THE SEVENTEENTH FARADAY LECTURE.

DELIVERED BEFORE THE CHEMICAL SOCIETY ON DECEMBER 15th, 1938.

Monolayers on Solids.

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J. WILLARD GIBBS proved that if any substance added to a pure solvent gives a solution whose surface tension decreases as the concentration of the solute increases, there must be an accumulation or adsorption of solute molecules in the free surface.

Similar adsorption can occur at other phase boundaries. With solid–gas or solid–liquid interfaces, although we cannot observe directly the lowering of surface tension, we can often detect the presence of the adsorbed film in other ways. The adsorption of gases by charcoal cooled in liquid air and the adsorption of vapours by silica gel are familiar examples.

With porous substances of this kind there is difficulty in determining the extent of the area of the solid–gas interface. With plane surfaces of solids, preferably cleavage surfaces such as those given by mica or calcite, the area is known, but the amount adsorbed is so small that it is not easily measured. However, with gases at low pressures and sensitive manometers, one can measure the amount of gas adsorbed per unit area.

The presence of adsorbed films on plane surfaces is frequently indicated by marked changes in many of the properties of the surface. For example, in the case of metals, minute amounts of certain adsorbed gases alter the contact potential and produce enormous changes in electron emission and catalytic activity. These films often behave as catalytic poisons in heterogeneous gas reactions. Films of many organic substances adsorbed on solids modify the contact angles observed when a drop of liquid is placed on the surface.

To understand effects of this kind we need to know the nature of these adsorbed films. We should know, for example, what types of force hold the adsorbed substance on the surface, how thick is the film, what is the arrangement of molecules or atoms within the film, and how do the properties of the film depend upon this structure. Since the forces at air–liquid or liquid–liquid interfaces do not differ essentially from those at air–solid or liquid–solid interfaces, any theoretical or experimental knowledge that we may acquire with regard to any one type of interface should help us in developing a general theory of adsorption phenomena. Thus, studies of surface tension, even of pure liquids, should throw light on the nature of the forces which cause adsorption.

Early theories of surface tension (Thomas Young, 1805; Laplace, Gauss, etc.) treated liquids as continuous fluids between whose elements of volume forces acted. Much later, van der Waals, in his theory of the continuity of the liquid and gaseous states, analysed the nature of the surface in more detail. In these theories the forces between the molecules or the elements of volume within the liquid were thought to be physical forces resembling in many ways gravitation or the interaction between electrically charged particles. They were assumed to be forces that acted at a distance through intervening matter, unaffected by the presence of that matter. The transition between liquid and vapour phases at an interface was thus taken to be continuous, without any abrupt change in the density or other properties.

Similarly, in the early theories of adsorption the film was assumed to have a structure analogous to that of the atmosphere of the earth, the forces exerted upon the molecules by the substrate playing the rôle of gravitation in the atmosphere. The molecules, however, were taken to be spheres which exerted forces on other molecules according to some function of the distances between molecular centres. Such theories could not take into consideration the wealth of knowledge of chemical structures which organic chemists had already obtained.

Nature of Forces.—The forces that hold bodies together in our three-dimensional world have been given many names. The so-called chemical forces, which correspond to covalent bonds, act between atoms within molecules, as, for example, between carbon and hydrogen atoms in molecules of methane. These forces are characterised by their specificity, being dependent upon the particular nature of the atoms that are joined and even upon the neighbours of these atoms. Electronic resonance may greatly modify the magnitude of the forces.

The familiar van der Waals forces, such as those that are involved in the liquefaction of methane at low temperatures, are non-specific attractive forces which result from the mutual interactions of electronic shells.

For stable equilibrium, attractive chemical forces and van der Waals forces must be balanced by repulsive forces which prevent the interpenetration of electronic shells and so keep the molecules from coming too close together.

Since atoms and molecules are built of electrons and atomic nuclei, it has long been recognised that all forces within matter are essentially electrical in nature. However, the three types of force which we have just discussed are so intimately associated with quantum phenomena that the electrical aspects are not apparent to the chemist. Electric forces which are more strictly of the Coulomb type, varying according to the inverse square law, have become increasingly important within recent years. Thus according to the older theory of electrolytic dissociation, positive and negative ions in aqueous salt solutions remain apart because the high dielectric constant of the solvent reduced the Coulomb attraction. The independent response of the two types of ions to electric fields became the basis of the theories of electrode potentials.

The crystal structures of inorganic salts that have been revealed by X-ray methods prove that these solids are held together by the Coulomb attraction between ions. By taking into account these electric forces it has been possible to calculate the compressibilities, heats of vaporisation and other properties of these crystals.

The Debye–Hückel theory of electrolytes is based on a consideration of the electric forces between the ions and the effect of thermal agitation. Debye also showed that many properties of pure liquids and solutions depend upon the presence of dipoles, whose interaction can be calculated from the Coulomb law.

Before clear ideas had developed in regard to the structure of solids, many properties of matter were described in terms of forces of cohesion and adhesion. To-day we no longer think of these as particular kinds of force: they are rather taken to be examples of forces of the types we have already considered. The great cohesion (hardness) shown by a diamond thus results from the strong covalent bonds that link together all neighbouring carbon atoms, while the low cohesion (softness) of solid paraffin involves mainly the relatively weak van der Waals forces between the hydrocarbon chains. We therefore do not consider that there are any unknown or mysterious forces primarily responsible for cohesion and adhesion.

Range of Forces.—There has been general recognition of the fact that in the structure of matter there are examples of forces having both long and short ranges. The chemist has dealt particularly with forces of short range. He has taken it for granted, as a result of a long experience, that chemical reactions between molecules occur only when the molecules are in contact with one another. He assumes, therefore, that the forces involved in chemical phenomena are of very short range, comparable with the radii of atoms.

Elementary consideration of the work necessary to break a brittle material or to cleave crystals such as mica shows that intense forces originating from the surface of a solid body can extend only to very short distances. Thomas Young, over a century ago, proved that the forces involved in surface tension must have a range of the order of 10^{-8} cm. or 1 A., but in later years this conclusion seems to have been largely forgotten.

The later physicists (prior to 1920) who dealt with surface tension and adsorption usually regarded the forces as essentially long-range forces which act over distances large compared with those between atoms and molecules. This assumption was made, I believe, largely by force of habit rather than because of definite experimental evidence.

Common observation of large electrically charged bodies shows that electrostatic forces can extend through large distances. Forces which are significant in the structure of matter must correspond to potential energies which are at least of the order of kT (about 0·025 electron volt at room temperature), which is a measure of the energy of thermal agitation.

The energy involved in chemical interactions is usually very much larger than this. The Coulomb law allows us to estimate the distances within which such forces may be significant. Thus the potential energy between two electrons is equal to kT when the distance between them is 560 A. On the other hand, in water (dielectric constant 80) the corresponding distance is only 7 A.

With multivalent ions and particularly with large colloidal particles the effective distances, which increase in proportion to the product of the charges on the interacting particles, may become relatively great. Colloids whose micelles carry charges of 10 or more units may show effective ranges of several hundred or even several thousand Ångström units. Concentrations of electrolytes of the order of 10^{-3} M can greatly reduce the range because of the segregation of ions of one sign around each ion of the opposite sign, in accordance with the Debye–Hückel theory.

Electric forces of very long range can be observed in the space charge phenomena which occur in electric discharges in high vacuum or in gases at low pressures (Langmuir, *Physical Rev.*, 1913, **2**, 450). Consider, for example, a nearly uniform volume distribution of particles having charges of one sign only (ions or electrons). The number of particles in successive concentric shells of equal thickness increases in proportion to the square of the radius. With an inverse-square law of force between particles the shells give contributions to the potential at the origin which increase in proportion to the radius, so that the effect of the outer shells is much more important than that of the inner ones. The forces due to space charge thus extend throughout any region in which the particles are predominantly of one sign, and are frequently observable at distances of several cm.

Debye has shown (" Polar Molecules," Chemical Catalog Co., New York, 1929) that many of the dielectric properties of liquids and solutions depend on the dipole moments of their molecules. In these cases the dipoles are oriented by an applied external field. Dipoles can also be oriented by the local fields of ions or of other dipoles. Let us consider the magnitude and range of the forces involved.

The interaction between a dipole and an ion gives a force which varies with the inverse cube of the distance and depends upon the orientation of the dipole. Molecules of water which have a high dipole moment, 1·87 Debye units (1 unit equals 10^{-18} c.g.s. units), should theoretically require a field of the order of 10^7 volts per cm. to orient the majority of them against the effect of thermal agitation. A field of this magnitude would exist at a distance of 12 $D^{-1/2}$ A. from a univalent ion, where D is the dielectric constant. If we should take $D = 80$, the distance would be only 1·3 A.

It is well known that small ions in aqueous solutions are hydrated. Such effects are now generally explained in terms of hydrogen bonds rather than electric attractions of the ions for the dipoles. A single layer of completely oriented water molecules on a plane surface would give a double layer potential of 15 volts if the dipole moment should remain 1·87 units. The mutual depolarisation of the dipoles in such layers must evidently reduce the moment to a relatively small value. The dipole theory of the origin of the forces thus loses its usefulness in cases where the dipole molecules are closely packed.

When the dipoles are at distances from ions so great that the forces give only a small orienting effect, the effective dipole moment instead of being μ reduces to $\mu^2F/3kT$, where F is the field strength. Under these conditions the average force exerted by the ion on the dipole is one of attraction and varies with the inverse fifth power of the distance. The potential energy involved is negligible compared to kT for dipoles of ordinary magnitude at distances of more than 3 A. in the case of univalent ions, but this effective range varies with the square root of the charge on a multivalent ion and so may be considerably larger in the case of colloidal particles.

Dipole molecules when completely oriented exert forces on one another which vary with the inverse fourth power of the distance. Under conditions which give incomplete orientation, the force is proportional to the inverse seventh power. Only when the dipoles are practically in contact can the energies be comparable with kT.

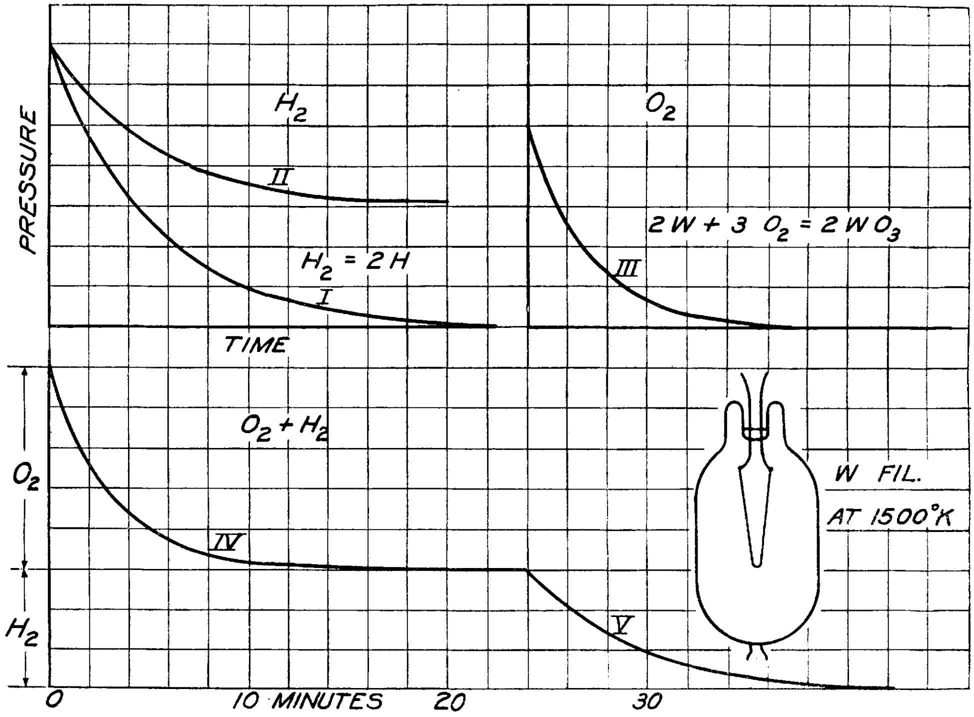
The van der Waals forces which act even between non-polar molecules also vary with the inverse seventh power of the distance. Therefore, between individual molecules these forces will have still shorter ranges than the dipole forces. The other types of force which we have considered, the chemical forces corresponding to covalent bonds, and the repulsive forces due to the impenetrability of electronic shells, have extremely short ranges of action, being limited in general to distances even much less than 1 A.

There is no logical reason to assume that the forces involved in the formation of adsorbed films are essentially different from those that are active within three-dimensional solid or liquid phases. At the boundary between phases the forces are naturally unsymmetrically distributed, and this produces the characteristic phenomena of adsorption. However, the nature and range of action of the forces should not be altered by this assymmetry.

Experiments with Tungsten Filaments.—My own interest in phenomena at surfaces arose from studies of the interactions between hot tungsten filaments and low pressures of various gases introduced into the surrounding bulb (Langmuir, *J. Amer. Chem. Soc.*, 1915, **37**, 1139).

FIG. 1.

Clean-up of oxygen and hydrogen by a heated tungsten filament.



Tungsten filaments possess particular advantages in studies of adsorption phenomena, since they can be heated in vacuum for considerable times even at temperatures as high as 3000° K., at which all other substances vaporise. The surface of the filament can be freed from all contamination by flashing it for a few seconds at a very high temperature. The ease of temperature measurement by optical pyrometers or from the current–voltage characteristics, and the rapidity with which temperature changes can be produced are further important advantages. The electron emission from the filament serves as a very sensitive indicator of the presence of adsorbed films.

With hydrogen at a low pressure, such as 10 baryes (*ca.* 0·01 mm. of mercury), the heating of the tungsten filament to 1500° K. caused a gradual disappearance of the hydrogen as shown in curve I of Fig. 1 (Langmuir, *ibid.*, 1912, **34**, 1310). After 20 minutes, practically all the hydrogen had disappeared. A second supply of hydrogen disappeared more slowly (curve II). With a bulb containing two filaments, it was readily proved that the gas was not absorbed by the filament but disappeared because a monatomic layer of hydrogen atoms was adsorbed on the surface of the bulb. The hydrogen adsorbed on the glass was found capable of reacting with oxygen at room temperature after the filament had been allowed to cool, indicating that the hydrogen remained in a very active state. The maximum amount of adsorption occurred when the bulb was immersed in liquid air, and corresponded to about $1{\cdot}5 \times 10^{15}$ atoms of hydrogen per cm.^{2} of glass surface, which is equal to the number of spheres of diameter 2·8 A. which can be packed per cm.^{2} into a close-packed hexagonal lattice.

Since the diameter of the hydrogen atoms is somewhat less than 2·8 A., those in the adsorbed film are not in contact with one another. Hydrogen atoms incident upon such an adsorbed film presumably combine with any hydrogen atoms which they may strike to form molecules which escape from the surface. The failure to obtain thicker films of hydrogen evidently depends upon this reactivity. The forces that hold the atoms on the surface are thus of short range and are related to the chemically unsaturated nature of the atomic hydrogen.

When a tungsten filament is heated to about 1500° K. in oxygen at 100 baryes or less, the oxygen reacts with the tungsten to form the oxide WO_3, which evaporates from the filament at this temperature as fast as it is produced, leaving no visible film on the surface and producing no change in the radiating characteristics of the filament (Langmuir, *ibid.*, 1913, **35**, 105). The decrease of pressure, as shown in curve III of Fig. 1, corresponds to a unimolecular reaction, the rate being proportional to the pressure.

