Physical Adsorption

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1. General Introduction

Since the coordination sphere of the atoms at the surface is not saturated, they exert residual forces, which can be utilized for bonding with incoming gas molecules. When a surface is in equilibrium with a gas, one finds an increased concentration of gas molecules in the intermediate vicinity of the surfacethan in the bulk gas phase. This preferential accumulation of gas molecues at the surfce is called adsorption. This type of accumulation takes place normally regardless of the nature of the gas or the surface, though the extent of adsorption and the degree of interaction and so activation may vary widely from system to system. In a heterogeneous reactions catalyzed by solids, at least one of the reactants must be attached in some way for a significant period of time to the surface of the solid catalyst. This can be achieved through the phenomenon of adsorption.

Since the phenomenon of adsorption is thermodynamically a spontaneous process, it should be accompanied by a decrease in the free energy the system. When the gas molecules is adsorbed from the gas phase, it loses certain degree of freedom (one or more degree of translational and rotational motion) and hence, the process is attended with a decrease in entropy, or ΔS is negative. It is therefore, clear from the thermodynamic relation, $\Delta G=\Delta H-T\Delta S$

that the adsorption is exothermic.

1.2 Physical adsorption and chemisorption:

All known adsorption processes can broadly be divided into two types, physical adsorption and chemisorption according to the forces involved in the binding at the surface. Physical adsorption results from intermolecular forces, which normally arise from the interaction of permanent dipoles, induced dipoles and quadruples and hence are akin to the condensation of vapor to form a liquid. For this reason physical adsorption is also known as van der Walls adsorption. On the other hand, chemisorption involved rearrangement of the electrons of the interacting gas (adsorbate) and the solid (adsorbent) resulting in the formation of chemical bonds. Since chemisorption can, for all practical purposes, be regarded as a chemical reaction, it is essentially restricted to the surface of adsorbent and so results in only a layer of molecule thick on the surface. Our concept of chemisorption is closely linked to our ideas of what constitutes a chemical bond.

Usually the distinction between chemisorption and physisorption is not clear-cut. Empirically it is often possible to distinguish between the two types, but as is two of most classification there are cases where the distinction is so ill defined that one has to use several criteria to decide the group to which the adsorption belongs. These criteria are listed below.

Criterion 1a: Magnitude of heat of adsorption

The heat of adsorption is of the same order of magnitude as the heat of liquefaction of the adsrobate and is rarely more than twice or thrice as large. In physical adsorption normally the heat liberated per mole of gas adsorbed is of the order of 8-25 kJ/mol though occasionally values as large as 85 kJ/mol have been reported. During chemisorption much larger values of heat of adsorption are encountered and they are of the same order of magnitude as the heat liberated in the corresponding bulk chemical reaction. For example, the heat of chemisorption of oxygen on metals are of the order of 400kJ/mol. Generally the heat of chemisorption is rarely less than 85 kJ/mol , but values as low as that associated with physical and adsorption are also known for some chemisorption processes.

Criterion 1b: Variation of heat of adsorption with coverage

The heat of adsorption can vary with surface coverage mainly due to the inherent heterogeneity of the surface as well as due to lateral interaction effect. All the atoms on the surface are not in identical environment and so the surface is heterogeneous. These effect are particularly marked for chemisorption process .The lateral interaction forces being invariably repulsive, can cumulatively contribute to a decrease in the heat of adsorption with coverage just as inherent heterogeneity of the surface does.

Criterion 2: Specificity:

Since physical adsorption is akin to condensation, it will occur with any system of gas and solid provided that the conditions of temperature and pressure are suitable. ON the other hand, chemisorption is highly specific, and will take place only when the gas is capable of forming a chemical bond with the surface atoms.

Criterion 3: Reversibility:

Physically adsorbed gas can be removed at the same temperature at which adsorption takes place by decrease of pressure, though the process may be slow. The slowness would be due to diffusion effect. The removal of a chemisorbed layer, however, required much more severe conditions like high temperatures or use of particle beams to displace the species from the surface.

Criterion 4: Extent of adsorption:

Under Under appropriate conditions of temperature and pressure, physical adsorption can proceed to multi-molecular layers while in contrast, chemisorption ceases once a mono-molecular layer is formed. It must be noted however, that subsequent physical adsorption on chemisorbed layer is possible.

Criterion 5: Pressure dependence:

Since physical adsorption is akin to the condensation process, it takes place to an appreciable extent only at pressures and temperatures close to those required for liquefaction. If p is the equilibrium pressure of the adsorbed film and p_0 is the vapor pressure the bulk liquid at the temperature of adsorption, then it is generally observed that adsorption is not significant at values of p/p_0 of the order of 0.01. This criterion may not be strictly applicable for adsorbents with very fine pores. Chemisorption process, on the other hand, proceeds at much lower pressure and at much higher temperatures.

Criterion 6: Rate of adsorption:

Physical adsorption simulating liquefaction requires no activation and can occur very rapidly. On the other hand, chemisorption like most chemical processes required activation and hence, takes place rather slowly. The application of this criterion is subject to many complications.

a) With highly porous or finely powdered adsorbents the passage of gas into adsorbent mass is often slow particularly at low pressures.

b) Precise measurements of rate of adsorption may be hampered by the establishment of pseudo-equilibrium, that is the outer sides of the adsorbent are covered thickly with the adsorbate and the subsequent re-adsorption of the adsorbed film to gibe rise to a uniform coverage may be a slow process. Thus physical absorption can also appear to be a slow process.

Criterion 7: Rate of desorption:

The activation energy for desorption from physically adsorbed layer is rarely greater than a few kJ/mole, whereas the activation energy for desorption from chemisorbed layers is generally greater than 85 kJ/mol, the value being almost invariably greater than or equal to the heat of chemisorption.

2..SOME QUANTITATIVE ASPECTS OF ADSORPTION

When a molecule with a certain kinetic energy strike a surface then its fate can be one of the following: (a) it can be reflected back without any energy changes; (b) it can penetrate into the solid and result in absorption, which is usually an endothermic process; (c) it can hinge on the surface for a period of time τ , the mean residence time of molecules on the surface. In the last case the gas molecule exchanges some energy with the solid and the process as we have already seen, is usually exothermic (the concept of endothermic chemisorption as proposed by deBoer will involve prior dissociation of the adsorbed molecules).

The validity of the statement that the gas molecule striking the surface exchanges energy with the solid surface can be easily demonstrated with molecular beam experiments, (Refer to Fig.1). The energy analysis of gas molecules in the secular as well as of non-secular directions will give information on the extent of energy exchange at the surface. Under these circumstances, the number of molecules which will be concentrated or adsorbed on the surface will depend on the number of molecules which strike the surface and on the duration of their stay. If ‘n’ molecules strike unit area (1 cm^2) of a surface per unit time (1 second) and remain there for an average time τ seconds, then the number of molecules which one will find at any instant on 1 cm^2 of the surface, i.e. the number of molecules adsorbed per cm^2 of the surface is given by

$$\sigma = \eta\tau \text{ molecules per unit area} \qquad (1)$$

Both the parameters η and τ are of great importance for the phenomenon of adsorption and hence requires consideration.

The number of collisions, n is the number of molecules striking each cm^2 of the surface per unit time (sec^{-1}) and can be derived from the kinetic theory of gases as

$$n = \frac{N_p}{(2\pi MRT)^{1/2}} \qquad (2)$$

Where p is the pressure in dynes cm^{-2}

R= the gas constant= $8.31 X 10^7$ erg. K^{-1} $mole^{-1}$

M= Molecular weight of the adsorbate

N= Avogadro number = $6.023X10^{23}$ molecule g^{-1} $mole^{-1}$

T= Temperature (K)

Table.1. Some gas parameters as a function of pressure:

	Pressure of gas		
	1atm	1μ	10^{-5}μ
Mean Free Path,L	10^{-5} cm	7cm	7km
Average number of collision per molecules(Sec^{-1})	$5x10^{9}$	$6.5x10^{3}$	$6.7x10^{-2}$ (0ne per fifteen sec)
Number of molecules per cm^3	25×10^{18}	33×10^{12}	33×10^{7}
Number of molecules striking a cm^{2}of a surface per second(n)	$\sim3\times10^{23}$	$\sim3.5\times10^{17}$	$\sim3.5\times10^{12}$
Time to cover(seconds)1 cm^3(10A°^{2}/molecules)	3×10^{9}	3×10^{-3}	3×10^{2}

substituting the constants in Equation 2, one obtains

$$n = 2.62X\ 10^{19} \frac{p}{(MT)^{1/2}} \qquad (3)$$

if one has to express p in terms of mmHg , the expression for n becomes

$$n = 3.52X\ 10^{22} \frac{p}{(MT)^{1/2}} \qquad (4)$$

Typical values for three common gases H_2, N_2 and O_2 at room temperature and 760 mm Hg are $11.0\ X\ 10^{23}$, $2.94\ X\ 10^{23}$ and $2.75\ X\ 10^{23}$ molecules cm^2 sec^{-1} respectively.

One notices that nearly 2 moles of hydrogen gas collide with each cm^2 of the surface every second at atmospheric pressure. To provide an idea of the value of n in Equation 1 in molecular terms, some gas parameters as a function of pressure are assembled in Table. 1. In this table the value of the mean free path L is roughly given by the relation,

$$L = 10^{-5} \times \frac{T}{273} \times \frac{760}{p} \quad \text{or} \quad L = 2.784 \times 10^{-5}\, T/p \qquad (5)$$

Where T is the temperature in Kelvin and p the pressure in mmHg.

