Physical, analytical, and inorganic chemistry

Physical chemistry

- Catalysis
- Surface chemistry
- Phase rule
- Colloids

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Catalysis

Catalysis type

Characteristics of catalytic reactions

Promoters

Catalytic poisoning

Autocatalysis

Negative catalysis

Activation energy

Theories of catalysis

Catalysis

The term catalysis was used by Berzelius when he realized that some substances can increase the speed of a reaction without being consumed in that reaction. These substances which increase the rate of the reaction were termed positive catalysts and the process was called positive catalysis. It was believed that the function of these catalysts is to loosen the bonds between the atoms in the reacting molecules.

On the other hand, there are some cases in which the catalyst was found to decreases the rate of the reaction and as a consequence, they were termed negative catalysts and the process is termed negative catalysis. A catalyst therefore can be defined as a substance which alters the rate of a reaction while it remains chemically unchanged at the end of the reaction. The term catalysis refers to the process in which a substance is used to alter the rate of a reaction and the catalyst which enhances or increases the rate of a reaction it is called a positive catalyst and the process is called positive catalysis. When the catalyst decreases the rate of a reaction it is called a negative catalyst (or an Inhibitor) and the process is called negative catalysis (or Inhibition).

Types of catalysis

There are two main types of catalysis: (a) Homogeneous catalysis and (b) Heterogeneous catalysis.

(a) Homogeneous catalysis: in homogeneous catalysis, the catalyst and reactants are in the same phase.

Examples of homogeneous catalysis:

(i) In the oxidation of (SO_2) to (SO_3) with nitric oxide (NO) as a catalyst:

$2SO_2 + O_2 + \xrightarrow{[NO]} 2SO_3 + [NO]$

the reactants and the catalyst are all gases and hence the reaction belongs to homogeneous catalysis.

(ii) The hydrolysis or inversion of cane sugar in the presence of H_2SO_4 a as catalyst:

$C_{12}H_{22}O_{11} + H_2O \xrightarrow{[H_2SO_4]} C_6H_{12}O_6 + C_6H_{12}O_6 + [H_2SO_4]$

Cane sugar glucose fructose

both of the reactants and the catalyst are in the liquid phase and as a results it is an example of homogeneous catalysis.

Heterogeneous catalysis

In heterogeneous catalysis, the catalyst and the reactants are present in different phases. For example, when the reactants are in the gas phase and the catalyst is a solid the process is termed heterogeneous catalysis. Contact catalysis is an example where the reaction occurs through contact of the reactants with the catalyst surface and the catalyst is usually used of a finely divided metal.

Examples of heterogeneous catalysis

(i) The reaction of (SO_2) with (O_2) in the presence of finely divided platinum, (Pt) (or vanadium pentoxide, (V_2O_5)), is an example of heterogeneous catalysis.

$2SO_2 + O_2 + \xrightarrow{[Pt]} 2SO_3 + [Pt]$

gas gas solid

(ii) The decomposition of an aqueous solution of hydrogen peroxide (H_2O_2) is catalyzed by manganese dioxide (MnO_2) or platinum, (Pt) in the colloidal form, and consequently the process belongs to heterogeneous catalysis

$2H_2O_2 \xrightarrow{[Pt]} 2H_2O + O_2 + [Pt]$

liquid   solid

Properties of catalytic reactions

(1) No change occurs in the catalyst at the end of the reaction. This means that there is no change in the chemical composition or in the mass of the catalyst by the end of the reaction. However, the physical nature may be changed. For example, in the thermal decomposition of potassium chlorate ($KClO_3$) the granules of the catalyst (MnO_2) are changed to a finely divided powder by the end of the reaction.

(2) Only a small quantity of the catalyst is required for a reaction. For example, few mgs of finely divided platinum is sufficient to catalyze the decomposition of a large amount of hydrogen peroxide (heterogeneous catalysis). However, a relatively large amount of some catalysts should be used to be effective in some cases. For example, for $AlCl_3$ (a Lewis acid) to function as an efficient catalyst in the Friedel- Crafts reaction:

$C_6H_6 + C_2H_5COCl \xrightarrow{AlCl_3} C_6H_5COC_2H_5 + HCl$

a relatively large percentage of it is required.

Also, in the case of homogeneous catalysis like the hydrolysis of an ester in the acidic or the basic medium:

$RCOOR + H_2O \xrightarrow{H^+ \text{ or } OH^-} RCOOH + ROH$

The rate of the reaction increases with increasing the concentration of H^+ or OH^-, respectively.

(3) In heterogeneous catalysis the catalyst becomes more active when it is used as a finely divided powder or in its colloidal state. Platinum in the colloidal state, as an example, will have much more catalytic activity than when it is used in the bulk form.

(4) A catalyst is specific in its action. For example, C_2H_5OH gives C_2H_4 over aluminum oxide (Al_2O_3):

$$C_2H_5OH \xrightarrow{Al_2O_3} CH_2CH_2 + H_2O \text{ (dehydration)}$$

But on copper (Cu) it gives the aldehide (CH_3CHO):

$$C_2H_5OH \xrightarrow{Cu} CH_3CHO + H_2 \text{ (dehydrogenation)}$$

(5) In general, a catalyst cannot initiate a reaction. However, there are certain cases where the reactants do not react for a very long period under the reaction conditions. For example, the case of a mixture of H_2 and O_2 at room temperature, there will be no reaction for a very long time, however, in the presence of platinum black catalyst they react in a short time

$$H_2 + O_2 \xrightarrow{\text{room temp}} \text{no reaction}$$

$$2H_2 + O_2 \xrightarrow{\text{Pt black}} 2H_2O$$

Another example is the reaction of H_2 and Cl_2 to form HCl. In dry containers there is no reaction for a long period of time however, when there is moisture in the reaction vessel, it occurs easily. So, it is considered that the catalyst can initiate a reaction.

