solutions investigated, the absorption index diminishing approximately 1% for a rise in temperature of one degree.

6. In liquid ammonia rough measurements of concentration showed the absorption index to be proportional to the total concentration of metal.

7. In methylamine the absorption index, at the wave length of the band maximum is also proportional to the total concentration of metal. At shorter wave lengths, however, deviations were observed, the absorption increasing more rapidly with concentration than Beers' law would demand. The ratio of the absorption index at $650\mu\mu$ to that at $530\mu\mu$ increases not only with increasing concentration of the metal but also with increasing concentration of the reaction product of the metal with methylamine, and probably also with increasing temperature.

8. These observations can be accounted for by the following hypotheses: The color in all cases is due to electrons combined with the solvent. In ammonia the dissociation of the metal into electrons is nearly complete, and the concentration of electrons uncombined with solvent is negligible compared with that of the solvated electrons. In other words, the solvation of the electrons is nearly complete. In methylamine, on the other hand, the concentration of un-ionized metal is no longer negligible and is responsible for the increased absorption at the shorter wave lengths. The solvation of the electrons in methylamine is incomplete and diminishes as the temperature is increased.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

THE ADSORPTION OF GASES ON PLANE SURFACES OF GLASS, MICA AND PLATINUM.

BY IRVING LANGMUIR.

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In his studies of the continuous change from the liquid to the vapor state, at temperatures above the critical, van der Waals developed the theory that at the boundary between a liquid and its vapor there is not an abrupt change from one state to the other, but rather that a transition layer exists in which the density and other properties vary gradually from those of the liquid to those of the vapor.

This idea of the continuous transition between phases of matter has been applied very generally in the development of theories of surface phenomena, such as surface tension, adsorption, etc.

Eucken,[1] for example, in dealing with the theory of adsorption of gases, considers that the transition layer is a sort of miniature atmosphere, the molecules being attracted to the surface by some kind of "action at a

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[1] Eucken, *Verh. deut. physik. Ges.*, 16, 345 (1914).

distance." Bakker[1] has a very similar theory to account for surface tension phenomena. He assumes that the molecules in the transition layer are attracted towards one another with a force which is an inverse exponential function of the distance between them.

Colloid chemists have of necessity given a great deal of attention to the phenomena of adsorption. Although several "chemical theories of adsorption" have been proposed, most workers in this field favor the view that adsorption is a "physical" phenomenon.

During the year 1914, in connection with studies of electron emission[2] and chemical reactions at low pressures,[3] I became much interested in the phenomena of adsorption, and developed a theory[4] which has been strikingly verified by a large number of experiments carried out since that time. According to this theory there is an abrupt change in properties in passing through the surface of any solid or liquid. The atoms forming the surface of a solid are held to the underlying atoms by forces similar to those acting between the atoms inside the solid. From Bragg's work on crystal structure and from many other considerations we know that these forces are of the type that have usually been classed as chemical. In the surface layer, because of the asymmetry of the conditions, the arrangement of the atoms must always be slightly different from that in the interior. These atoms will be unsaturated chemically and thus they are surrounded by an intense field of force.[5]

From other considerations, I was led to believe that when gas molecules impinge against any solid or liquid surface they do not in general rebound elastically, but condense on the surface, being held by the field of force of the surface atoms. These molecules may subsequently evaporate from the surface.[6] The length of time that elapses between the condensation of a molecule and its subsequent evaporation depends on the intensity of the surface forces. Adsorption is the direct result of this

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[1] Bakker, *Z. physik. Chem.*, **89**, 1 (1915).

[2] Langmuir, *Phys. Rev.*, **2**, 450 (1913); *Physik. Z.*, **15**, 520 (1914).

[3] Langmuir, THIS JOURNAL, **37**, 1155 (1915).

[4] A preliminary account of this theory was given in a paper read before the New York section of the American Chemical Society in March, 1915. (See THIS JOURNAL, **37**, 1165 (1915).) A more detailed account was read (April, 1915) before the American Phys. Soc. (See *Phys. Rev.*, **6**, 79 (1915).)

[5] After the development of this theory and the publication of the abstracts already referred to, I found that Haber (*J. Soc. Chem. Ind.*, **33**, 50 (1914) and *Z. Elektrochem.*, **20**, 521 (1914)) in a short discussion of a paper by Marc, had already suggested, on the basis of Bragg's theory, that adsorption may be the result of unsaturated chemical forces at the surface of a solid body.

[6] A full discussion of the evidence in support of this condensation—evaporation theory has been given in the *Phys. Rev.*, **8**, 149 (1916). Further evidence has recently been presented in the *Proc. Nat. Acad. Sci.*, **3**, 141 (1917).

time lag. If the surface forces are relatively intense, evaporation will take place at only a negligible rate, so that the surface of the solid becomes completely covered with a layer of molecules. In cases of true adsorption this layer will usually be not more than one molecule deep, for as soon as the surface becomes covered by a single layer the surface forces are chemically saturated. Where, on the other hand, the surface forces are weak the evaporation may occur so soon after condensation that only a small fraction of the surface becomes covered by a single layer of adsorbed molecules. In agreement with the chemical nature of the surface forces, the range of these forces has been found to be extremely small, of the order of 10^{-8} cm. That is, the effective range of the forces is usually much less than the diameter of the molecules. The molecules thus usually orient themselves in definite ways in the surface layer since they are held to the surface by forces acting between the surface and particular atoms or groups of atoms in the adsorbed molecule.

This theory has been tested by a large number of experiments in this laboratory. In every case the results have furnished striking confirmation of the correctness of the theory. In two recent papers on the "Constitution and Fundamental Properties of Solids and Liquids"[1] I have presented a large amount of evidence in support of the above theory of adsorption emphasizing particularly the chemical nature of the forces involved. This chemical theory of adsorption is essentially different from previous chemical theories of this phenomenon. The earlier workers believed that definite chemical compounds were formed on the surface, whereas according to the present theory, the adsorbed atoms are chemically combined to the surface atoms of the solid (or liquid) *but these in turn are chemically combined to those below them*, and so on throughout the whole mass of the solid. Although the forces involved in the formation of such adsorbed layers are not different from those in the formation of chemical compounds, yet the chemist has not devised any terminology for such types of chemical combinations and, therefore, often fails to realize the similarity between these phenomena and those typical chemical phenomena to which his language applies more directly.

In the two papers referred to, a large number of experiments are described which prove that true adsorbed films do not exceed one molecule in thickness. In the first paper (Part I, pages 2269 to 2292) the evidence was for the most part indirect and was based primarily on observations of the electron emission from heated filaments in various gases at low pressures and of the velocity of chemical reactions in gases at low pres-

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[1] Part I, THIS JOURNAL, **38**, 2221 (1916) and Part II, *Ibid.*, **39**, 1848 (1917). These articles will be referred to in the remainder of the present paper simply as Part I and Part II, respectively.

sures. In the second paper (Part II, pages 1858 to 1898),[1] direct proof is given that thin oil films on the surfaces of liquids, as well as adsorbed films of substances dissolved in liquids do not normally exceed one molecule in thickness. With saturated surfaces the adsorbed surface layer consists of a single layer of tightly packed molecules. In fact, methods were developed by which it was possible to measure the lengths and cross-sections of these adsorbed molecules and to determine with certainty how they were orientated on the surface.

The theory of surface tension which I developed in 1916[2] and which was later elaborated by W. D. Harkins,[3] also furnishes striking proof that the surface layers in pure liquids are normally of the thickness of a single molecule, and that these molecules are orientated in definite ways. Although with liquids, direct proof of the existence of these monomolecular films was obtained, the evidence in the case of adsorption by solid bodies was indirect. Only in one instance, namely the adsorption of atomic hydrogen on glass surfaces (see Part I, page 2270) was direct evidence of this kind found. The theory outlined above leads inevitably to the conclusion that films of gas adsorbed on plane surfaces of solids should have no greater tendency to exceed one molecule in thickness than do those on liquids. But the conclusions drawn by most previous investigators of adsorption of gases by solids have been that such adsorbed films have a thickness relatively large compared to the dimensions of a molecule. A discussion and a criticism of much of the published work have been given in Part I, on pages 2283–5, and in Part II, on page 1904.

There appear to be three main reasons which have led these investigators to conclude that adsorbed films are relatively thick. In most cases the experiments have been carried out with porous materials such as charcoal, so that it has not been possible to determine with certainty the effective adsorbing surface. Other workers have employed metal foil or other surfaces of known area, but in order to get sufficiently large surfaces have packed so much foil, etc., into small vessels that enormous numbers of capillary spaces were formed. They then employed saturated or nearly saturated vapors bringing about actual condensation of liquid in the capillary spaces. The third cause of error has consisted in the use of substances which actually dissolve the vapor thought to be adsorbed. The so-called adsorption of water vapor by glass is an example of this kind.

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[1] See also a shorter and earlier paper on "The Shapes of Group Molecules Forming the Surfaces of Liquids," Langmuir, *Proc. Nat. Acad. Sci.*, **3**, 251 (1917).

[2] Abstract published in *Met. Chem. Eng.*, **15**, 468 (1916) and in part reprinted in Part II, page 1849.

[3] W. D. Harkins, THIS JOURNAL, **39**, 354 and 541 (1917).

The experiments to be described in the present paper[1] were undertaken to determine whether, if these three sources of error were eliminated, the quantities of gases adsorbed by solids would not be in agreement with the new theory of adsorption. Since it was necessary to use relatively large surfaces of solid bodies it was hardly practicable entirely to avoid capillary spaces, but by using gases at pressures much below their saturation pressures the danger of the condensation of liquid in the capillary spaces was avoided. It was decided to work with gases at very low pressures, partly to overcome the above difficulty, but more particularly to make it easier to measure small quantities of adsorbed gases. With a vacuum system of one-half liter capacity a single cubic millimeter of gas will give a pressure of 2 bars (dynes per sq. cm.). A pressure of 0.01 bar may be easily read on an ordinary McLeod gauge so that these small volumes of gas may be measured with sufficient accuracy. The diameter of molecules of ordinary permanent gases averages about 3×10^{-8} cm. There are thus about 10^{15} molecules per sq. cm. in a monomolecular layer, corresponding to 0.04 cubic millimeter of gas per sq. cm. at ordinary temperature and pressure; therefore, with surfaces of about a square meter, the amount of gas required to cover the surface with a single layer of molecules is 400 cubic millimeters.

Three substances were tried, mica, glass and platinum. Mica and glass had the advantage that they could be obtained in thin sheets and that the surfaces would probably be smoother than most other substances that could be used. Platinum was tried as an example of a metallic surface; to be sure that the surface was not covered with a layer of oxide or other surface film which might *absorb* gases, it was necessary to use a non-oxidizing metal such as platinum.

Before taking up the details of the experiments let us consider the general theory of adsorption.

THEORY OF ADSORPTION ON PLANE SURFACES.

The plane faces of a crystal must consist of atoms forming a regular plane lattice structure. The atoms in the cleavage surface of crystals like mica are those which have the weakest stray fields of force of any of the atoms in the crystal. It is probable that in mica the hydrogen atoms cover most, if not all, of the surface, since hydrogen atoms when chemically saturated by such elements as oxygen possess only weak residual valence. In the case of glass, and other oxygen compounds like quartz or calcite, the surface probably consists of a lattice of oxygen atoms. The surface of crystals thus resembles to some extent a checkerboard. When molecules of gas are adsorbed by such a surface these molecules take up definite positions with respect to the surface lattice and

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[1] These experiments were carried out during the latter half of 1916. A brief summary of the most important results was published in "Part II" page 1904.

thus tend to form a new lattice above the old. A unit area of any crystal surface, therefore, has a definite number of "elementary spaces," each capable of holding one adsorbed molecule or atom. In general, these elementary spaces will not all be exactly alike. There will frequently be cases where there are two or three different kinds of spaces. For example, in a mica crystal it may be that both oxygen and hydrogen atoms, arranged in a regular lattice, form the surface in such a way that different elementary spaces are surrounded by different numbers or arrangements of atoms. In Fig. 1 is given a conceivable arrangement of oxygen and hydrogen atoms in a surface lattice:

H O H H O H
H H O H H O
O H H O H H
H O H H O H
H H O H H O
O H H O H H

Fig. 1.

If the adsorbed molecules take up positions over the centers of the squared formed by 4 of the surface atoms, it is seen from this diagram that there are two kinds of elementary spaces, those represented by $\begin{matrix}\text{H} & \text{O}\\ \text{H} & \text{H}\end{matrix}$ and those represented by $\begin{matrix}\text{H} & \text{O}\\ \text{O} & \text{H}\end{matrix}$. For each of the latter there are two of the former kind of space. In case the adsorbed atoms arrange themselves directly above the surface atoms, there would still be two kinds of elementary spaces. From considerations of this kind we see that a crystal surface may have spaces of only one kind, or may have two, three, or more different kinds of spaces representing definite simple fractions of the surface.