It is of interest to inquire what fraction of all the molecules of oxygen that strike the surface of the filament react to form an oxide. The kinetic theory of gases leads to the equation

$$\mu = p/(2\pi mkT)^{1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where μ is the rate of arrival of the gas molecules expressed in molecules cm.$^{-2}$ sec.$^{-1}$, and m is the mass of the molecule. By inserting numerical values this equation becomes

$$\mu = 2{\cdot}65 \times 10^{19} p(MT)^{-1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where M is the molecular weight of the gas (oxygen atom = 16) and p is expressed in baryes. By comparing the observed rate of clean-up of the gas with the rate calculated by this equation it was possible to find ϵ, the fraction of all the impinging molecules which react on striking the filament. For filament temperatures from 1200° to 2000° K. the value (Langmuir, *ibid.*, p. 105) of ϵ is given by

$$\log_{10} \epsilon = 1{\cdot}76 - 5940/T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

so that at $T = 1500°$, $\epsilon = 0{\cdot}0063$. The temperature coefficient corresponds to an activation energy of 27 kg.-cals.

The pressures in these experiments were so low that the reaction cannot be due to the simultaneous arrival of two molecules of oxygen from the gas at a given point on the filament surface. The formation of the trioxide must therefore depend on an adsorbed film of oxygen, which permits three oxygen atoms to come into contact with a single tungsten atom.

The presence of such an adsorbed film of oxygen is manifested also by many other properties of the filament. For example, the electron emission at 1500° K. is reduced to about 1/10,000 of that observed before the oxygen is admitted, but this emission is independent of the oxygen pressure and remains indefinitely at this low value, even after the oxidation of the tungsten has consumed nearly all residual oxygen. By introducing cæsium vapour, every trace of gaseous oxygen is immediately removed, yet this does not increase the emission at 1500° K.

After the filament temperature, however, has been raised to 2000° K. for 20 seconds, the electron emission at 1500° K. increases 100-fold, showing a partial evaporation of oxygen from the surface of the filament. Experiments at a series of temperatures below 2000° each followed by a test of activity at 1500°, gave a temperature coefficient for the rate of evaporation of the oxygen which corresponded to an activation energy or a heat of evaporation of 160 kg.-cals. per g.-atom. Extrapolation indicates that at 1500° K. several years would be necessary for the evaporation of the film.

The extraordinary stability of this adsorbed film of oxygen on tungsten is also shown by many chemical properties. For example, the film acts as a catalytic poison; it prevents the heated filament from dissociating hydrogen into atoms or ammonia into its elements. Curves IV and V in Fig. 1 illustrate typical results (*idem*, *Chem. Reviews*, **1933**, **13**, **147**) obtained when a mixture of oxygen and hydrogen at low pressure is introduced into a bulb containing a tungsten filament at 1500° K. For the first 24 minutes the oxygen disappeared at exactly the same rate as though no hydrogen had been present. Analyses of the gas in the bulb at the end of this time showed that the remaining gas was pure hydrogen, and that none of this gas had disappeared up to this time. After the pressure of oxygen had fallen to an extremely low value (about 10^{-3} barye), the hydrogen suddenly began to disappear (curve V) at the same rate as if no oxygen had previously been present.

In view of the fact that the oxygen film in absence of hydrogen would not have evaporated appreciably in less than a year at 1500° K., it is remarkable that in the presence of hydrogen the effect of the oxygen disappears abruptly after 24 minutes. Measurements of electron emission have shown that there is a sudden increase of emission at this point. These observations prove that the film of oxygen is unaffected by the hydrogen as long as a minute trace of gaseous oxygen is present, but below this critical pressure the hydrogen is very effective in reacting with and removing the adsorbed oxygen. It appears that hydrogen can react with the oxygen only after it is adsorbed on the tungsten in spaces between the oxygen atoms.

Since oxides of tungsten are easily reduced by hydrogen at temperatures below 1000°, the inability of the hydrogen to react with the complete film of oxygen on tungsten proves that this film does not consist of any of the oxides of tungsten. If, however, the film consists of a complete layer of oxygen atoms chemically bound to the tungsten atoms of the surface, the oxygen may be just as incapable of reacting with hydrogen as is the oxygen in such a compound as calcium oxide. When two hydrogen atoms are adsorbed on the tungsten, adjacent to an oxygen atom, a mere shifting of electrons in the metal can permit the hydrogen atoms to attach themselves by covalency bonds to the oxygen, thus saturating the oxygen and allowing it to escape from the underlying tungsten.

These alterations in the properties of the surface of the tungsten filament produced by the presence of oxygen are due to a monatomic layer of oxygen atoms held very firmly to the tungsten atoms. The fact that complete and incomplete monatomic layers of oxygen behave so differently toward hydrogen emphasises the importance of contacts between atoms. The hydrogen cannot dissociate unless it comes into contact with tungsten atoms. The oxygen adsorbed atoms cannot leave the tungsten until they can react with hydrogen atoms adsorbed on tungsten in adjacent spaces. Thus the complete monatomic layer of oxygen is a catalytic poison for the dissociation of hydrogen, while bare spots on the tungsten surface act as a catalyst for the interaction of the oxygen and hydrogen.

An extensive set of experiments was carried out in 1919 by my assistant, Mr. S. P. Sweetser, who studied the interaction of oxygen and hydrogen in contact with a tungsten filament over a wide range of filament temperatures. With the filament at 1500° K. in a mixture of oxygen and hydrogen no appreciable amount of hydrogen disappears until the kink is reached, as shown in Fig. 1. The pressure corresponding to this kink measures the amount of hydrogen, while the decrease in pressure that occurs before the kink gives the amount of oxygen. We are thus provided with a simple and accurate method of analysing mixtures of oxygen and hydrogen.

When filament temperatures ranging from 1700° to 2300° K. are used, the pressure at the kink is less than the partial pressure of the hydrogen originally present, but an analysis of the residual gas made at any time after the kink shows that the gas is pure hydrogen.

Table I contains a brief summary of the previously unpublished results of these experiments. The volume of the bulb with the attached McLeod gauge was 5·5 l. The filament had a surface of 2·5 cm.^{2}. Before the filament was heated, the bulb was filled to a total pressure of about 12 baryes with a mixture containing two volumes of hydrogen to one of oxygen. The filament was then heated to the temperature given in the first column. The time in seconds at which the kink in the curve occurred is shown in col. 2. Col. 3 gives the percentage of the original amount of hydrogen which remained in the gas at this critical point, the oxygen having all disappeared at this time.

TABLE I.

The rate of disappearance of hydrogen from mixtures of oxygen and hydrogen in contact with heated tungsten filaments.

T.	t, secs.	% H_2.	[illegible] before.	ϵ_2 after.	ϵ_0.
1570°	1500	100	—	0·00010	0·0095
1710	270	97	0·00003	0·00030	0·0193
1870	175	92	0·00022	0·0013	0·038
2050	115	79	0·0010	0·0048	0·073
2210	54	72	0·0028	0·0099	0·118
2380	28	60	0·0086	0·0185	0·184
2520	16	50	0·017	0·022	0·253

By repeating each of these runs several times, but interrupting the experiments at predetermined times to make an analysis of the gas by the method just described, it was possible to determine the rates at which the hydrogen and the oxygen disappeared before the critical time had been reached. At any given temperature the rate of decrease of the hydrogen pressure was approximately proportional to the pressure of the hydrogen, but independent of the pressure of the oxygen. The value of ϵ_1 in col. 4 gives this rate of reaction in terms of the fraction of the hydrogen molecules incident upon the filament which disappear before the critical time has been reached. Col. 5, under the heading ϵ_2, shows the corresponding value of ϵ for the clean-up of the hydrogen after the critical time. In the last column, under the heading ϵ_0, is the value of ϵ given by equation (3) for the normal rate of clean-up of oxygen by a tungsten filament at the temperature T.

A study of these and other data has led me to the following conclusions. The adsorbed film of oxygen consists of a single layer of firmly bound oxygen atoms nearly completely covering the surface. These atoms, however, do not react directly with one another and with tungsten to form the oxide WO_3 even at the highest temperatures. At very high temperatures, such as 2000° or more, the adsorbed oxygen evaporates as free atoms, not as molecules.

Oxygen molecules which strike the surface already covered with the adsorbed oxygen films condense on the surface to form a second layer, probably of atoms held to the underlying atoms by forces much like those that hold together the two atoms of oxygen in peroxides. The atoms in the second layer, however, are held by forces that are small compared with those that hold the first layer, so that at temperatures above 1200° K. they evaporate at a relatively high rate and therefore only a minute fraction of the surface is covered by this second layer. Each atom in the second layer moves freely over the surface until one of three things happens: (1) It evaporates; (2) it reacts with two oxygen atoms in the first layer and with an underlying tungsten atom to form WO_3, which evaporates, leaving a hole or gap in the first adsorbed layer; (3) it drops from the second layer into any of these holes formed in the first layer and thus provides the mechanism by which the oxygen content of the first layer is held constant.

This theory explains the fact that the rate of formation of WO_3 is proportional to oxygen pressure over a wide range of pressure. The amount of oxygen in the second layer is proportional to the oxygen pressure. The fraction of the surface which is bare (holes in the oxygen film) is independent of the pressure, since both the rate of formation of the holes and the rate of filling up the holes are proportional to the pressure. The electron emission and the rate of clean-up of hydrogen, as measured by ϵ_1 in Table I, are thus independent of the oxygen pressure.

At much lower oxygen pressures with very high filament temperatures, particularly above 2200° K., the rate of evaporation of oxygen atoms from the first layer begins to be of increasing importance, so that the fraction of the surface which is bare under these conditions no longer remains independent of the oxygen pressure. The rate of formation of WO_3 at these low pressures then has a negative temperature coefficient; at the highest temperatures the atoms evaporate before they have a chance to form WO_3. Numerous experiments in our laboratory have demonstrated this negative temperature coefficient of reaction velocity at pressures less than 0·1 barye and at temperatures above 2300°, and have also shown that the oxygen which escapes from the filament is then atomic oxygen which reacts with and oxidises metallic tungsten previously evaporated on to the bulb.

When hydrogen and oxygen are both present in the bulb the hydrogen molecules are not able at any temperature to react directly with the oxygen in either the first or the second adsorbed layer. However, if they reach the tungsten surface through the holes in the first layer they dissociate into atoms and react immediately with an adjacent oxygen atom. Thus when the oxygen pressure falls below the critical value, the hydrogen completely removes all the oxygen from the surface, and it does this suddenly. The data for ϵ_0 and ϵ_1 in Table I show that before the critical pressure is reached the value of ϵ for the oxygen clean-up is several hundred times as great as that for the hydrogen. This greater effectiveness of the oxygen is accounted for by the presence of mobile oxygen atoms in a second layer, and the absence of a mobile layer of hydrogen. Thus the holes in the first layer can be filled by oxygen from molecules which may have struck almost any part of the surface, but only the hydrogen molecules which make direct hits in the holes are able to interact with oxygen atoms and so increase the size of the holes. The pressure of the oxygen is thus several hundred times greater than that of the hydrogen at the time when the kink occurs.

In some unpublished experiments made a few years ago by Dr. J. Bradshaw Taylor, oxygen at low pressure was admitted into a bulb cooled in liquid air, whose inner surface was covered with a deposit of metallic cæsium. In the bulb was also a tungsten filament which had previously been flashed to 3000° to clean its surface. After the oxygen was pumped out, the bulb was warmed to room temperature so that every trace of remaining oxygen would react with cæsium. The filament was then heated to 1600° K. and was found to have the same electron emission as if it had been heated to 1600° K. in contact with oxygen at low pressure. This experiment proves that an amount of oxygen sufficient to form a monatomic layer condenses on a filament at very low temperatures and remains on the filament when it is heated 1600° K. The layer cannot consist of more than one layer of atoms, since the oxygen at low temperatures cannot penetrate into a tungsten filament, although it does so at temperatures above 1200° K., and thus no oxides of tungsten could have been formed.

The poisoning effect of a monolayer of oxygen atoms on the dissociation of hydrogen and on many other chemical reactions bears a close resemblance to the phenomena of passivity of chromium as shown by its electrochemical behaviour and the resistance of polished chromium to oxidation. Since chromium and tungsten are in the same group of the Periodic Table, it would seem that a single complete layer of oxygen atoms tightly bound to the atoms of the chromium surface should be adequate to explain many of the features of passivity (Langmuir, *Trans. Amer. Electrochem. Soc.*, 1916, **29**, 260).

Films of Thorium on Tungsten.—A study of the electron emission from tungsten filaments containing approximately 1% of thorium oxide showed (*idem, Physical Rev.*, 1923, **22**, 357) that after proper heat treatment of the filament the electron emission at an arbitrarily chosen temperature (testing temperature) of 1500° K. was about 100,000 times greater than that from a pure tungsten filament. To bring the filament into this condition it is heated for short time intervals at a series of increasing temperatures, the final heating being for about 30 seconds at 3000° K. In this way a fine-grained filament is produced which contains a low concentration of metallic thorium formed by the reduction of the thorium oxide while oxygen diffuses out of the filament. It is then necessary to activate the filament by heating it for a considerable time at a temperature in the neighbourhood of 2100° K. which permits the thorium to diffuse to the surface without too great loss from the surface by evaporation.

Under these conditions the thorium accumulates on the surface as a single layer of atoms, thus giving a concentration near the surface far higher than in the interior of the filament. The fact that the thorium diffuses from a region of low concentration to one of high concentration indicates that we are dealing with a typical case of adsorption. A comparison of the properties of thorium and tungsten shows that the surface energy of thorium should be much lower than that of tungsten, and therefore, according to Gibbs's theorem, one should expect a stable adsorbed film of thorium.

The activity of the filament can be determined by measuring the emission at the testing temperature of 1500° K. By raising the temperature to 1900° K. an emission of over 0·5 amp./cm.^{2} can be be maintained for many thousands of hours, although to obtain a similar emission from pure tungsten one would have to heat the filament to 2500° K., and the life would then be much shorter than that of the thoriated filament.

The effect of the thorium monolayer which forms on the surface is to raise the electron emission from the filament. Since the emission can be easily measured with an accuracy of about 1%, while a complete monolayer gives a 100,000-fold increase, we have here an extremely sensitive method of detecting adsorbed atoms on a surface. For a quantitative determination of the amount of thorium on the surface it is necessary, however, to know the relationship between the emission and the amount of adsorbed thorium. Since thorium is a metal which has a much higher atomic volume than tungsten, it should have a lower electron affinity, and therefore atoms of thorium on the surface should be positively charged. This charge induces a negative charge in the surrounding tungsten, so that, according to the usual image theory, the external field produced by a thorium atom is equivalent to that of a dipole. If the dipoles are sufficiently far from one another, the dipole moment given by one thorium atom will not modify that of its neighbours. It follows then that at low surface concentrations the contact potential increases linearly with the surface concentration of the thorium. The electron emission, however, which is a kind of evaporation phenomenon, varies exponentially with the contact potential. Thus the logarithm of the emission should increase linearly with σ, the number of thorium atoms per cm.^{2} of surface.

If one cleans the surface of the filament by flashing at 2800° K. and then maintains the filament at 2100° K., one would expect the thorium to arrive at the surface at a nearly constant rate, at least until the supply of metallic thorium in the filament begins to be exhausted. From time to time one can lower the filament temperature to 1500° K. to measure the electron emission. It is found, in fact, that for moderate increases in emission, of several hundred-fold, the logarithm of the emission i increases linearly with the time, which indicates that the change in log i is a measure of the amount of thorium present.