The time τ:

As stated earlier there are two possible things that can happen to a molecule striking a surface, it can either be influenced by the forces at the surface or it can rebound and return immediately to the gas phase. If it comes under the influence of the surface forces it may either remain on the surface for a short time and then return to the gas phase, or may stay there more or less permanently.

When the case of a molecule striking the surface and rebounding instantaneously to the gas phase is compared with that of a molecule returning after a brief period of stay on the surface one notices very important differences concerning the direction in which the molecules leave the surface. In the case of the rebounding molecule which returns to the gas phase instantaneously, the direction in which it is reflected from the surface is related to the direction of incidence as in the reflection of light. If, however, the molecule remains on the surface for a short time before returning to the gas phase, there is no such relation and hence, no preferred orientation in any particular direction. The molecules in this case are scattered in all directions from the surface. This is one way to determine whether or not a molecule remains on the surface for a finite time. Experimentally, however, a difficulty may arise on account of the unevenness of the surface. If the surface is rough, even elastically reflected molecules will be scattered in all directions. Therefore, in order to find out experimentally whether it is genuine case of adsorption, scattering surface should be perfectly smooth or even.

In the case of the reflection of light, it is known that to avoid scattering, the unevenness of the surface must be such that the projection of the average height of the incident beam must be less than the wavelength of the light used. If h is the average height of the roughness on the surface and θ the angle of incidence of he light of wavelength, λ, then the condition for reflection is $h \cos \theta < \lambda$.

Extending the same condition for reflection of molecules striking a surface, let us consider λ as the wavelength of the material wave corresponding to the molecules. This is given by the relation $\lambda = h/m\mu$, where, h is the Planck's constant, m is mass of the gas molecules and μ is the average velocity of the molecules, ($\lambda \approx 10^{-8}$ cm for beams of light molecules, the wavelength of red light $\approx 7\text{x}\ 10^{-5}$ cm) one can see that the condition of evenness required for reflection of molecular beams is about 100 times more exacting than that for reflection of light.

On such ideal smooth surface, it was found that with beams of light molecules such as hydrogen and helium the predominant phenomenon was reflection. With beams of heavier molecules like neon, argon and oxygen, there was very little or no reflection. For a beam of oxygen molecules ($\lambda \approx 0.28 \text{ x } 10^{-8}$ cm) no reflection was found in the secular direction. It is therefore deduced that all the molecules hindered for some time on the surface before leaving the surface.

Experiments of the exchange of thermal energy between the impinging molecules and the surface also provide additional evidence for a time lag between impact of a molecule on the surface and its leaving the surface. These experiments also provide a measure of the extent of adsorption. When the molecules of a gas at a temperature T_2 here will be an exchange of heat if the time of secular contact is long enough. In the case of secular reflection, there will be hardly any exchange of energy. Complete exchange of heat will be found only when the impinging molecules stay on the surface for length of time which is large (say 100 times) compared with the period of vibration of surface atoms $\sim 10^{-13}$ sec). For a smaller time of contact, there will be only a partial exchange of heat and the molecules returning from the surface will have a temperature T_2', intermediate between T_1 and T_2. To express the extent to which the impinging gas molecules "accommodated" their temperature to that of the surface, Knudsen defined and accommodation coefficient α given by the relation.

$$\alpha = \frac{T_2' - T_1}{T_2 - T_1} \qquad (6)$$

The solid surface is assumed to undergo no change in temperature of its functions like a thermostat. The two extreme cases of no energy interchange $T_2' = T_1$ and complete equilibration $T_2' = T_2$ correspond to $\alpha = 0$ and $\alpha = 1$. When the molecules fail to reach thermal equilibrium with the surface before leaving it $T_2 > T_2' > T_1$), α will be less than unity. The experimental method employed by Roberts for determining the accommodation coefficient is described below:

A fine metal filament of diameter about 0.07 mm and length about 18 cm is stitched in a cylindrical glass vessel, which is kept in a thermostat oil bath at the temperature T1. The wire is maintained at a temperature, T_2 , about 20° above T_1 by passing a suitable electric current through it. A slow stream of purified (free of oxygen and other impurities) neon gas (which is practically non-absorbable) is passed through the vessel at a low pressure (0.1mm Hg) such that the mean free path of the gas molecules is large compared with the diameter of the wire. Under these circumstances, the number of gas molecules 'n' striking a square cm of the surface of the wire per second is given according to kinetic theory:

$$n = \frac{p}{(2\pi mkT_1)^{1/2}} \tag{7}$$

Where p is the pressure of the gas in dynes cm^{-2}, k, the Boltzmann constant and T_1 the temperature of the gas molecules striking the surface of the wire. This temperature is taken as equal to that of oil bath T_1. The energy brought up thereby to unit area of the wire per second is

$$n \times 2kT_1 = \frac{p}{(2\pi mT_1)^{1/2}} \times 2kT'_2 \tag{8}$$

Since $2kT_1$ is the average energy per molecule of the gas at tmperature T_1.

Under steady state, the number of molecules leaving unit area per second must be equal to the number striking it, but these molecules are supposed to be at the temperature T_2'(> T_1). And the energy carried away by these molecules is given by

$$n \times 2kT'_2 = \frac{p}{(2\pi mT_1)^{1/2}} \times 2kT'_2 \tag{9}$$

The net energy loss by conduction from the wire in ergs cm^{-2} sec^{-1} is given by

$$q_c = \frac{p}{(2\pi mkT_1)^{1/2}} \times 2k(T'_2 - T_1) \tag{10}$$

Where k is in ergs K^{-1}

Equation (10) can be rewritten using the Knudsen relation as

$$(T_2' - T_1) = \alpha\,(T_2 - T_1) \qquad (11)$$

$$q_c = \frac{p}{(2\pi mkT)^{1/2}} \times 2k\alpha\,(T_2\text{-}T_1) \qquad (12)$$

Substituting for m = M/N and k as i$1.38\mathrm{x}10^{-16}$ergs K^{-1} q_c is given by

$$qc = 7.3\mathrm{x}10^{3}\ \frac{\rho}{(MT_1)^{1/2}} \times \rho\alpha\,(T_2\text{-}T_1)\ \mathrm{ergscm^{-2}\ sec^{-1}} \qquad (13)$$

Neglecting heat losses due to radiation and conduction through the ends, which are usually small, qc may be equated to the energy supplied to the wire to maintain it at the temperature T_2 . Since all quantities other than α is known in Equation (13), α can be calculated. Roberts obtained α value close to zero for pure neon gas withT_2 values of 79 and 295 K. When a minute trace of hydrogen is admitted with neon, the accommodation coefficient rose immediately to about 0.18 at 295 K and to 0.28 at 79 K . Roberts also found that if the tungsten surface was previously covered with chemisorbed oxygen atoms, even inert gases like helium and neon (which gave $\alpha \approx 0$ on the clean surface) gave appreciable α values ($\approx$ 0.3 at 295 K). the values increased significantly as the temperature of the wire was lowered.

The results of determination of accomodation coefficient show that while in certain cases (e.g. neon on clean tungsten) α =0 there are many cases where α has higher values, sometimes approaching 1 (e.g. neon on oxygen covered tungsten surface; hydrogen on clean tungsten). In the later case, α increases with decreasing temperature. As already explained $\alpha > 0$ corresponds to situations where the impinging gas molecules stay on the surface long enough for energy transfer to occur before returning to the gas phase .The accommodation coefficient can also be considered to be a direct measure of the fraction of the surface covered.

Attempts have also been made to measure the time of residence τ in a direct way. Hoist and Clausing reported in 1962, some interesting experiments in which a narrow beam of molecules was directed against a fast rotating disc. If the molecules really stayed for some time on this place before evaporating, they will have traveled a short distance with the rotating plate before being scattered. The molecules leaving the surface will naturally go helter and shelter in all directions, thereby being no preferred direction. If the molecules leaving the surface are, however, made to condense on a stationary plate which is strongly cooled, the center of the spot of condensed molecules, will not coincide with the opening through which the original beam of molecules emerged but will be displayed by a certain distance on the direction of rotation on the rotating plate. The extent of this displacement will depend on τ as well as on the speed of the rotating plate. Since the evaporating molecules have an extra component of velocity due to the speed of the rotating disc, correction has to be applied to the measured displacement. It was ,however, realized that the direct measurement of τ by this procedure was rather difficult. All that could be established at that time was that cadmium vapor molecules impinging on glass surfaces at 200K do have a finite time of residence though the actual value can be anywhere between 10^{-6} to 10^{-12} sec. In 1930, Clausing had worked out a more reliable indirect method for determining τ. This method was based on the estimation of the velocity with which the gas molecules passed through narrow capillaries. When the pressure is sufficiently low so that mutual collisions are minimized the molecules collide only with the walls of the capillary and remain there for a time τ before leaving surface. The average time taken by a molecule in order to pass through such a capillary of length

$$\bar{t} = (l^2 / 2d\bar{u}) + (l^2 \tau / 2d^2)$$

‘l’ and diameter ‘d’ is given by equation (14)

When u is the mean velocity of the molecules. When t is measured, τ can be estimated by means of the following expression (15)

$$\tau = [2d^2 / l^2][\bar{t} - (l^2 / 2d\overline{u})] = [(2d^2 \bar{t} / l^2) - (d / \overline{u})]$$

Clausing obtained a value of 75 x 10^{-5} sec. for argon flow in glass capillaries and the value decreased with increase of temperature (3.1 x 10^{-5} sec. 90K).

