UNIVERSAL
LIBRARY

OU_150602

UNIVERSAL
LIBRARY

Osmania University Library

Call No. 533.1/R645 Accession No. 20401

Author Roberts, J.K.

Title Some problems in adsorption.

This book should be returned on or before the date last marked below.

Cambridge Physical Tracts

GENERAL EDITORS

M. L. E. OLIPHANT, PH.D., F.R.S.
Professor of Physics in the University of Birmingham

J. A. RATCLIFFE, M.A.
Lecturer in Physics in the University of Cambridge

SOME PROBLEMS IN ADSORPTION

CAMBRIDGE
UNIVERSITY PRESS
LONDON: BENTLEY HOUSE
NEW YORK, TORONTO, BOMBAY
CALCUTTA, MADRAS: MACMILLAN
TOKYO: MARUZEN COMPANY LTD

All rights reserved

SOME PROBLEMS IN ADSORPTION

by

J. K. ROBERTS

Assistant Director of Research in Colloid Science,
University of Cambridge

CAMBRIDGE
AT THE UNIVERSITY PRESS
1939

PRINTED IN GREAT BRITAIN

GENERAL PREFACE

It is the aim of these tracts to provide authoritative accounts of subjects of topical physical interest written by those actively engaged in research. Each author is encouraged to adopt an individualistic outlook and to write the tract from his own point of view without necessarily making it "complete" by the inclusion of references to all other workers or to all allied subjects; it is hoped that the tracts may present such surveys of subjects as the authors might give in a short course of specialized lectures.

By this means readers will be provided with accounts of those subjects which are advancing so rapidly that a full-length book would be out of place. From time to time it is hoped to issue new editions of tracts dealing with subjects in which the advance is most rapid.

M. L. E. O.
J. A. R.

CONTENTS

AUTHOR'S PREFACE

The idea of starting the experimental investigations described in this tract arose in the following way. Knudsen was the first to realize that, when the relevant dimensions of the apparatus used are small compared with the free path of the gas molecules, kinetic theory calculations in connexion with various transport phenomena can be carried out exactly. He performed a number of very beautiful experiments to test this view, thus making a great advance in the application of this theory, and it can fairly be said that the phenomena occurring in the gas phase were completely elucidated by his work. In dealing with the exchange of energy between a solid and a gas at a different temperature he used a quantity called the accommodation coefficient, which is a measure of the extent to which the gas molecules leaving the solid are in thermal equilibrium with it. Experimental determinations of this quantity for various gases were made by him and other workers, and Baule later worked out a straightforward classical theory of the collisions of the gas molecules with the atoms of the solid. By making some reasonable simplifying assumptions it was possible to use Baule's theory to obtain an expression for the accommodation coefficient of a given monatomic gas and a given solid which contained no arbitrary constant. The values so calculated were very much smaller than the measured values. Another point that was noticed was that, while the theory indicated that the value of the accommodation coefficient should depend on the ratio of the masses of the gas and solid atoms, the experiments showed that for a given gas the accommodation coefficient under comparable conditions was nearly the same for all the metals tried. These two results together suggested that the metals were all covered with adsorbed layers of impurity, the composition of which was of course

unknown so that any application of a mechanical theory was impossible. It was obvious then that to obtain experimental results that would be useful in testing any theory it was essential to work under such conditions that the adsorbed layers could be removed and the surface kept free from impurities. When these conditions were fulfilled the change was so striking that it seemed important to extend the investigations to as wide a range of interactions between gases and solids as was possible, and in particular to study the structure and behaviour of adsorbed films of gases built up on a known substrate. It is evident that both structure and behaviour will be profoundly affected if the film is formed not on a crystalline metal but on top of films of impurities. An account of this study forms the main part of the tract. It is hardly necessary to say that there is now no need to discuss the simple classical theory of collisions which formed the starting point of the work because this was quickly superseded by a quantum mechanical treatment.

J. K. ROBERTS

DEPARTMENT OF COLLOID SCIENCE
CAMBRIDGE
June 1939

Chapter I

EXPERIMENTAL METHODS

§ 1·1. General introduction.

The aim of the work to be described here has been to obtain experimental data which should form part of the basis of a mechanical or physical theory of the interaction between gas atoms or molecules and solids, and to develop, as far as possible, some aspects of the mechanical picture of the events occurring at the surface.

It was thought that, if any advance in our knowledge of the fundamental facts in this field was to be made, it was essential to obtain experimental results under such conditions that the natures of the gas and solid atoms concerned in any interaction were known. There is little difficulty in this as far as the gas is concerned, but with the solid special care must be taken. In general it is best to work with a metal so that all the atoms are of the same nature. At the beginning of the experiment the metal must be freed from all adsorbed films of impurities and precautions must be taken to remove all adsorbable impurities from the gas so that the surface remains clean during the course of the experiment. In addition to the fact that the gas and solid atoms are known, experiments carried out under such conditions have the advantage that the system is a comparatively simple one. On the other hand a surface covered with adsorbed films of impurity of unknown structure and composition is a highly complicated system, and it would be expected on general grounds that results of a much more fundamental character would be obtained when working with the simple than with the composite system.

Apart from this particular application of it the idea of starting with simple systems has been an essential one in the development of the work. Only in this way is it possible to build up

a detailed picture of what is happening. We are concerned with the phenomena which occur when a gas atom approaches a solid surface. It may either make a collision and rebound, an interchange of energy in general taking place, or else it may remain an appreciable time on the surface, i.e. be adsorbed. The behaviour would be expected to be simplest with helium, for here the attractive forces between gas atoms and the surface are very weak, so that adsorption effects would be practically absent except at very low temperatures, and collisions with the accompanying interchange of energy would alone be involved. In the first experiments, therefore, the interchange of energy between helium and a tungsten surface was studied. To do this the accommodation coefficient of Knudsen (1) was measured. This quantity is defined as follows. The gas atoms striking the surface of the solid (see fig. 1) are at temperature T_1. After leaving it they will not in general be in thermal equilibrium with it, i.e. they will not be at temperature T_2, but will on the average have energy corresponding to a temperature T_2'. The accommodation coefficient a is defined by the equation

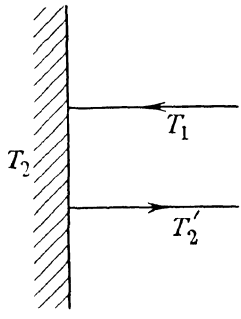

Fig. 1.

$$a=\frac{T_2'-T_1}{T_2-T_1}. \qquad (1\cdot1)$$

The details of the measurement of a and the proof that to a first approximation it is a constant will be considered below. It will be seen that, if $a=1$, the gas molecules leaving the surface are in equilibrium with it, and, if $a=0$, there is no net interchange of energy between the gas and the solid.

In previous experiments by various workers in which an ordinary wire was used, it was found that the accommodation coefficient of helium at room temperature was always about 0·3. When such precautions are taken as are necessary to ensure that

the surface of the tungsten is bare there is a striking change and a value in the neighbourhood of 0·05 or 0·06 is obtained (2). Not only is the actual magnitude of the accommodation coefficient affected but the nature of its variation with temperature is quite different. Soddy and Berry (3) found for helium with ordinary platinum wire a value of 0·28 in the neighbourhood of 20° C. and of 0·36 in the neighbourhood of −185° C. With bare tungsten on the other hand the temperature variation is shown by the points in fig. 2. The general run of these points suggests

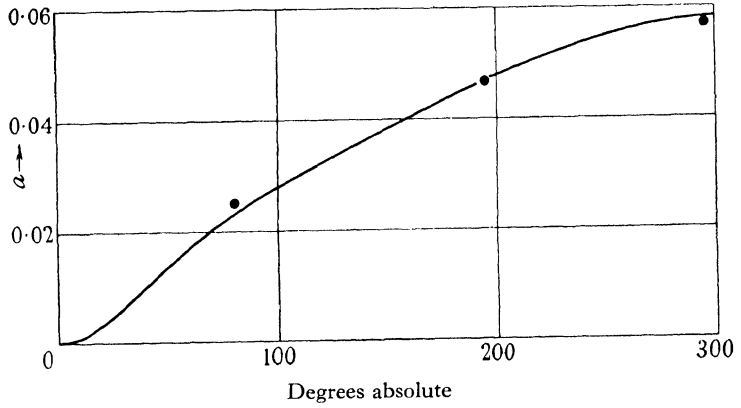

Fig. 2. Variation of accommodation coefficient of helium with temperature.

that the accommodation coefficient approaches zero as the absolute zero is approached, but no doubt the lowest parts of the curve would not be realized in practice owing to condensation of the helium on the surface.

The following (4) physical picture explains this falling off at low temperatures. To begin with, let us regard the solid as an assembly of Planck oscillators all of identical frequency ν as in Einstein's original theory of the temperature variation of the specific heat of solids. When a gas atom interacts with such an assembly, energy transfers can take place only in amounts of $nh\nu$, where n can have the values 0, 1, 2, 3, etc. At temperatures at which the mean thermal energy is smaller than $h\nu$ a considerable

number of the oscillators will be in the ground state. When a gas atom interacts with an oscillator in the ground state, the only possible interchange of energy is that in which the gas atom gives up energy to the oscillator and the smallest energy that the oscillator can take is $h\nu$. The number of gas atoms that have energy $h\nu$ to give up becomes progressively smaller as the temperature gets lower, and thus the proportion of gas atoms which can undergo a change of energy on interacting with the solid becomes smaller and smaller as the temperature approaches the absolute zero. If the solid is not regarded as an assembly of oscillators all having identical frequencies but having frequencies distributed over a range from o to ν_m, the above considerations show that at sufficiently low temperatures only the lower frequency oscillators will be appreciably affected by collisions with gas atoms. Therefore the number of oscillators so affected becomes fewer and fewer as the temperature becomes progressively lower, and as a result the interchange of energy, other things being equal, becomes less and less efficient. Thus for a small temperature difference between solid and gas the accommodation coefficient becomes smaller and smaller.

Devonshire (5), in one of a series of papers by Lennard-Jones and his co-workers, has followed up the work of Fowler and of Jackson and Mott and others (6) in developing the detailed quantum mechanical theory of collisions of gas atoms with solids. The efficiency of energy interchange between the gas atom and the oscillations of the solid depends, among other things, markedly on the masses of gas and solid atoms, which are known, and on the law of force between the gas atom and the atom of the solid. Devonshire assumes that the potential energy when their centres are at a distance z apart is given by a Morse function

$$De^{-2\kappa(z-b)} - 2De^{-\kappa(z-b)}.$$

This is plotted in fig. 3 which shows the meanings of b and of D, which is closely related to the heat of adsorption. The further constant κ determines the rate at which the repulsive potential

energy rises when the atoms are closer together than b. The greater κ is, the sharper is this rise and, other things being equal, the greater is the accommodation coefficient. For helium D is small and the curve in fig. 2 is the theoretical curve for a one-dimensional model for $\kappa = 2 \times 10^8$ and $D = 0$ multiplied throughout by a roughness factor 1·06* to make it fit the experimental point at 195° K.

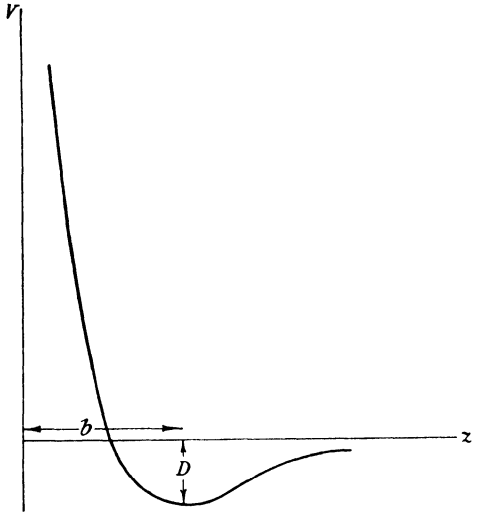

Fig. 3. Potential energy V of two molecules a distance z apart showing meaning of D and b in the Morse function.

As we have mentioned, the behaviour with helium would be expected to be simpler than with any other gas because of the smallness of D (fig. 3). The next step was to use neon for which

* Actual surfaces are never absolutely plane. The effect of any roughness is to increase the measured accommodation coefficient over that for a smooth surface, because a certain number of the gas molecules after making a collision with and leaving one part of the surface will strike it again in another place. Thus to obtain the accommodation coefficient for a smooth surface, which is what is required for comparison with the theory, the measured values at various temperatures must all be reduced by dividing by a roughness factor or equally the theoretical values can all be multiplied by the factor. The actual value of this factor cannot be known without direct observation of the shape and size of the irregularities on the surface. For a general discussion of this point see Roberts (7).

D will certainly be appreciable. This makes the curve showing the variation of a with temperature fall off less slowly than it would if D were zero, and Devonshire(5) has shown that an accurate experimental determination of the shape of this curve would make it possible to deduce the values of the constants in the Morse function. Experiments on this problem are at present under consideration. The early experiments so far carried out have determined only the relative behaviour of helium and neon but have not given the shape of the neon curve with sufficient accuracy for the above purpose. The important point about the neon results from our present point of view is the very large difference between the accommodation coefficient for a surface covered with adsorbed films (about 0·6) and for a clean surface (about 0·07). This suggests that the accommodation coefficient of neon is very sensitive to the presence of adsorbed films on the surface and that therefore it can be used satisfactorily as an indicator in studying the adsorption of gases on bare tungsten. This is the starting point of the work we shall now discuss.

§ 1·2. The measurement of accommodation coefficients.

We need consider only the accommodation coefficients of monatomic gases and are therefore not concerned with any difficulties that may arise if the accommodation coefficient for rotational energy is not the same as that for translational energy.*

Suppose that a fine wire maintained at temperature T_2 by an electric current is stretched down the centre of a cylindrical glass tube at temperature T_1 containing a monatomic gas at such a low pressure p dynes per cm.^{2} that the mean free path of the gas atoms is long compared with the radius of the tube and that the diameter of the wire is small compared with that of the tube. Under these conditions any molecule leaving the wire makes many collisions with the tube before returning to the wire again and it may be assumed that the molecules striking the wire are at the temperature T_1 of the tube. Suppose there

* For a discussion of this point see Rowley and Bonhoeffer(8).

are $f(c)\,dc$ molecules per c.c. with velocities lying between c and $c+dc$. The number of such molecules of mass m striking unit area of the wire per second is $\frac{1}{4}f(c)\,c\,dc$ and the energy brought up to unit area of the wire per second by such molecules is $\frac{1}{8}mf(c)\,c^3\,dc$. The total energy brought up to unit area of the wire per second is

$$\frac{m}{8}\int_0^\infty f(c)\,c^3\,dc.$$

Since

$$f(c)=\frac{4n}{\sqrt{\pi}}\left(\frac{m}{2kT_1}\right)^{\frac{3}{2}}e^{-\frac{mc^2}{2kT_1}}c^2,$$

where n is the number of atoms per c.c., the total energy brought up to unit area of the wire per second is

$$n\left(\frac{2k^3T_1^3}{\pi m}\right)^{\frac{1}{2}},$$

and the total number of molecules striking unit area of the wire per second is

$$n\left(\frac{kT_1}{2\pi m}\right)^{\frac{1}{2}}=\frac{p}{(2\pi mkT_1)^{\frac{1}{2}}},$$

where p dynes cm.$^{-2}$ is the pressure. The expression for the energy brought up to unit area of the wire per second may be written

$$\frac{p}{(2\pi mkT_1)^{\frac{1}{2}}}\,2kT_1.$$

Let $n_c\,dc$ be the number of molecules with velocities between c and $c+dc$ leaving unit area of the wire per second. These molecules are not in thermal equilibrium with the wire at temperature T_2 but have mean energy corresponding to a temperature T_2'. Their distribution of velocities will not therefore be strictly Maxwellian but the departure from such a distribution becomes smaller as T_2-T_1 becomes smaller.* We assume a Maxwellian distribution so that

$$n_c=Ac^3e^{-\frac{mc^2}{2kT_2'}}.$$

* For a discussion of this see Knudsen(1).

The total number of molecules leaving unit area of the wire per second is

$$\int_0^\infty n_c dc = A\frac{2k^2T_2'^2}{m^2}.$$

In the steady state the number of molecules leaving unit area of the wire per second must equal the number striking it so that

$$A\frac{2k^2T_2'^2}{m^2} = \frac{p}{(2\pi mkT_1)^{\frac{1}{2}}}.$$

This condition determines the constant A. The energy carried away from unit area of the wire per second is

$$\frac{Am}{2}\int_0^\infty c^5 e^{-\frac{mc^2}{2kT_2'}} dc = 4A\frac{k^3T_2'^3}{m^2} = \frac{p}{(2\pi mkT_1)^{\frac{1}{2}}} 2kT_2',$$

and the difference between the energy carried away from unit area of the wire per second and the energy brought up to it or the net energy loss in ergs per unit area per second is

$$\frac{p}{(2\pi mkT_1)^{\frac{1}{2}}} 2k(T_2' - T_1),$$

where k is in ergs, etc. Using equation (1·1), this becomes

$$\frac{ap}{(2\pi mkT_1)^{\frac{1}{2}}} 2k(T_2 - T_1) \text{ ergs per cm.}^2 \text{ per sec.},$$

or

$$\frac{7{\cdot}3 \times 10^3 ap(T_2 - T_1)}{(MT_1)^{\frac{1}{2}}} \text{ ergs per cm.}^2 \text{ per sec.},$$

where M is the molecular weight referred to $O_2 = 32$ and p is the pressure in dynes per cm.^{2} The heat loss q in calories per cm.^{2} per second is therefore given by

$$q = 1{\cdot}74 \times 10^{-4} \frac{ap}{\sqrt{MT_1}}(T_2 - T_1). \qquad (1{\cdot}2)$$

All the quantities in this equation except a can be measured and thus a is determined. The wire is placed in one arm of a Wheatstone bridge. q is obtained by measuring the current through the bridge and the temperature excess of the wire

$T_2 - T_1$ is found from its resistance. The pressure is measured on a Macleod gauge. It must be shown experimentally that the value of a obtained does not depend on p or on $T_2 - T_1$. The fact that this last condition is fulfilled establishes the correctness of the assumptions on which equation (1·1) is based.

Actually it is not necessary to work at such low pressures that the free path λ is long compared with the radius of the containing tube, but it is sufficient that λ should be long compared with the diameter of the wire. Molecules leaving the wire on the average travel a distance λ before making a collision and then make many collisions with other gas molecules before returning to the wire. The passage of the heat from a circle of radius λ to the outside of the tube may be treated as ordinary gas conduction. Simple numerical calculations show that the temperature drop in the gas is small compared with the temperature difference between the wire and the gas at a distance λ from it.* Thus the molecules striking the wire can be taken as being at the temperature T_1 of the outer tube. The above theory is the same as that first given and tested by Knudsen (1).

In order to be able to measure the accommodation coefficient for a bare surface and to study the adsorption of known gases on such a surface it is necessary to work under carefully controlled conditions and the essential parts of the apparatus that has been used for this purpose are shown in fig. 4. The tungsten wire of diameter 0·0066 cm. and about 18 cm. long was contained in the tube A. The neon was continuously circulated by a diffusion pump through the charcoal tubes B immersed in liquid air to remove from it any adsorbable impurities coming from the glass. There were liquid air traps between the charcoal tubes and the rest of the apparatus and two liquid air traps between the tube containing the wire and the Macleod gauge. All the usual precautions necessary for obtaining the best vacuum were taken.

After the neon at a pressure of about 0·1 mm. of mercury had

* See for example Blodgett and Langmuir (9).

circulated for some time, the wire, which had previously been thoroughly outgassed, was heated to a temperature well above 2000° K. so as to remove all adsorbed impurities from its surface. It was connected to a Wheatstone bridge and, when it had cooled down, a measured current was passed through it

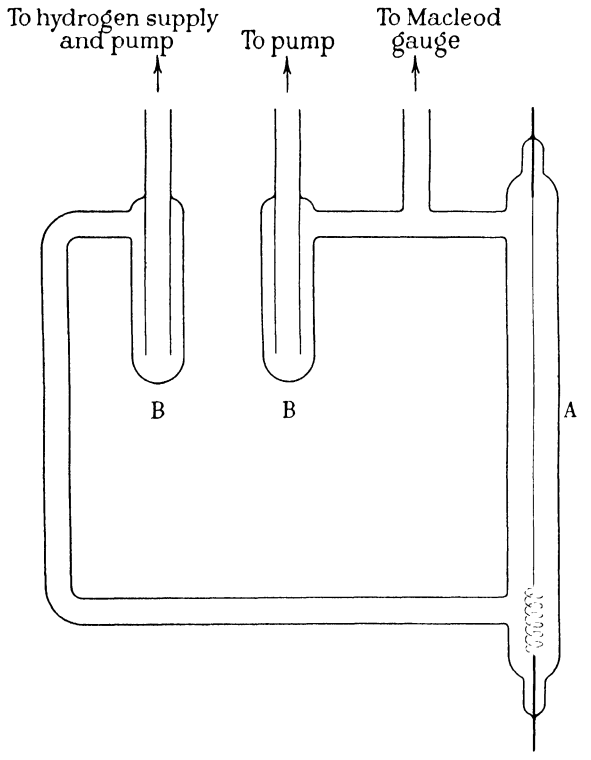

Fig. 4. Apparatus for measuring accommodation coefficients.

sufficient to raise its temperature about twenty degrees above that of the oil bath in which the containing tube was immersed. Taking the time of starting the experiment as the moment when the flashing current was cut off, readings of resistance as a function of the time were taken and the pressure was read on the Macleod gauge. After the temperature coefficient of

resistance for the wire had been determined it was possible to deduce from each reading a value of the accommodation coefficient.* These values are plotted in the first part of the curves of fig. 5 which refer to experiments at 295° K. and 79° K. They show a very slow drift with time, presumably due to the adsorption on the wire of very small residual traces of impurity in the neon. Extrapolation to zero time gives the accommodation coefficient for a clean wire.† At the time indicated by the arrow

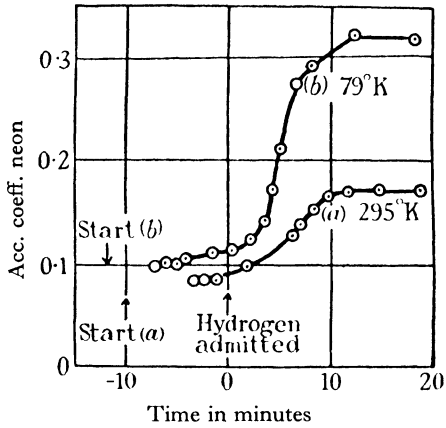

Fig. 5. Effect on accommodation coefficient of neon of admitting a trace of hydrogen, when the tungsten surface is clean.

one dose of hydrogen contained between two taps forming a gas pipette and sufficient to produce a pressure of about 10^{-4} mm. of mercury in the apparatus was admitted so that it had to pass through a charcoal tube before reaching the wire. The accommodation coefficient rose rapidly to a final steady value. This indicates adsorption of the hydrogen on the tungsten. The final steady value was not affected if very much larger doses of hydrogen were admitted which suggests that a complete monomolecular layer is formed even when the hydrogen is present

* For the correction for radiation and end losses see Roberts(2).

† See Roberts(10), footnote on p. 447, and Michels(11).

at a partial pressure of only 10^{-4} mm. of mercury, and this view is completely confirmed by the experiments of a different kind described in the next section. To show that the effects observed were not due to the adsorption of traces of oxygen in the hydrogen the experiments were carried out admitting, instead of hydrogen, the same volume of air at the same pressure as the hydrogen. No trace of the phenomena described above was observed; this means that the charcoal tubes were able to remove completely this relatively very large amount of oxygen.

Blodgett and Langmuir(9) had previously measured the accommodation coefficient of hydrogen with a tungsten surface. Their experiments showed certain changes in the accommodation coefficient according to the heat treatment of the wire and they interpreted these as due to changes in an adsorbed film of hydrogen on the surface. The present experiments show conclusively that their view that a hydrogen film is formed on a bare tungsten surface is correct.

The rapid adsorption of hydrogen on tungsten occurs only when the surface of the metal is bare, and earlier workers,* using tungsten powder and the usual methods of cleaning such powders, did not observe it, from which it must be concluded that these methods do not in fact produce a bare metal surface at all. In this connexion some results obtained by Burdon(13) are of interest. He has shown that, when a new surface of mercury is formed in the presence of hydrogen at a pressure of 400 mm. of mercury, a monomolecular film of the gas is adsorbed on the surface and held tenaciously, the rate of loss being inappreciable when the pressure is reduced to 2×10^{-4} mm. If on the other hand the new surface is first formed in a vacuum and hydrogen then admitted, no such adsorption occurs, presumably because the surface is immediately contaminated. It is a striking fact that this rapid adsorption of hydrogen occurs on two metals so different as tungsten and mercury provided

* For example Frankenburger and Hodler(12). For a discussion of the earlier work see Roberts(10).

the proper precautions are taken to expose a bare surface to the gas, but that in the absence of the necessary precautions no appreciable adsorption is observed in either case.

It is important to investigate as fully as possible the properties of the hydrogen film and films of other simple gases on tungsten and any other metal that can be cleaned satisfactorily. An understanding of these simplest systems is fundamental to our knowledge of the nature of adsorption processes in general.

§ 1·3. The measurement of the heat of adsorption.

The experiments on the accommodation coefficient indicate that a complete monomolecular film is formed at a very low pressure of hydrogen. This, and the fact that the adsorption takes place rapidly, suggests the possibility of measuring the heat of adsorption on a single fine wire. It is of course necessary to use a wire or fine strip if it is to be cleaned before the hydrogen is admitted to it.

The idea underlying the method was that the wire on which the adsorption took place should itself form the calorimeter. There is a great advantage in having the heat liberated just where it is wanted, and in knowing the apparent area of the surface on which adsorption takes place. The thermal capacity of the wire is known from its diameter and length (in the actual experiment these were 0·0066 and 28·2 cm. respectively) and the density and specific heat of the material of which it is made are also known. If its mean rise of temperature when the adsorption takes place can be measured, the total heat given out by the adsorption process is obtained.

The apparatus(10) is shown in fig. 6. The wire was contained in a tube *W* protected from mercury and other vapours by liquid air traps. This tube, and the tube *G* containing a Pirani gauge, were immersed in a large Dewar vessel filled with oil The necessary small amount of hydrogen was obtained by expanding one charge of the gas pipette *P*, which was connected to the hydrogen reservoir, into a large volume *B* (not shown), and then

admitting to the part of the apparatus containing the wire the amount of this expanded gas contained in the small volume A between the two mercury cut-offs.

The actual experimental procedure in its simplest form was as follows:

(i) The wire was flashed and, when the flashing current was cut off, it was connected to a sensitive bridge in which a Paschen galvanometer was used. As the wire cooled down the galvano-

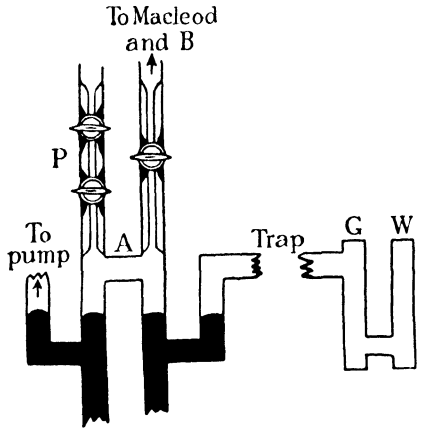

Fig. 6. Apparatus for measuring heat of adsorption of hydrogen.

meter showed a drift with time. After about 10 min. this drift was sufficiently slow to be easily followed and controlled by altering one of the other arms of the bridge. When this stage was reached the apparatus was cut off from the pumps, the hydrogen charge was prepared, and regular readings of the galvanometer deflexion and time were taken. The hydrogen in A was then admitted to the apparatus, and the galvanometer showed a deflexion in the direction corresponding to a rise in the temperature of the filament as shown in fig. 7. The time of admission, the maximum reading, and the time of its occurrence were noted. The deflexion of the Pirani gauge was read at the

same time. The hydrogen was now pumped out, and the deflexion of the Pirani gauge measured as a check.

