

THE HEATS OF ADSORPTION AND THE KINETICS OF ADSORPTION.

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The Heat of Adsorption.

During an adsorption process the energy levels of the adsorbed molecules and of the atoms composing the surface undergo modification, and also, as in most physical and chemical processes, there is a residuum of energy which is liberated as heat. The latter is called the heat of adsorption. This heat is the algebraic sum of the various energy changes occurring during the adjustment of the surface and molecular fields, and hence it is not possible to deduce from it the actual values of the changes in potential energy which take place at the surface. Nevertheless, there seems to be some correspondence between the magnitudes

of the heat of adsorption and of the potential energy changes. This correspondence is sufficiently exact to enable us roughly to classify adsorption processes by its aid.

Such a classification is possible because the energies associated with the rotational, vibrational and electronic levels of molecules respectively are of widely different magnitudes. At low temperatures, only changes in rotational levels and the kinetic energies of the molecules would be expected to occur on adsorption. Thus, at such temperatures, the potential energy changes and also the heat of adsorption must be small

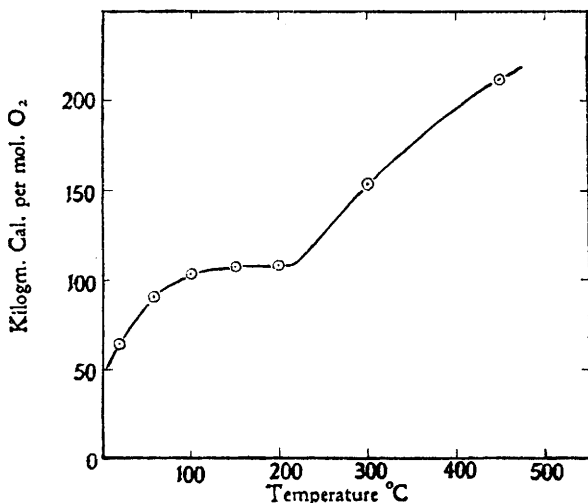


FIG. 1.—Heat of adsorption. Oxygen on charcoal.

in magnitude. As the temperature is raised, there successively appear changes in the vibrational and electronic levels, and since the rotational, vibrational-rotational, and the electronic-vibrational-rotational levels are usually widely separated on the energy scale, there must occur on raising the temperature discontinuous changes in the magnitude of the residuum of energy which is liberated as heat.

Systematic measurements of the heats of adsorption have very rarely been made over a wide range of temperatures. The experimental data which are available have either been calculated by the application of thermodynamics to the adsorption isobar for a narrow range of temperatures or else have been measured experimentally for temperatures in the neighbourhood of 0° C. Sufficient has, however, been done for us to observe the trend of the values of the heat of adsorption with increase in temperature. That discontinuities do occur is abundantly evident from the work of H. S. Taylor on activated adsorption on many surfaces. Also, measurements of the heats of adsorption of oxygen on charcoal between 20° C. and 350° C. provide clear evidence for the same view (Fig. 1).

Adsorption at Low Temperatures.

When adsorption occurs at low temperatures, the heats of adsorption are not very much greater in magnitude than the kinetic energies of the adsorbed molecules. Thus, for the permanent gases adsorbed on mica at temperatures between -180° C. and -80° C., the heats of adsorption¹ range between 500-2000 calories pro mol. Also, the heat of adsorption of hydrogen on metals at these temperatures is of the same order.² These small heats of adsorption may be taken to indicate

¹ Langmuir, *J.A.C.S.*, **40**, 1361, 1918; Bawn, *J.A.C.S.*, **54**, 72, 1932.

² Benton and White, *J.A.C.S.*, **53**, 3301, 1931.

that the changes in potential energy which occur during adsorption are small in magnitude, and this is supported by the fact that the gases adsorbed under these conditions are not specially active chemically. The heats of adsorption are of the same order as those to be expected from the magnitude of the van der Waals' forces between the normal surface atoms and normal adsorbed molecules.³

Adsorption at Room Temperatures.

Since the heat of adsorption includes some of the energy of translation, rotation, etc., of the adsorbed molecule, it would be expected that it would increase with rise in temperature. This is found to be the case. Gases like nitrogen and ammonia adsorbed on charcoal at room temperatures give heats of adsorption of 4000-8000 calories.⁴ The heats of adsorption at room temperatures are sometimes found to depend on the number of gas molecules adsorbed per unit area of surface.⁵ For small amounts adsorbed, quite high values may be obtained. Thus, the differential heats of adsorption of oxygen on charcoal range between 90 in the initial stages of the adsorption to 4 cal. in the neighbourhood of saturation.⁶ The occurrence of such large energy changes demonstrates the occurrence of large changes in the potential energies of the surface atoms and of the adsorbed molecules. These are of such a magnitude that it may be that they are a consequence of chemical combination of the adsorbed molecule with the surface.

