Surface chemistry: كيمياء السطح

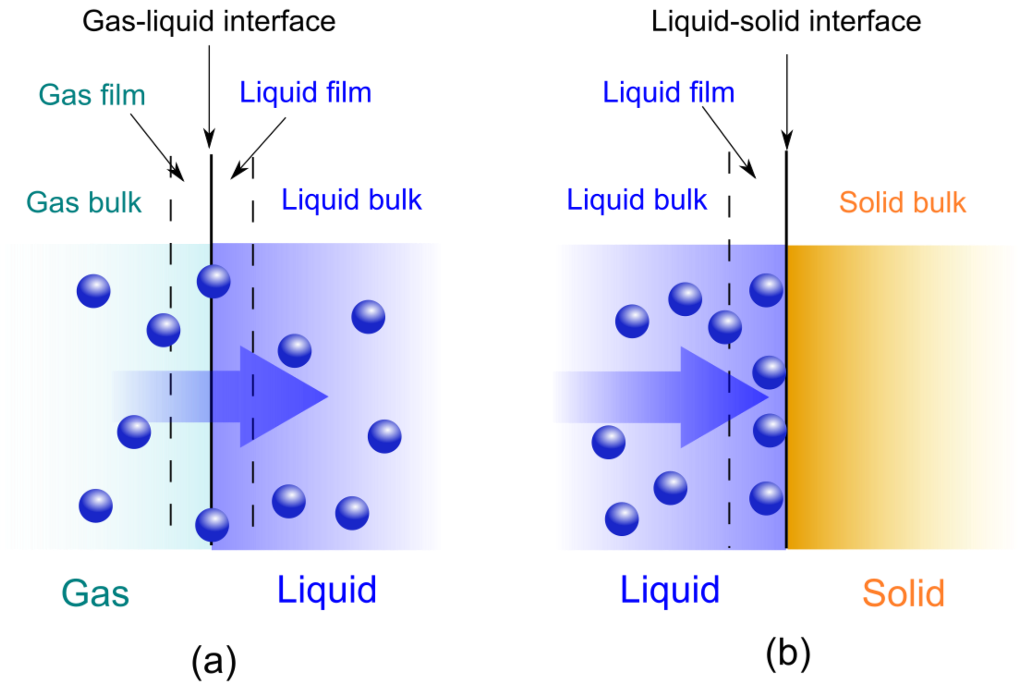
Surface chemistry can be defined as the study of chemical reactions and physical processes that occur at the different surfaces interfaces. Surface science is the study of physical and chemical phenomena that occur at the interface of **two different phases**, including each of the following cases:

1-solid–liquid interfaces,

2-solid–gas interfaces,

3-solid–vacuum interfaces, and

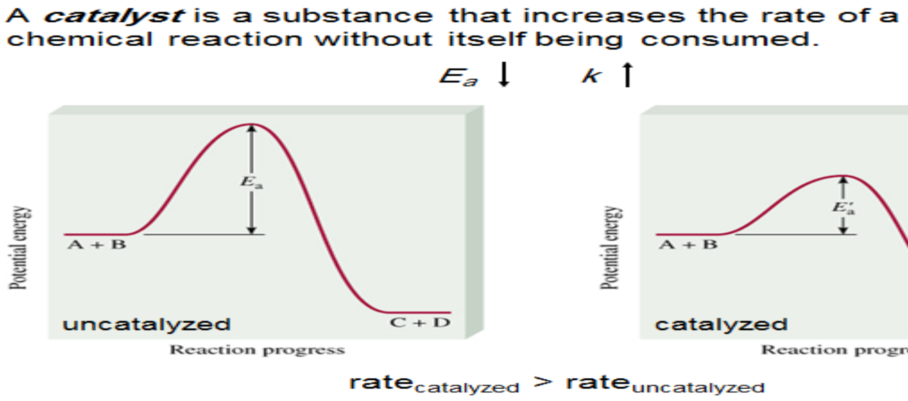
4- liquid–gas interfaces.



The surface science encompasses concepts such as heterogeneous catalysis, semiconductor device fabrication, fuel cells, self-assembled monolayers, adhesives processes and other surface processes such as chemical corrosion.