Each kind of elementary space will, in general, have a different tendency to adsorb gases. As the pressure of gas is increased the adsorption will then tend to take place in steps, the different kinds of spaces being successively filled by the adsorbed molecules. The quantities of gas adsorbed in the different steps should in general bear simple stoichiometric ratios to each other. For example, suppose adsorption takes place more readily in the spaces represented by $\begin{matrix}\text{H} & \text{O}\\ \text{O} & \text{H}\end{matrix}$ in Fig. 1 than in the spaces $\begin{matrix}\text{H} & \text{O}\\ \text{H} & \text{H}\end{matrix}$. Then the first step in the adsorption will be to saturate the $\begin{matrix}\text{H} & \text{O}\\ \text{O} & \text{H}\end{matrix}$ spaces and in the second step the $\begin{matrix}\text{H} & \text{O}\\ \text{H} & \text{H}\end{matrix}$ spaces will be saturated. Since there are twice as many of the second kind as of the former, the second step will represent just twice as much gas as the first step. When different gases are adsorbed alternately by the same crystal surface the maximum amounts of gas adsorbed will often be related in a simple stoichiometric manner. Thus, if each elementary space holds one adsorbed molecule, equal volumes of different gases will be adsorbed. It may, however, happen that two or three molecules of one gas can occupy a space previously occupied by a single molecule of another gas. In this case the maximum volumes adsorbed will bear the relation 1 : 2 or 1 : 3. Where more than one molecule can occupy a single elementary space the forces holding the successive molecules will usually differ. Thus the first molecule may be held by a strong force, but when the space is shared by a second molecule the force holding each of the two may be much weaker. This will lead to a tendency for the adsorption to occur in steps just as though there were several kinds of elementary spaces. On the other hand, it may sometimes happen that the forces holding each of two molecules may be greater than the force holding a single one. Adsorption would then not occur in steps, but according to laws quite different from those where only one molecule occupies an elementary space.

The molecules of many gases will be so large that they cannot occupy adjacent elementary spaces on the crystal surface. This may cause one-half or a third of the elementary spaces to be occupied, in which case stoichiometric relation might still exist. It may happen more often that molecules are only slightly too large for the elementary spaces so that they occupy adjacent spaces only by crowding each other. Phenomena of this kind are very familiar to organic chemists, under the name "Steric hindrance." This crowding of the molecules may, in many cases, completely obliterate the stoichiometric relations that would otherwise occur. The effect of steric hindrance will be to make it difficult to saturate the surface with any adsorbed substance. The exact fraction of the elementary spaces which may be filled will depend on a large number of factors such as the shape and elastic properties of the molecules and their mobility on the surface.

With amorphous substances like glass, the surface atoms are probably not arranged in a regular lattice formation. There will therefore be an indefinite number of different kinds of elementary spaces. We should not expect the adsorption to occur in steps representing stoichiometric proportions of gas. The number of elementary spaces may, however, be quite definitely determinable so that the maximum amounts of different gases adsorbed may still stand in stoichiometric relations.

We have so far considered only cases in which the maximum amount of adsorbed substance is primarily determined by the surface lattice of the solid on which the adsorption occurs. In the study of the spreading of oil films on water[1] it was found that stoichiometric relations frequently

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[1] See Part II pages 1866 and 1902.

occurred between the maximum amounts of different oils adsorbed per unit area. In every case, however, the space occupied per molecule depended on the nature and shape of the adsorbed molecule rather than upon the structure of the surface of the water. In a similar way, with solid bodies, the properties of the adsorbed molecules may often determine the amount adsorbed, especially where the mobility of the adsorbed molecules is great or where the forces acting between adjacent adsorbed molecules are comparable with those holding the molecules on the surface.

From the above considerations it is apparent that the phenomena of adsorption cover nearly the whole of the chemistry and physics of surface action. The complexity and variety of processes involved in adsorption are thus about as great as those in physical and chemical changes of state in homogeneous media. In the study of adsorption we should therefore expect to find many different types of adsorption phenomena and, in general, unless great care is taken to simplify the experimental conditions, we should expect the observed phenomena to be of the utmost complexity. It is then no longer reasonable to look for a single equation which, for all cases, will give the relation between the pressure and the quantity of adsorbed gas. Instead of that, we should look for a number of different limiting equations each covering a definite type of adsorption. Only by careful control of the experimental conditions will it be possible to study each type separately.

Let us now attempt to develop a quantitative theory of adsorption for each of the simple limiting conditions which we may hope to be able to study experimentally.

Case I. Simple Adsorption.—We will first consider adsorption on a plane surface having only one kind of elementary space and in which each space can hold only one adsorbed molecule.

The rate at which gas molecules come into contact with a surface is given by the equation[1]

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

Here m is the number of grams of gas striking the surface per sq. cm. per second, M is the molecular weight, T the absolute temperature, p the pressure in bars, and R the gas constant 83.2×10^6 ergs per degree. If we let μ represent the number of gram molecules of gas striking each sq. cm. per second, then $\mu = m/M$, whence from (1)

$$\mu = \frac{p}{\sqrt{2\pi MRT}} \qquad (2) \qquad = 43.75 \times 10^{-6} \frac{p}{\sqrt{MT}} \qquad (3)$$

Of all the molecules striking the surface a certain fraction, which we

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[1] This equation is a simple modification of the equation giving the rate of effusion of gases through small openings (Meyer's *Kinetic Theory of Gases*, German edition, 1899, p. 82). Its derivation was given by the writer in *Phys. Rev.*, **2**, 331 (1913).

may call α, will condense and will be held by the surface forces until the molecules evaporate again. As was mentioned above, there is good experimental evidence that α is in general very close to unity. The rate at which gas condenses on a bare surface will thus be $\alpha\mu$.

Let N_0 represent the number of elementary spaces per sq. cm. of surface. Then, in accordance with the assumptions we have made, the number of gas molecules adsorbed cannot exceed N_0 except by the formation of additional layers of molecules. The forces acting between two layers of gas molecules will usually be very much less than those between the solid surface and the first layer of molecules.[1] The rate of evaporation from the second layer will, therefore, be so much more rapid than from the first, that the number of molecules in the second layer will be negligible. When a molecule strikes a portion of the surface already covered it thus evaporates so quickly as to be in effect equivalent to a reflection. Therefore, the rate of condensation of the gas on the surface is $\alpha\theta\mu$, where θ represents the fraction of the surface which is bare. Similarly the rate of evaporation of the molecules from the surface is equal to $\nu_1\theta_1$, where ν_1 is the rate at which the gas would evaporate if the surface were completely covered and θ_1 is the fraction actually covered by the adsorbed molecules. When a gas is in equilibrium with a surface these two rates must be equal, so we have

$$\alpha\theta\mu = \nu_1\theta_1. \tag{4}$$

Furthermore,

$$\theta + \theta_1 = 1 \tag{5}$$

whence

$$\theta_1 = \frac{\alpha\mu}{\nu_1 + \alpha\mu}. \tag{6}$$

Let us place

$$\frac{\alpha}{\nu_1} = \sigma_1. \tag{7}$$

Equation 6 then becomes

$$\theta_1 = \frac{\sigma_1\mu}{1 + \sigma_1\mu}. \tag{8}$$

If η be the number of gram molecules of gas adsorbed per unit area of surface, then η is given by

$$\frac{N}{N_0}\eta = \theta_1 = \frac{\sigma_1\mu}{1 + \sigma_1\mu}, \tag{9}$$

where N is the Avogadro constant 6.06×10^{23} molecules per gram molecule.

Equation 9 gives the desired relation between the pressure of a gas, which by (3) is proportional to μ, and η, the amount adsorbed on a plane

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[1] The case where this assumption does not hold will be considered under Case VI.

surface. The values of μ and η can be determined experimentally and from these data by means of Equation 9, N_0 and σ_1 can be calculated.

The quantity σ_1 which we shall call the "relative life," is related in a simple way to the "average life" of an atom of adsorbed gas on the surface. It is readily seen that the average life of all the atoms which *condense* on the surface is equal to $N_0/N\nu_1$, while the average life τ of all the atoms which *strike* the surface, is $N_0\alpha/N\nu_1$. From this, by Equation 7, we obtain

$$\tau = \frac{N_0\alpha}{N\nu_1} = \frac{N_0\sigma_1}{N}, \tag{10}$$

whence

$$\eta = \frac{\tau\mu}{1 + \sigma_1\mu}. \tag{11}$$

For very low pressures, $\sigma_1\mu$ becomes negligible compared to unity, so that as a first approximation

$$\eta = \tau\mu. \tag{12}$$

At these low pressures the amount adsorbed thus decreases rapidly as the temperature is raised, since by (10) τ is inversely proportional to ν_1, the rate of evaporation.

On the other hand, at higher pressures, $\sigma_1\mu$ becomes very large compared to unity, so that η, the amount adsorbed, approaches a definite limit or saturation value

$$\eta_\infty = \frac{\tau}{\sigma_1} = \frac{N_0}{N}, \tag{13}$$

corresponding to the case where every elementary space contains one adsorbed molecule. At these higher pressures the amount adsorbed does not vary with the temperature except in so far as N_0 is dependent on temperature.

The rate at which the adsorption equilibrium is reached is related to τ, the average life of a molecule on the surface. Equation 8 holds after equilibrium has been reached. By an analogous method of derivation it may be readily shown that the rate at which the adsorption equilibrium is reached is given by the following equation:

$$\frac{N_0}{N}\frac{d\theta'}{dt} = \alpha\mu - (\nu_1 + \alpha\mu)\theta' \tag{14}$$

Here θ' represents the instantaneous value of θ_1. Integration gives

$$t = \frac{N_0}{N\nu_1(1 + \sigma_1\mu)} \ln \frac{\theta'}{\theta_1 - \theta'}, \tag{15}$$

The time $t_{1/2}$ required for the equilibrium to go half way to its final value is obtained by placing $\theta' = {}^1/_2\theta_1$. If we then combine this result with Equation 10 we obtain

$$t_{1/2} = \frac{\tau \ln 2}{\alpha(1 + \sigma_1\mu)}. \tag{16}$$

Since α is close to unity the "half period" in reaching equilibrium is always less than τ, the average life of an adsorbed molecule. At high pressures when the surface is nearly saturated, the equilibrium is reached still more rapidly.

Case II. More than One Kind of Elementary Space.—Let us assume that the surface contains several different kinds of elementary spaces representing the fractions β_1, β_2, β_3, etc., of the surface so that

$$\beta_1 + \beta_2 + \beta_3 + \ldots = 1 \tag{17}$$

With crystal surfaces the quantities β_1, β_2, etc., will generally be simply related (stoichiometric relations). Since each of the different kinds of elementary spaces affects the adsorption independently, the result is the same as if the total surface were divided into certain fractions, β_1, β_2, etc. For each of these surfaces an equation of the type of Equation 8 will hold. The total amount adsorbed η will thus be given by

$$(N/N_0)\,\eta = \beta_1\theta_1 + \beta_2\theta_2 + \beta_3\theta_3 + \ldots \tag{18}$$

where θ_1, θ_2, θ_3, etc., represent the fractions of the various surfaces occupied by the adsorbed molecules.

This equation may also be written

$$\frac{N\eta}{N_0} = \frac{\beta_1\sigma_1\mu}{1 + \sigma_1\mu} + \frac{\beta_2\sigma_2\mu}{1 + \sigma_2\mu} + \text{etc.} \tag{19}$$

For very small pressures, where the second terms in the denominators are negligible, the amount of adsorbed gas is proportional to the pressure, but increases much more slowly at higher pressures. If the relative lives σ_1, σ_2, etc., are markedly different from each other then it is seen that the adsorption will occur in definite steps as the pressure increases. Thus, if σ_1 is much larger than σ_2, the first term in (19) will approach the limiting value β_1, before the second term has become appreciable. At still higher pressures the second term will also approach its limiting value, β_2.

Case III. Adsorption on Amorphous Surfaces.—In general with crystal surfaces there are probably only a few different kinds of elementary spaces, but with amorphous bodies such as glass, the elementary spaces, may all be unlike. In such cases we may consider the surface divided into infinitesimal fractions, $d\beta$, each element having its corresponding value of σ. If the "law of distribution" of the relative life σ over the surface is known, then a formula can readily be derived giving the amount of adsorption as a function of the pressure. In general, we may therefore place

$$\frac{N}{N_0}\,d\eta = \frac{\sigma\mu\,d\beta}{1 + \sigma\mu} \tag{20}$$

or

$$\frac{N\eta}{N_c} = \int_0^1 \frac{\sigma\mu\,d\beta}{1 + \sigma\mu} \tag{21}$$

where σ is a function of β. The exact form of this function can only be determined by a more intimate knowledge of the nature of amorphous surfaces than we now possess. It may, however, be possible by careful experimental determinations of η as a function of μ to draw certain useful conclusions as to the nature of the function $\sigma(\beta)$. Equation 21 should also apply to adsorption by porous bodies.