The processes which give rise to abnormally high heats of adsorption may be classified into two main groups, (1) reversible changes and (2) irreversible changes. In the first class, the adsorbed molecules can be recovered on desorption in an unchanged state, and in the second, desorption results in the volatilisation of some of the surface atoms in chemical combination with the adsorbed gas.

Reversible Adsorption at Moderate and High Temperatures.

The adsorption of hydrogen or carbon monoxide on metals and metallic oxides is in the majority of cases reversible at room temperatures, and the heats of adsorption lie between 10,000-30,000 cal./mol., whereas at lower temperatures the heats obtained with the same substances are of the order 1000-2000 calories. There is a complete change in the character of the adsorption process as the temperature is increased, for the adsorption isobar shows a minimum in several cases.⁷

Heats of adsorption of 30,000 cal. are of too large a magnitude to be due to the changes in potential energy which arise under the influence of the normal van der Waals' forces. Besides, these high temperature adsorption processes possess quite large critical increments.⁸

Benton and White² refer to these reversible adsorption processes as chemisorption, but H. S. Taylor leaves the question of their nature

³ Lennard-Jones and Dent, *Trans. Far. Soc.*, **24**, 92, 1928.

⁴ Cf. Hückel, *Adsorption und Kapillarkondensation*, p. 34.

⁵ This does not happen in many cases. In the adsorption of gases on metals, for example, the heat of adsorption is independent of the surface covered. Cf. Ward, *Proc. Roy. Soc.*, **133A**, 506, 1931, and Maxted and Hassid, *J.C.S. In press*.

⁶ Garner and Blench, *J.C.S.*, **125**, 1288, 1924; Garner and McKie, *J.C.S.*, **2451**, 1927; Keyes and Marshall, *J.A.C.S.*, **49**, 156, 1927.

⁷ Benton and White, *J.A.C.S.*, **52**, 2325, 1930; Taylor and Williamson, *J.A.C.S.*, **53**, 2168, 1931; Taylor and McKinney, *J.A.C.S.*, **53**, 3604, 1931.

⁸ Cf. H. S. Taylor, *J.A.C.S.*, **53**, 578, 1931.

more open by describing them as "activated" adsorption. This term "activated" is used to indicate that they possess a temperature coefficient, but it might also have been used to mean that the adsorbed molecules were in an active state. The latter seems to be true, for activated adsorption occurs at those temperatures for which the surface is catalytically active.⁸ In view of the fact that these processes possess a critical increment it is reasonable to refer to them as reversible activated adsorption.

The work of Ward⁵ on the adsorption of hydrogen on copper leads him to suggest that the slow reversible adsorption is due to lattice or intergranular diffusion. The heats of adsorption are so high that the adsorption process cannot be of the van der Waals' type. They are independent of the area of surface covered, which appears to conflict with the variable chemical activity of the surface atoms. Similar results have recently been obtained by Maxted.⁹ The theory that the rate of activated adsorption is actually governed by the rate of diffusion presents difficulties in that it does not explain the high temperature coefficient of the process, for diffusion processes normally increase as \sqrt{T} . If the slowness of the rate be due to diffusion, it follows that the diffusion must be of an activated type. (See later.)

Irreversible Adsorption.

The adsorption of oxygen on tungsten and of oxygen on charcoal are of this type, for on desorption, oxides of tungsten and carbon are liberated. Very few heats of adsorption have been measured in this class. For oxygen on charcoal, the heats are 70-200 cal./mol. oxygen adsorbed;⁶ and for oxygen on tungsten, 160 cal.¹⁰ These heats are much larger than those for reversible adsorption but this may be accidental, for irreversible chemical change does not necessarily take place with a very large heat of reaction. Gases adsorbed on surfaces irreversibly do not appear to be chemically reactive, in contradistinction to the reversible adsorption on metals and oxides. For example, hydrogen which is not appreciably adsorbed on carbon at room temperatures will not react with adsorbed oxygen nor is any water formed if oxygen and hydrogen are admitted simultaneously to the carbon.