τ can also be determined from the value of the temperature and heat of adsorption in accordance with the following equation due to Frenkel

$$\tau = \tau_0 e^{-Q/RT} \qquad (16)$$

Where τ_0 is a constant = h/kT ≈ 10^{-12} to 10^{-14} sec. It follows from Frenkel's Equation that the heat of adsorption, Q. is the determining factor for the magnitude of τ. Indeed it is the heat of adsorption, which measures the energy of interaction between the surface and impinging gas molecules, that is mainly responsible for the residence of molecules on the surface, which so results in the phenomenon of adsorption. It is therefore appropriate to refer τ as the measure of adsorption. In Table. 2 the typical values of τ calculated for adsorption at room temperature are given for various values of heat of adsorption.

It is seen from Table 2 that the time of residence of molecules on the surface is very small δ of the order of microseconds even for fairly strong interaction energies of the order of 45 kJ. However, even shorter duration of stay can lead to appreciable adsorption, because the number of molecules present on the surface is given by $n\tau$ of molecules reaching the surface per unit time. The later is usually very large of the order of 10^{23} Even so, one has to compare this product with the number of molecules present 1 cm^2 crosssection of the gas; to see if there is any appreciable increase in concentration. The number of molecules in 1 cm^3 of gas at NTP being about 25 x10^{18}, the number at a cross section of 1 cm^2 is equal to ~8.5 x10^{12}. Unless the concentration of molecules at an interface is significantly larger than this, this is about ten times, one cannot recognize it as adsorption. For a surface concentration of ~10^{13} per cm^2, τ should be not less than 10^{-10} sec; for which the ratio of Q/T should be about 14. In other words, there will be appreciable adsorption at room temperature only if the heat of adsorption exceeds 17.64 kJ. If the heat of adsorption is reduced to one third i.e. 5.88 kJ, the temperature should be reduced to 100K (-173°C) for measurable adsorption which for individual molecules can vary widely from10^{-13} seconds to much larger. In the same way the heat of adsorption, Q,is equal to Nq where q is the average heat of interaction of a molecule with a surface .

Table 2:Values of τ at room temperature for various assumed values of Q

($\tau_{o=10}{}^{-13}$sec)

Q kJ/mol	K cal/mole	τ seconds
0.42	0.1	$1.2\text{x}10^{-13}$
6.3	1.5	$1.3\text{x}10^{-12}$
14.7	3.5	$4\text{x}10^{-11}$
16.8	4.0	$1\text{x}10^{-10}$
42.0	10.0	$3.2\text{x}10^{-6}$
63	15.0	$1.8\text{x}10^{-2}$
84.0	20.0	100
105.0	25.0	$6.5\text{x}10^{5}$(1week)
126.0	30.0	$4\text{x}10^{9}$(1century)

3.Adsorption equilibrium

According to the concepts of molecular kinetics the phenomenon of adsorption is attributed to the time lag between the arrival and departure of molecules at the surface in the course of their collisions with the later. As in any chemical process, a condition of equilibrium will be reached, when the number of molecules striking the surface and lingering on equals the number of molecules that are evaporating. A molecule which is adsorbed on the surface will leave the surface when it picks up an amount of energy equals to or greater than the heat of adsorption. This acquisition of energy can take place through fluctuations of thermal energy of the surface and the transfer of kinetic energy of the molecules on the adsorbed layer. From statistical considerations the number of molecules, which have this, acquired and required minimum energy, Q will at any moment be proportional to $e^{-Q/RT}$. At any instant, therefore, the number of molecules leaving the surface will be proportional to the number of molecules adsorbed n_a and (ii) the Boltzmann factor $e^{-Q/RT}$ i.e.

$$n_v = k_v n_a e^{-Q/RT} \qquad (1)$$

This is reckoned for unit time (1 sec) and unit area (1 cm^2). Since n_v has the units of molecules cm^{-2} sec^{-1} and n_c has the units of molecules cm^{-2}, the proportionality constant k_v should have the dimension of sec^{-1}. In other words it has the dimensions of frequency. One can show this in another way. From the fundamental considerations described earlier,

$$n_a = n\tau = n\tau_0 e^{-Q/RT} \qquad (2)$$

$$n = n_a (1/\tau_0 e^{-Q/RT}) \qquad (3)$$

Where n is the number of molecules striking the surface per cm^2 per second. Since as a condition of equilibrium $n = n_v$, one can see by comparison,

$$n = n_v = n_a (1/\tau_0 e^{-Q/RT}) \qquad (4)$$

or $$n_v = k\, n_a e^{-Q/RT} \qquad (5)$$

Therefore one can write $k = 1/\tau_0 = v_0$

Considering that n is a function of P and T, using Equation (2) one can write the following equilibrium relations:

$$n_{a(eq)} = f(P,T)$$

Whence (i) $[n_{a(eq)}]_T = f(P)$ adsorption isotherm

(ii) $[n_{a\,(eq)}]_P = f(T)$ adsorption isobar

(iii) $[n_{a\,(eq)}]_T = f(T)$ adsorption isostere

Of the above three, the most commonly determined relation is the adsorption isotherm. Isotherms are essentially plots of free energy change as a function of amount adsorbed. They can be used for obtaining information on the adsorption process and on the fraction of the surface covered by the adsorbate. Brunauer et al have classified all the isotherms obtained at temperatures below the critical temperature of the gas into five types based on their shapes as shown in Figure 2. Isotherms of type I are associated with systems where adsorption proceeds only up to a coverage of mono molecular layer. The other four isotherms result from multi- molecular layer formation Types IV and V arise from adsorption on porous adsorbents, wherein in addition to multilayer formation, simultaneous capillary condensation can occur.

4.Unimolecular Adsorption

An adsorption isotherm is the relation between the amount of gas adsorbed on a given surface at constant temperature and the pressure of the gas in equilibrium with it. Langmuir derived a mathematical expression for the adsorption isotherm on the basis of a model he proposed. He suggested (for the purpose of argument) that the surface could be considered to be comprised of number of elementary 'sites', the number of such sites per unit area of the surface depending entirely on the structural characteristics of the solid i.e. its lattice parameters. Specifically, each atom or ion on of surface of a solid was considered to constitute a potential site for adsorption. Unlike the atoms or ions in the interior of the solid which are surrounded uniformly on all sides by other atoms or ions of the solid lattice, an atom or ion in the surface layer is surrounded by less number of atoms or ions and are therefore subjected to an imbalance of valence forces leading to the surface possessing surface energy (analogous to surface tension) and the surface atoms being left free with unsaturated valences. These surface atoms tend to become saturated thereby decreasing the 'surface energy' also. These unsaturated valence forces are of extremely short rage and fall off exponentially with distance from the surface. Ordinarily they are too weak to permeate through a molecule or atom held by the surface atom. This led Langmuir to postulate as the basis for his theory of unimolecualr adsorption that each elementary site on the surface can accommodate one and only one molecule of the adsorbed species. In other words, only those molecules, which fall on sites, which are unoccupied, have any chance of being adsorbed. Molecules striking parts of the surface, which are already covered by adsorption are elastically reflected back. Therefore, the number of molecules that would be adsorbed on the surface will be related to the number of those striking the unoccupied sites and not tot he total number striking the entire surface.

Consider the adsorption on unit area ($1cm^2$) of the surface. If n_s is the number of sites per unit area and n_a is the number of sites occupied at any given time, the number of sites that are vacant and still available for adsorption at that time is (n_s-n_a) sites per cm^2. The fraction of the total surface that is vacant is equal to [(n_s- n_a)/n_s]. If the number of molecules striking one cm^2 of the entire surface (occupied and unoccupied sites) at the relevant temperature and pressure is n, the number $n*$ striking the vacant sites is given by:

$$n* = n\left[\left(n_s - n_a\right)/n_s\right]. = n\left[\left(1 - n_a\right)/n_s\right] \ cm^{-2}\ sec^{-1} \quad (1)$$

It is obvious that n_a is also the molecules adsorbed on 1 cm^2 of the surface

$$n_a = n* \tau = n* \tau_0 e^{-Q/RT} \quad (2)$$

This may be regarded as a fundamental equation for adsorption leading to monolayer formation .

Now for simple calculations by using a single value of Q over the entire course of the adsorption from sparse coverage to near saturation, Langmuir made two further assumptions,

1. All the elementary sites of a given surface are equally active for adsorption, in the sense that the heat of adsorption has the same value for every one of them.
2. There are no interactions of any kind between the adsorbed molecules that would involve energy change other than the heat of adsorption. The only interaction to be considered is that between adsorbed molecule and the adsorbing surface element.

These assumptions help to eliminate from consideration the only possible causes for the variation of heat adsorption with surface sites and interaction among the adsorbed species. The only justification for these assumptions is that they lead to a simple treatment.