However, when the activity becomes still greater, log i increases much more slowly and finally approaches a limiting value. The higher the activating temperature, the lower this limit becomes. Qualitatively, at least, this indicates that the final surface concentration represents a balance between the rate of diffusion of the thorium to the surface and the evaporation from the surface. By flashing the filament for short time intervals at a series of higher temperatures, and observing the effect on the electron emission at the testing temperature, one can measure this rate of evaporation and its temperature coefficient. It is found that the heat of evaporation corresponds to 173 kg.-cals., while that of tungsten as determined by the rate of loss of weight is 210 kg.-cals.

The non-linear increase in log i with time at the higher surface concentrations suggests that the evaporation of the thorium takes place relatively more rapidly when the thorium atoms become crowded on the surface. It was first assumed that the linear relation between log i and σ was applicable, at least approximately, over the whole range of values of σ. The maximum value σ_1 thus corresponded to a complete monolayer of thorium. The fraction θ of the surface covered by the thorium, or covering fraction, can be defined as equal to σ/σ_1.

Interpreted in this way, the experimental data on the activation of thoriated filaments between 1950° K. and 2050° K. led to the conclusion that the rate of growth of the thorium film could be expressed by the equation

$$d\theta/dt = k(1 - \theta) \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

where k increases with temperature and depends upon the rate of diffusion of thorium from the interior of the filament.

To account for the factor $(1 - \theta)$ the hypothesis was made that the thorium atoms which arrived from the interior pushed the " adatoms " (adsorbed atoms) off the surface if they arrived at places already occupied. This forced evaporation was referred to as " induced evaporation " to distinguish it from that which occurs spontaneously at a given temperature from the film, even when thorium does not arrive from the interior.

Becker and Brattain (*Physical Rev.*, 1926, **28**, 341) and Brattain and Becker (*ibid.*, 1933, **43**, 428) have shown that with monolayers of barium, cæsium, or thorium on tungsten the curve giving log i as a function of θ is approximately linear only at low values of θ, while at higher values log i increases to a maximum and then decreases. To determine this relationship in the case of thorium films they evaporated thorium at a constant rate from a heated thorium filament on to a neighbouring cold tungsten filament, and from time to time measured the electron emission from the tungsten filament at a testing temperature. When these results were compared with the data that I had obtained during the spontaneous activation of thoriated filaments between 1950° K. and 2050° K., it was found (Langmuir, *J. Franklin Inst.*, 1934, **217**, 543) that the non-linear increase of log i with time was fully accounted for by the non-linearity of the relation between log i and θ, and thus the hypothesis of induced evaporation could be discarded. As a matter of fact, the analysis of the data showed that θ increased linearly with time until spontaneous evaporation brought θ nearly to its limiting value.

From the data of these experiments it was possible to determine the actual rate of evaporation of thorium ν, in atoms per sq. cm. per sec., as a function of T and θ. In the range from $\theta = 0{\cdot}2$ to $\theta = 0{\cdot}6$, ν varies in proportion to $\epsilon^{H\theta}$, where $H = 8{\cdot}1$. A ten-fold increase in θ from 0·07 to 0·7 gives a 730-fold increase in ν, which means that the average life of a thorium atom on the surface decreases in the ratio 73 to 1 in this range.

This rise in ν at the higher values of θ results from the repulsive forces between the dipoles of the adsorbed thorium atoms which tend to drive these atoms off the surface. As θ approaches unity, ν increases so rapidly that the amount of thorium accumulating at the surface never exceeds that which corresponds to a monolayer. The measurements show that the maximum in the electron emission occurs when $\theta = 0{\cdot}7$.

When layers of thorium deposited by evaporation on to a tungsten filament reach a thickness several times that of a monolayer, the electron emission is about one-third of that corresponding to the optimum emission at $\theta = 0{\cdot}7$. The electrical properties of a surface covered by a complete monolayer, $\theta = 1$, are substantially the same as those of a thick film of the same material.

Numerous experiments have proved that thorium atoms migrate over the surface of a tungsten filament at appreciable rates at temperatures a few hundred degrees lower than those at which the thorium evaporates from the surface. For example, thorium deposited on one side of the filament may be made to diffuse uniformly over both sides of the filament by prolonged heating of the filament at the proper temperature.

Adsorption by van der Waals Forces.—The cases of adsorption which we have just been considering, where atoms of oxygen or thorium are bound firmly to the surface of the tungsten filament, even at very high temperatures, prove that in some cases at least the forces involved in adsorption are comparable with those which hold together the atoms of even the most stable chemical compounds. They also prove that the effective range of action of these forces is small even when compared with atomic diameters. Since adsorption involves the same types of forces as those involved in the ordinary three-dimensional states of matter, we should expect to find types of adsorption corresponding to even the weak van der Waals forces, which hold together the molecules of non-polar liquids such as the liquid hydrocarbons or liquefied inert gases. In order to gain knowledge of adsorption of these types, experiments were undertaken to measure the adsorption of such gases as argon, nitrogen, hydrogen, oxygen, and methane on plane surfaces of glass and mica (Langmuir, *J. Amer. Chem. Soc.*, 1918, **40**, 1361). Most previous work on adsorption had been done with porous substances, such as charcoal, where the extent of the surface was unknown, and therefore the thickness of the adsorbed film could not be determined. The experiments soon showed that the amounts of these so-called permanent gases adsorbed on the plane surfaces at room temperature are negligibly small compared with the amount needed to form a monolayer of molecules. At liquid-air temperatures, however, the amount adsorbed increases at first about in proportion to the pressure, but at higher pressures reaches a limiting value which in every case studied corresponds to less than a monolayer.

Evidently, therefore, even with these cases of adsorption which involve merely van der Waals forces, the effective range of action of the forces responsible for the adsorption is less than the molecular diameter, so that we are still clearly dealing with forces which act between atoms or molecules in contact.

Condensation–Evaporation Theory of Adsorption on Solids.—With adsorbed films of both oxygen and thorium on tungsten we have seen that the number of atoms in the film at any given time depends upon a balance between the rate of arrival of the oxygen or thorium on to the surface and the rate of loss of material from the surface by evaporation or by a chemical reaction. When we are dealing with the surface of a solid in contact with a gas which can become adsorbed we can therefore analyse the mechanism in terms of condensation and evaporation. This leads us to a theory not only of the equilibrium but also of the kinetics of adsorption phenomena.

According to this theory, the condensation and evaporation processes are independent of one another; that is, the probability that a given adsorbed atom will evaporate in any short time interval is not influenced by the time that has elapsed since its condensation upon the surface. If we divide the rate of evaporation ν, expressed in atoms cm.$^{-2}$ sec.$^{-1}$, by σ, the number of adsorbed atoms cm.$^{-2}$, we obtain the average probability per second for the evaporation of individual atoms. The reciprocal of this, τ, is thus the average life of an adsorbed atom on the surface. We thus have

$$\tau = \sigma/\nu \quad \dots\dots\dots\dots \quad (5)$$

One of the important characteristics of adsorption is expressed by an adsorption isotherm, which relates the pressure or concentration in the volume phase to the amount of substance adsorbed on the surface under the conditions of equilibrium. According to the condensation–evaporation theory (Langmuir, *J. Amer. Chem. Soc.*, 1918, **40**, 1361), the general equation for the adsorption isotherm is

$$\nu = \alpha\mu \quad \dots\dots\dots\dots \quad (6)$$

where μ is the rate of arrival of the molecules on the surface, as given by equation (1), and α is the condensation coefficient which, naturally, cannot exceed unity. In general, ν and α are functions of σ and T, the temperature.

These functional relationships determine the nature of the adsorption isotherm. It is, of course, possible that ν and α depend not only on σ but also on various other factors characteristic of the surface, or upon the forces which the surface exerts upon the adatoms. Thus, because of a lack of homogeneity of the surface there may be more than one way in which a given adatom may be held on the surface, or the adsorbed substance can exist on the surface in two states, for example, in the form of atoms or of molecules. We may postpone the consideration of such complicating factors and limit ourselves at present to cases in which the adsorbed film may be regarded as a " surface phase " characterised by two degrees of freedom (Langmuir, *J. Chem. Physics*, 1933, **1**, 3), such as σ and T.

The adsorption isotherm is the relation between p, σ, and T which exists under equilibrium conditions. According to equations (1) and (6), this relation depends only on the ratio ν/α, which in general is a function of σ. Since this isotherm expresses the equilibrium condition, it should be derivable by statistical methods from energy and entropy considerations.

The kinetics of the adsorption process involves a knowledge of $\alpha\mu$, the rate of condensation, and ν, which are equal only under equilibrium conditions. These quantities cannot be determined by thermodynamic considerations but must depend upon the mechanism of the adsorption process.

Let us consider in more detail the condensation process (Langmuir, *Physical Rev.*, 1916, **8**, 149). In the classical kinetic theory of gases it is usually considered that molecules rebound from one another elastically, and it is therefore frequently assumed that molecules make similar elastic collisions with a solid surface. We must, however, recognise an essential difference between the two cases. The molecule approaching the solid is attracted and acquires an additional energy when it reaches the surface. The impact against the surface is delivered to several atoms which can dissipate their excess energy to still others.

A calculation based on the heat conductivity of solids indicates that even within the duration of a collision (*ca.* 10^{-13} sec.) a large fraction of the heat may be carried away. In general, therefore, we should expect the condensation coefficient α to approximate to unity; that is, all molecules that strike the surface condense upon it. Only when the rate of evaporation of these molecules from the surface is so high that the average life τ is less than about 10^{-13} sec. should there be any failure of the adsorbed molecules to reach thermal equilibrium before leaving the surface. This case, which corresponds to an accommodation coefficient materially less than unity, has been observed when molecules of permanent gases, particularly hydrogen and helium, strike a surface having a temperature different from that of the gas. These cases of low accommodation coefficient occur under just those conditions where we may assume that the life τ of the adsorbed molecule is of the same order of magnitude as the duration of the collision. When τ has much larger values, experiments show that the condensation coefficient α is close to unity.

If the gas pressure is raised or the temperature of the surface is lowered, σ must ultimately increase to a point where there is no longer room for additional molecules in the first layer in contact with the solid; a further increase in σ would require the formation of a second layer.

Because of the short range of the forces that act on the adatoms, the life τ_2 of an atom in the second layer is usually very different from the life τ_1 of a similar atom in the first layer, since the atom in the two cases in question is in contact with atoms of an entirely different character. There are two cases to be considered according as τ_2 is greater or less than τ_1 (Langmuir, *J. Amer. Chem. Soc.*, 1932, **54**, 2810).

Case I. The second layer is held by stronger forces than the first, $\tau_2 \gg \tau_1$. An example of this kind has been found experimentally (*idem, Proc. Nat. Acad. Sci.*, 1917, **3**, 141) in the condensation of mercury or cadmium atoms allowed to strike a cooled glass surface. These atoms have a much greater affinity for one another than they have for glass. The cadmium atoms in the second layer, being in contact with underlying cadmium atoms, evaporate much more slowly than single atoms in the first layer.

In these experiments cadmium was introduced into a well-exhausted spherical glass bulb. By immersing one half of the bulb in cold water and applying a flame to the other half, all the cadmium was driven to the lower hemisphere. This cadmium-covered hemisphere was then lowered into an oil bath at 170° c. A portion of the uncovered hemisphere was cooled to — 40° c., and another region was cooled by a wad of cotton dipped in liquid nitrogen (— 196° c.). A visible deposit of cadmium formed within 30 seconds on the surface cooled to — 196°, and this continued to grow in thickness, forming a mirror, even after the spot was allowed to warm to room temperature, but on the surface cooled to — 40° and on the uncooled parts no deposit appeared within 10 minutes.

The vapour pressure of solid cadmium (International Critical Tables) is given by

$$\log_{10} p = 11{\cdot}689 - 5693/T \ (p \text{ in baryes}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

At 170° c. the vapour pressure of cadmium is thus $p = 0{\cdot}0069$ barye. By equation (2) we can calculate the rate ν at which the atoms evaporate from this surface. Since only one hemisphere supplies the vapour, the rate μ at which the atoms arrive on the opposite hemisphere is only half as great. We thus find $\mu = 4{\cdot}1 \times 10^{15}$ atoms cm.$^{-2}$ sec.$^{-1}$. A monolayer of cadmium atoms contains about 10^{15} atoms em.$^{-2}$. Therefore it takes 0·25 sec. at this temperature to form a monolayer when the incident atoms condense and remain on the surface. Under these conditions the cadmium deposit formed in 30 secs. on a spot cooled by liquid nitrogen contains 125 atomic layers ($\theta = 125$).

The fact that no visible film appears on the surface at — 40° c. indicates that the life τ_1 of the cadmium atoms on the bare glass surface even at this low temperature is very small compared to the life ($\tau_2 = 0{\cdot}12$ sec.) of the atoms on a cadmium surface at 170° c. For a cadmium surface at — 40° c., $\tau_2 = 3 \times 10^{10}$ secs. Thus the rate of evaporation of cadmium atoms from a glass surface at — 40° c. exceeds that of the evaporation of atoms from a cadmium surface at the same temperature by a factor much greater than 10^{11}.

If the forces of interaction between atoms are of such short range that they act only when the atoms are in contact, a film of cadmium on glass having a surface concentration considerably less than that of a monolayer may suffice to prevent the evaporation of atoms incident on a surface at room temperature. Experiments were therefore undertaken to determine how large the covering fraction θ needs to be in order that the invisible or latent deposit formed at very low temperatures should be capable of being developed at room temperature by a supply of vapour from cadmium at 170° c.

Latent deposits corresponding to $\theta = 0{\cdot}016$, formed in one minute from cadmium at 60° c., were developable into visible spots in about 30 secs. The rate of development increased appreciably as θ was raised to 0·12 (from cadmium at 78° c.), but still heavier latent deposits gave no further increase in the rate of development.

When θ was reduced to 0·008 (one minute at 54° c.) the latent deposit was developable within one minute from vapour at 170° c., if the temperature of the deposit was allowed to rise only to — 40° c. after being formed at the temperature of liquid nitrogen. However, if this latent deposit, before development, was allowed to warm to room temperature the development occurred extremely slowly. The same slow development was obtained when the latent deposit, after having been warmed to room temperature, was cooled to — 40° c. It appears, therefore, that the latent deposit with this low value of θ evaporates when the temperature is raised from — 40° to + 20° c., although with higher θ it does not evaporate in this range. Evidently, as θ increases, clusters of 2, 3, or more atoms begin to form, and these are more stable than single atoms.

If the cadmium-covered hemisphere is heated to 220° c., a deposit forms within 15 secs. over the whole of the uncovered hemisphere (at 20° c.) even when no latent deposits have previously been formed. This deposit, however, is very different from that built up on a latent deposit. Instead of being a silver-like mirror, it has a fog-like appearance, and microscopic examination shows that it consists of myriads of small well-separated crystals. Even if the deposition is continued for a considerable time, the crystals remain separate although they continue to grow in size.

The formation of fog-like deposits under these conditions is readily explainable by the condensation–evaporation theory when $\tau_2 \gg \tau_1$. Thus, if vapour from cadmium at 170° c. strikes glass at 20° c., the life τ_1 of single atoms on glass is so short that almost every atom evaporates before it comes into contact with another atom and therefore no deposit appears. When, however, the vapour source is heated to 220° c., which raises ν 19-fold, it often happens that an atom condenses on the surface in a position adjacent to an atom which has not yet evaporated. In this way, clusters of atoms are formed which are far more stable than single atoms and serve as nuclei for the growth of crystals.