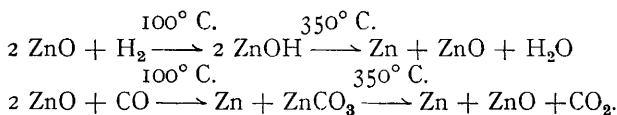
The transition from reversible to irreversible chemisorption has been observed in the case of hydrogen and carbon monoxide¹¹ on $\text{ZnO}-\text{Cr}_2\text{O}_3$ at 90° to 180° C. The heats of adsorption of these gases at room temperatures are 20-30 cal.; the values for the adsorption above the transition temperature have not yet been determined. If hydrogen or carbon monoxide is adsorbed on $\text{ZnO}-\text{Cr}_2\text{O}_3$ at room temperature at a pressure of 10^{-3} to 10^{-4} cm., and the temperature is rapidly raised to 90° to 180° C., the adsorbed hydrogen or carbon monoxide is desorbed unchanged. The pressure of the gas rises rapidly to a maximum, and then falls more slowly to zero, due to subsequent readsorption (Fig. 2) After the second adsorption, the gases can only be removed from the surface on raising the temperature to 350° C. and then the gaseous products consist of water and carbon dioxide respectively. On desorption, oxygen atoms are removed from the surface at the same time as the adsorbed gas. The latter type of adsorption is thus an example of irre-

⁸ *J.S.C.*, 3313, 1931.

¹⁰ Langmuir and Kingdon, *Physic. Rev.*, **24**, 570, 1924.

¹¹ Garner and Kingman, *Nature*, **126**, 352, 1930; *Trans. Far. Soc.*, **27**, 322, 1931.

versible chemi-sorption. The chemical change which results is very probably the combination of the gases with the oxygen on the surface to give OH and CO_3 groups. Thus,



If such be the case, then the process occurring at 20°C. cannot consist in the adsorption of hydrogen or carbon monoxide on the oxygen atoms of the catalyst. Kingman¹² has investigated the nature of the processes which occur during the adsorption of hydrogen on both the freshly-prepared and on the strongly reduced catalyst, and from the fact that the reversible type of adsorption increases in magnitude as the surface is reduced, concludes that the reversible adsorption occurs on the metal atoms. Thus, it is very probable that the "activated" reversible adsorption on metals and on oxides occurs on the same centres. There was also evidence in Kingman's work, that there are two different kinds of reduced centres on which the hydrogen is adsorbed, which in view of the complexity of the catalyst $\text{ZnO}-\text{Cr}_2\text{O}_3$ is what would be expected.

There have been distinguished at least three kinds of adsorption on oxide catalysts: (1) adsorption due to van der Waals' forces, (2) reversible chemi-sorption, and (3) irreversible chemi-sorption. It is of interest in this connection that Langmuir claims to have detected the existence of three types of adsorption of oxygen on tungsten.

The Rate of Adsorption.

The surfaces of catalytic substances resemble that of charcoal in that their main area is internal to the external surface of the grains composing the solid. A gas undergoing adsorption penetrates into the interior along passages the smallest of which may be of molecular size. Thus the rates at which a gas is adsorbed will depend partly on the rate of diffusion and partly on the true rate of adsorption, the latter being defined as the rate at which adsorption occurs on a plane surface directly accessible to the gas. Only when the rate of adsorption is much slower than the rate of diffusion will the rate of disappearance of the gas give

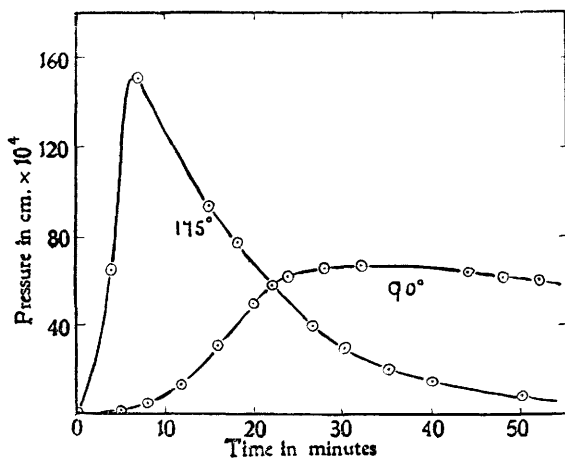


FIG. 2.—Desorption and readsorption of hydrogen on $\text{ZnO} \cdot \text{Cr}_2\text{O}_3$.

the true rate of adsorption. Under these conditions, the pressure of the gas throughout the adsorbent will be in equilibrium with that in the free space.

