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Catalyst and catalysis

Definition:

Generally, the process by which a catalyst affects a reaction, speeds up or slows down, is called catalysis.

A catalyst is defined as any substance “organic, synthetic, or metal” that works to accelerate a chemical reaction by reducing its activation energy (E_a) without affecting in any way the possibilities for this reaction within a chemical system.

Scientifically, catalyst within the catalysis lowers the value of activation energy and therefore increases the rate of reaction, without being consumed in the reaction and without it is changing the original energies (i.e. enthalpy “ΔH” or free energy “ΔG” states) of neither the reactants nor the products. Therefore, the required energy to allow the reactants to enter the transition state to react and thereby to initiate the reaction is seen to be extensively reduced by applying the more stable and active catalyst to the reaction.

E_a is the activation energy in kJ.mol^{-1}, which is defined as the energy that must be overcome in order for a chemical reaction to occur, it may otherwise be denoted as the minimum energy necessary for a specific reaction to occur. The classical exponential law of Arrhenius can be applied to estimate the kinetic parameters for the reaction:

$$k = A.\exp\left(-E_a/RT\right)$$

Where k is the rate constant (i.e. reaction rate coefficient), A is the attempt frequency of the reaction (i.e. an empirical relationship between the temperature and the rate coefficient), which denotes the total number of collisions between reactant molecules having the correct orientation so as to lead to products, T is the absolute reaction temperature in degree Kelvin (i.e. the reactor bed temperature), and R is symbolized as the molar gas constant with the value of 8.314×10^{-3} kJ.mol$^{-1}\cdot$K^{-1}. The Boltzmann constant ($K_B = 1.38066\times10^{-23}$ J.K^{-1}) is usually used instead of the gas law constant, when E_a is given in molecular units (i.e. Joules per molecule).

Adding the catalyst diminishes decomposition temperature and promotes decomposition speed, hence makes a chemical process more efficient and reduces pollution by saving energy while minimising unnecessary products and by-products.

For example; the following chemical reaction reaches the equilibrium at 50% of the conversion of SO_2 into SO_3 as shown in Figure 1:

$$SO_2 + {}^1\!/_2 O_2 \xleftrightarrow{753K,1.013bar} SO_3$$

Using the catalyst leads to reduce both the reaction time and the cost by means of increasing the speed of the reaction.

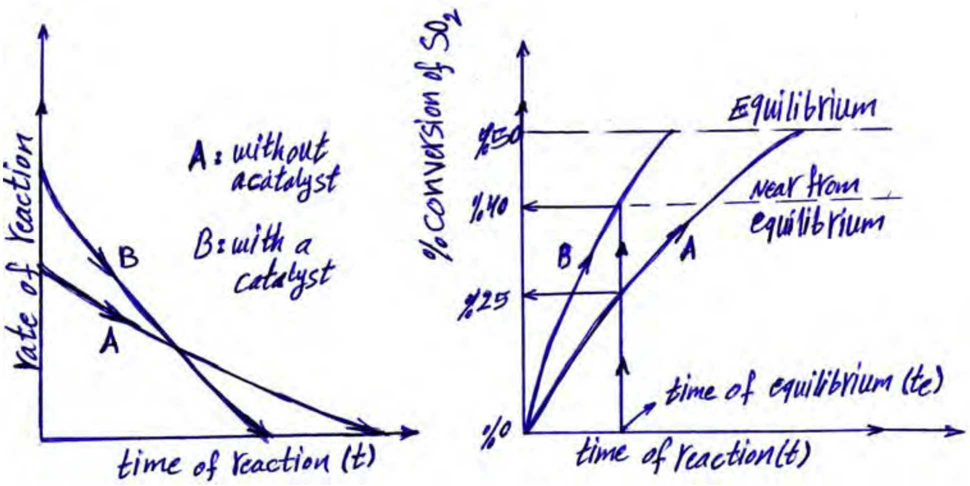


Figure 1: The effects of the catalyst on both the time and the rate of chemical reaction.

In fact, the possibilities for the reaction described in terms of thermodynamics by means of the Gibbs free energy of the materials involved in the reaction – the reaction proceeds spontaneously if $\Delta G < 0$ and vice versa, as shown in Figure 2.