The phenomena involved in the formation of the latent deposits, the mirror-like and the fog-like deposits of cadmium, although typical of many cases of condensation on solid surfaces, are evidently not those characteristic of adsorption. One striking difference is that the cadmium deposits are formed only when the vapour is strongly supersaturated, while adsorbed films are produced from vapours or gases at pressures far below saturation.

Case II. The first layer is held more strongly than the second, $\tau_2 \ll \tau_1$. In this case, as the gas pressure rises, the number of adsorbed atoms in the first layer increases until the surface becomes nearly completely covered with a monolayer, but yet, since the life of the atoms in the second layer is so small, no appreciable number of adatoms is present in a second layer. When, however, the pressure is raised until the vapour becomes nearly saturated, the number of atoms in the second layer increases rapidly, so that bulk condensation, involving the formation of many layers, begins as saturation is reached. A theory of the formation of these polyatomic layers with nearly saturated vapours was proposed in 1918 (Langmuir, *J. Amer. Chem. Soc.*, **40**, 1374), and in 1933 was further developed and applied to experimental data on the condensation of cæsium vapour on tungsten (Taylor and Langmuir, *Physical Rev.*, **44**, 453).

The pressure required for the formation of a nearly complete monolayer may be far less than that which gives multilayers (saturated vapour). The ratio of these two pressures is of the order of τ_2/τ_1. In the case of cæsium vapour adsorbed on tungsten (*loc. cit.*), the life τ_1 of isolated adatoms is given by

$$\log_{10} \tau_1 = -\,12{\cdot}373 + 14061/T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

when τ_1 is expressed in seconds. The life τ_M of cæsium atoms which lie in the surface of solid metallic cæsium is (*idem, ibid.*, 1937, **51**, 753)

$$\log_{10} \tau_M = -13{\cdot}201 + 3979/T \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The latent heat of evaporation of adsorbed cæsium atoms on tungsten is thus 3·5 times (*i.e.*, 14061/3979) as great as that of metallic cæsium—an indication of the strong forces that hold the adatoms. At 20° c., equation (8) gives $\tau_1 = 4 \times 10^{35}$ seconds, while equation (9) gives $\tau_M = 2{\cdot}4$ seconds (vapour pressure 0·0011 barye). A life of 2·4 seconds for the adatoms on tungsten occurs, by equation (8), at 830° c. An analysis of the experimental data (*idem, loc. cit.*, 1933, p. 455) has shown that the life τ_2 of cæsium atoms in a second layer on tungsten is about $\frac{1}{6}$ of τ_M. Undoubtedly for the third and subsequent layers τ does not differ appreciably from τ_M. Since therefore $\tau_3/\tau_2 = 6$, while $\tau_1/\tau_2 = 10^{35}$, we see that a complete monolayer of cæsium gives to a tungsten surface properties that are remarkably close to those of metallic cæsium.

The fact that adsorbed films are normally monolayers thus results from the common occurrence of large values for the ratio τ_1/τ_2. There is usually a wide range of pressures over which typical adsorbed films are nearly complete monolayers. Only when the properties of the adsorbed substance and the substrate are nearly identical (τ_1 and τ_2 nearly equal), or when $\tau_2 \gg \tau_1$ (Case I), does this tendency to form monolayers disappear.

Hyperbolic Adsorption Isotherm.—A simple form of isotherm, which has been extensively applied by many investigators to the analysis of experimental data, is represented by the hyperbolic equation

$$q = ap/(b + p) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Here, q is the amount of gas adsorbed when the surface is in equilibrium with the gas at a pressure p, while a and b are constants for any given temperature. This equation was derived (Langmuir, *J. Amer. Chem. Soc.*, 1918, **40**, 1361) from equation (6) by placing

$$\nu = \nu_1\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and

$$\alpha = \alpha_0(1 - \theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where ν_1 and α_0 are constants, and θ represents the fraction of the surface covered by adatoms. These substitutions give

$$\theta = \alpha_0\mu/(\nu_1 + \alpha_0\mu) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

which is of the same form as the hyperbolic equation (10).

Equations (11) and (12) were based upon particular mechanisms of evaporation and condensation. It was assumed that all the adatoms are located in definite positions, or "elementary spaces," whose number and arrangement are determined by the structure of the substrate. In accordance with a convenient nomenclature recently introduced by Bragg and Williams (*Proc. Roy. Soc.*, 1934, *A*, **145**, 699) in treating an analogous problem, we shall use the term "site" for a region in which the adsorbed particle is held on the surface in such a way that it has a minimum of potential energy. Let σ_1 be the number of such sites per unit area. The covering fraction θ is thus defined by

$$\theta = \sigma/\sigma_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The assumption underlying equation (11) is that the life of an atom in a site is not affected by the presence of atoms in other sites.

Equation (12) was based on the assumption that the atoms from the gas phase which strike a bare part of the surface condense and have a life τ_1, while the incident atoms that strike parts of the surface already covered, although they may condense on the surface, re-evaporate so quickly that they make no appreciable contribution to σ. The fraction of the surface bare is $(1 - \theta)$. It was thus crudely assumed that the fraction of atoms that condense on the bare surface is proportional to $(1 - \theta)$.

It has recently been pointed out (Langmuir, *Chem. Reviews*, 1933, **13**, 147, see p. 171) that the physical assumptions underlying this factor $(1 - \theta)$ are very improbable. The experiments on the adsorption of cæsium vapour by tungsten (Taylor and Langmuir, *Physical Rev.*, 1933, **44**, 423) have proved that all the cæsium atoms which strike the surface, even at high temperature, condense, although the surface may be as much as 98% covered with adatoms. This must mean that the atoms incident on the surface move to vacant sites because of surface mobility.

Even if there were no mobility at all we cannot justify the factor $(1 - \theta)$ in equation (12) if the sites are closely adjacent to one another. In this case it is more reasonable to assume that $(1 - \theta)$ should be replaced by $(1 - \theta^4)$.

Some of the fundamental postulates made in the derivation of equation (13) do not involve the particular mechanism that was assumed:

1. The adsorption sites are all identical.
2. At any given time only a negligible fraction of the sites contain more than one adatom each.
3. The potential energy of an adatom in a site is independent of the presence of adatoms in other sites; in other words, the adatoms in separate sites exert no forces on one another.

I will show later that from these postulates we can derive the hyperbolic adsorption isotherm by purely statistical methods. Any mechanism which is compatible with these postulates and with the reversibility principle must give the same isotherm, although each separate mechanism may give a different equation for the kinetics of the adsorption process.

For example, let us consider that all atoms that strike the surface are able, because of their mobility, to move into vacant sites before they evaporate. Then equation (12) is to be replaced by

$$\alpha = 1 \qquad (15)$$

If, now, the adsorption is to occur in sites in accord with our three postulates, the isotherm must be of the hyperbolic form of equation (13). Therefore in this case we find by equations (6) and (15) that the evaporation ν, instead of increasing in proportion to θ by equation (11), is given by

$$\nu = A\theta/(1 - \theta) \qquad (16)$$

From this, by equations (5) and (14), we conclude that the life τ of an atom on the surface is no longer independent of the presence of other atoms, for it is given by

$$\tau = \tau_0(1 - \theta) \qquad (17)$$

A careful analysis shows that this shortening of the life τ as θ approaches unity results from strong repulsive forces between pairs of atoms which occasionally occupy single sites.

Cæsium Films on Tungsten.—The ionising potential of cæsium is 3·9 volts, which is lower than that of any other chemical element, cæsium being the most electropositive substance. The heat of evaporation of electrons from tungsten corresponds to 4·6 volts; thus the energy necessary to detach an electron from a cæsium atom is 0·7 electron volt less than that required to extract an electron from metallic tungsten. Experiments have shown that each cæsium atom which strikes a tungsten filament at high temperature loses its electron and escapes as a cæsium ion if the filament is surrounded by the proper electric field. The electric current which flows from the tungsten thus gives a quantitative measure of the number of cæsium atoms that strike the filament, and therefore by equation (1) it gives an accurate determination of the vapour pressure of the cæsium (Taylor and Langmuir, *Physical Rev.*, 1937, **51**, 753). If the current were measured by an electrometer sensitive to currents of 10^{-17} amp., it should be possible to detect a cæsium vapour pressure as low as 10^{-15} barye, which corresponds to a concentration of only 0·02 cæsium atom per cm.^{3}.

I believe there is no case better adapted to a complete study of the mechanism of adsorption phenomena than that of the adsorption of cæsium on tungsten. Not only can the number of cæsium atoms on the surface of the filament at any given time be measured accurately, but in the same apparatus the contact potential, the rate of evaporation ν_a

of cæsium atoms, the rate of evaporation ν_p of cæsium ions, and the rate of evaporation of electrons ν_e can be simultaneously measured as a function of the filament temperature and σ. From these data it becomes possible to calculate the forces acting between the adatoms, to measure the heats of evaporation, and to check these data against thermodynamic equations.

The escape of cæsium ions from the heated tungsten surface is an evaporation phenomenon, and thus below about 1000° K. the atoms that strike the surface accumulate. As the surface concentration σ builds up, the rate of atom evaporation increases, but if the filament is at room temperature, there is no appreciable evaporation until the surface becomes covered by a complete monatomic film of cæsium.

When the covering fraction θ is less than 0·08, a sudden heating of the filament to high temperature causes all the adsorbed cæsium atoms to evaporate as ions. If the filament is surrounded by a negatively charged cylinder, this sudden burst of ions produces a momentary current which can be measured by a ballistic galvanometer or electrometer. With a good electrometer it should be possible, by allowing the cæsium atoms to accumulate on the filament for 24 hours, to detect the presence of cæsium vapour even with pressures as low as 10^{-26} atm., which is the pressure corresponding to a concentration of one atom of cæsium in every five cubic metres of space.

A second method of measuring σ, applicable to all values of θ, involves the sudden evaporation of the cæsium as atoms, in the presence of a retarding field which prevents the escape of ions. This burst of atoms falls on a parallel neighbouring tungsten filament heated above 1300° from which these atoms escape as ions. The ballistic kick of current from this second filament thus measures σ on the first filament.

The conversion of cæsium atoms into ions by a heated tungsten filament depends upon the ionising potential of cæsium being less than the heat of evaporation of electrons from tungsten. Potassium and rubidium, which have ionising potentials less than 4·6 volts, therefore also form positive ions when their atoms strike a hot tungsten surface, but sodium, with an ionising potential of 5·1 volts, gives no appreciable positive current.

By using a thoriated tungsten filament, the heat of evaporation of electrons can be lowered from 4·6 to 3·1 volts, lower than the ionising potential of cæsium. Thus, cæsium atoms do not readily form ions on a tungsten surface completely covered with thorium atoms. On the other hand, by forming on the tungsten surface a film of adsorbed oxygen, the electron emission from the tungsten is greatly reduced and the heat of evaporation rises to 5·6 volts. A filament with such a film is capable of yielding positive ions even with atoms of sodium or lithium (Taylor, *Z. Physik*, 1928, **52**, 846; *Physical Rev.*, 1930, **35**, 375).

At a given filament temperature, such as 1000° K., and at low θ, the ion evaporation rate ν_p (observable only with accelerating fields) is several thousand times greater than the atom evaporation rate ν_a. At $\theta = 0{\cdot}01$, ν_p reaches a maximum; and at higher values of θ it decreases rapidly, becoming less than ν_a at $\theta = 0{\cdot}08$. A minimum value of ν_p is reached at $\theta = 0{\cdot}5$, the value of ν_p then being only 10^{-6} as great as the maximum at $\theta = 0{\cdot}01$.

With cæsium vapour saturated at 20° C. (10^{-3} barye) the electron emission ν_e increases to a maximum of 10^{-5} amp. cm.$^{-2}$ when the filament temperature is raised to 700° K. Under these conditions, which give $\theta = 0{\cdot}55$, the emission is 10^{25} times greater than from pure tungsten at the same temperature in absence of cæsium. At still higher filament temperatures the emission rapidly decreases because of loss of cæsium from the surface.

If the filament temperature is kept constant and θ is increased by raising the cæsium vapour pressure, the emission rises to a maximum at $\theta = 0{\cdot}67$. We have seen that with thorium and barium films on tungsten a similar maximum of emission occurs at about the same value of θ.

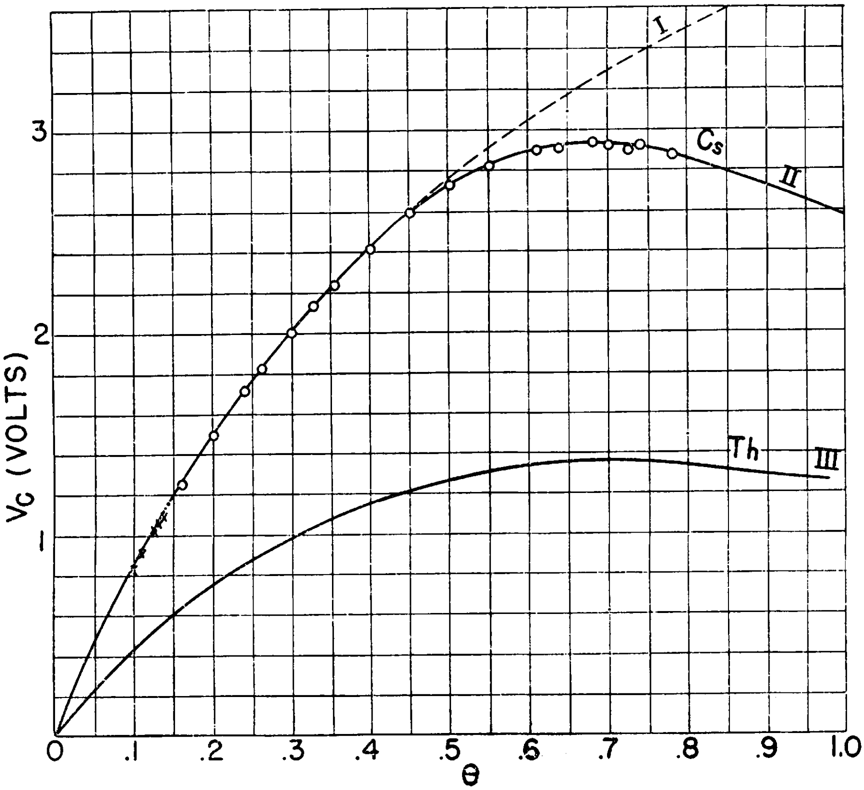
From measurements of ν_e, the contact potential V can be calculated by the Boltzmann equation

$$\nu_e/\nu_W = \exp(V\boldsymbol{e}/\boldsymbol{k}T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where ν_W is the electron emission from pure tungsten at the same temperature. The contact potential is measured with respect to a pure tungsten surface. The points marked by circles in Fig. 2 (curve II) give the values of V calculated from ν_e in this way. Curve III gives corresponding data for the contact potentials observed with a film of thorium on tungsten.

FIG. 2.

Contact potentials of monolayers of cæsium and thorium on tungsten.



Each cæsium adatom constitutes a dipole of moment M. The contact potential of the surface can be calculated by the equation

$$V = 2\pi\sigma_1\theta M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Table II gives for films of cæsium and thorium on tungsten the dipole moment M, calculated from the contact potential by equation (19). The decrease in M as θ increases results from the partial depolarisation of each dipole by the intense electric field produced by neighbouring dipoles. These fields are of the order of 5×10^7 and 8×10^7 volts cm.$^{-1}$ for thorium and cæsium respectively at $\theta = 0{\cdot}7$.

