

system, it is nevertheless possible to divide all adsorptions into two main types: physical adsorption and chemisorption.

### 2.1.1. Physical adsorption and chemisorption

In principle, the distinction between these two types of adsorption is clear cut. Physical adsorption is caused by the forces of molecular interaction which embrace [1] permanent dipole, induced dipole and quadrupole attraction. For this reason, it is frequently designated van der Waals adsorption. Chemisorption, on the other hand, involves the rearrangement of the electrons of the interacting gas and solid, with consequential formation of chemical bonds. In other words, physical adsorption is akin to the condensation of a vapour to form a liquid, or to the liquefaction of gases, and chemisorption can be regarded as a chemical reaction which is restricted to the surface layer of the adsorbent. It is evident from these definitions that as our concept of what constitutes a chemical bond alters, so also will our concept of chemisorption.

Experimentally, it is frequently possible to distinguish between the two types of adsorption, but in some instances the distinction is so ill defined that several criteria have to be employed before a decision can be reached. The magnitude of the *heat of adsorption* forms the basis of one, and probably the best (but see Section 3.2.8), of these criteria. During physical adsorption the heat liberated per mole of gas adsorbed is generally in the region of 2-6 kcal, but values as large as 20 kcal mole<sup>-1</sup> have been reported [2]. For example, the heats of physical adsorption of argon [3] and krypton [4] on graphitized carbon black are, respectively, 2.70 and 3.90 kcal mole<sup>-1</sup>, the heats of liquefaction being 1.55 and 2.31 kcal mole<sup>-1</sup> at the corresponding temperature. Seldom does the heat of physical adsorption exceed the heat of liquefaction of the gas in question by more than a factor of two or three (but see Table 1 of this chapter). During chemisorption larger values for the heat of adsorption are usually encountered; the heat of chemisorption of oxygen on some metals may, for instance, be a few hundred kcal mole<sup>-1</sup>. Generally, heats of chemisorption are rarely less than 20 kcal mole<sup>-1</sup>, but values as low as those associated with physical adsorption are known, and evidence has recently come to light to demonstrate the occurrence of endothermic adsorption (see Section 2.2.3).

A second criterion used to distinguish experimentally between chemisorption and physical adsorption is the *rate* at which the process occurs. It is argued that, since physical adsorption simulates liquefaction, the same dispersion forces being at work, it should, like liquefaction, require no activation and therefore occur very rapidly. Chemisorption, on the other hand, should, like most chemical processes, require activation. This criterion of rate proves to be a useful guide but, just as for the heat of adsorption, it can be misleading if it alone is the sole criterion used. Thus, chemisorption of

## CHAPTER 2

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### 2.1. The Nature of Adsorption

From the definition of heterogeneous catalysis, it follows that at least one of the reactants must become attached in some way, and for a significant period, to the surface of the solid catalyst. As the process of attachment is of central importance in catalysis, it is imperative that we first concern ourselves with the precise details of the nature of this process. Indeed, there is little hope that we can ever fully appreciate the mechanism of heterogeneous catalysis unless we first comprehend the characteristics of adsorption.

The forces acting at the surface of a solid, be it a catalyst or not, are unsaturated. Hence, whenever a fresh surface is exposed to a gas a higher concentration of gas molecules will result on the surface compared with that in the gas phase. This preferential concentration of a molecule at the surface is termed adsorption. Although the strength of adsorption, that is, the tightness with which molecules of the adsorbate are attached to the adsorbent, together with the extent of adsorption, may vary widely from system to

hydrogen and oxygen on many clean metal surfaces is essentially a non-activated process, as evidenced by the fact that, at liquid nitrogen temperature, the process takes place extremely rapidly. Moreover, there is another difficulty which may render this criterion untenable. Physical adsorption on a porous solid, such as hydrocarbons on a silica-supported alumina catalyst, may take place very slowly, if diffusion of the adsorbate along the pores is the rate-determining step. This could easily be mistaken for activated chemisorption.