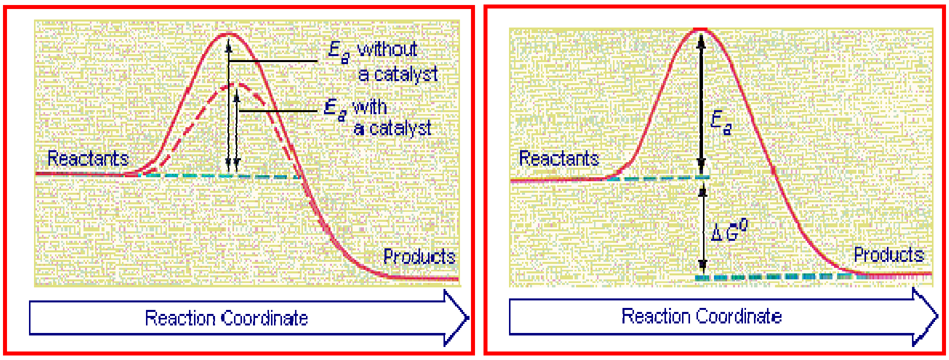


Figure 2 The left diagram shows that reactants can be converted into products, when the free energy of the system overcome the activation energy for the reaction, while the right diagram shows that catalysts provide a new mechanism by supplying acidic sites for the adsorption and dissociation of the reactants in order to increase the rates of reactions.

The change in free energy (ΔG), which is related to the reaction enthalpy (ΔH) and reaction entropy (ΔS) by the equation:

$$\Delta G = \Delta H - T.\Delta S$$

is equal to the difference between the respective energies of formation of products and reactants from their elements at the reaction temperature (T) :

$$\Delta G = G\ \text{(products)} - G\ \text{(reactants)}$$

In terms of partial pressures (P), the equilibrium constants (Kp = [P (products) / P (reactants)], is given by the expression:

$$\Delta G = -R.T.\ \ln Kp$$

$$Kp = \exp\left(\frac{\Delta S - \dfrac{\Delta H}{T}}{R}\right)$$

Where ΔH is the enthalpy of transition (KJ.mol^{-1}), which measures the heat content. Changes of state or phase of matter are also accompanied by enthalpy changes, and if ΔH is positive, the reaction is endothermic such as in a melting process – heat is absorbed by the system. In contrast, if ΔH is negative, the reaction is exothermic such as in a freezing process – heat is desorbed from the system.

According to the transition state theory the activated complex can be formed by either the left or the right diagram as shown in Figure 3.

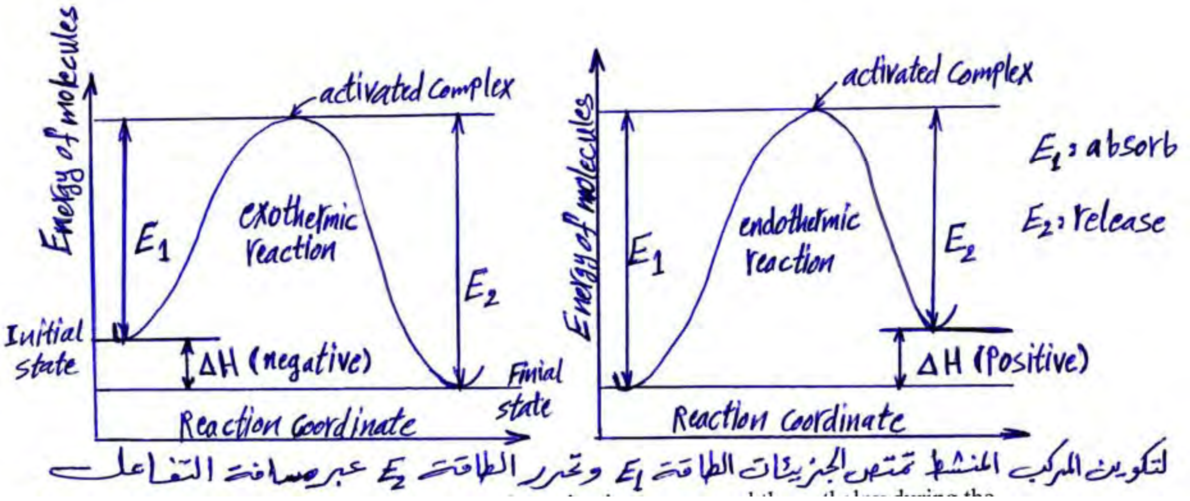


Figure 3: The relationship between the activation energy and the enthalpy during the reaction.

Classification of catalyst:

A catalyst can be either hetero-geneous or homo-geneous with bio-catalysts (enzymatic) are often seen as a separate group. Accordingly, there are two types of reactions:

1- Homogenous Reaction

In this type of reaction both the catalyst and the reactants are existing in the same phase (e.g. either the catalytic reactions in most of the liquid phase or the noncatalytic reactions in most of the gaseous phase).