Therefore assuming that the heat of adsorption and hence the time of adsorption ($\tau = \tau\ e^{-Q/RT}$) to be independent of the surface coverage, one may write for the number of molecules adsorbed per cm^2 of the surface.

$$n_a = n* \tau = n[(1 - n_a)/n_s] \quad (3)$$

Rearranging the terms

$$na = n_s n\tau/(n_s + n\tau) \quad (4)$$

The extent of adsorption may be expressed in terms of the fraction of the surface covered θ given by , n_a/n_s. Therefore, divinding the Equation (4) by n_s one gets

$$\theta = (n_a/n_s) = (n\tau)/(n_s + n\tau) = (n/n_s)\tau \,/\, 1+(n/\, n_s\,)\, \tau \qquad (5)$$

where n is the number of molecules striking 1 cm^2 surface per second which can be calculated from the kinetic theory as

$$n \;=\; (NP) / (2\pi MRT)^{1/2} \;=\; Zp \qquad (6)$$

Where Z is the collision number, $N/(\,2\pi MRT)^{/1/2}$

$$\theta \;= [Z\tau / n_s].p/ [1 + (Z\tau/n_s)].p \qquad (7)$$

With Z, τ, and n_s all constants at constant temperature, one can denote $Z\tau/n_s$ by an isothermal constant ‘b’. Therefore,

$$\theta \;= (bp) / (1+bp) \qquad (8)$$

Where

$$b \;= (Z\tau/n_s) = \;(N / \surd 2\pi MRT) \times \;\; (\tau\, e^{Q/RT}) /n_s \;\; = (N / \surd 2\pi MRT)\, (1/\, \nu_0 n_s).eQ^{/RT} \qquad (9)$$

The first term $(N/\surd 2\pi MRT)$ is the number of molecules (Z) striking each cm^2 of the surface per second at unit pressure of 1 dyne per cm^2. But it is more usual to express pressure in mmHg. Substituting R in ergs/K one gets.

$$Z = \;(3.5 \times 10^{22}) / (\surd MT)\ cm^{-2}\, sec^{-1}\ mmHg \qquad (10)$$

which for light gases at room temperature will be roughly of the order of 10^{20} cm^{-2} sec^{-1}. It should be remembered that the values of Z and b are directly related to the unit of pressure chosen . v_o has the unit of frequency and is usually if the order of 10^{12} to 10^{14} , n_s is the number of elementary sites or surface atoms per cm^2 is of the order of 10^{14} to 10^{15}. Thus $(v_0 n_s)$ will vary between 10^{26} and 10^{29} and is generally of the order of 10^{28}.

Therefore, the magnitude of b will be of the order of 10^{-8} $e^{Q/RT}$ if the unit of pressure is mmHg.

Since

$$b = \;[N / (2\pi MRT)^{1/2}]\; (\,\tau / n_s) \qquad (11)$$

Reckoing, as before, the unit of pressure as 1mm Hg and

$$n_s \cong 10^{15} \qquad (12)$$

$$b=[10^{20}/10^{15}]\ \tau \qquad (13)$$

$$\tau=10^{-5}b \qquad (14\ )$$

The values of both and b and τ depend on the ratio of Q/T which virtually controls the extent of coverage at any given pressure. Calculated values of b and τ for some typical values of Q/T are given Table.3

Table.3. Typical values of b and τ at certain values of Q/T

Q/T (J/K)	Q/T (Cals/K)	$e^{Q/RT}$	b	τ(Sec)
4.2	1	1.65	$1.65x10^{-8}$	$\sim x\ 10^{-13}$
8.4	2	2.72	$2,72x10^{-8}$	$\sim x\ 10^{-13}$
21.0	5	$1.2x10^{1}$	$1.2x10^{-7}$	$\sim x\ 10^{-12}$
42	10	$1.5x10^{2}$	$1.5x10^{-6}$	$\sim x\ 10^{-11}$
63	15	$2x10^{3}$	2.210^{-5}	$\sim x\ 10^{-10}$
84	20	$2x10^{4}$	$2x10^{-4}$	$\sim x\ 10^{-9}$
105	25	$3x10^{5}$	$3x10^{-3}$	$\sim x\ 10^{-8}$
126	30	$3x10^{6}$	$3x10^{-2}$	$\sim x\ 10^{-7}$
136.5	32.4	$1x10^{7}$	$1x10^{-1}$	$\sim x\ 10^{-6}$
168	40	$5x10^{8}$	5	$5\ x\ 10^{-5}$
210	59	$7x10^{10}$	$7x10^{2}$	$7\ x\ 10^{-3}$
252	60	$1x10^{13}$	$1x10^{5}$	1
420	100	$5x10^{21}$	$5x10^{13}$	$5\ x\ 10^{8}$

Langmuir derived the isothermal relation between the extent of adsorption and the equilibrium pressure namely $\theta = bp/(1+bp)$ using a purely kinetic approach .The fundamental assumption made by Langmuir are (i) atoms (or molecules) of the gas are adsorbed without any fragmentation on to definite points of attachment on the surface of the adsorbent, (ii) each point of attachment can accommodate one and only one adsorbed atom and (iii) the energies of the states of any adsorbed atom are independent of the presence or absence of other adsorbed atoms on neighboring points of attachment. Of all the molecules striking a surface on a bare sites, a definite fraction α will be adsorbed and held by the surface forces for a definite time. If the fraction the site already filled is θ, then the rate at which molecules will be adsorbed is $k_a(1-\theta)p$ .while the rate of desorption from the surface can be denoted as $k_d\,\theta$, where kd is the desorption constant when the surface is fully covered. At equilibrium the number of molecules in the adsorbed state is equal to the molecues desorbed or at equilibrium the number of molecues in the adsorbed state at any instant is constant and hence

Comment [KCL1]:

$$k_a p(1-\theta) = k_d\,\theta \qquad (15)$$

Denoting $b = k_a/k_d$ (16)

One obtains: $bp = \theta/(1-\theta)$ or$\theta = bp/(1+bp)$ (17)

In order not to obscure the essential thermodynamic character of the adsorption isotherm, Fowler has formulated a statistical derivation which depends only on the whole set of states, adsorbed and free accessible to the molecule. According to this derivation the constant b in the isotherm equation has been shown to be

$$Q = \frac{h^3}{(2\pi m)^{1/3}\,(k/T)^{5/2}} \quad \frac{f_a(T)}{f_g(T)}\, e^{q/kT} \qquad (18)$$

Where f_a (T) and f_g(T) are the internal partition functions for a molecule in the adsorbed and gaseous states respectively. q is the energy required it transfer a molecule from the lowest adsorbed to the lowest gaseous state. Other forms of derivation based on the theory of absolute reaction rates, Maxwell Boltzmann distribution law, law of mass action and Infinitesimal Carnot cycle have also been formulated.

The shape of the isotherm predicted by the Langmuir equation (Equation 17)

$$\theta = bp / (1+bp) \qquad (17)$$

has been found to be in qualitative agreement with experimental isotherms. Thus at low pressure $b<<1$, the equation simplifies to $\theta \cong bp$, indicating a linear increase of adsorption with pressure. At high pressure when $bp >> 1, \theta = 1$; the surface becomes saturated with a mono-molecular layer of adsorbate .At this point, increase of pressure produces no further increase in adsorption. Between these extremes, however, θ increases at a steadily declining rate with pressure.

The shape of adsorption isotherm, particularly with respect to its slope and the pressure at which it indicates saturation depends entirely on the magnitude of the constant b, which in turn, as already pointed out, depends on the values of Q/T. This is illustrated by the isotherms shown in Fig.3, where curves A,B,C and D correspond to b values 10^{-3},10^{-2}, 10^{-1} and respectively. In curve A for which the value of b is the lowest, the adsorption increases gradually with pressure throughout the pressure range, whereas in curve D with b=1 saturation is attained at a very low pressure of few millimeters.

If modification is imposed on the original assumption of Langmuir that each adsorption molecule occupies n adjacent sites, then the rate at which molecules pass into adsorbed state is given by

$$\alpha\ Zp(1-\theta)^n \qquad (19)$$

and the isotherm takes the form

$$\theta = bp^{1/n} /(1+ bp)^{1/n} \qquad (20)$$

If on adsorption, each diatomic molecule dissociates into two atoms, and each atom is accommodated on one single site, then one gets an isotherm equation

$$\theta = bp^{1/2} / (1+ bp^{1/2}) \qquad (21)$$

which is of some importance in practical chemisorption.

To test the application of Langmuir model to experimental data, the isotherm equation has to be expressed in a linear form .The three forms in which this can be done are given in Table. 4. A typical set of experimental data plotted in terms of three linear forms are shown in Fig. 4 of the three forms, the second form appears to be the most satisfactory, both the intercept and the slope have fairly large values and the points are more evenly spaced than in the other two plots. Since b and v are usually large, the values of $1/v_mb$ and $1/v_m$ (where v_m is the volume required to form a saturated monolayer on the surface) hence the intercept and the slope in the corresponding plots tend to be small, making it difficult to evaluate the parameter v_m and b. Moreover, the initial points are compressed towards the origin adding further to the inaccuracy of the plots. However,linear form most commonly used for verifying the applicability of the Langmuir isotherm is the first one.