As well as the rate of adsorption, the *rate of desorption* is frequently a useful guide in deciding which type of adsorption obtains. It will emerge later (Section 2.2), when the energetics of adsorption are discussed, that the activation energy of desorption from the physically adsorbed state (assuming an adsorbent of low porosity) is rarely more than a few kilocalories per mole, whereas the activation energy for desorption from the chemisorbed state is generally greater than 20 kcal mole<sup>-1</sup>, being almost invariably greater than or equal to the heat of chemisorption.† It is for this reason that the ease of desorption noted on warming a system from liquid air temperatures to -78°C or to room temperature is often employed [5, 6] as a preliminary means of ascertaining the nature of the adsorption.

Another useful criterion is based on the *temperature range* over which the adsorption occurs. Physical adsorption should occur only at temperatures close to the boiling-point of the adsorbate at the operative pressure, whereas chemisorption, being associated with much stronger forces, should be capable of occurring at temperatures well above the boiling-point of the adsorbate at the operative pressure. Although unquestionably useful, this test can also prove misleading if the adsorbent is highly porous. On such a solid, physical adsorption may be quite extensive, even though the ratio  $p/p_0$  of the pressure of the gas to the saturated vapour pressure (s.v.p.) at the operative temperature is as low as 10<sup>-6</sup> or less; that is, even though the temperature is very much in excess of the boiling-point of the adsorbate. The boiling-point of argon is 87.4°K and  $p_0$  at 160°K is ~10<sup>5</sup> mm Hg. Therefore, on the basis of previous experience, we can expect physical adsorption to take place at an equilibrium pressure of 1 mm Hg when the temperature is 160°-87.4°=72° above the boiling-point of argon. To appreciate why this is possible, it is instructive first to consider, as did Zsigmondy [7], the classical Kelvin (Thomson [8]) equation (see Section 4.3.1), which relates the vapour pressure above a planar liquid surface to the vapour pressure above a curved surface, as of a meniscus of liquid inside a cylindrical capillary. The Kelvin equation is:

$$\ln \left( \frac{p}{p_0} \right) = \frac{-2 \sigma \bar{V} \cos \alpha}{rRT} \quad (1)$$

† Substances which are desorbed in the ionic form may have heats of desorption less than the heats of adsorption. The respective values for caesium on tungsten are 54 and 63 kcal mole<sup>-1</sup> [2].

where  $p$  is the vapour pressure above a surface the radius of curvature of which is  $r$ ,  $p_0$  is the vapour pressure above the planar surface,  $\sigma$  the surface tension of the liquid,  $\bar{V}$  the molar volume of the liquid,  $\alpha$  the angle of contact,  $R$  the gas constant and  $T$  the absolute temperature. Now, if we suppose that a highly porous adsorbent consists of numerous cylindrical pores of mean radius  $r$ , and that the adsorbate within the pores has properties characteristic of the bulk liquid phase, the system should conform to equation (1).  $p/p_0$  now being the ratio of the equilibrium adsorption pressure and the s.v.p. of the adsorbate. Clearly, the smaller the value of  $r$ , the smaller the ratio  $p/p_0$  and the greater the temperature, above the boiling-point, at which physical adsorption can take place.

A fourth criterion which helps to distinguish adsorption types is based on the extent of *specificity* in gas-solid interaction. Since chemisorptions are chemical reactions confined to the surfaces of solids, and since chemical reactions are specific, so also are chemisorptions in the sense that, if a gas is chemisorbed by a given solid under certain conditions, it does not follow that the same gas will be chemisorbed by another solid of equivalent surface cleanliness and under identical conditions. Obviously, the chemical potentials of the interacting substances and of the possible surface products govern the feasibility of the chemisorption. Physical adsorption, however, is effectively the process whereby condensation of gas occurs, the adsorbate being capable of building up to one or many layers on an inert solid. Like all the other criteria that have been discussed thus far, this one also has its limitations. There is little doubt [9] that the adsorbent is not always "chemically" inert, and that specificity, to some degree, may obtain even in physical adsorption.