(ii) The volume A was then refilled from B so that the pressure in it was practically the same as in (i). This hydrogen was admitted to the evacuated apparatus without flashing the wire. The deflexion of the Pirani gauge was measured and was greater than for the same amount of hydrogen in (i) because

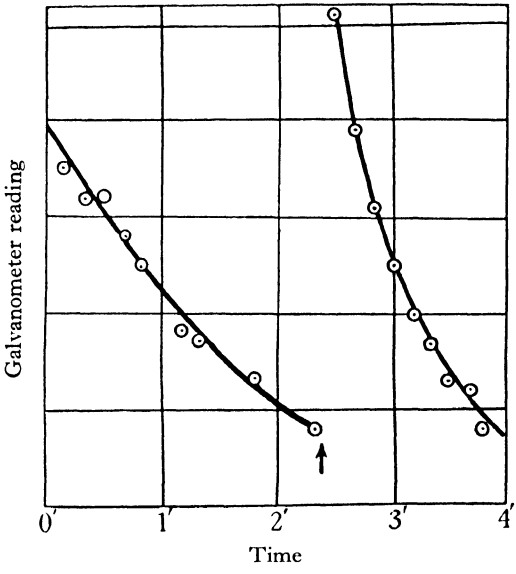

Fig. 7. Effect of heat of adsorption of hydrogen in raising the temperature of a bare tungsten filament.

there was no adsorption on the unflashed wire. At the same time it was observed, as would be expected, that there was practically no deflexion of the Paschen galvanometer. The Pirani gauge was calibrated by diminishing the bridge sensitivity in a known ratio and comparing the gauge directly with a Macleod gauge.

Provided the volume of the apparatus is known, the Pirani gauge readings give directly the amount of gas adsorbed on the

wire in (i). The volume was determined in the ordinary way by expanding air at a few cm. pressure from a measured volume into the apparatus, and measuring the pressure change.

To obtain the temperature rise of the filament from the readings a correction had to be made for the cooling during the time when the deflexion was occurring. This correction, which was small and never more than about 10 per cent of the total deflexion, was obtained in the usual way by a study of the slope of the temperature-time curve at different points. The change of resistance corresponding to a given deflexion was obtained by altering by a small known amount a large shunt in the opposite arm of the bridge, the resistance of which was equal to that of the filament. The temperature change was deduced from the temperature coefficient of resistance of the tungsten as determined in an independent experiment. The heat evolved in the adsorption process is given by $msAT$, where m is the mass of the wire, s the specific heat, and AT the rise of temperature.

The above description gives the principle of an experiment which determines the average heat of adsorption when the surface was fully covered at the end of the experiment. This procedure was not followed exactly, but the amount of hydrogen admitted in one charge of A was made less than was necessary to cover the surface completely. When the first charge was admitted there was a heating effect, but there was no pressure change sufficient to be indicated on the Pirani gauge (that is, it was less than 2 or 3×10^{-7} mm.). Thus even at these low pressures adsorption was complete and rapid. Charge after charge was admitted, and the heating effect measured each time. Finally, when saturation was reached, the Pirani gauge showed a deflexion, and from this it was possible to deduce the amount admitted at each charge and so to obtain the variation of heat of adsorption as the surface became progressively more covered.

§ 1·4. The amount of hydrogen adsorbed on tungsten.

We shall first consider the number of molecules adsorbed and the number of tungsten atoms in the surface. It has been usual following Langmuir(14) to assume that with aged tungsten the 110 plane is the important one in the surface, but R. P. Johnson(15) has shown that this is not necessarily correct and that the 100 plane must also be considered. Tungsten is a body-centred cubic lattice and the arrangements of the atoms in these two planes are shown in fig. 8. The numbers of atoms per cm.^{2} are for the 110 plane $14{\cdot}24 \times 10^{14}$ and for the 100

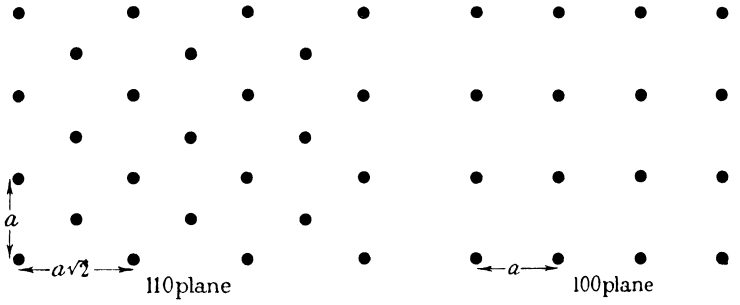

Fig. 8. Arrangement of atoms in surface planes of tungsten. $a = 3{\cdot}15 \times 10^{-8}$ cm.

plane $10{\cdot}07 \times 10^{14}$. The effective apparent superficial area of the filament was 0·55 cm.^{2} after correcting for short lengths at the ends, which during the flashing were below 2000° K., and which therefore would not be completely freed from any adsorbed oxygen and would not therefore be available for the adsorption of hydrogen. Thus, if the wire were smooth, the number of tungsten atoms in the surface would be $7{\cdot}8 \times 10^{14}$ for the 110 plane and $5{\cdot}5 \times 10^{14}$ for the 100 plane. If the surface is not smooth, we have to multiply these numbers by a factor ρ which is greater than unity.

The total numbers of molecules adsorbed in five independent experiments were respectively 4·2, 4·4, 4·3, 3·3 and $3{\cdot}8 \times 10^{14}$ respectively. We take the largest $4{\cdot}4 \times 10^{14}$ as being nearest to

the correct value and assume that the lower values are due to slight contamination of the wire before the hydrogen was admitted. We compare this with what would be expected for different types of adsorbed film on an area of 0·55 cm.^{2} We shall consider three types:

(*a*) If the hydrogen were adsorbed as undissociated molecules with one molecule for each tungsten atom, the total number of molecules adsorbed would be $\rho \times 7{\cdot}8 \times 10^{14}$ for the 110 plane and $\rho \times 5{\cdot}5 \times 10^{14}$ for the 100 plane.

(*b*) If the hydrogen were adsorbed as undissociated molecules and if the occupation of a given site made it impossible for any of the four neighbouring sites to be occupied, the number of molecules adsorbed would be $\rho \times 3{\cdot}9 \times 10^{14}$ for the 110 plane and $\rho \times 2{\cdot}75 \times 10^{14}$ for the 100 plane.

(*c*) If the hydrogen were dissociated on adsorption and if there were one atom for each tungsten atom in the surface, the number of adsorbed molecules would be $\rho \times 3{\cdot}9 \times 10^{14}$ for the 110 plane and $\rho \times 2{\cdot}75 \times 10^{14}$ for the 100 plane.

A reasonable value of ρ can be taken as somewhere between 1 and 2. Thus for either type of surface plane both (*b*) and (*c*) are in accord with the experimentally determined number of adsorbed molecules. It should be mentioned here that we shall see in sections 3·1 and 5·3 that the numbers in (*b*) should be reduced by about 20 per cent and those in (*c*) by about 8 per cent.

It is usually assumed that hydrogen adsorbed on metals is either held by van der Waals forces in the molecular form or else dissociated and the two atoms held separately by chemical forces, and Lennard-Jones[16] has considered this point of view in detail. The high heat of adsorption discussed in the next section and the stability of the film show that here we have to do with chemisorption and we shall assume as a working hypothesis that it is (*c*) or adsorption with dissociation that occurs. The possibility of (*b*), i.e. the chemisorption of undissociated molecules, cannot be excluded by these experimental results, but its occurrence is unlikely. This process will be discussed in

chapter v. One of the main objects of future work must be to decide whether (*b*) or (*c*) is the actual process, particularly for other gases.

In connexion with (*c*) it can be seen from fig. 8 that, for both the 110 and the 100 planes, each site for adsorption has four nearest neighbours and that no two neighbours of a given site are neighbours of each other. The importance of this will be seen in section 2·3.

§ 1·5. Variation of heat of adsorption of hydrogen on tungsten with fraction of surface covered.

We assume that in the final film $4{\cdot}4 \times 10^{14}$ molecules are adsorbed and that variations in the amount adsorbed in different

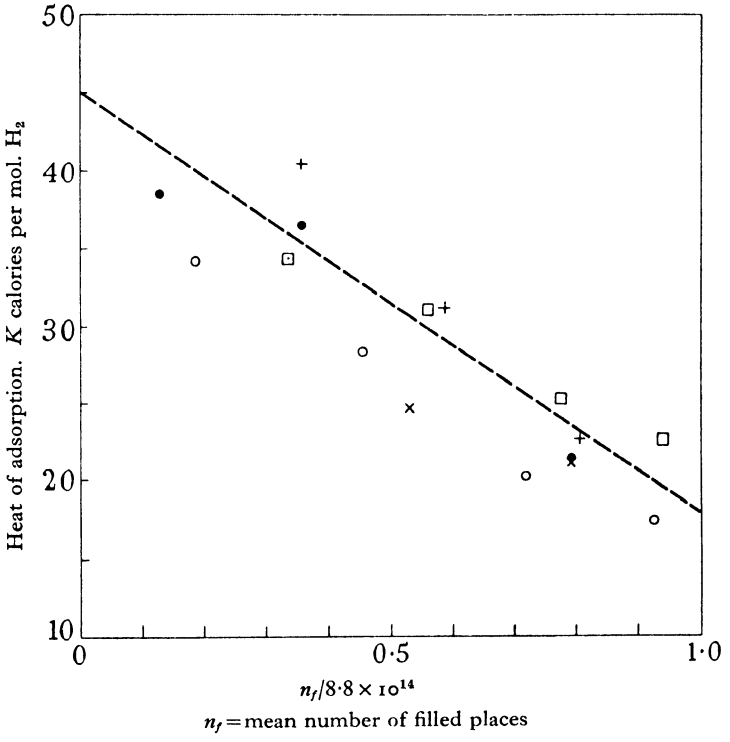

Fig. 9. Relation between heat of adsorption and amount adsorbed.

experiments are due to slight initial contamination of the wire. The measured values of the heat of adsorption are plotted against the ratio of n_f, the number of filled places, to $8{\cdot}8 \times 10^{14}$ in fig. 9 for the five different experiments, a different sign being used for each experiment. The relative values of the heats for the successive admissions in a particular experiment can be fixed with a much higher accuracy than the absolute values which are used in comparing different experiments. The results indicate a relation between heat of adsorption and amount adsorbed, which is linear or nearly linear. When $n_f = 0$ we obtain by extrapolation a heat of adsorption of 45,000 calories per mol. H_2 and of 18,000 calories when $n_f = 8{\cdot}8 \times 10^{14}$.

A consideration of the results collected in fig. 9 indicates immediately the theoretical developments that are necessary to make a full interpretation possible. It cannot be supposed that the large and regular change in the heat of adsorption as the surface becomes covered is for a smooth wire surface due to variations in the activity of different parts. There must therefore be strong repulsive forces between adsorbed particles and to understand the phenomena involved it is necessary to develop the theory of adsorption when such repulsive forces are taken into account. We shall discuss this problem in the next chapter.

Chapter II

THE THEORY OF HEAT OF ADSORPTION WITH INTERACTION BETWEEN ADSORBED PARTICLES

§ 2·1. Langmuir's theory of adsorption on definite sites.

A fundamental advance in the theory of adsorption was made when Langmuir introduced the idea that, owing to the regular arrangement of the atoms in the surface of a solid, the force acting on a gas atom near the surface would not depend only on the distance of the gas atom from the surface, but would vary over the surface so as to be much stronger at some points than at others. He proposed that the effect of this could be taken into account by assuming that there is a definite number, which we shall call n_s, of sites per unit area of solid surface on which adsorption of gas atoms or molecules can take place, and that, when these sites are all occupied, the force acting on a molecule approaching the surface is so small that no further adsorption occurs.

We suppose that each gas molecule that is adsorbed occupies one site, and it is convenient as an introduction to our problem to consider the simplest application of this idea to the deduction of the Langmuir adsorption isotherm in which the effects of forces between adsorbed particles are neglected. Let a fraction θ of the sites be occupied when equilibrium is established with a gas at pressure p dynes per cm.^{2} and temperature T. The number of molecules striking unit area of the solid per second is $p(2\pi mkT)^{\frac{1}{2}}$. If a fraction α of those striking vacant sites condense, the number condensing on unit area per second is

$$\alpha(1-\theta)\, p(2\pi mkT)^{-\frac{1}{2}},$$

where θ is the fraction of the sites that are occupied and α is called the Condensation Coefficient. If we assume that there is no interaction between adsorbed particles, the number evaporating per second is proportional to the number present, i.e. to θ, and is put equal to $A\theta$ per unit area, where A is a function of the temperature. For equilibrium the rates of condensation and of evaporation are equal. Thus

$$\frac{\theta}{1-\theta} = Bp, \qquad (2{\cdot}1)$$

where B is a function of the temperature. This is the Langmuir Adsorption Isotherm.

§ 2·2. Mobile and immobile adsorbed films.

When we begin to formulate the theory of heat of adsorption, taking into account the effects of interaction between adsorbed particles, it is at once evident that there will be a profound difference between the behaviour of mobile and immobile films, and we shall be able to show that the results plotted in fig. 9 are quite inconsistent with what would be expected of a mobile film but are in accord with what would be expected of an immobile one.

By a mobile film we mean one in which the energy of activation necessary to enable an adsorbed particle to move from a given site to a neighbouring vacant site is much less than kT, so that the particles move freely from one site to another. This free movement enables the film to take up equilibrium configurations during the occurrence of any process. Thus for a mobile film we assume that at each instant the particles on the surface may be treated as having an equilibrium Boltzmann distribution under the influence of the forces between them.

For an immobile film, on the other hand, we suppose that the energy of activation necessary to enable a particle to move from one site to another is so much greater than kT that, for the times with which we are concerned in any given experimental investigation, the particles may be treated as remaining fixed on

the sites on which they are first adsorbed. For such a film the distribution at any instant will not necessarily be an equilibrium distribution.*

These two extreme cases can be dealt with theoretically as we shall show. The methods of statistical mechanics can be applied to the equilibrium distribution in the mobile film and to some problems for the immobile film for which in addition special semi-empirical methods have been devised to obtain those necessary results which cannot be deduced statistically. Intermediate cases undoubtedly occur in which the particles can move from site to site but in which there is an appreciable time lag in setting up the equilibrium distribution if this is distributed in any way.

The following simple physical considerations illustrate how the behaviour of mobile and immobile films may be different. Consider the simplest case of all, the formation of a film in which there is repulsive interaction between adsorbed particles and in which each adsorbed molecule occupies one site on the surface. We suppose that interaction is appreciable only between particles adsorbed on neighbouring sites, and that adsorption occurs on the simple quadratic lattice of sites formed by the intersections of the lines in fig. 10. The adsorbed particles are represented by the black dots, and it will be seen that, with the arrangement represented, half the sites are occupied and no two neighbouring sites are occupied, i.e. $\theta = 0{\cdot}5$ and the interaction energy is zero.

This is the state of lowest energy for $\theta = 0{\cdot}5$ and, if the film is mobile, the mutual repulsive forces between the adsorbed particles will tend to make them arrange themselves in this state of lowest energy, but in accordance with Boltzmann's law

* It should be mentioned here that, apart from mobility of the adsorbed particles, evaporation and condensation will set up an equilibrium distribution of particles on the surface. In general, however, the temperature at which free mobility sets in will be lower than that at which appreciable evaporation occurs, so that the assumption that mobility is negligible implies the assumption that evaporation is also negligible.

the thermal motion of the particles will cause a configuration of higher energy to be taken up. If we neglect the effect of the thermal motion and assume that the system is always in the state of lowest energy, the heat of adsorption will remain constant at, say, q_0 calories per particle adsorbed up to $\theta = 0{\cdot}5$. It will then fall and remain constant at $q_0 - 4V$ from $\theta = 0{\cdot}5$ to $\theta = 1$, where V is the interaction energy between two particles

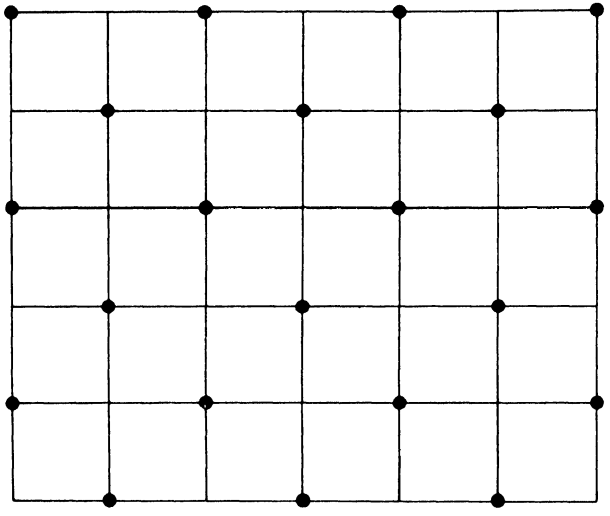

Fig. 10. State of lowest energy for adsorbed film on quadratic lattice with repulsion between particles adsorbed on neighbouring sites.

adsorbed on neighbouring sites. If the heat is plotted against θ, the curve will have a sharp step at $\theta = 0{\cdot}5$ (see curve (*a*), fig. 12). The only effect of the Boltzmann distribution will be to round off the sharp corners as shown in the other curves in fig. 12.

For the immobile film, on the other hand, if we assume that the probability that a molecule condenses when it strikes a vacant site is independent of the state of occupation of neighbouring sites, the distribution of the particles on the surface will be random, and the average number of occupied sites around any vacant site on which adsorption takes place will be

strictly proportional to θ. Thus the heat of adsorption will be accurately a linear function of θ, changing from q_0 at $\theta = 0$ to $q_0 - 4V$ at $\theta = 1$.

Other illustrations will be given later.

§ 2·3. The equilibrium distribution of particles on the surface in a mobile film.

In order to determine how the heat of adsorption varies as more and more of the sites on the surface become occupied, it is necessary to know how the energy of the adsorbed film varies with θ. That is, if the interaction energy is appreciable only between particles adsorbed on neighbouring sites, it is necessary to know, for a given value of θ, the average number of pairs of interacting particles on the surface. The method of solving such problems, which we shall now discuss, was first given by Peierls(1) in connexion with a development of some work by Fowler(2) on critical condensation conditions when there are attractive forces between adsorbed particles.

We shall suppose that there is one layer of N_s possible sites for adsorption arranged in a regular array in such a way that each site has z nearest neighbours, and that there is an interaction energy V for each pair of neighbouring adsorbed atoms, V being positive if the force between the particles is repulsive. For particles not adsorbed on neighbouring sites we assume that the interaction energy is negligible. This assumption is justified for all forces except dipole forces, which we discuss separately in chapter VI.

Let there be θN_s occupied sites in all and let us consider various arrangements of these occupied sites. If, in any given arrangement, X pairs of neighbouring sites are occupied, the relative probability of such an arrangement is, by Boltzmann's law,*

$$e^{-XV/kT} = \eta^X, \qquad (2{\cdot}2)$$

* This is true only if we assume that the vibrational partition function $v_s(T)$ for an adsorbed particle is not affected by the state of occupation of neighbouring sites. We make this assumption throughout. A full examination

where η is defined by

$$\eta = e^{-V/kT}. \qquad (2{\cdot}3)$$

We select a group of sites consisting of site o, which we call the central site, and sites 1 to z, its z neighbours, which we call the first shell, and we define a set of numbers $\theta_0, \theta_1 \ldots \theta_z$ which are 1 or o according to whether the corresponding sites are occupied or unoccupied. For example, in fig. 11, such a group is shown in a simple hexagonal array, particles being represented by black dots. Here we have $\theta_0 = \theta_2 = \theta_3 = \theta_5 = 1$, and

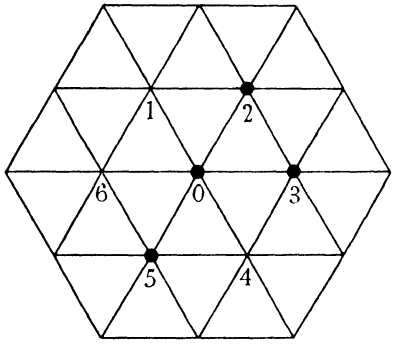

Fig. 11. Group of sites on hexagonal lattice.

$\theta_1 = \theta_4 = \theta_6 = 0$, and the number of occupied neighbouring sites in the group is 4. We want to find the relative probability that $\theta_0, \theta_1 \ldots \theta_z$ shall have an assigned set of values.

Consider one particular arrangement (arrangement 1) in which $\theta_0, \theta_1 \ldots \theta_z$ have this assigned set of values, and in which there are n pairs of neighbouring occupied sites among the sites o to z. The relative probability of this particular arrangement is

$$\eta^n \psi_1(\theta_1 \ldots \theta_z)\, \eta^{\Gamma_1},$$

where ψ_1 represents the effect of interactions between particles on first shell sites and particles on neighbouring outer sites and

of its validity is important and a first step in this direction has been made by Rushbrooke(3) for the case when there are attractive forces between adsorbed particles.

is equal to η raised to a power equal to the number of such interactions, and Y_1 is the number of pairs of occupied neighbouring sites among the outer sites. For a second arrangement in which $\theta_0 \ldots \theta_z$ still have the same set of values, we shall use ψ_2 and Y_2 and so on. The relative probability that $\theta_0 \ldots \theta_z$ shall have the assigned set of values is then

$$\eta^n\{\psi_1(\theta_1 \ldots \theta_z)\,\eta^{Y_1}+\psi_2(\theta_1 \ldots \theta_z)\,\eta^{Y_2}+\ldots\}, \qquad (2{\cdot}4)$$

where the sum in the brackets is taken for all possible arrangements of the $\theta N_s-(\theta_0+\theta_1+\ldots+\theta_z)$ atoms on the outer sites. Expression (2·4) may be written in the form

$$\eta^n\psi(\theta_0 \ldots \theta_z)\{\eta^{Y_1}+\eta^{Y_2}+\ldots\}, \qquad (2{\cdot}5)$$

where

$$\psi=\frac{\Sigma\psi_1\eta^{Y_1}}{\Sigma\eta^{Y_1}}. \qquad (2{\cdot}6)$$

We cannot determine ψ and the last term in brackets exactly as a function of $\theta_0, \theta_1 \ldots \theta_z$, but obtain a first approximation by using averages. Consider the (N_s-z-1) outer sites separately. When $(\theta_0+\theta_1+\ldots+\theta_z)$ changes, the number of particles on the outer sites is also altered, and this affects both the interaction energy of the particles on the outer sites and the number of ways of arranging them. If all the $\theta N_s=M$ particles are adsorbed on these outer sites, let their average total interaction energy be E_0. Further suppose that the average interaction energy between a particle on a first shell site and particles on outer sites is $V_{12}(\theta)$, and that this is not appreciably altered by changes in the number of particles on outer sites occasioned by changes in $\theta_0 \ldots \theta_z$. The interaction energy for a fixed value of θ and an assigned set of values of $\theta_0 \ldots \theta_z$ is, on the average,

$$nV+(\theta_1+\ldots+\theta_z)\,V_{12}(\theta)+E_0-\frac{dE_0}{dM}(\theta_0+\ldots+\theta_z). \qquad (2{\cdot}7)$$

For a given value of θ the relative probability of this assigned set of values of $\theta_0 \ldots \theta_z$ is

$$\eta^n\xi^{\theta_1+\ldots+\theta_z}\xi^{\theta_0+\theta_1+\ldots+\theta_z}, \qquad (2{\cdot}8)$$

where $$\zeta = e^{-V_{12}(\theta)/kT}, \qquad (2\cdot9)$$

and where the term in ξ is introduced to represent the effect of the alteration in the energy and the number of possible configurations of particles on outer sites.*

Expression (2·8) can be written

$$\xi^{\theta_0}\eta^n\epsilon^{\theta_1+\ldots+\theta_z}, \qquad (2\cdot10)$$

where $$\epsilon = \xi\zeta. \qquad (2\cdot11)$$

* That a term of this sort, i.e. some function of θ raised to the power $\theta_0+\ldots+\theta_z$, is probably of the right type to represent the effect of the outer sites is indicated by considering the effects of the energy and of the number of configurations separately, although as expression (2·5) shows they are in fact not separable.

If only the energy were affected, expression (2·7) shows that the relative probability would contain a term $e^{\frac{1}{kT}\frac{dE_0}{dM}(\theta_0+\ldots+\theta_z)}$, i.e. a function of θ raised to the power $(\theta_0+\ldots+\theta_z)$.

Now consider the number of configurations. The number of ways of arranging M particles on N sites is ${}_NC_M$. When N and M are large,

$$\frac{{}_NC_{M-(\theta_0+\ldots+\theta_z)}}{{}_NC_M} = \left(\frac{M}{N-M}\right)^{\theta_0+\ldots+\theta_z} = \left(\frac{\theta}{1-\theta}\right)^{\theta_0+\ldots+\theta_z},$$

if $M=\theta N$. This again is of the same type, i.e. a function of θ raised to the power $(\theta_0+\ldots+\theta_z)$.

When ξ is evaluated, it is found for the special case considered that, when θ is nearly unity, it does in fact contain (see equation (2·15) for large values of ϵ) a term $\theta/(1-\theta)$ being equal to $\theta\eta^{-z}/(1-\theta)$. Thus, when θ is nearly unity, the two effects are separated, the term $\theta/(1-\theta)$ representing the effect of the changes in the number of possible configurations in the particles on the outer sites and the term η^{-z} the effect of changes in their energy, since, when θ approaches unity, $\frac{dE_0}{dM}$ clearly approaches zV. Similarly, when θ is small, ϵ is small and $\xi = \frac{\theta}{1-\theta}$. The term $\xi^{\theta_0+\ldots+\theta_z}$ therefore takes account of the alteration in the number of configurations of particles on outer sites but does not include any effect due to their mutual interaction energies. This is correct, as at low θ the effect of the energy will obviously be small.

It is convenient to discuss here also the term ζ. We have introduced it in the above way to show that a term of the form $\zeta^{\theta_1+\ldots+\theta_z}$ is probably of the right type to represent to a first approximation the rather complicated effect of interactions between particles on first shell sites and those on outer sites. The effect is complicated for the reason that, if the first shell is occupied, there is, because of the repulsive force, a diminished chance of finding adsorbed atoms on sites adjoining the first shell. This, conversely, will increase the chance that a site in the first shell is occupied. As we shall see, we really treat ζ as a variable, the value of which is to be chosen in such a way as to make each first shell site an average site.

By writing down all the possible combinations of values of $\theta_0 \ldots \theta_z$ and using (2·10) to give the relative probability of each we can obtain an expression in terms of ϵ for the probability of finding one of the first shell sites, say site 1, occupied. That is, we find the average value of θ_1. Since every site must be an average site, the average value of θ_1 must be equal to θ. This condition fixes the value of ϵ.