TABLE II.

Dipole moments and lives of adsorbed cæsium and thorium atoms on tungsten.

θ.	$M \times 10^{18}$; Cs on W.	$M \times 10^{18}$; Th on W.	τ, secs.; Cs on W at 30° c.	θ.	$M \times 10^{18}$; Cs on W.	$M \times 10^{18}$; Th on W.	τ, secs.; Cs on W at 30° c.
0·0	16·2	3·9	4×10^{35}	0·9	4·5	—	10^{12}
0·1	13·0	3·3	$1{\cdot}4 \times 10^{32}$	0·95	4·0	—	10^{7}
0·5	8·2	1·9	3×10^{21}	1·0	3·6	—	0·4
0·7	6·3	1·5	2×10^{17}	2·0	—	—	2·4

We saw that the repulsive forces between thorium adatoms on tungsten cause a shortening of the life τ in the ratio 73 : 1 as θ increased from 0·07 to 0·7. In the case of cæsium films on tungsten the decrease in τ with increase in θ, as shown in the last column of the table, is much more marked. The most rapid change in log τ occurs as θ approaches unity. This is clearly the effect produced by the crowding of the atoms in the monolayer as saturation is approached.

The forces between the cæsium adatoms are of two kinds. First, there is the long-range repulsive force f between any two dipoles, as given by

$$f = (3/2)M^2/r^4 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (20)$$

where r is the distance between the adatoms. Secondly, there is the short-range force that prevents two adatoms from occupying the same site at the same time. It has been possible to develop a quantitative theory by which the variation in ν_a as a function of θ can be calculated from the dipole moment M obtained by measurements of the electron emission. We shall outline this theory.

Adsorbed Films as Two-dimensional Gases.—An adatom on the surface of a crystalline solid has a potential energy which depends on the position of the atom with respect to the lattice of the underlying solid. By considering these forces and the forces f between pairs of adatoms, we can derive a two-dimensional equation of state (Langmuir, *J. Amer. Chem. Soc.*, 1932, **54**, 2817),

$$F = \sigma kT + (1/4)\sigma\Sigma(rf) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (21)$$

where the summation extends over all adatoms which act upon any one of them, and F is the spreading force, in dynes/cm., with which the adatoms tend to distribute themselves over the surface because of their Brownian movement and mobility. Under equilibrium conditions, neither the mobility nor the forces between the adatoms and the substrate influence F.

When there are no forces of interaction between the adatoms, the adsorbed film behaves as an ideal two-dimensional gas, the equation of state being

$$F = \sigma kT \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (22)$$

This equation is analogous to the ordinary ideal-gas law for three-dimensional gases, *viz.*,

$$p = nkT \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (23)$$

The forces of interaction between adatoms may be of many types. In the development of the kinetic theory of gases, particular laws of force were postulated for special cases and corresponding equations of state were derived theoretically. Similarly, we may make various assumptions regarding the interactions of adatoms and obtain, by equation (21), many types of equation of state for adsorbed films.

From any such equation of state, which expresses F as a function of σ and T, a corresponding adsorption isotherm, giving p as a function of σ and T, can be derived by means of the thermodynamical equation of Gibbs

$$\mathrm{d}F/\mathrm{d}\ln p = \sigma kT \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (24)$$

It was found by J. Traube in 1891 that in very dilute aqueous solutions, surface-active substances depress the surface tension in proportion to their concentration. This lowering of the surface tension γ can be looked upon as being due to the spreading force F exerted by the molecules in the adsorbed film, so that

$$F = \gamma_0 - \gamma \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (25)$$

where γ_0 is the surface tension of the pure solvent. Thus Traube's observation means that in very dilute solutions, F increases in proportion to p. By substituting $p = \text{const.} \times F$ in equation (24), it was shown (Langmuir, *J. Amer. Chem. Soc.*, 1917, **39**, 1888) that the ideal two-dimensional gas law, (22), applies to dilute films. The equation was originally given in the form

$$Fa = kT \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (26)$$

where a, the area of the surface divided by the number of adsorbed molecules, is equal to $1/\sigma$.

To take into account the short-range forces that prevent any two adsorbed molecules from occupying the same space at the same time, Volmer and I independently proposed the equation

$$F(a - a_0) = \boldsymbol{k}T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

where a_0 is constant. The factor $(a - a_0)$ corresponds to the analogous factor $(v - b)$ in the van der Waals equation of state for gases. In the derivation of the latter equation, by assuming that b is small compared to v, it is found that b is four times the actual volume of the molecules in the gas, these molecules being regarded as hard elastic spheres. By similar reasoning, which is valid only for low surface concentrations, Volmer (*Z. physikal. Chem.*, 1925, **115**, 253) showed that a_0 in equation (27) should be twice the actual projected area of the adsorbed molecules. The application for which I proposed equation (27), however (*Colloid Symposium Monograph*, 1925, **3**, 72), was one which involved high surface concentrations and the quantity a_0 was thus interpreted as the limiting value of a as F was made to increase indefinitely. On this basis, a_0 is the reciprocal of σ_1 as given in equation (14), and therefore the equation of state (27) can be written

$$F = \sigma_1\boldsymbol{k}T\theta/(1 - \theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Although this equation serves as a useful rough approximation to cover the range in θ from zero to 1, it cannot be regarded as having a sound theoretical basis. To compare the many equations of state that can be derived on the basis of different postulates regarding the forces of interaction it will be convenient to express any equation of state in the form

$$F = \sigma_1\boldsymbol{k}T\theta/\mathrm{Y}(\theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

where Y(θ) is a function of θ which must approach unity at low values of θ and approach zero when θ becomes nearly unity. If we put $\mathrm{Y}(\theta) = 1 - \theta$, we evidently obtain (28).

Tonks (*Physical Rev.*, 1936, **50**, 955) has made a study of the complete equation of state for one-, two-, and three-dimensional gases of hard, elastic spheres. For low values of θ he obtains a result which is equivalent to the following

$$\mathrm{Y}(\theta) = 1 - 1{\cdot}814\theta + 0{\cdot}72\theta^2 \ldots \quad . \quad . \quad . \quad . \quad . \quad (30)$$

The limiting expression for values of θ approaching unity is

$$\mathrm{Y}(\theta) = 1 - \theta^{1/2} = (1/2)(1 - \theta) + (1/8)(1 - \theta)^2 \ldots \quad . \quad . \quad . \quad (31)$$

At high values of θ, Tonks shows that the adatoms are forced into approximately hexagonal, close-packed arrangements, the centre of each atom being able to move only within a small hexagonal region.

The rather complicated empirical interpolation formula for the whole range of θ which Tonks gives can be much more simply represented (within about 1%) by the equation

$$\mathrm{Y}(\theta) = (1 - \theta)/(1 + \theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

Fig. 3 gives Y(θ) for several typical equations of state. Curve I, a straight line, $\mathrm{Y}(\theta) = 1 - \theta$, corresponds to equation (28). Curve II, the hyperbola of equation (32), gives the following equation of state :

$$F = \sigma_1\boldsymbol{k}T\theta(1 + \theta)/(1 - \theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

By means of (24) we can obtain from each of these equations of state the corresponding adsorption isotherm. Thus from (28) (curve I), we get

$$\ln(p/\theta) = \theta/(1 - \theta) - \ln(1 - \theta) + \text{const.} \quad . \quad . \quad . \quad . \quad (34)$$

while from (33) (curve II), we find

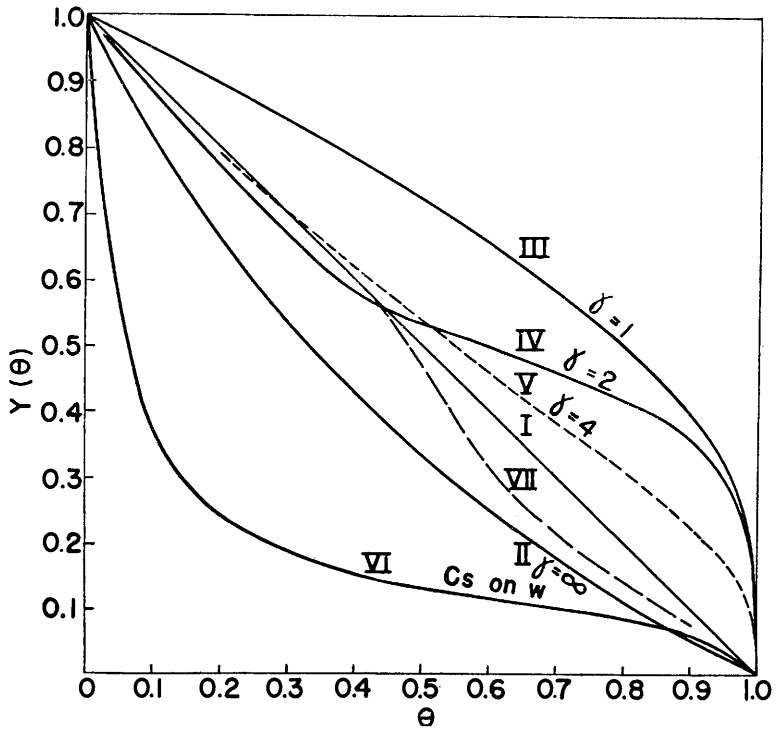
$$\ln(p/\theta) = 2\theta/(1 - \theta) - 2\ln(1 - \theta) + \text{const.} \quad . \quad . \quad . \quad . \quad (35)$$

Just as we have used a function Y(θ) to compare various equations of state by equation (29), we can now use another function Z(θ) to characterise the adsorption isotherms which may be put in the form

$$p = B\theta/\mathrm{Z}(\theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

Here B is a constant which depends on temperature, and $Z(\theta)$, like $Y(\theta)$, is a function which approaches unity at low values of θ and approaches 0 when θ becomes nearly unity. Curves I and II in Fig. 4 represent the $Z(\theta)$ function for the isotherms of equations (34) and (35).

FIG. 3.



A comparison of equations of state of typical adsorbed films. $F = \sigma_1 kT\theta/Y(\theta)$.

The straight line (curve III in Fig. 4) gives the function $Z(\theta) = 1 - \theta$, which corresponds to the hyperbolic isotherm of equation (10). By eliminating p between (10) and (24), we find that the equation of state that corresponds to this hyperbolic isotherm is

$$F = -\sigma_1 kT \ln(1 - \theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

from which we find, by (29),

$$Y(\theta) = -\theta/\ln(1 - \theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

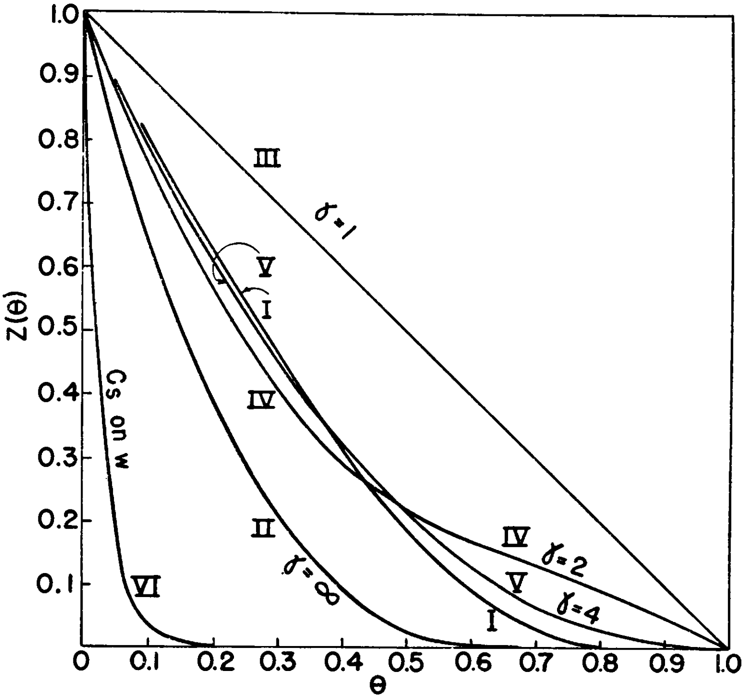
Curve III in Fig. 3 is a graph of this function.

The marked difference in the equations of state represented by (33) and (37) (curves II and III) results from the different types of force of interaction assumed in the derivation of these equations. Thus Curve II, equation (33), is based upon intense forces of repulsion between adatoms that act only when the centres of the atoms are a definite distance d apart, d being the diameter of the atom. On the other hand, Curve III, in Fig. 3, equation (37), involves only forces of interaction that prevent any two atoms from occupying the same site at the same time—forces that depend on the underlying lattice.

Adsorption Isotherms and Equations of State for Atoms having Diameters greater than the Shortest Distances between Sites.—In the derivation of the hyperbolic isotherm, equation (10), it was assumed that each adsorption site can contain one, but never more than one, adatom. It is evident that if the diameter d of the adatoms is greater than the shortest distance d_s between sites, then the presence of each adatom prevents other atoms from occupying certain neighbouring sites. Under these conditions, therefore, the hyperbolic isotherm cannot apply.

In Fig. 5 the small black dots represent sites which form a square lattice. The adatoms, shown as large circles, have diameters greater than the lattice constant of the sites, the ratio d/d_s being 1·25. Let us draw a circle of radius d about the centre of any adatom, taking as an example the atom whose co-ordinates (x, y) are (7, 12). The five sites that lie within this circle cannot be occupied by other atoms; they form a pattern which we shall call the *exclusion pattern.* Let E be the number of sites in the exclusion pattern of an adatom; in the example of Fig. 5, $E = 5$. If the diameter of the atom were slightly greater than $1{\cdot}41 d_s$ we would have $E = 9$.

FIG. 4.



A comparison of adsorption isotherms of typical adsorbed films. $p = B\theta/Z(\theta)$.

Let σ_s be the *total* number of sites per unit area and σ_E be the number of sites per unit area that *lie within exclusion patterns* of adatoms. If σ_f is the number of *free sites* per unit area, then evidently

$$\sigma_f = \sigma_s - \sigma_E \quad \dots\dots\dots \quad (39)$$

The small circles in Fig. 5 denote free sites; *i.e.*, places into which atoms can go.

The adatoms of Fig. 5 can be divided into two groups, as shown by the two types of hatching of the large circles, according as the sum, $x + y$, of the co-ordinates of each of the atoms is an odd or an even integer. The broken lines mark the boundaries between odd and even surface phases. For example, the adatom at (5, 14) belongs to the odd phase because $5 + 14 = 19$ is an odd integer.