Although no single foolproof test is available to assess the type of adsorption in any given system, the above-mentioned criteria, taken collectively, leave little doubt as to the type which prevails. There are also other, rather special, criteria (see Section 3.3.1) which, taken singly even, afford sufficient evidence to indicate the category of the adsorption. For example, a substantial change of magnetic susceptibility of an adsorbent during adsorption may constitute convincing evidence that the process is chemical [10]. Again, if the surface area of the solid is known, the extent of adsorption can sometimes be used as an indication, for it is doubtful whether chemisorption can ever exceed more than a monolayer, whereas physical adsorption can extend to multilayers [11].

## 2.2. The Energetics of Adsorption

Since it is well established (see Section 2.4.1.3) that heterogeneous catalysis is usually a consequence of the fact that the activation energy of a reaction is lowered as a result of chemical combination between the catalyst and at least one of the reactants, it is profitable to discuss the general nature and extent

of the energy changes involved in adsorption. To appreciate the way in which the energetics of chemisorption are normally expressed, we shall first consider the simpler problem of the energetics of physical adsorption, which are also relevant to the question of catalysis.

### 2.2.1. Depiction of adsorption processes by potential energy diagrams: heat of adsorption

It was shown by Lennard-Jones [12, 13] over thirty years ago that, by calculating the van der Waals fields outside solid surfaces, it is possible to estimate the magnitude of the heats of physical adsorption of certain gases on the surfaces of the solids. In the intervening years numerous theoretical studies have been carried out (see Refs. 1, 2, 14) to compute the dependence of the potential energy of an adsorbate molecule upon its distance from the adsorbent surface. It has emerged [1] that different theoretical approaches are required for different systems if satisfactory agreement is ever to be reached between the calculated and observed heats of physical adsorption. For example, a certain equation may be applicable for the interaction between an inert gas and the surface of an alkali halide, but be quite inappropriate for the same gas and a metal or other good electrical conductor. It is not here necessary to enumerate the various types of physical interaction which are now known [2] to demand distinct theoretical treatment; all that is necessary is to appreciate that the interaction energy responsible for physical adsorption can, in principle, and for most systems, be represented by an equation similar to that which Lennard-Jones successfully employed for the potential energy of gas molecules as they approach each other:

$$E = -ar^{-m} + br^{-n} \quad (2)$$

In equation (2),  $a$ ,  $b$ ,  $m$  and  $n$  are constants, and  $r$  is the separation distance. The first of the terms on the right-hand side arises from attractive forces, and the second from repulsive forces, between the interacting species. Lennard-Jones chose [13, 15] values of 6 and 12 for  $m$  and  $n$  respectively. The first of these choices was theoretically justified in view of London's work [16] on dispersion forces, which were shown to fall off with the seventh power of distance; the second,  $n=12$ , had no theoretical significance and was chosen for computational convenience. The constant  $a$  presented relatively little difficulty, its value being calculable from such properties as the atomic susceptibilities and polarizabilities. However, much uncertainty, which still persists, attached to the calculation of the "repulsive" constant  $b$ . Largely because of this, it is not yet possible to calculate, *a priori*, the complete potential energy equation for gas molecules. The current procedure is to adjust the value of  $b$  so that a "correct" value is obtained for the separation of two gas molecules in the equilibrium condition when the attractive and repulsive forces between the

molecules are equal [17]. Thus, at the equilibrium distance,  $r_0$ , we have that  $dE/dr=0$ , so that equation (2) yields:

$$mar_0^{-m-1} - bnr_0^{-n-1} = 0 \quad (3)$$

or

$$b = \frac{m}{n} ar_0^{(n-m)} \quad (4)$$

The total decrease  $E_0$  in potential energy at the equilibrium distance is therefore given by:

$$E_0 = ar_0^{-m} \left( \frac{m}{n} - 1 \right) \quad (5)$$

Clearly, the theoretical value of  $E_0$  can be made to coincide with the observed energy of interaction by adjusting  $b$  through equations (4) and (5).