We shall carry out the detailed calculations for the case in which no two neighbours of a given site are neighbours of each other. This practically restricts the application of the results to $z=2$, i.e. to linear chains which are of trivial importance, and to $z=4$, which, as has been pointed out in section 1·4, is the application we require. The importance of this restriction is that with it

$$n=\theta_0(\theta_1+\ldots+\theta_z), \tag{2·12}$$

and we obtain simple algebraical expressions for all our quantities instead of having to tabulate the results and use numerical methods. Using (2·12) in (2·10), the relative probability of a given set of values of $\theta_0 \ldots \theta_z$ becomes

$$\xi^{\theta_0}\eta^{\theta_0(\theta_1+\ldots+\theta_z)}\epsilon^{(\theta_1+\ldots+\theta_z)}. \tag{2·13}$$

We now determine ϵ by calculating the average occupation of site 1. If $\theta_0=0$, the average value of θ_1 is given by

$$\frac{\Sigma\epsilon^{1+\theta_2+\ldots+\theta_z}}{\Sigma\epsilon^{1+\theta_2+\ldots+\theta_z}+\Sigma\epsilon^{0+\theta_2+\ldots+\theta_z}},$$

the sums (see footnote, p. 30) being for all combinations of values of $\theta_2 \ldots \theta_z$; that is by

$$\frac{\epsilon}{1+\epsilon}.$$

Similarly, if $\theta_0=1$, the average value of θ_1 is

$$\frac{\eta\epsilon}{1+\eta\epsilon}.$$

Taking the two results together, the overall average value of θ_1 is

$$(1-\theta)\frac{\epsilon}{1+\epsilon}+\theta\frac{\eta\epsilon}{1+\eta\epsilon}.$$

This must be equal to θ and, therefore,

$$\frac{\theta}{1-\theta}=\frac{\epsilon(1+\eta\epsilon)}{1+\epsilon}. \qquad (2{\cdot}14)$$

For a given value of η (i.e. of V/kT) this equation enables us to obtain ϵ as a function of θ, and gives us all the results we require for the calculation of heats of adsorption.

Let us consider some examples of the application of these results. If $\eta=4\times10^{-2}$, which (see section 2·6) corresponds approximately to $e^{-V/kT'}$ at 700° K. for a film of hydrogen if it is atomic, we obtain from equation (2·14) that, at $\theta=0{\cdot}4$, $\epsilon=1{\cdot}67$, and, at $\theta=0{\cdot}6$, $\epsilon=15$. If at $\theta=0{\cdot}4$ the central site is occupied, the probability that site 1 is occupied is $\eta\epsilon/(1+\eta\epsilon)$ or 0·063; if the system were in the state of lowest energy discussed in section 2·2, this probability would be zero, while for a random distribution (i.e. no interaction between adsorbed particles) it would be 0·4. If at $\theta=0{\cdot}6$ the central site is vacant, the probability that site 1 is vacant is $1/(1+\epsilon)$ or 0·063; if the system were in the state of lowest energy, this probability would be zero, while for a random distribution it would be 0·4.

Although we do not need it at present,* it is convenient to consider here the determination of ξ. To do this we calculate the average value of θ_0. This is

$$\frac{\Sigma\xi(\eta\epsilon)^{\theta_1+\ldots+\theta_z}}{\Sigma\xi(\eta\epsilon)^{\theta_1+\ldots+\theta_z}+\Sigma\epsilon^{\theta_1+\ldots+\theta_z}},$$

the sums as before being taken for all possible combinations of values of $\theta_1 \ldots \theta_z$.† This average value of θ_0 must also be equal to θ and we have therefore

$$\frac{\xi(1+\eta\epsilon)^z}{\xi(1+\eta\epsilon)^z+(1+\epsilon)^z}=\theta,$$

* The results obtained in the rest of this section are used only in the last footnote. It may be omitted if wished.

† $\Sigma\epsilon^{\theta_1+\ldots+\theta_z}=1+{}_zC_1\epsilon+{}_zC_2\epsilon^2+\ldots+{}_zC_z\epsilon^z=(1+\epsilon)^z$.

or
$$\frac{\theta}{1-\theta}=\xi\left(\frac{1+\eta\epsilon}{1+\epsilon}\right)^{z}. \qquad (2\cdot15)$$

Dividing this by (2·14), we obtain

$$\xi=\epsilon\left(\frac{1+\epsilon}{1+\eta\epsilon}\right)^{z-1}. \qquad (2\cdot16)$$

After ϵ has been determined as a function of θ from (2·14), equation (2·16) enables us to determine ξ as a function of θ.

§ 2·4. The variation of heat of adsorption with fraction of sites occupied for simple adsorption into a mobile film.

The application of these results in connexion with heats of adsorption has been given by Wang(4). The simplest is to a system in which each adsorbed particle occupies one site and there is no dissociation. The heat of adsorption per molecule q is the decrease in the energy of the system when one molecule is adsorbed, and is given by

$$q=u-\frac{\partial U}{\partial(N_s\theta)}, \qquad (2\cdot17)$$

where u is the energy of a molecule in the gas phase and U the total energy of the molecules in the adsorbed film. $N_s\theta$ is of course the total number of adsorbed molecules. U is given by

$$U=U_0+\bar{X}V, \qquad (2\cdot18)$$

where U_0 is the energy of the adsorbed molecules apart from the effect of interactions and $\bar{X}$ is the average number of interacting pairs of molecules for a given value of θ. $\bar{X}$ is equal to $\frac{1}{2}zN_s\theta$ times the average value of θ_1 when $\theta_0=1$, the factor one-half being introduced so that each pair shall be reckoned once only. That is

$$\bar{X}=\tfrac{1}{2}zN_s\theta\frac{\eta\epsilon}{1+\eta\epsilon}.$$

Using (2·14) this becomes

$$\bar{X}=\tfrac{1}{2}N_sz\left[\theta-\frac{1-\{1-4(1-\eta)\theta(1-\theta)\}^{\frac{1}{2}}}{2(1-\eta)}\right]. \qquad (2\cdot19)$$

Using (2·19) in (2·18) and (2·17), we obtain

$$\frac{q-q_0}{V}=-\frac{z}{2}\left[1-\frac{1-2\theta}{\{1-4(1-\eta)\,\theta(1-\theta)\}^{\frac{1}{2}}}\right], \qquad (2\cdot20)$$

where q_0 is the heat of adsorption of a molecule on a bare surface, i.e. the heat of adsorption when $\theta=0$.

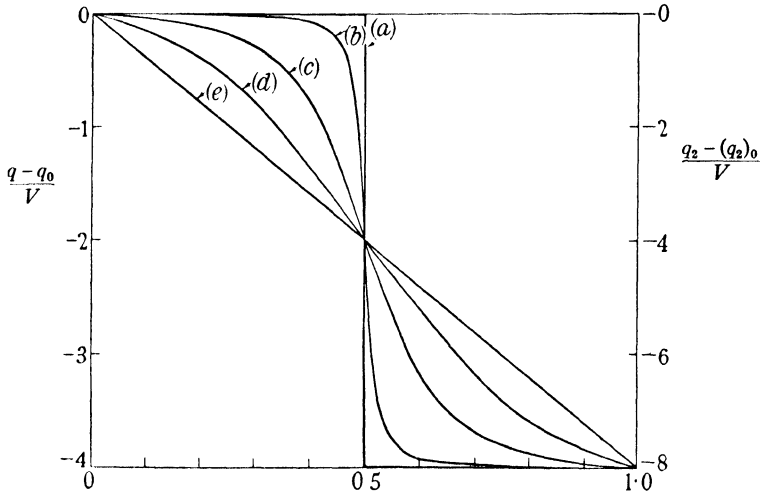

Fig. 12. Variation of heat of adsorption with fraction of surface covered. Curve (*a*) $\eta=e^{-V/kT}=0$; (*b*) $\eta=3\cdot6\times10^{-3}$; (*c*) $\eta=8\cdot2\times10^{-2}$; (*d*) $\eta=0\cdot368$; (*e*) $\eta=1$. The scale on the left is for the heat of adsorption q when there is no dissociation and that on the right is for the heat per molecule q_2 when there is dissociation. The subscript 0 refers to $\theta=0$, and V is the interaction energy between particles adsorbed on neighbouring sites. The calculations are for $z=4$.

Values of $(q-q_0)/V$ for $z=4$ and for various values of η are plotted against θ in fig. 12. The curve for $\eta=0$ corresponds to the case discussed in section 2·2 when the system is always in the state of lowest energy, and that for $\eta=1$ corresponds to a random distribution.

§ 2·5. Variation of heat of adsorption with fraction of sites occupied in a mobile film for adsorption with dissociation.

The results in the last paragraph enable us to obtain the variation of the heat of adsorption q_2 of a diatomic molecule which dissociates on adsorption. This is defined as the decrease in energy when one molecule is adsorbed. If q_1 is the heat of adsorption of an atom,

$$q_2 = 2q_1 - q_d, \tag{2·21}$$

where q_d is the heat *required* to dissociate a molecule. From equation (2·20),

$$\frac{q_1 - (q_1)_0}{V} = -\frac{z}{2}\left[1 - \frac{1-2\theta}{\{1-4(1-\eta)\theta(1-\theta)\}^{\frac{1}{2}}}\right],$$

where $(q_1)_0$ is the heat of adsorption of an atom on the bare surface and V is the interaction energy between two *atoms* adsorbed on neighbouring sites. Using this in equation (2·21), we obtain

$$\frac{q_2 - (q_2)_0}{V} = -z\left[1 - \frac{1-2\theta}{\{1-4(1-\eta)\theta(1-\theta)\}^{\frac{1}{2}}}\right], \tag{2·22}$$

where $(q_2)_0$ is the heat of adsorption of a molecule on the bare surface. Apart from the factor one-half this is the same as equation (2·20), and the curves plotted in fig. 12 for $z=4$ apply to this case also provided the scale of ordinates on the right-hand side of the figure is used.

In comparing these calculations with the experimental results for hydrogen plotted in fig. 1, we note that $(q_2)_1 - (q_2)_0 = 8V$. The difference between the heats of adsorption at $\theta=0$ and $\theta=1$ is 27,000 calories per mol. This gives $V = 2{\cdot}3 \times 10^{-13}$ erg per pair of atoms* and at 300° K., the temperature at which

* The justification for assuming that in this case only nearest neighbours interact is as follows. The only long range forces that are likely to arise are forces between electrostatic dipoles. Assuming that the whole variation in the heat was due to repulsion between dipoles the author(5) has shown that

the experiments were carried out, $\eta = \epsilon^{-V/kT} = 3{\cdot}6 \times 10^{-3}$. Thus, if the film were mobile, we should expect a relation between heat of adsorption and θ like curve (*b*) in fig. 12. A comparison with the experimental results in fig. 1 shows immediately that the actual variation is nothing like this, and we therefore examine the behaviour that would be expected if the film were not mobile but immobile.

§ 2·6. The theory of heat of adsorption for an immobile film.

For an immobile film, in which each particle occupies one site and in which the probability of condensation on a vacant site is independent of the state of occupation of neighbouring sites, we have at any stage a geometrically random distribution of occupied sites and we have already seen in section 2·2 that the heat of adsorption is a linear function of θ. If we are considering a process in which diatomic gas molecules dissociate on adsorption and the two atoms occupy two neighbouring vacant sites on the surface, we do not have a random distribution of occupied sites, because, if a given site is occupied, we know that one of the neighbouring sites must be occupied by the other atom of the diatomic molecule. In this case we have a geometrically random distribution of *pairs* of occupied sites. We now consider the relevant properties of such a distribution.

The statistical methods discussed in section 2·3 are being extended to cover this case (see section 3·1). This extension has not yet been carried sufficiently far to obtain the heats and we shall therefore discuss an empirical method which has been

the dipoles would be of such strength that the contact potential between bare tungsten and hydrogen-covered tungsten would be 5·2 volts. Bosworth (6) has measured this and shown that it is 1·04 volts. Thus the dipoles are about one-fifth as strong as would be required to account for the whole thermal effect and, since the interaction energy is proportional to the square of the dipole strength, electrostatic forces would account for only about 4 per cent of the whole. The remaining 96 per cent is due to short range forces which can be assumed to be effective only between nearest neighbours.

developed to give the results we require(7) and which is applicable to a large number of similar problems. We use a model of the surface with all the sites numbered and fill pairs of neighbouring sites at random by drawing a numbered card representing one site and a number 1, 2, 3 or 4 representing the orientation of the second site with respect to the site so chosen. If either site is occupied, the draw is rejected. Pre-

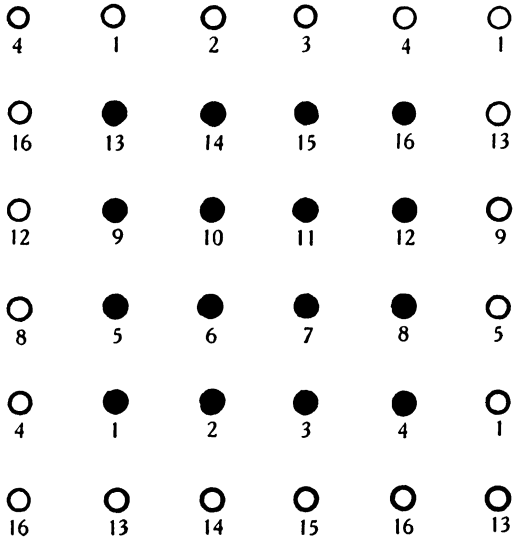

Fig. 13. Model for obtaining properties of immobile films.

cautions must be taken to eliminate edge effects. Some simple numerical calculations on linear chains of sites showed that, if the sites were arranged on a circle so as to eliminate edge effects completely, accurate results could be obtained by considering comparatively few sites. Exactly the same method can be applied to a quadratic two-dimensional array of sites by imagining them arranged on circles round a cylinder and then imagining the two ends of the cylinder joined together to form

a ring. This arrangement can be represented on a plane. To show this we consider only sixteen sites represented by black dots in fig. 13. When these are bent round, site 2 comes next to site 14, site 9 next to site 12 and so on. This is shown by duplicating these sites as shown by the circles. Each corner site, for example 1, occurs four times in this arrangement. If a site like 1 is occupied, this must be indicated on *all* the four 1 sites, but this of course counts as only one particle on the surface. With this arrangement all the sites are identical; each has four nearest neighbours and no two neighbours of a given site are neighbours of each other.

The model had one hundred sites and at each stage in the process of filling it up, i.e. for each θ, a record was made of the total number of available pairs of vacant sites and of the fractions $x_6, x_5 \ldots x_0$ of these which were surrounded respectively by 6, 5 ... 0 vacant sites. If χ_2 is the heat of adsorption of a molecule on a bare surface when the diatomic molecule dissociates on adsorption but the two atoms remain immobile on the two neighbouring sites on which they are first adsorbed, the heat of adsorption q_i for the immobile film is given by

$$q_i = \chi_2 - V(x_5 + 2x_4 + 3x_3 + 4x_2 + 5x_1 + 6x_0). \quad (2{\cdot}23)$$

It will be seen that $(q_2)_0$, the heat of adsorption of a molecule on a bare surface if the film is *mobile*, is given by

$$(q_2)_0 = \chi_2 + V. \quad (2{\cdot}24)$$

Thus

$$\frac{q_i - (q_2)_0}{V} = -1 - (x_5 + 2x_4 + 3x_3 + 4x_2 + 5x_1 + 6x_0). \quad (2{\cdot}25)$$

The values of $\{q_i - (q_2)_0\}/V$ obtained in this way are plotted in fig. 14. It is convenient to present the results in this form as it reminds us that the initial heat of adsorption into a mobile film is, other things being equal, different from that into an immobile film.

It is at once evident that the nearly linear relation is in accord with the experimental results for hydrogen, from which we conclude that the hydrogen film on tungsten at room temperature is immobile.

For comparison the straight line is drawn from the point (0, −1) to (1, −7). This is obtained if, when each molecule is adsorbed and the two atoms remain fixed on two neighbouring

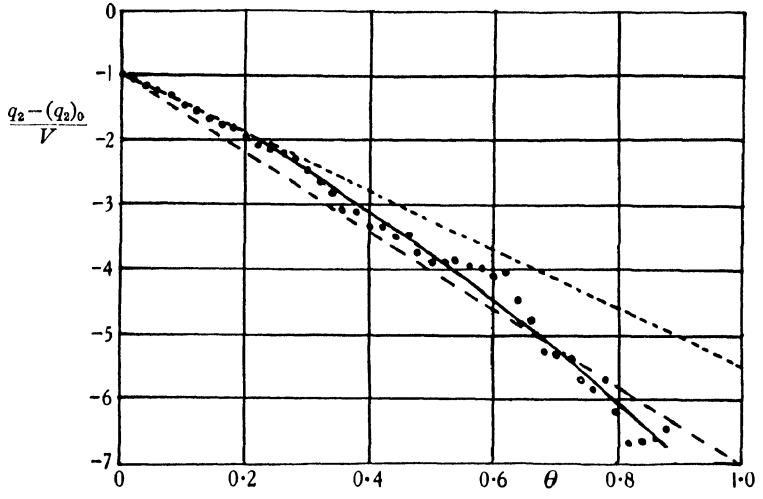

Fig. 14. Variation of heat of adsorption with θ for immobile film.

sites, the particles already on the surface are arranged so that there is a random distribution of single occupied sites. The conclusion that the hydrogen film is immobile was originally drawn from a comparison with this case(5), since it was evident that the behaviour with a random distribution of pairs of occupied sites would not differ greatly from it.

Finally it may be pointed out that, as we shall see in the next chapter, an immobile film of this type is complete when θ is in the neighbourhood of 0·9.* The total change in the heat of

* For a further discussion of the shape of the curve in fig. 14 see Roberts (7).

adsorption from $\theta = 0$ to the complete film is approximately $6V$, so that, using the data in the last section, we have $V = 3{\cdot}1 \times 10^{-13}$ erg per pair of hydrogen atoms on the tungsten surface, i.e. at a distance $2{\cdot}6 \times 10^{-8}$ cm. apart if the surface plane is the 110 plane and $3{\cdot}1 \times 10^{-8}$ cm. if it is the 100 plane.

§ 2·7. The assumption of a fixed interaction energy between particles on neighbouring sites.

The solution of the problem of the distribution of adsorbed particles would be extremely complicated if an attempt were made to take into account the fact that the energy of a single adsorbed atom in its lowest state is a continuously varying function of its position on the surface. For this reason the simplifying assumption has been made that the particles are adsorbed on definite sites and that the interaction energy V between particles adsorbed on neighbouring sites is a constant.

In fig. 15 the lower full curves show a two-dimensional cross-section of how the energy of a single adsorbed particle in its lowest state might be expected to vary with its position on the surface. A and B are "sites" for adsorption. The distance between A and B is 3 of the arbitrary units of length used. The upper curves show the mutual potential energy of two adsorbed particles at various distances apart. The actual value V of this energy when the distance is equal to AB is the same in (a), (b) and (c), but the variation with distance is different in the three cases. In (a) it has an intermediate value, in (b) it is rapid, and in (c) it is slow. The lower dotted curves show the potential energy of two particles adsorbed in their lowest states on neighbouring sites and arranged in each case symmetrically about the point o.

If as in (b) the rate of variation with distance apart of the mutual potential energy of two particles on neighbouring sites is large compared with the rate of variation of the potential energy of a single particle with its position, the interaction energy

between two particles adsorbed on neighbouring sites will be considerably less than V, provided the relevant outer neighbouring sites, which are not shown on the diagram are vacant. It will be seen that in an extreme case of this type the variation

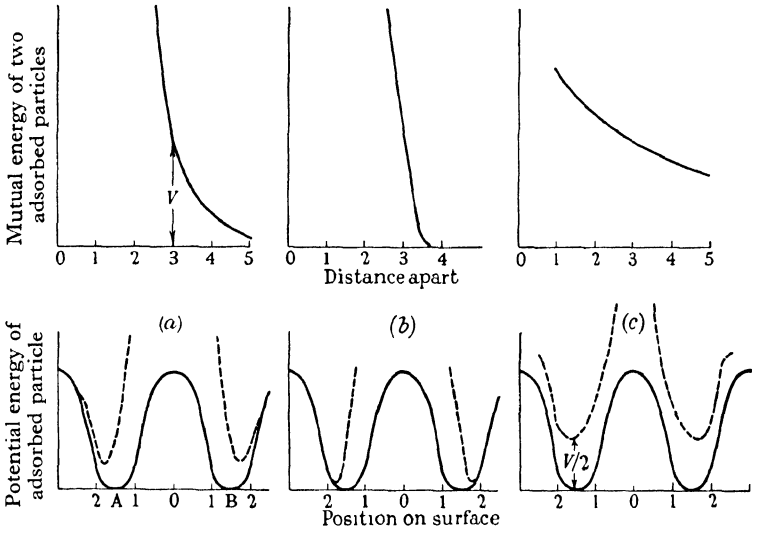

Fig. 15. The upper curves show the variation with distance apart of the potential energy of two adsorbed atoms due to the mutual repulsive forces. The lower full curves show the variation in the potential energy of a single adsorbed atom in its lowest state at different places on the surface, and the dotted curves show how this is modified when two particles in their lowest states are adsorbed on two neighbouring sites in similar positions, i.e. in positions symmetrical about o. If the particles are at a distance apart equal to the distance between the lowest points of the full curves, the interaction energy V is the same in the three cases but the slopes of the upper curves are very different. In (*a*) the heat of adsorption of the second particle would be about $q_0 - V/2$; in (*b*) about $q_0 - V/4$; in (*c*) about $q_0 - V$. The length and energy scales respectively are the same in the upper and lower figures.

of heat of adsorption with θ for mobile and immobile films would be more similar than in the model considered before, since for low values of θ the heat would in both cases vary slowly with θ. One step in obtaining a general idea of the behaviour will be to consider quantitatively the limiting case in which the

potential energy of a single particle is assumed to be uniform over the surface. This has been discussed statistically by Wilkins(8).

If on the other hand the rate of variation with distance of the mutual potential energy of two particles is as in (*c*) small, the model used earlier in this chapter represents the actual behaviour closely. The shapes of the curves in fig. 15 are not yet known for any particular case and any further discussion of this point must be deferred until the whole question has been examined in detail. It is hoped shortly to carry out this examination.

Chapter III

THE PROCESS OF THE FORMATION OF ADSORBED FILMS

§ 3·1. The kinetics of the formation of immobile adsorbed films with dissociation.

If there is no dissociation and each adsorbed particle occupies one site only and if we assume that the probability of condensation on a vacant site is independent of the state of occupation of neighbouring sites, an assumption that we shall make throughout the whole of our treatment (see section 4·4), the rate of condensation of particles is, as shown in section 2·1, independent of whether the film is mobile or immobile or of whether there is or is not interaction between adsorbed particles. On the other hand, if dissociation occurs on adsorption, there is a marked difference between the various types of film. Since we have already shown in section 2·6 that the hydrogen film is immobile at room temperature, we shall commence by considering this type.

As an immobile film formed by the dissociation of diatomic gas molecules and the adsorption of the two atoms on neighbouring sites is gradually built up, certain individual surface sites will find themselves surrounded by four filled places. Such sites will not be able to take any part in the adsorption process and will remain bare. The complete film therefore of necessity has gaps or holes in it.* The number of these holes can be determined using the model described in section 2·6 and

* It may be mentioned here that any immobile film, in which each particle in the gas phase does not on adsorption occupy one site only, will have similar gaps (see Roberts(1) and section 5·3) and that such gaps will probably be important as centres of catalytic activity (see Roberts(2)).

is about 8 per cent of the number of sites on the surface. The presence of the holes must be taken into account in considering the kinetics of the formation of the film.

We suppose as before that each site has four nearest neighbours and that no two neighbours of a given site are neighbours of each other. If there are n_s sites per unit area, the number of pairs of neighbouring sites per unit area is $2n_s$. If a molecule condenses on two neighbouring sites and if all the six sites (cf. fig. 13) which are neighbours to these two sites are vacant, the number of available pairs of sites is reduced by $1+6$. If the number of adsorbed atoms on unit area of the surface is θn_s, let $f(\theta)$ be the number of available pairs of sites. The main kinetic problem is the determination of $f(\theta)$. When one further molecule condenses, we have

$$d\theta = 2/n_s, \tag{3·1}$$

and

$$df(\theta) = -1-6\gamma(\theta), \tag{3·2}$$

where $\gamma(\theta)$ is the average fraction which is vacant of the six sites surrounding a pair of vacant sites. Thus

$$\frac{df(\theta)}{d\theta} = -\frac{n_s}{2}\{1+6\gamma(\theta)\}.$$

If as before we determine at each stage of filling up the model the fractions $x_6, x_5, x_4 \ldots x_0$ of the total number of pairs of vacant sites surrounded respectively by $6, 5, 4 \ldots 0$ vacant sites, then

$$6\gamma(\theta) = 6x_6+5x_5+4x_4+3x_3+2x_2+x_1,$$

and

$$\frac{df(\theta)}{d\theta} = -\frac{n_s}{2}(7x_6+6x_5+5x_4+4x_3+3x_2+2x_1+x_0).$$

or

$$\frac{df(\theta)}{d\theta} = -3{\cdot}5n_s\,g(\theta), \tag{3·3}$$

where

$$g(\theta) = \tfrac{1}{7}(7x_6+6x_5+5x_4+4x_3+3x_2+2x_1+x_0).$$

Integrating equation 3·3 after inserting numerical constants to

fit the values of $g(\theta)$ obtained from the model we obtain for $\phi(\theta)$, which we define as $f(\theta)/2n_s$,

$$\phi(\theta)=\frac{f(\theta)}{2n_s}=1-1{\cdot}75(\theta-0{\cdot}3215\theta^2-0{\cdot}0833\theta^3-0{\cdot}0175\theta^5).$$

This makes $f(\theta)=0$ when $\theta=0{\cdot}92$, i.e. takes account of the 8 per cent of isolated sites.*

The rate of condensation of molecules on unit area is

$$\frac{\alpha_2 p_2}{(2\pi m_2 kT)^{\frac{1}{2}}}\phi(\theta), \tag{3·4}$$

where α_2 is the condensation coefficient, i.e. the fraction which condenses of the molecules incident on a part of the surface where two neighbouring sites are vacant, p_2 is the pressure in dynes per cm.^{2}, and m_2 is the mass of a molecule. $p_2/(2\pi m_2 kT)^{\frac{1}{2}}$ is the number of molecules striking unit area per second. Thus

$$\frac{d\theta}{dt}=\frac{2}{n_s}\frac{\alpha_2 p_2}{(2\pi m_2 kT)^{\frac{1}{2}}}\phi(\theta), \tag{3·5}$$

and

$$\int_0^{\theta}\frac{d\theta}{\phi(\theta)}=\frac{2}{n_s}\frac{\alpha_2 p_2}{(2\pi m_2 kT)^{\frac{1}{2}}}t, \tag{3·6}$$

if $\theta=0$ at $t=0$. Values of the integral obtained from equation 3·6 by numerical integration are given in Table I. It may be mentioned that, as we shall see in section 3·3, fig. 20, the $\theta-t$

Table I

θ	$\int_0^{\theta}\frac{d\theta}{\phi(\theta)}$	θ	$\int_0^{\theta}\frac{d\theta}{\phi(\theta)}$
0·1	0·110	0·65	1·665
0·2	0·245	0·70	2·065
0·3	0·413	0·75	2·635
0·4	0·630	0·80	3·495
0·5	0·927	0·85	5·135
0·6	1·360	0·90	9·235

* For the numerical details see Roberts(3). A statistical method of treating this problem has been developed and the results will be described in a paper by Roberts and Miller which will appear shortly (2a).

curve for this type of adsorption is very similar to that marked $\eta = 1$ in fig. 19 for adsorption with dissociation into a mobile film with no interaction between the adsorbed atoms(3).