There is no doubt that diffusion phenomena do determine the rate if the velocity of adsorption is very rapid. For example, the adsorption of small amounts of oxygen on a clean carbon surface is complete within two or three seconds and the whole of the adsorption is found to occur entirely on the grains forming the outside of the carbon mass.¹³ The rate of reaction is here much more rapid than the rate of diffusion. When the carbon is nearly saturated with oxygen, the rate of adsorption becomes measurable and proportional to the pressure. This is, however, what would be expected at low pressures, if the rate were determined by the rate of diffusion of oxygen through capillaries to the active carbon atoms on which reaction occurred, so that it cannot be concluded that even near saturation, diffusion effects are absent. Any measurements of rates are suspect until it has been definitely shown that diffusion effects are absent.

The recent work of Benton and White and of H. S. Taylor has, however, demonstrated that at low temperatures, adsorption of oxide and metal catalysts reaches equilibrium within a few minutes. If at low temperatures, gases can diffuse into the body of the catalyst and reach equilibrium in a very short time, it is clear that the diffusion effects of the same kind must be negligible at higher temperatures. It is, however, possible that at low temperatures the adsorption is limited to the external surface and the larger capillaries, and that at high temperatures, on account of increased molecular mobility on the surface, diffusion occurs into the intergranular spaces.

At very low temperatures, Benton and White find that adsorption is not instantaneous, although at higher temperatures it is so. Bawn, working in this laboratory, finds that although carbon monoxide at -78° reaches its equilibrium value on mica almost instantaneously, this is not the case at liquid air temperatures. At the latter, adsorption is not complete until after forty-five minutes. Since the heat of adsorption was quite small, the process which occurs is no doubt of the ordinary van der Waals' type, so that there is no question here of a critical increment for the process. The explanation of the result presents difficulties on the usual conception of the mode of action of the van der Waals' forces.

At moderate and high temperatures, the rates of adsorption usually observed often obey a very complex law. This is true for some of the oxide catalysts for which the rates of diffusion as measured at low temperatures are very rapid. In the initial stages of the adsorption, the rate of adsorption varies as a high power of the pressure, but in the final stages it often proceeds at a rate proportional to the square of the pressure.¹² Such complexities may be ascribed to a limited extent to the variation in the activity of the surface atoms of the adsorbent, but not entirely, for the first quantities of gas are often adsorbed on the outermost grains of the adsorbent.

In the case of the adsorption of hydrogen on carbon¹⁴ at $400-500^{\circ}\text{C.}$, conditions were found under which the critical increment of the process did not vary very greatly from the initial to the final stages of adsorption. These conditions were such that the amounts of gas employed were much

¹³ Bull, Hall and Garner, *J.C.S.*, 837, 1931.

¹⁴ Kingman, *This vol.*, 269.

smaller than those required for saturation. The critical increment of the process ranges from 27,500 to 31,000 calories and is practically constant after the first few minutes. Since, on desorption, hydrogen is the main product, the process belongs to the reversible class. It is thus suitable for the study of the kinetics of "activated" adsorption. It is found that the velocity of adsorption is given by

$$-\frac{dx}{dt} = ke^{-E/RT} \cdot p \cdot (N - N'),$$

where N is the number of carbon atoms which are available for the adsorption and N' is the number saturated with hydrogen at any time. N is not, however, constant, but practically doubles between 400-500° C. The critical increment of the increase in N is, however, very small compared with E , so that its neglect in the calculation of E by the method of Taylor and Williamson does not lead to appreciable error.

The above equation was derived on the assumption that diffusion effects do not enter into the rate of adsorption, and this is supported by the fact that it is possible to account for the changes in the rates of adsorption at constant temperature by an equation of the above type, in which the rate is given as proportional to the uncovered area of the carbon. On further consideration, however, the accuracy with which this equation fits the experimental results cannot be adduced, as was first thought, in proof of the absence of diffusion effects.

Activated Diffusion.

If activated adsorption occur on *activated* atoms which possess a life of the order of 10^{-13} second, so that the atom holding the adsorbed molecule is rapidly activated and deactivated, then it is possible to account for the independence of the heat of adsorption with the surface covered. If the rate of activation and deactivation of the surface atoms be independent of their chemical activity, then there will be no preponderance of adsorption on a few surface atoms of a special kind. The adsorption will be distributed equally over the whole surface.