Table.4. Linear forms of Langmuir isotherm

Form	Plot	Intercept	Slope
$(p/v) = [1/(V_mb)] + [(p/v_m)]$	(p/v) vs p	$1/v_mb$	$1/v_m$
$(v/p) = v_mb - bv$	(v/p) vs v	v_mb	-b
$(1/v) = (1/v_m) + (1/v_mb)(1/p)$	1/v vs 1/p	$1/v_m$	$1/v_mb$

From the data for equilibrium adsorption at difference temperatures (at least two) the heat of adsorption can be deduced by means of the Clausius–Clapeyron equation

$$(d\ln p/dT)_v = Q/RT^2$$

Where p is the equilibrium adsorption pressure required for fixed amount of adsorption at the temperature T, and Q is the heat of adsorption in calories per mole of the gas adsorbed. In order that the Langmuir isotherm equation be applicable to the experimental adsorption data obtained, not only should the data give a linear plot for p/v Vs .p but the assumed condition of constancy of the heat of adsorption with surface coverage must also be fulfilled because this is implicit in the derivation of the Langmuir equation.

However, usually is found that the heat of adsorption decreases monotonically with the extent of adsorption though some times complex variations have been observed.

The variation of Q with θ means that the assumption of surface homogeneity and absence of interaction between the adsorbed species - either or both of them are not realized in practice. Normally, the surface sites are heterogeneous in activity for variety of reasons namely the inevitable existence of textural irregularities such as cracks and crevices, pores and pockets, edges and corners of crystallites, polycrystallinity of the exposed surface and so on. As a result, the more active sites will be occupied first followed by sites of lesser activity giving rise to the observed decrease of Q with θ. Interactions between the adsorbed molecules or atoms may either be repulsive or attractive in character, depending on the nature of the adsorbed species and the degree of surface coverage. It is obvious that the interactions will have appreciable effect on Q only at moderate or high coverages, i.e. when the adsorbed molecules come within interaction range of one another. The sharp fall in the heat of adsorption observed at low coverages must therefore be attributed to surface heterogeneity, the effect of which persists throughout the coverage and on which the effect of surface interactions is super-imposed at higher coverages.

Whatever be the cause of variation of the heat of adsorption, it is obvious that the Langmuir isotherm assuming constancy of the heat of adsorption cannot be valid in practical situations. Langmuir himself realized that Q and consequently the constant b could vary due to surface heterogeneity and tried to provide for this variations by dividing the surface intoseveral groups of sites, each group being homogeneous with itself, but different from the rest. In such a case, the adsorption isotherm will be composite of several terms, one for each group sites. The θ_i the fraction of sites of group i that is covered at an equilibrium pressure p is given by

$$\theta_i = (b_i p) / (1+ b_i p)$$

Where bi (Qi) pertains to the group i .

If $n_1\theta_1$, $n_2\theta_2$, n_3 θ_3………………..n_i θ_i represent the fractions of the total number of sites per unit area of the entire surface which is occupied, then the total fraction covered at any given pressure is

$$\theta = \sum_{i=1}^{i=i} n_i\theta_i \qquad (24)$$

The use of summation sign implies a finite number of groups of sites and a discrete variation inactivity from group to group. If as is more likely, the gradation of activity is continuous, the summation has to be replaced by an integration, thus,

$$\theta=\delta=\int\theta_q n_q d_q \qquad (25)$$

The last mentioned integration can be carried out only if the distribution function i.e.how the number site varies with Q is known. It is possible to consider various kinds of distribution functions for this variation and accordingly one can derive the isotherm equations. Let us consider some typical cases.

Zeidowich suggested a Boltzmann distribution of sites according to activity, that is an a exponential dependence of n_q on Q by the following equation

$$n_q=n_0 e^{-Q/Q m} \qquad (26)$$

Where n_0 and Q_m are constants.

combining this relation for n_q with Langmuir equation for adsorption on sites of a particular activity (Q) that is

$$\theta = \frac{b_q p}{1+ b_q p} = \frac{b_0 e^{Q/RT} p}{1+b_0 e^{Q/RT} p} \qquad (27)$$

where b_0 is a constant for a particular adsorbate – adsorbent system, one gets

$$\theta = \int \frac{b_0 e^{Q/RT} p}{1+b_0 e^{Q/RT} p} n_0 e^{-Q/Qm} dQ \qquad (28)$$

This is a modified form of the Lamgmuir isotherm allowing for the variation of Q with θ. From this, if Q>>.RT, that is the heat of adsorption considerably exceeds the thermal energy the integration is possible and it yields.

$$\theta = (b_0p)^{RT/Q_m}.n_0.Q_m \qquad (29)$$

This is the familiar Freundlich isotherm equation which was originally proposed on empirical grounds based on data which did not obey Langmuir equation. From this the heat of adsorption is obtained by applying the Clausius – Clapeyron equation which gives

$$Q = - Q_m \text{ In}\theta + Q_m \text{ In}(n_0 Q_m) \qquad (30)$$

Now when $p = 1/b_0$, $\theta = n_0 Q_m$ at all temperature as per the isotherm equation (29). Under these circumstances, the heat of adsorption $Q = 0$ as per equation (30). At pressures greater than $(1/b_0)$, θ is greater than $n_0 Q_m$ as per the isotherm equation. However, when $\theta > n_0 Q_m$, then the value of Q is negative meaning that the adsorption process is endothermic. This is not correct on thermodynamic grounds already considered. Therefore, setting $\theta = n_0 Q_m$ is the maximum adsorption, and the scale of θ is suitably rearranged so that $\theta = n_0 Q_m$ corresponds to complete saturation, the isotherm equation becomes

$$\theta = (b_0p)^{RT/Q_m} \qquad (31)$$

and the corresponding equation for the heat of adsorption takes the form, $Q = - Q_m \ln \theta$. In this later form the isotherm equation (31) resembles the original empirical Freundlich equation, namely

$$V = cp^{1/n} \qquad (32)$$

Since b_0 and RT/Q_m are isothermally constant and Q_m is always greater than RT. Thus Halsey and Taylor using Zeldowitsch's assumption regarding surface heterogeneity provided a theoretical basis for the Freundlich isotherm. The applicability of the Halesy Tylor equation to experimental data can be tested in the same way as the Freundlich isotherm, i.e. by plotting log θ vs log p. If v_m is the volume of the gas in the saturated monolayer (i.e corresponding to θ = 1) and the v is the volume adsorbed at any pressure p ($<1/b_0$) then

Comment [KCL2]:

$$v = v_m \theta = v_m (b_0p)^{RT/Q} m \qquad (33)$$

Taking logarithms

$$\text{Log } v = \text{Log } v_m + (RT/Q_m) \text{ Log } b_0 + (RT/Q_m) \text{ Log } p \qquad (34)$$

For all temperatures, $v = v_m$ when $p = 1/b_0$, that is the value of monolayer saturation volume is independent of temperature. In other words, plots of log v vs log p for different temperatures give a family of straight lines, which meet at a common point. The point of intersection corresponds to v_m, the saturated monolayer volume of adsorption. Typical plot of log v vs log p for hydrogen adsorption on a tungsten powder is reproduced in Fig.5, which denotes that all isotherm data for a given adsorbate on given adsorbent coverage to a point . With such a derivation by Halsey and Taylor, the Freundlich isotherm can now be regarded as a modification of the langmuir isotherm for adsorption on a heterogeneous surface. The modification is based on the assumption of a Boltzmann distribution of activity among the sites. It leads to a logarithmic decrease of heat of adsorption with coverage and also indicates a unimolecular saturation value, which is independent of temperature.

Relatively a few experimental data conform to logarithmic variation of Q with θ, while much of the data follow a pattern where the heat of adsorption decreases linearly with coverage which can be, as stated earlier, due to: (i) The inherent surface heterogeneity with an equal distribution of sites of activity, which is rather improbable and (ii) repulsive interactions. This briefly is the basis of Temkin isotherm, which is derived by inserting in the Langmuir isotherm the condition that the heat of adsorption decreases linearly with θ i.e., as per the equation

$$Q = Q_0\,(1—\alpha\theta) \qquad (35)$$

Where α is the proportionality constant and Q_0 is the maximum value of the heat of adsorption obtained at he lowest coverage i.e. as $\theta \to 0$.

For a single value of Q, the Langmuir isotherm $\theta = bp/(1+bp)$ may be simply transformed into the form

$$\theta/(1-\theta) = bp = b_0pe^{Q}{}_{0}(1-\alpha\theta)/RT \qquad (36)$$

$$= (b_0e^{Q/RT})\, e^{-Q}{}_{0}{}^{\alpha\,\theta/RT}.p \qquad (37)$$

$$= B_0e^{Q}{}_{o}{}^{\alpha\,\theta/RT} \qquad (38)$$

Where $B_0 = b_0e^{Q_0 / RT}$, which is independent of θ. Taking logarithms and rearranging

$$\ln B_0p = (Q_0 \alpha\theta) /RT + \ln [\theta/(1-\theta)] \qquad (39)$$

Now, if one restricts to the middle range of coverage, where ln [θ/(1-θ)} varies very slowly with θ and if θ = 0.5, this term ≅ 0 and may therefore be neglected . Under these conditions, the above equation simplifies to

$$\ln B_0 p = (Q_0 \alpha\theta) / RT \qquad (40)$$

Where $\theta = (\mathrm{In}B_0p)\, RT/Q_0\alpha = (RT/Q_0\alpha)\, \mathrm{In}B_0 + (RT/Q_0\alpha)\, \mathrm{In}\ p$ (41)

This isotherm, characterized by logarithmic variation of p with θ is the Temkin isotherm. It should be emphasized that this equation holds only for intermediate coverage say θ = 0.3 to 0.6 and not for θ ≅ 0 or θ ≅ 1.