To study the formation of hydrogen films on tungsten, Bosworth(4) has used the contact potential method of Langmuir and Kingdon(5) as developed by Reimann(6) and applied by Bosworth and Rideal(7) to the study of sodium films on tungsten.

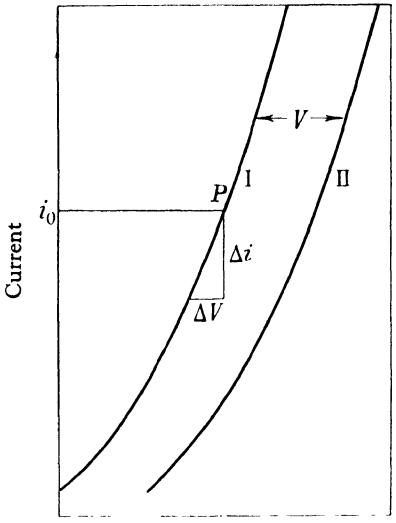

Fig. 16.

In this method the electron current from an incandescent filament maintained at a fixed temperature to a nearby cold filament is plotted as a function of the voltage between the two filaments, a curve like curve I in fig. 16 being obtained. We shall suppose that curve I refers to a cold tungsten filament with a bare surface. If now an adsorbed film is deposited on the cold surface, the incandescent filament being at such a high temperature that it remains bare, and the experiment is repeated, the whole curve is bodily displaced to II through a distance V equal to the contact potential between the cold bare surface and

the cold surface with the adsorbed film on it. The procedure is to determine the calibration curve. Then with the cold surface bare we start with a current say i_0 corresponding to a point P on the calibration curve. If now adsorption occurs and the current

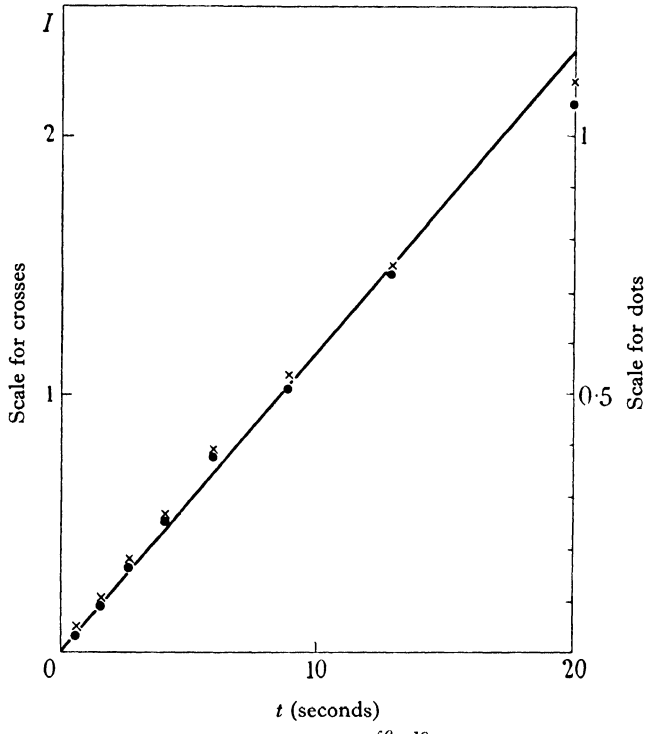

Fig. 17. Relation between $I = \int_0^{\theta} \frac{d\theta}{\phi(\theta)}$ and the time t.

changes by Δi, the contact potential between the bare cold surface and the cold surface with the adsorbed film on it is ΔV. The advantage of the method is that with a short period recording galvanometer comparatively rapid adsorption processes can be followed.

Bosworth found that the contact potential of the tungsten with a hydrogen film on it in its final steady state was 1·04 volts

against bare tungsten, the sign being the same as for tungsten with an oxygen film and opposite to that with an alkali metal film. If this corresponds to a film with $\theta = 0{\cdot}92$, we assume that for $\theta = 1$ the contact potential would be 1·12 volts and thus, if V_θ is the contact potential at any stage in building up the film, we assume that $\theta = V_\theta / 1{\cdot}12$. Bosworth followed the relation between V_θ and the time t as the film built up and thus obtained the relation between θ and t. For each value of θ we obtain by interpolation from Table I the value of the integral* on the left of equation (3·6). These values plotted against the time are shown as crosses in fig. 17—the values plotted as points are discussed in chapter v.

The relation between $\int_0^\theta \frac{d\theta}{\phi(\theta)}$ and t is approximately linear and this is what would be expected for an immobile film, and this behaviour is very different from that of a mobile film (see section 3·3).

§ 3·2. Some properties of oxygen films.

We shall now consider some experimental results with oxygen films on tungsten which are consistent with what would be expected if the well-known stable film of oxygen had in it holes of the type discussed in section 3·1. Using the method involving the measurement of the heat of adsorption the author(1) has shown that in addition to the well-known stable film, the heat of adsorption of which is greater than 100 kilocalories per mol., and the amount in which is approximately one atom of oxygen per atom of tungsten, some oxygen is adsorbed with a heat of 40 or 50 kilocalories per mol. This additional oxygen can be removed by heating to a comparatively low temperature (about 1000° K.). Owing to certain complications and difficulties in working with oxygen, which we need not discuss here, it is extremely difficult to obtain an accurate measure of the amount so adsorbed, but it appears to be less

* The values plotted in fig. 17 are not the same as those in Bosworth's fig. 4 which refer to a first approximation theory given earlier by the author.

than a complete film and the most likely explanation of its presence is that it consists of molecules held by the bare tungsten atoms in the gaps in the atomic film. The estimated amount so adsorbed agreed with what would be expected on this view, but, although this result is suggestive, it would be unwise owing to the difficulties already mentioned to regard it as definite experimental proof of the existence of the holes (see section 7·2).

Van Cleave(8) has carried out some experiments using the accommodation-coefficient method. The technique was the same as that described in section 1·2 for hydrogen, except that the oxygen was admitted so that it could reach the wire without having to pass through a charcoal tube. Admission of oxygen causes the accommodation coefficient of neon to rise from 0·06, the value for a bare surface, to above 0·3. As the earlier experiments by the author had shown, moderate heating of the wire after the deposition of oxygen reduces the accommodation coefficient to a value in the neighbourhood of 0·2 and a low value corresponding to bare tungsten is obtained only after heating to about 2000° K. The actual relation between the accommodation coefficient a measured at *room temperature* and the mean temperature to which the wire with the oxygen film on it had been heated for 1 min. in neon free from oxygen* is shown in fig. 18. The value 0·2 obtained after heating over a considerable range of temperature presumably corresponds to the presence of the well-known stable film. It will be seen that removal of this film begins at temperatures of about 1750° K. Heating the wire to temperatures between about 1500 and 1700° K. caused an *increase* in the value of the accommodation coefficient. This effect is presumably due to some rearrangement in the film, a possible interpretation being that the film becomes mobile and that at these temperatures there is an appreciable probability that two gaps should come together and be filled up from

* There were residual traces of oxygen in the neon and the values plotted were obtained by extrapolation to the time at which the heating current was switched off as described in section 1·2.

residual traces of oxygen in the gas phase. It is evident that this cannot be regarded as direct experimental proof for the existence of holes in the stable film, but it is consistent with the behaviour that would be expected from a film containing such holes.*

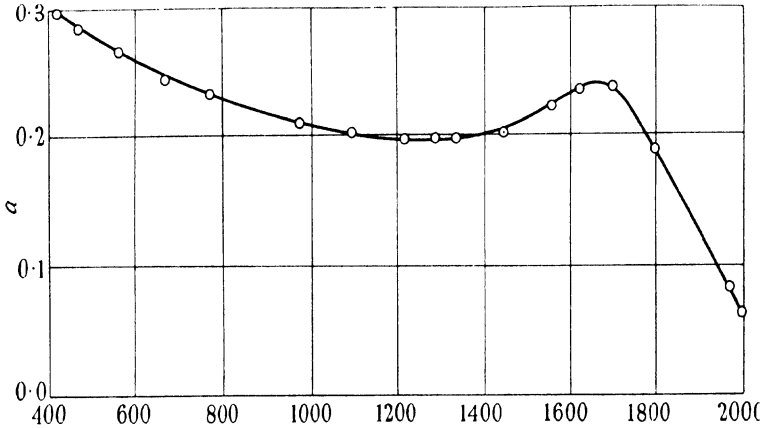

Fig. 18. Accommodation coefficient a of tungsten wire at room temperature as function of the temperature to which it has been heated for 1 min. in neon containing a trace of oxygen.

§ 3·3. The kinetics of the formation of mobile films with dissociation.

We shall commence the study of mobile films, in which there is repulsive interaction between adsorbed particles and no two neighbours of a given site are neighbours of each other, by considering the states of lowest energy as we did in section 2·2 in connexion with heats of adsorption. When $\theta = 0{\cdot}5$ the particles will be arranged as shown in fig. 10, that is no two neighbouring sites will be vacant and no further adsorption of diatomic molecules with dissociation will be possible. The curve showing the relation between θ and the time will obviously be of the type marked $\eta = 0$ in fig. 19, the shape of the earlier part being calculated as shown below.

* It may be mentioned here that Van Cleave found evidence that oxygen can be adsorbed on the top of the first film and not in the gaps only. This is a further indication of the complicated nature of the processes involved in connexion with the adsorption of oxygen (see chapter VII).

When we take into account the effect of the thermal motion of the particles in making configurations other than that of lowest energy occur, it is evident from the above considerations that there will be a rapid change in the rate of formation of the film in the neighbourhood of $\theta = 0{\cdot}5$. The reason for this is that, for $\theta \geqslant 0{\cdot}5$, configurations with two neighbouring vacant sites cannot occur without causing an increase in the number of neighbouring sites occupied, i.e. an increase in the interaction energy of the adsorbed particles. For example in fig. 10, if particle on a site which we shall call site 1 moves to a neighbouring site, adsorption can occur on site 1. Since, by Boltzmann's law, the occurrence of such configurations is relatively improbable, the rate of condensation becomes slow.

We obtain the formula for the rate of condensation as follows(9). If the central site is vacant, the chance that site 1 is vacant is, by expression (2·13), given by $1/(1+\epsilon)$. The probability that the central site is vacant is $1-\theta$. Thus the probability that a molecule striking the surface at a given place finds two neighbouring sites vacant is $(1-\theta)/(1+\epsilon)$. The rate of condensation of molecules per unit area is

$$\frac{\alpha_2 p_2}{(2\pi m_2 kT)^{\frac{1}{2}}} \frac{1-\theta}{1+\epsilon}, \tag{3·7}$$

where, as before, α_2 is the probability that a molecule condenses when it strikes the surface at a place where two neighbouring sites are vacant. Thus, if there is no re-evaporation, we have, as in equation (3·5),

$$\frac{d\theta}{dt} = \frac{2}{n_s} \frac{\alpha_2 p_2}{(2\pi m_2 kT)^{\frac{1}{2}}} \frac{1-\theta}{1+\epsilon}, \tag{3·8}$$

where n_s is the number of sites per unit area. Integrating this equation we obtain

$$\int_0^\theta \frac{1+\epsilon}{1-\theta}\, d\theta = \frac{2}{n_s} \frac{\alpha_2 p_2}{(2\pi m_2 kT)^{\frac{1}{2}}} t, \tag{3·9}$$

if $\theta = 0$ at $t = 0$. At constant pressure and temperature this equation shows that t is proportional to $\int_0^\theta \frac{1+\epsilon}{1-\theta}\, d\theta$, so that, if

we want to see how θ varies with t, we plot θ as a function of $\int_0^\theta \frac{1+\epsilon}{1-\theta}\,d\theta$. This is done in fig. 19 for various values of $\eta = e^{-V/kT}$.

If $\eta = 1$, i.e. the interaction energy between neighbouring adsorbed atoms is negligibly small, we have a random distri-

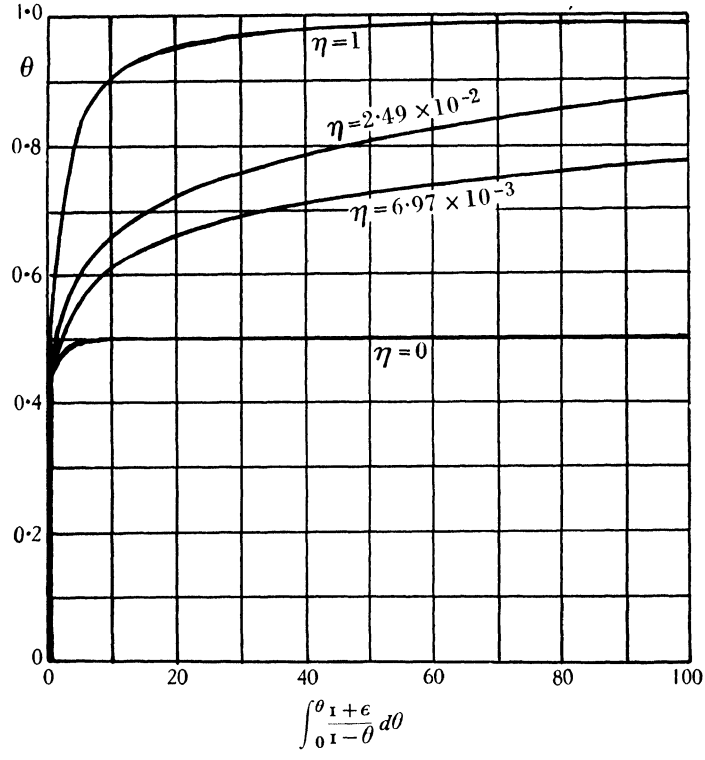

Fig. 19. Relation between θ and the time for the formation of a mobile film.

bution and the probability of finding two neighbouring sites vacant becomes $(1-\theta)^2$. If we write $(1-\theta)^2$ instead of $(1-\theta)/(1+\epsilon)$, equation (3·9) becomes

$$\int_0^\theta \frac{d\theta}{(1-\theta)^2} = \frac{2}{n_s}\frac{\alpha_2 p_2}{(2\pi m_2 kT)^{\frac{1}{2}}}t. \qquad (3\cdot10)$$

This can of course be integrated. It is interesting to compare

this equation for condensation into a film in which there is a random distribution of single occupied sites with equation (3·6),

$$\int_0^\theta \frac{d\theta}{\phi(\theta)} = \frac{2}{n_s}\frac{\alpha_2 p_2}{(2\pi m_2 kT)^{\frac{1}{2}}}\, t,$$

which refers to a film in which there is a random distribution of pairs of occupied sites. We suppose that α_2, p_2, n_s, m_2 and T

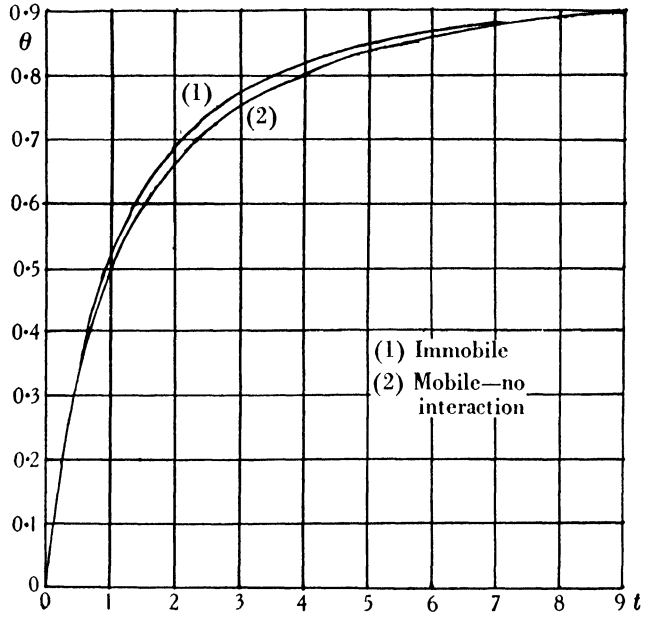

Fig. 20. Rate of formation of immobile film and mobile film with no interaction.

are the same in the two cases. The relative times taken from 0 to θ are then proportional to the integrals on the left side of the two equations. θ is plotted as a function of these two integrals in fig. 20. It will be seen that the two curves are very similar and that they cross just below $\theta = 0{\cdot}9$. The reason for this is that the curve for the immobile film approaches a limiting value of $\theta = 0{\cdot}92$ while the other approaches a limiting value of $\theta = 1$.

Chapter IV

EVAPORATION PROCESSES AND THE PRODUCTION OF ATOMIC HYDROGEN

§ 4·1. The production of atomic hydrogen by hot tungsten.

When a tungsten filament is heated to a sufficiently high temperature in hydrogen contained in a glass vessel the walls of which are cooled in liquid air, Langmuir(1) showed that there is a continuous diminution of pressure and interpreted this as being due to the production by the hot tungsten of atomic hydrogen which is adsorbed on the surface of the glass. In order to investigate the rate of production quantitatively it is essential to use an efficient method of trapping the atoms, since, if it can be assumed that any atom produced is trapped before it combines with another atom, the rate of disappearance of gas, obtained from the volume of the vessel and the rate of diminution of pressure, gives a measure of the rate of production of atoms. Langmuir's measurements themselves showed that glass cooled in liquid air is not consistently efficient in this way, since the rate of production of atoms under definite conditions appeared to be very variable.

Atomic hydrogen is known to react with molybdenum oxide. In order to trap the atoms efficiently, and obtain accurate measurements of their rate of production, Bryce(2) deposited this oxide to a depth of more than fifty layers on the walls of the vessel containing the tungsten by heating a subsidiary molybdenum filament in oxygen. After this oxygen had been pumped off, the experiment on the production of atomic hydrogen was begun, the vessel containing the filament being immersed in melting ice to keep the temperature constant. The results obtained showed that the earlier estimates of the rate

of production under given conditions were too low by a factor at least as great as two hundred. From this, and the fact that subsidiary experiments showed that there was no fatigue effect in the molybdenum oxide, it can be concluded that the oxide is a much more efficient and reliable trap than the glass surface cooled in liquid air. Some considerations given below indicate, as we shall see, that the trapping must be almost 100 per cent efficient.

With the filament at a fixed temperature the effect of varying the pressure on the rate of production of atoms is shown in Table II. It may be mentioned that the smaller rates at the

Table II

Central filament temperature	Mean pressure p mm. mercury	Volume at N.T.P. dissociated per cm.^{2} per sec. v cm. sec.$^{-1}$	$v/p^{\frac{1}{2}}$
1148° K.	$3{\cdot}50 \times 10^{-3}$	$2{\cdot}13 \times 10^{-6}$	$0{\cdot}36 \times 10^{-4}$
	12·5	6·1	0·55
	31·0	9·5	0·53
	37·2	8·1	0·42
1243	2·40	8·6	1·75
	4·59	19·4	2·86
	10·3	24·2	2·35
	12·5	31·3	2·79
	17·5	36·0	2·72
	24·4	40·3	2·58
	32·8	50·3	2·78
	37·0	51·1	2·66
	37·0	49·0	2·55
1338	4·87	72·9	10·4
	11·7	120	11·1
	15·3	130	10·5
	35·2	215	11·5
	36·0	225	11·8
1420	13·0	400	35·0
	36·4	703	37·0

lowest temperature could not be measured as accurately as the others. It will be seen from the constancy of the sets of numbers in the last column that at constant filament temperature the

rate of production is proportional to the square root of the hydrogen pressure.

The variation of the rate of production with filament temperature was accurately determined. After correcting for the distribution of temperature along the filament, the results showed that n, the number of hydrogen atoms produced per cm.^{2} per sec., is given by

$$n = 2{\cdot}5 \times 10^{24} p_{mm}^{\frac{1}{2}} e^{-45000/RT}, \qquad (4{\cdot}1)$$

where p_{mm} is the pressure in mm. of mercury and $R = 1{\cdot}985$ cal. deg.$^{-1}$ T is the temperature of the tungsten and the gas is at 0° C. The experimental results on which this equation is based cover a temperature range from 1148 to 1420° K. and a pressure range from 3×10^{-3} to $3{\cdot}7 \times 10^{-2}$ mm. of mercury.

It is evident that to explain these results we must consider in some detail the various processes occurring at the surface, including the evaporation from it of adsorbed particles.

§ 4·2. Groups of processes occurring at the surface.

In the case of adsorption without dissociation there are only two processes to be taken into account: (1) Condensation of molecules, and (2) Evaporation of molecules. When each molecule occupies one site on the surface and when there is no interaction, we have seen in section 2·1 that the condition of balance between these two processes leads to the Langmuir adsorption isotherm.

When dissociation occurs on adsorption there are more possible processes at the surface to be considered and in discussing the equilibrium problem we must also take into account the fact that at a given temperature and pressure the gas in its equilibrium state contains both undissociated and dissociated molecules. The equilibrium condition for the reaction

$$H_2 = 2H$$

in the gas phase is $$p_1 = 10^3 K^{\frac{1}{2}} p_2^{\frac{1}{2}}, \qquad (4{\cdot}2)$$

where p_1 and p_2 are the partial pressures in dynes per cm.^{2} of the atomic and molecular forms respectively and K is the equilibrium constant with pressures measured in atmospheres. For the sake of definiteness we consider the case of hydrogen although the treatment applies equally well to any diatomic molecule with two similar atoms.

Suppose the gas is contained in a tungsten box maintained at the required temperature T, the surface of the metal being free from oxygen and other adsorbed impurities. Quite apart from any reactions taking place in the gas phase, the processes occurring at the surface must themselves be able to set up and maintain the degree of dissociation of the hydrogen corresponding to the temperature of the walls and the pressure in the box. There are three pairs of surface processes to be considered and, according to the principle of detailed balancing, each pair of these must balance individually. These processes are:

(i) (*a*) Evaporation of atoms from the adsorbed film.
(*b*) Atom from the gas strikes the surface where there is a vacant site and sticks.

(ii) (*a*) Two neighbouring adsorbed atoms combine and evaporate as a molecule.
(*b*) Molecule strikes surface where two neighbouring sites are vacant and is adsorbed as atoms.

(iii) (*a*) Gas atom strikes adsorbed atom, combines with it and the two evaporate as a molecule.
(*b*) Gas molecule strikes the surface where there is one vacant site or more, one atom is adsorbed, the other goes into the gas phase.

In order to make the physical meaning of the theory clear we shall consider in the next section (4·3) the balance between these processes[3] and the theory of the production of atomic hydrogen on the assumption that there is no interaction between adsorbed atoms[4]. In section 4·5 we shall see how the interactions can be taken into account and shall show that as far as the production

of atomic hydrogen is concerned the inclusion of the effect of the interactions produces no important difference(5). We shall therefore give the full numerical comparison between theory and experiment in section 4·3 in connexion with the simple theory.

§ 4·3. Theory of equilibrium and of the production of atomic hydrogen neglecting interactions.

The numbers of atoms and molecules (subscripts 1 and 2 respectively) from the gas striking unit area of the wall per second are p_1/μ_1 and p_2/μ_2, where $\mu_1=(2\pi m_1 kT)^{\frac{1}{2}}$ and $\mu_2=(2\pi m_2 kT)^{\frac{1}{2}}$. We now write down the equations, neglecting the effects of interactions, for the balance of the three pairs of processes enumerated in the last section. From (i) we have

$$B_1\theta=\frac{\alpha_1 p_1(1-\theta)}{\mu_1}, \qquad (4\cdot3)$$

where B_1 is the number of atoms evaporating per second per unit area from a complete film and α_1 is the probability that an atom from the gas phase is adsorbed when it strikes a place on the surface where there is a vacant site.

From (ii) we have

$$B_2\theta^2=\frac{\alpha_2 p_2(1-\theta)^2}{\mu_2}, \qquad (4\cdot4)$$

where B_2 is the rate of evaporation of molecules from unit area of a complete film and α_2 is the probability that a molecule is adsorbed when it strikes a place on the surface where two neighbouring sites are vacant.

From (iii) we have

$$\frac{B_3 p_1\theta}{\mu_1}=\frac{B_4 p_2(1-\theta)}{\mu_2}, \qquad (4\cdot5)$$

where B_3 is the probability that a gas atom striking an adsorbed atom combines with it, the two evaporating as a molecule, and B_4 the probability that a molecule, which strikes a place on the surface where there is a vacant site, breaks up so that one atom is adsorbed and the other escapes into the gas phase.

Substitute the value of p_1 given by equation (4·2) in equations (4·3), (4·4) and (4·5), and we obtain respectively

$$\frac{\theta}{1-\theta}=\frac{10^3K^{\frac{1}{2}}}{\mu_1}\frac{\alpha_1}{B_1}p_2^{\frac{1}{2}}, \tag{4·6}$$

$$\frac{\theta}{1-\theta}=\frac{1}{(\mu_2)^{\frac{1}{2}}}\left(\frac{\alpha_2}{B_2}\right)^{\frac{1}{2}}p_2^{\frac{1}{2}}, \tag{4·7}$$

$$\frac{\theta}{1-\theta}=\frac{(m_1/m_2)^{\frac{1}{2}}B_4}{10^3K^{\frac{1}{2}}B_3}p_2^{\frac{1}{2}}. \tag{4·8}$$

Each of these equations is of the form

$$\frac{\theta}{1-\theta}=Ap_2^{\frac{1}{2}}, \tag{4·9}$$

where A is constant at constant temperature. This is the form of the isotherm (cf. section 4·7), and it is evident that the three expressions for A must all be the same, which gives relations between α_1, B_1, α_2, B_2, B_3 and B_4.

Two of the processes discussed give rise to the presence of atoms in the gas phase. These are (i) (*a*) in which atoms evaporate from the adsorbed film, and (iii) (*b*) in which a gas molecule strikes a bare tungsten atom, one atom being adsorbed, the other going into the gas phase. The fact that at a given temperature the rate of production of hydrogen atoms is proportional to the square root of the pressure shows either that process (i) (*a*) is the important one and the film is very sparsely occupied, or that process (iii) (*b*) is the important one and the film is nearly complete.

Let us consider the first possibility. If θ is small, equation (4·9) shows that $\theta \propto p_2^{\frac{1}{2}}$ and, since the rate of evaporation of atoms is proportional to θ, this will also be proportional to $p_2^{\frac{1}{2}}$. If, on the other hand, θ is not small, the $p_2^{\frac{1}{2}}$ law no longer holds. For example, if θ is nearly unity, the rate of evaporation is independent of p_2.

Now consider the second possibility. If θ is nearly unity, we have $(1-\theta) \propto p_2^{-\frac{1}{2}}$. The number of atoms produced by process

(iii) (b) is proportional to the product of the number of molecules striking unit area per second and of the number of vacant places per unit area, i.e. to $p_2(1-\theta)$, or to $p_2^{\frac{1}{2}}$. If θ is not nearly unity, the $p_2^{\frac{1}{2}}$ law no longer holds.

