in the second column, while λ, the internal latent heat of evaporation at the boiling point, is given in the third. It is seen that the maximum range of the values of λ/T is only from 10 to 41, and, since this ratio in (28) occurs under the radical, the value of α_2 only varies within the ratio 1 to 2. The values of α_2 and P calculated by taking $n = 1$ are also given in Table II.

These data are calculated for the temperature of the boiling point. At lower temperatures α_2 would be larger so that P would be still smaller than the values given in the table.

In the above discussion we have derived a method of calculating the probability that an atom on the surface of a solid may have a sufficient velocity to cause an incident molecule to be reflected. The calculation was based, however, on the assumptions:

1. That the forces and motions involved are all normal to the surface.
2. That the collisions are perfectly elastic and that the work done on the incident particle by the attractive forces all appears as kinetic energy of this particle.

It is certain that the first assumption cannot correspond to the facts. The directions of motion of the incident particles after the collisions are probably distributed uniformly in all directions so that the chance of an atom being reflected is *very much* less than that given by P.

It is also probable that the second condition is not fulfilled, which must result in a still further decrease in the amount of reflectivity. Some idea of the rapidity with which adjacent atoms in a solid reach thermal equilibrium may be obtained from a consideration of the heat conductivity.

The problem is similar to that of a calculation of the "time of relaxation" for a gas. The distribution of velocities among the molecules of a gas in the steady state is given by Maxwell's distribution law. If a deviation from this law is brought about in some manner, and the gas is then left to itself, the distribution will rapidly return to that of Maxwell. The time required for the abnormal condition to subside is measured by the "time of relaxation," which Maxwell defines as the time needed for the deviation (measured in terms of kinetic energy) to fall to $1/e$th of its original value.

The following roughly approximate method will enable us to estimate the order of magnitude of the time of relaxation in a solid body.

Let us imagine that a single layer of atoms on the surface of a solid is at a temperature T, while the underlying layers of atoms are at zero temperature. If h is the heat conductivity of the solid, and σ is the distance between adjacent atoms, then the heat flowing between the first and second layers will be hT/σ per sq. cm. if we neglect the change in temperature of the second layer. The number of atoms in the surface layer will be $1/\sigma^2$ per sq. cm. and the heat capacity of each atom is $3k$, where k is the Boltzmann gas constant 1.37×10^{-16} erg./deg. We thus obtain

$$\frac{hT}{\sigma} = -\frac{3k}{\sigma^2} \cdot \frac{dT}{dt}, \tag{31}$$

or

$$ln\frac{T_0}{T} = \frac{h\sigma}{3k}t. \tag{32}$$

If we let T_0/T equal e, then t will become equal to the time of relaxation, which we may represent by t_r, thus

$$t_r = \frac{3k}{h\sigma}. \tag{33}$$

The times of relaxation for various substances as calculated by this equation are given in the fourth column of Table III. The data used in the calculation, h and σ, are given in the second and third columns. The values of σ were calculated from the density ρ and atomic weights A given in the fifth and sixth columns. For such substances as calcite and glass A was taken to represent the average atomic weight of all the atoms in the substance. The seventh column gives τ the natural period of oscillation of the atoms of the substance.

TABLE III.

Substance.	h erg/cm. sec.	σ cm.	t_r sec.	ρ g/cm^3.	A	τ sec.	$\frac{t_r}{\tau}$
	$\times 10^{7}$	$\times 10^{-8}$	$\times 10^{-15}$			$\times 10^{-15}$	
Copper.......	3.84	2.3	0.46	8.9	64.	180	.0026
Tungsten.....	1.25	2.5	1.3	19.	184.	170	.0077
Platinum......	0.7	2.5	2.3	21.5	195.	210	.011
Mercury......	.082	2.9	17.	13.6	200.	640	.027
Quartz........	.09	2.3	20.	2.6	20.	186	.11
Rock salt.....	.06	2.8	25.	2.2	29.	250	.10
Calcite........	.034	2.3	53.	2.7	20.	138	.38
Soda-glass.....	.01	2.4	170.	2.5	21.	200	.85
Ice...........	.004	2.2	470.	0.9	6.	370	1.3
Sulfur........	.0026	2.9	550.	2.1	32.	460	1.2
Paraffin.......	.0025	2.0	790.	0.9	4.6	440	1.8

This natural period is the reciprocal of ν the atomic frequency (Eigenschwingungen). The atomic frequency may be calculated in any one of a half dozen different ways[1] with substantially similar results. The values given in the table have been obtained from the compressibilities K by means of Einstein's[2] equation

$$\tau = \frac{1}{\nu} = 3.5 \times 10^{-8} A^{\frac{1}{3}} \rho^{\frac{1}{6}} K^{\frac{1}{2}}. \tag{34}$$

Objections may be raised against the use of this equation for the calculation of the periods of oscillations of the atoms of compounds, but it is not likely that the order of magnitude of the result will be in error. Koref[3] calculates by other methods that in a rock salt crystal the fre-

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[1] Harkins and Hall, J. Amer. Chem. Soc., *38*, 207, 1916.