Catalyst and catalysis phenomenon: التحفيز و العامل الحفاز

As catalysis a surface phenomenon, catalyst is defined as a substance, which accelerates the rate of a chemical reaction and itself unchanged and not consumed in the overall reaction with a lowering of activation energy (Ea) for the catalyzed reaction. Catalysis is a phenomenon of altering the rate of a reaction in the presence of a catalyst as shown below.

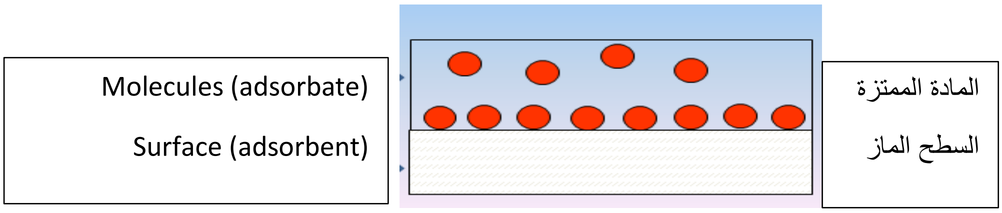


A *catalyst* is a substance that increases the rate of a chemical reaction without itself being consumed.

Figure: Schematic description for the effect of catalyst on altering rate of catalyzed reaction[to the left unanalyzed , to the right is the catalyzed reaction]

Adsorption, desorption and absorption:الامتزاز والابتزاز والامتصاص

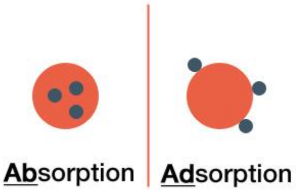
Adsorption is the adhesion and or accumulation of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. This process can be represented as follows:

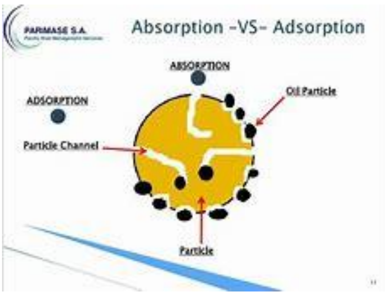


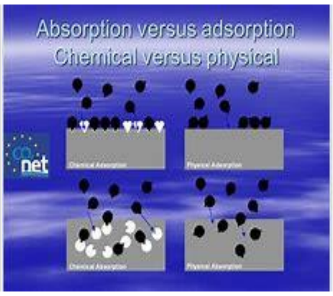
Adsorption: Adsorption is a surface phenomenon is present in many natural, physical, biological and chemical systems and is widely used in industrial applications such as heterogeneous catalysts, activated charcoal and environmental applications.

Desorption: Is a process in which the adsorbate molecules are left the adsorbent surface due to elevation of temperature and/or reducing pressure. Example of this process as in evaporation of vapor molecules from the surface upon increasing temperature. Releasing of gas molecules from charcoal by heating or vacuuming.

Absorption: is a process that occurs when molecules or atoms are “sucked” inside of a volume of other surface. It has to completely enter into the pores of other substance. This may be a chemical process (reaction) or physical process (dissolving into a liquid) process. So that adsorption process occurs at the surface only while absorption occurs inside the pores of the desired surface For example, absorption of CO_2 molecules in the inner pores of activated carbons, as shown below:







Desorption versus adsorption: الامتزاز والابتزاز

Desorption is a surface phenomenon that is opposite to adsorption for the same system (adsorbate/ adsorbent), it is a phenomenon whereby adsorbate molecules are released away from or through an adsorbent surface.

The term sorption: مصطلح الامدصاص

The term sorption involves both of adsorption and absorption together(i.e. sorption= adsorption+ absorption) for the same surface.

امدصاص= امتزاز + امتصاص

Introduction to Molecular Adsorption

Adsorption of molecules on to a surface is a necessary step to any surface chemical processes. For example, in the case of a surface catalyzed reaction it is possible to break down the completely continuously cycling process into the following five basic steps, these also called steps of catalytic process:

1.Diffusion of reactants to the active surface sites,

2.Adsorption of one or more reactants onto the active surface site,

3.Surface reaction,

4.Desorption of products from the surface,

5.Diffusion of products away from the surface

Types of Adsorption: أنواع الامتزاز

Based on type of forces of attraction existing between adsorbate and adsorbent, adsorption can be classified into two main types. These are physical Adsorption and chemical Adsorption.