(6) A catalyst does not affect the final position of equilibrium.

In a reversible reaction the catalyst accelerates both of the forward and the backward reactions equally so, the equilibrium constant remains unchanged (as long as the reaction temperature is constant). For example, consider the reaction between the reactants A and B to form the products C and D as follows: A + B = C + D.

At the beginning of the reaction the concentrations of A and B are at maximum value and therefore the rate of the forward reaction is highest. After a certain time, the concentrations of both A and B decreases so the forward reaction rate decreases till the equilibrium is established.

On the other hand, at the beginning of the reaction the concentrations of both of C and D are zero and hence the rate of the backward reaction is zero. As the time passes, the rate of the reverse reaction increases (because the concentration of C and D increases with time) till the equilibrium is established. The rates of the forward reaction and the reverse reaction then are equal at equilibrium but the time required for establishing equilibrium is shorter in case of the catalyzed reaction. The catalyst used in the process shortens the time required to attain equilibrium but cannot supply the required energy to change the equilibrium constant and thus cannot alter the % yield.

(7) Effect of temperature: a change in the catalytic reaction temperature changes the reaction rate as it does for the same reaction in the absence of the catalyst. However, some catalysts are physically changed (coagulated) by increasing the reaction temperature and as a result their catalytic activity decreases. An example of this phenomenon is the colloidal

solution of platinum, an increase in the temperature may cause coagulation for its particles and a corresponding decrease in its activity. In such cases where increasing the temperature affects the nature of the catalyst, the optimum temperature (where the catalyst exhibits maximum efficiency) should be determined practically.

Catalytic poisoning

The presence of small amounts of certain impurities with the reactants makes the heterogeneous catalyst ineffective. The substance which destroys the activity of the catalyst is called a poison and the process is called catalytic poisoning. The poison is adsorbed on the catalyst surface and the extent by which the activity is decreased depends on the amount of poison adsorbed on the surface. The catalyst may regain its catalytic activity when the catalyst leaves the surface (desorbed). In some cases a catalytically inert compound is formed on the catalyst surface due to adsorption of the poison and the catalyst can be regenerated only by a special chemical reaction.

Examples:

(i) In the contact process for the production of sulfuric acid, presence of a small amount of arsenic (As) destroys the activity of the platinum catalyst and makes it catalytically inert.

(ii) In Haber process for the production of ammonia, the presence of carbon monoxide (CO) with hydrogen reduces the activity of the catalyst and decreases the rate of the reaction.

(iii) In the catalytic decomposition of hydrogen peroxide, presence of hydrogen cyanide (HCN) destroys the activity of the catalyst.

Activation of catalysts

It is generally important to increase the activity of the catalysts in different catalytic processes. A well-known approach by which the activity of the catalyst can be increased is by the addition of a small quantity of a second material to a catalyst to increase its activity. The substance which promotes the activity of a catalyst is called a promoter. In Haber process for the production of ammonia, aluminum oxide is used to activate iron (the catalyst). Copper and tellurium increase the activity of nickel catalyst in the hydrogenation of oils. The action of activators can be explained by the changes in the lattice parameters, like spacing and the increase in the amount of peaks and cracks on the catalyst surface and also, the adsorbed molecules probably become more active on the surface of the catalyst in the presence of the activator.

Autocatalysis

When one of the products of a reaction acts as a catalyst for that reaction, the phenomenon is called autocatalysis. For example, when copper reacts with nitric acid, the reaction rate increases after the formation of nitrous acid during the reaction. Also, during the hydrolysis of ethyl acetate, the speed of the reaction increases after the formation of acetic acid which catalyze the reaction as an autocatalyst.

The rate of reaction between potassium permanganate and oxalic acid increases after the formation of Mn^{2+} during the reaction. This ability of Mn^{2+} to speed up the reaction can be noticed when Mn^{2+} is added in the beginning of the reaction, where the reaction occurs at high speed.

Activation energy

A reaction occurs by the collisions between the reactant molecules. At low temperatures, the molecules do not have enough energy so the collisions are not effective. No reaction occurs between molecules unless they have a minimum amount of energy (the activation Energy). Increasing temperature increases the kinetic energy of the molecules and increases the chance for an effective collision leading to a reaction.The activated molecules on collision form an activated complex at first. As a result of breaking of bonds and formation of new ones, the activated complex dissociates to yield molecules of the product.

The role of the catalyst

The catalyst decreases the activation energy of the reaction by providing a new pathway for the reaction. In the presence of the catalyst a larger number of effective collisions occur compared with the number of effective collisions of the same reaction without a catalyst (at the same temperature) and thus the presence of the catalyst speeds up the reaction.

Theories of catalysis

(1) The Intermediate Compound Formation Theory:

The intermediate compound formation theory explains homogeneous catalytic reactions. The catalyst role according to this theory is to provide a new pathway of lower activation energy for the reaction. The catalyst forms an intermediate compound with one of the reactants. The intermediate compound is highly reactive and it reacts with the second reactant to yield the product and the catalyst is regenerated. Consider the general reaction:

$A + B + [C] \rightarrow AB + [C]$

According to this theory the reaction proceeds as follows:

$A + C \rightarrow AC$

$AC + B \rightarrow AB + C$

Example 1

$\mathbf{2C_2H_5OH + [H_2SO_4] \rightarrow C_2H_5OC_2H_5 + H_2O + [H_2SO_4]}$

$\mathbf{C_2H_5OH + H_2SO_4 \rightarrow C_2H_5HSO_4 + H_2O}$

$\mathbf{C_2H_5HSO_4 + C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2SO_4}$

Example 2

$\mathbf{C_6H_5COCl + C_6H_6 + [AlCl_3] \rightarrow (C_6H_5)_2CO + HCl + [AlCl_3]}$

a- $\mathbf{C_6H_5COCl + AlCl_3 \rightarrow C_6H_5COClAlCl_3}$

b- $\mathbf{C_6H_5COClAlCl_3 + C_6H_6 \rightarrow (C_6H6)_2CO + HCl + AlCl_3}$

Example 3

$\mathbf{SO_2 + O_2 + H_2O + [NO] \rightarrow H_2SO_4 + [NO]}$

a- $\mathbf{O_2 + 2\,NO \rightarrow 2NO_2}$

b- $\mathbf{NO_2 + SO_2 \rightarrow SO_3 + NO}$

c- $\mathbf{SO_3 + H_2O \rightarrow H_2SO_4}$

(ii) The adsorption theory

Here the main function of the catalyst is to adsorb the reacting molecules on its surface. Adsorption increases the concentration of the reactants on the surface and the reaction rate increases (the law of mass action).

