The Dynamics of Adsorption

In typical environments where gas molecules and solid surfaces coexist, a vast number of collisions between the two occur each second. However, the interaction between a molecule and a solid surface at the point of collision may not be exactly what you imagine.

When a molecule approaches a surface from an arbitrary direction and strikes the surface, one of two things happens. Either the molecule rebounds like a billiard ball striking the cushion of a billiard table or the molecule sticks to the surface. Those that stick remain for a short time, then fly off at an angle unrelated to the angle at which they arrived. The latter phenomenon is the more normal one.

As molecules strike repeatedly upon the solid surface and linger for a time, there develops a higher concentration of gas molecules at this surface than in the bulk of the gas. This is somewhat analogous to the fact that you will find a higher concentration of automobiles at an intersection with a stop sign compared to the concentration of autos along comparable section of street leading to the intersection. In the case of gas molecules, the phenomenon is called adsorption. You may expect to find adsorption of molecules in every case where a surface is exposed to a gas.

Closely examining the surface upon which the molecules are adsorbing reveals that both the molecules composing the solid material and the adsorbed molecules are vibrating. These vibrations are expected since we know that the average kinetic energy (motion) of molecules is zero only at the temperature of absolute zero. The absorbed gas molecule attaches to an adsorption site and rides the "bucking" surface until thrown off to rejoin the chaos in the gas phase. It may happen that before being ejected free of the surface, the adsorbed molecule will be bumped around to many other adsorption sites. The intensity and frequency of the surface motion are directly related to the temperature of the solid surface and the kinetic energy of the molecules.

How does a gas molecule riding the vibrating surface of a solid differ from one bouncing around in the bulk of the gas? Energy. The adsorbed molecule has traded a higher energy state (that of a gas molecule) for a lower energy state (that of an adsorbed molecule). The difference in the two energy states is called the heat of adsorption (Q) and this is the quantity of energy liberated when the molecule is adsorbed. Likewise, it is the minimum quantity of energy regained by the molecule in order to break away from the surface (desorb) and rejoin the gaseous state. The energy for revaporization is derived either from a firm jolt from a surface molecule or from a collision by one of the gas molecules that continually collide with the surface and the adsorbed molecules.

The number of molecules (a) that concentrates at the surface is dependent on the number (n) that strikes the surface and upon the time (t) that they remain on the surface. The number of molecules striking a unit area of surface per unit time, n, for a gas system is expressed by

$n = 1/4 \ N \ v$

where n is the number of molecules striking a unit area of surface per second, N the number of molecules in 1 cm3 of gas, and v the average velocity of the gas molecules.

This is an important formula in the theory of surface reactions. It also applies directly to the problem of gaseous effusion, because if an area of the solid surface is open to form a pore (d >> mean free path), the rate of effusion into the pore opening is exactly equal to the rate at which molecules would strike that area.

In regard to adsorption, the number of molecules adsorbed on to a unit surface is expressed by the formula,

$$a = nt$$

where n is the number of molecules striking a unit area of surface per second, and t the time the molecules remains on the surface.

When a surface is initially exposed to a gas, the surface, if properly degassed beforehand, will have no gas molecules upon it. As gas molecules strike it and remain for a time, the average number of molecules on the surface increases with each additional time interval. After a number of intervals, the rate at which molecules are leaving the surface (desorbed) will equal the rate at which molecules are being adsorbed and the average number of molecules per unit area of surface per interval of time will become constant. This condition is called dynamic equilibrium.

Since the vibration of the surface molecules is a function of temperature, it might be expected that the time (t) which an adsorbed molecule remains on the surface is greatly dependent of temperature. Although the relationship exists, the heat of adsorption (Q) is mainly responsible for the length of time during which the adsorbed molecules stay at the surface before re evaporating. The heat of adsorption is a characteristic of the gas-surface interaction. How the time of adsorption (t) is related to both the absolute temperature (T) and the heat of adsorption (Q) is expressed in the formula

$$t = t_o e^{Q/RT},$$

where R is the molar gas constant and to the period of vibration of the surface at the adsorption site.

Physical adsorption is characterized by relatively small heats of adsorption-- about 5 kcal per mole, or less. All gases exhibit physical adsorption, but in some cases a second type of adsorption, chemisorption, may ensue. This type adsorption involves forces and energies similar to those concerned in chemical combination-- about 10 to 100 kcal per mole. Although physical adsorption occurs in all cases, chemisorption is observed only when some kind of chemical interaction is possible.

Using de Boer's value of $t_o = 10^{-13}$ sec for room temperature, the following table is generated represents only approximations. At lower temperatures the value of t is greater leading to stronger adsorption. As a reference, values of 3.5 to 4 kcal per mole for Q are typical for gases like argon, oxygen, nitrogen and carbon monoxide at various surfaces.

Table of Energies of Adsorption and Times of Adsorption

Representative Molecules for Q value	Q	T
(H2)	1.5 kcal/mole	1.2×10^{-13} sec
(Ar, O2)	3.5 kcal/mole	4.0×10^{-11} sec
(N2, CO2)	4.0 kcal/mole	1.0×10^{-10} sec
(many organic molecules)	10 kcal/mole	3.2×10^{-6} sec
	15 kcal/mole	1.8×10^{-2} sec
	20 kcal/mole	1.0×10^{-2} sec
	25 kcal/mole	About 1 week
	30 kcal/mole	More than 100 years
	40 kcal/mole	More than 10-9 years (approx. age or the earth)

* Most of the information on gas adsorption presented here was taken from J.H. de Boer's book, The Dynamical Character of Adsorption, Oxford Press, 1953.