Physical Adsorption or Physisorption: الامتزاز الفيزيائى او الامتزاز الطبيعى

In this type of adsorption no chemical reaction occurs between adsorbate molecules and the adsorbed surface (adsorbent). Adsorbed molecules are attracted with the surface by columbic attraction, Van Der Waals forces and or hydrogen bonding. This occur normally at low temperature and high pressure. The following steps represents main concepts of natural adsorption:

1-The gas molecules adhere to the surface of the solid via van der Waals forces between them.

2-The process is exothermic, the enthalpy of condensation of vapor (20-40 kJ/mole)
3-Adsorbate can be adsorbed on a multy of layers of adorbate,
4-This process is a reversible/(adsorption/desorption),
5-It is called natural adsorption,
6-Normally occurs at lower temperatures, as the temperature increases, the process of physisorption decreases and vice versa.

Chemical Adsorption or Chemisorption:الامتزاز الكيميائى

In this type of adsorption real chemical bonding occurs between adsorbate molecules and the adsorbed surface sites (adsorbent). This process leads to a chemical reaction and its requires an activation energy more than 40 kJ/mol., formed product release from the surface by desorption process.

1-Chemical interaction between the adsorbate and adsorbent. Therefore formed bond is much stronger than that for physical adsorption,
2-Heat adsorption around 400-80 kJ/ mole and $\Delta H > 40$ kJ/mol.,
3-It is a irreversible process,
4-Only a monomolecular layer of adsorbate formed,
5- It is a specific adsorption,
6- Occurs at higher temperatures with the increases in temperature, Chemisorption first increases and then decreases.

Factors affecting on adsorption processes: العوامل المؤثرة على الامتزاز

1-Temperature

For a physical adsorption (natural adsorption), increases at low temperature conditions and vice versa for a chemical adsorption. For the first type, it can be presented as follows:

$$A + B \Leftrightarrow AB + Heat$$

2-Pressure

As depicted by Adsorption Isotherm, with the increases in pressure, adsorption increases up to a certain extent until saturation level is achieved. After saturation level is achieved no more adsorption takes place no matter can be further adsorbed how high pressure is applied.

3-Surface Area of the adsorbent:

Adsorption is a surface phenomenon therefore; it increases with increase in surface area of the adsorbent surface. The surface area of adsorbent is mainly dependent on the type and numbers of pores and active sites that are available at the surface. So that highly porous materials have high surface area, for example charcoal have a surface area around 400 m^2/gm

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Applications of Adsorption:تطبيقات الامتزاز

There are many types of applications of adsorption involving industrial, environmental, pharmaceutical, medical and catalytic applications. Below are some examples of these applications:

1. Charcoal is used as a decoloriser as it adsorbs the coloring matter from the colored solution such as industrial wastewaters and sewage water.

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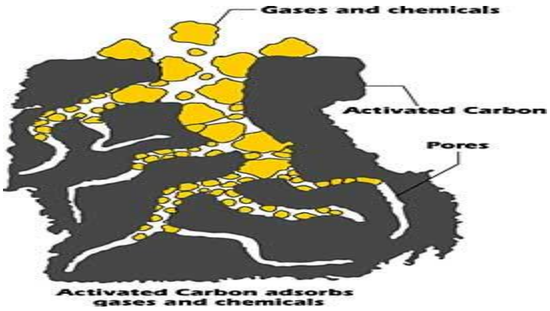
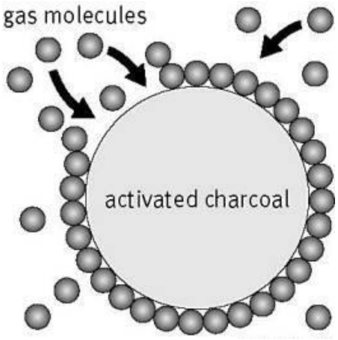


2. Silica gel adsorbs moisture from the desiccators as well as another applications in adsorbing of wide range of gases and organic pollutants,

3. Activated charcoal is used in gas masks as it adsorbs all the toxic gases and vapors and purifies the air for breathing. Beside that AC used in many environmental applications via removing polluted dyes from industrial wastewaters.