The three equations pertaining to the unimolecular adsorption, namely the original Langmuir equation, the Halsey equation and the Temkin equation and their characteristic features are summarized in Table 5. together with that for simple Henry equation.

To make sure that a particular set of experimental data truly obeys a particular isotherm equation one has to look for two conditions.

1) The Q-θ variation must be of the form implied by the isotherm equation.

2) The experimental data must cover the appropriate range of θ.

For example for testing the obedience to the Langmuir or to the Freundlich isotherm, the data must apply to the widest possible rage of coverage , in testing the Temkin isotherm coverage’s must be between about 30 and 60 percent.

Multimolicular Adsorption

The assumption of unimolicualrity of adsorption that there can be no more that a single layer of the adsorbed molecules or atoms on the surface 8s the important aspect of Langmuir theory. This assumption alone accounts for the characteristic curve shape of the isotherm tending asymptotically towards a saturation values at high pressures as shown in the figuere 1. However, not all isotherms obtained pertain to his shape and one finds frequently isotherms of the types II to V as shown in figure 1. The question that arises naturally is how could these observations be accounted for?

these assumption of unimolecularity means essentially the molecules that strike on those places where molecules are already adsorbed will either be elastically reflected or be held only for a short time(~10-^{13}) sec. This considerations generally satisfied when adsorption occurs as a result of short rage chemical valence forces, which do not penetrate through the primary adsorbed layer. If. However the adsorption and the temperature and pressure are favorable for such forces to become effective, it would be possible for several layers of molecules to be adsorbed on the surface, as a result of cohesive forces exerted by the molecules of he adsorbate. The theory of multimolecular adsorption was then therefore developed by Brunauer, Emmet and Teller in 1938 and the isotherm

The important assumptions of this theory are similar to that of Langmuir theory except that requiring that the adsorbed layer has to be unimolecular. The assumptions are:

1. The adsorption energy is supposed to remain constant from zero coverage to full coverage in the primary layer of the adsorbate and in the each of he layers above.

2. Molecules of any layers are not interacting with one another in any manner though they attract and retain molecules striking them form the gas phase.

The state of affairs of the surface when the equilibrium is reached at any given pressure can therefore represented formally as in Figure 5 with varying numbers of molecules being adsorbed only one side. Under equilibrium situation conduct8ve for multi molecular adsorption, it need not be assumed that the thickness of the adsorbed layers is uniform over the entire region. It is possinbelas hsown figure 5 that at one and their same item parts of the surface are bare some parts are covered with two layers, and so on. In other words, the entire surface of areas may be composed of a part s0 which is bar and s1, s2, s3, etc, which are covered with 1,2,3, etc. layers of adsorbate as shown in Figure 5 though into in orderly fashion. This situation leads to the just definition that the entire surface of area is given by:

$$s = s0 + s1 + s2 + s3 + \ldots\ldots\ldots\ldots + si = \sum_{i=0}^{i=\alpha} si\ (cm^2) \qquad (42)$$

When steady state is reached, the rate of condensation on the bare surface is balanced by the of adsorption from the second layer and so on. Thus there will be several pairs of condensations and evaporation’s between s_0, s1, s2 and s_2, s2, s3 that can be expressed by the equations

Layer 1 $k_1s_0P=k_{-1}s_1e^{-Q_1/RT.}ds_0/dt = 0$ (43)

Layer 2 $k_2s_1P=k_2s_2e^{-Q_2/RT.}ds_1/dt = 0$ (44)

Layer 3 $k_3s_2P=k_3s_3e^{-Q_3/RT.}ds_2/dt = 0$ (45)

Layer 4 $k_4s_3P=k_is_ie^{-Q_i/RT.}ds_i/dt = 0$ (46)

where $k_1,k_2,k_3\ldots$ki represent the condensation coefficients and $k_{-1},k_{-2},k_{-3},\ldots$..ki the evaporation coefficients, $Q_1,Q_2,Q_3\ldots$Qi the heats of adsorption in the layers denoted by the subscript. It is necessary to that one introduce further definitions before he produces with the

derivation of the multimolecular adsorption isotherm. It is reasonable to assume that the evaporation condensation properties of the molecules in the second and higher layers are the same as those on the surface of the liquid. One can therefore equate the heats of adsorption

Q_2,Q_3,Q_4 etc to the heats of liquefaction.

there fore $Q_{2=}\ Q_{3=}\ Q_{4=}\ Q_{5\ldots\ldots}\ Q_{I=}$ latent heat of condensation of the adsorbate.

similarly if one compares the ratio of condensation and evaporation coefficients to that applicable for a condensed liquid film then:

$$ki/k\text{-}l = kl/k\text{-}l = \ldots\ldots ki/k\text{-}I = kl/k\text{-}l = L \qquad (6)$$

The total volume of adsorbate condensed is given by

$$v = v_0 \sum_{i=0}^{\alpha} isi\ (cm^3) \qquad (7)$$

Where v0 is the volume adsorbed in one monolayer/cm^2,

Therefore $\sum is_i$

$$v/sv_0 = v/vm = \frac{\qquad}{\sum s_i} \qquad (8)$$

Where v_m is the total volume of adsorbate required to form one monolayer over the entire surface.

Now returning to the equilibrium equation….,it is clear that s_1,s_2,s_3…….is can all be expressed in terms of so as follows :

$$s_1 = (k_1/k_{-1})pe^{Q1/RT} s_0 = Ys_0 \qquad (9)$$

Where, $Y = (k_1/k_{-1})pe^{Q1/RT} s_0$

$$s_2 = (k_2/k_{-2})\, pe^{Q1/RT} s_1 = L\, pe^{Q_2/RT} xs_i = xys_0 \qquad (10)$$

$$x = (k_2/k_{-2})\, pe^{Q1/RT} \quad s = Lpe^{Q}2^{/RT}$$

(11)

$$s_3 = xs_2 = x^2 s_1 = x^2ys_0$$

$$s_i = xs_{i-1} = x^{i-1} ys_0 = x_i(y/x)s_0 = x^icts_0$$

$$\text{Where, } c = (y/x) = \frac{(k1/k\text{-}1)}{(kL/k\_l)} e^{(Q1\text{-}QL)/RT} \qquad (12)$$

Now, v the total of the gas adsorbed at any given stage of the multimolecualr adsorption equilibrium can be expressed by the sum:

$$v = s_1v_0 + 2s_2v_0 + \ldots\ldots\ldots\ldots is_iv_0 \qquad (13)$$

$i = \alpha \qquad i = \alpha$

$$= v_0 \sum is_i = v0 \sum is_I \qquad (14)$$

i =0 i = i

$$\nu \;/\; \nu m = \frac{\nu_o \sum_{i=1}^{i=\alpha} si}{\nu_o \sum_{i=0}^{i=\alpha} si} = \frac{s_o \sum_{i=1}^{i=\alpha} ix^i}{s_o + \sum_{i=1}^{i=\alpha} si}$$

Now (15)

$$\text{or} \quad \nu / \nu m = \frac{s_o \sum_{i=1}^{i=\alpha} ix^i}{s_o + c\, s_o \sum_{i=1}^{i=\alpha} xi} = \frac{c \sum^{i=\alpha} ix^i}{1 + c \sum x^i}$$

$\sum_{i=1}^{i=\alpha} x^i$ = x/1-x (sum of infinite geometric progression)

$$\sum_{i=1}^{i=\alpha} ix = x \sum_{i=1}^{i=\alpha} ix^{i-1} = x \frac{d}{dx} \sum_{i=1}^{i=\alpha} x^i = x \frac{d}{dx}\left(\frac{x}{x-1}\right) = \frac{x}{(1-x)^2}$$

Therefore $\nu \;/\; \nu m = \dfrac{cx/(1-x)^2}{1 + \left(cx/_{1-x}\right)} = \dfrac{cx}{(1-x)(1-x+cx)}$ (16) & (17)

or $\nu = \nu_m \, cx / (1-x)(1-x+cx)$

The equilibrium between condensation and evaporation of molecules at the surface of a liquid can be expressed by the equation

$$k_l s_l P_o = K_{-L} s_L e^{-QL/RT} \qquad (18)$$

Where s_l is the extent of the liquid surface and p_o the saturation vapour pressure at the concerned temperature. This gives for p_o,

$$p_o = k_{-l}/k_l \, e^{-QL/RT} \qquad (19)$$

According to the definition of

$$X = (k_{-l}/k_l)\ p\ e^{QL/RT} \tag{20}$$

So that x can be equated to p/po which is called relative pressure

Therefore the isotherm equation takes the from

$$\nu = \frac{\nu_m C\left({}^{p}\!/_{po}\right)}{\left(1-{}^{p}\!/_{po}\right)\left(1-{}^{p}\!/_{po}+c\,{}^{p}\!/_{po}\right)} \tag{21}$$

The is the Brunauer-Emmer-Teller (BET) equation for multilayer adsorption on a free surface. It is seen from the equation that when the pressure approaches the saturation pressure i.e. when p/po → 1, v → α or infinite number of layers can build up provided the adsorption takes place on a free surface.