If the theoretical difficulties in evaluating potential functions are quite considerable for gas phase molecules, the problems encountered when the interaction involves a condensed phase are not likely to be easier. When an adsorbate molecule approaches a surface, it is, effectively, interacting with a large number of atoms simultaneously, and the total potential energy of the interaction is an infinite series composed of terms similar to those contained in equation (2), with the appropriate value of  $r$  being used in each case. Although the form of the potential energy function, which is dependent upon the structure of the solid, cannot be written down in such a way as to be applicable to all known systems of physical adsorption, and although precise calculations are still impossible, we can at least assert that an equation such as equation (2) gives, in most instances, the correct shape of the potential energy diagram depicting physical adsorption, and frequently leads to values of heats of adsorption in reasonable agreement with those obtained experimentally [18]. To take a specific example, Kiselev [18] and his associates calculated the potential energies (and, hence, the heat of adsorption) of vapours of non-polar substances on graphitized carbon black, using the following potential-equation:

$$E = -C_{11} \sum_j r_{ij}^{-6} - C_{12} \sum_j r_{ij}^{-8} + B \sum_j \exp \left( -\frac{r_{ij}}{\rho} \right) \quad (6)$$

where  $i$  is the force centre of the adsorbate molecule; the dispersions  $C_{11}$  and  $C_{12}$  are calculable from magnetic susceptibility and polarizability data using formulae previously derived by Kirkwood [19] and Müller [20];  $\rho$  is an exponential repulsion constant; the constant  $B$  is adjustable in much the same way as constant  $b$  in equation (2). Table 2.1 shows some of the results quoted by Kiselev. Apart from showing that equation (6), (i) predicts the correct sequence of adsorption energy values, and (ii) leads to satisfactory agreement between observed and "computed" values, Table 2.1 also shows the type of energies we can anticipate in physical adsorption.

TABLE 2.1. Energies of adsorption (kcal mole<sup>-1</sup>) on the surface of graphitized carbon blacks at half coverage (after Kiselev [18])

Adsorbate	Energy of adsorption	
	Calculated (equation (6))	Observed
Hydrogen	0.90	0.91
Deuterium	0.95	0.95
Nitrogen	2.6	2.8
Propane	6.8	6.5
n-Hexane	12.4	12.5
Benzene	10.3	10.0
n-Octane	16.1	16.0

Figure 1 represents the general shape of the potential energy curve relating to the physical adsorption of a gas molecule  $M_2$  on the surface of a solid S. It can be seen from this figure that the heat of adsorption is given by the difference in energy between the states X where the molecule is infinitely removed and Y where it is at its equilibrium distance from the surface. The potential energy increases rapidly with decreasing distance from the surface, since repulsive forces must dominate ultimately (state Z) to satisfy the physical requirement that two species cannot occupy the same space.

By analogy with what has already been said concerning physical adsorption, we would expect the potential energy diagram depicting the chemisorption of a reactive atom, such as atomic hydrogen, on a solid surface to be as

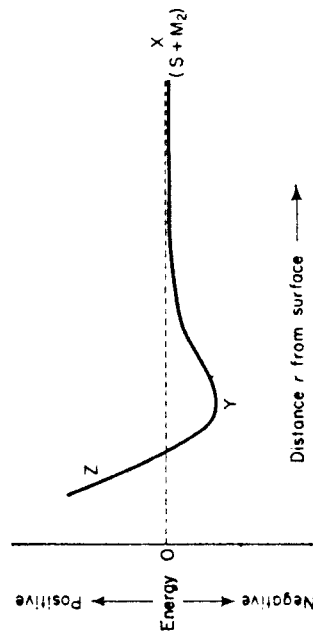


FIG. 1. Potential energy curve relating to the physical adsorption of a molecule  $M_2$  on the surface of a solid S.

shown schematically in Fig. 2. Such a Lennard-Jones plot, as it is sometimes designated, is reminiscent of the Morse curve used [21] to represent the electronic energy of a molecule. At separation distances  $r$  not far removed from  $r_0$ , the equilibrium separation, the curve takes a parabolic form given by:

$$E = +Q \{-1 + \sigma(r - r_0)^2 + \dots\} \quad (7)$$

where  $\sigma$  is a constant, and  $Q$  is the heat or energy of adsorption (see Fig. 2). The heat of adsorption (per g atom) is again equal numerically to the difference between the corresponding levels X and Y, and it is to be noted that the heat of desorption is equal to the same difference in energy levels.