We shall now show that both processes lead to the same law of variation with temperature and to one which is in agreement with that determined experimentally. Consider first the evaporation of atoms from a sparsely covered surface. If we use equation (4·6) to obtain the relation between θ and p_2, we have when θ is small

$$\theta = \frac{10^3 K^{\frac{1}{2}}}{\mu_1}\frac{\alpha_1}{B_1} p_2^{\frac{1}{2}}.$$

This gives the equilibrium covering when the gas and solid are at the same temperature T. It can be taken as giving a first approximation to the covering when the solid is at a temperature T, at which the degree of dissociation is small, but the gas is at 0° C. In considering this latter case and working to this approximation we can regard μ_1 as constant, since it varies only as $T^{\frac{1}{2}}$ and any changes in it are negligible compared with those in K which is an exponential function. Thus we can write for $B_1\theta$ the rate of production of atomic hydrogen by evaporation

$$B_1\theta = \text{const. } K^{\frac{1}{2}}\alpha_1 p_2^{\frac{1}{2}}, \qquad (4\cdot10)$$

where α_1 is the condensation coefficient for hydrogen atoms striking bare metal atoms. The adsorption of a hydrogen atom on tungsten is a highly exothermic process (6) and it would not be expected that α_1 would vary rapidly with temperature (see section 4·4). If we regard α_1 as constant, then at constant pressure the temperature variation of the rate of production of atomic hydrogen is due entirely to the temperature variation of $K^{\frac{1}{2}}$.

Now consider the other process. The rate of production of atomic hydrogen is equal to

$$\frac{B_4 p_2(1-\theta)}{\mu_2}.$$

If θ is nearly unity, we have from (4·8),

$$1-\theta=\frac{10^3K^{\frac{1}{2}}B_3}{(m_1/m_2)^{\frac{1}{2}}B_4p_2^{\frac{1}{2}}}.$$

Thus we have for the rate of production of atomic hydrogen per unit area per second

$$\frac{B_4p_2(1-\theta)}{\mu_2}=\frac{10^3K^{\frac{1}{2}}}{\mu_1}B_3p_2^{\frac{1}{2}}. \qquad (4\cdot11)$$

As before we may neglect the temperature variation of μ_1. B_3 is the probability that, when an atom from the gas phase strikes an adsorbed atom, the two combine and evaporate as a molecule. A large amount of heat is evolved when this takes place. We assume that B_3 is, to a first approximation, independent of the temperature. At constant pressure the variation with temperature of the rate of production of atomic hydrogen is due entirely to the temperature variation of $K^{\frac{1}{2}}$ as in the first process considered. This result is important since it shows that a determination of the temperature variation does not enable us to decide between the two processes.

We shall now show that this theoretical temperature variation agrees with that determined experimentally. Values of $\log_{10}K$ calculated from the data given by Giauque(7), but using the value 101,000 calories for the heat of dissociation from spectroscopic data instead of the older value 102,800 used by him, are given in Table III. If values of $\log_{10}K^{\frac{1}{2}}$ deduced from these

Table III

T	$\log_{10}K$
298·1° K.	−77·139
500	−39·332
1000	−16·797
1500	− 9·181
2000	− 5·332
2500	− 3·003

are plotted against $1/T$, a linear relation is obtained over the required temperature range and, using values of $K^{\frac{1}{2}}$ from this

plot, the relative rates of production of atomic hydrogen at the tungsten surface at various temperatures can be obtained immediately if the above theoretical views are correct. Thus, if the rate at one temperature (the highest) is taken as known, those at other temperatures can be calculated. The results of this calculation together with the measured rates are given in Table IV. The agreement is satisfactory.

Table IV

Temperature	Rate of production of H atoms per cm.^{2} per sec. at $p = 1{\cdot}25 \times 10^{-2}$ mm. mercury	
	Observed	Theoretical
1420° K.	316×10^{14}	(316×10^{14})
1338	115×10^{14}	103×10^{14}
1243	32×10^{14}	22×10^{14}
1148	7×10^{14}	4×10^{14}

In order to decide which of the two processes is the important one it is necessary to determine experimentally whether the surface is sparsely or nearly fully covered in the above experiments. This has been done by Bosworth(8) using the method of contact potentials described in section 3·1. He has shown that, under the conditions obtaining in Bryce's experiments, the covering would always be greater than 0·6 or 0·7. We therefore conclude that the second process considered above, in which a molecule strikes a bare place on the surface, one atom being adsorbed and the other passing into the gas phase, is under the conditions of Bryce's experiments the one primarily responsible for the production of atomic hydrogen.

Lennard-Jones* has pointed out that, since all the other quantities in equation (4·11) are known, an estimate can be made of the value of B_3. Using the above values of K and the values of the rate of production of H atoms given in Table IV, we obtain values of B_3 ranging from 1·1 at 1420° K. to 1·8 at

* Professor Lennard-Jones pointed this out to me in private conversation.

1148° K. Remembering the approximations made in the theory we are certainly justified in concluding that B_3 is not far from unity—it cannot actually of course be greater than unity—that is, when an atom from the gas phase strikes an adsorbed atom, they almost certainly combine and evaporate as a molecule. The fact that the experimental results treated in this way lead to a value of B_3 which is nearly unity is an indication of the efficiency of the molybdenum oxide in trapping the hydrogen atoms.

§ 4·4. Some general results.

In section 4·5 we shall consider a fuller treatment including the effects of interactions. We shall devote this section to a discussion of some of the fundamental assumptions which we shall have to use in that fuller theory. The adsorbed particles can be regarded as oscillators moving in various quantum states in the field at the surface of the solid and Lennard-Jones and Devonshire(9) have discussed the excitation of such oscillators and the evaporation of the particles by interaction with the elastic waves of the solid. This treatment supersedes completely all earlier attempts, such for example as that given by the author(10), to obtain formulae for evaporation based on a classical picture. They have shown how calculations can be carried out for the case when the oscillations are normal to the surface, so that the state can be specified by one quantum number, and when only one quantum of thermal vibration of the solid is transferred at a time. This practically restricts the treatment to atoms or molecules held by van der Waals forces, since only these would be likely to be evaporated by one such quantum.* They assume that the potential energy between the adsorbed

* Strachan(11) has later shown that the probability of the simultaneous transfer of several quanta of energy by the solid is small. Lennard-Jones and Goodwin(12) have therefore examined the possibility that the energy necessary to excite and evaporate adsorbed atoms held by chemical forces may come from the metallic electrons. It has not been possible to carry the calculations in this case quite as far as in that considered by Lennard-Jones and Devonshire.

particle and the surface can be represented by a Morse function (see section 1·1). The interesting result has been obtained that even at very low temperatures evaporation in two stages is relatively very frequent. The two stages involved are, first,

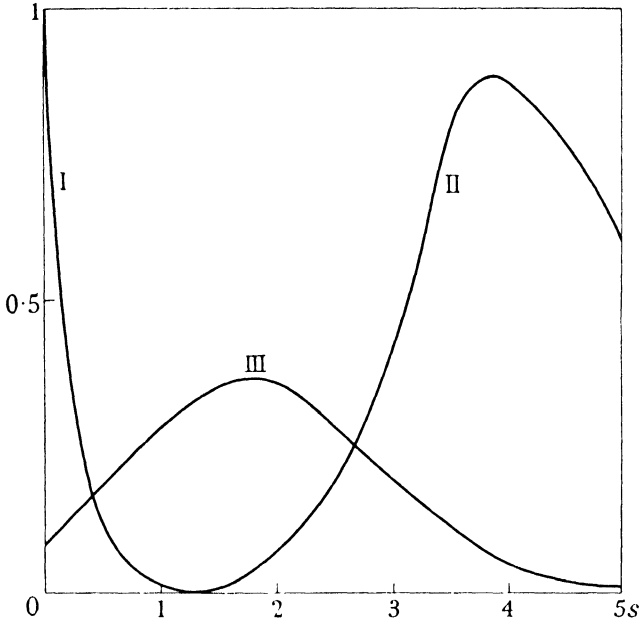

Fig. 21. The probability of evaporation of an adsorbed molecule from various quantum states s of vibration perpendicular to the surface of a solid. Curve I gives the relative population of the various states, curve II the relative probability of evaporation from each state, and curve III on a different scale the product of curves I and II ($T=30°$ K., $\Theta=510°$ K.).

excitation to a higher vibrational level and then communication from the solid of a further quantum sufficient to cause evaporation. This mechanism is illustrated by fig. 21 in which curve I gives the relative populations of the various states, curve II the relative probability of evaporation from each state and curve III, on a different scale, the product of curves I and II, i.e. the relative numbers of evaporating particles coming from the different states. The calculations were made for $T=30°$ K., for

a solid with a characteristic temperature $\Theta = 510°$ K., and for a heat of desorption from the lowest state of 1000 calories per mol. It will be seen that evaporating particles are most likely to come from the second state and that almost as many come from the fourth state as from the ground state, in spite of the relatively low populations of the second and fourth states. It may be mentioned that the only points on these curves which are significant are those lying immediately above the abscissae corresponding to $s = 0, 1, 2$, etc.

Lennard-Jones and Devonshire analyse the assumption that for a given desorption process the rate of evaporation of particles per unit area is proportional to

$$A\theta e^{-\chi/kT}, \qquad (4{\cdot}12)$$

where χ is the energy of desorption per molecule from the lowest state and A is a constant. In this formula, as in their theory, it is tacitly assumed that there is no interaction between adsorbed particles. They carry out calculations for particles of molecular weight 2 and for a heat of desorption of 1000 calories per mol. and $\Theta = 510°$ K. at $T = 30$ and $T = 300°$ K. and show that A is not constant but that

$$\frac{A_{300}}{A_{30}} \simeq 6.$$

The essential thing from our point of view is that their calculation justifies the use of formula (4·12), because over this range of temperature and for the given value of χ the term $e^{-\chi/kT}$ varies by a factor of about 10^7, so that the correct formula with A a function of T and formula (4·12) with A constant and a slight adjustment in the value of χ would be completely indistinguishable in any experimental investigation.

We shall make a similar assumption throughout the subsequent treatment and shall suppose that, when there is an interaction energy V (positive if the force is repulsive) between particles adsorbed on neighbouring sites, the relative probability

of evaporation of a particle on a site with $\theta_1+\ldots+\theta_z$ neighbouring sites occupied contains a factor

$$e^{-\{\chi-(\theta_1+\ldots+\theta_z)V\}/kT},$$

and that the term corresponding to the A term in (4·12) does not vary appreciably with T or with $\theta_1+\ldots+\theta_z$. Although A is undoubtedly in fact a function of T and of $\theta_1+\ldots+\theta_z$, the essential point is that in the important temperature range $\{\chi-(\theta_1+\ldots+\theta_z)\,V\}/kT$ is assumed to be sufficiently large for variations in the exponential term occasioned by changes in $\theta_1+\ldots+\theta_z$ or in T to swamp completely the accompanying changes in A. Lennard-Jones and Devonshire have, as we have seen, justified the assumption of an effectively constant A at different temperatures for van der Waals' adsorption and for no interaction between adsorbed particles. We extend it to cover the effect of interaction between adsorbed particles and processes in which the heat of adsorption indicates that chemisorption is involved.

Lennard-Jones and Devonshire have also examined the theory of condensation for a similar model and have shown that for a molecule striking a vacant site the condensation coefficient varies little with temperature, being 0·081 at 30° K. and 0·103 at 300° K. This provides some support for the assumption we have made about condensation coefficients in section 4·3.

§ 4·5. Theory of equilibrium and of production of atomic hydrogen including effect of interactions.

We now consider the balance between the three pairs of processes given in section 4·3, taking into account, however, interactions between the adsorbed atoms(5). We assume as before that each site has z nearest neighbours, that no two neighbours of a given site are neighbours of each other, and that there is an interaction energy V between atoms adsorbed on neighbouring sites and no appreciable interaction energy if they are at a greater distance. The relative probability of a given

arrangement of atoms on the central site o and its neighbours 1 ... z, specified as before by the numbers $\theta_0, \theta_1 \ldots \theta_z$, is given by equation (2·13).

Let us first consider the pair of processes (i). If, as before, we write $\eta = e^{-V/kT}$, the expression for the rate of evaporation of atoms from sites surrounded by $(\theta_1 + \ldots + \theta_z)$ occupied sites will, as discussed in the preceding section, contain a factor

$$\eta^{-(\theta_1+\ldots+\theta_z)}.$$

Since we are discussing the evaporation of an atom from the central site, we consider only arrangements in which the central site is occupied, i.e. $\theta_0 = 1$. The relative probability of an assigned set of values of $\theta_1 \ldots \theta_z$ is, by equation (2·13), given by

$$(\eta\epsilon)^{\theta_1+\ldots+\theta_z},$$

so that the rate of evaporation from unit area of the surface is given by

$$B_1\theta \frac{\Sigma(\eta\epsilon)^{\theta_1+\ldots+\theta_z}\eta^{-(\theta_1+\ldots+\theta_z)}}{\Sigma(\eta\epsilon)^{\theta_1+\ldots+\theta_z}},$$

or by

$$B_1\theta \frac{\Sigma\epsilon^{\theta_1+\ldots+\theta_z}}{\Sigma(\eta\epsilon)^{\theta_1+\ldots+\theta_z}},$$

where $B_1\theta$ would be the rate of evaporation of atoms per unit area for a given θ if the atoms were arranged in such a way that there were no interactions.* Since the sums are to be taken for all possible combinations of the various values of $\theta_1 \ldots \theta_z$, this becomes

$$B_1\theta\left(\frac{1+\epsilon}{1+\eta\epsilon}\right)^z. \qquad (4\cdot13)$$

The rate of the inverse condensation process per unit area is

$$\alpha_1 \frac{p_1}{\mu_1}(1-\theta), \qquad (4\cdot14)$$

* B_1 and other similar quantities used in this section are not the same as the corresponding quantities in section 4·3, but they have a similar significance and, since the theories with and without interaction will never be used together, no confusion can arise from using the same symbols in the two theories.

where as before we assume that α_1, the probability that an atom condenses when it strikes a vacant site, is independent of the state of occupation of neighbouring sites. For the balance of processes (i), we have, then,

$$\frac{\theta}{1-\theta} = \frac{\alpha_1 p_1}{B_1 \mu_1}\left(\frac{1+\eta\epsilon}{1+\epsilon}\right)^z. \tag{4·15}$$

Now consider (ii) the evaporation and condensation of molecules. We have already seen in equation (3·7) that the rate of condensation of molecules on unit area per second is

$$\frac{\alpha_2 p_2}{\mu_2}\frac{1-\theta}{1+\epsilon}. \tag{4·16}$$

In the inverse evaporation process atoms on sites 0 and 1 combine and evaporate. The probability that site 0 is occupied is θ. If site 0 is occupied, the probability that site 1 is also occupied is, from (2·13),

$$\frac{\Sigma(\eta\epsilon)^{1+\theta_2+\ldots+\theta_z}}{\Sigma(\eta\epsilon)^{\theta_1+\theta_2+\ldots+\theta_z}} = \frac{\eta\epsilon}{1+\eta\epsilon}.$$

That is, the probability that sites 0 and 1 are occupied together is

$$\theta\frac{\eta\epsilon}{1+\eta\epsilon}.$$

The rate of evaporation will contain a factor depending on the state of occupation of the sites surrounding 0 and 1. We continue to specify the occupation of the sites around 0 by $\theta_1 \ldots \theta_z$ and specify the occupation of those round 1 by $\theta_1' \ldots \theta_z'$ with $\theta_1' = \theta_0$. No other dashed site coincides with an undashed site. From considerations exactly similar to those leading to expression (4·13) the average rate of evaporation of molecules per unit area of surface is

$$B_2\theta\frac{\eta\epsilon}{1+\eta\epsilon}\frac{\Sigma(\eta\epsilon)^{1+\theta_2+\ldots+\theta_z}\eta^{-(\theta_2+\ldots+\theta_z)}(\eta\epsilon)^{1+\theta_2'+\ldots+\theta_z'}\eta^{-(\theta_2'+\ldots+\theta_z')}}{\Sigma(\eta\epsilon)^{1+\theta_2+\ldots+\theta_z}(\eta\epsilon)^{1+\theta_2'+\ldots+\theta_z'}},$$

where the sums are to be taken for all possible combina-

tions* of values of $\theta_2 \ldots \theta_z$, $\theta_2' \ldots \theta_z'$. This expression is equal to

$$B_2\theta\frac{\eta\epsilon}{1+\eta\epsilon}\left(\frac{1+\epsilon}{1+\eta\epsilon}\right)^{2z-2}. \qquad (4\cdot17)$$

For the condition of balance of processes (ii) obtained by equating (4·16) and (4·17) we have, since, by (2·14),

$$\frac{\theta}{1-\theta}=\frac{\epsilon(1+\eta\epsilon)}{1+\epsilon},$$

$$\frac{\theta}{1-\theta}=\left(\frac{\alpha_2 p_2}{B_2\mu_2}\right)^{\frac{1}{2}}\frac{1}{\eta^{\frac{1}{2}}}\left(\frac{1+\eta\epsilon}{1+\epsilon}\right)^{z}. \qquad (4\cdot18)$$

We now consider the third pair of processes. When a hydrogen atom from the gas phase strikes an adsorbed atom and the two combine and evaporate as a molecule, there is a considerable evolution of heat. We assume that the frequency of occurrence of this process per unit area is given by

$$\frac{B_3 p_1\theta}{\mu_1}, \qquad (4\cdot19)$$

with B_3 to a first approximation independent of the temperature and of the state of occupation of surrounding sites. In the inverse process, when a molecule from the gas phase strikes an unoccupied site (the central site) and one atom is adsorbed and the other escapes to the gas phase, the energy *absorbed* is

$$q_d-(q_1)_0+V(\theta_1+\ldots+\theta_z), \qquad (4\cdot20)$$

where q_d is the energy of dissociation per molecule in the gas phase and $(q_1)_0$ the heat of adsorption of an atom on a bare surface. The frequency of occurrence of this process is therefore taken as containing a factor $\eta^{\theta_1+\ldots+\theta_z}$. If the central site is vacant, the relative probability of a configuration of given

* It may be mentioned that θ_2', etc. are not all necessarily independent of θ_2, etc., but with the present method of averaging this interdependence must be neglected (see section 4·7).

$\theta_1 \ldots \theta_z$ is by (2·13) given by $\epsilon^{\theta_1+\ldots+\theta_z}$. Thus the frequency of occurrence of this process per unit area per second is

$$\frac{B_4 p_2(1-\theta)}{\mu_2} \frac{\Sigma(\eta\epsilon)^{\theta_1+\ldots+\theta_z}}{\Sigma\epsilon^{\theta_1+\ldots+\theta_z}},$$

which is equal to

$$\frac{B_4 p_2(1-\theta)}{\mu_2}\left(\frac{1+\eta\epsilon}{1+\epsilon}\right)^z. \tag{4·21}$$

For the equilibrium of the pair of processes (iii) we obtain from (4·19) and (4·21)

$$\frac{\theta}{1-\theta}=\frac{B_4}{B_3}\left(\frac{m_1}{m_2}\right)^{\frac{1}{2}}\frac{p_2}{p_1}\left(\frac{1+\eta\epsilon}{1+\epsilon}\right)^z. \tag{4·22}$$

Substituting the value of p_1 given by equation (4·2) in (4·15) and (4·22), the three equations (4·15), (4·18) and (4·22) which give $\theta/(1-\theta)$ become respectively

$$\frac{\theta}{1-\theta}=\frac{10^3K^{\frac{1}{2}}}{\mu_1}\frac{\alpha_1}{B_1}p_2^{\frac{1}{2}}\left(\frac{1+\eta\epsilon}{1+\epsilon}\right)^z, \tag{4·23}$$

$$\frac{\theta}{1-\theta}=\left(\frac{1}{\mu_2\eta}\right)^{\frac{1}{2}}\left(\frac{\alpha_2}{B_2}\right)^{\frac{1}{2}}p_2^{\frac{1}{2}}\left(\frac{1+\eta\epsilon}{1+\epsilon}\right)^z, \tag{4·24}$$

$$\frac{\theta}{1-\theta}=\frac{1}{10^3K^{\frac{1}{2}}}\left(\frac{m_1}{m_2}\right)^{\frac{1}{2}}\frac{B_4}{B_3}p_2^{\frac{1}{2}}\left(\frac{1+\eta\epsilon}{1+\epsilon}\right)^z. \tag{4·25}$$

These are all of the form

$$\frac{\theta}{1-\theta}=Bp_2^{\frac{1}{2}}\left(\frac{1+\eta\epsilon}{1+\epsilon}\right)^z. \tag{4·26}$$

This is the isotherm which we shall discuss in section 4·7. The different expressions for B must all be equal, which gives us relations between α_1, B_1, α_2, B_2, B_3, B_4 similar to those between the corresponding quantities in section 4·3.

We now apply these results to the production of atomic hydrogen and show that the same results are obtained as in section 4·3 where the effects of interaction were neglected. The

rate of evaporation of atoms from unit area of the surface is, by expression (4·13), given by

$$B_1\theta\left(\frac{1+\epsilon}{1+\eta\epsilon}\right)^z.$$

Substituting the value of θ given by (4·23) in this, it becomes

$$(1-\theta)\frac{10^3}{\mu_1}K^{\frac{1}{2}}\alpha_1 p_2^{\frac{1}{2}}.$$

If θ is small, we may put $(1-\theta)=1$, and this expression is then the same as that in (4·10), and may be discussed in the same way.

The rate of production by the other process given by expression (4·21) is

$$\frac{B_4 p_2(1-\theta)}{\mu_2}\left(\frac{1+\eta\epsilon}{1+\epsilon}\right)^z.$$

Using the value of $1-\theta$ given by (4·25), this becomes

$$\theta\frac{10^3}{\mu_1}K^{\frac{1}{2}}B_3 p_2^{\frac{1}{2}}.$$

When θ is nearly unity, this is the same as the expression in (4·11) and may be discussed in the same way.

§ 4·6. True and apparent heats of evaporation of adsorbed films.

In a number of experiments, particularly with oxygen on tungsten, the heat of adsorption has been deduced from measurements of the relative rates of evaporation of adsorbed films at different temperatures. Various electrical methods have been used to measure the amount of oxygen on the surface.

Langmuir and Kingdon [13] showed that an adsorbed film of caesium on tungsten or on tungsten already covered with oxygen increases enormously the electron emission at a given temperature. Further, when there is an oxygen film on the tungsten, the caesium film is much more stable than on bare tungsten. The effect of this is evident if a filament is heated to

a temperature in the neighbourhood of about 800–1000° K. in the presence of caesium vapour at a pressure corresponding to the vapour pressure of caesium at about 20° C. Under these conditions an oxygen covered filament has much more caesium on it than a bare tungsten filament and the emission from it is much greater. Langmuir and Villars(14) have made this fact the basis of a method of measuring the amount of oxygen on a tungsten surface. In applying this method to determine relative rates of evaporation of oxygen they allowed the evaporation to proceed for a measured time at a high temperature (1856–2070° K.). They then cooled the filament down to a temperature in the range 800–1000° K. in the presence of caesium vapour and measured the emission. Assuming that a given emission under definite conditions corresponds to a given fraction of surface covered with oxygen, they were able to deduce relative rates of evaporation at different temperatures.

Johnson and Vick(15) measured the thermionic emission at a fixed high temperature from a tungsten filament and studied directly the effect of an oxygen film on the thermionic current. As the film evaporated the emission increased and a cathode ray oscillograph was used to follow the changes. Their system had the advantage of involving only tungsten and oxygen. Bosworth and Rideal(16) have given a preliminary account of similar experiments in which the contact potential method described in section 3·1 was used.

The heat of adsorption per particle, which we shall for convenience call the apparent heat of evaporation q_a, is in all these experiments deduced from the rate of evaporation r by means of the formula

$$q_a = -k \frac{d \log r}{d(1/T)}, \qquad (4{\cdot}27)$$

where k is Boltzmann's constant. Langmuir and Villars found an apparent heat of 164,000 calories per mol. for small values of θ and state that the value becomes less as θ increases but give no details. Johnson and Vick found 147,000 for small θ.

Bosworth and Rideal found 150,000 for small θ diminishing to about 70,000 as θ increases.

In this section our object is to discuss the meaning of the heats deduced in this way when there is interaction between adsorbed particles. For simple adsorption, in which each particle in the gas phase occupies one site for adsorption, the true heat of adsorption is obtained, but in other cases this is not generally true[17] and to interpret the results correctly we must know the nature of the desorption process involved. To illustrate this we shall discuss the relevant physical processes involved in connexion with adsorption with dissociation and shall consider evaporation in which the only important process is the recombination of adsorbed atoms and subsequent evaporation of molecules.

First consider the true heat of adsorption when $\theta = 0$. A gas molecule strikes the surface and the two atoms are adsorbed on two neighbouring sites. The energy of the system is diminished by χ_2, where χ_2 is the heat of adsorption when the two atoms remain on neighbouring sites and all surrounding sites are vacant. In the normal state of the system with only two atoms on the surface they are on neighbouring sites for only a very small fraction of the total time. In passing to this normal state there is a further diminution of the potential energy of the system by V, where V is the interaction energy between atoms adsorbed on neighbouring sites. The true heat of adsorption $(q_2)_0$ is therefore given by

$$(q_2)_0 = \chi_2 + V. \qquad (4{\cdot}28)$$

When $\theta = 0$, we may consider in the following way the apparent heat of evaporation deduced from the temperature variation of the rate of evaporation. In the limit there are just two atoms left on the surface. Except for a very small fraction of the total time they will not be on neighbouring sites. In order to evaporate as a molecule they must occupy neighbouring sites and when they do so the potential energy of the system is

increased by V. When they evaporate the potential energy* is further increased by χ_2, so that the heat factor in the exponential term in the expression for the rate of evaporation is $\chi_2 + V$, and this is the apparent heat of evaporation obtained from the variation of the rate with temperature. We have therefore for $\theta = 0$

$$(q_a)_0 = (q_2)_0 = \chi_2 + V. \tag{4·29}$$

When $\theta = 1$, the following considerations apply to the true heat of adsorption. In the limit there are two vacant sites left on the surface. Except for a very small fraction of the total time these will not be neighbours. When they are neighbours, the potential energy is greater by V than it is in the normal state. When a molecule from the gas phase comes and occupies these two sites, the energy of the system is diminished by $\chi_2 - (2z-2)\,V$. The total change in energy in going from the normal state with two vacant sites to the final state with all sites occupied is therefore $\chi_2 - (2z-2)\,V - V$, so that $(q_2)_1$, the true heat of adsorption with $\theta = 1$, is, for $z = 4$, given by

$$(q_2)_1 = \chi_2 - 7V. \tag{4·30}$$

Since the surface is fully covered, no reorganization is necessary before evaporation can occur, and therefore the heat factor in the exponential term in the expression for the rate of evaporation is $\chi_2 - (2z-2)\,V$, which is the energy that a molecule must acquire† in order to leave the surface. This is the apparent heat of evaporation deduced from the variation of the rate of evaporation with temperature. Thus, for $z = 4$, we have

$$(q_a)_1 = \chi_2 - 6V. \tag{4·31}$$

Therefore, from (4·29), (4·30) and (4·31),

$$(q_2)_1 - (q_2)_0 = -8V, \tag{4·32}$$

and

$$(q_a)_1 - (q_2)_0 = -7V. \tag{4·33}$$

* We may in connexion with these simple physical considerations neglect the contribution of changes in kinetic energy to heats of adsorption.