Case IV. Each Elementary Space Can Hold More than One Adsorbed Molecule.—Let us assume that each elementary space can hold n molecules. The rates of evaporation of the molecules will depend upon the number of molecules in the spaces. Let ν_n be the rate of evaporation from a space containing n molecules. It is probable that the reflection coefficient α may also vary according to the number of molecules in a space. Let α_n be the reflection coefficient corresponding to spaces containing $n - 1$ molecules. Let θ represent the fraction of the elementary spaces which contain no adsorbed molecules, θ_n the fraction of spaces containing n molecules. Then

$$1 = \theta + \theta_1 + \theta_2 + \ldots + \theta_n. \tag{22}$$

And the total quantity of adsorbed gas η is given by (see Equation 9).

$$\frac{N\eta}{N_0} = \theta_1 + 2\theta_2 + 3\theta_3 + \ldots n\theta_n. \tag{23}$$

When equilibrium has been reached we have

$$\begin{aligned} \alpha_1\theta\mu &= \nu_1\theta_1 \\ \alpha_2\theta_1\mu &= \nu_2\theta_2 \\ \alpha_3\theta_2\mu &= \nu_3\theta_3,\ \text{etc.} \end{aligned} \tag{24}$$

whence if we place $\alpha_n/\nu_n = \sigma_n$

$$\begin{aligned} \theta &= \theta_1/\sigma_1\mu \\ \theta_2 &= \sigma_2\mu\theta_1 \\ \theta_3 &= \sigma_2\sigma_3\mu^2\theta_1 \\ \theta_4 &= \sigma_2\sigma_3\sigma_4\mu^3\theta_1,\ \text{etc.} \end{aligned} \tag{25}$$

Substituting these in 22 and 23 and eliminating θ_1 we find

$$\frac{N\eta}{N_0} = \frac{\sigma_1\mu + 2\sigma_1\sigma_2\mu^2 + 3\sigma_1\sigma_2\sigma_3\mu^3 + \ldots}{1 + \sigma_1\mu + \sigma_1\sigma_2\mu^2 + \sigma_1\sigma_2\sigma_3\mu^3 + \ldots}. \tag{26}$$

In this equation there are only a limited number of terms in the numerator and denominator; for example, suppose each elementary space can hold two molecules, then σ_3, σ_4, etc., are each equal to zero, so that there are only two terms in the numerator and three in the denominator. An equation of this general form may be expected to hold in other cases where adjacent molecules influence each other's rate of evaporation.

Case V. Atomic Adsorption.—In the cases considered above, molecules of adsorbed substance have acted as indivisible units; that is, when a molecule evaporated from the surface it contained the same atoms as when it was first adsorbed. There is good evidence that the forces which hold adsorbed substances act primarily on the individual atoms rather than on the molecules. When these forces are sufficiently strong, it may happen that the atoms leaving the surface become paired in a different manner from that in the original molecules.

For example, consider the adsorption of a diatomic gas such as oxygen on a metallic surface. Let us assume that the atoms are individually held to the metal, each atom occupying one elementary space. The rate of evaporation of the atoms is negligibly small, but occasionally adjacent atoms combine together and thus nearly saturate each other chemically, so that their rate of evaporation becomes much greater. The atoms thus leave the surface only in pairs as molecules. Starting with a bare surface, if a small amount of gas is adsorbed, the adjacent atoms will nearly always be the atoms which condensed together when a molecule was adsorbed. But from time to time two molecules will happen to be adsorbed in adjacent spaces. One atom of one molecule and one of the other may then evaporate from the surface as a new molecule, leaving two isolated atoms which cannot combine together as a molecule and are therefore compelled to remain on the surface. When a stationary state has been reached there will be a haphazard distribution of atoms over the surface. The problem may then be treated as follows:

Let θ_1 be the fraction of the surface covered by adsorbed atoms, while θ is the fraction which is bare. In order that a given molecule approaching the surface may condense (and be retained for an appreciable time) on the surface, two particular elementary spaces must be vacant. The chance of one of these spaces being vacant is θ; that both shall be vacant is θ^2. The rate of condensation is thus equal to $\alpha\theta^2\mu$. Evaporation only occurs when adsorbed atoms are in adjacent spaces. The chance that an atom shall be in a given space is θ_1. Therefore, the chance that atoms shall be in adjacent spaces is proportional to θ_1^2. The rate of evaporation of molecules from the surface is therefore equal to $\nu_1\theta_1^2$, where, as before, ν_1 is the rate of evaporation from a completely covered surface. For equilibrium we then have the condition

$$\alpha\theta^2\mu = \nu_1\theta_1^2 \qquad (27)$$

The number of gram molecules η of oxygen (O_2) adsorbed per unit area is given by

$$\frac{2N\eta}{N_0} = \theta_1. \qquad (27a)$$

By combining these two equations with $\theta + \theta_1 = 1$, we may express η in terms of μ by means of a quadratic equation. Of most practical interest, however, is the case where the total amount of adsorption is only sufficient to cover a small fraction of the surface. We can, therefore, place approximately $\theta = 1$ and obtain

$$\frac{2N\eta}{N_0} = \sqrt{\sigma\mu} \tag{28}$$

where $\sigma = \alpha/\nu_1$.

Thus, in this case, even at relatively low pressures, the total amount of adsorbed gas varies in proportion to the square root of the pressure. If three instead of two elementary spaces are occupied by the atoms of each molecule, then the square root relation expressed by (28) becomes a cube root relation.

Case VI. Adsorbed Films More than One Molecule in Thickness.—With gases or vapors at pressures much below saturation the surface of a solid tends to become covered with a single layer of molecules. The reason for this is that the forces holding gas molecules (or atoms) on to the surface of solids are generally much stronger than those acting between one layer of gas molecules and the next. When the vapor becomes nearly saturated, however, the rate of evaporation from the second layer of molecules is comparable with the rate of condensation so that the thickness of the film may exceed that of a molecule. These thicker films may also occur in those cases where the forces acting between the first and second layers of adsorbed molecules are greater than those holding the first layer to the surface. An example of this latter kind has been found experimentally in the condensation of cadmium vapor on glass surfaces.[1]

Let θ be the fraction of the surface which is bare, while θ_n represents the fraction of the surface covered by a layer n molecules deep. Let ν_n be the rate of evaporation of molecules from the nth layer, and α_n be the reflection coefficient of molecules striking the n–1st layer. For simplicity we shall assume that each elementary space can hold only one molecule. The problem is then identical with that considered under Case IV. Equations 22, 23 and 24 are applicable without alteration and the solution of the problem is thus given by Equation 26. In Case IV, however, all except the first few of the coefficients, σ_1, σ_2, etc., were equal to zero, while in the present problem the higher coefficients would tend to be equal to each other but different from zero. Both numerator and denominator of Equation 26 then become infinite series. We should expect the relative life, σ_1, of molecules in the first layer to be very different from that in the second and subsequent layers. There may be a small difference between σ_2 and σ_3, but as the number of layers increases still further the values of σ should remain practically constant.

By a simple transformation, Equation 26 may be converted to a form

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[1] Langmuir, *Proc. Nat. Acad. Sci.*, 3, 141 (1917).

in which infinite series are avoided. Dividing both numerator and denominator by the numerator, the equation takes the form

$$\frac{N\eta}{N_0} = \frac{\sigma_1}{1/\mu + a + b\mu + c\mu^2 + \ldots} \tag{29}$$

where

$$\begin{aligned} a &= \sigma_1 - 2\sigma_2 \\ b &= \sigma_2(4\sigma_2 - 3\sigma_3 - \sigma_1) \\ c &= 2\sigma_2(6\sigma_2\sigma_3 - 2\sigma_3\sigma_4 + \sigma_1\sigma_2 - \sigma_1\sigma_3 - 4\sigma_2^2), \text{ etc.} \end{aligned} \tag{30}$$

If σ_1, σ_2, σ_3, etc., are equal, all the coefficients in (29) after a are zero. If σ_1 and σ_2 are different, but all subsequent values of σ (*i. e.*, σ_3, σ_4, etc.) are equal to σ_2, then all the coefficients in (29) after b are zero. Equation 29 thus takes a very simple form and shows that at very low pressures η is proportional to μ, but at pressures close to saturation η begins to increase rapidly and becomes infinite when saturation is reached.

Discussion of Theoretical Results.

As far as I am aware no single equation has as yet been proposed which is satisfactorily applicable to adsorption in general. Freundlich[1] has used the following equation

$$q = ap^{1/n}$$

to express the relation between q, the quantity of adsorbed gas, and p, the pressure, n being a constant greater than unity. As a matter of fact this equation agrees very poorly with experiment when the range of pressures is large. An examination of the data presented by Freundlich shows that for low pressures or high temperatures $1/n$ approaches unity while at high pressures or low temperatures $1/n$ often becomes as small as 0.1.

These facts are readily explained on the basis of the theory given in the present paper. At low pressures or at high temperatures, $\sigma_1\mu$ becomes very small, so that in Equation 9 this term in the denominator may be neglected compared to unity. The amount of adsorbed gas η thus varies in proportion to the pressure (μ), which is equivalent to saying that $1/n$ in Freundlich's equation is equal to unity. At high pressures or low temperatures the amount of adsorbed gas, according to Equation 9, tends to reach a limiting value (saturation). As this limit is approached the value of $1/n$ in Freundlich's equation must gradually decrease. As is to be expected, however, Equation 9 does not give quantitative agreement with experimental data on adsorption by porous bodies. The transition from the part of the curve where η is proportional to μ, to the part where η is constant, takes place over much too small a range of pressures. When we take into account, as was done in Cases II and III, any lack of homogeneity of the surface, we obtain Equations 19 and 21, in which the

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[1] *Kapillarchemie*, Leipzig, 1909.

transition takes place as gradually as desired. It is true that these equations are inconvenient to use in practice, but this fact should not be used as an argument that they do not actually represent the facts. It must be remembered that the phenomena of adsorption by porous bodies are inherently very complex and that we should not expect them to be represented by a simple formula.

Experimental evidence that atomic adsorption (Case V) actually occurs and is of great importance in chemical reactions has been discussed at some length in "Part I," pages 2287 to 2296.

EXPERIMENTAL PART.

I. Experiments with Mica.—Large pieces of high grade muscovite were split to a thickness of about 0.04 mm., rejecting all pieces which showed any fissures. The outside pieces were discarded and the others were never touched except by forceps or by the edges. The mica was cut into strips and done up in bundles by brass paper fasteners, the individual pieces of mica being separated by narrow strips of thin sheet iron placed near their ends. The iron had been thoroughly cleaned by heating to a bright red heat in pure dry hydrogen. The total surface of the mica was 5750 sq. cm. and that of the iron 310 sq. cm.; the weight of the mica was 24.3 g.; the iron 31.3, the brass 3.1 g.

The bundles of mica were placed in a glass tube 4 cm. in diameter by 10 cm. long. A similar tube was used as a blank; it contained no mica, but contained the same amount of iron and brass as did the tube with the mica. Both tubes were connected by tubing, 2.5 cm. in diameter, through traps kept continuously immersed in liquid air and through mercury seals, to a McLeod gauge. There was provision for exhausting the tubes or the gauge by a glass condensation pump. The gases delivered by this pump were collected in a system "C" of known volume where the pressure could be measured by a second McLeod gauge. A bypass allowed the gas to be returned at will back to the part of the system "B" connected to the bulb containing the mica. All joints were of sealed glass and there were no stopcocks, only mercury seals being used. The volumes of all parts of the system were carefully measured before assembling.

From the foregoing description it is seen that the system was divided into three parts: A, the bulb containing the mica, together with the liquid air trap; B, the part connected to the first McLeod gauge, and C, the part into which gas was delivered by the condensation pump. The blank bulb will be referred to as A′. The volumes of the parts were:

$$A = 593 \text{ cc.};\ A' = 628 \text{ cc.};\ B = 722 \text{ cc.};\ C = 1138 \text{ cc.}$$

Two methods were used in measuring the amount of gas adsorbed by the mica.

Method I.—A and B were exhausted, A was then closed and the gas was allowed to enter B. From the observed pressure the amount of gas in B was calculated. The gas was then allowed to expand into A, and the pressure was again noted. From this pressure and the volume of A + B the amount of gas in the space was calculated. The difference between this amount and that previously found in B alone gave the amount of gas adsorbed on the mica. A was again closed and B was pumped out. The gas was allowed to expand into B and the pressure was noted. The amount of gas in A + B was then greater than that previously in A. The difference gave the amount of adsorbed gas which had been released from the mica by the lowering of pressure. In this manner the amount of gas absorbed at two pressures was obtained.