Having outlined the present status concerning the calculation of the

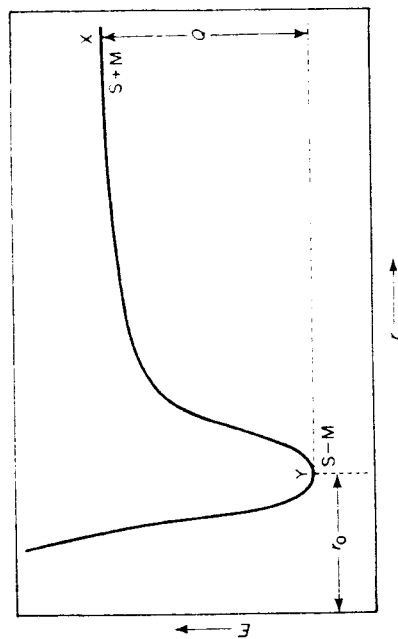


FIG. 2. Schematic representation of the chemisorption of a reactive atom M on the surface of a solid, S.  $Q$  is the heat or energy of adsorption, and  $r_0$  the equilibrium separation distance.

potential energy of physical adsorption, the question naturally arises as to the feasibility of calculating the potential energy curve for chemisorption. It has to be stated, at the outset, that a complete theoretical computation, from first principles, is not possible. This is partly because of the inadequacy of our present knowledge of the forces involved in chemisorption, partly because of our ignorance of the precise structure, electronic and otherwise, of the surface layers of solids, and not least because of—to use the language of the quantum mechanist—our inability to solve the many-body problem [22]. However, the general shape of the potential energy curve may be constructed (with greater or lesser precision, depending upon the nature of the chemisorbed link with which we shall deal later) provided that we know the heat of adsorption and some other information, such as the bond dissociation energies of the adsorbate. It follows, therefore, that the task of constructing a realistic potential energy curve depicting a particular chemisorption devolves upon our obtaining a reliable value for the heat of that adsorption. It will emerge shortly that the potential energy curves for chemisorption are almost invariably constructed from the observed, rather than the calculated, heat of adsorption (that is, the curves are derived semi-empirically), the prime reason for this being, again, our inability to calculate heats of adsorption with the necessary precision.

### 2.2.2. Potential energy diagrams describing chemisorption

Having discussed, at some length, the difficulties encountered in calculating heats of adsorption, we now return to the original theme of depicting chemisorption by means of Lennard-Jones plots, it being understood that, so long as heats of adsorption are known, it is always possible to evaluate the shape of these plots and, if certain additional information is available, this can be done with considerable precision.

We may begin by recalling the work of Eley and Rossington [34], which dealt with the dissociative adsorption of hydrogen on the surfaces of Group IB metals. They observed the heat of adsorption  $Q$  of hydrogen on copper to be  $8.0 \text{ kcal mole}^{-1}$ , and the activation energy of desorption of hydrogen molecules from the surface to be  $13.0 \text{ kcal mole}^{-1}$ . They could therefore draw the Lennard-Jones plot shown in Fig. 3. Curve A refers to the physical adsorption of molecular hydrogen, and curve B to the chemisorption of atomic hydrogen to form two covalent bonds:



The heat of adsorption of hydrogen as two atoms,  $8.0 \text{ kcal mole}^{-1}$ , is clearly equal to  $2Q_a - D(\text{H}-\text{H})$ , where  $Q_a$  stands for the heat of adsorption of the atomic hydrogen, and  $D(\text{H}-\text{H})$  the bond dissociation energy of the hydrogen molecule.

Figure 3 shows how, in energetic terms, hydrogen can be dissociatively adsorbed by a metal without the prior dissociation of the molecule in the gas phase: so long as the physically adsorbed molecule can acquire adequate activation, that is, get sufficiently near to the metal surface so as to reach the point X on curve A, it can transfer to curve B and become chemisorbed in the dissociated state. The height of X above the potential energy minimum is clearly the activation energy of desorption,  $13.0 \text{ kcal mole}^{-1}$ , and the height of X above the level of zero energy is the activation energy of adsorption.