† Apart from any heat of activation in the adsorption process, see Roberts(5).

These simple considerations show therefore that there is a difference between the true and apparent heats.

We have already obtained an expression for the variation of true heat of adsorption with fraction of sites occupied in equation (2·22). This gives also, of course, the true heat of

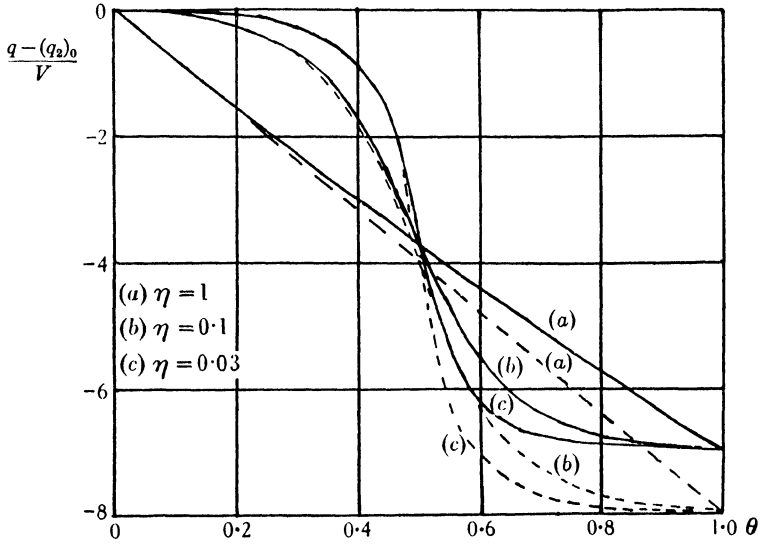

Fig. 22. $\frac{q_a-(q_2)_0}{V}$ (full lines) and $\frac{q_2-(q_2)_0}{V}$ (broken lines) plotted as a function of θ.

evaporation and the heat obtained from isotherms measured at different temperatures by use of the appropriate analogue of the Clausius-Clapeyron equation.* We have already in expression (4·17) obtained r the rate of evaporation of recombined molecules from the surface. From the considerations in section 4·4 it is evident that B_2 in equation (4·17) may be written as

$$B_2 = A_2 e^{-\chi_2/kT}, \qquad (4{\cdot}34)$$

* See for example Wang(18).

where A_2 is to a first approximation independent of the temperature. Using this we have, from (4·17),

$$r = A_2\theta \frac{\eta\epsilon}{1+\eta\epsilon} e^{-\chi_2/kT}\left(\frac{1+\epsilon}{1+\eta\epsilon}\right)^{2z-2}. \qquad (4\cdot35)$$

Substituting the value of r given by (4·35) in (4·27) and using the relation $\theta/(1-\theta)=\epsilon(1+\eta\epsilon)/(1+\epsilon)$ from (2·14), we obtain

$$q_a = \chi_2 - (2z-2)V + \frac{2\eta x V}{\{(x-1)^2+4x\eta\}^{\frac{1}{2}}} \times \left\{\frac{2z-1}{(x-1)+\{(x-1)^2+4x\eta\}^{\frac{1}{2}}} - \frac{1}{(x+1)+\{(x-1)^2+4x\eta\}^{\frac{1}{2}}}\right\}, \qquad (4\cdot36)$$

where $x=\theta/(1-\theta)$. Remembering that, from (4·29), we have $(q_a)_0=(q_2)_0=\chi_2+V$, we can obtain from this equation values of $\{q_a-(q_2)_0\}/V$. These are plotted against θ as full lines in fig. 22 and values of $\{q_2-(q_2)_0\}/V$ as broken lines for various values of η and for $z=4$. The differences indicated by equations (4·32) and (4·33) are evident in the figure.*

§ 4·7. The adsorption isotherm.

A great advance in the theory of adsorption was made when Fowler(19) showed that the Langmuir Adsorption Isotherm can be deduced from statistical considerations only, without postulating any particular mechanism by which the equilibrium state is attained. In addition he has shown that, when diatomic molecules consisting of two similar atoms dissociate on adsorption and each atom occupies one site, the statistical method leads to an isotherm of the same form as that deduced from kinetic considerations in equation (4·9), on the assumption that there is no interaction between adsorbed atoms.

One way in which the statistical method is important is that it shows which of the assumptions leading to any particular result are essential and which are irrelevant. For example, in deducing the Langmuir isotherm the essential assumptions are

* For a further discussion see Roberts(17).

(i) that there are a definite number of sites for adsorption, (ii) that one gas molecule and one only can be adsorbed on each site, and (iii) that there is no interaction between adsorbed molecules, i.e. that the energies of the states of any adsorbed molecule are independent of the state of occupation of neighbouring sites. The fact that a particular mechanism of condensation and evaporation leads to the correct form of the isotherm merely means that the mechanism has been formulated and written down in a consistent manner. If, in connexion with any particular model of adsorption, we are interested in the mechanisms of condensation and evaporation, it is obviously essential that our formulation of these processes should be consistent with the laws of thermodynamics; that is, it is essential that our formulation of the processes should lead to an isotherm of the same form as that obtained for the same model from statistical considerations.

In order to make the comparison in the present case we must express the constant B in equation (4·26) as a function of the temperature. Let χ_1 be the heat of desorption of an atom from a site surrounded by vacant sites and from the state of lowest energy to the state of lowest energy in the gas phase. Let χ_2 be the heat of desorption as a molecule of two atoms adsorbed on neighbouring sites, the surrounding sites being vacant and each atom in its state of lowest energy, the molecule after desorption being in the state of lowest energy in the gas phase.* Let χ_d be the heat of dissociation of a gas molecule in the state of lowest energy into two atoms also in the state of lowest energy. The law of conservation of energy gives

$$\chi_2 = 2\chi_1 - V - \chi_d. \qquad (4{\cdot}37)$$

We now make use of the considerations discussed in section 4·4 and write

$$B_1 = A_1 e^{-\chi_1/kT}, \qquad (4{\cdot}38)$$

$$B_2 = A_2 e^{-\chi_2/kT}, \qquad (4{\cdot}39)$$

* This differs from the definition of χ_2 given before in that we now specify the change as from one state of lowest energy to another. For practical purposes the difference is negligible.

and, using the result given in equation (4·20) and neglecting as discussed in the last footnote the difference between q_d and χ_d and between $(q_1)_0$ and χ_1,

$$B_4 = A_4 e^{(\chi_1 - \chi_d)/kT}. \tag{4·40}$$

A_1, A_2 and A_4 are to a first approximation independent of the temperature. Further the van't Hoff equation of the isochore of reaction for the dissociation of hydrogen in the gas phase may be written

$$\frac{\partial \log K}{\partial T} = \frac{\chi_d}{kT^2}.$$

To the approximation to which we are working we treat χ_d as a constant. Integrating this we have

$$K = \kappa e^{-\chi_d/kT}, \tag{4·41}$$

where κ is independent of T. Using equations (4·37) to (4·41) in (4·23) to (4·25), the latter are all seen to be of the form

$$\frac{\theta}{1-\theta} = A e^{(\chi_1 - \frac{1}{2}\chi_d)/kT} p_2^{\frac{1}{2}} \left(\frac{1+\eta\epsilon}{1+\epsilon}\right)^z. \tag{4·42}$$

The expressions for A are respectively

$$\frac{\alpha_1}{A_1} \frac{10^3 \kappa^{\frac{1}{2}}}{\mu_1}, \quad \left(\frac{\alpha_2}{A_2 \mu_2}\right)^{\frac{1}{2}}, \quad \frac{A_4}{B_3} \frac{(m_1/m_2)^{\frac{1}{2}}}{10^3 \kappa^{\frac{1}{2}}}.$$

As far as the important terms in T are concerned equation (4·42) is of the same form as the isotherm which Wang[18] in his equations 2 and 9 deduced from statistical considerations using the method of Peierls.

This agreement is important; for, as has already been pointed out at the beginning of this section, it means that our formulation of the rates of the various processes is consistent. In this connexion particular mention should be made of the rates of condensation and evaporation of molecules given in expressions (4·16) and (4·17). Expression (4·16) was deduced using the general assumptions that we make throughout. In obtaining (4·17) a difficulty was mentioned in connexion with the method

of averaging. We can now say that, if (4·16) is correct, (4·17) is correct (see, however, footnote on p. 25).

We need not illustrate the actual form of the isotherms (see Wang[18]), as at present there are no experimental results available for comparison. Some points of importance in connexion with them may be noted. Wang has shown that, if there is repulsive interaction between adsorbed particles, the first approximation treatment which we have given leads to an isotherm in which there is no point of inflexion. Chang[20] has shown that, if the approximation is carried further and the effect of long distance order is included, there is in some cases a point of inflexion, but numerical calculation shows that this occurs only when θ varies slowly with p and it would be difficult to detect the effect experimentally. In connexion with points of inflexion in isotherms it has often been stated that, if the surface is not uniform in that various sites on it have different energies of adsorption associated with them quite apart from any interaction between the adsorbed particles, the adsorption isotherm will show steps. Wang[18] (p. 136) has shown that this is not so.

§ 4·8. The displacement of hydrogen by oxygen.

We shall conclude this chapter by describing some effects which take place when oxygen is admitted to a tungsten surface already covered with hydrogen[6]. Using the accommodation coefficient of neon as an indicator, it was shown that oxygen is adsorbed on such a surface. The bare tungsten was first covered with hydrogen so that the accommodation coefficient rose from 0·06 to 0·16. Oxygen was then introduced and after several admissions the accommodation coefficient rose to 0·36.

This adsorption was investigated, using the apparatus for measuring heats of adsorption. The bare wire was completely covered with hydrogen. A charge of oxygen of $1{\cdot}2 \times 10^{14}$ molecules was then admitted, which is rather less than one-third of the amount necessary to form a complete film. A large amount

of heat was developed in the wire of the same order as would have been developed if it had been bare and all the oxygen had been adsorbed. At the same time the pressure gauge showed a deflexion slightly larger than corresponded to the total amount of oxygen in the charge as determined later after all adsorption was completed. We thus have an amount of heat developed in the wire of the same order as would correspond to the adsorption of the complete charge on a bare tungsten surface, while at the same time the pressure measurements indicate no adsorption at all.

The only possible explanation of this is that the oxygen is adsorbed on the tungsten and throws the hydrogen off into the gas phase. The gas cannot be water vapour, as this would be taken up by the liquid air traps, the vapour pressure of ice at liquid air temperatures being quite negligible. The pressure developed when the oxygen was admitted corresponded to $0{\cdot}9 \times 10^{14}$ molecules, assuming the gas to be hydrogen, and the total charge of oxygen was $1{\cdot}2 \times 10^{14}$ molecules, so that roughly speaking each molecule of oxygen adsorbed throws off a molecule of hydrogen.

Consider the energy balance in this process. The measured heat of adsorption for the process is of the order 100–130 kilocalories per mol. O_2. The heat of desorption of hydrogen molecules (i.e. the measured heat of adsorption) is about 20 kilocalories per mol. H_2 for a covered surface. The total amount of heat, i.e. 120–150 kilocalories per mol., is of the order that can be made available by the adsorption of oxygen on tungsten. If, on the other hand, the hydrogen were thrown off as two separate atoms, the heat of desorption would be 120 kilocalories per mol. H_2. Adding this to the measured heat of adsorption for the process, we obtain altogether 220–250 kilocalories per mol. This amount of heat cannot be made available by the adsorption of oxygen on tungsten. The hydrogen could only be thrown off as atoms if the heat of adsorption of an oxygen molecule on bare sites surrounded by places occupied

by hydrogen were much greater than that of oxygen on a bare surface. If this were so, the heat of adsorption of hydrogen on a surface partially covered with oxygen would be greater than that of hydrogen on a bare surface. This has been measured and has been shown, in fact, to be less than that of bare tungsten (the measured values were 20–30 kilocalories per mol. H_2). We conclude, therefore, that the hydrogen must be thrown off as molecules and not as separate atoms. A detailed investigation of this process may be expected to give interesting information concerning the properties of both hydrogen and oxygen films.

Chapter V

SOME OTHER TYPES OF ADSORPTION

§ 5·1. The distribution of particles in a mobile film when each particle occupies more than one site.

In chapters II, III and IV we have considered the theory of adsorption of diatomic molecules with dissociation when each adsorbed atom occupies one site and each site is surrounded by four neighbouring sites. It was pointed out in section 1·4 that the amount of hydrogen adsorbed on tungsten could equally well be explained on the view that the hydrogen is adsorbed as molecules without dissociation and that, if a given site is occupied, the size of the molecules is such that no adsorption can occur on the four neighbouring sites. This also applies to the amount of oxygen in the stable film on tungsten. When such a film is complete there are half as many adsorbed molecules as there are metal atoms in the surface, i.e. the number of adsorbed gas atoms is equal to the number of metal atoms in the surface. It is therefore important to develop the theory of this type of film to see if there is any crucial experimental test which would enable us to decide definitely to which of the two types a given film belongs.

The theory of the production of atomic hydrogen on the basis of adsorption with dissociation accounts for the experimental results satisfactorily (section 4·3). This suggests that at the temperatures 1150–1420° K. at which the experiments were carried out the hydrogen film is an atomic one. Blodgett and Langmuir(1) in the experiments already mentioned in section 1·2 measured the accommodation coefficient a of hydrogen with a tungsten filament at a mean temperature of 357° K., the hydrogen being at 80° K. They showed that, if the filament was

heated in the hydrogen to a temperature of about 600–1000° K. before the measurement was made, the value of a obtained was lower than that given by a filament that had not been heated higher than about 400 or 500° K. after admitting the hydrogen. They interpreted this result as meaning that there are two types of adsorption of hydrogen on tungsten and suggested that the simplest assumption was that at low temperatures the hydrogen is adsorbed in the molecular form while in a film formed at higher temperatures it is atomic. They point out that Bonhoeffer and Farkas(2) have suggested that the ortho-para hydrogen conversion of hydrogen on tungsten can be explained if it is assumed that a film formed at room temperature is atomic and that, if this contention is accepted as correct, it would appear to be necessary to conclude from their experiments that there are two types of atomic adsorption.

There is a real difficulty here because, whatever view may be taken of the detailed mechanism by which the conversion goes, it is difficult to explain its occurrence on the surface without postulating dissociation of the hydrogen when it is adsorbed at room temperature. There is the further consideration in favour of dissociation on adsorption that it is difficult to picture how the hydrogen can be held by chemical forces unless it is dissociated into atoms, because the electrons in the molecule form a closed shell. On the other hand, if the atomic nature of the film at room temperature is accepted, it seems equally difficult to devise a plausible model of the two types of atomic adsorption demanded by Blodgett and Langmuir's result. The weight of the evidence appears to be in favour of an atomic film to which the considerations brought forward in this chapter will not apply. With oxygen, which we now consider, these difficulties do not arise.

Johnson and Henson(3) have used the method developed by Johnson and Vick and described in section 4·6 to study the formation of an oxygen film on tungsten at high temperatures (2100–2400° K.). They have found that in this temperature

range there is an apparent energy of activation for the adsorption process. The experiments indicated that under given conditions the rate of adsorption increases with the temperature and, if the same law continued to ordinary temperatures, it would there be negligibly small. They suggest therefore that in this case there are two types of adsorption, some sort of molecular adsorption at low temperatures and atomic adsorption at high, the occurrence of the latter requiring an energy of activation. Here then there is sufficient evidence to suggest the desirability of examining the properties of molecular films.

We have already seen in section 1·4 that there is some doubt about the actual crystal plane that predominates in the surface of a tungsten filament. From the present point of view this is of considerable importance as the 110 and the 100 planes would behave differently. We shall first consider the 110 plane in which the atoms are arranged as shown in fig. 23 and shall assume that, if a molecule is adsorbed on a given site (say site 0 in the figure), the neighbouring sites are not available for the adsorption of another molecule. We assume that, when two molecules are adsorbed on sites like 0 and 5, the nearest sites on which adsorption can take place, there is an interaction energy V between them due to their mutual repulsive forces, but that at greater distances, for example on sites 1 and 2, the interaction energy is negligible.

Let us first consider the states of lowest energy for a film of this type. Up to $\theta = \frac{1}{3}$ it is possible, as shown in fig. 24, to arrange the particles on the surface so that the interaction energy is zero. The small dots in the figure represent vacant sites and the large ones particles. It is not possible to put more particles on the surface or to arrange them differently without introducing interactions. Up to $\theta = \frac{1}{3}$ the heat of adsorption will remain constant at q_0. An examination of fig. 24 shows that no further adsorption can occur without breaking up this configuration. Some rearrangement such as the following is necessary. Particle 1 moves to site 3 and particle 2 to site 4 simultaneously. Particle 5

then moves to site 6 and site 7 is available for the adsorption of an extra particle. In order to put in this one extra particle we have introduced six interactions and its heat of adsorption is

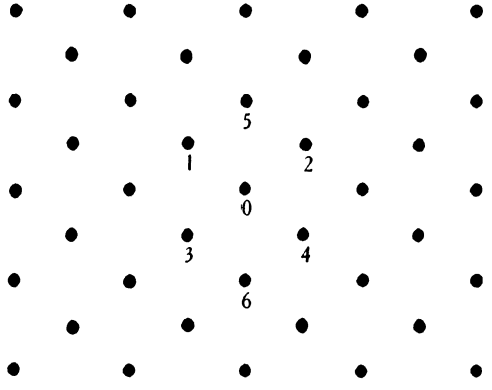

Fig. 23. Group of sites on 110 plane of tungsten.

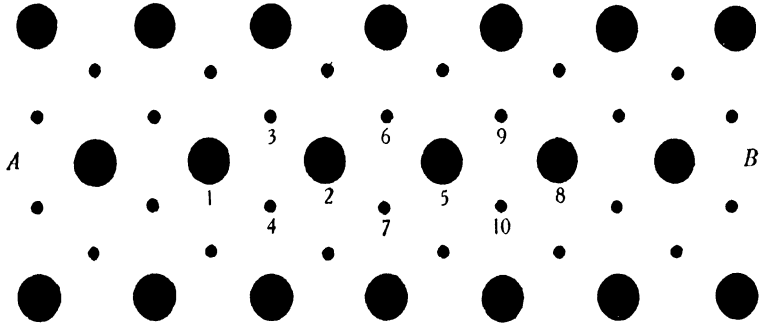

Fig. 24. State of lowest energy when $\theta = \frac{1}{3}$.

anomalous. The extra energy can be regarded as a sort of activation energy for starting the rearrangement right along the chain *AB*, since, once the rearrangement has proceeded to this extent, particle 8 can move to site 9 leaving site 10 vacant for an extra particle and so on along the line on both sides, each particle added introducing three interactions so that the heat of

adsorption per particle is $q_0 - 3V$. This holds till we get to the ends of the line where actually the heat is higher than $q_0 - 3V$. When the total number of sites is large, the anomalies at the beginning and end of a line are negligible and the relation between $(q - q_0)/V$ and θ is shown by the heavy line in fig. 25. This behaviour will be approached when V/kT is large, i.e. when $\eta = e^{-V/kT}$ approaches zero, and the curve is marked $\eta = 0$.

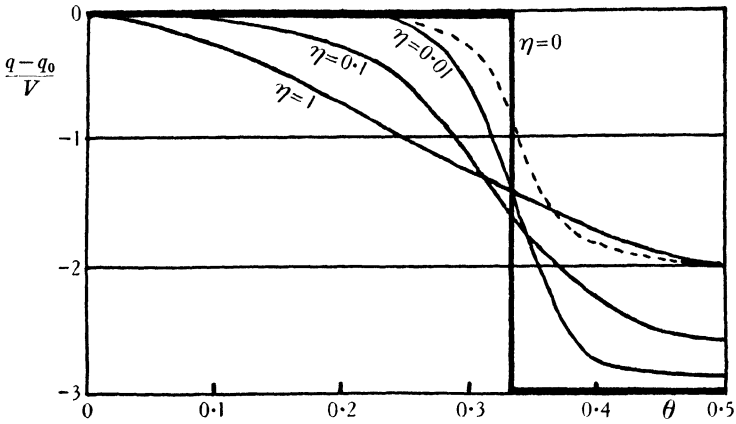

Fig. 25. Variation of heat of adsorption with θ. The full lines are true heats of adsorption and the broken line the apparent heat of evaporation when $\eta = 0{\cdot}01$.

When on the other hand V/kT is very small, i.e. $\eta = 1$, the distribution of particles on the surface is random at all stages of filling up the film and there is never any necessity to break up a configuration of lowest energy. The heat of adsorption for $\theta = 0{\cdot}5$ is the heat corresponding to the filling up of the last gap in this random distribution and is $q_0 - 2V$. For the random distribution the relation between heat of adsorption and θ is approximately linear* and is shown by the curve marked $\eta = 1$

* The relation is not strictly linear because, even when there is no appreciable interaction between adsorbed particles on sites like 0 and 5 in fig. 23, i.e. V/kT small, the fact that site 0 is a site on which adsorption can take place affects the state of occupation of site 5. In other words site 5 is not an average site, the reason for this being that, if adsorption can take place on the vacant site 0, sites 1 and 2 must also be vacant, and a site which

in fig. 25. The actual shape of this curve and of those for values of η between 0 and 1 have been calculated by the author(4).

The behaviour in the region $\theta = 0{\cdot}5$, when the film is nearly complete, is remarkable. For a given system, i.e. a given value of V, the heat of adsorption varies markedly with T and increases as T increases. It is important to note that for this type of system this does not, as might be supposed, *necessarily* mean that, as the temperature is raised, the type of adsorption changes. Any further discussion of this point would be premature as yet, but it must be pointed out that very complicated variations of heat of adsorption with temperature and with θ can arise for quite simple systems when there are forces between the adsorbed particles.

§ 5·2. The kinetics of adsorption and evaporation in a mobile film on the 110 plane of tungsten when each particle occupies more than one site.

Similar considerations will apply to the rate of condensation during the formation of the film and for small values of η we should expect a rapid diminution in this rate in the neighbourhood of $\theta = \frac{1}{3}$.

Let n_s be the number of sites per unit area. If re-evaporation of particles is negligible, $n_s \dfrac{d\theta}{dt}$ the rate of condensation per unit area is given by

$$n_s \frac{d\theta}{dt} = \frac{\alpha p}{\mu} \phi(\theta), \qquad (5{\cdot}1)$$

where p is the gas pressure in dynes per cm.^{2}, $\mu = (2\pi mkT)^{\frac{1}{2}}$ and α is the condensation coefficient, i.e. the chance that a molecule condenses when it strikes a vacant site surrounded by four vacant sites. $\phi(\theta)$ is the probability that any given site is vacant

is a neighbour to two vacant sites is not an average site. Only for an average site can it be stated that the probability of its being occupied is θ. Thus, when site 0 and its four neighbours are vacant, the probability of finding site 5 occupied is not exactly θ. The relation between heat of adsorption and θ would be strictly linear only if this probability were θ.

and is surrounded by four vacant sites. If we integrate this equation, it becomes

$$\int_0^{\theta} \frac{d\theta}{\phi(\theta)} = \frac{\alpha p}{\mu n_s} t, \qquad (5{\cdot}2)$$

where $\theta = 0$ when $t = 0$. Values of this integral I have been

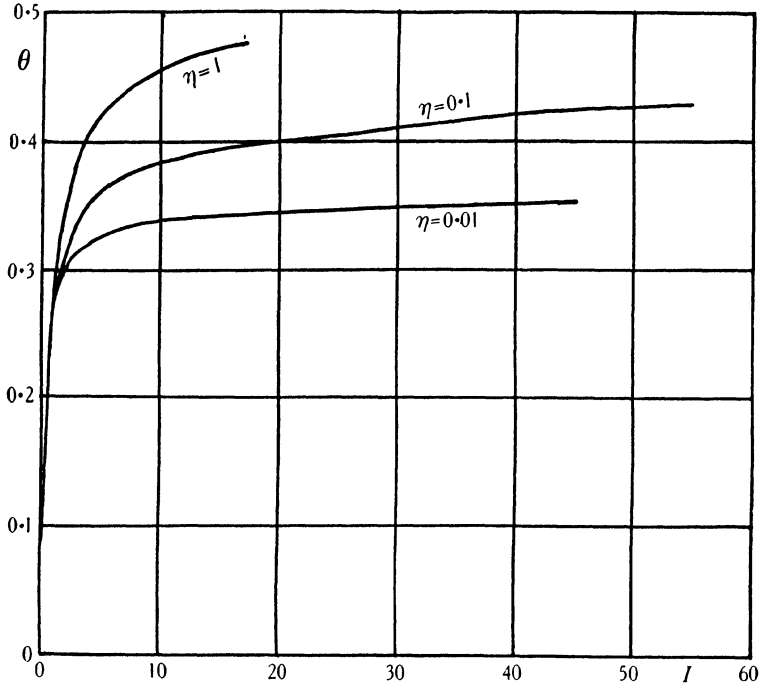

Fig. 26. Rate of formation of film. I is the integral on the left-hand side of equation (5·2) and is proportional to the time.

calculated by the author(4) (equation 12) for various values of η. Since I is proportional to t, we can see how θ varies with t by plotting the relation between θ and I. This is done in fig. 26 and it will be seen that for small η there is as we should expect a rapid diminution in the rate of formation of the film near $\theta = \frac{1}{3}$.

A formula for the rate of evaporation r per unit area can also

be obtained by using the statistical method(4), and the apparent heat of evaporation q_a deduced from the formula

$$q_a = -kd \log r/d(1/T)$$

can also be obtained. Values of $(q_a - q_0)/V$ obtained in this way for $\eta = 0{\cdot}01$ are shown by the broken line in fig. 25. It will be seen that in this case, as in that considered in section 4·6, there is a marked difference between the apparent heat deduced in this way and the true heat. Even for this small value of η the value of $(q_a - q_0)/V$ is -2 at $\theta = 0{\cdot}5$. The reason for this is evident when the process of evaporation from a complete film is considered. The heat term in the exponential part of the expression for the rate of evaporation is simply the energy $q_0 - 2V$ required to remove a single particle from the complete film. This is independent of η and is the apparent heat obtained from the application of the formula $q_a = -kd \log r/d(1/T)$.

§ 5·3. Properties of immobile films on tungsten in which each particle occupies more than one site.

If the particles in the adsorbed film are immobile in the sense discussed in section 2·2 and there is no re-evaporation and if the probability that a molecule striking a suitable vacant site on the surface will condense is independent of the state of occupation of near sites, the relation between heat of adsorption and fraction of sites occupied is approximately linear.

Whenever the spacing of the adsorbed particles in an immobile film differs from that of the underlying solid atoms, the author(5) has shown that the final film will have gaps in it. The number of gaps in the present case has been obtained(4) using the model described in section 2·6. If there are N_s sites for adsorption in all and if for a given value of θ there are N sites available for adsorption, we define $f(\theta) = N/N_s$. If the film were arranged in such a way that it contained the maximum number of particles, $f(\theta)$ would be zero when $\theta = 0{\cdot}5$. Actually it was found to be zero when $\theta = 0{\cdot}4$, so that the effect of the gaps is

to diminish the amount in the final film by about 20 per cent. The details of the kinetics of the formation of the immobile film need not be discussed here.

§ 5·4. General summary.