Method II.—A and B were filled with gas at a pressure usually as high as the McLeod gauge would read, and the pressure was recorded. The amounts of gas adsorbed in A were not always known. B and C were then well exhausted and each part closed off. The gas was allowed to expand from A to B and from the pressure the amount of gas released from the mica was calculated. Then A was closed off and the gas in B was pumped into C. The gas in A was again allowed to expand into B and the released gas determined. This process could be repeated as often as desired. Finally, all the gas from A and B was pumped over into C, where it was measured. In this way the total amount of gas originally introduced into A was found. To save time, gas was sometimes pumped from B over to C without closing A; the amounts of gas thus removed could always be determined by noting the pressure changes in C.

In making the calculations no corrections were made for adsorption of gas by the walls of the apparatus as previous experience had demonstrated that the adsorption at room temperature was wholly negligible.

When the bulbs A and A′ were cooled by liquid air or solid ether it was necessary to correct for the decrease in pressure caused by this cooling. Complications were produced by the fact that when differences of temperature exist, the pressures in different parts of the system are different. At very low pressures these pressures are proportional to the square roots of the absolute temperatures. This effect, known as thermal effusion, which has been described in detail by Knudsen,[1] is very important at low pressures; it begins to be important when the mean free path of the gas molecules becomes comparable with the diameter of the tubing used. To determine this correction experiments were made with the blank bulb, using hydrogen at various pressures from 5 bars to 100 bars. The system A + B was filled with hydrogen at the given pressure. By cooling the bulb A in liquid air the pressure in A + B decreased in a definite ratio. At different pressures different ratios were obtained. At

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[1] Knudsen, *Ann. Physik*, 31, 205 (1910).

5 bars' pressure and below the ratio was constant and agreed with the theory that the pressure in the bulb and in B varied in proportion to the square root of the temperature. At 60 bars' pressure and above the ratio was again constant and the results indicated that the pressures in A and B were equal. The transition curve between these two ratios was plotted as a function of the pressure. Curves for other gases than hydrogen were then prepared from this on the assumption that the ratios for different gases would be the same for pressures at which the free paths of the molecules were equal. The fact that at both high and low pressures the ratios found with hydrogen agreed well with calculated ratios proved that there was no measurable adsorption of hydrogen by glass or mica even at liquid air temperatures. The use of hydrogen for calibration purposes was thus justified.

Preliminary Tests.—Before obtaining the correction curves just referred to, some experiments were undertaken to see if any adsorption by the mica could be detected at room temperature without previously heating the mica to drive off adsorbed moisture, etc. Nitrogen, hydrogen, oxygen and carbon dioxide, at pressure of about 10 bars, were tried, using Method I, but in no case was any appreciable adsorption noted. Both with the bulb containing the mica and with the blank bulb, the quantities of gas in A + B checked within one or two per cent. with those in B before A was opened. The bulbs A and A′ were then thoroughly baked out to drive off gases. Bulb A, containing the mica, was heated for 3 hours to about 300°, the maximum temperature being 304°, while bulb A′ was heated 4 hours to a maximum temperature of 312°. Until near the end of the time of heating, there was no liquid air on the trap near A, but it was used on an appendix attached to the system C. The moisture and carbon dioxide were thus collected in a small volume. By sealing off this appendix by a mercury seal and removing the liquid air the quantity of moisture plus carbon dioxide was measured. The appendix was then cooled to —78° and the carbon dioxide, without the water vapor, was allowed to expand into C, where its pressure was measured. The other gases evolved from the bulbs A and A′ were transferred by a Töpler pump from C into a miniature gas analysis apparatus, where they were mixed with an excess of oxygen and burned in contact with a platinum wire. The contraction in volume and the amount of carbon dioxide found by the combustion gave the data by which the amount of hydrogen, carbon monoxide and nitrogen were determined.

The total gases evolved from the bulbs and contents are given in Table I.

The carbon monoxide was undoubtedly given off by the iron strips used as spacers. The water vapor given off by the blank bulb is about what is usually obtained from a glass surface of this area. The inside surface of the bulb was 340 sq. cm., so that about 1.3 cubic mm. of water vapor was given off by each sq. cm. of surface. Previous experiments with lamp bulbs[1] had given 1.0 cu. mm. per sq. cm. at 200°; 1.5 at 350°; and 2.2 at 450°.

TABLE I.

Gases Evolved by Heating to About 300° Volumes in Cubic mm. at 20° and 760 mm.

Gas.	Bulb A (containing mica).	Bulb (blank).
H_2O	925	432
CO_2	352	216
N_2	27	4
CO	111	56

The 1.3 cu. mm. per sq. cm. corresponds to 33×10^{15} molecules per sq. cm., assuming closely packed cubical molecules of the same density as liquid water. It has already been pointed out (Part I, p. 2284) that these large quantities of water are to be regarded as dissolved by the glass rather than adsorbed by it. The difference between the 925 cu. mm. given off by A and the 432 given off by A′ represents the moisture given off by the 5750 sq. cm. of mica. This corresponds to 0.086 cu. mm. per sq. cm. or 2.1×10^{15} molecules per sq. cm., and represents a layer of adsorbed water two molecules deep.

When it is remembered that mica contains about 18% of combined water, it is remarkable that no larger part escapes during prolonged heating to 300°. It is probable that mica cleaves along planes containing combined water molecules, so that the freshly prepared surfaces are covered by a single layer of water molecules, but these form a very intimate part of the surface structure only given off with difficulty on heating. This surface in contact with moist air may then adsorb a second layer of water molecules which would be held very much more loosely. It would be interesting to determine whether the moisture is in fact given off in two steps while the temperature is gradually raised.

The difference between the amount of carbon dioxide given off by A and by A′ represents 0.024 cu. mm per sq. cm. of mica or 0.59×10^{15} molecules per sq. cm. The number of molecules of CO_2 required to form a monomolecular layer is about 0.77×10^{15}. It thus appears that the total gas given off by the mica corresponds to a double layer of water molecules and a single layer of carbon dioxide molecules. The amounts of nitrogen given off were comparatively negligible.

After baking out the bulb, experiments on adsorption at room temperature were continued. Nitrogen was first tried but no adsorption could be detected. Upon attempting to measure the adsorption of oxygen a remarkable irreversible disappearance of oxygen with the bulb A at room temperature was noted.

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[1] Langmuir, *Trans. Am. Inst. Elec. Eng.*, **32**, 1921 (1913), and "Part I," p. 2283.

The oxygen in B was allowed to expand into A + B at a pressure of about 11 bars. Within one minute the amount of the oxygen had fallen from 13.8 to 7.4 cu. mm.; in two minutes to 5.7; in 3 minutes to 4.6; in 5 minutes to 3.4; in 10 minutes to 1.9; and in 20 minutes to 1.1. About an hour later 41.0 cu. mm. more of oxygen was introduced. In one minute the amount of oxygen had decreased to 39.5; in two minutes to 37.6; in 5 minutes to 34.9; in 10 minutes to 30.9; in 20 minutes to 27.1; in 45 minutes to 22.6, and in 15 hours to 6.2. After this fresh quantities of oxygen showed no signs of disappearing. Heating the bulb to 300° did not cause the oxygen to be given up again. This effect was undoubtedly due to the presence of the iron strips. The total amount of oxygen which disappeared was 47.5 cu. mm., corresponding to 0.15 cu. mm. per sq. cm. of iron surface, or to 3.8×10^{15} molecules per sq. cm., enough oxygen to give a layer several molecules deep. It is remarkable that the iron was capable of taking up this oxygen at room temperature, after having been heated to 300° for 4 hours, even although it had previously been exposed to the air for several days. A possible explanation seemed to be that the oxygen was used to oxidize carbon monoxide from the iron. The liquid air on the trap was therefore replaced by solid carbon dioxide (—78°) but only 8 cu. mm. of carbon dioxide was released, proving that only a small fraction, if any, of the oxygen had been consumed by reacting with carbon monoxide.

The data given above show that 6 or 7 cu. mm. of oxygen disappeared during the first minute, but that thereafter the rate was about one cu. mm. per min. This seems to indicate that oxygen enough to form a monomolecular layer (probably about 5–8 cu. mm.) reacted with the iron practically instantaneously, but that the reaction then proceeded much slower, time being required for the oxygen to penetrate into the surface film formed. That the reaction should not cease with the formation of a monomolecular layer is not surprising, for at somewhat higher temperatures we know that the oxidation of iron continues until the relatively very thick, iridescent films are formed.

According to this interpretation of the results, the sudden disappearance of the first 6 to 7 cu. mm. of oxygen corresponds to an *adsorption,* while the slow disappearance of the additional quantity was due to *absorption.* The strong affinity between iron and oxygen, however, made the action wholly irreversible, so that the oxygen could neither be removed by pumping nor driven off by heating.[1]

Adsorption Experiments with the Bulb Cooled by Liquid Air.—Be-

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[1] Unfortunately oxygen was accidentally introduced into bulb A′ without measuring it, so that this absorption of oxygen could not be studied with the blank. In several other experiments in this laboratory I have had similar experiences with bulbs containing iron, so that I feel confident that the explanation here given is the correct one.

cause of the poor conduction of heat through gases at very low pressures and the small amount of radiation at low temperatures, the mica in bulb A did not reach temperature equilibrium for about an hour. Thus, if the bulb was immersed in liquid air just prior to the introduction of a gas the pressure continued to decrease for about an hour, but if the liquid air was applied several hours before introducing the gas the equilibrium was reached very much more rapidly. In one typical experiment in which the bulb had been kept cold several hours, there was 104.5 cu. mm. of nitrogen in B. After opening A, the following observations of the total quantity of free gas in A + B were made: one minute, 87.0 cu. mm.; two minutes, 84.7; 4 minutes, 81.0; 7 minutes, 76.7; 10 minutes, 74.0; 13 minutes, 72.8; 18 minutes, 71.7; 23 minutes, 71.5. The equilibrium was reached much more quickly with bulb A′. It is probable that the true adsorption takes place extremely rapidly, but that the rate of disappearance of the gas in these experiments was determined by the slow diffusion of the gas (especially at low pressures) through the spaces between the mica strips. After exhausting B and allowing the gas in A and adsorbed on the mica, to expand into B, the pressure in B always increased to its final value within less than 30 seconds. To reduce as far as possible the time necessary to reach equilibrium, the bulb A or A′ being experimented with, was kept cooled by liquid air continuously night and day during the course of the experiments.

The following will serve as an example of a measurement of adsorption in bulb A cooled by liquid air (see Table VIII). The parts A and B were exhausted to good vacuum (0.02 bar), A was sealed off and pure methane was introduced into B to a pressure of 157 bars, representing 112.0 cu. mm. of gas. The bulb A was then opened and the pressure fell in the course of about 15 minutes to 13.4 bars, representing a total of 27.0 cu. mm. of free gas in A + B. The difference between 112 and 27 or 85 represents the amount of gas adsorbed in A. The bulb A was now sealed off while B was exhausted. The free gas in A amounted to 17.4 cu. mm. When A was opened the pressure in B immediately rose to 11.1 bars, representing 22.0 cu. mm. The difference between 22.0 and 17.4, or 4.6 cu. mm., is the amount of adsorbed gas released from A when the pressure was lowered from 13.4 to 11.1 bars. The results of this experiment therefore indicate that 85.0 cu. mm. was adsorbed at 13.4 bars and that 80.4 cu. mm. were adsorbed at 11.1 bars.

A summary of all the results obtained with the bulbs A and A′, cooled by liquid air, is given in the following tables.

The columns headed p give the pressures in bars, while the observed amount of gas adsorbed (in cu. mm. at 20° and 760 mm. pressure) is given under $q_{obs.}$.

TABLE II.

Adsorption of Nitrogen on Mica (90° K.).

Method I.

$a = 0.085$.	Bulb A.	$b = 32.5$.	Bulb A'.	
p.	q_{obs}.	q_{cal}.	p.	q_{obs}.
37.5	24.2	24.6	48.5	8.8
25.7	22.7	22.4	32.3	7.8
4.04	7.55	8.3	..	..
2.8	6.8	6.2	..	..

TABLE III.

Adsorption of Methane on Mica (90° K.).

Method I.

$a = 0.107$.	Bulb A.	$b = 97$.	Bulb A'.	
p.	q_{obs}.	q_{cal}.	p.	q_{obs}.
19.2	65.0	65.0	44.5	17.6
15.2	59.9	60.0	30.5	15.0
1.6	11.7	14.2	0.8	3.7
1.2	11.2	11.1	..	..
0.4	4.0	4.0	..	..

TABLE IV.

Adsorption of Carbon Monoxide on Mica (90° K.).

Method I.

$a = 0.65$. Bulb A. $b = 58.3$.		Bulb A'.	
p.	q_{obs}.	p.	q_{obs}.
24.3	53.8	49.1	5.8
16.8	52.3	32.0	5.5

TABLE V.

Adsorption of Argon on Mica (90° K.).

Method I.

$a = 0.065$. Bulb A. $b = 30.0$.		Bulb A'.	
p.	q_{obs}.	p.	q_{obs}.
41.5	21.8	52.8	0.8
28.6	19.5	33.9	—1.2

(Adsorption too small to measure)

TABLE VI.

