

CHAPTER I

EXPERIMENTAL METHODS

1.1. General Introduction

The classical experiments of Langmuir showed that, when a clean surface of a solid or a liquid is exposed to an impurity, a monomolecular layer of the impurity is often formed on the surface and contaminates it. In the study both of the behaviour of surfaces and of surface reactions it is of considerable importance to understand the properties of such monomolecular films. Furthermore, many properties of surfaces, for example, the interchange of energy between a solid surface and a gas,* depend in a very noticeable way on the presence of gas atoms or molecules adsorbed on the surface. To understand the processes which take place at the surface it is necessary to study the properties of such films and the physical mechanism by which they are formed. It is the purpose of this monograph to consider some of the experimental results concerning films of gases and vapours adsorbed on solid surfaces and to present the statistical thermodynamical theory in terms of which the properties of these films can be described.

It was first realized by Knudsen (1911, 1915) that, when the relevant dimensions of the apparatus used are small compared with the free path of the molecules, calculations based on the kinetic theory of gases can be carried out exactly. He performed a number of very beautiful experiments which substantiated this view, thus making a great advance in the theory, since 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, Knudsen introduced a quantity called the accommodation coefficient. It is a measure of the extent to which the gas molecules leaving the solid are in thermal equilibrium with it and is defined in the following way. Gas atoms at temperature T_1 strike a solid surface which is at temperature T_2

* This is discussed further below.

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(see fig. 1). On leaving the surface, the gas atoms will not in general be in equilibrium with it, i.e. they will not be at the 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

$$a = \frac{T'_2 - T_1}{T_2 - T_1}. \quad (1.1)$$

The details of the measurement of a and the proof that to a first approximation it is a constant, will be considered below. For a equal to unity the gas molecules leaving the surface are in equilibrium with it, while for a zero there is no net interchange of

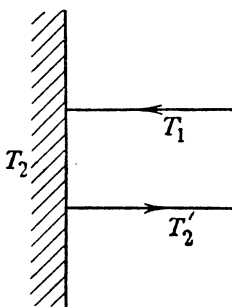


Fig. 1.

energy between the gas and the solid. Experimental determinations of a for various gases were made by Knudsen and other workers. On the basis of suitable simplifying assumptions, Baule worked out a classical theory of the collisions of the gas molecules with the atoms of the solid. This gave 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 consistently very much smaller than the measured values. Further, while the theory indicated that 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 of unknown composition, so that the application of a physical theory was impossible.

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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. To carry out experiments under these conditions formed the starting-point of the experiments initiated by Roberts in 1931. The experiments were extended to a wide range of interactions between gases and solids and to the study of the structure and behaviour of adsorbed films of gases built up on a known substrate. Their purpose was to obtain experimental data which should provide the basis for a physical theory of the interaction between gas atoms and solids. It should, perhaps, be noted here that there is no need to discuss Baule's simple classical theory of collisions, for it was quickly superseded by a quantal treatment.

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 was essential, for only in this way was it possible to build up a detailed picture of what was 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

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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 his first experiments Roberts studied the interchange of energy between helium and a tungsten surface by measuring the accommodation coefficient.

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

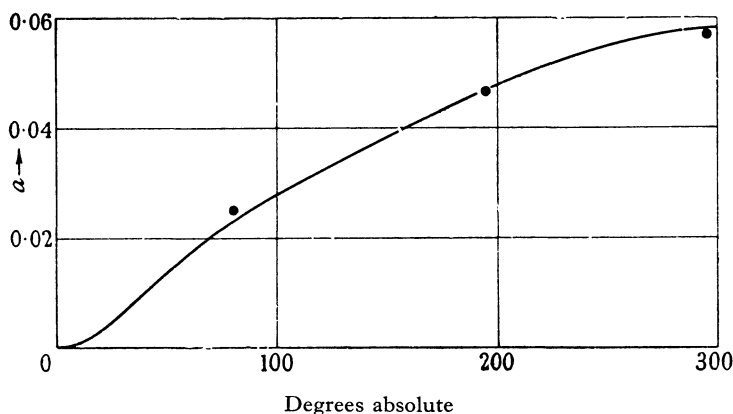


Fig. 2. Variation of accommodation coefficient of helium with temperature.

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 (Roberts 1932*a*). 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 (1911) 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 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 (Roberts 1932*b*) 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 $n h \nu$, 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 a 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 0 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, fewer and fewer oscillators are affected as the temperature falls. As a result, the interchange of energy, under comparable conditions, becomes less and less efficient. Thus for a small temperature difference between solid and gas the accommodation coefficient becomes smaller and smaller.