For purposes of testing adherence of experimental data to this isotherm equation, it is transferred into a linear form

$$x / \nu\ (1-x) = 1 / \nu_m\, c + ((c-1) / \nu_m\, c)x \tag{22}$$

The a plot of x/v (1-x) vs. x should be a straight line for the experimental values of v at several relative pressures. From the slope and intercept of this straight line, value of the parameters v_m and c can be obtained.

If instead of multimolecular adsorption on a free surface, adsorption takes place in fine capillaries, then the maximum number of layers that can be adsorbed is finite and is limited to say 'n'. Imposing this upper limit to the summations in the derivation of the BET equation gives the relation.

$$\nu = \frac{\nu_m cx}{1-x}\ \frac{\left[1-(n+1)x^n+nx^{n+1}\right]}{\left[1-x+cx=cx^{n+1}\right]} \tag{23}$$

The slopes of isotherms with various values of n are shown in Figure 6. In this equation n can take two extreme values namely 1 and α. When it takes a value of 1

$$\nu = \frac{\nu_m cx}{1-x}\,\frac{\left[1-2x+x^2\right]}{\left[1-x+cx-cx^2\right]}$$

$$= \frac{\nu_m cx}{1+x} = \left(\frac{\nu_m c}{po}\right)\frac{p}{\left[1+\left(\frac{c}{po}\right)p\right]} = \frac{\nu_m bp}{1+bp} \qquad (24)$$

Where b = c/pi. One can immediately recognize that this is the same as the Langmuir equation for uni molecular adsorption.

At other extreme when n = α, it reduces to the simple form given in equation 21

$$v = v_m \, cx \,/\, (1-x)\,(1-x+cx) \qquad (25)$$

Most of the experimental data fit in with this equation for adsorption on free surface as seen from the linear plots of x/v(1-x) vs. x. When the data do not fit into this equation, then it is suspected that the cause of this deviation can be to n taking a definite value which is deduced by trial and error, first obtaining approximate value of v_m and c from the plot of x/v (1-x) vs, x in the low pressure region, where at least, the adsorption should still be as though on a free surface.

The constant c is given by the expression

$$c = \left(\frac{k1}{k-1}\right)\left(\frac{k_l}{k_{-l}}\right)e^{(q1-ql)RT} \qquad (26)$$

$$c = \frac{\left(\frac{k_1}{k_{-L}}\right)e^{QL/RT}}{\left(\frac{k_L}{k_{-L}}\right)e^{QL/RT}} \qquad (27)$$

Now the quantity $k_1 e^{-Q1/RT}$ represents the number of molecules evaporating per unit time from an adsorption site and its reciprocal, can therefore be regarded as the average life time τ, of a molecule in the adsorbed state in the first layer. Similar expressions can be written for subsequent layers so that

$$C - (k_1\tau_1 / k_L / \tau_L) \qquad (28)$$

c is seen thus seen to be proportional to the relative life time of the molecules in the first and higher layers. Since all layers beyond first layer have evaporation-condensation properties of the bulk liquid, c also denotes the relative life time of the molecules in the first layers and in the bulk liquid respectively.

Secondly, when the temperature of the experiment is close to the boiling point of the liquid form of the adsorbate the adsorption-desorption characteristics in the primary layer(k_1/k_{-1})

will be similar to the condensation -evaporation co-efficient on the surface of the liquid k_1/k_{-1} so that one can consider

$$(k_1/k_{-1}) = (k_1/k_{-L}) \qquad (29)$$

therefore $$c \cong e^{(Q1-QL)/RT} \qquad (30)$$

from which knowing Q_L, the heat of liquefaction, one can calculate Q_1 the heat adsorption in the first layer.

The parameter v_m denotes the volume (in cm^3) of the gaseous adsorbate required to cover the entire surface of the adsorbent with a uni molecular layer. It can be converted into the number of molecules using the Avogadro number. Then it the area covered by each adsorbed molecules a_m is known * (* The methods of determining a_m and typical values of a_m for various adsorbates are given in Appendix I), the area of the entire surface can be estimated. The value of v_m is thus a measure of the surface area of the adsorbent.

If the BET equation is rewritten in the form,

$$\frac{p}{v(po-p)} = \frac{1}{v_m c} + \left(\frac{c-1}{v_m c}\right)\left(\frac{p}{po}\right) \qquad (31)$$

then one can plot the experimental data in the form of v/v_m vs. p/po which gives isotherm shapes of the type II as long as c is greater than 2. When c is less than 2 but is still positive, then isotherms with shape III is obtained. Typical v/v_m vs, p/po plots calculated as per the BET equation for various values of c are given in Figure 7. It is seen that the isotherms possess points of inflection as long as c exceeds 2 ; this point is near to the point where v/v, = 1 i.e. where the adsorption is equal to v_m.

Type III isotherms normally contain a long straight line portion. The point at which this linear (Fig. 8) portion begins has been termed point B and was considered by Emmet and Brunauer to indicate the completion of the monolayer, i.e. the volume adsorbed at point B, $v_B = v_m$. Earlier they has suggested that the volume adsorbed corresponding to point A represented the monolayer capacity. However, estimation by various investigators showed that the ratio of v_B/v_m can vary between 0.75 to 1.53 thus casting serious limitation on the use of point B method for the determination of the monolayer capacity. The value of v_B/v_m is close to 1 when the correct range of the linearity of the BET plot is chosen such the p/po at the point B is well within the liner range chosen.

The following points form the basis for formulating that a point B, the monolayer completion should have taken place.

1. According to simple BET equation with its assumptions on the homogeneous nature of the surface and absences of interactions among adsorbed molecules, the differential heat of adsorption Q should decrease from the value of Q_1 to the latent heat of condensation Q_L at the point where monolayer is complete. However, the two assumptions may not strictly hold good and hence one would not observe such an abrupt change in the heat of adsorption at the completion of the monolayer. Secondly, this expectation is based on the assumption that the primary layer is complete before subsequent layers are formed which is not strictly true is actual experimental conditions and is also not implied in the derivations of the BET equation.

2. The change is molar entropy of the adsorbed gases against the amount adsorbed should be distingusly different for the primary layers and subsequent layers. Experimentally it has been observed that entropy variation curves with amount

adsorbed showed minimum corresponding to the point B, indicating the completion of the monolayer.

Calculation of the specific surface area of samples from monolayer capacity:

It has been shown the treatment of experimental data according to the BET equation can give the value of v_m which is equal to the monolayer capacity. The specific surface area S (m^2/g) can then be related to the monolayer capacity using a relation

$$S = \frac{v_m}{22414} \times N \times A_m \times 10^{-20} \qquad (32)$$

Where v_m is expressed in cm^3 of gas adsorbed per gram of the adsorbent. N, the Avogadro number and A_m the molecular cross sectional area of the adsorbate in A^2, i.e. the area which an adsorbed molecule occupies on the surface of a solid when monolayer is completed. If instead of v_m the monolayer saturation quantity is expressed as grams per gram of the adsorbent then the equation takes the form

$$\frac{X_m}{M} \times N \times A_m \times 10^{-20} \qquad (33)$$

Where M is the molecular weight of the adsorbate used. If the amount adsorbed is expressed in moles per gram of the solid then

$$S = X_m N A_m \times 10^{-20} \qquad (34)$$

It is clear that the use of these formulate for determining the surface area of the sample requires the knowledge of the cross sectional area of the adsorbate. The accurate determination of this quantity is difficult because of the ignorance as to the exact mode of packing of the adsorbed molecules in a completed monolayer (see however Appendix 1).
General applicability and importance of BET theory:

In most cases, the original equation for adsorption of a free surface fits the experimental data accurately and can be used over the entire course of the isotherm ranging from early stages of uni molecular coverage to the advanced stages of multilayer adsorption without having to make any changes in the equation. The equation has been tested thoroughly by many authors and has been found to be applicable to all known types of physical adsorption covering a wide range of adsorbates and adsorbents. This is exemplified by the straight line plots obtained for the adsorption of different gases and vapors on various adsorbents shown in Figure 8,9. The values of constants obtained from these isotherms are given in Table 6 and 7.Table: 6 Values of constants of the BET equation for the adsorption of nitrogen at 90K

Substance	**V_m cm^3/g**	**Q_1-Q_L Cals/Mole**
Un promoted iron catalyst	0.12	794
Fe-Al_2O_3catalyst	2.78	774
Fe-Al_2O_3-K_2O catalyst	0.76	911
Fe-K_2O Catalyst	0.12	772
Fused Cu catalyst	0.05	776
Commercial Cu catalyst	0.10	834
Cr_2O_3 gel	50.5	738
Cr_2O_3 glowed	6.14	835
Silica gel	127.0	794
Glass Spheres	0.1	900

Table: 7 Values of constant of the BET equation for the adsorption of various gases on silica gel.