Ward⁵ has shown that the rate of diffusion at constant temperature is proportional to the amount adsorbed on the readily accessible areas, not proportional to p , the pressure of the gas. The diffusion into the interior of the solid must therefore occur via the adsorption space, that is, within the sphere of action of the surface forces. This is what would be expected if the capillaries were of molecular size. Knudsen¹⁵ has shown that the rates of diffusion in capillaries of diameters less than the mean free path of the gas molecules obey another law than that obeyed at higher pressures, and he postulated surface flow in explanation of this fact.

The problem of activated diffusion thus resolves itself into a study of mechanism of surface flow. The concentration in the adsorption space at the outermost end of the capillary is proportional to the fraction of activated atoms, $e^{-E/RT}$, and to $p \cdot e^{Q/RT}$, where Q is the heat of adsorption. Thus, the surface concentration $= k \cdot p \cdot e^{(Q-E)/RT}$. The rate of flow along the capillary will be inversely proportional to the duration of time the molecules remain adsorbed at one spot, that is, to $e^{-D/RT}$. D and Q will normally cancel, so that the rate of diffusion will be proportional

¹⁵ *Ann. Physik*, **28**, 75, 1908.

to $e^{-E/RT}$, and the activation energy of diffusion becomes the energy of activation of the surface atoms.

The rate of diffusion will also be some function of $N - N'$ (see above), hence the results obtained for the activated adsorption of hydrogen on carbon cannot be taken to mean that diffusion effects are absent.

A summary of the data at present available on the heat of activated adsorption and the activation energy is given in the table. It will be

Gas.	Surface.	Heat of Adsorption. (<i>Q</i> , Cal.).	Heat of Activation. (<i>E</i> Cal.).
H ₂	Carbon	—	30
H ₂	Al ₂ O ₃	—	27.5
H ₂	Cu	33	14.1
H ₂	MnO	—	12–20
H ₂	MnO . Cr ₂ O ₃	20	6–10
CO	Pd	15	9

seen that E is less than Q in all cases for which data have been obtained. Since the activation energies vary with the surface, they cannot therefore consist in an electronic activation of the adsorbed molecule. There appear to be two possibilities, (1) that a hydrogen molecule becomes adsorbed on the surface when it collides with the surface atoms with kinetic energies equal to the above values; the additional energy required for activation is supplied by the surface atoms, or (2) it is the surface atoms which are activated. From the argument developed on p. 264, it will be seen that the latter is considered to be the more likely.

The Transition between the Various Types of Adsorption.

The isobars for hydrogen on nickel, on manganous oxide-chromic oxide, and on carbon, and of hydrogen and carbon oxide on zinc oxide-chromium oxide show a minimum at a temperature which varies with the chemical nature of the system investigated. There is thus a region of temperature over which adsorption increases with rise in temperature. In the case of reversible adsorption, the values for the adsorption in this region are reproducible as long as the temperature is not radically changed.² Taylor refers to the equilibria which are attained in the transitional regions as pseudo-equilibria. It is not clear what is meant by this term, for in no case is thermodynamic equilibrium ever attained.

The positive temperature coefficient in the transitional regions can be accounted for as follows. If E is the activation energy of the surface atoms and Q is the heat of adsorption, then the number of surface atoms N' which are activated = $N \cdot e^{-E/RT}$, where N is the total number of surface atoms, and the number of activated atoms which are covered with molecules of adsorbed gas will be $N'' = N \cdot e^{(Q-E)/RT} \cdot k \cdot p$. Over the transitional regions, $Q - E$ must first possess a negative value, which as the temperature increases becomes zero and then positive. The activation energy of the surface atoms is likely to increase with temperature, therefore Q must also increase. There are few data bearing on the change in Q with temperature, for the heats of adsorption are usually measured in a Bunsen ice calorimeter or else with a thermocouple calorimeter at room temperatures. In the case of the adsorption of oxygen on carbon, measurements are available above room temperatures.

The values increase from 70 to 110 cal. between 20° and 100° C., and then become practically constant for another 100° C. This is what would be expected of the heat of adsorption in the transitional regions.

The causes underlying increases of this type would possibly be different for the two types of transition, and there is perhaps little justification for speculation until the physical basis of reversible activated adsorption is better understood. It may, however, be mentioned that the number of times the surface atoms will be activated in unit time will increase with increase in temperature. Thus, the heat liberated on adsorption would be expected to be greater at higher temperatures.

I am glad to acknowledge many helpful discussions with Professor Lennard-Jones on problems of adsorption from which many of the above ideas have emerged.

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