4 .Adsorption processes are useful in carrying out heterogeneous catalysis. This plays important role in the industry as more than 85% of industrial processes are performed with using catalysis phenomenon.

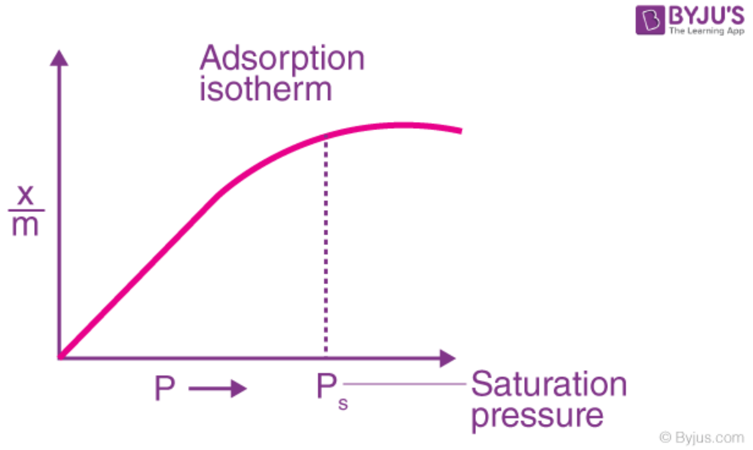
Activation of Adsorbent: تنشيط السطح الماز

Activation of adsorbent surface is performed to provide more number of vacant sites on surface of adsorbent. This can be done by breaking solid crystal in small pieces, heating charcoal at high temperature, breaking crystals of solid into powder or other methods suitable for particular adsorbent.

Adsorption Isotherm: ايزوثرم الامتزاز- متساوي درجة حرارة الامتزاز

The process of adsorption is usually studied through a graph that is called as an **adsorption isotherm**. It is the graph between the amounts of adsorbate (x) that is adsorbed on the surface of adsorbent (m) as a function of pressure(P) or concentration(C) at a constant temperature (T).

An adsorption isotherm is a graph that represents the variation in the amount of adsorbate(x) that is adsorbed on the surface of the adsorbent with the change in pressure at a constant temperature. The graph below shows the isotherm proposed by Freundlich



As we know from Le Chatelier’s principle, the direction of equilibrium in a reaction shifts in the direction in which stress is relieved. So, here we can see that upon application of excess pressure on the system, the equilibrium shifts in the direction where the number of molecules decreases so that the pressure in the system decreases.

From the graph, we also observe that after attaining a pressure P_s, that is the saturation pressure, the variation in the amount of adsorbent adhering to the adsorbate becomes zero. This happens because the surface area available for adsorption is limited and as all the sites are occupied, a further increase in pressure does not cause any difference. Different adsorption isotherms have been proposed by different scientists namely,

1-Freundlich adsorption isotherm

2-Langmuir adsorption isotherm

3-BET adsorption isotherm

Basic Adsorption Isotherm: مبادئ ايزوثرمات الامتزاز

1-Freundlich adsorption isotherm متساوي درجة الحرارة لامتزاز فرندلج

In 1909 AC, Freundlich, reported an empirical expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This type of adsorption isotherm is fitted with physical adsorption (multy layers adsorption) .This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation or simply Freundlich Isotherm. This relation can be written as follows:

$x/m= K_f P^{1/n}$ or $x/m= K_f C^{1/n}$

$q_e=k_f P^{1/n}$ $q_e=k_f C_e^{1/n}$

$\log x/m = \log k_f + 1/n \log P$ or it can be written as:

$\log q_e = \log k_f + 1/n \log C_e$

Whereas, (qe) is the amount of adsorbate at equilibrium per unit mass of adsorbent (mg/gm), Ce, is the concentration (mg/L) of adsorbate in solution at equilibrium. This equation can be plotted as follows:

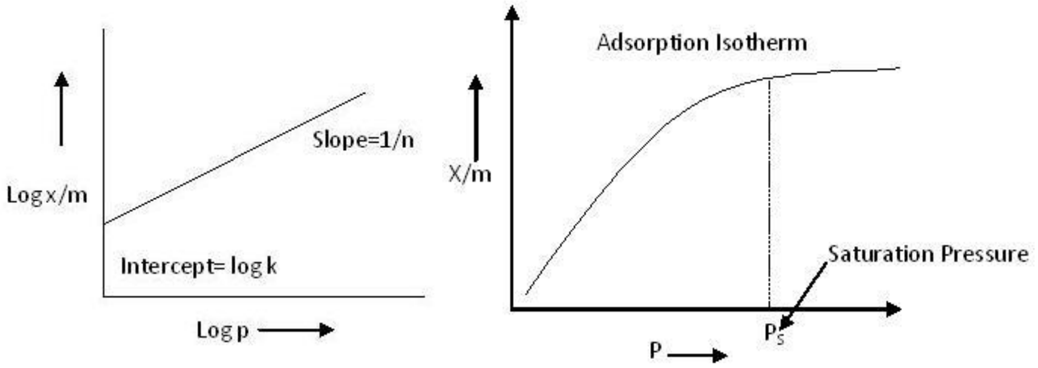


Figure :Non-linear and linear Freundlich adsorption isotherm

Where (x) is the mass of the gas adsorbed on mass (m) of the adsorbent at pressure p and k, n are constants whose values depend upon adsorbent and gas at particular temperature. Though Freundlich Isotherm correctly established the relationship of adsorption with pressure at lower values, it failed to predict value of adsorption at higher pressure.

2-Langmuir Adsorption Isotherm: متساوي درجة الحرارة لامتزاز لانغموير

In 1916 AC, Arvin Langmuir proposed another Adsorption Isotherm known as Langmuir Adsorption isotherm. This type of adsorption isotherm is fitted with chemical (monolayer adsoprion) .This isotherm was based on different assumptions on which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules. Based on this theory, he derived Langmuir Equation, which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure.

$$\theta = \frac{KP}{1 + KP}$$

$$k = k_{ads}/k_{des}$$

Where θ the number of sites of the surface which are covered with gaseous molecule (surface coverage, θ= 0-1.0), P represents pressure and K is the equilibrium constant for distribution of adsorbate between the surface and the gas phase.The basic limitation of

Langmuir adsorption equation is that it is valid at low pressure only. Based on this relation, two cases can be reported as follows:

1-At lower pressure,

Regarding to main Langmuir equation: $\theta = \frac{KP}{1 + KP}$

KP is so small, that factor (1+KP= 1) in denominator can almost be ignored. So Langmuir equation reduces to the form,

$\theta = KP$ (direct proportionality between adsorption capacity and p or concentration)

2-At high pressure:

KP is so large, that factor (1+KP= KP) in denominator is nearly equal to KP. Therefore, Langmuir equation reduces to: $\theta = 1$.

Also Langmuir adsorption model can be demonstrated by the following equation:

$$[1/q_e = 1/q_m + 1/K_L q_m C_e] \quad \text{Langmuir equation}$$

In above equation, C_e is the concentration of adsorbate in solution in (mg L^{-1}) at equilibrium, and q_e (mg g^{-1}) is the concentration of the molecules at equilibrium and the amount of adsorbed molecules on the surface of the adsorbent at any time, respectively. q_{max} shows the maximum adsorption capacity (mg g^{-1}) and K_L represents the Langmuir constant (L mg^{-1}).

The Langmuir-adsorption model predicts an asymptotic approach to monolayer surface

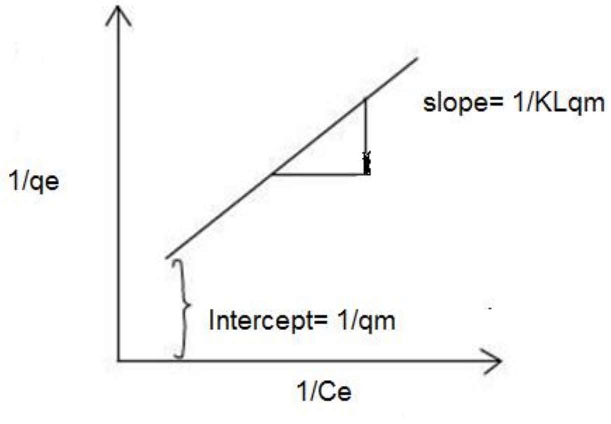


Figure: plotting of Langmuir equation