Adsorption of Oxygen on Mica (90° K.).

Method I.

$a = 0.0805$.	Bulb A.	$b = 20.0$.	Bulb A'.	
p.	q_{obs}.	q_{cal}.	p.	q_{obs}.
42.0	15.0	15.4	50.2	3.7
28.4	14.3	14.0	32.8	4.5
4.65	5.25	5.45	..	...
3.36	4.18	4.26	..	...

TABLE VII.

Adsorption of Nitrogen on Mica (90° K.).

Method II.

		$a = 0.156$.	$b = 38.9$.	Freundlich's formula. $q_F = 8.4\,p^{0.417}$.	
p.	q_{obs}.	q_{cal}.	Difference.	q_F.	Diff.
34.0	33.0	32.8	—0.2	36.8	+3.8
23.8	30.8	30.7	—0.1	31.6	+0.8
17.3	28.2	28.4	+0.2	27.3	—0.9
13.0	25.5	26.0	+0.5	24.2	—1.3
9.5	23.9	23.2	—0.7	21.2	—2.8
7.4	21.6	20.8	—0.8	19.1	—2.5
6.1	19.0	19.0	0.0	17.7	—1.3
5.0	17.0	17.0	0.0	16.3	—0.7
4.0	15.1	15.0	—0.1	14.9	—0.2
3.4	13.4	13.5	+0.1	13.9	+0.5
2.8	12.0	11.8	—0.2	12.9	+0.9

TABLE VIII.

Adsorption of Methane on Mica (90° K.).

Method II.

$a = 0.168$. $b = 123$.

p.	q_{obs}.	q_{cal}.	Diff.
13.4	85.0	84.8	—0.2
11.1	80.4	79.8	—0.6
9.6	75.9	75.6	—0.3
8.55	71.6	72.4	+0.8
7.4	67.9	68.1	+0.2
6.68	64.2	64.9	+0.7
5.85	61.2	60.8	—0.4

TABLE IX.

Adsorption of Methane on Mica (90° K.).

Method II.

		$a = 0.123$. $b = 108.0$.		$a_1 = 0.19$. $b_1 = 83.2$	$a_2 = 0.0181$. $b_2 = 35.4$.
p.	q_{obs}.	q_{cal}.	Diff.	q_{cal}.	Diff.
122.0	104.0	101.6	—2.4	104.2	+0.2
83.0	98.6	98.5	—0.1	99.3	+0.7
45.0	90.2	91.5	+1.3	90.4	+0.2
25.8	82.2	82.2	0.0	80.2	—2.0
17.3	71.2	73.5	+2.3	71.8	—0.4
12.8	60.6	65.9	+5.3	65.6	+5.0
8.0	52.7	53.6	+0.9	54.6	+1.9
5.2	43.7	41.8	—1.9	44.3	+0.6
3.7	36.3	33.8	—2.5	36.2	—0.1
2.7	30.6	27.0	—3.6	29.9	—0.7

An examination of these data shows that the adsorption increases with the pressure at first nearly linearly, but at higher pressures seems to approach saturation. Since we are dealing with plane crystal surfaces and with gases far below saturation, it is of interest to see if the formulas developed for simple adsorption (Case I) apply to these data. Inspection of Equation 9 shows that in this case q and p in Tables II to IX should be related by an equation of the form

$$q = \frac{abp}{1 + ap}, \qquad (31)$$

where a and b are constants related to σ_1, N_0, M and T of Equations 3 and 9.

Equation 31 can be rewritten

$$\frac{p}{q} = \frac{1}{ab} + \frac{p}{b}. \qquad (32)$$

If the results agree with this equation, then when we plot p/q as a function of p we should obtain a straight line of slope $1/b$ having the intercept $1/ab$ on the Y axis. The experimental data from each of the Tables II to IX have been plotted in this manner and a straight line has been drawn to pass as nearly as possible through these points. From the slopes and Y intercepts of these lines the values of a and b as given in the tables have been calculated.

The values of $q_{cal.}$ given in the tables have been calculated by means of Equation 31 from these values of a and b. The best data are those of Tables VII, VIII and IX. Reference to Tables VII and VIII shows that $q_{cal.}$ agrees with $q_{obs.}$ within experimental error, indicating that the adsorption takes place according to Equations 31 and 9. The data do not, however, agree at all well with Freundlich's adsorption formula. When the data, given for example, in Table VII, are plotted on logarithmic paper the points lie along a curved line. At the lowest pressures (3 bars) the slope of this line corresponds to an exponent 0.684 while at the highest pressures (100 bars) the exponent decreases to 0.20. Drawing a straight line as nearly as possible through the points leads to the equation $q_F = 8.4\, p^{0.417}$. The last two columns of Table VII show that the agreement with the experimental results is very poor. The data in the other tables fit in equally badly with the observed values.

In Table IX, where there is a much greater range of pressures, the agreement between $q_{obs.}$ and $q_{cal.}$ (Col. 4) is much less satisfactory. It was therefore attempted to express the results in terms of Equation 19 (Case II) using only two terms. By a somewhat laborious method of trial the constants $a_1 = 0.19$, $b_1 = 83.2$, $a_2 = 0.0181$, and $b_2 = 35.4$, were found to give best agreement. The last two columns of Table IX give the results calculated in this manner. The results appear to lie within the experimental error. The observed value of q corresponding to the pressure 12.8 is undoubtedly in error, as it cannot be made to fit into a smooth curve with the other data.

The data obtained with the blank bulb were rather meager. Except in the case of nitrogen (Table II) the amount of adsorption by the blank bulb does not exceed 10 or 20% of that in the bulb containing the mica. With nitrogen the fraction was about one-third. No attempt was made to subtract the adsorption in the blank from that in the other bulb in order to obtain the adsorption by the mica itself as the accuracy of the results hardly warrants such a calculation. The results therefore obtained from bulb A are to be considered as being 10 to 30% too high.

The results obtained with the same gas at different times, as for example with nitrogen in Tables II and VII, and with methane in Tables III, VIII and IX, do not agree very well with each other. It is likely that this variation may be due to the rise in the temperature of the liquid air as the nitrogen gradually boils out and leaves the oxygen. No record was kept of these temperature changes.

Adsorption with the Bulb Cooled by Frozen Ether.—Some data were obtained with the bulb A cooled by frozen ether (155° K.). These are given in Tables X and XI. No measurements were made with bulb A′ at this temperature.

TABLE X.

Adsorption of Various Gases on Mica (155° K.).

Method I. Bulb A.

Gas.	p.	q_{obs}.	q_{cal}.	a.	b.
N_2	65.8	6.2	6.3	0.0176	11.8
	37.5	4.8	4.7	..	..
	3.9	0.43	0.75	..	..
	2.2	0.43	0.43	..	..
CH_4	61.6	8.9	8.9	0.009	25.0
	35.9	6.1	6.1	..	..
	4.1	0.40	0.89	..	..
	1.3	0.46	0.29	..	..
CO	64.3	6.2	...	0.0069	20.0
	37.1	4.1	...	..	..
Ar	63.0	6.8	...	0.024	11.2
	36.0	5.2	...	..	..
O_2	65.2	3.5	...	0.043	4.7
	36.4	2.9	...	..	..
CO_2	42.0	48.2	48.5	0.071	65.0
	26.4	42.6	42.1	..	..
	1.31	5.38	5.5	..	..
	1.14	4.82	4.85	..	..

The amount of adsorption at this temperature was from 5 to 20% of that observed with the same gas at the lower temperature. For this reason the experimental errors are relatively greater.

TABLE XI.

Adsorption of Carbon Dioxide on Mica (155° K.).

Method II. Bulb A.

$a = 0.085$. $b = 57.3$.

p.	q_{obs}.	q_{cal}.	Diff.
172.0	55.0	53.6	—1.4
98.0	49.9	51.1	+1.2
41.4	44.6	44.6	0.0
20.6	35.2	36.4	+1.2
11.9	26.9	28.8	+1.9
7.3	21.1	22.0	+0.9
4.8	16.9	16.6	—0.3
3.19	13.8	12.2	—1.6
2.06	9.2	8.6	—0.6
1.60	6.2	6.9	+0.7

II. Experiments with Glass.—Nearly 200 microscope cover glasses 2.5 cm. in diameter and 0.14 mm. thick furnished the adsorbing surface for this experiment. The glasses were separately slightly bent by momentarily heating in a gas flame so that they would not pack together when placed loosely into the bulb. The total surface of the glasses used was 1966 sq. cm. and their volume was 13.6 cu. cm. They were placed in a bulb (A) 15 cm. long and 3.6 cm. inside diameter having a volume of 164 cc. Another similar bulb (A′) (volume 152 cc.) was used as a blank. These bulbs were connected to the same vacuum system as used in the experiments with mica, but to reduce the uncertainty in the volume cooled by liquid air, the tube connecting the bulb to the system was made 1.2 cm. instead of 2.5 cm. in diameter, and similar reduction was made in the dimensions of the liquid air traps. These changes considerably increased the accuracy of the results. The bulbs, cover glasses and liquid air traps were thoroughly cleaned before sealing to the vacuum system by heating with conc. sulfuric acid and potassium bichromate and washing well with distilled water.

Great care was taken in calibrating the apparatus with the bulbs and traps cooled to different temperatures. It was thought that some errors might be caused by a diffusion pump effect, owing to mercury vapor passing from the mercury seals into the liquid air trap. This might cause the pressure in the bulbs to be somewhat greater than indicated by the gauge. Experiments were therefore undertaken at a wide range of pressures, cooling the traps by ice. The diffusion pump effect was found to be negligible at pressures above 10 bars and at lower pressures the maximum error produced was not over a few per cent. These small corrections were applied in calculating the amounts of gas adsorbed.

On baking out bulbs A and A′ at 300° for one hour the quantities of gas given in Table XII were evolved.

Table XII.

Gases Evolved by Heating Bulbs to 300°. Volumes in Cubic mm. at 20° and 760 mm.

Gas.	Bulb A (containing cover glasses).	Bulb A′ (blank).	Cover glasses.
H_2O	476.0	122.0	354.0
CO_2	82.0	18.0	64.0
Non-condensable gases (N_2?)	62.0	13.0	49.0

The "non-condensable" gas was probably all nitrogen, as previous experience had shown that nitrogen is the only "non-condensable" gas given off in heating glass. The inside surface of bulb A′ was about 180 sq. cm., so the amounts of gas given off from this bulb per sq. cm. were 0.68 cu. mm. of water vapor, 0.10 of carbon dioxide, and 0.07 of nitrogen. These quantities are less than those found with the blank bulk in the experiments with mica. The shorter time of heating accounts for the difference.

The amount of gas given off by the cover glasses per sq. cm. corresponds to 0.18 cu. mm. of water vapor (4.5×10^{15}) molecules; 0.032 of carbon dioxide (0.81×10^{15} molecules); and 0.025 of nitrogen (0.63×10^{15} molecules). These amounts correspond to the following number of layers of molecules: 4.5 for water vapor, 1.05 for carbon dioxide, and 0.9 for nitrogen. The previous heating of the glass for bending probably accounts for the relatively low values for water vapor. It should be noted that the amounts of nitrogen and carbon dioxide correspond to monomolecular layers of these gases.

Experiments were undertaken to detect adsorption of various gases with bulbs A and A′ at room temperature and at pressures ranging from 30 to 110 bars. With hydrogen, nitrogen, carbon monoxide, argon and methane no adsorption could be observed, that is, the adsorption was less than 0.5 cu. mm. when 100 cu. mm. of gas was admitted to bulb A. With carbon dioxide, however (using solid ether on the trap), about 1.0 cu. mm. of gas was apparently adsorbed in bulb A at a pressure of 110 bars. The results obtained with bulbs A and A′ immersed in liquid air are given in Tables XIV to XVII. It is seen that the adsorption observed with

Table XIII.

Adsorption of Carbon Monoxide on Glass (90° K.).

Method II.

Bulb A.				Bulb A′.	
$b_1 = 6.6$.	$a_2 = 0.083$.		$b_2 = 16.2$.		
p.	q_{obs}.	q_{cal}.	Diff.	p.	q_{obs}.
61.6	20.0	20.2	+0.2	82.0	1.0
31.5	18.5	18.4	−0.1	40.1	0.7
17.3	16.2	16.2	0.0	..	...
9.7	14.0	13.9	−0.1	..	...
5.8	11.8	11.9	+0.1	..	...
2.7	9.6	9.6	0.0	..	...
1.4	8.3	8.2	−0.1	..	...

Table XIV.

Adsorption of Argon on Glass (90° K.).

Method II.

$a = 0.0511$.	Bulb A.		$b = 11.8$.	Bulb A′.	
p.	$q_{obs.}$	$q_{cal.}$	Diff.	p.	$q_{obs.}$
73.0	9.4	9.3	−0.1	76.0	1.0
37.3	7.5	7.75	+0.25	37.5	0.6
19.6	6.3	5.93	−0.37	..	...
10.6	4.3	4.15	−0.15	..	...
5.7	2.56	2.67	+0.11	..	...
2.2	1.20	1.20	0.0	..	...
1.0	0.40	0.57	+0.17	..	...