(iii) The Modern Theory of Contact Catalysis

This theory combines the intermediate compound formation theory and the adsorption theory. The free valence electrons on the catalyst surface play an important role in the catalytic reaction according to this theory. Due to the presence of these free electrons on the catalyst surface it becomes a center of attraction for the reacting molecules which form chemical bonds with the surface and become more active.

. . . .
. . . . Ni-Ni-Ni-Ni. . . . . .
. . . . Ni-NIi-Ni-Ni . . . . . .
. . . . Ni-Ni-Ni-Ni . . . .
. . . . Ni-Ni-Ni-Ni . . . .

The mechanism of heterogeneous catalysis involves four steps according to this view:

1. Adsorption of the reactant molecules (chemisorption)

2. Formation of an activated complex: this unstable intermediate is formed when adjacent reacting molecules join or attaches one another.

3. Decomposition of the activated complex to form the products.

4. Desorption of products molecules: the products particles then are desorbed or they leave the catalyst surface for new reactants.

The modern theory of contact catalysis explains:

(i) Why subdivision of the catalyst makes it more efficient: subdivision increases the surface area of the catalysts and increases the number of free valence electrons on the solid catalyst surface. Colloidal Pt is an efficient catalyst and also metals in a state of fine subdivision (or in the colloidal state) are rich in free valence electrons and accordingly they are more efficient catalysts than when they exist in their bulk forms.

(ii) The phenomenon of catalytic poisoning: The poison molecules block the free valence bonds on the catalyst surface due to preferential adsorption of the poison molecules on the surface or due to some chemical combinations of the reacting molecules with the surface.

(ii) Why promoters increase the efficiency of the catalyst: A promotor increases the valence bonds on the catalyst surface and it changes the crystal lattice dimensions and thereby increasing the surface active sites.

H------------- H

------ Ni ------Ni --------------- Cu

------ Ni ------Ni -------------- Ni

(iv) It explains the specificity of the catalysts.

ACID–BASE CATALYSIS

Many homogeneous catalytic reactions are known where the catalyst is an acid or a base. These reactions are referred to as acid-base catalysts. Catalysis is brought about by protons supplied by the strong acid and in base catalysis the catalysis is caused by OH^- ions supplied by the strong bases. As was mention before, the inversion or hydrolysis of cane sugar in the presence of sulfuric acid is an example for this kind of catalysis. Another example for acid-base catalysis is the reaction between acetic acid and ethanol to form ethyl acetate in the presence of sulfuric acid.

Surface Chemistry

Adsorption and Adsorbents

Adsorption is a surface phenomenon in which some material molecules are concentrated at the surface of a solid (or a liquid). It is important to distinguish adsorption which is a surface phenomenon from **absorption**. As was previously mentioned, adsorption is a surface phenomenon in which a layer (or more than one layer) of the molecules of a substance is formed on the surface of another substance and it is usually important to identify the nature of bonding between the surface and the molecules attached to it (the **adsorbate**). The expression absorption, on the other hand, refers to the homogeneous penetration of substance molecules into the body of a second substance as in the case of absorption of water in a sponge.

Generally, porous materials are preferred in adsorption studies due to their high surface areas.

The expression **sorption** is used to mean adsorption and absorption (when it is difficult or not important to distinguish adsorption from absorption).

There are many substances which are known as excellent adsorbents like charcoal which is well known to has high potential for the adsorption of large volumes of gases and also the removal of dyes from solutions. Alumina, silica gel, chromium oxide and zinc oxide are also known as adsorbents.

The amount of adsorbate and the strength of bonds they form with the surface depend on the nature of both the adsorbate and the adsorbent.

The adsorbents are selective, for instance, nickel has high adsorption capacity for hydrogen but adsorbs nitrogen very little.

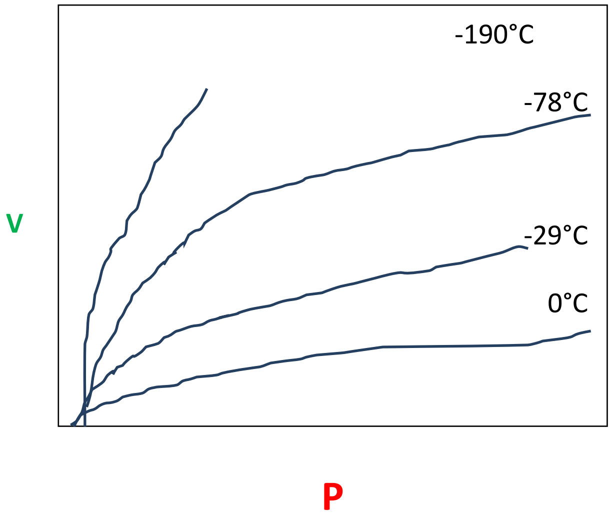
Surface area and the nature of the surface play an important role in adsorption processes.

The degree of adsorption of a gas increases with increasing pressure and decreasing temperature. Le Chatelier principle can be used to explain why adsorption decreases with increasing temperature, where adsorption is an exothermic process (meaning, heat is given out during adsorption).