Gas	Temperature°C	v_m cm^2/g	surface area m^2/g	Q_I-Q_L Cals/mole
Nitrogen	195.8	135	560	719

Nitrogen	183.0	127	534	794
Argon	183.0	122	464	594
Oxygen	183.0	132	477	586
Carbon monoxide	183.0	132	550	973
Carbon dioxide	78	102	455	1335
Butane	0	28	387	930

It is interesting to note from the Table 6 that the values of Q1-Q2 for the adsorption of nitrogen changes little for adsorbent to adsorbent . It is 840±70 Cals/mole for most of the adsorbents. This is in agreement with the concept of non-specificity of physical adsorption. It is seen from he values in /Table 7 that the surface area values deduced from the adsorption of five gases, nitrogen, oxygen, argon, CO, CO_2, average around $500m^2/g$ with a maximum deviation of 10%. However it is noticed that when butane is used as the adsorbate, the value obtained for surface area is nearly 20% less which could be due to (I) non accessibility of fine pores for the big butane molecule and or (ii) the inaccuracy of using the cross sectional area of butane molecules assuming a spherical shape.

Application to surface area measurements , It is clear that the BET equation is ideally suited for the determination of surface areas of finely divided solids. There are many advantages is using this equation over other methods. The chief advantage are:

1. Compared to other physical techniques based on measuring the average crystallite size ‘l’ form which surface area is deduced using a relation S= 6/dl where d is the density , like x-ray line broadening, electron microscopy , small angle x-ray scattering (SAXS). magnetic methods and Mossbauer spectroscopy the technique of adsorption measurements and the apparatus required for it are relatively simple.. For comparison, the surface area values determined for several substances by nitrogen (Sa) and electron microscopy(Sm) are given in table 8.

Table 8: Comparison of surface areas of samples determined adsorption measurements ass well as by electron

Substance	S_m	S_A	S_A / S_m
Grade 6carbon	76.95	110	1.43
P33 Carbon	21.6	20.7	0.96
Shawinigan acetylene carbon	60.05	64.5	1.08
Lampblack carbon	23.5	25.5	11.09
Thermax carbon	6.50	7.63	1.17
Thermax carbongraphitized	6.45	6.37	0.99
Sphereon 6carbon	94	114	1.21
Vilcan3 carbon	74	71.5	0.97
Sterling S carbon	26	27.9	1.07
Anatase	9.5	10.65	
Zinc oxide	4.3	4.2	
Cristobalite silica virgin	5.0	6.1	
Cristobalite silicaetched	4.9	4.9	1.0
Fused silica virgin	5.2	6.0	
Fused silica etched	4.0q	4.3	

2. The accuracy attained is usually high. Values agreeing within 10% absolute values are obtained without any difficulty, Rarely, on account of uncertainties with respect to accessibility of all the pores and the estimated area per adsorbed molecule ,larger derivation upto25% may rise.

3. Determination of surface area of sample under various pretreatment conditions like sintering with various gases can be carried on the same sample on which other properties of the sample have to be measured.

The adsorption measurement for this work are usually determined at temperature very close to the boiling point of the adsorbate , the usual choice is nitrogen at it is inexpensive .easily obtained ,inert towards most of the its solids and is able to penetrate even the finest pores .Occasionally,however ,as in the case of non-catalysts, nitrogen may chemisorb on the solid even at low temperature s and may therefore, be preferable to use a more inert gas like argon. For determination of low surface areas such as those of metal filaments and single crystals low pressure techniques have to be employed; and for these krypton is the usual adsorbate.

For purpose of routine testing of powdered materials .a simplified Bet liner equation is possible, though with some sacrifice of accuracy. Because of the usually large value of c (of the order of 100) the intercept $1/V_mc$ is generally small and negligible compared to the slope .So one can write without any serious error,

$$x/(1-x) \cong \left[c-1/v_mc\right] \qquad (35)$$

Again, since>>1is this equation reduces to

$$v_m = v(1-x) \qquad (36)$$

which enables the determination of v_m from a single value of v .It is pointed out that this value of v should be determined at a relative pressure between 0.05 and 0.35.since in the normal BET plot the intercept is usually small ,and the knowledge of both intercept and slope is necessary to obtain the value of v_m Key et al have proposed a modified equation for obtaining the value of v_m directly .Dividing the BET equation throughout by x and rearranging the terms one obtains an alternative equation

$1/v(1-x)=1/v_m +(1/ v_m c)(1-x/x)$ (37)

plotting 1/v(1-x)Vs (1-x/x) yields straight lines ,the intercept of this gives the value of v_m straight –away

Harkins-Jura equation:

Harkins-Jura have presented an alternative approach for the low temperature physical adsorption of gases .They have considered the process to be phenomenologically analogous to the spreading of condensed film on liquid surfaces .On this basis they have suggested the following equation for the adsorption isotherm.

$\text{Iogp(or Logp}/p_0)=B-(A/v^2)$ (38)

where v is the volume of gas adsorbed at the pressure p, A and B are constants .The plot of logp(or)Logp/p_0 Vs $1/v^2$ gives a straight line with a negative slope ,from which the surface area can be calculated by the relation

$\text{Area}=K(-\text{slope})^{1/2}$ (39)

The constant K was determined independently from the heat of immersion measurement .It will be different from liquids and will also be dependent on temperature .For nitrogen at its boiling point (-195.8°C)K=4.06 .Values of area found by this method are general in agreement with those determined by BET equation .The only advantages of the adsorbate molecule .since the same adsorption data can be used for both of methods ,it may perhaps be worthwhile to calculate the surface area by both of them so that the values obtained by Harkins-Jura equation can be used to check the values obtained by the application of BET equation

Application of BET equation to type III isotherms:

There are few experimentally obtained isotherms which are convex to the pressure axis and pertain the type III of the classification shown in Fig1 .This type of variation implies that the process of adsorption is cooperative in nature ,that is the already adsorbed molecules influences the easier further adsorption of molecules ,meaning thereby that the attraction between the molecules is greater than attraction between the adsorbent and adsorbate .For a quantitative measure of interaction between adsorbate molecules, one can ,for the first approximation ,consider the latent heat of evaporation .Q_L as a measure and for the adsorbate-adsorbent interaction ,the differential heat of adsorption Q.In this case type III isotherms will result when $Q \approx Q_{L.}$

The adsorbate-adsorbent interaction will also be enhanced by further interaction a like hydrogen bonding ,which probably occurs in water and ammonia adsorption .This type of interaction will result in the type III isotherm. If instead the surface itself contains hydroxyl groups then the adsorbent-adsorbate interaction will predominate and thus result in type II isotherm .similarly benzene molecules can also interact with surface hydroxyl groups of specific adsorbents like silica by quadruple –dipole interactions and will result in type II isotherms .while on dehydrated surfaces its adsorption yields type III isotherms.The presence of hydrogen bonding or dipole –quadruple interaction between the surface hydroxyl groups and the adsorbate molecules like water or benzene can be demonstrated by replacing the surface hydroxyl groups by groups likes –Osi(CH_3)

Applying BET equation to type III isotherms and imposing the condition that $Q_1 \approx_{:} Q_L$ so that c takes the value of 1 gives a relation .Substituting c=1in the BET equation

,

$$\frac{p}{v(po-p)} = \frac{1}{v_m c} + \left(\frac{c-1}{v_m c}\right)\left(\frac{p}{po}\right) \qquad (40)$$

p 1
------------------- = -----------------------

$v(p^0-p)$ V_m

so that BET plot becomes a straight line parallel to the p/p^0 axis and at a distance $1/V_m$ from it

If on the other hand c=2 one obtains

$$\frac{p}{v(p^0-p)} = \frac{1}{2v_m} + \frac{1}{2v_m} \times \frac{p}{p^0} \qquad (41)$$

so that slope and intercept are now equal to $1/2v_m$

Strictly speaking one cannot make an accurate a BET plot when the isotherm obtained is of type III and the calculation of v_m is unceasingly inaccurate when the value of c approaches unity. The slope of the BET plot is given by

Slope $s=c-1/ v_mc$ (42)

so that the value of V_m is given by

st

$v_m=c-1/c_s$ (43)

so that the value of v_m is sensitive to the value of c especially when c tends to unity .Therefore ,the direct use of conventional BET equation to type III isotherm is not suitable and therefore one has to seek an alternative procedure for determining the value of v_m .From the BET equation one can directly determine the value of $p/_{p0}$ corresponding to monolayer saturation by substituting $v=v_m$ and $c=1$

$(p/p^0)_m$ =-1+√c/c-1 (44)

as equal to 0.5 when c=2 the$(p/p^0)_m$ =0.41.As the value of c decreases from unity the value of$(p/p^0)_i$ncreases.

There are not many experimental data available to test the validity of BET equation to type III isotherm and even for those cases where data is available(representative from data collected are given in table9)the BET analysis is not as the estimate from type III isotherms is some times off from the estimate from type II isotherms by suitable choice by pretreatment or adsorbate by more than 20%.At the present stage development ,it seems better not to attempt BET analysis for the surface area determinations
when type III isotherm is obtained experimentally

Table9 :Values of monolayer saturation volumes obtained from $(p/p^0)_m$ values for type III isotherms and the corresponding values for type II isotherms by BET analysis using suitable adsorbate or pretreatment:

Adsorbent Adsorbatefor typeIII isotherm V_mg/g Adsorbatefor typeIII isotherm V_mg/g Kaolin0.5µstokesdiameter CCI_4 0.0122 O_2 0.0183 Magnesia CCI_4 0.098 O_2 0.0331 Calcium Carbonate n-butane 0.0021 n-butane on heat treated sample 0.019

Isotherms of types IV and V are obtained for porous solids only and this will be taken up for consideration in a subsequent chapter