[2] Ann. Phys., *34*, 170, 1911.

[3] Phys. Ztsch., *13*, 186, 1912.

quency of the sodium atom is 6.8×10^{12} and that of the chlorine is 5.5×10^{12} The atomic frequency calculated from the value of τ in Table III. is 4×10^{12}, which is not greatly different from Koref's results.

The last column of the table gives the ratio of the time of relaxation to the natural period of oscillation of the atoms. In the case of the metallic substances this ratio is very much less than unity, which must mean that thermal equilibrium is established between adjacent atoms in a small fraction of the time necessary to complete a single oscillation.

Under these conditions it is apparent that our second assumption (elasticity in collisions) is not justified in the case of metals. It is probable, in fact, that atoms of metal vapor striking the surface reach practically perfect thermal equilibrium with adjacent atoms before they can possibly escape again from the surface. The amount of reflection during the condensation of metallic vapors is therefore probably extremely small. Since the high heat conductivity of metals is related to their electrical conductivity, we may conclude that "free electrons" play an important part in the mechanism of the condensation of metallic vapors.

From Table III. we see that even in the substances of low heat conductivity such as ice or sulfur, the "rate of relaxation" is so high that the collisions must be far from elastic. A slight loss of energy to adjacent atoms, must have a very great effect in decreasing the chance that an incident atom or molecule will be able to escape, so that even with non-metallic substances it is probable that the reflection of molecules occurs to a much smaller degree than would be estimated from the values of P given in Table II.

However, it would not be safe to conclude that in all cases where molecules strike similar molecules (or atoms) on a surface that the reflectivity must be negligibly small. We have seen that there is evidence that metals in contact with hydrogen even at low pressures have their surface completely covered with a layer of hydrogen atoms or molecules. The accommodation coefficient 0.25 observed for hydrogen in contact with platinum, indicates that a considerable fraction of the hydrogen molecules striking other hydrogen atoms or molecules on the surface is reflected. The reasons for the high reflectivity in this case probably are:

1. The heat of condensation λ is very small. By Table II. we see that λ for liquid hydrogen at its boiling point is only 205 calories per gram molecule. It is probable, however, that the hydrogen atoms on a metal surface are held by very strong chemical forces[1] so that they are much

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[1] There is reason to think that for the condensation of the first layer of atoms of hydrogen on platinum the value of λ is about 40,000 calories per gram molecule.

more thoroughly saturated than the atoms or molecules in liquid hydrogen. There is good reason to think, therefore, that such a layer of hydrogen atoms would exert only very weak attractive forces on incident hydrogen molecules, and that the value of λ for the condensation of the second layer would be much less than 205 calories.

We see by equation (28) that a small value of λ would tend to increase the number of atoms reflected.

2. The temperature is very high compared to the boiling point of hydrogen, and this fact, according to (28) and (30), would tend to increase the chance of reflection. It may also decrease λ. Although the heat of evaporation of liquids decreases to zero when the critical temperature is reached, we must not consider that λ also disappears at this temperature. In the sense in which we are using this quantity it represents the work done in separating the atoms of the solid or liquid to an infinite distance from each other. This quantity evidently may have considerable values even at temperatures much above the critical temperature.

3. The atoms forming the adsorbed layer on the surface may be so rigidly held by the underlying metal as to greatly increase the tendency for the weakly attracted incident atoms to be reflected. In deriving equation 28 it was assumed that during the time of a collision, the atom on the surface is free to move according to the usual laws of elastic collisions. If the adsorbed atoms are rigidly held to the metal atoms the effective mass of the adsorbed atoms would be greatly increased. According to equation (27), this would tend to increase the reflectivity.

Another effect produced by the close coupling of the adsorbed atoms to the metal and the loose coupling to the incident atoms is to lengthen the time of relaxation of the incident atoms.