Gases has a definite value for the heat of adsorption on a certain solid, however, the value of heat of adsorption is dependent on the degree of surface coverage or the amount of substance adsorbed as will be discussed later.

Adsorption isotherm

The adsorption depends on many factors like temperature, the nature of the adsorbate and the adsorbent, the concentration or pressure of the adsorbate, the amount of adsorbent …etc. In the study of the phenomenon of adsorption it is frequently desired to obtain the adsorption isotherm. The results (data) of an adsorption experiment are presented in a graph known as the adsorption isotherm. In the adsorption experiment, the amount of gas adsorbed, at constant temperature, by a certain quantity of an adsorbent (e.g. one gram) as a function of the pressure is determined and the data are presented in a graph. The graph shows the pressure (cm Hg) on the abscissa and the amount of gas (volume, cc at STP) on the ordinate, see below.



Classification of adsorption (gas/solid)

An adsorption can be classified depending on the features of the bonding forces involved whether they are physical forces or chemical ones that are responsible on the adsorption. Two main categories of adsorption can be identified (based on the observed characteristics and experimental results). The two categories are physical adsorption and chemical adsorption. It is important first to consider some thermodynamics functions related to the adsorption process:

Let us consider the following relation from thermodynamics

$\Delta G = \Delta H - \mathbf{T\Delta S}$

ΔG, is known as the free energy, ΔH, is the enthalpy and ΔS, is the entropy of the process. It is important to investigate the sign of this function for a certain process. A negative value for the free energy is required for the process to be spontaneous.

There is always heat given out due to adsorption and thus ΔH for adsorption is always negative. Also, before adsorption the gas molecules have high kinetic energy and high entropy. When they become attached to the surface due to the adsorption process, they will have lower entropy. For ΔG to be spontaneous, it must be negative and thus the value of ΔH must be more negative than TΔS.

The difference between physical adsorption and chemical adsorption

A number of points need to be clear to identify the adsorption process as a physical adsorption or a chemical one. The value of the heat of adsorption, the temperature suitable for adsorption to occur, the shape of the adsorption isotherm, if the amount of adsorption depends on the adsorbate, the adsorbent, or both, the number of layers of adsorbate molecules formed on the surface of the adsorbent and if the adsorption involves activation energy, need to be considered.

Physical adsorption

Physical adsorption involves physical forces (Van der Waals forces).

It usually occurs at heat below the b. p. of the gas and the heat of adsorption ΔH is less than about 10 Kcal/mole. This amount of energy is comparable with the heat of vaporization and condensation where the same types of forces are involved (between the surface and the gas molecules in case of adsorption and between gas molecules themselves in case of condensation and vaporization).

The quantity of gas adsorbed depends on how easy the gas is liquefied. The easier the gas is liquefied the more will be the amount of it adsorbed on the adsorbent surface.

Physical adsorption tends to have a positive slope with increasing the gas pressure where at the vapor pressure of the gas, the curve ascends vertically due to condensation.

It is also known that no activation energy is involved in physical adsorption and also the physical adsorption is reversible and multi layersare formed in that type like the adsorption of carbon dioxide on charcoal.

Chemisorption

This type of adsorption Involves chemical forces between the adsorbate molecules and the surface i.e. it involves electron transition between the adsorbate molecules and the surface, and as a result the heat of adsorption is greater than about 10 K cal/mole.

No relation exists with how easy the gas is liquefied and adsorption occurs at high temperature (remember that catalytic reactions involve chemical adsorption and occur at high temperature). The adsorption isotherm also shows an Initial steep rising (showing a strong affinity or tendency of the surface to adsorb gas molecules). At higher partial pressure the isotherm gradually flattens off, where the surface exhibits lower tendency for more adsorption.

The chemical adsorption includes formation of a chemical bond between the adsorbate molecule and the surface and therefore the quantity of gas adsorbed is a function of both the adsorbent and the gas molecules (the adsorbate).

An activation energy may be involved in the chemical adsorption and a monolayer is formed in this type of adsorption which is also irreversible like the adsorption of oxygen on carbon.

Freundlich adsorption isotherm

Freundlich adsorption isotherm can be used to study adsorption of gases on solid adsorbents and it also can be used to study adsorption from solutions. In the case of adsorption of gases on a solid, the effect of changes in gas pressure on the amount of it adsorbed by a certain amount of the adsorbent (e.g. 1 g) at constant temperature is studied. The empirical relation used is given as follows:

$$a = KP^n$$

a, is the amount of gas adsorbed by a mass unit of the adsorbent (1 g) at a pressure p of the gas.

The constants K and n are specific for the adsorbent and adsorbate at the specified conditions.

Freundlich equation can also be written in the logarithmic form:

$$\text{Log } a = \log K + n \log P$$

When the experimental results can be explained by Freundlich adsorption isotherm, n and K are determined (from slope and intercept of the straight line of log a vs. log P, respectively). It is known that Freundlich equation gives satisfactory results for experimental data in a narrow range of pressure. It also can be used for the study of the adsorption from solutions.

Adsorption from solutions

Adsorption from solutions is an important phenomenon in many different fields like color removal from solutions by activated charcoal.

Freundlich isotherm can be used to study the adsorption from solutions and the following form can be used:

$a = KC^n$

where C is the concentration of the adsorbate

It is noteworthy that adsorption from solution is more complex than adsorption of gases andonly one layer is formed.

*In chemical adsorption (chemisorption) it is supposed that only one layer of the adsorbate molecules is formed (monolayer). It is not practical to assume that more than one layer is formed in chemisorption because chemisorption requires a direct contact between the adsorbent surface and the molecules of adsorbate (contrary to physical adsorption)

*In physical adsorption many layers are presumably formed especially at low temperature and high pressure.