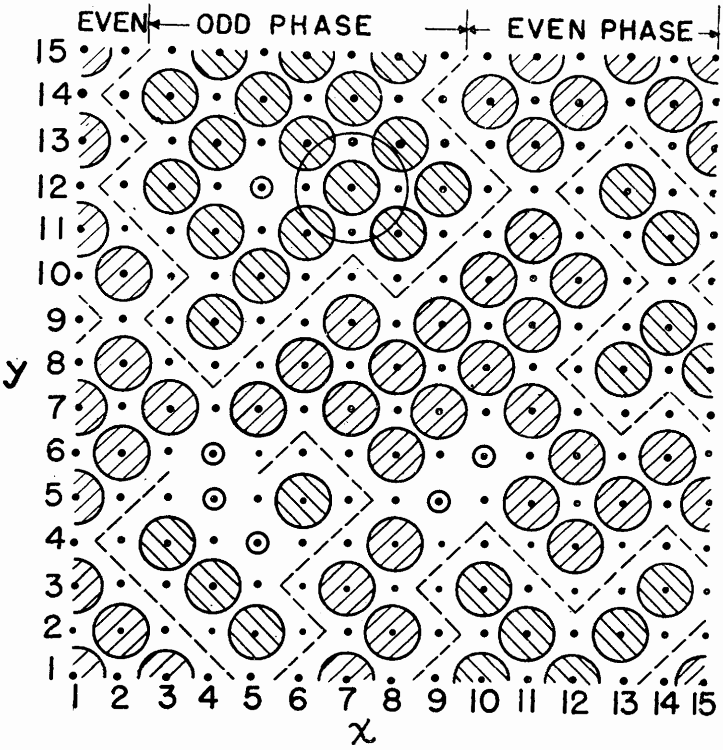
In order to get the densest possible packing of adatoms within a given area, it is necessary that all the atoms in that area should belong to the same surface phase. With this closest packing, the number of adatoms per unit area σ_1 is half σ_s, the surface concentration of sites. Let us define a quantity γ by

$$\gamma = \sigma_s/\sigma_1 \quad \dots\dots\dots \quad (40)$$

In the particular case illustrated in Fig. 5 we have $\gamma = 2$. If the adatoms have diameters less than d_s every site can be occupied, and therefore $E = 1$ and $\gamma = 1$. With adatoms of larger diameter γ increases. Thus if d is slightly greater than $\sqrt{2}\, d_s$, $E = 9$ and $\gamma = 4$.

Let us make the problem of the adsorption isotherm definite by assuming that the presence of an adatom in a given site has no effect on the adsorption in sites that lie outside of its exclusion pattern. To calculate the adsorption isotherm we shall adopt a generalisation of a rigorous statistical method used by Hückel (" Adsorption und Kapillar-Kondensation," Akad. Verlagsgesellschaft, Leipzig, 1928, p. 157) in his derivation of the hyperbolic isotherm, equation (10).

FIG. 5.



Typical arrangements of adatoms on a square lattice for the case $\gamma = 2$, E = 5, $d_s = 1·0$, d = 1·25, e = 0·69.

Consider a gas of pressure p in equilibrium with an adsorbed film of gas on the surface of a crystal. Select a particular atom of gas and follow its history as it moves back and forth between the gas and the surface phases. Since this atom, when it condenses on the surface, can go only into free sites, the total probability that it is on the surface at any given time is proportional to σ_f. There is an equal probability that any other atom in the system will be found on the surface, and since the number of such atoms is proportional to the pressure, the adsorption isotherm can be written

$$\sigma = Ap\sigma_f \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

where A is an undetermined constant which depends on temperature.

For the special case of adatoms having diameters less than d_s, we have $E = 1$, $\sigma_E = \sigma$, $\sigma_1 = \sigma_s$, and therefore by equations (40), (39), and (14), $\gamma = 1$ and $\sigma_f = \sigma_1(1 - \theta)$. By substituting these values in (41) we can derive the hyperbolic isotherm of equation (10).

For the general case, where γ may have values greater than unity, the isotherm,* for low values of θ, is expressible as a series

$$\theta = A\gamma p(1 - K_1\theta + K_2\theta^2 + K_3\theta^3 + \ldots) \quad . \quad . \quad . \quad . \quad (42)$$

The coefficient K_1 can be calculated by considering that at low values of θ, where the higher-order terms are negligible, the exclusion patterns of separate atoms do not overlap, and therefore $\sigma_E = \sigma E$. Introducing this into equation (39), and eliminating σ_s by (40), we obtain a value of σ_f which by (41) gives $\theta = Ap(\gamma - E\theta)$. A comparison with (42) shows that

$$K_1 = E/\gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

The calculation of K_2 requires consideration of the overlapping of the exclusion patterns between pairs of adatoms. For the case illustrated in Fig. 5 with $\gamma = 2$, (42) becomes †

$$\theta = 2Ap(1 - 2{\cdot}5\theta + 1{\cdot}5\theta^2 + 0{\cdot}75\theta^3 + \ldots) \quad . \quad . \quad . \quad . \quad (44)$$

The corresponding equation of state can be calculated by equation (24). It can be expressed in the form of equation (29) by placing

$$Y(\theta) = 1 - 1{\cdot}25\theta + 0{\cdot}48\theta^2 + 0{\cdot}22\theta^3 \ldots \quad . \quad . \quad . \quad . \quad (45)$$

Curve IV of Fig. 3, in the range $\theta < 0{\cdot}4$, is a plot of this function, while Curve IV of Fig. 4, in the same range, is a plot of $Z(\theta)$ obtained by comparing equations (36) and (44).

The peculiar conditions that arise, in the case $\gamma = 2$, when θ becomes large are illustrated in Fig. 5. This diagram of a typical arrangement of adatoms was constructed by placing adatoms one after the other in free sites selected at random by drawing numbered cards from a shuffled pack.

If such a surface array of adatoms is in equilibrium with a gas, we see by equation (41) that, as the pressure p is increased indefinitely, the number of free sites, σ_f, must approach zero; but it is not evident that σ must approach its maximum value σ_1, which corresponds to $\theta = 1$. In Fig. 5 six free sites are shown, but only five of these can be filled by adatoms, since the two adjacent sites (4, 5) and (4, 6) cannot both be filled. A large increase in pressure would cause most of these free sites to be filled, but even if all should be filled, only 83 out of the 225 sites would be occupied, giving a limiting value of $\theta = 0{\cdot}74$.

The two rows of excluded sites along each boundary between the odd and even phases are responsible for the failure of θ to become unity when the free sites are made to disappear. Thus the deficiency of adatoms caused by the boundaries, which we shall denote by θ_L and which is measured by $1 - \theta$, varies in proportion to the total length of the phase boundaries per unit of surface. As a unit for measuring both the lengths of the boundaries

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* The theory of adsorption on crystal lattices which is outlined in these pages was developed early in 1936 but has not yet been published in detail. However, a paper presenting the results was read before the American Physical Society (*Physical Rev.*, 1936, **50**, 393), and the generalised adsorption isotherm with a curve for the case $\gamma = 2$ were incorporated in Tonks's paper of 1936 (*loc. cit.*). Roberts (*Proc. Roy. Soc.*, 1935, *A*, **152**, 472) and Morrison and Roberts (*ibid.*, 1939, *A*, **173**, 1, 13) have considered the irreversible adsorption of oxygen molecules to give pairs of adjacent adatoms ($E = 2$). Chang and Fowler (*Proc. Camb. Phil. Soc.*, 1938, **34**, 224) have dealt with the effects of attractive and repulsive forces between adjacent adatoms and have shown that in the latter case a surface superlattice may result.

(Note added, March 15th, 1940) Roberts has summarised theoretical developments in this field in a booklet, " Some Problems in Adsorption," Cambridge University Press, 1939. A more detailed analysis of the condensation of atoms to form an immobile adsorbed film for the case $\gamma = 2$, $E = 5$ has recently been published by Roberts (*Proc. Cambridge Phil. Soc.*, 1940, **36**, 53). The adsorption isotherm obtained by Roberts and others for this case is essentially different from that given in the present paper. The derivations of the adsorption isotherms for the cases $\gamma = 2$, $E = 5$ and $\gamma = 4$, $E = 9$ are contained in a paper by Tonks, which was recently submitted to the *Journal of Chemical Physics.* He shows that Roberts' application of Bethe's statistical method to this problem is incorrect.

† The coefficient of the last term was calculated by Tonks.

and the unit of area, let us choose the distance between adjacent adatoms within a single phase:

$$a_1 = \sqrt{2} \times d_s = 1/\sqrt{\sigma_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

The total length of boundaries per unit area expressed in this way in terms of a_1 and $(a_1)^2$ is a dimensionless quantity which we shall represent by L. The actual length of the boundaries (in cm.) per unit of surface (in sq. cm.) is thus L/a_1. At high pressures which make the number of free sites negligible we then have

$$\theta_L = 1 - \theta = L/2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

Any random one-way process of building up the adsorbed film ($\gamma = 2$) thus leads to a pseudo-saturation in which θ approaches a limiting value $1 - \theta_L$. Numerous experiments with balls of $\frac{1}{2}$ inch diameter, randomly placed on a square lattice formed with $\frac{3}{8}$-inch balls, have demonstrated that this limiting value of θ is always very close to 0·73. If, however, we provide a mechanism of equilibration by removing balls at random and replacing them among the free sites by random selection, we find that the phase boundaries slowly shift their positions and decrease in length, causing an increase in θ. An examination of the mechanism of these slow changes, as well as a consideration of the associated free-energy changes, shows that at very high pressures the final equilibrium state should be one in which only a single surface phase is present over any given finite area.

Equation (41) is applicable, not only to this final state of true equilibrium, but also to the the rapidly established pseudoequilibrium that exists during the slow equilibration process. The number of free sites, if small compared to the number of occupied sites, is given by $\sigma_f = \sigma_1(1 - \theta_L - \theta)/(1 - 0{\cdot}4\theta_L)$; and therefore equation (41) gives the following adsorption isotherm for the pseudoequilibrium:

$$\theta = Ap(1 - \theta_L - \theta)/(1 - 0{\cdot}4\theta_L) \quad . \quad . \quad . \quad . \quad . \quad . \quad (48)$$

If the equilibrium is disturbed by a sudden change in pressure, there will be a relatively rapid change in θ to bring about a new equilibrium given by equation (48) with the new value of p but with the old value of θ_L.

The final equilibrium state, reached only after the slow changes in the phase boundaries have been completed, is given by (48) if we put $\theta_L = 0$. This equation is a limiting expression applicable only for high values of θ. Dr. Tonks has made a careful study (unpublished work) of the second- and third-order effects and has obtained an expression for the adsorption isotherm for $\theta > 0{\cdot}5$:

$$\theta = Ap(1 - \theta)[1 - 3(1 - \theta)^2 + 5(1 - \theta)^3] \quad . \quad . \quad . \quad . \quad . \quad (49)$$

The $Z(\theta)$ function for this isotherm is represented in Fig. 4 by the portion of Curve IV that extends from $\theta = 0{\cdot}5$ up to $\theta = 1$. A double logarithmic plot of $Z(\theta)$ as a function of $1 - \theta$ has been published by Tonks (*loc. cit.*, 1936), but the derivation was not given. The part of curve IV in Fig. 4 that corresponds to $\theta < 0{\cdot}5$ was calculated from (44).

Because the two series used in calculating $Z(\theta)$ for curve IV do not converge rapidly for values of θ between 0·3 and 0·7, this intermediate part of the curve must be regarded as an empirical extrapolation. However, several points in this intermediate range have been checked by experiments in which $\frac{1}{2}$-inch steel balls, placed at random on a square lattice of $\frac{3}{8}$-inch balls, were subjected to prolonged equilibration by a random selection process.

The equation of state that corresponds to this adsorption isotherm is represented by its $Y(\theta)$ function in curve IV of Fig. 3. These curves and equations (44)—(49) all apply to the case illustrated in Fig. 5, where $E = 5$, $\gamma = 2$ and $d_s < d < 1{\cdot}41d_s$.

With still larger adatoms of diameters from $1{\cdot}42d_s$ to $2d_s$, we have $E = 9$ and $\gamma = 4$. Dr. Tonks has found that the limiting expressions for this case are

$$\theta = Ap(1 - 2{\cdot}25\theta + 1{\cdot}0\theta^2 + \ldots) \quad . \quad . \quad . \quad . \quad . \quad . \quad (50)$$

and

$$\theta = (A/2)p(1 - \theta)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (51)$$

Although the exact form of this isotherm for intermediate values of θ would be difficult to calculate, it seems that a good approximation is given by an equation of the type

$$\theta = Ap(1 - \theta)^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (52)$$

If we put $n = 2{\cdot}25$ we obtain an isotherm which agrees well with (50) when θ is small, and with (51) when θ is large. Curve V in Fig. 4 is a plot of function $Z(\theta) = (1 - \theta)^{2\cdot25}$ which represents the isotherm of (52).

The equation of state that corresponds to (52) is given by

$$F = \sigma_1 kT[(1 - n)\theta - n \ln (1 - \theta)] \quad . \quad . \quad . \quad . \quad . \quad . \quad (53)$$

This reduces to (37) if $n = 1$, while for the case $n = 2{\cdot}25$ it gives the function $Y(\theta)$, shown by curve V, in Fig. 3.

With further successive increases in adatom diameter, or progressive decrease of lattice constant, d_s, both E and γ increase by irregular steps so that K_1, which depends upon E/γ, by equation (43), shows both positive and negative increments. However, as E and γ increase without limit, an integration process shows that K_1 and K_2 in (42) approach the limits $K_1 = 3{\cdot}63$ and $K_2 = 2{\cdot}72$. If the corresponding equation of state is calculated by (24), we obtain the same series expression for $Y(\theta)$ that is given by (30). Thus the case in which γ is infinite is equivalent to that of the adsorption of rigid spheres not held in fixed sites (mobile monolayers). Curves II in Figs. 3 and 4, which are based on equations (32) and (35), apply to this case and are therefore properly marked $\gamma = \infty$.

We have so far considered only square lattices in illustrating the effects of making the adatom diameter greater than d_s. Similar effects occur with other types of lattice. An interesting example is found when adatoms are placed upon a substrate consisting of a plane hexagonal close-packed arrangement of atoms such as that in the 111-face of a face-centred cubic crystal. If each adatom makes contact with three substrate atoms, there are twice as many adsorption sites as there are substrate atoms. The shortest distance, d_s, between sites is only 58% of the distance, d_0, between substrate atoms. Thus, only if the adatom diameter d is less than $0{\cdot}58d_0$ does the hyperbolic adsorption isotherm apply. When the adatoms are as large as the substrate atoms, only half the sites can be filled and we have $\gamma = 2$ and $E = 4$.

Curves III and II in Figs. 3 and 4 represent the extreme types of equation of state and adsorption isotherm that result directly from the lattice-like arrangement of the atoms in the substrate. These cases that we have considered, however, involve only repulsive forces that prevent two adatoms from occupying the same site or sites that lie closer than a minimum distance d.

If we take into account attractive forces that cause clustering of atoms, such as those which Mayer and his co-workers (*J. Chem. Physics*, 1937, **5**, 67, 74; 1938, **6**, 87; Band, *ibid.*, 1938, **7**, 324) have successfully used in deriving equations of state for gases, we should obtain curves for $Y(\theta)$ and $Z(\theta)$ that lie above the curves III in Figs. 3 and 4. With two-dimensional gases, however, because of the orientation of molecules or the polarisation of atoms by the substrate, we should expect repulsive forces to predominate and so obtain curves that may lie even below Curve II.

Equation of State for Cæsium Adatoms on Tungsten.—Taylor's studies of the evaporation of cæsium adatoms from a tungsten surface have provided data for the calculation of the isotherm and the equation of state for the whole range in θ from 0 to 1. The measurements of electron emission permit the determination of the dipole moment and thus the long-range repulsive forces between the adatoms. By allowing for these known forces we can then find the effect of the short-range forces.

Col. 2 of Table III gives Taylor's data for ν_a, the rate of evaporation of adatoms (atoms cm.$^{-2}$ sec.$^{-1}$) at 800° K. as a function of θ. The limiting value of ν_a/θ as θ approaches 0 is found to be $2{\cdot}24 \times 10^9$, and therefore $Z(\theta)$, defined by equation (36), is equal to $2{\cdot}24 \times 10^9\, \theta/\nu_a$, as given in col. 3 of Table III, and in Curve VI of Fig. 4. The effect of the strong repulsive forces between the cæsium adatoms is here manifested by the very small values of $Z(\theta)$; when $\theta > 0{\cdot}6$, $Z(\theta)$ is less than 10^{-5} as great as for any of the other isotherms.