In making a general comparison between the different types of film we shall first summarize the differences between films formed on the 110 plane of tungsten (*a*) by the dissociation of diatomic molecules with two similar atoms, each atom occupying one site, and (*b*) by adsorption without dissociation, the size of the molecules being such that, if a molecule is adsorbed on a given site, the four neighbouring sites are not available for the adsorption of another molecule. We assume that there is a large repulsive interaction between adsorbed particles, i.e. that V/kT is fairly large.

Let us first consider mobile films in equilibrium. For the two types of film the qualitative behaviour will be similar and at a certain stage in the process under consideration there will be rapid changes in the heat of adsorption or the apparent heat of evaporation and in the rate of formation of the film if there is no appreciable re-evaporation. For the film formed with dissociation the changes occur when it contains one-half the maximum number of particles and for the other type when it contains two-thirds the maximum number.

With immobile films the relation between heat of adsorption and amount adsorbed is nearly linear in both cases. The variation in the rate of formation with amount adsorbed is not very different in the two cases but for the film formed with dissociation the amount in the final film differs by 8 per cent from that in a complete mobile film, while for the other type the amount in the final film differs by about 20 per cent from the amount in the complete mobile film. To show that any difference between the variation in the rate of formation with amount adsorbed does not provide an experimental method for distinguishing between the two types, we have plotted as dots in

fig. 17 the values of $\int_0^{\theta} \frac{d\theta}{\phi(\theta)}$ that would be obtained for a molecular film of the type we are discussing from the same observations as those to which the crosses in the same figure refer. These crosses are deduced on the assumption of adsorption with dissociation.

If on the other hand the 100 plane predominates, the surface atoms are arranged in a simple square lattice. For a mobile film on a lattice of this type the changes in the rate of formation and in the heat of adsorption occur when the film is half complete for the film formed with dissociation. The change in the heat also occurs when the film is half complete for molecular adsorption in which the final film contains half as many molecules as there are atoms in the surface. There is no effect of interaction energy on the rate of formation of the molecular film. Thus the two types of mobile film could be distinguished by studying the rate of formation. For an immobile film formed with dissociation the final amount would differ by 8 per cent from that in a complete mobile film, while for an immobile film formed without dissociation the final amount would differ by about 20 per cent from that in a complete mobile film.

The behaviour is summarized further in Table V. It will be seen from the table that a definite decision between the two types of adsorption can be obtained, whichever plane predominates, by a study of the difference between the amounts in the final immobile film and the complete mobile film. The results obtained by Van Cleave with oxygen on tungsten and given in fig. 18 have been tentatively interpreted as being due to the difference between the amounts in the final immobile film and in a complete mobile film. The accommodation coefficient for the final immobile film is 0·2 and it rises to 0·24 when the film is heated, this rise being interpreted as due to the possibility of adsorbing additional oxygen in a mobile film. The accommodation for a bare surface is 0·06 and, if we assume that the change in accommodation coefficient is proportional to θ,

we have for the ratio of the amount in the final immobile film to that in the complete mobile film $0{\cdot}14/0{\cdot}18 = 0{\cdot}78$. This agrees with 0·8 which would be expected for the molecular film but not with 0·92 which would be expected for the film formed with dissociation. In so far then as the interpretation of the

Table V

Value for mobile film of θ/θ_f at which change in true and apparent heats and in rate of formation occurs				Ratio of amounts in final immobile film and in complete mobile film			
100 plane		110 plane		100 plane		110 plane	
Dissoc.	Without dissoc.*	Dissoc.	Without dissoc.	Dissoc.	Without dissoc.	Dissoc.	Without dissoc.
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{2}{3}$	0·92	0·80	0·92	0·80

θ_f = value of θ when film complete.

* There is no effect on the rate of formation in this case due to the interaction energy.

nature of the rise in fig. 18 is correct, this suggests that the oxygen film is molecular.

We shall return in chapter VII to an account of some recent experiments on the properties of oxygen films on tungsten. These experiments have a bearing on the question we have just discussed and illustrate the application of the general methods that have been developed. It is suggested that this chapter should be read at this stage rather than after chapter VI.

§ 5·5. Hexagonal lattices.

To illustrate how, for a mobile film, the type of lattice can affect the variation of heat of adsorption with fraction of surface covered, we shall consider briefly the simple hexagonal lattice illustrated in fig. 27 in which each site has six neighbouring sites and shall take the simplest case in which each particle

occupies one site. We assume as before that there is repulsive interaction and an interaction energy V between particles on neighbouring sites.

We consider the states of lowest energy. All the sites marked 1 in the figure can be occupied without introducing any interactions. When they are all occupied, $\theta = \frac{1}{3}$. Up to this we have

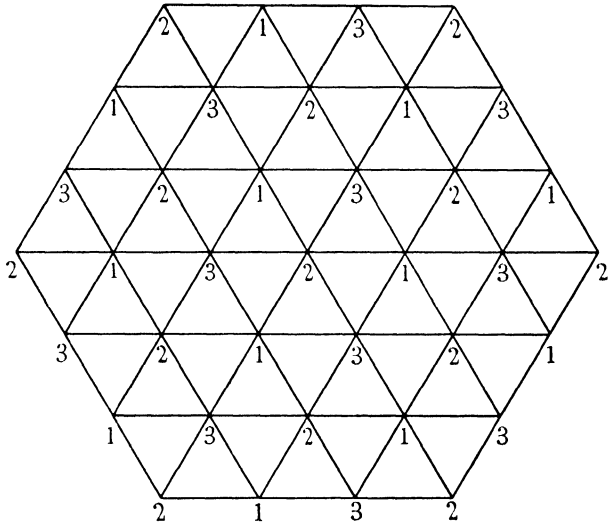

Fig. 27. States of lowest energy for hexagonal lattice with repulsion between particles adsorbed on neighbouring sites.

a constant heat of adsorption q_0 per molecule. It is not possible to put more molecules on the surface without introducing interactions and the next stage consists in filling up the group of sites marked 2. When these are all occupied, $\theta = \frac{2}{3}$, and during this stage the heat of adsorption is $q_0 - 3V$. The final stage consists in filling up the remaining sites marked 3. During this stage the heat of adsorption is $q_0 - 6V$. Thus, if the system is in the state of lowest energy throughout, the variation of heat of adsorption with fraction of sites occupied is shown by the curve with two steps in fig. 28.

For a random distribution of particles, i.e. at very high temperatures, we should have the straight line from q_0 at $\theta = 0$ to $q_0 - 6V$ at $\theta = 1$. For intermediate temperatures the curve would be like the curve with two steps but with the corners

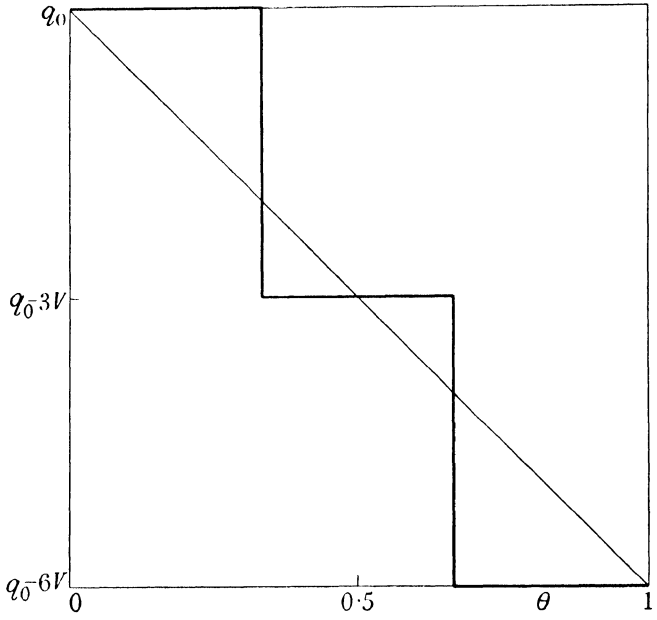

Fig. 28. Variation of heat of adsorption with θ for hexagonal lattice.

more or less rounded. Wang (6) has worked out the detailed theory for a hexagonal lattice but taking into account long range (dipole) interaction between adsorbed particles and has shown that in this case too the relation between heat of adsorption and θ has two steps in it.

Chapter VI

SOME EFFECTS OF DIPOLE INTERACTIONS

§ 6·1. Introduction.

We have seen that the variation of heat of adsorption with amount adsorbed is very different for different types of film and that an experimental determination of this variation can give definite information as to the nature of the film. Up to the present we have considered only those cases in which the force between adsorbed atoms is repulsive and where it falls off so rapidly with distance that only the interaction between nearest neighbours need be considered. In this chapter we shall calculate the effects that may arise when the interaction between adsorbed molecules arises partly from van der Waals' *attractive* forces and partly from repulsions between permanent or induced dipoles and shall consider the bearing of the calculations on a number of experimental results. In this complicated case we shall make approximations which simplify the calculations, but we shall see that the nature of the final result obtained shows that the approximations introduced cannot affect this result seriously.

It has of course been pointed out in various connexions that permanent or induced dipoles in adsorbed molecules will affect heats of adsorption. For example, if a molecule with a permanent dipole moment is adsorbed on the surface of a metal, there is an attractive force between the dipole and the metal and the potential energy can be calculated using the method of electric images.* This potential energy will contribute to the heat of adsorption.

If all the ions in the surface plane of an ionic crystal have the same charge, there is an electrostatic field near the surface.

* See for example de Boer(1).

Lenel(2) has pointed out that the presence of such a field which will induce dipoles in adsorbed molecules can account for the difference between the heats of adsorption of argon on KCl (simple cubic) and on CsCl (body centred cubic) crystals.* Lennard-Jones and Dent(5) have considered the electrostatic field near the surface of an ionic crystal in which each ion is surrounded by four ions of different sign (e.g. simple cubic KCl). They have pointed out that there is a strong field immediately above a given ion but that the energy of adsorption due to electrostatic forces *plus* van der Waals forces is in fact greatest above a point equidistant from four ions where the electrostatic field is zero. In this, and in all the cases that have been considered, attention has been fixed on the actual heat of adsorption of a single particle on the surface. In this chapter on the other hand the *variation* of heat of adsorption with fraction of surface covered will be discussed(6).

Let us then consider molecules with permanent dipole moments adsorbed on a conductor in such a way that the moments are all parallel to each other and normal to the surface. When there is only one molecule on the surface, there will be a term in the potential energy arising from the attraction between the dipole in the molecule and its electric image. When the surface is fully covered, the corresponding term will arise from the force between the dipole in the molecule and its own electric image together with the electric images of all the other adsorbed molecules. All the electric images taken together approximate to two infinite parallel sheets of charges of opposite sign and their net effect is smaller than that of a single image. Thus, as the surface becomes covered, this term in the heat of adsorption undergoes considerable variation in such a way as to make the heat of adsorption decrease. The direct repulsive forces between neighbouring adsorbed dipoles also causes the heat to decrease as the surface becomes covered.

* Bradley(3) has worked out a theory of the formation of multilayers based on the view that the induced dipoles in one layer will themselves induce dipoles in the layer above. See also de Boer and Zwikker(4).

In connexion with films of caesium atoms held on the surface of tungsten as positive ions, each ion and its electric image being equivalent to a dipole, Langmuir(7) has pointed out that a number of parallel dipoles exert mutual depolarizing effects on each other, and he and Taylor(8) have shown directly that the electric moment per adsorbed caesium atom diminishes considerably as the number of adsorbed atoms increases. We shall not consider films in which the adsorbed atoms are held as positive ions, but those in which the adsorbed molecules have permanent or induced dipole moments. The essential thing from our point of view is that, whenever dipoles are lined up parallel to each other, they exert a mutual depolarizing effect, which must be taken into account.

§ 6·2. Some properties of arrays of dipoles near a metal.

In this section we shall collect together the necessary results connected with the properties of arrays of dipoles near a metal. We consider a very large number of similar dipoles. In the initial state they are a large distance apart and are all a large distance from a plane metal surface, so that they are effectively outside each other's influence and effects due to the presence of the metal are negligible. The moment of each is M_p. In the final state they are arranged with their moments parallel to each other in a simple square pattern a distance a apart and each a distance x from the metal surface. The field acting on each due to their mutual effects and the effects of all the images is Z_1 and the dipole moment of each is M_1 and is given by

$$M_1 = M_p + \sigma Z_1, \qquad (6\cdot1)$$

where σ is the polarizability. We want to calculate the change in energy in passing from the initial to the final state. We carry out the calculation in the following stages.

(i) When they are outside each other's influence, alter each dipole so that its moment becomes M_1.

$$\text{Work done } \textit{on} \text{ each} = \tfrac{1}{2}\sigma Z_1^2.$$

(ii) Keeping the moments constant, move them so that they are arranged in a square lattice in a plane parallel to the metal but a long way from it with their dipole moments parallel to each other and normal to the plane, the distance apart being a.

$$\text{Work done } \textit{on} \text{ each} = \frac{1}{2}\frac{9M_1^2}{a_3}.$$

This follows from the result obtained by Topping(9) that the energy of a dipole in such an array due to its interaction with all the others is $\frac{9M_1^2}{a^3}$, i.e. that the field at a given dipole due to all the others is parallel to the dipole and equal to $9M_1/a^3$. The total energy of all the dipoles, the total number being N, is $\frac{N}{2}\frac{9M_1^2}{a^3}$, the factor one-half being introduced so that each interaction may be reckoned once only. Thus the work done on each in forming the array is $\frac{1}{2}\frac{9M_1^2}{a^3}$.

(iii) Keeping the moments constant and the plane of the array parallel to the surface of the metal, move the array towards the metal until the centre of each dipole is at a distance x from it.

$$\text{Work done } \textit{by} \text{ each dipole due to the effect of its own image and the images of all the others} = \tfrac{1}{2}M_1 Z_i,$$

where Z_i is the field at any dipole due to all the images when the dipoles are at a distance x from the metal and is given by

$$Z_i = \sum_{r=0}^{r=\infty} g_r M_1 \frac{8x^2 - r^2}{(4x^2 + r^2)^{\frac{5}{2}}}, \qquad (6{\cdot}2)$$

where r is the distance from the molecule under consideration of a site for adsorption (see fig. 29), g_r is the number of sites at a distance r, and the sum is to be taken for all possible values of r from 0 to ∞. This result is established by considering the work done by one dipole A due to the normal component* of

* Only normal components need be considered because of the symmetry of the arrangement.

the field arising from any one image B (see fig. 29) as follows. The force towards the surface on the dipole of moment M_1 due to the effect of the image B is

$$6M_1^2 \frac{x(8x^2-r^2)}{(4x^2+r^2)^{\frac{7}{2}}}.$$

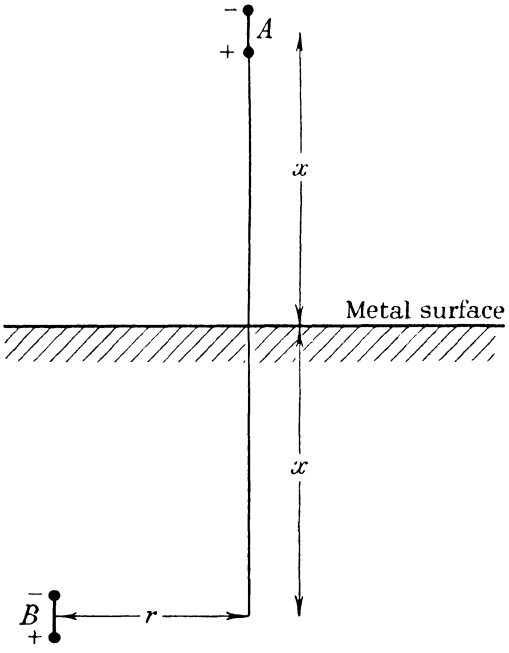

Fig. 29.

Work done *by* the dipole from ∞ to x is

$$-\int_{\infty}^{x} 6M_1^2 \frac{x(8x^2-r^2)}{(4x^2+r^2)^{\frac{7}{2}}}\,dx,$$

or

$$\tfrac{1}{2}M_1^2 \frac{8x^2-r^2}{(4x^2+r^2)^{\frac{5}{2}}}.$$

Adding with appropriate signs the work done *by* the dipole in (i), (ii) and (iii), and remembering that

$$Z_1 = Z_i - \frac{9M_1}{a^3}, \tag{6·3}$$

and using (6·1), we obtain

Total work done *by* each dipole in forming the array near the metal

$$= \tfrac{1}{2} M_p Z_1. \qquad (6{\cdot}4)$$

Using (6·2) and (6·3), the field Z_1 is given by

$$Z_1 = \frac{M_1}{4x^3} + M_1 \left\{ \sum_{r=a}^{r=\infty} g_r \frac{8x^2 - r^2}{(4x^2 + r^2)^{\frac{5}{2}}} - \frac{9}{a^3} \right\}. \qquad (6{\cdot}5)$$

The first term arises from the image of the dipole under consideration and the second from the images of all the other dipoles. The last term represents the direct effect of the other dipoles.

These calculations apply to a film in which every site is occupied, i.e. $\theta = 1$, and for such a film are exact. If a fraction θ of the total sites is occupied, we shall assume that

$$Z_\theta = \frac{M_\theta}{4x^3} + \theta M_\theta \left\{ \sum_{r=a}^{r=\infty} g_r \frac{8x^2 - r^2}{(4x^2 + r^2)^{\frac{5}{2}}} - \frac{9}{a^3} \right\}, \qquad (6{\cdot}6)$$

where the sum is still to be taken over *all* the sites. This involves the assumption that the dipoles are all of the same strength, i.e. that each has the average strength M_θ given by

$$M_\theta = M_p + \sigma Z_\theta, \qquad (6{\cdot}7)$$

and that they are distributed at random, any effects due to clustering being neglected. We shall discuss later the effects of these assumptions. M_θ can be eliminated between (6·6) and (6·7) giving Z_θ explicitly as a function of M_p, σ and θ. The energy U_d of the film due to dipole interactions is from (6·4) given by

$$U_d = -\tfrac{1}{2} N_s \theta M_p Z_\theta, \qquad (6{\cdot}8)$$

where N_s is the total number of sites for adsorption. This assumes that for an incomplete film only the normal component of the field at a given dipole need be taken into account. The

contribution of dipole interactions to the heat of adsorption per molecule is $-\frac{\partial U_d}{\partial(N_s\theta)}$ and is given by

$$-\frac{\partial U_d}{\partial(N_s\theta)}=\tfrac{1}{2}M_p\left(Z_\theta+\theta\frac{\partial Z_\theta}{\partial\theta}\right). \qquad (6\cdot9)$$

§ 6·3. Numerical calculations on the adsorption of polar molecules on metals.

These considerations are likely to be applicable only to the adsorption of vapours. For these, in addition to the dipole forces, there will be attractive van der Waals forces between adsorbed molecules. These forces may be assumed to be appreciable only when molecules are adsorbed on neighbouring sites. The potential energy V_a of two molecules adsorbed on neighbouring sites is negative and may be taken as approximately one-sixth of the latent heat of vaporization per molecule.

In order to give some numerical examples we consider NH_3 and SO_2 at 273 and 263° K. respectively. The known properties are given in Table VI. v is the volume per molecule at the boiling point. We take a, the distance between nearest neighbours on the surface, which will be determined by the solid lattice, but the exact value of which we do not know, as a little greater than $v^{\frac{1}{3}}$. We assume that the distance x of the dipoles

Table VI

	$-V_a$ ergs per gram	$\eta=e^{-V_a/kT}$	$M_p(10)$ e.s.u.
NH_3	$6\cdot4\times10^{-14}$	5·37	$1\cdot5\times10^{-18}$
SO_2	7×10^{-14}	6·70	$1\cdot6\times10^{-18}$

	$\sigma(11)$ cm.^{3}	$v^{\frac{1}{3}}$ cm.	a cm.
NH_3	$2\cdot3\times10^{-24}$	$3\cdot45\times10^{-8}$	4×10^{-8}
SO_2	$4\cdot2\times10^{-24}$	$4\cdot2\times10^{-8}$	$4\cdot4\times10^{-8}$

from the surface is equal to $a/2$. With this assumption $\sum_r$ in equations (6·5) and (6·6) is equal to* $-1{\cdot}64/a^3$.

The results are plotted in fig. 30*a*. Curves I show the variation in heat of adsorption with θ if the only forces between the adsorbed molecules are van der Waals attractive forces. They were calculated using equation (2·20) which takes account of the tendency to form aggregates. Curves II were obtained from equation (6·9) which takes no account of the effect of forces between adsorbed molecules on the arrangement of the adsorbed film. Curves III represent the sum of I and II. It is not suggested that curves III will show the actual resultant variation but the essential point is that the calculations show that the effects of van der Waals attractions and of dipole interactions are opposite in sign and of the same order so that the resultant variation with θ is very much smaller than would be expected from a consideration of forces of one type only. It is important to notice that the actual change from $\theta=0$ to $\theta=1$ is obtained accurately from these calculations and the approximations only affect the shapes of the curves joining the extreme values. These shapes are also affected by the type of lattice as we have seen in chapter v. In connexion with the actual shapes, it may be pointed out that, if the total effects at $\theta=1$ are approximately of the same magnitude, the short range van der Waals attraction will necessarily be greater than the long range dipole repulsion between molecules on neighbouring sites. Thus on the whole there will be a tendency to aggregate on the surface and I will still have S-shaped forms as shown, but the S-shape will be less marked. Also II will tend to be distorted in the direction of making their shapes a mirror image of I. The net effect will be to make III less wavy in form.

For comparison the heats of adsorption for SO_2 on charcoal

* This was obtained as follows. The effect due to the nearest twenty-four images was calculated directly. The distance from the centre of the farthest away of these is $2{\cdot}83a$ and that of the nearest one in the next shell is $3a$. The effect of the remainder was calculated by integrating from $2{\cdot}9a$ to ∞ assuming a uniform distribution of density M/a^2 per unit area (see Roberts(6), p. 1343).

measured by Williams[12] are plotted with the same scale of ordinates in fig. 30*b*. The initial rapid drop is always found in

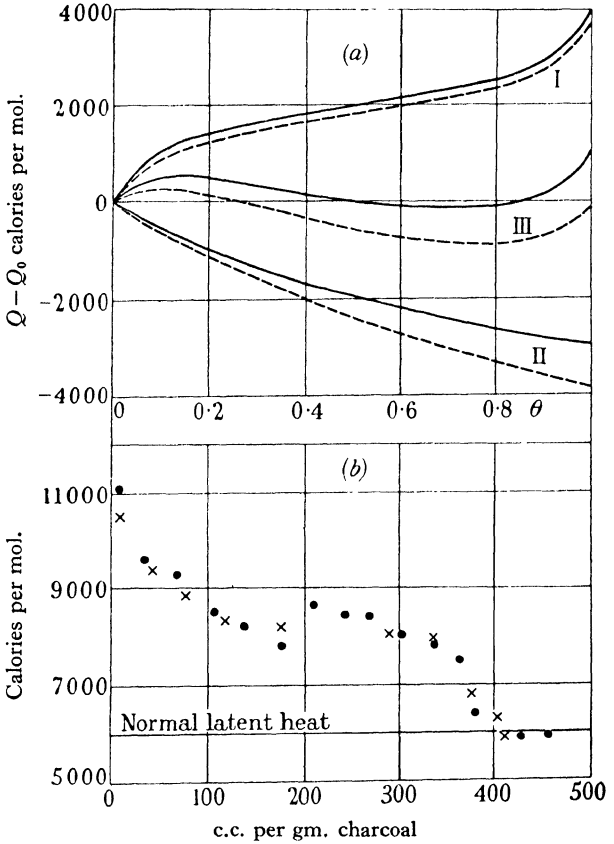

Fig. 30(*a*). Variation of heat of adsorption Q with θ, Q_0 is the heat when $\theta = 0$. I, effect of van der Waals forces alone; II, effect of electrostatic forces; III, combined effect. Full curves SO_2; broken curves NH_3.

Fig. 30(*b*). Variation of heat of adsorption of SO_2 on charcoal with amount adsorbed (Williams).

experiments with charcoal* and is presumably due to adsorption in crevices where an adsorbed atom is influenced by an abnormally high number of atoms of the solid. At 400 c.c. per

* Cf. for example, Barrer[13].

gram the adsorption isotherm (not reproduced here) bends up rapidly and, as will be seen from the figure, the heat is the normal latent heat, so that here condensation in bulk has begun. The main point is that between the initial drop to about 9400 calories and the point (about 300 c.c. per gram), where effects due to the formation of multilayers begin to set in, the variation in heat of adsorption is small.

§ 6·4. Dipoles induced in non-polar atoms or molecules adsorbed on ionic crystals.

Lennard-Jones and Dent(5) have considered the electrostatic field near the surface of an ionic crystal in which each ion is surrounded by four ions of different sign. They have pointed out that there is a strong field immediately above a given ion but that the energy of adsorption due to electrostatic forces plus van der Waals forces is in fact greatest above a point equidistant from four ions, where the electrostatic field is zero. Lenel(2) has shown that the heat of adsorption of argon on body-centred cubic CsCl crystals is greater than on simple cubic KCl crystals and that the difference is due partly to the fact that on the 100 plane, the cleavage plane, of the body-centred crystal the adsorbed atom is close to five atoms of the solid, while in the case of the simple cubic crystal it is close to four atoms only. It is also due to the fact that in the cleavage plane of CsCl all the ions are of the same sign and induce dipoles in the argon atoms, while in KCl the considerations brought forward by Lennard-Jones and Dent apply and the atoms are adsorbed at points equidistant from four ions where the electrostatic field is zero and residual effects due to the inhomogeneity of the field are small. As in the case of adsorption on metals we shall consider here the variation of heat of adsorption with amount adsorbed rather than the actual heat of adsorption of a single particle(14).

Consider the complete film, $\theta = 1$, adsorbed on a surface in which all the ions are of the same sign. We have a large number of atoms with no permanent dipole moment arranged in a square

array at a distance a apart. On account of symmetry the resultant field Z_1 at each atom is normal to the surface and is made up of Z_e, the field due to the ions in the crystal, and of the field due to the induced dipoles each of moment M_1; i.e.

$$Z_1 = Z_e - 9\frac{M_1}{a^3}. \qquad (6{\cdot}10)$$

M_1 is given by

$$M_1 = \sigma\left(Z_e - \frac{9M_1}{a^3}\right), \qquad (6{\cdot}11)$$

where σ is the polarizability.

As in section 6·2 we have to calculate the change in energy when a large number of atoms pass from a state in which they are a large distance apart and a large distance from the surface of the crystal to a state in which they are arranged in a simple square pattern a distance a apart and each at a distance x from the surface of the crystal where the field due to the ions in the crystal is Z_e. We carry out the calculations in the same stages as before.

(i) When they are outside each other's influence, alter each atom so that it acquires a dipole moment of strength M_1.

$$\text{Work done } \textit{on} \text{ each} = \tfrac{1}{2}\sigma Z_1^2.$$

(ii) Keeping the moments constant, move them so that they are arranged in a square lattice in a plane parallel to the crystal but a long way from it with their dipole moments parallel to each other and normal to the plane.

$$\text{Work done } \textit{on} \text{ each} = -\frac{1}{2}\frac{9M_1^2}{a^3}.$$

(iii) Keeping the moments constant and the plane of the array parallel to the surface of the crystal move the array towards the crystal until the centre of each dipole is at a distance x from it where the field due to the ionic lattice is Z_e, this being reckoned positive if it attracts the dipoles towards the surface.