Langmuir adsorption isotherm

In this case, it is assumed that adsorption leads to the formation of a monolayer of the adsorbate on the adsorbent surface. Based on this assumption, Langmuir could obtain an important relation between the gas pressure and the amount of gas adsorbed at constant temperature:

The Langmuir adsorption isotherm

$p/y = a/y_m + P/y_m$

As was previously mentioned, the basic postulate is that in chemisorption a monolayer is formed. Adsorption involves attachment of the adsorbate molecules with the surface of the solid adsorbent to form adsorbed molecules. In the different stages of adsorption, some adsorbed molecules also tend to leave the surface of the adsorbent (desorption). This means that adsorption and desorption occurs simultaneously. At each stage, adsorption and desorption continues till equilibrium is established (the rate of adsorption equals the rate of desorption).

The rate of desorption is proportional to the fraction of the surface covered with adsorbate molecules (θ).

The rate of desorption = $K_1 (\theta)$

On the other hand, the rate of adsorption at any stage is proportional to the pressure (P) and also to the fraction of the surface not yet covered with molecules ($1 - \theta$).

The rate of adsorption= $K_2P (1 - \theta)$

K_1 and K_2 are the proportionality constants

At equilibrium:

$K_1 (\theta) = K_2P (1 - \theta)$and,

$\theta = P/a+P$

where, $a = (K_1/K_2)$

θ may be defined as:

$\theta = y/y_m$

y is the amount of gas adsorbed at any given pressure (P)

y_m is the amount of gas required to form a monolayer.

substitution for $\theta = y/y_m$

$y/y_m = P/a+P$

$p/y = a/y_m + P/y_m$

$1/y_m$ and a/y_m can be determined, respectively, from the slope and intercept of the straight line (p/y vs. p).

There are two cases need to be considered:

The first case:

At the first stage of the adsorption, when p is small, it can be neglected compared to (a).

So, $\theta = P/a+P$, is simplified to:

$\theta = KP$

Which means that the fraction covered θ is proportional to the pressure

The second case:

at high temperature:

a, can be neglected in the denominator so,

$\theta = 1$

This means that at high pressure and at a constant temperature the amount of gas adsorbed is constant; a case arises when the surface is completely covered with the adsorbate to form the monolayer.

The Langmuir adsorption isotherm data can be used to estimate the surface area of solid adsorbent:

Slope = $1/y_m$ and intercept = a/y_m

If y_m is the amount of gas at STP required to form the monolayer, the number of adsorbate molecules adsorbed is:

$(y_m/22.4)\ (6 \times 10^{23})$

If the area covered by one molecule is (Z)

The total surface area of the adsorbent (1 g) is:

$(y_m/22.4)\ (6 \times 10^{23})\ (Z)$

- Applications of adsorption:

Estimation of solids surface area from the data of adsorption

Chromatography, Extraction, ….. etc.

Phase rule

The phase in any system (a thermodynamic system at equilibrium) can be defined as a part of that system which is physically distinct and chemically uniform and it is separated from other parts (phases) of the system by a separation surface (which allows the transfer of mater from one phase to another) and it exists in a state of equilibrium with other phases of the system. Because different identical regions form one phase, a phase is any amount of material, which is homogeneous throughout, whether it is exists as one piece or more, and it can be separated from other phases mechanically.

The high diffusion of gases makes them completely miscible and therefore they form one phase. Liquids form one or more phases depending on their mutual miscibility. In a mixture of water and ethanol as an example, there is no surface separating them i.e. they are completely miscible at all ratios and as a result they form one liquid phase. Benzene and water, on the other hand, are immiscible and hence they form two distinct liquid phases. Partially immiscible liquids form one or more liquid phases depending on the ratio of each in the mixture.

Different solids, on the other hand, form different phases. The decomposition of calcium carbonate to form calcium oxide and carbon dioxide involves three phases, two solids ($CaCO_3$ and CaO) beside the gas phase (CO_2). Also, different allotropic forms of the same solid form different phases for example, two forms of sulfur (will be encountered when we study the sulfur system) rhombic and monoclinc form two different solid phases. One phase transfers to the other at a definite temperature depending on the pressure of the system.

In the phase rule: $F=C-P+2$, P is the number of phases which are at a state of equilibrium (on the phase diagram of a one component system, the area represents one phase, a line represents two phases at equilibrium and a triple point represents three phases at equilibrium, $p=1,2$ and 3, respectively). In the water system, there are three phases, solid (ice), liquid and vapor. The presence of aany of them or more at equilibrium depends on the values of pressure and temperature.

The number of components

The no of components of a system at equilibrium is the smallest number of the chemical species required to determine the composition of each phases and all phases in the system quantitatively. In the water system, H_2O can be used to express the composition of each phase. In the equilibrium between the solid and the vapor phase of NH_4Cl, the composition of each phase can be expressed by NH_4Cl (one component) although the vapor consists of a mixture of equivalent amounts of NH_3 and HCl. However, if conditions could be adjusted to separate HCl or NH_3 from the gaseous mixture, then the no of components is 2. In the phase rule C is the number of components (in the water system and in the sulfur system the number of components C is 1)

Number of degrees of freedom

It is the minimum no of independent variables required to completely specify the system (meaning, all the intensive properties become specified). The number of degrees of freedom is the number of independent variables that can be independently varied without the disappearance or the appearance of a new phase. In the phase diagram of a one component system for example, in any area which represents one phase, pressure and temperature cab be varied independently without appearing of a new phase or disappearance of the phase specified by this area.

On any line, which represents the equilibrium between two phases, the number of degrees of freedom is 1.Choosing a point on that line at a certain temperature, the pressure is already specified i.e there is only one pressure corresponding to this value of temperatureand changing this value of pressure will shift the equilibrium towards the area of the one phase, meaning one phase disappears.