Devonshire (1937), in one of a series of papers by Lennard-Jones and his co-workers, has followed up the work of Jackson, Mott and others (Jackson 1932; Jackson and Mott 1932; Jackson and Howarth 1933, 1935; Landau 1935) in developing the detailed quantum 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

assumed that the potential energy between a gas atom and an atom in the surface of the solid when their centres are at a distance z apart is given by a Morse function

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

This is plotted in fig. 3, in which the meanings of b and of D are shown; D is closely related to the heat of adsorption. The third constant κ determines the rate at which the repulsive potential energy increases when the atoms are closer together than b . The greater κ is, the more sharply does the repulsive potential increase 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.

As has been mentioned, the behaviour with helium would be expected to be simpler than with any other gas because of the small value of D (fig. 3). The next gas used was neon, for which D is 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 (1937) 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. The experiments described here 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 results for neon from the 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

* 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. The value of this factor can be determined only by direct observation of the shape and size of the irregularities on the surface. For a general discussion of this point see Roberts (1930).

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.

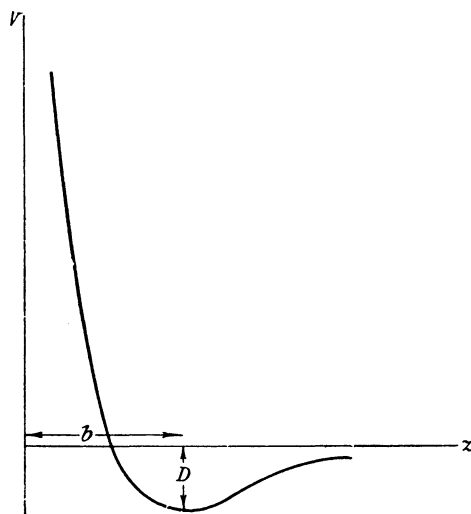


Fig. 3. Potential energy V of two molecules a distance z apart showing the meanings of D and b in the Morse function.

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 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 are $f(c)dc$ molecules per cm^3 with velocities lying between c and $c+dc$ cm. per sec. The

* For a discussion of this point see Rowley and Bonhoeffer (1933).

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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

$$\frac{1}{8}m \int_0^{\infty} f(c) c^3 \, dc.$$

Since

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

where n is the number of atoms per cm.³, the total energy brought up to unit area of the wire per second is

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

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 exactly Maxwellian, but the departure from such a distribution becomes smaller as $T_2 - T_1$ becomes smaller.* We assume a Maxwellian distribution so that

$$n_c = A c^3 e^{-mc^2/2kT'_2}.$$

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

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

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

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

* For a discussion of this see Knudsen (1911, 1915).

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

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

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 measured in ergs. Using equation (1.1), this becomes

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

$$\text{or} \quad \frac{7.3 \times 10^3 ap(T_2 - T_1)}{(MT_1)^{\frac{1}{2}}} \quad \text{ergs per cm.}^2 \text{ per sec.,}$$

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

$$q = 1.74 \times 10^{-4} \frac{ap}{\sqrt{(MT_1)}} (T_2 - T_1). \quad (1.2)$$

All the quantities in this equation except a can be measured and thus a is determined. The wire was placed in one arm of a Wheatstone bridge. q was 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 was 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 l is long compared with the radius of the containing tube, but it is sufficient that l should be long compared with the diameter of the wire. Molecules leaving the wire travel, on the average, a distance l 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 l 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

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the wire and the gas at a distance l 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 (1911, 1915).

In order to be able to measure the accommodation coefficient for a bare surface and to study the adsorption of known gases on

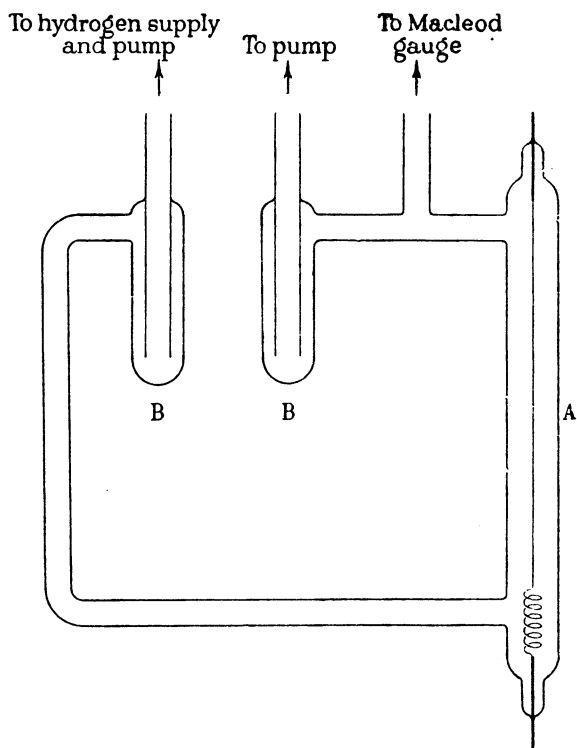


Fig. 4. Apparatus for measuring accommodation coefficients.

such a surface it is necessary to work under carefully controlled conditions. The essential parts of the apparatus that were 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

* See, for example, Blodgett and Langmuir (1932).