Table XV.

Adsorption of Oxygen on Glass (90° K.).

Method II.

$a = 0.079$.	Bulb A.		$b = 8.46$.	Bulb A′.	
p.	$q_{obs.}$	$q_{cal.}$	Diff.	p.	$q_{obs.}$
71.0	7.1	7.15	+0.05	81.0	−0.1
35.5	6.3	6.24	−0.06	39.0	+0.1
18.5	5.0	5.01	+0.01	..	...
9.7	3.5	3.66	+0.16	..	...
5.0	2.19	2.40	+0.21	..	...
1.3	1.15	0.79	−0.36	..	...
0.7	0.63	0.44	−0.19	..	...

Table XVI.

Adsorption of Methane on Glass (90° K.).

Method II.

$b_1 = 2.0$.	Bulb A. $a_2 = 0.0638$.		$b_2 = 22.4$.	Bulb A′.	
p.	$q_{obs.}$	$q_{cal.}$	Diff.	p.	$q_{obs.}$
67.0	20.3	20.2	−0.1	80.0	0.2
34.8	17.3	17.5	+0.2	39.0	0.3
19.3	14.3	14.4	+0.1	..	...
11.6	11.3	11.5	+0.2	..	...
7.0	9.0	8.9	−0.1	..	...
3.4	6.14	5.98	−0.16	..	...
1.9	4.35	4.42	+0.07	..	...

Table XVII.

Adsorption of Nitrogen on Glass (90° K.).

Method I.

$a = 0.088$. Bulb A. $b = 13.5$.		Bulb A′.	
p.	$q_{obs.}$	p.	$q_{obs.}$
73.0	11.7	82.4	+0.8
36.5	10.3	40.8	−0.7

bulb A′ was practically negligible, the small amounts recorded being not much greater than the experimental errors.

The results with carbon monoxide (Table XIII) do not give a straight line when $p/q_{obs.}$ is plotted against p and therefore do not satisfy Equation 31, but the results are well expressed by the equation

$$q = b_1 + \frac{a_2 b_2 p}{1 + a_2 p}. \tag{33}$$

This equation is readily deducible from Equation 19 (Case II), by making σ_1 so large that unity is negligible compared with $\sigma_1\mu$. In other words, the data of Table XIII indicate that the adsorption of carbon monoxide occurs in two stages. At pressures lower than those used in the experiment (1.4 bars), a part of the surface becomes saturated with 6.6 cu. mm. of gas. Over the range of pressures used, adsorption then proceeds in a normal manner and the rest of the surface tends to become saturated at the highest pressures by taking up an additional 16.2 cu. mm. of gas. It should be noted that at the end of this experiment all the gas was pumped from the systems A and B into C. The total volume of the gas then in C was 5.3 cu. mm. less than the amount originally let into the system. It appears, therefore, that some carbon monoxide is so strongly adsorbed on glass surfaces (or possibly by the mercury of the condensation pump) that it cannot readily be removed by pumping. A similar phenomenon, although much less strongly marked, was observed in the adsorption of methane, Table XVI. In this case 2.0 cu. mm. was strongly adsorbed at pressures below 1.9 bars, while at high pressures 22.4 cu. mm. more was needed to saturate the surface.

The data obtained on adsorption by glass agrees with Equations 31 and 33 within the experimental error. The magnitude of these errors is shown by the results with the bulb A′. In some cases negative values for the adsorption were obtained, the largest negative value being —0.7 cu. mm.

Discussion of Results with Mica and Glass.—The results have shown clearly that equations of the type of (9) or (19) are applicable to adsorption of gases by plane surfaces of glass or mica. It now remains to calculate the constants N_0, σ and β from the experimental data, and to see whether these values of N_0 correspond to adsorbed layers not exceeding one molecule in thickness in accordance with the proposed theory of adsorption.

By dividing Equation 31 by b and comparing with (9) we find the following relations:

$$\sigma\mu = ap \tag{34}$$

$$N_0 q = bN\eta \tag{35}$$

Now q and η are proportional to one another, q being the number of cu. mm. of gas adsorbed on the surface s of the glass or mica, and η being the corresponding number of molecules per sq. cm. Since one cu. mm. of gas at 20° and 760 mm. pressure is 4.16×10^{-8} gram molecules we have

$$\eta = 4.16 \times 10^{-8}\, q/s. \tag{36}$$

Substituting this in (35) and placing $N = 6.06 \times 10^{23}$ molecules per gram molecule we have

$$N_0 = 25.2 \times 10^{15}\, b/s. \qquad (37)$$

Dividing (34) by Equation 3 gives

$$\sigma = 22860\, a\sqrt{MT}, \qquad (38)$$

where M is the molecular weight of the gas and T is the temperature at which the adsorption takes place. From Equations 37 and 38 the coefficients N_0 and σ can be directly calculated from the experimental data on b and a. Tables XVIII, XIX and XX give a summary of the results. The values of b given in previous tables have here been calculated over to the basis of cu. mm. of gas per sq. meter of surface in order to make the results for mica and glass comparable. In other words, the values of b' are equal to b/s.

As a test for the correctness of our theory of adsorption it is of especial interest to compare the values of N_0 in these tables with the number of molecules required to cover the surface with a single layer. In the first place, it should be noted that the order of magnitude of the values of N_0 is in good agreement with that of the number of elementary spaces on the surfaces of solids. Thus, if the average distance between atoms is 3×10^{-8} cm. the area covered by each is about 9×10^{-16} sq. cm. and the number of atoms per sq. cm. is about 10^{15}.

TABLE XVIII.

Adsorption by Mica at 90° K.

Gas.	Table.	Number of obs.	a.	b'. Cu. mm. per sq. meter.	σ. Seconds.	N_0 molecules per sq. cm.	β.
N_2	2	4	0.085	56.5	97,000	0.142×10^{15}	0.22
N_2	7	11	0.156	67.6	178,000	0.170×10^{15}	0.26
CH_4	3	5	0.107	169.0	92,000	0.426×10^{15}	0.68
CH_4	8	7	0.168	214.0	145,000	0.54×10^{15}	0.86
CH_4	9	10	0.19[1] 0.018	145.0[1] 61.5	164,000[1] 15,600	0.365×10^{15}[1] 0.155×10^{15}	0.58 0.25
CO	4	2	0.65	100.0	740,000	0.252×10^{15}	0.38
Ar	5	2	0.065	52.2	88,000	0.131×10^{15}	0.17
O_2	6	4	0.080	34.8	97,000	0.088×10^{15}	0.11

TABLE XIX.

Adsorption by Mica at 155° K.

Gas.	Table.	Number of obs.	a.	b'. Cu. mm. per sq. meter.	σ. Seconds.	N_0.	β.
N_2	10	4	0.0176	20.5	26,000	0.052×10^{15}	0.08
CH_4	10	4	0.009	43.5	10,000	0.109×10^{15}	0.17
CO	10	2	0.0069	34.8	10,000	0.088×10^{15}	0.13
Ar	10	2	0.024	19.5	43,000	0.049×10^{15}	0.06
O_2	10	2	0.043	8.2	69,000	0.021×10^{15}	0.03
CO_2	10	4	0.071	113.0	134,000	0.284×10^{15}	0.47
CO_2	11	10	0.085	99.0	160,000	0.250×10^{15}	0.41

[1] The first values correspond to a_1 and b_1 while the second correspond to a_2 and b_2.

TABLE XX.

Adsorption by Glass at 90° K.

Gas.	Table.	Number of obs.	a.	b'. Cu. mm. per sq. meter.	σ. Seconds.	N_0.	β.
CO	13	7	... 0.083 [1]	33.6 82.4	 95,000	0.085×10^{15} 0.208×10^{15}	0.13 0.32
Ar	14	7	0.051	60.0	70,000	0.151×10^{15}	0.20
O_2	15	7	0.079	43.0	97,000	0.108×10^{15}	0.14
CH_4	16	7	... 0.064 [1]	10.2 114.0	 55,000	0.026×10^{15} 0.288×10^{15}	0.04 0.36
N_2	17	2	0.088	69.0	101,000	0.174×10^{15}	0.26

The approximate number of molecules needed to form a monomolecular layer may be estimated from the density of the adsorbed substance in the liquid state. Thus, the "molecular volume" of liquid nitrogen is 35.5 cu. cm. Dividing this by $N = 6.06 \times 10^{23}$, and taking the cubic root, gives for the diameter of the molecule (assumed cubical) the value 3.88×10^{-8} cm. The number per sq. cm. is therefore 0.66×10^{15}. In a similar way we obtain for methane, 0.63×10^{15}; for carbon monoxide, 0.66×10^{15}; for argon and oxygen, 0.77×10^{15}; and for carbon dioxide, 0.61×10^{15}.

The observed values of N_0 are all less than these calculated results. The ratios between N_0 and the numbers of molecules in a monomolecular layer as given above, are given under the heading β in the last column in Tables XVIII, XIX and XX. This ratio represents the fraction of the saturated solid surface covered by adsorbed molecules on the assumption that the size of the adsorbed molecules is the same as that in the liquefied gas. These experiments therefore prove that even with saturated surfaces of mica and glass the amounts of gas adsorbed are always less than the amounts needed to form a monomolecular layer. In this connection it should also be remembered that the results given for the adsorption by mica are somewhat too high, since they were not corrected for the adsorption by the blank bulb.

The fact that β is so variable and so much less than unity suggests that the adsorption of most of these gases does not occur over the whole surface, but only where the arrangement of the surface atoms is such as to give particularly strong stray fields of force. The adsorption thus takes place in the manner discussed under Case II or Case III, but over a large part of the surface the value of σ is so small as to be negligible under the conditions of these experiments.

If we arrange the gases in order, according to the amounts required to saturate the surface, as indicated by b', N_0 or β we find that this order is the same in all three sets of experiments, namely, methane, carbon monoxide, nitrogen, argon and oxygen—methane being the most and oxygen

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[1] Values corresponding to a_1 and a_2, respectively.

the least adsorbed. The order of the boiling points of these gases is methane, oxygen, argon, carbon monoxide and nitrogen. The high boiling point of methane is probably related to the large values of β for this gas. Carbon monoxide, however, is much more strongly adsorbed and oxygen much less adsorbed than would be expected from their boiling points. It seems that the unsaturated carbon atom of the carbon monoxide plays an important part in the adsorption of this gas. The small adsorption of oxygen is perhaps due to the surface of mica and glass being covered with chemically saturated oxygen atoms. The chemical inertness of argon as compared to nitrogen also seems to play a part in the relative adsorption of these gases.

An inspection of the tables shows that the values of a or σ are much more erratic than those of b or N_0. The order in the different tables is different and they bear little relationship to other properties of the gases. In fact even in experiments with the same gas, variable results for a were obtained. It is probable that the rate of evaporation of the molecules, on which a and σ are dependent, is very sensitive to slight changes, in the arrangement of the surface atoms of the solid such as may be caused by temperature changes or the previous adsorption of the gases. Effects of this kind were frequently observed (not published) during the course of experiments on the evaporation and condensation of cadmium on glass surfaces.

It is of interest to compare the "relative lives" σ in the tables, with the values of σ corresponding to the evaporation of gas from the liquefied gas at the same temperature. For a liquid in equilibrium with its saturated vapor an equation analogous to Equation 4 must hold, namely

$$\alpha\mu = \nu, \tag{39}$$

where $\alpha\mu$ is the rate of condensation and ν is the rate of evaporation. As before, we may place $\alpha/\nu = \sigma$, so that the equation reduces to $\sigma\mu = 1$. The value of σ may thus be calculated by Equation 3 from the vapor pressure of the liquefied gas at the temperature of the experiment. Table XXI gives the results for the different gases at 90° and 155° K.

TABLE XXI.

"Relative Lives." σ of Molecules in the Surfaces of Liquefied Gases in Seconds.

Gas.	T = 90°.	T = 155°.
N_2	0.30	0.013
CH_4	5.5	0.070
CO	0.50	0.021
Ar	0.96	0.022
O_2	1.24	0.029
CO_2	..	16.5

The values of σ give the time in seconds required for the evaporation of one gram molecule per sq. cm. Comparing these results with the "relative lives" of the adsorbed molecules on the mica and glass surfaces, we see that the latter are many thousands or even millions of times greater. The ratio between the two lives are summarized in Table XXII.

TABLE XXII.

Relative Increase in "Life" of Molecules on the Surface Caused by Adsorption.

Gas.	Adsorbed on mica. 90° K.	Adsorbed on mica. 155° K.	Adsorbed on glass. 90° K.
N_2	440,000	2,000,000	330,000
CH_4	24,000	140,000	10,000
CO	1,500,000	480,000	190,000
Ar	92,000	.....	73,000
O_2	80,000	.....	78,000
CO_2	.....	9,000	.....