On the triple point (at which three lines intersects) neither temperature nor pressure can be changed independently and thus the system has a number of degrees of freedom of zero. Meaning we can specify neither temperature nor pressure and the system determines this triple point. One cannot change the temperature (or pressure) and still at the same point so any change in the temperature or pressure leads to the disappearance of one phase.

Phase diagram

It is the diagram which presents the conditions (values of the variable like temperature and pressure) of equilibrium between different phases in the system. These phase diagrams help predicting the changes in phases when one of these variables (like temperature and pressure) changes and shows the conditions at which phases are stable. Two co-ordinates or three are required, respectively, when there are two and three variables are needed to specify the system completely.

One component system

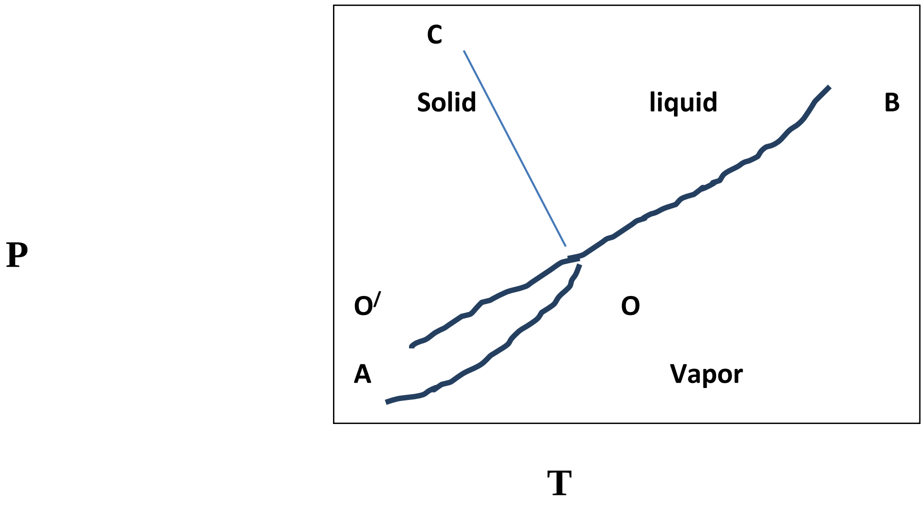
For one component systems, the maximum number of degrees of freedom is when there is only one phase, meaning: F=1-1+2 = 2. This means that phase diagrams can be established by controlling two variables, temperature and pressure to completely specify the system (the system then is bivariant and an area represents this one phase at equilibrium). Equilibria involving lower degrees of freedom in one component systems are represented by lines (the system is monovariant or univariant) when there are two phases are at equilibrium and triple points (the system is invariant) represent equilibrium between three phases in the diagrams. From the phase rule it can be predicted that the maiximum number of phases which can co-exist at equilibrium is three, 0 = 1-P+2 or P=3.

The water system

It is well known that water exists in three different states, solid, liquid and vapor.These can form three different two-phase equilibria (solid – vapor, solid – liquid and liquid-vapor) and one three –phase equilibrium (solid – liquid- vapor).

Applying the phase rule to the previous equilibria gives rise to three bivariant areas, each of which represents one of the three phases and three univariant lines. Each represent the three two phase equibria in addition to a single invariant triple point for the three –phase equilibrium state.

The phase diagram of water (below) consists of three areas representing the existence of the three phases, three curves (OA, OB and OC) each of which represent the state of equilibrium between two phases and one triple point (O) representing the equilibrium between the three phases.



Curve (OA) is the vapor pressure curve of ice or the sublimation curve of ice. It gives the vapor pressure of ice in equilibrium with water vapor at many different temperature values. There is only one pressure corresponding to any temperature where the ice and water exists in a state of equilibrium. On each curve the number of degrees of freedom is one and the system is univariant, F=1-2+2 = 1. The OA curve has a positive slope (the volume of vapor produced is larger than the corresponding volume of ice transformed) and thus the vapor pressure increases with increasing temperature.

Curve (OB) is the vapor pressure curve of water or the vaporization curve of water. It gives the vapor pressure of water in equilibrium with liquid at different temperatures. It extends up to the critical temperature and along this curve at any temperature there is only one pressure at which water and its vapor exists in a state of equilibrium. The curve also has a positive slope (for the same reason as before, the water vapor has larger volume than liquid water). The number of degrees of freedom is one and the system is univariant.

Curve (OC) represents the melting point curve of ice (or the freezing point of water). It shows how the freezing point of ice changes with pressure. It has a negative slope (notice that contrary to the previous two cases, ice volume is greater than the corresponding volume of liquid water). The degree of freedom on this curve is also one and the system is monovariant. At any chosen temperature there is only one corresponding pressure where ice and liquid water co-exists at equilibrium.

Metastable curve O**O**/: it represents the case when liquid water is cooled below its freezing point without the appearance of ice. It can be considered as an extension for curve OB. Over $OO^{/}$ water and its vapor co-exists in a state of metastable equilibrium. The supercooled water is metastable with respect to ice thus the addition of a piece of ice leads to the immediate transformation of the super-cooled water into the stable solid phase (ice). It is clear that the vapor pressure of the supercooled water is higher than that of ice.

The phase diagram is divided into three areas each corresponds to a single stable phase. The degree of freedom in each is two and the system is bivariant meaning, to define a point in an area, the two variables should be specified and also it means that one can vary independently pressure or temperature without the disappearance of this phase.

F=1-1+2 = 2.

At the triple point O (the three curves intersect and only at which ice, water and water vapor are existing at equilibrium. At this point neither temperature nor pressure can be changed. A slight change in any of the two values specified for the temperature and pressure shifts the equilibrium and results in the disappearance of one phase. The system corresponding to this state is then invariant and the degree of freedom is zero: F=1-3+2 = 0.

