THE ADSORPTION KINETICS FOR MOLECULES ATTACHED AT MORE THAN ONE POINT

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The extremely short range of atomic forces limits the effectiveness of adsorptive forces to a region within an atomic diameter of the surface. Furthermore, the portions of this force region directly overlying the surface atoms would be the seat of forces enormously more intense than the regions in between these atoms. Such a structure of the adsorptive forces leads to the conception that the separate atoms of the adsorbed molecule are attached to the separate atoms of the surface. Insofar as the geometric arrangement of the relevant atoms does not permit this, the adsorbed molecule will be stretched, an action which must play a part in catalysis.

Recent experiments of Beebe, Taylor and others on "differential" heats of adsorption show that when some gases are adsorbed on certain surfaces, less heat is evolved for the first portions of gas adsorbed than for later portions, indicating that the heat of adsorption is not the only factor determining the life of an adsorbed molecule on the surface. In other of the experiments, the molecules first adsorbed did evolve more heat than the later ones.

From the above remarks, where it was concluded that the atoms of an adsorbed molecule should be considered to be separately attached to individual atoms of the surface, a certain kinetic complexity arises in the process of desorption which offers a possible explanation of these interesting results on "differential" heats of adsorption in the case of molecules with more than one atom.

Consider a molecule, $A-B$, adsorbed on a surface, the atoms of which are represented by $S$ in the figure 1a. If, in desorption, the bonds are broken by separate elementary acts, the possibility is that unless both the $A-S$ and the $B-S$ bonds are broken within a very short time, the atom first knocked loose will have an opportunity of becoming attached again, so that if this time interval is short enough, molecules of this type could leave the surface less often than those attached by a single bond involving...
an amount of energy greater than the sum of the heats of linkage for both the A—S and B—S bonds.

Let us represent a second of time by the straight line $S_0S_1$ (Fig. 1b). When A is knocked loose, let the average time it is loose before returning to the surface be $\alpha$, the corresponding time for B being $\beta$. Let the number of vibrations of the underlying surface atoms (all alike) per second be $M$. If the distribution of energy among these vibrations be Maxwellian, $e^{-E_A/RT}$ would be the probability of a given vibration breaking the A—S bond and $Me^{-E_A/RT}$ would be the approximate number of times per second each surface atom would vibrate with sufficient energy to break the A—S bond, $E_A$ being the energy necessary to break the bond. The corresponding number for the B atom would be $Me^{-E_B/RT}$.

Now let us lay off upon the line representing a second $Me^{-E_B/RT}$ segments each of length $\beta$. Then if we lay off, arbitrarily, a segment $\alpha$ in length, the chance that it has a point in common with a $\beta$ segment (the condition assumed to be necessary for desorption) would be the same as the chance of a point falling within one of the latter segments if each end of each of these were enlarged by $\frac{\alpha}{2}$. This probability would be the ratio of the sum of the enlarged segments to the length representing a second, or $Me^{-E_B/RT}(\alpha + \beta)$.

If, when the A—B-molecule leaves the surface, it is instantly replaced, one would then expect $Me^{-E_A+E_B/RT}(\alpha + \beta)$ molecules to leave the pair of surface atoms per second, this being the number of $\alpha$ segments having a point in common with a $\beta$ segment. If there are a great many $(P)$ molecules attached to the surface in this way, the rate at which they would be desorbed per second would then be $PM^2e^{-E_A+E_B/RT}(\alpha + \beta)$.

If the molecules were attached by a single point, and this bond involved energy $(E_A + E_B) = E_T$, the rate at which they would come off would be $2PMe^{-E_A/RT}$. In deriving the last expression, as before, the probability of a given vibration breaking a given bond would be $e^{-E_A/RT}$, and the number of times a given molecule would be desorbed each second (if the molecules are instantly replaced each time) would be $Me^{-E_A/RT}$. Since the surface could now accommodate $2P$ molecules, the rate of desorption would be $2PMe^{-E_A/RT}$.

The singly and doubly attached molecules would thus come off at equal rates if $M(\alpha + \beta) = 2$, otherwise not. If the doubly attached molecules were desorbed by a single extremely violent vibration at one of the atoms, the necessary energy of the act must exceed $E_A + E_B$ because some energy would be used up in stretching the A—B bond.

Such a kinetic complexity may also have something to do with the alleged rough proportionality between the association of substances and their boiling points.
CHARACTERISTICS OF HOMOGENEOUS, EXOTHERMIC GAS REACTIONS

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Previous investigations have shown that such gases as methane and hydrogen react slowly with oxygen in vessels of glass, silica or porcelain at temperatures in the neighborhood of 500°C. These reactions, if purely homogeneous, would be of considerable interest in their relation to gaseous combustion processes in general. However, the difficulty of obtaining reproducible measurements of reaction rate indicates that catalytic action by the walls of the reaction vessel is to be taken into consideration. Indeed, it has been questioned whether any homogeneous reaction whatever occurs under these conditions. In order to obtain evidence on this point, and if possible to isolate the homogeneous reaction, we have recently carried out experiments in which the suppression of the wall reaction was attempted. Our results indicate some success in this regard. Considerable decreases in reaction rate have been effected. In addition we have obtained results which seem to necessitate the predominance of a homogeneous gas reaction under certain circumstances, and which reveal something of its nature. We find that the rates of these oxidation reactions may be greater in an empty reaction tube of Pyrex glass than in a tube filled with broken Pyrex, although the latter should favor the surface reaction. Further, this result is the more pronounced after poisoning. We desire to cite some of the evidence which leads to these conclusions, and to discuss briefly its implications.

The activity of a contact catalyst can usually be diminished by exposure to a substance which adheres to its surface, and which is itself inert. For the present purpose we chose to try potassium chloride. The first experiments were made on 50 per cent methane-oxygen mixtures by the flow method. A reaction tube of Pyrex was made up, washed out with nitric acid and water, and tested. The tube was then rinsed out first with a