Second Case. Unlike Atoms.—So far, we have considered the condensation of a vapor on a solid whose surface consists of the same kind of atoms. If atoms of a light gas strike the surface of a solid consisting of heavy molecules, the case becomes more complicated, since we must use equation (27) instead of (28). Let us consider the case of hydrogen molecules striking an absolutely clean surface of tungsten or other heavy metal. For such a case we may put approximately $\gamma = .01$, so that, if we place $T_2 = T_1 = T$ and $R = 2$, equation (27) becomes:

$$\alpha_2 - 4.95\,\alpha_1 = -\,0.058\frac{n}{n+1}\sqrt{\frac{\lambda}{T}}. \tag{35}$$

From this equation we may estimate the amount of reflection which would occur if the directions of all motions and forces were normal to the surface. Under actual conditions the amount of reflection would be considerably smaller. In making this calculation we substitute in (35) the value of n, λ, and T and then choose particular values of α_1, and find α_2 by the equation. Thus if we place $n = 1$ and $\lambda = 40{,}000$, we find the pairs of values of α_1 and α_2 given in the first two columns of Table IV.

TABLE IV.

α_1	α_2	P_1	P_2
+0.	−0.34	1.00	0.28
+0.1	+0.15	0.98	0.60
0.2	+0.65	0.94	0.87
0.3	+1.14	0.87	0.98
0.4	+1.64	0.79	1.00
0.5	+2.14	0.69	1.00
1.0	+4.61	0.22	1.00

The value of α_2 gives the maximum (positive) velocity which an atom of the solid may have and still cause the reflection of an atom colliding with it. Thus from the table we see that if a molecule of hydrogen (A) starts from rest ($\alpha_1 = 0$) and is attracted towards the metal surface, it will only be reflected if the metal atom which it strikes is moving *towards* it with a velocity numerically in excess of that corresponding to $\alpha_2 = 0.34$. If, however, the hydrogen molecule starts with an initial velocity (normal to the surface) corresponding to $\alpha_1 = 0.1$ we see that it may be reflected even if it strikes a metal atom moving *away* from it with a velocity as large as that corresponding to $\alpha_2 = 0.15$.

The probability that a molecule striking the surface should have a velocity greater than α_1 is given by

$$P_1 = e^{-\frac{3}{2}\alpha_1^2}. \tag{36}$$

On the other hand, the probability P_2 that a molecule on the surface should have a velocity component less than that corresponding to α_2 may be readily calculated by means of equation (30). The probabilities P_1 and P_2 have been entered in Table IV. From these data we see for example, that 87 per cent. of all the incident molecules have velocities towards the surface greater than that corresponding to $\alpha_1 = 0.3$. In order that these molecules may be reflected it is necessary that α_2 shall not exceed 1.14, but according to the fourth column we see that 98 per cent. of the metal atoms have a value of α_2 less than 1.14.

From these data by approximate integration of $\int P_2 dP_1$, it can be shown that of all molecules striking the surface 97.3 per cent. would be reflected if we could assume all motions and forces to have directions normal to the surface. This figure gives us an upper limit for the amount of reflection. This result is not greatly different if we take other values for λ or n. Thus if we take λ or n (or both) equal to zero, we obtain in a similar manner to that used above, the value 98.7 per cent. for the maximum possible reflectivity. On the other hand if we take $n = \infty$ and $\lambda = 40{,}000$ we find 95.1 per cent.

In many chemical and physical problems it is important to know how closely the reflectivity can approach 100 per cent. Thus in calculating the vapor pressure from the rate of evaporation, we made use of $(1 - r)$. (See equation (1).) In this case, where $\gamma = 1$, we have seen that we may always place $r = 0$. Similarly in estimating the velocity of a chemical reaction we may use an equation similar to (1) in which we use ϵ in place of $(1 - r)$.

In studying the mechanism of such reactions we need to know the order of magnitude of $1 - r$. Thus suppose in a given case we find that only one molecule reacts out of every thousand striking the surfaces, that is $\epsilon = 0.001$. In interpreting this result we need to know whether it is possible that 99.9 per cent. of the molecules are actually reflected.

From the calculations given above, it appears that the reflectivity can in no case exceed 99 per cent., and must in all probability be much less than this. Therefore a value of ϵ as small as .001 must be accounted for in some other way than by reflectivity, as for example by assuming that the greater part of the surface is covered with a material on which the given reaction does not take place.

The smallest accommodation coefficient that has been observed is 0.19 (hydrogen). This corresponds according to Baule's theory (equation 8), to a reflectivity of about 83 per cent., a value which is in reasonable agreement with the upper limit of 95–99 per cent. calculated above.

It thus seems extremely probable that when gas molecules strike solid bodies in no case are more than 90 per cent. of the molecules reflected.

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(*To be continued.*)