The Sulfur system

At room temperature rhombic is the stable phase of Sulfur. At atmospheric pressure, subtle heating converts rhomic Sulfur to monoclinc Sulfur at the transition point of about 96°C..

Monoclinic Sulphur when cooled slowly to room temperature converts back to the rhombic phase and each of the two solid forms of Sulfur can be co-existed together in equilibrium with vapor or with liquid.

When rhombic phase Sulfur is subjected to a high rate of heating it does not transfer to the monoclinic phase but persists in the rhombic phase till melts at a temperature lower than the melting point of the monoclinic phase at the same pressure.

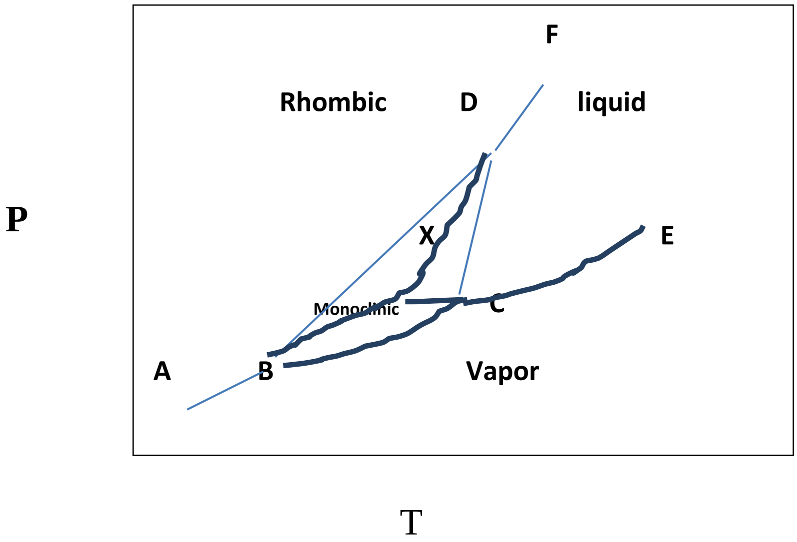
Sulfur then has four phases (two solid phases, liquid and vapor).

From the phase rule it can be predicted that the four phases cannot co-exist at equilibrium because the number of degrees of freedom cannot be a negative.

F= 1-4+2 = -1

It also can be predicted from the phase rule that the phase diagram of the Sulfur system consists of four areas, corresponding to the four different single pure phases. Taking into consideration the three-phase equilibria, there will be four triple points corresponding to the four possible three-phase equilibria: Rhombic – monoclinc- vapor, Rhombic –monoclinc-liquid, Rhombic-liquid-vapor and monoclinic-liquid-vapor.

In addition, there should be six lines for the six two-phase equilibria: Rhombic –vapor line (AB), Rhombic-monoclinic (line BD), Rhombic-liquid (line DF), monoclinic-liquid (line CD), monoclinic-vapor (line BC) and finally, the vapor-liquid equilibrium (line CE).



The metastable equilibrium at X is only observed when there is a rapid change of the temperature so that there is no sufficient time for the slow phase transition (rhombic to monoclinic).

Heating rhombic Sulfur slowly will convert to monoclinc at a point on (BD) then melts at a point at (CD) and boil at a point on (CE). However, if the heating rate is fast, Rhombic will melt at a point on (XD) and melt at a point on (CE).

It is obvious that from the Sulfur system that no additional information can be extracted from the phase rule to distinguish metastable equilibria.

Colloidal solutions

Thomas Graham classified soluble substances as colloids and crystalloids. This classification is based on the ability of their solutions to diffuse across vegetable or animal membranes. Crystalloid solutions are able to pass across such membranes but colloid solutions cannot. However, by using suitable methods, any substance can be prepared in the colloidal conditions or the colloidal state. Particle sizes in colloidal solutions are between those of true solutions (less than about 10 Angstrom= 1 nm) and those of coarse suspensions (more than about 1000 Angstrom= 100 nm). Particles in a colloidal solution therefore cannot be seen by the naked eye or by the ordinary microscope (compare particle size in a colloidal solution with the wavelength of visible light) But due to the ability of colloidal particles to scatter light, halos are formed around them when they illuminated by a converging beam of light. Colloidal particles therefore can be seen under the ultra-microscope which uses an intense converging beam of light. The photographs of colloidal particles can be obtained by using the electron microscope (a beam of electrons of very short wavelength is used in the electron microscope, $\lambda=h/mv$).

Colloidal solutions are heterogeneous systems. This means that a colloidal solution comprises two phases. The first phase is the dispersion medium (or the outer phase) and the second is dispersed phase (or the inner phase).

Different systems can be encountered due to different combination of phases: a gas dispersed in a liquid, a gas dispersed in a solid, a liquid dispersed in a gas,a liquid dispersed in a liquid, a liquid dispersed in a solid,a solid dispersed in a gas, a solid dispersed in a liquid (sol) and a solid dispersed in a solid. Two gases cannot form a heterogeneous system due to the diffusion rates. Among the previous systems, sols will be studied in some details.

Sols

As was mentioned before, a solis a heterogeneous system in which a solid, having particles in the range 1-100 nm, is dispersed in a liquid. Sols formed by dispersing a solid in water, as the dispersion medium, are called hydrosols.

Hydrophilic sols are formed when substances directly form sols with water. These are reversible sols. When precipitated, (coagulated) reversible sols can directly be reconverted to the colloidal state. Hydrophobic sols, on the other hand, are formed when the substances to be transformed to the colloidal sate do not directly form sols with water. These are Irreversible sols and therefore, when precipitated they cannot directly be reconverted to the colloidal state.

Preparation of colloidal solutions

A colloidal solution can be prepared either by breaking up a substance (in its bulk form) to get it dispersed in the dispersion medium with its particles in the range of colloidal size or by allowing ions or molecules of a substance to form larger particle shaving dimensions in the colloidal range. These two approaches may be referred to as the dispersion methods and the condensation methods, respectively, for the preparation of colloidal solutions.