Because the chemisorption of nitrogen on iron, as well as that of hydrogen on silver and gold, is an activated process, the Lennard-Jones plots in these cases would also be drawn such that the height of the intersection point X above the energy zero would be equal to the corresponding activation energy of adsorption. For surfaces which have been stringently cleaned, chemisorption of gases at liquid air temperatures (*ca*  $-193^\circ\text{C}$ ) may occur at an extremely fast (frequently immeasurably fast) rate, thus revealing that there is no activation energy of adsorption. Trapnell [35] gives a comprehensive list of metals and oxides which display this behaviour towards hydrogen, carbon monoxide, carbon dioxide, oxygen, ethylene and other gases. One example is the chromia-carbon monoxide system and the nickel-hydrogen system is another. In the potential energy diagrams depicting these non-activated chemisorptions, the point X must fall below the level of zero energy.

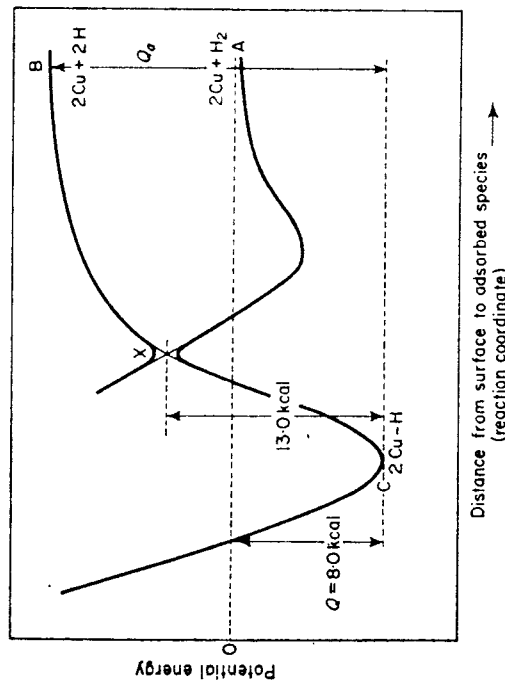


FIG. 3. Lennard-Jones curves for the copper-hydrogen system [34]. Curve A refers to the physical adsorption of molecular hydrogen, and curve B to the chemisorption of atomic hydrogen. The intersection of the two curves is slightly rounded, as expected from the non-crossing rule [37] between two states.

### 2.2.3. Endothermic adsorption

The view is frequently expressed that endothermic adsorption cannot occur. This is tantamount to stating that all adsorptions are exothermic processes. The problem of ascertaining the veracity of this statement is not simply a matter of academic interest. As will be shown (Section 5.4.3), endothermic adsorption may play a prominent role in certain heterogeneously catalysed reactions, and the importance of endothermic adsorption has been recently emphasized by de Boer [45] and by Schwab [46]. We shall deal with the reasons for initially accepting, and later retracting, the notion that endothermic adsorptions are impossible.

The justification generally produced for the statement that adsorptions are always exothermic is a thermodynamic one: since the Gibbs free energy  $G$  must decrease for any spontaneous process, and since chemisorption is one such process which is always accompanied by a decrease in entropy (the number of degrees of freedom in the adsorbed state being less than the number in the gaseous state), then, according to the second law of thermodynamics, which leads to the equation

$$\Delta G = \Delta H - T\Delta S, \quad (22)$$

$\Delta H$ , the enthalpy or heat of adsorption, must be negative; that is, adsorption is always exothermic. (An exothermic adsorption is one that, in the field of chemisorption and heterogeneous catalysis, is said to have a positive heat of adsorption. For example in Fig. 2,  $Q = -\Delta H$ , where  $-\Delta H$  is another notation for the heat of adsorption.)

For the overwhelming majority of adsorptions, this argument would be valid. It may well be that the argument applies invariably to physical adsorptions, where it can be shown [47], using equations derived from statistical mechanics, that, even when the adsorbed species is extremely mobile, the entropy of a species in the adsorbed state is always less than the entropy in the gaseous state. That endothermic physical adsorption has never been reported is, therefore, not surprising.