The forces involved in the adsorption of these gases are thus very much more intense than those holding the molecules of the liquids together. This increase is most marked in the cases of carbon monoxide and nitrogen, and least marked with carbon dioxide and methane.

III. Experiments with Platinum.—The platinum used in these experiments was a piece of pure platinum foil 15.3 × 10.2 cm. with a thickness of 0.0010 cm. The weight was 4.03 g. and the total surface 312 sq. cm. The platinum foil was cleaned by heating to a bright red heat for several minutes in a Bunsen flame, boiling in hydrochloric acid, and finally washing thoroughly in distilled water. The sheet was folded or crimped so that it could be placed in a tube 1.8 cm. inside diameter without providing capillary spaces due to contacts between different parts of the platinum surface. A similar glass tube (volume 30 cu. cm.) without platinum served as a blank. The vacuum system was the same as in the experiments with glass.

After exhausting the bulb and drying the system for 24 hours by cooling an appendix in liquid air, the bulb containing the platinum was baked out for one hour at 350° with the condensation pump operating continuously. This heating caused the evolution of 18.3 cu. mm. of hydrogen, 5.8 of carbon monoxide, 17.7 of carbon dioxide, 92 of water vapor and 1.2 of some noncondensable gas probably mostly nitrogen. A similar heating of the blank bulb gave only 55 cu. mm. of water vapor, 4.6 cu. mm. of carbon dioxide and 0.5 cu. mm. of nitrogen. The smaller amounts of water vapor and carbon dioxide given off from this bulb are probably to be accounted for by the fact that the blank bulb before baking out was dried at room temperature several days by a trap cooled in liquid air. The combustible gases hydrogen and carbon monoxide must have come entirely from the platinum. The volume of these gases, however, is only about one-tenth of the volume of the platinum.

In the first tests to measure adsorption it was found that the quantities of gas adsorbed were negligibly small, never more than a few tenths of a cu. mm. The gases tried were hydrogen, oxygen and carbon monoxide, with the bulb at room temperature and also cooled by liquid air. Since the calculated amounts of these gases required to form a monomolecular layer over the surface of the platinum range from 8 to 10 cu. mm., the amount of adsorption by this platinum foil was much less than that observed with either mica or glass.

Hydrogen (111 cu. mm.) and oxygen (102 cu. mm.) were now introduced together into the system (pressure 120 bars). At room temperature and at liquid air temperatures no adsorption and no reaction between the gases were noted, but when the bulb with the platinum was heated to 130° the gases slowly reacted to form water vapor, which condensed in the liquid air trap. At 240° the reaction became very rapid and continued until within fifteen minutes, the total volume of gas had decreased to 1.6 cu. mm. Not only had all the hydrogen reacted with the oxygen, but the excess of 46 cu. mm. of oxygen had also disappeared. It is probable that this oxygen reacted with hydrogen and carbon monoxide dissolved in the platinum which had not been removed by baking out at 350° in vacuum. With the bulb at 275°, hydrogen was now admitted. In the course of a few minutes 3.1 cu. mm. disappeared, but continued heating caused no further disappearance. After pumping out the hydrogen, oxygen was admitted with the bulb at the same temperature. About 4.0 cu. mm. of this gas disappeared. A mixture of 106 cu. mm. of oxygen with 93 of carbon monoxide was then admitted with the bulb at room temperature. This mixture contained an excess of 59 cu. mm. of oxygen above that necessary to react with the monoxide. Although carbon monoxide and oxygen usually require a higher temperature than hydrogen-oxygen before reaction begins, the platinum now caused these gases to react slowly at room temperature, the amount of gas decreasing from 200 to 157 cu. mm. in half an hour. Upon heating to 250° the reaction continued more rapidly until only 39 cu. mm. of oxygen remained. This indicates that besides the oxygen which reacted with the carbon monoxide an additional quantity of 20 cu. mm. reacted with something from the platinum. This treatment lasting several hours, seemed, however, to have removed nearly the last of this oxidizable substance from the platinum.

The platinum was now found to be in a permanently active condition towards oxygen-hydrogen, as well as towards oxygen-carbon monoxide. That is, it caused the catalytic combination of these gases even at room temperature. The activation had been brought about, as in many other similar experiments in this laboratory, by heating the platinum with a *mixture* of hydrogen and oxygen. Heating in either gas alone does not cause activation. It is also remarkable that the oxygen does not react with the oxidizable impurity in the platinum until after the activation of the platinum.

The next experiment showed that the quantities of oxygen and carbon monoxide which disappeared when these gases were brought into contact with the platinum were not in stoichiometric ratio, but depended on the previous history of the platinum. Thus, if the platinum had previously been in contact with the oxygen an abnormally large amount of carbon monoxide disappeared when a mixture of the gases was introduced into the bulb. Similarly, after an excess of carbon monoxide had been used, there was an abnormal disappearance of oxygen.

TABLE XXIII.

Disappearance of Oxygen and Carbon Monoxide in Presence of Platinum Foil at 200° C.

Run.	Gas.	Initial amount.	Final amount.	Abnormal disappearance.
1	$2CO + O_2$	43.2	...	...
	CO	34.4	19.0	15.4
2	$2CO + O_2$	45.4	...	...
	CO	33.4	32.6	0.8
3	$2CO + O_2$	59.7	...	...
	O_2	21.6	13.0	8.6
4	$2CO + O_2$	59.0	...	...
	O_2	19.6	19.4	0.2
5	$2CO + O_2$	0.0	...	...
	CO	6.0	0.04	6.0

These phenomena are illustrated by the data given in Table XXIII, which were obtained with the bulb at 200°. Prior to Run 1 the platinum had been in presence of an excess of oxygen. In the first run a mixture of gas consisting of 63.2 cu. mm. of carbon monoxide with 14.4 of oxygen was prepared in the part of the system denoted by B. This mixture may be looked upon as consisting of 43.2 of a mixture of equivalent parts of carbon monoxide and oxygen, together with an excess of 34.4 of carbon monoxide. When the bulb A was opened the gas immediately began to disappear, fully half of it going within the first minute, although about 20 minutes was needed for the pressure to become steady. There remained only 19.0 cu. mm. of carbon monoxide. There was thus an abnormal disappearance of 15.4 cu. mm. of carbon monoxide. In the second run an excess of carbon monoxide was again used, but this time practically the whole of the excess of carbon monoxide remained. In the next two runs (3 and 4) the mixtures contained an excess of oxygen. In the first of these runs there was an abnormal disappearance of 8.6 cu. mm. of oxygen, but practically none in the second run. In the fifth run no oxygen was added. The 6 cu. mm. of carbon monoxide disappeared completely. Judging from the first run, a much larger quantity would have disappeared if it had been present.

These results prove that either gas, added in excess, becomes adsorbed on the platinum and subsequently reacts with the other gas when brought into contact with it. For example, the abnormal disappearance of 15.4 cu. mm. of carbon monoxide in the first run may be explained by assuming that part of this gas reacted with oxygen previously adsorbed and that another part became adsorbed on the platinum in place of the oxygen thus removed. To determine the actual amounts of oxygen and carbon monoxide required additional information. A series of runs was therefore made in which the amount of carbon dioxide formed by the reaction was measured. As the previous runs had shown that it was unnecessary to have oxygen and carbon monoxide present together in order to observe these adsorption phenomena, it was decided to introduce the gases alternately to the bulb containing the platinum. The results of these experiments are summarized in Table XXIV. As an explanation of the meaning of the data given in the table, let us consider the first two runs in more detail.

TABLE XXIV.

Treatment of Platinum Alternately with Oxygen and Carbon Monoxide.

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
			Initial amount,	Contraction,	CO_2 formed,	Adsorbed.			
Run.	Gas.	Temp.	cu. mm.	cu. mm.	cu. mm.	O_2.	CO.	Loss of O_2.	Loss of CO.
1......	CO	200°	35.9	15.6	11.2	5.6	4.4		0.5
2......	O_2	200	30.0	8.5	3.9	6.6	3.9	1.4	
3......	CO	200	25.0	14.8	10.5	5.2	4.3		0.4
4......	O_2	330	29.0	12.7	3.9	10.8	3.9	5.6	
5......	CO	330	29.9	13.4	10.5	5.2	2.9		1.7
6......	O_2	330	29.6	8.9	1.2	8.3	1.2	4.7	
7......	CO	100	28.4	11.5	7.3	3.6	4.2		0.1
8......	O_2	100	27.4	5.6	4.1	3.5	4.1	—0.1	
9......	CO	100	26.6	11.4	7.3	3.6	4.1		0.5
10......	O_2	20	26.6	4.5	3.6	2.7	3.6	0.6	
11......	CO	20	27.8	8.5	4.2	2.1	4.3		0.8
12......	O_2	20	29.0	4.5	3.5	2.8	3.5		

Just prior to Run 1 the platinum had been in contact with an excess of oxygen at 200°. While the bulb was maintained at this temperature it was well exhausted and the liquid air was removed from the trap to release all condensed carbon monoxide. After replacing the liquid air, carbon monoxide (35.9 cu. mm., Col. 4) was introduced. The pressure began to decrease immediately and in a few minutes the quantity of gas had decreased to 20.3 cu. mm. This contraction of 15.6 cu. mm. (Col. 5) indicated a disappearance of this quantity of carbon monoxide. This residue was then pumped out and the liquid air was again removed from the trap. The carbon dioxide (11.2 cu. mm., Col. 6) which was thus released and measured, was produced by the combustion of 5.6 cu. mm. oxygen (Col. 7) adsorbed on the platinum, together with 11.2 out of the 15.6 cu. mm. of carbon monoxide which disappeared. The remainder of the carbon monoxide, namely 4.4 cu. mm. (Col. 8), was presumably adsorbed on the platinum.

In the second run 30.0 cu. mm. of oxygen was introduced. The contraction was 8.5 cu. mm. and 3.9 cu. mm. of carbon dioxide were formed. This carbon dioxide must have been produced by the reaction of 1.95 cu. mm. of oxygen with 3.9 cu. mm. of carbon monoxide (Col. 8) adsorbed on the platinum. The remainder of the 8.5 cu. mm. of oxygen which disappeared, namely 6.6 cu. mm. (Col. 7), was presumably adsorbed by the platinum.

The 4.4 cu. mm. of carbon monoxide (Col. 8) adsorbed in Run 1 and the 3.9 cu. mm. found in Run 2 should agree except for a possible loss of adsorbed gas from the platinum while the bulb is being exhausted prior to the succeeding run. The corresponding pairs of values are indicated by brackets and the corresponding differences are given in Col. 10. An examination of the table shows that in every case the second value is lower than the first, indicating that a small fraction of the carbon monoxide actually escapes in this manner, especially when the platinum is at the highest temperatures. This conclusion was also confirmed by later direct observations.

In a similar way, the values for the amounts of oxygen adsorbed occur in pairs as indicated by brackets. In this case also, with one exception, the first value is larger than the second. Subsequent experiments have shown that adsorbed oxygen cannot be driven off the platinum by heating to 330°, so this loss of oxygen cannot be due to this cause. It is more probable that a trace of the oxidizable matter (probably hydrogen) still remained in the platinum and that part of this reacted with oxygen. This conclusion is supported by the fact that the loss (Col. 9) was much greater at 330° than at 200° and was negligible at 100° and at 20°.

A comparison of Tables XXIII and XXIV shows that the "abnormal disappearance" of oxygen and carbon monoxide due to adsorption is in no wise dependent on the presence of both gases. Thus, in Table XXIII 15.4 cu. mm. of carbon monoxide and 8.6 cu. mm. of oxygen disappeared after runs in the other gas. Runs 1 and 2, of Table XXIV, give 15.6 cu.

mm. of carbon monoxide and 8.5 cu. mm. of oxygen as the disappearance at the same temperature. From these results the amounts of gas adsorbed by the platinum (not removable by exhausting) were as given in Table XXV.

TABLE XXV.

Amounts of Oxygen and Carbon Monoxide Adsorbed by Platinum.

	Oxygen.		Carbon monoxide.	
Temp.	Cu. mm.	N_0.	Cu. mm.	N_0.
20° C.	2.1	0.17×10^{15}	3.6	0.29×10^{15}
100	3.6	0.29	4.1	0.33
200	5.4	0.44	3.9	0.32
330	5.2	0.42	1.2	0.10

The number of molecules adsorbed per sq. cm. of surface, tabulated in the columns headed N_0, is thus somewhat greater than the number adsorbed by mica and glass (see Tables XVIII, XIX and XX), but still never exceeds the amounts corresponding to a layer of tightly packed molecules.