Work done *by* each dipole from ∞ to x

$$= \int_{\infty}^{x} M_1 \frac{dZ}{dx}\, dx = M_1 Z_e.$$

Adding the three amounts of work together and remembering that the first two must be taken as negative, we obtain

Total work done *by* each dipole in forming the array near the crystal $= \frac{1}{2}M_1 Z_e$. (6·12)

If a fraction θ of the sites is occupied, we assume as before that

$$Z_\theta = Z_e - \theta \frac{9M_\theta}{a^3}, \tag{6·13}$$

$$M_\theta = \sigma\left(Z_e - \theta \frac{9M_\theta}{a^3}\right),$$

or

$$M_\theta = \frac{\sigma Z_e}{1 + 9\dfrac{\sigma\theta}{a^3}}, \tag{6·14}$$

and that the energy of each dipole is

$$\tfrac{1}{2}M_\theta Z_e. \tag{6·15}$$

These equations may be discussed in the same way as equations (6·6), (6·7) and (6·8). If there are N_s sites for adsorption, the energy U_d of the adsorbed film due to electrostatic interactions is from equations (6·14) and (6·15) given by

$$U_d = -\tfrac{1}{2}N_s\theta \frac{\sigma Z_e^2}{1 + \dfrac{9\sigma}{a^3}\theta}. \tag{6·16}$$

The contribution of electrostatic interactions to the heat of adsorption per molecule is $-\dfrac{\partial U_d}{\partial(N_s\theta)}$ and is given by

$$-\frac{\partial U_d}{\partial(N_s\theta)} = \frac{1}{2}\frac{\sigma Z_e^2}{\left(1 + \dfrac{9}{a^3}\sigma\theta\right)^2}. \tag{6·17}$$

We must now calculate the electrostatic field Z_e near the 100 plane, the cleavage plane, of a body-centred ionic crystal of the CsCl or CsI type. In this plane all the ions are of the same sign and are arranged in a square pattern at a distance

a apart. In the plane below the ions are of the opposite sign and are below the centres of the squares and so on. The distance between successive planes is $0{\cdot}5a$. For the surface layer 1, for layer 3 and all the odd layers the point at which the field is required is above the centre of a square in the ion pattern, while for layer 2, layer 4 and all the even layers it is above an ion. The field due to a given layer will at large distances approximate to

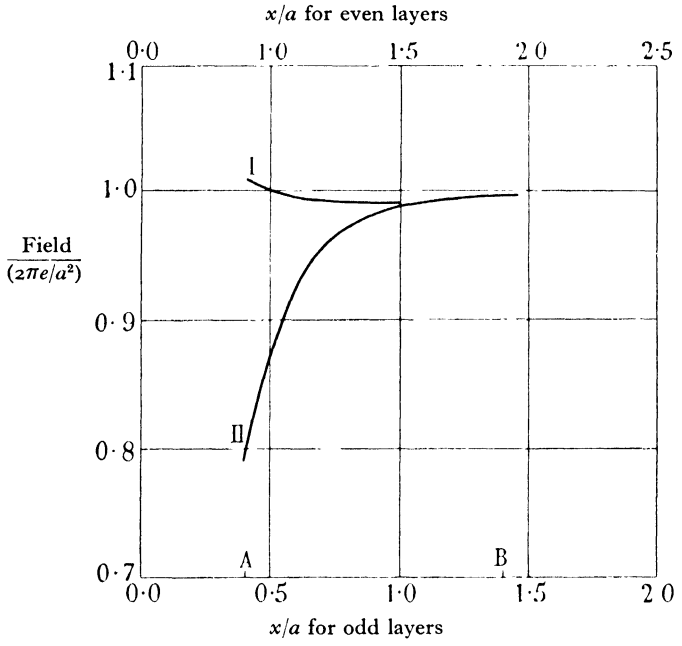

Fig. 31. Field due to odd and even layers near the 100 plane of a body-centred alkali halide crystal. Curve I, even layers; Curve II, odd layers.

$(2\pi e/a^2)$ where e is the charge on a particle. The actual fields were calculated by summing for the nearest 16 particles for the odd layers and 25 particles for the even layers and integrating for the more distant particles. If x is the distance of a point from a layer, we plot in fig. 31 the value of Field/$(2\pi e/a^2)$ as a function of x/a for both odd and even layers without regard for sign. The scale of x/a for odd layers is shown at the bottom

of the figure and for even layers at the top, the latter being displaced 0·5 with respect to the former. To obtain the resultant effect due to an odd layer and the even layer immediately below it, we take the difference between the ordinates of the two curves at the abscissa corresponding to the odd layer. Thus for a point $0{\cdot}4a$ above the odd surface layer the resultant field is the difference at A plus the difference at B and so on. It is evident that only the difference at A need be taken into account. It can be seen that the field due to the surface odd layer is less than that due to the even layer below it, i.e. that the field is in the opposite direction to that which might be expected at first sight. In Table VII we give values.

Table VII

Distance from 1st layer	$Z_e/(2\pi e/a^2)$
$0{\cdot}4a$	0·2193
$0{\cdot}5a$	0·1338
$0{\cdot}6a$	0·0702
$0{\cdot}7a$	0·0374

§ 6·5. Numerical calculations for argon on caesium iodide.

For caesium iodide $a = 4{\cdot}56 \times 10^{-8}$ cm. and $2\pi e/a^2 = 1{\cdot}442 \times 10^6$ e.s.u., a is also the nearest distance between atoms in the adsorbed film, i.e. the a of equation (6·17). At $0{\cdot}4a$ from the top layer the field is $3{\cdot}16 \times 10^5$ e.s.u. and at $0{\cdot}5a$ it is $1{\cdot}93 \times 10^5$ e.s.u., and we shall carry out the calculations for these two distances. Actually the plane of argon atoms is $0{\cdot}4a$ above the surface layer when the latter consists of caesium and $0{\cdot}6a$ when it consists of I ions. The value of V_a, the potential energy between argon atoms $4{\cdot}56 \times 10^{-8}$ cm. apart, taken from a large scale plot by Orr of the formulae for the potential curves derived from an analysis of the virial coefficients[15],[16], is $0{\cdot}96 \times 10^{-14}$ ergs and σ, the polarizability[17], is $1{\cdot}63 \times 10^{-24}$ cm.^{3}

As in section 6·3 we plot separately in fig. 32 the effects on

the heat of adsorption of the van der Waals attraction at 80° K. (curve I) and of the electrostatic interaction (curves II (*a*) at a distance 0·4*a* and II (*b*) at 0·5*a*). At $\theta=0$ and at 0·4*a* the electrostatic effect contributes 1160 calories per mol. to the heat of adsorption and, at 0·5*a*, 430 calories per mol. The resultant

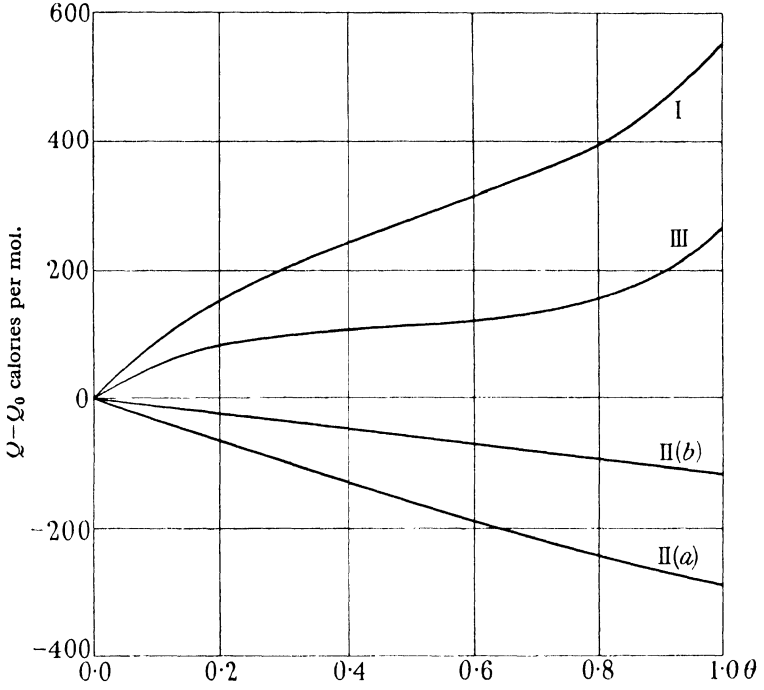

Fig. 32. Variation with θ of heat of adsorption of argon on CsI. Q_0 is the heat when $\theta=0$. Curve I, van der Waals forces alone at 80° K. Curves II(*a*) and (*b*), electrostatic forces alone at 0·4*a* and 0·5*a*. Curve III, resultant of I and II(*a*).

effect from I and II (*a*) is shown in curve III. The same remarks as to the effect of the approximation on the actual shape of this final curve apply as in section 6·3. For the surfaces which consist of iodine ions the effect of the electrostatic on the variation of the heat will be smaller, so that the net resultant variation will lie somewhere between curve I and curve III and

rather nearer curve III, and as before the rise at $\theta = 1$ will be partly masked in practice by the beginning of the formation of the second film. The essential point is that, in agreement with some experimental results of Orr,* the total variation is considerably smaller than would be expected from the van der Waals forces alone. It may be pointed out that in the numerical calculations we have only used known atomic or crystal data and no data derived from adsorption measurements.

* Quoted by Roberts and Orr(14).

Chapter VII

SOME PROPERTIES OF OXYGEN FILMS ON TUNGSTEN

§ 7·1. Experimental method.

Since the preceding chapters were written some experimental investigations by the author and J. L. Morrison(1) on oxygen films on tungsten have been completed. These show the application and development of a number of the ideas developed earlier in this tract. A brief outline of this work will be given here.

The accommodation coefficient method was modified in such a way as to enable the actual pressure of oxygen at the wire to be obtained. The principle of the method will be understood by reference to fig. 4, although the actual apparatus differed in detail from that illustrated there. The oxygen was admitted from a gas pipette to a large calibrated bulb of about two litres capacity, so that the partial pressure in this bulb was known. It then passed through a long fine capillary tube and entered the apparatus at a point near the side tube leading to the Macleod gauge. Here it divided into three streams. The first filled the Macleod gauge and, once equilibrium was established, ceased. The second flowed to the near charcoal tube and was taken up by the charcoal. The third flowed past the wire to the other charcoal tube. The resistance to the flow of oxygen arose in part from the effect of collisions with the walls of the tubes and in part from the fact that it was diffusing through neon. The dimensions of the tubes were so chosen that in the capillary tube the resistance was primarily due to collisions with the walls, the effect due to the presence of the neon being only a correction, while in the other parts of the apparatus the resistance was

primarily due to the presence of the neon and the wall effect was only a correction. Under these conditions the flow could be accurately calculated and the partial pressure of the oxygen at any point and in particular at the wire could be deduced. The conditions obtaining at the surface of the charcoal were investigated in subsidiary experiments and it was found that a small correction was necessary for the fact that the charcoal was not perfectly efficient in taking up oxygen. The pressure of oxygen at the wire depended markedly on the neon pressure and it was a satisfactory test of the theory of the method to find that consistent results were obtained when this pressure was varied in the ratio 2 : 1.

§ 7·2. Three different types of oxygen film.

With the wire used the accommodation coefficient of neon with bare tungsten was 0·057. When oxygen was admitted and

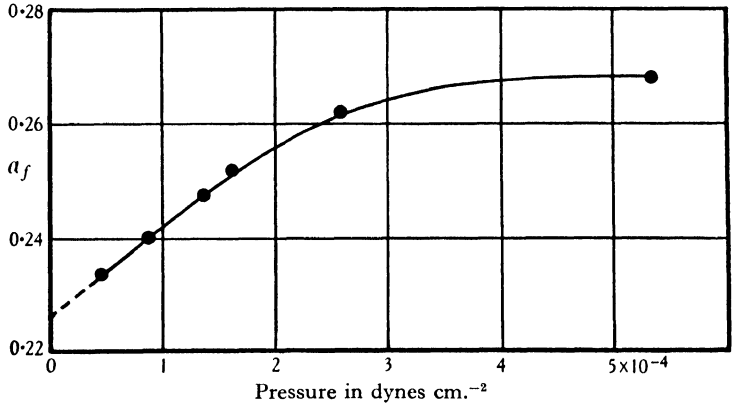

Fig. 33. Relation between a_f, the final steady value of the accommodation coefficient of neon, and the partial pressure of oxygen.

adsorbed on the tungsten, this rose to a final steady value a_f which depended on the pressure of oxygen at the wire. a_f is plotted against the oxygen pressure in fig. 33. Extrapolating the curve, we see that at very low pressures the value of

$a_f = 0{\cdot}226$ would be reached, although of course the time taken to reach it would be considerable. This suggests two types of adsorption, a very stable film corresponding to $a = 0{\cdot}226$ and a less stable one on top of it, the population in which depends on the pressure. Further investigation showed, however, that the film corresponding to $a = 0{\cdot}226$ is itself composite. Heating this film to a temperature of about 1100° K. reduced the accommodation coefficient to 0·177 and, until it was heated to above 1700° K., no further evaporation took place.*

The stable film which does not begin to evaporate appreciably until above 1700° K. can be presumed to be immobile, that is, each particle remains where it is first attached. If it is assumed that the film is atomic, each molecule dissociating on adsorption and the two atoms occupying two neighbouring vacant sites, the final film will have 8 per cent of holes in it consisting of isolated uncovered single sites (see section 3·1). As we have seen in section 3·2, it would be expected that such sites would exert a greater attraction for impinging oxygen molecules than the other parts of the surface and that oxygen molecules would be strongly adsorbed on them. The most likely explanation of the results is then that the state $a = 0{\cdot}177$ produced by heating the film to about 1100° K. corresponds to the stable atomic film with 8 per cent of gaps in it unfilled. The state $a = 0{\cdot}226$ reached at very low pressures corresponds to the stable film with the 8 per cent of gaps occupied by molecules. The higher values, shown in fig. 33, are due to the presence of an adsorbed film on top of this structure, the equilibrium amount in this last film depending on the pressure of oxygen in the gas phase.

The form of the isotherm for this last film was investigated. The highest pressure at the wire which could be measured accurately was about $9{\cdot}8 \times 10^{-3}$ dyne cm.$^{-2}$ For convenience

* The value 0·177 corresponds to 0·20 given by Van Cleave and referred to in section 3·2. These small differences are not relevant from the present point of view and may be due to slight variations in the roughness of different samples of tungsten. The rise when the tungsten was heated above about 1400° K. shown in fig. 18 was also observed in the present experiments.

in plotting, the results for these higher pressures are not shown in fig. 33. At higher pressures than this the necessary conditions for the theory to be applicable were not satisfied. At $9{\cdot}8 \times 10^{-3}$ dyne cm.$^{-2}$ the final steady value a_f of the accommodation coefficient was 0·320. When the pressure of the oxygen in the large bulb from which the oxygen diffused through the capillary tube was increased 4 times, the value of a_f was 0·340, and, when it was increased about 10 times, a_f was 0·352. The pressures at the wire in these two experiments could not be deduced accurately but they must have been of the order of 4 and 10 times that in the experiment in which a_f was 0·320. It is thus evident that at these pressures the value of a_f is changing very slowly with increase of pressure and that the final value corresponding to a complete film cannot lie far from 0·36.

Let us consider the 100 plane of tungsten (see fig. 8). The sites in the upper layer we are considering will be arranged in the same way as the atoms in the surface so that the distance between nearest neighbours will be $3{\cdot}15 \times 10^{-8}$ cm. The diameter of the oxygen molecule is[2] $3{\cdot}64 \times 10^{-8}$ cm. Thus it is probably not possible to pack oxygen molecules on the surface so that every site is occupied, but easily possible to pack them so that, if a given site is occupied, the surrounding four sites are vacant as considered in section 5·1 for the 110 plane. In this case the complete film with $a_f = 0{\cdot}36$ will correspond to $\theta = 0{\cdot}5$, if we neglect the fact that the underlying structure is not completely uniform in that places where undissociated molecules are adsorbed on vacant sites surrounded by four occupied sites will differ from sites occupied by atoms. We therefore take the value of θ corresponding to any value of a_f as

$$\theta = 0{\cdot}5 \frac{a_f - 0{\cdot}226}{0{\cdot}36 - 0{\cdot}226}.$$

We shall not discuss the isotherm deduced in this way in any detail, but it is interesting to note that from the values of θ so obtained and the corresponding pressures in the range of low values of θ, where the relation between the two is linear, it can

be shown that the mean life of an adsorbed molecule in this second layer is not less than about 2 seconds.

It is important to consider the actual changes in a. During the formation of the first stable layer with the gaps unfilled, a changes by $0{\cdot}177-0{\cdot}057$ or by $0{\cdot}120$. When the gaps are filled, a changes by $0{\cdot}226-0{\cdot}177$ or by $0{\cdot}049$. When the second layer is formed, a changes by $0{\cdot}360-0{\cdot}226$ or by $0{\cdot}134$. If there are only 8 per cent of gaps, the second change seems disproportionately large compared with the other two. If on the other hand the oxygen in the first stable layer were adsorbed as undissociated molecules, the adsorption of such a molecule on a given site excluding the possibility of adsorption on the four neighbouring sites as considered in section 5·3, the gaps in the film reduce the amount in it by 20 per cent. It will be shown in a paper that will be published shortly(3) that the number of molecules that can be adsorbed per unit area over these gaps is in the neighbourhood of $0{\cdot}2n_s$, while the number in the second layer is in the neighbourhood of $0{\cdot}5n_s$. Thus for a film of this type it would be much easier to account for the relative changes in a in the different stages. We have already seen in section 5·4 that another result for oxygen is in more satisfactory numerical agreement with what would be expected for this type of film than with what would be expected for a film in which the first stable layer was atomic.

Whatever may be the nature of the first stable film, the essential point that is established by these experiments is that there are the three types of adsorbed film and that the most reasonable way of accounting for these is to suppose that the first consists of a very stable film on the tungsten, that the second consists of molecules adsorbed in the gaps in this stable film and that the third consists of molecules in a second layer.

§ 7·3. The kinetics of the adsorption of oxygen.

It is easy to see that the kinetics of the formation of the oxygen film will be profoundly affected by the existence of the upper

layer. A molecule which strikes a site in the stable film which is already occupied is not immediately permanently adsorbed, but the fact that there is a second molecular layer formed, the amount in which depends on the pressure of the gas, must mean that molecules have a finite life on the surface in this upper layer, where they will presumably be mobile. Thus, even if the first site which a molecule tries is occupied, it may still find its way to a vacant place in the stable layer by moving over the surface. Let θ be the fraction of sites occupied in the stable layer. The effect of the presence of the upper mobile layer is to make the rate of adsorption into the stable layer vary slowly with θ, particularly when θ is small.

By working at very low pressures and measuring the gradients of curves giving the relation between the accommodation coefficient and the time, it was possible to investigate the variation of $d\theta/dt$ with θ. At these pressures the amount actually present in the upper layer at any instant was very small and any direct effect of it on the accommodation coefficient was negligible. The results obtained were in agreement with what would be expected for the type of system to which oxygen has been shown in section 7·2 to belong. It may be mentioned that, although it is difficult to measure gradients accurately, this is the best way to use the results, because the relation between $d\theta/dt$ and θ is much more characteristic and varies much more from one type of film to another than other relations that can be used, for example, the relation between θ and t.

REFERENCES

Chapter I

(1) Knudsen, *Ann. Physik*, **34**, 593 (1911); **46**, 641 (1915).
(2) Roberts, *Proc. Roy. Soc.* A, **135**, 192 (1932).
(3) Soddy and Berry, *Proc. Roy. Soc.* A, **84**, 576 (1911).
(4) Roberts, *Trans. Faraday Soc.* **28**, 395 (1932).
(5) Devonshire, *Proc. Roy. Soc.* A, **158**, 269 (1937).
(6) Jackson, *Proc. Camb. Phil. Soc.* **28**, 136 (1932); Jackson and Mott, *Proc. Roy. Soc.* A, **137**, 703 (1932); Jackson and Howarth, *Proc. Roy. Soc.* A, **142**, 447 (1933); **152**, 515 (1935); Landau, *Phys. Z. Sowjet*, **8**, 489 (1935).
(7) Roberts, *Proc. Roy. Soc.* A, **129**, 152 (1930).
(8) Rowley and Bonhoeffer, *Z. physik. Chem.* B, **21**, 84 (1933).
(9) Blodgett and Langmuir, *Phys. Rev.* **40**, 78 (1932).
(10) Roberts, *Proc. Roy. Soc.* A, **152**, 445 (1935).
(11) Michels, *Phys. Rev.* **52**, 1067 (1937).
(12) Frankenburger and Hodler, *Trans. Faraday Soc.* **28**, 229 (1932).
(13) Burdon, *Proc. Phys. Soc.* **47**, 460 (1935).
(14) Langmuir, *J. Amer. Chem. Soc.* **54**, 2819 (1932).
(15) R. P. Johnson, *Phys. Rev.* **54**, 459 (1938).
(16) Lennard-Jones, *Trans. Faraday Soc.* **28**, 333 (1932).

Chapter II

(1) Peierls, *Proc. Camb. Phil. Soc.* **32**, 471 (1936).
(2) Fowler, *Proc. Camb. Phil. Soc.* **32**, 144 (1936).
(3) Rushbrooke, *Proc. Camb. Phil. Soc.* **34**, 424 (1938).
(4) Wang, *Proc. Roy. Soc.* A, **161**, 127 (1937).
(5) Roberts, *Proc. Roy. Soc.* A, **161**, 141 (1937).
(6) Bosworth, *Proc. Camb. Phil. Soc.* **33**, 394 (1937).
(7) Roberts, *Proc. Camb. Phil. Soc.* **34**, 399 (1938).
(8) Wilkins, *Proc. Roy. Soc.* A, **164**, 496 (1938).

Chapter III

(1) Roberts, *Proc. Roy. Soc.* A, **152**, 473 (1935).
(2) Roberts, *Nature*, **135**, 1037 (1935).
(2*a*) Roberts and Miller, *Proc. Camb. Phil. Soc.* **35**, 293 (1939).
(3) Roberts, *Proc. Camb. Phil. Soc.* **34**, 399 (1938).
(4) Bosworth, *Proc. Camb. Phil. Soc.* **33**, 394 (1937).
(5) Langmuir and Kingdon, *Phys. Rev.* **34**, 129 (1929).
(6) Reimann, *Phil. Mag.* **20**, 594 (1935).
(7) Bosworth and Rideal, *Proc. Roy. Soc.* A, **162**, 1 (1937).
(8) Van Cleave, *Trans. Faraday Soc.* **34**, 1174 (1938).
(9) Roberts, *Proc. Roy. Soc.* A, **161**, 141 (1937).

Chapter IV

(1) Langmuir, *J. Amer. Chem. Soc.* **34**, 1310 (1912); **37**, 417 (1915); *General Electric Review*, **29**, 153 (1926).
(2) Bryce, *Proc. Camb. Phil. Soc.* **32**, 648 (1936).
(3) Roberts, *Proc. Camb. Phil. Soc.* **32**, 152 (1936).
(4) Roberts and Bryce, *Proc. Camb. Phil. Soc.* **32**, 653 (1936).
(5) Roberts, *Proc. Roy. Soc.* A, **161**, 141 (1937).
(6) Roberts, *Proc. Roy. Soc.* A, **152**, 445 (1935).
(7) Giauque, *J. Amer. Chem. Soc.* **52**, 4816 (1930).
(8) Bosworth, *Proc. Camb. Phil. Soc.* **33**, 394 (1937).
(9) Lennard-Jones and Devonshire, *Proc. Roy. Soc.* A, **156**, 6 (1936).
(10) Roberts, *Trans. Faraday Soc.* **31**, 1710 (1935).
(11) Strachan, *Proc. Roy. Soc.* A, **158**, 591 (1937).
(12) Lennard-Jones and Goodwin, *Proc. Roy. Soc.* A, **163**, 101 (1937).
(13) Langmuir and Kingdon, *Proc. Roy. Soc.* A, **107**, 61 (1925).
(14) Langmuir and Villars, *J. Amer. Chem. Soc.* **53**, 486 (1931).
(15) Johnson and Vick, *Proc. Roy. Soc.* A, **151**, 308 (1935).
(16) Bosworth and Rideal, *Physica*, **4**, 925 (1937); **5**, 170 (1938).
(17) Roberts, *Proc. Camb. Phil. Soc.* **34**, 399 (1938).
(18) Wang, *Proc. Roy. Soc.* A, **161**, 127 (1937).
(19) Fowler, *Proc. Camb. Phil. Soc.* **31**, 260 (1935).
(20) Chang, *Proc. Camb. Phil. Soc.* **34**, 224 (1938).

Chapter V

(1) Blodgett and Langmuir, *Phys. Rev.* **40**, 78 (1932).
(2) Bonhoeffer and Farkas, *Z. physik. Chem.* B, **12**, 231 (1931). For a later discussion see Farkas, *Orthohydrogen, Parahydrogen and Heavy Hydrogen.* (Camb. Univ. Press 1935.)
(3) Johnson and Henson, *Proc. Roy. Soc.* A, **165**, 148 (1938).
(4) Roberts, *Proc. Camb. Phil. Soc.* **34**, 577 (1938).
(5) Roberts, *Proc. Roy. Soc.* A, **152**, 473 (1935).
(6) Wang, *Proc. Camb. Phil. Soc.* **34**, 247 (1938).

Chapter VI

(1) de Boer, *Electron Emission and Adsorption Phenomena.* (Camb. Univ. Press, 1935.)
(2) Lenel, *Z. physik. Chem.* B, **23**, 379 (1933).
(3) Bradley, *J. Chem. Soc.* p. 1799 (1936).
(4) de Boer and Zwikker, *Z. physik. Chem.* B, **3**, 407 (1929).

(5) Lennard-Jones and Dent, *Trans. Faraday Soc.* **24**, 92 (1928).
(6) Roberts, *Trans. Faraday Soc.* **34**, 1342 (1938).
(7) Langmuir, *J. Amer. Chem. Soc.* **54**, 2798 (1932).
(8) Langmuir and Taylor, *Phys. Rev.* **44**, 423 (1933).
(9) Topping, *Proc. Roy. Soc.* A, **114**, 67 (1927).
(10) *Trans. Faraday Soc.* **30**, Appendix (1934).
(11) Zahn, *Phys. Rev.* **27**, 455 (1926).
(12) Williams, *Proc. Roy. Soc. Edin.* **37**, 161 (1917).
(13) Barrer, *Proc. Roy. Soc.* A, **161**, 476 (1937).
(14) Roberts and Orr, *Trans. Faraday Soc.* **34**, 1346 (1938).
(15) Fowler, *Statistical Mechanics*, 2nd edition, p. 306. (Camb. Univ. Press, 1936.)
(16) Herzfeld, *Phys. Rev.* **52**, 374 (1937).
(17) C. and M. Cuthbertson, *Proc. Roy. Soc.* A, **84**, 13 (1910).

Chapter VII

(1) Roberts and Morrison, *Proc. Roy. Soc.* A, in course of publication.
(2) Jeans, *Dynamical Theory of Gases*. (Camb. Univ. Press, 1925.)
(3) Roberts, *Proc. Camb. Phil. Soc.* **36** (1940).

INDEX

CAMBRIDGE: PRINTED BY W. LEWIS, M.A., AT THE UNIVERSITY PRESS