For several chemisorptions, however, there is cogent evidence that endothermic processes have been observed [45, 46, 48-51]. In the chemisorption of molecular hydrogen on glass, the heat of adsorption is negative [50]. The heat of adsorption is also negative (that is  $\Delta H$  is positive) when hydrogen is dissociatively adsorbed on iron surfaces contaminated with sulphide ions [45]. There are other instances of chemisorption where endothermicity is strongly suspected, but not yet incontrovertibly established. Molecular hydrogen at 0°C on Group IB metals and on cadmium is one example [52], molecular oxygen on silver is another [45, 49].

Before considering the detailed energetics of endothermic adsorption, it is pertinent to consider, in general terms, how it is that we can account for the absence of endothermic physical adsorption while also accepting the existence of endothermic chemisorptions. In physical adsorption, the entropy change is always negative, since we have essentially a condensation process, analogous to liquefaction, on the adsorbent. Because the number of degrees of freedom of the adsorbed species is less than the number it possessed prior to adsorption, and because the entropy of the adsorbent is unaltered (since there is no chemical interaction, but see Ref. 52), the entropy change  $\Delta S$  is negative, and so, from equation (22),  $\Delta H$  must be negative. In chemisorption, on the other hand, a surface reaction takes place involving the rupture and creation of chemical bonds. In the same way that some chemical reactions are endothermic, so also it may be expected that some surface reactions can be endothermic.

In an adsorption process which is endothermic, the entropy change must be not only positive, but the  $T\Delta S$  term must also exceed numerically the  $\Delta G$  term (equation (22)). The implication of this conclusion meets with some scepticism in view of the popular conception that the entropy of adsorption is always negative. Consequently, it is useful, for heuristic purposes, to visualize the following hypothetical system. A gas molecule  $M_2$  is dissociatively chemisorbed on the surface of a solid S. Suppose the strength of the S—M bond is equal to half the strength of the M—M bond. Now, if the adsorbed atoms M have complete two-dimensional mobility, it would then follow that a positive entropy change  $\Delta S$  would result, corresponding to a net gain of one degree of freedom, and the free energy change associated with this thermally neutral process ( $\Delta H=0$ ) would be equal solely to the  $T\Delta S$  term.

However, positive values for the entropy of adsorption are also likely to originate from another source: the change in entropy of the adsorbent itself. Thus, during chemisorption, even if, as is usual, the entropy of the species adsorbed decreases on adsorption, due largely to reduction in the number of degrees of freedom, this decrease may be exceeded by a concomitant increase

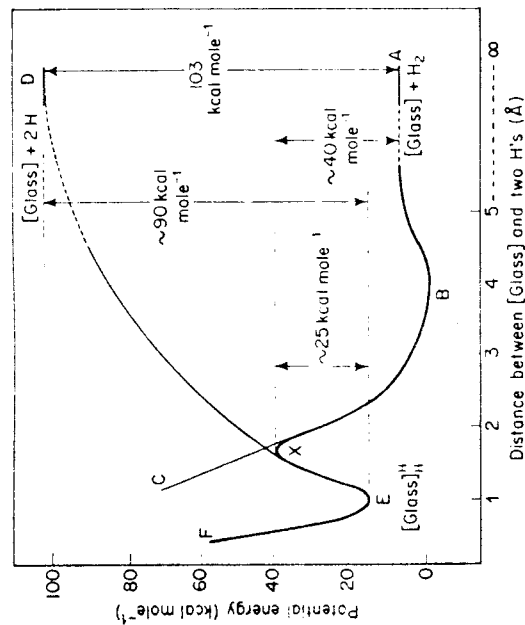


FIG. 6. The endothermic chemisorption of hydrogen on glass: the heat of adsorption is about  $-15$  kcal mole $^{-1}$  [2].

in the entropy of the adsorbent. This, in turn, would lead to an endothermic process if the  $T\Delta S$  term were greater numerically than the  $\Delta G$  term.

Energetically, it is not difficult to envisage endothermic adsorptions. Figure 6, which is taken from the work of de Boer [2], shows two potential energy curves; one refers to the chemisorption of atomic hydrogen on glass, the other to the physical adsorption of molecular hydrogen on the same adsorbent. The energy level of the two hydrogen atoms adsorbed on glass is above that of gaseous molecular hydrogen (for exothermic adsorptions the situation is reversed, compare Fig. 3). The path of endothermic adsorption is ABXEF.