The results of Table XXV indicate that the amounts of oxygen adsorbed increase as the temperature increases, while with carbon monoxide the adsorption decreases at the higher temperatures. To throw more light on these effects of temperature and also to see whether, under other conditions, greater quantities of gas could not be adsorbed, another series of experiments was undertaken. To remove all traces of oxygen and carbon dioxide from the platinum, it was heated and exhausted at 360° and an excess of carbon monoxide was introduced. After the bulb was cooled to room temperature the excess of carbon monoxide was pumped out. No appreciable amount of carbon monoxide came off the platinum while pumping. However, by heating the bulb to 360°, 4.8 cu. mm. of carbon monoxide was driven off and by continued pumping for an hour with the bulb at this temperature another 0.9 cu. mm. was obtained. The platinum still retained about 1.2 cu. mm. of carbon monoxide, for when oxygen was introduced some of this disappeared and 1.2 cu. mm. of carbon dioxide were produced. Runs of this kind were repeated several times with concordant results. From this it may be concluded that at room temperature, platinum thoroughly saturated with carbon monoxide has adsorbed on it about 6.9 cu. mm., corresponding to $N_0 = 0.56 \times 10^{15}$, which checks well with the amount to be expected in a monomolecular layer. Carbon monoxide driven off the platinum at 360° is completely readsorbed when the platinum is cooled to room temperature.

The behavior of oxygen films adsorbed by platinum is quite different. To saturate the platinum thoroughly it was heated to 360° for several hours in presence of 3 separate portions of oxygen until no further disappearance of oxygen occurred. The oxygen was pumped out with the bulb still hot, an excess of carbon monoxide was introduced; 14.4 cu. mm. of this disappeared immediately and 11.8 cu. mm. of carbon dioxide were formed. This indicates that at 360°, 5.9 cu. mm. of oxygen had been adsorbed on the platinum and that this was replaced by 2.6 cu. mm. of carbon monoxide. On allowing the bulb to cool, an additional amount of 4.4 cu. mm. of carbon monoxide was adsorbed by the platinum, making a total of 7.0 cu. mm. in good agreement with the 6.9 cu. mm. recorded above. Cooling the bulb in liquid air caused no perceptible increase in the amount adsorbed. The amount of oxygen adsorbed at 360°, namely, 5.9 cu. mm., is somewhat greater than that previously observed at 330° (see Table XXV). It corresponds to $N_o = 0.48 \times 10^{15}$. In another case the platinum was again thoroughly saturated with oxygen at 360° and was allowed to cool in this gas, but there was no evidence of either an increase or a decrease in the adsorption. On heating again to 360° no oxygen was evolved. The oxygen thus seems to be held to the platinum much more firmly than the carbon monoxide.

The adsorption of these gases by platinum is clearly due to very strong chemical forces of the type represented by primary valence. The action with oxygen seems to be wholly irreversible, so that this gas can be removed from the platinum only by reaction with carbon monoxide, hydrogen, etc. With carbon monoxide, the gas is partly driven off by heating, but only with relative difficulty. This behavior is in marked contrast with that observed in the adsorption of gases by mica and glass, where forces involved are of the secondary valence type. The specific nature of the adsorption of gases by platinum offers further confirmation of this conclusion. Qualitative observations have shown that hydrogen is adsorbed in quantities similar to those of oxygen and carbon monoxide, but that carbon dioxide, nitrogen, etc., are not appreciably adsorbed by the platinum at room temperature.

To throw more light on this distinction between the two types of adsorption some experiments were undertaken to measure the adsorption of carbon monoxide and oxygen by platinum cooled by liquid air. Very interesting results were obtained. The platinum was first treated with an excess of carbon monoxide and heated in a good vacuum to 360°. The bulb was cooled by liquid air and then carbon monoxide was introduced in successive small quantities. The first 4 cu. mm. were adsorbed practically completely as soon as introduced. On further additions the amount adsorbed increased only very slowly until at a pressure of 16 bars it was 4.8 cu. mm. The liquid air was now removed and the bulb was immediately packed in loose cotton, so that it would warm up slowly. The pressure rose in 1.5 minutes from 16.0 to 18.6 bars and then very gradually decreased to 16.8. The increase in pressure from 16.0 to 16.8

corresponded closely to the expansion of the gas in the small volume of the bulb previously cooled by liquid air, so that the increase in pressure to 18.6 bars indicated unmistakably that roughly 3 cu. mm. of gas adsorbed on the platinum at liquid air temperatures, was released by a moderate rise in temperature and that this gas became readsorbed when the temperature approached room temperature. A check run with the blank bulb did not show any corresponding release or adsorption of gas during warming.

It is evident from these data that at liquid air temperature platinum adsorbs carbon monoxide in much the same way that glass does, that is, by secondary valence forces. With a moderate rise in temperature this gas is released, but in the neighborhood of room temperature the reaction velocity becomes sufficient for the platinum to react (primary valence) with the carbon monoxide to form a much more stable adsorbed film.

To study the behavior of the platinum towards oxygen under similar conditions, the platinum was first freed from carbon monoxide as far as possible by prolonged exhaustion at 360°. Previous experience had shown that only 1.2 cu. mm. of carbon monoxide remain after such treatment. The bulb was now cooled by liquid air and small quantities of oxygen were introduced. Six-tenths cu. mm. disappeared by adsorption without perceptibly increasing the pressure and then 1.3 cu. mm. more were adsorbed while the pressure rose to 18 bars. On removing the liquid air as before, the pressure rose somewhat (18.9 bars), but not more than corresponded to the expansion of the gas in the bulb. The pressure then gradually decreased, so that when the bulb had reached room temperature it was only 18 bars. On standing overnight the pressure finally decreased to 17.3 bars. This indicated that 1.9 cu. mm. more of oxygen had been adsorbed by the platinum on warming up to room temperature, making a total of 3.8 cu. mm. adsorbed. On heating the bulb to 360° there was a further disappearance of 2.4 cu. mm. of oxygen and a production of 1.22 cu. mm. of carbon dioxide, which was probably formed by the oxidation of the 1.2 cu. mm. of carbon monoxide presumably originally present on the platinum. Of the oxygen which disappeared, 2.1 cu. mm. therefore were probably adsorbed, making a total of 5.9, in good agreement with results previously obtained at this temperature. There is no doubt therefore that the adsorption of oxygen by the platinum increased steadily from about 0.6 cu. mm. at liquid air temperatures up to nearly 6.0 at 360°.

Some further work was done with the platinum foil in studying the velocity of the reaction between oxygen and carbon monoxide, and between oxygen and hydrogen. This may be reported on at a later time. The results, however, were rather erratic, owing to unaccountable changes in the catalytic effectiveness of the platinum. From time to time the reaction velocity would become relatively very slow, although no foreign gas in quantity sufficient to form a monomolecular layer seemed to be present. Heating the platinum in presence of a mixture of oxygen and hydrogen always restored the activity. It was thought that mercury vapor or water vapor might account for the variations in reaction velocity, but this was not borne out by experiments made to test this point.

It was my intention to make a thorough study of the causes underlying the activation and passivation of the platinum as well as to study the adsorption of hydrogen and other gases by the platinum at various temperatures. Unfortunately, the work has had to be discontinued indefinitely before results along these lines were obtained.

Summary.

According to the theory previously developed, gaseous molecules impinging on a solid or liquid surface do not in general rebound elastically from the surface, but condense on it, and are held or adsorbed on the surface by forces similar to those holding the atoms or group molecules of solid bodies. If these forces are weak the "life" of the adsorbed molecules on the surface is short, so that the number of molecules adsorbed at any time is relatively small. On the other hand, when the forces are strong the rate of evaporation of the molecules may be so slow that the surface becomes practically completely covered by a monomolecular layer of adsorbed molecules. In the present paper this theory is extended and is developed along quantitative lines.

The theory requires that in typical cases of true adsorption the adsorbed film should not exceed one molecule in thickness. This is contrary to the usual viewpoint. The discrepancy is accounted for by the fact that nearly all investigators have worked with porous bodies in which the adsorbing surface is indeterminate or have used nearly saturated vapors so that condensation of liquid occurred in capillary spaces. Others have mistaken solution or *ab*sorption for true adsorption.

The mechanism of adsorption is discussed at some length. The forces causing adsorption are typically chemical and exhibit all the great differences in intensity and quality characteristic of chemical forces. The adsorption of so-called permanent gases by solids usually involves only secondary valence forces. A great many cases of adsorption, particularly by metals, are caused by primary valence forces. Under certain conditions stoichiometric relations should govern the amounts of gas adsorbed on saturated surfaces. These relationships may fail to hold because of steric hindrance effects between the adsorbed molecules.

Equations are developed which give the relation between the amount of adsorbed gas and the pressure and other variables under various assumed conditions. No single equation other than purely thermodynamic ones should be expected to cover all cases of adsorption any more than a

single equation should represent equilibrium pressures for all chemical reactions.

Experiments were undertaken to measure the adsorption of several common gases by plane surfaces of mica, glass, and platinum. By using pressures of 100 bars (approximately 0.1 mm. of mercury) or less, small quantities of gas were more easily measured and the danger of condensation of liquefied gas in capillary spaces was avoided.

At room temperature the adsorption by mica and glass was negligible, certainly not over one per cent. of the surface being covered by a single layer of molecules. At —183° and at —118° C., relatively large amounts of gas were adsorbed, except in case of hydrogen. At the higher pressures used, the surfaces tended to become saturated with gas. The maximum quantities adsorbed even with saturated surfaces were always somewhat less than the amounts to be expected in a monomolecular layer. The results are summarized in Tables XVIII, XIX and XX. The amounts of the different gases adsorbed by saturated surfaces of mica and glass were always in the following order: hydrogen, oxygen, argon, nitrogen, carbon monoxide, methane, and carbon dioxide.

The amounts of these gases adsorbed by mica and glass varied with the pressure in accordance with Equation 9, which was deduced for the case of simple adsorption. The adsorption of these gases was easily and quickly reversible.

The phenomena observed with platinum were quite different. No adsorption of gases could be observed even at —183°, until the platinum had been "activated" by heating to 300° in a mixture of hydrogen and oxygen at low pressure. After this activation, hydrogen and oxygen or carbon monoxide and oxygen reacted together readily at room temperature in contact with the platinum. The platinum was then found capable of adsorbing oxygen, carbon monoxide or hydrogen. The maximum quantities of oxygen and carbon monoxide corresponded to monomolecular layers. The oxygen could not be driven off either by heat or by pumping. When the platinum was in contact with an excess of oxygen the amount of oxygen adsorbed increased as the temperature was raised, but the action was irreversible. Adsorbed carbon monoxide could not be removed by pumping at room temperature, but at 300° part of it could be pumped off. When oxygen was brought in contact with carbon monoxide adsorbed on the platinum it reacted rapidly to from carbon dioxide, which at room temperature showed no tendency to be adsorbed on the platinum. In a similar way carbon monoxide brought into contact with adsorbed oxygen reacted immediately. These cases of adsorption are clearly due to chemical forces of the primary valence type.

Further work needs to be done to determine the cause of the activation of the platinum.

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

SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

THE REFRACTIVE INDEX AND SOLUBILITIES OF THE NITRATES OF LEAD ISOTOPES.

BY THEODORE W. RICHARDS AND WALTER C. SCHUMB.

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Many investigations during the last few years have shown that among all the properties of the isotopes of lead which have been investigated only those which concern mass and radioactivity differ in different specimens.[1]

Most of these investigations (although not all of them) have concerned the metallic form of the isotopes, but it is worth while also to investigate very fully the salts. Among other properties, the comparative refractive indices of like salts of different isotopes seemed to be worth studying, for obvious reasons. The comparison of solubilities also seemed worthy of more accurate determination than has yet been accorded it.[2] Accordingly, both of these subjects have been studied in the present investigation; and the results are recorded herewith.

I. The Refractive Indices of the Nitrates of Lead Isotopes.

The method of total reflection employing a crystal refractometer of the Abbé type, improved and manufactured by Zeiss, was used for the determination, since this is an accurate method and requires only a small, smooth, plane surface of the crystal. The microscopic method of immersion in liquid of equal refractive index is troublesome and less accurate, while the method of minimum deviation requires a crystal of some size possessing an accurately measured transparent crystal angle between perfectly plane surfaces.

The nitrate was chosen for the present purpose, since it is isotropic

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[1] See, for example, "Reports on Radioactivity," by F. Soddy, in the *Annual Reports of the Progress of Chemistry*, published by the Chemical Society (London); also five papers in THIS JOURNAL, Richards and Lembert, **36**, 1229 (1914); Richards and Wadsworth, **38**, 221, 1658 and 2613 (1916); Richards and Hall, **39**, 531 (1917). Comment by Soddy, THIS JOURNAL, **39**, 1614 (1917). The exceedingly small differences in spectra found by Harkins and Aronberg (*Proc. Nat. Acad. Sci.*, **3**, 710 (1917)) may perhaps be referred to differences in mass.

[2] Fajans and Fischler, *Z. anorg. allgem. Chem.*, **95**, 284 (1916); Fajans and Lembert, *Ibid.*, **95**, 297 (1916). They determined the solubilities of ordinary and radioactive lead nitrates, and found no difference greater than the wide range, 0.75%, of their experimental error.