TABLE III.

Data for cæsium films on tungsten at 800° K.

1. θ.	2. ν_a.	3. $Z(\theta)$.	4. F.	5. $Y(\theta)$.	6. V.	7. $M \times 10^{18}$.	8. F_M.	9. F_s.	10. $Y'(\theta)$.
0	0·00	1·000	0·00	1·000	0·0	16·2	0·00	0·00	1·000
0·01	$3{\cdot}2 \times 10^{7}$	0·707	0·46	0·850	0·106	15·7	0·06	0·004	0·99
0·02	$9{\cdot}0 \times 10^{7}$	0·500	1·06	0·741	0·208	15·2	0·26	0·016	0·98
0·05	$6{\cdot}3 \times 10^{8}$	0·178	3·6	0·539	0·48	13·9	1·6	0·103	0·95
0·10	$6{\cdot}4 \times 10^{9}$	0·035	10·4	0·377	0·87	13·0	6·0	0·43	0·90
0·2	$2{\cdot}7 \times 10^{11}$	$1{\cdot}7 \times 10^{-3}$	31·9	0·244	1·50	11·2	22·2	2·0	0·80
0·3	$6{\cdot}3 \times 10^{12}$	$1{\cdot}1 \times 10^{-4}$	62·6	0·187	2·00	9·93	45·9	5·0	0·70
0·4	$1{\cdot}1 \times 10^{14}$	$8{\cdot}3 \times 10^{-6}$	101·4	0·154	2·42	9·01	75·3	10·5	0·599
0·5	$1{\cdot}5 \times 10^{15}$	$7{\cdot}3 \times 10^{-7}$	148	0·132	2·74	8·15	106	23	0·467
0·6	$2{\cdot}1 \times 10^{16}$	$6{\cdot}4 \times 10^{-8}$	204	0·115	2·89	7·18	129	52	0·312
0·7	$3{\cdot}0 \times 10^{17}$	$5{\cdot}2 \times 10^{-9}$	272	0·101	2·92	6·23	142	103	0·210
0·8	$7{\cdot}6 \times 10^{18}$	$2{\cdot}4 \times 10^{-10}$	367	0·085	2·87	5·34	142	194	0·139
0·9	$3{\cdot}0 \times 10^{20}$	$6{\cdot}8 \times 10^{-12}$	587	0·060	2·72	4·50	130	422	0·077
0·95	$3{\cdot}1 \times 10^{26}$	$6{\cdot}8 \times 10^{-18}$	990	0·038	2·66	4·17	114	840	0·042
1·00	∞	0	∞	0·000	2·62	3·90	120	∞	0·000

The values of F in col. 4 have been calculated directly from ν_a by means of equation (24), and from these the values of $Y(\theta)$, as defined by (29), have been obtained (col. 5 of Table III and curve VI of Fig. 3). We see that the effect of the repulsive forces is to cause a rapid decrease in $Y(\theta)$, and consequent increase in F, in the range in θ from 0—0·1, with a slower decrease at higher values of θ until, at $\theta = 0{\cdot}87$, the curve crosses Curve II.

Col. 6 of Table III and the full-line curve of Fig. 2 contain the contact potential V of the cæsium-covered surface against pure tungsten, as defined by equation (18). Between $\theta = 0{\cdot}15$ and 0·78, they are based directly upon measurements of the electron emission, ν_e, but outside this range, the curve may be looked upon as extrapolated.

Col. 7 gives the dipole moment M calculated from V by (19). The force f acting between dipoles is given by (20).

It is seen from (21) that the spreading force F can be regarded as consisting of three components,

$$F = F_0 + F_s + F_M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (54)$$

where F_0 is the contribution, σkT, of the Brownian movement, as given by the ideal-gas law of equation (22); F_s is the component which involves the *short-range* forces that act during contacts between atoms or that confine the atoms to definite sites. Finally, F_M is the contribution that results from the long-range repulsive forces due to the dipole moments of the adatoms. It has previously been shown (Langmuir, *J. Amer. Chem. Soc.*, 1932, **54**, 2822) that

$$F_M = 3{\cdot}34\sigma^{5/2}M^2 + 1{\cdot}53 \times 10^{-5}\sigma^2 T^{1/3} M^{3/4} I \quad . \quad . \quad . \quad . \quad (55)$$

where I is an easily determined integral whose numerical value can never exceed 0·89 and which is less than 0·2 for $\theta > 0{\cdot}3$.

The value of F_M calculated in this way from M and indirectly from the electron emission is given in col. 8, while the value of F_s calculated from the known value of F, by equation (54), is in col. 9.

It will be noted by comparing F_s and F_M that at low values of θ the contribution from the long-range force (F_M) is about 16 times that of the short-range forces. Above about $\theta = 0{\cdot}75$, the short-range component becomes greater than the long-range component. It is evident, therefore, that the experiments with cæsium films are particularly suitable for determining F_M at low values and F_s at large values of θ.

In the previous theories of the properties of cæsium films on tungsten (Taylor and Langmuir, 1933) it was assumed that the short-range forces together with F_0 gave contributions in accord with equation (28), corresponding to curve I in Fig. 3. These values of F_0 and F_s were then subtracted from F to obtain the values of F_M, and from these, M and V were calculated. The broken line (curve I) in Fig. 2 gives the values of V obtained in this way. In the range of θ from 0·15 to 0·5 they agreed well with the values experimentally determined from the electron emission.

The present lack of theoretical justification for the equation of state of curve I suggests that the discrepancy between curves I and II in Fig. 2 is due to incorrect values for F_s, assumed in the previous work.

A better procedure is to take the values of V in curve II and in col. 6 as being given directly by the experiments, and from these to calculate F_M and F_s in cols. 8 and 9. From $F_0 + F_s$ we can then obtain the corresponding value of $Y(\theta)$ defined by equation (29). These values, denoted $Y'(\theta)$ in the last column of Table III, are plotted in curve VII, Fig. 3. They represent the equation of state after elimination of the contribution of the long-range forces. They can thus be compared directly with the other curves, I—V in Fig. 3.

Up to $\theta = 0{\cdot}45$, curve VII coincides with curve I. The accuracy of this fit is of little significance, for it results from having used the isotherm of equation (28) for two of the components of F in constructing the lower part of the heavy-line curve in Fig. 2, a procedure justified by the agreement with the experimental values of V. Above $\theta = 0{\cdot}5$, curve VII falls consistently below curve I and approaches curve II.

Both cæsium and tungsten give body-centred cubic crystals, the lattice constant for cæsium being close to twice that of tungsten. Thus the number of sites for cæsium atoms on tungsten should correspond to $\gamma = 4$. Curve V in Fig. 3, which applies to this case, lies very close to curve I up to $\theta = 0{\cdot}4$. The agreement between curves VII and V in this range is compatible with the adsorption of cæsium atoms in definite sites in the tungsten surface.

Experiments on the mobility of cæsium adatoms on tungsten have shown (Langmuir and Taylor, *Physical Rev.*, 1932, **40**, 463; 1933, **44**, 454; Langmuir, *J. Franklin Inst.*, 1934, **217**, 555) that at low values of θ there is an energy barrier of 0·61 electron volt hindering the passage of adatoms between adjacent sites. Since the dipole moment and the heat of evaporation decrease greatly as θ increases, it appears probable that the magnitude of the barrier also decreases. Thus the difficulties in reaching high values of θ with random arrangements of adatoms when $\gamma = 4$ (illustrated in Fig. 5 for the case $\gamma = 2$) should force the atoms into positions between the fixed sites. This would account for the fact that curve VII at high values of θ departs from curve V and approaches curve II, which applies to the case where the atoms are no longer in fixed sites.

Since F_s is so much larger than F_M at high values of θ, the shape of curve VII at high values of θ should not depend greatly on the particular form of theory which has been used in calculating F_M from V. The small difference between curves VII and II in this range may be due to a slight residual effect produced by the lattice-like structure of the tungsten, or it may depend on the particular value of σ_1 used in these calculations. This value, $3{\cdot}56 \times 10^{14}$, was based upon the spacing of tungsten atoms in a 110 face of a tungsten crystal. Recent work by Johnson (*Physical Rev.*, 1938, **54**, 459), however, has raised doubt as to whether the surface of tungsten filaments consists wholly of these faces.

A further test of the theories that we have used in analysing the properties of cæsium films on tungsten is provided by measurements of the rates of evaporation, ν_p, of positive ions in accelerating fields. Thermodynamic reasoning involving the Saha equation has led (Langmuir, *J. Amer. Chem. Soc.*, 1932, **54**, 2826) to the equation

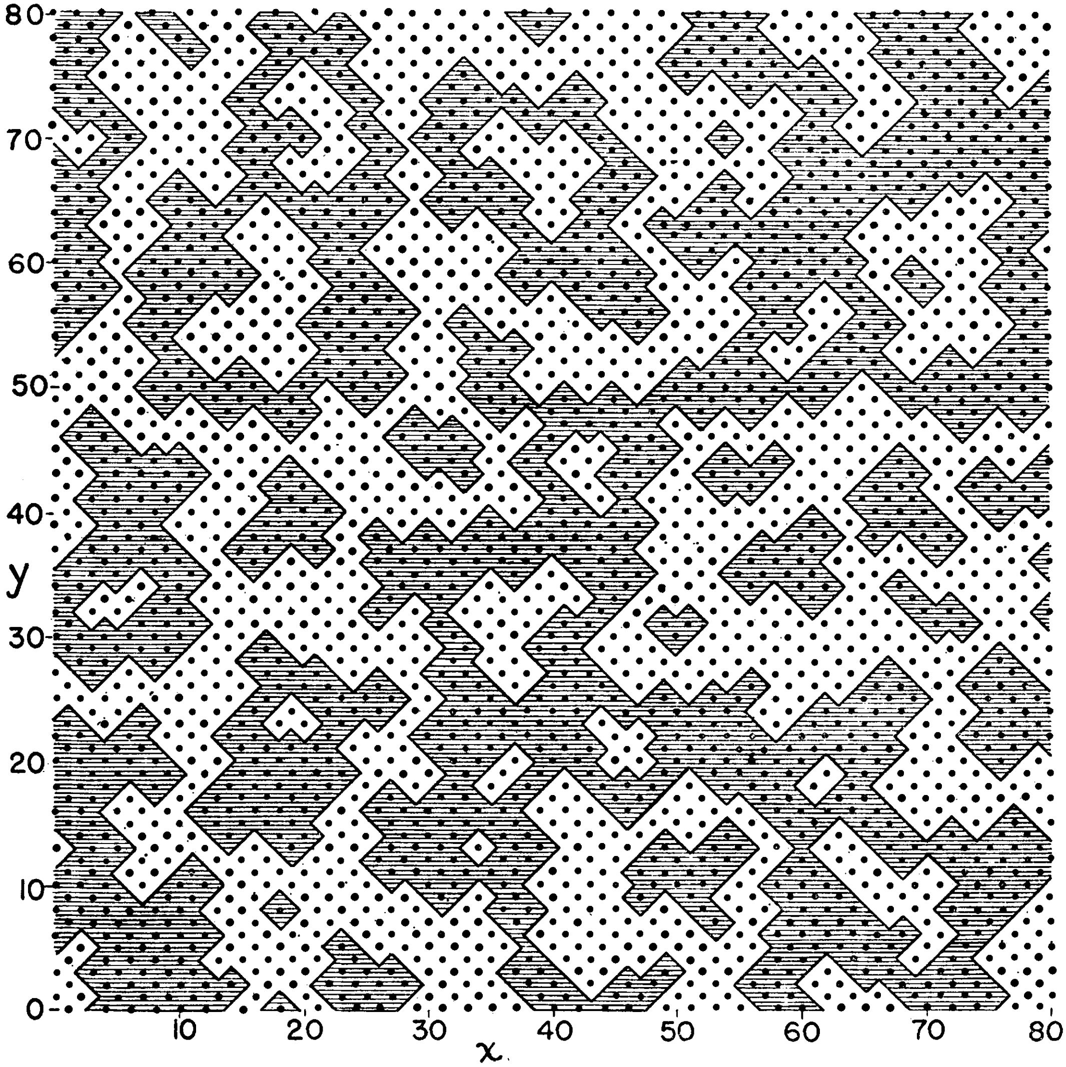
$$\ln (2\nu_p) = \ln \nu_a + (e/kT)(V_W - V_i - V) \quad . \quad . \quad . \quad . \quad (56)$$

where V_i is the ionising potential of cæsium (3·874 volts), and V_W is the energy of evaporation of electrons from tungsten (4·622 electron volts). Thus from the data for ν_a and V in cols. 2 and 6 of Table III it is possible to calculate, for any given value of θ, the corresponding value of ν_p. The five points marked by crosses on the lower part of the curve in Fig. 2 were determined by the converse process of substituting into equation (56) experimental values of ν_p and ν_a and solving the equation for V. The good agreement with the values found by the entirely independent method involving measurement of electron emission gives strong support to the theory.

Slow Approach to Final Equilibrium at High Pressures when $\gamma = 2$.—Fig. 5 illustrates a typical arrangement of adatoms on a square lattice for the case $\gamma = 2$ when atoms have been added to the surface until a state approaching pseudosaturation has been reached, with $\theta_L = 0{\cdot}26$.

Fig. 6 shows, on a much smaller scale, a larger surface which has been subjected to prolonged equilibration, sufficient to bring θ_L from its usual initial value of about 0·27 down to 0·20. The pressure is assumed to be so high that no appreciable number of free sites are present. The black dots in this figure denote adatoms, but the sites are not marked. The even and odd phases are represented by the hatched and unhatched areas respectively.

Fig. 6.



Typical arrangement of adatoms on a square lattice after partial equilibration, $\gamma = 2$, E = 5, $d/d_s = 1{\cdot}25$, $\theta = 0{\cdot}80$.

A well-known, but unproved, mathematical theorem states that in the construction of a map, with countries of any arbitrary shapes, four colours are needed to distinguish the separate countries so that the same colour will never appear on both sides of any boundary. It is evident, since we have only two surface phases in Fig. 6, that the shapes of the boundaries of these phases are subject to some restrictions. For example, they must be such that three boundaries never meet at a point. In general, therefore, the boundaries resemble contour lines on a map forming closed curves which often enclose others.

Across any finite square region selected from a larger area there is usually a single boundary that runs from one side of the square to the opposite side, but this prevents any boundary from extending between the other pair of sides. Thus, for example, in Fig. 6 there is a boundary that starts at the lower edge at a point $x = 39$ and extends to the upper edge at $x = 51$. There is, however, no boundary running from the left- to the right-hand edge.

A mathematical study of two-phase systems of this kind has led me to some equations (not previously published) which describe the distribution and other properties of these boundaries. Consider a straight line drawn at random across a typical arrangement of two phases. Let ρ be the average number of intersections per unit of length which this line makes with the envelopes or boundaries of the phases. The changes in distribution of envelopes that are brought about by equilibration produce a gradual decrease in ρ. We shall describe a film as being in the *initial state* if it has been built up to $\theta = 0{\cdot}73$, $\theta_L = 0{\cdot}27$, $\sigma_f/\sigma_1 = 0$, by a one-way process consisting of placing adatoms one by one into free sites selected at random.