A number of methods like the mechanical dispersion, ultrasonic dispersion, electro- dispersion and peptization can be used to reduce the dimensions of the particles of a substance to the dimensions of the particles in the colloidal state (1-100 nm). On the other hand, excessive cooling, lowering the solubility (by exchanging of the solvent), passing of a vapor of an element into a liquid and the chemical action belong to thesecond approach.

Dispersion methods

Mechanical dispersion

In mechanical dispersion, the substance is grounded, shaken with the dispersion medium and then passed to the colloid mill. The disc mill consists of two metal discs (nearly touching each other) rotating at a high speed in opposite directions. Particles of the coarse suspension (due to the shearing force between the two discs) yield particles having sizes in the colloidal range. The ball mill also is used for preparation of colloidal solution. Due to the special design of its internal surface and the high speed rotation of the ball mill, a coarse suspension is transformed into a colloidal dispersion.

Dispersion by ultrasonic vibrations

Ultrasonic vibrations also can cause the transformation of a coarse suspension to the colloidal dimensions. The mercury sol in water, in the presence of a stabilizing agent like citrate, can be prepared by this method.

Electro dispersion: The Bredig’s arc method consists in striking an arc between two electrodes (immersed in the dispersion medium) of a metal. Due to the intense heating of the arc the metal, which is to be transformed into the colloidal state, is vaporized at first and thenimmediately condensed in the cooled dispersion medium.Traces of an electrolyte (KOH) is used to stabilize the obtained sol.

Peptization: peptization is the converse of coagulation (coagulation occurs when a colloidal solution is broken down due to aging or removing the charge from the surface of dispersed particles, ..etc). In this case a colloidal solution is obtained as a result of the dispersion of a coagulated sol. A freshly prepared $Fe(OH)_3$-for example-when treated with $FeCl_3$ (used as a peptizing agent) forms a sol.

Condensation methods

Excessive cooling: e.g. a colloidal solution of ice in an organic solvent can be prepared by freezing a solution of water in the organic solvent.

Chemical actions: Like precipitation, oxidation, reduction, hydrolysis…etc.

Precipitation: when the solubility of the substance is small (like As_2S_3) it can be prepared by precipitation:

$As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$ (double decomposition)

Oxidation: $H_2S + O \rightarrow H_2O + S$

Reduction:

$2AuCl_3 + 3SnCl_2 \rightarrow 3SnCl_4 + 2Au$

$2H_2S + SO_2 \rightarrow 2H_2O + 3S$

Hydrolysis:

$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$

Properties of colloidal solutions:

1- Heterogeneity: A colloidal solution is a heterogeneous system consists of the dispersion medium like water and the dispersed phase (small particles of a substance). The ultramicroscope can be used to detect particles of the colloidal solution and photograph of the particles in a colloidal solution can be obtained by using the electron microscope.

2- The large increase in surface area. Due to the high surface area of colloidal systems, they exhibit a large increase in the surface chemical energy, adsorption capacity and catalytic efficiency.

3- Osmotic pressure: if a true solution is transformed to a colloidal solution, the osmotic pressure of the resulting colloidal solution is less than that of the original true solution. This is because of that osmotic pressure depends on the number of species in the solution. The number of species is greater in the original true solution.

4- Tyndall effect: particles of the colloidal solution scatter light. As a consequence, the path of a beam of light passing through the colloidal solution becomes illuminated and visible when observed from the side.

5- The Brownian movement: The suspended particles are in a constant zig-zag motion due to the collision between particles of the dispersed phase with particles of the dispersion medium. The Brownian movement becomes more intense as the particle size decreases.

6- Filterability: Colloidal solutions are heterogeneous and colloidal particles can be separated by ultrafilters.

7- Electrical properties: Particles of colloidal solutions have a charge on them due to: (1) the selective adsorption: when preparing a colloidal solution of (XY), the charge on (XY) depends on the adsorbed ion, whether it is X^+ or Y^-. This largely depends on which of these two ions exists in excess during preparation.

(2) self-dissociation: soap ($C_nH_{2n+1}COONa^+$) dissociates in solution to give ions. The hydrocarbon part of the molecules (negatively charged) have high affinity for one another and as a result they form molecular aggregates having sizes of the colloidal state. (3) Presence of acidic or basic groups: e.g. the protein molecule $H_2N\text{-}X\text{-}COOH$, the ionization and charge on molecules depend on the pH value. The molecules become positive $^+H_3N\text{-}X\text{-}COOH$ or negative $H_2N\text{-}X\text{-}COO^-$ depending on the pH value.

Isoelectric point:

The particles of the colloidal solution move under the effect of an electric field. The protein molecules are positive or negative depending on the pH. By changing the pH value, the type of charge on the molecule can be changed.For example from positive (+) to negative (-) andas a result, the direction of motion in the field is reversed. The isoelectric point is the pH where the protein molecule is neither negative nor positive, and hence do not move under the effect of the electric field.

8- Cataphoresis (electrophoresis): Because colloidal particles carry a charge on them, they migrate to the electrode of the opposite charge in an electric field. Cataphoresis is thus used to determine the type of charge on the colloidal particles.

9- electro osmosis: When the charged particles of a colloid is maintained stationary in the electric field, by using a diaphragm in the U-tube used for the experiment, the dispersion medium would move.

10- Color: The color of the colloidal solution depends on the wavelength of the scattered light, which in return is dependent on the particles sizes.

11- Coagulation: coagulation occurs when the particles of the dispersed phase precipitate due to breaking up of a colloidal solution due to the addition of an electrolyte (due to the neutralization or the removal of the charge from the particles surface). Aging also may result in the breaking up of a colloidal solution and its coagulation.