For a film in this initial state we find that $d\rho$, the probability per unit length that the straight line meets an envelope whose perimeter lies between λ and $\lambda + d\lambda$, is given by

$$\lambda \,.\, d\rho = H \,.\, d\lambda/\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (57)$$

where H is a pure number that is approximately 7. It will be convenient to express ρ and λ in terms of a_1, the unit of length, defined by equation (46), that we previously used to measure L. The actual length of an envelope, expressed in cm., is thus $a_1\lambda$. Equation (57) is applicable only to envelopes which are of sufficient size to contain large numbers of atoms; we shall see, however, that this restriction is of minor importance.

The frequency of intersection ρ between the straight line and the envelopes increases in proportion to L, the relative total length of the boundaries. We find in fact that

$$\rho = (2/\pi)L \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (58)$$

From (57) and (58), the following distribution law for envelopes of a film in the initial state can be derived:

$$N = \pi H/4\lambda^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

where N is the number of envelopes per unit area (in $a_1{}^2$ units) that have perimeters greater than λ.

Let us now subject the film to equilibration by successive removal of single adatoms, selected at random, and simultaneous return of an equal number of atoms to the surface by random choice of free sites. We shall assume that the pressure is so high that $\sigma_f \ll \sigma_1$. A measure of the amount of the equilibration is given by a quantity η, which may be defined as the ratio of the number of atoms removed from any given area A to the total number of atoms, σA, present on the same area, this latter number being kept constant by replacing as many atoms as are removed.

The mechanism of the slow shifts in the positions of the envelopes that cause the gradual shortening of the perimeters can be understood by examination of Figs. 5 and 6. The closed broken lines that form the envelopes have a number of external and internal corners, but the number of external corners must always be 4 more than the number of internal corners. For example, the envelope containing 18 adatoms that surrounds the hatched area about the point having co-ordinates (20, 40) in Fig. 6 has 7 external and 3 internal corners; its perimeter is $\lambda = 24$.

The removal of an adatom from an external corner gives two free sites, one belonging to each of the surface phases. In all other cases, however, only one site is made free. Whenever an atom is removed from an external corner there is thus a 50% chance that, by the filling of the resulting free sites, there will be a transfer of an adatom from the internal to the external phase. Since each envelope has 4 more external than internal corners, there is a constant tendency for adatoms to escape from any envelope.

Let us consider a particular envelope which in its initial state had a perimeter λ_0. Analysis shows that during the course of equilibration the perimeter λ decreases in accord with the equation

$$\lambda^2 = \lambda_0{}^2 - 2\epsilon^2\eta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

where ϵ^2, the ratio of λ^2 to the number of adatoms within a completely filled envelope, is approximately 36.

From (60) we can now determine the distribution function for envelopes during equilibration :

$$N = \pi H/4(\lambda^2 + 2\epsilon^2\eta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (61)$$

where N is the number of envelopes per unit area which have perimeters greater than λ.

These equations enable us to calculate L, the total length of the perimeters of all the envelopes per unit area. From this, by equation (47), we obtain

$$0_L = \pi^2 H/16\epsilon(2\eta)^{1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (62)$$

The total number of envelopes per unit area obtained by putting $\lambda = 0$ in (61) is

$$N_0 = \pi H/8\epsilon^2\eta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (63)$$

and the average perimeter of the envelopes (L/N_0) is

$$\lambda_{\text{av.}} = \pi\epsilon(\eta/2)^{1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (64)$$

Thus the average length of the perimeters increases with the square root of η, the amount of equilibration, while the total length of the envelopes decreases because of the more rapid decrease of their number.

From (62) and (47), by introducing the numerical values $H = 7$ and $\epsilon = 6$, we obtain

$$\eta = 0{\cdot}26/(1 - \theta)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (65)$$

an expression which applies to the slow changes in θ during equilibration when $\gamma = 2$ and the pressure is so high that the film is in a state of pseudosaturation. Thus the rate of approach to the final state ($\theta = 1$), which can be measured by $d\theta/d\eta$, varies as $(1 - \theta)^3$.

With adatoms which occupy a still greater number of sites, *i.e.*, when $\gamma > 2$, it is probable that saturation is even more difficult to attain and that the exponent of $(1 - \theta)$ in equation (65) should have some integral value greater than 2.

From our definition of η as a measure of the degree of equilibration, this quantity must increase in proportion to the time t, but we need now to examine its dependence on pressure. If atoms from the gas phase pass directly into free sites during equilibration, then the condensation coefficient α, in accord with equation (12), should vary in proportion to σ_f. Therefore η should depend upon the product $p\sigma_f$ and by equation (41) should be nearly independent of pressure if this is high enough to bring about pseudosaturation.

If, as was found for the condensation of cæsium on tungsten, the value of α is higher than that given by (12), the mechanism of equilibration must involve a low concentration of mobile atoms in a second adsorbed layer. It is also probable that surface mobility of the adatoms in the first layer contributes to the rate of equilibration.

Thus by hopping to an adjacent site it is possible for an adatom of one surface phase, if the atom is located at an external corner of the envelope of that phase, to pass into the other phase. For example, by Fig. 5 we see that the atom of the odd phase at $(x, y) = (8, 11)$ can pass into the even phase by hopping into the adjacent site at (8, 10). Let τ_K be the average life associated with this process, *i.e.*, τ_K is the average time that elapses before an adatom located at an external corner passes into the adjacent available site. Mechanisms of these types have been considered in some detail in connection with cæsium films on tungsten (Taylor and Langmuir, *Physical Rev.*, 1933, **44**, 423; see particularly pp. 455—458). Using the concepts and nomenclature there introduced, we obtain

$$\eta = (2t/\tau_0)(\tau_2/\tau_D + \tau_0/\tau_K) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (66)$$

where τ is the life of an isolated adatom in the first layer before the atom evaporates, τ_2 is the corresponding life for an isolated atom in the second layer, and τ_D is the average time that elapses before an atom in a given site in the second layer passes to an adjacent site (τ_D determines the surface diffusion coefficient of atoms in the second layer). The lives τ_0, τ_2, and τ_D do not depend upon pressure. There is, however, some reason to believe (see Langmuir, *J. Franklin Inst.*, 1934, **217**, 556, eqn. 24) that $1/\tau_K$ should increase slowly with pressure (linearly with log p). Thus surface mobility of adatoms in the first layer, if appreciable, should tend to make η increase slightly with pressure.

Similar calculations for the case $\gamma = 1$ (hyperbolic adsorption isotherm) show that the relaxation time τ for the rate of return of θ to equilibrium after a small disturbance is

$$\tau = \tau_0(1 - \theta)(1 - \theta + \tau_D/2\tau_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (67)$$

If τ_D/τ_2 can be neglected, this result means that the rate of approach to equilibrium varies in proportion to the square of the pressure; otherwise it varies with the first power of p. Equation (67) applies also to disturbances from a state of pseudoequilibration if we replace θ by $1 - \theta_L$ in accord with equation (47). A comparison of (67) and (65) shows a striking difference between the cases $\gamma = 1$ and $\gamma = 2$ in regard to the way the rate of approach to the final state depends upon θ. In the first case ($\gamma = 1$) the rate increases with pressure and *rises* rapidly as θ approaches 1, but in the second case ($\gamma = 2$) the rate is much slower, is nearly independent of pressure, and *decreases* rapidly as θ approaches 1.

The peculiar features that characterise adsorption in the case $\gamma = 2$ bear a close resemblance to those of many types of activated adsorption that have been reported recently.

At sufficiently low temperatures the so-called permanent gases, hydrogen, nitrogen, argon, etc., are adsorbed on surfaces by van der Waals forces. This kind of adsorption, which we shall call Type I, is characterised by rapidity and the relative ease with which saturation is attained. When the temperature is raised this adsorbed gas evaporates, but in some cases at a much higher temperature it is slowly readsorbed. With this kind of activated adsorption it is almost impossible to reach definite saturation. This distinction between van der Waals and activated adsorption was pointed out for the cases of carbon monoxide on platinum (Langmuir, *J. Amer. Chem. Soc.*, 1918, **40**, 1361, see especially p. 1399) and later for hydrogen, oxygen, and carbon monoxide on platinum (*idem, Trans. Faraday Soc.*, 1921, **17**, 607, 621). Taylor and others (*J. Amer. Chem. Soc.*, 1931, **53**, 578) have studied in detail many cases of activated adsorption.

From measurements of the adsorption of hydrogen by copper powder at temperatures from 25° to 200° c., Ward (*Proc. Roy. Soc.*, 1931, *A*, **133**, 506) concludes that this adsorption, which according to Taylor is of the activated type, takes place in two distinct steps, which we shall describe as being of types II and III. The introduction of gas gave an almost instantaneous adsorption (type II) of part of the gas, followed by a very slow adsorption (type III) which increased in proportion to the square root of the time, and thus did not give any definite saturation. The rate of type III adsorption was only very slightly dependent on the gas pressure. When during this slow adsorption the pressure was decreased in the ratio 2 : 1, there was a nearly instantaneous decrease in the amount of gas adsorbed, but the slow adsorption continued unchanged. Ward contends that the type III adsorption is caused by *solution* of the gas in the bulk metal, or in fissures (?), but Taylor (*Trans. Faraday Soc.*, 1932, **28**, 131) gives reasons for believing that it represents merely a continuation of the type II process.

Blodgett and Langmuir (*Physical Rev.*, 1932, **40**, 78) found two distinct types of true activated adsorption of hydrogen on tungsten filaments and proved that neither type involves solution in the metal.

Benton and White (*J. Amer. Chem. Soc.*, 1930, **52**, 2325; 1932, **54**, 1373, 1820) and Benton (*Trans. Faraday Soc.*, 1932, **28**, 202) recognise these three types in interpreting experiments on the adsorption of hydrogen and carbon monoxide by powders of copper, iron, or nickel. They find that the amount of gas taken up by the type III adsorption never exceeds that of type II, and they note that " in no case examined does solubility (type III adsorption) make its appearance until temperatures are reached at which there is a pronounced activated adsorption " (type II). A typical example is cited in which a given amount of iron powder instantly and reversibly adsorbed 3·0 c.c. of hydrogen at −195° c.

and 40 mm. pressure (type I). At $-78°$ c. only 0·05 c.c. was adsorbed at this pressure. At 0° c., 0·3 c.c. was taken up immediately, but a slow adsorption continued at a decreasing rate, giving a total adsorption of 3·28 c.c. in 35 days without signs of approach to a limiting value. At this time a quick change of temperature to 110° c. gave an *immediate release* of 1·22 c.c., but then during the next three days, 0·41 c.c. of gas was slowly *taken up*. These phenomena led Benton and White to believe that two different adsorption processes are " conclusively shown." They attribute type III to solution of gas in the metal, but are careful to state that it " may well be a second type of activated adsorption."

Taylor and Ogden (*Trans. Faraday Soc.*, 1934, **30**, 1178), in studies of the rate of adsorption of hydrogen and carbon monoxide by zinc oxide, find an instantaneous, followed by a slow adsorption varying approximately with the square root of the time and not appreciably dependent on pressure. They do not attribute this type III adsorption to solution.

The fact that the observed adsorption of type III is usually of the same order of magnitude as, although always less than, the type II adsorption, is strong evidence that solution in the metal is not involved; for otherwise we should expect, by suitable choice of the substrate metal or method of preparation of the powder, to obtain wide variations in the ratio of type III to type II.

The striking difference in the rates of adsorption characterising types II and III has sometimes been attributed to a non-homogeneous surface, some parts of which bind adsorbed molecules much more firmly than others. Such effects should be associated with decreases in the heat of adsorption, Q, as θ, the amount of adsorbed gas, increases. Changes of this kind in Q have sometimes been found, but in other cases which give characteristic adsorption of types II and III, no dependence of Q on θ has been observed (Ward, *loc. cit.*; Maxted and Hassid, J., 1931, 3313).

If we compare the observed characteristics of type III adsorption with those deduced theoretically for adsorption on crowded lattices (*i.e.*, when $\gamma > 1$), we find such striking similarity that we are led to suspect that in many cases adsorptions of type III and type II differ essentially only because of a crowding of adatoms which requires complicated rearrangements before a close-packed state can be reached. In particular, attention may be called to the relatively high rate of adsorption up to a rather definite point where $\theta = 1 - \theta_L$, by equation (47), followed by a rapidly established pseudoequilibrium with a slow upward drift in θ due to the gradual decrease in θ_L, equation (62), accompanying the redistribution of surface phases. By the postulates of our theory, the heat of adsorption is the same at high and at low values of θ. The marked decrease in the rate of adsorption at high θ is associated with the low entropy that results from the overcrowding of the lattice.

Several investigators have obtained approximately linear relationships between q, the amount adsorbed, and $\sqrt{t}$; but often the curves, with q as ordinate, show gradually decreasing slopes. Since, of course, there must be a limit to the amount of gas that can be adsorbed, the square-root law cannot apply for indefinitely large values of t. Let us examine some of these experimental data to see if the rates vary in proportion to the cube or some higher power of $(1 - \theta)$, in accord with equation (65).

Maxted and Moon (*Trans. Faraday Soc.*, 1936, **32**, 1375) found that 1 g. of platinum-black at 20° c. adsorbs 0·40 c.c. of ethylene within the first 5 minutes, and that this amount increases to only 0·70 c.c. after 1316 mins. Their results are accurately expressed by the equation $q = 0{\cdot}385 + 0{\cdot}0086\sqrt{t-2}$. It is also possible, however, to represent their data within the same time interval by

$$1/(1{\cdot}00 - q)^2 = 2{\cdot}95 + 0{\cdot}0054t \quad . \quad . \quad . \quad . \quad . \quad . \quad (68)$$

with a mean error of 0·010 c.c., which is probably within the experimental error, since only two significant figures are used in recording the data. This equation, which is based upon equation (65), shows that the limiting value of q is 1·00 c.c.; to reach 0·90 c.c. would require 12·5 days, and for 0·99 c.c. 3·3 years are needed.

Taylor and Strother (*J. Amer. Chem. Soc.*, 1934, **56**, 586), in studying the kinetics of the adsorption of hydrogen by zinc oxide at six temperatures between 0° and 302° c., observed three types of adsorption, I, II, and III. If the data for q are plotted against $\sqrt{t}$, lines are obtained which are fairly straight in the range $t = 5$—25 mins., but above that the slopes gradually decrease. However, when the cube roots of the rates of adsorption, *i.e.*, $(dq/dt)^{1/3}$, are plotted against q, straight lines are obtained whose intercepts on the q-axis give the limiting value of q for $t = \infty$. Thus all these data are well expressed by equations of the type of (65). For example, the data at 0° c. give $q = 2{\cdot}58$ c.c. after 5 mins. and $q = 4{\cdot}23$ c.c. at 400 mins., and the whole curve is represented by

$$1/(5{\cdot}00 - q)^2 = 0{\cdot}15 + 0{\cdot}0047t$$

within an average error of 0·027 c.c. Thus, in these experiments during the slow type III adsorption, θ increased from 0·52 to 0·84.

With activated adsorption on powdered or porous substrates one would perhaps hardly expect to find conditions that conform with those that we have postulated in our theory of adsorption on crowded plane lattices. However, the hyperbolic isotherm, originally derived for plane surfaces, has often been found to apply well to powdered substrates. When therefore we find empirically examples of type III adsorption which are in accord with equation (65), we may at least suspect that they represent cases of adsorption on overcrowded lattices. The postulates underlying the theory are in no way incompatible with activated adsorption. In fact, it is just in the case of activated adsorption, as contrasted with van der Waals adsorption, that we should find strong forces that bind atoms or molecules in definite sites in the surface.