2- Heterogeneous Reaction

In this type of reaction the catalyst and the reactants are existing in the different phase, as in the case of the following catalytic reactions:

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{Pt(s)} 2NH_{3(g)}$$

$$2NH_{3(g)} + 4O_{2(g)} \xrightarrow{Rh(s)} N_2O_{5(g)} + 3H_2O_{(g)}$$

$$C_4H_{10(g)} \xrightarrow{Pt(s)} C_2H_{4(g)} + C_2H_{6(g)}$$

$$CO_{(g)} + 2H_{2(g)} \xrightarrow{pt(s)} CH_3OH_{(g)}$$

Or in the case of the following noncatalytic reactions:

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$$

$$PbS_{(s)} + \frac{3}{2}O_{2(g)} \longrightarrow PbO_{(s)} + SO_{2(g)}$$

$$Zn_{(s)} + 2HCl_{(l)} \longrightarrow ZnCl_{2(l)} + H_{2(g)}$$

$$Zn_{(s)} + 2NaOH_{(l)} \longrightarrow Na_2ZnO_{2(l)} + H_{2(g)}$$

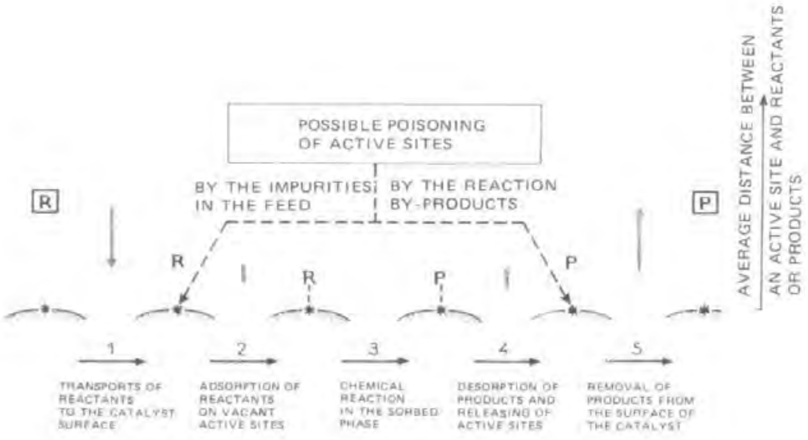
$$SO_{2(g)} + 2NaOH_{(l)} \longrightarrow Na_2SO_{3(l)} + H_2O_{(l)}$$

$$NH_{3(g)} + HCl_{(l)} \longrightarrow NH_4Cl_{(l)}$$

Mechanisms of heterogeneous catalysis:

Theoretically, the overall reaction that takes place throughout the active sites on the catalyst's surface follow a five-step mechanism, as shown in the schematic diagram in Figure 4. These stages are: –

1- Thermal decomposition, generally after the transport of reactants from the homogeneous phase (i.e gaseous or liquid) to the solid surface.
2- Primary catalytic reaction following absorption of reactants on specific sites of the surface so as to produce the intermediate chemisorbed species.
3- Secondary reactions between primary products in the sorbed phase.
4- Desorption of the products from the sorbed phase to release the sites.
5- Removal of the products from the catalyst surface into the homogeneous phase, and accumulation of polymerizable products from further reaction by their adsorption on the surface of the catalyst as coke.



(*) Active site on the surface of the catalyst

Fig. 2a. Elementary steps of heterogeneous catalysis.

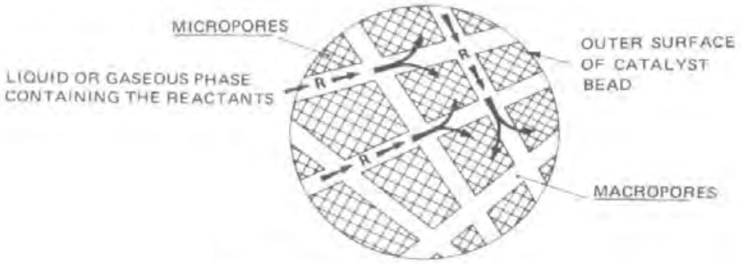


Fig. 2b. Porosity of a solid catalyst.

Figure 4 **(a)** Reaction occurs on the catalyst surface "heterogeneous catalysis", **(b)** Porosity

Properties of heterogeneous catalysts:

Heterogeneous catalysis is the common attractive method for activating reactions that are thermodynamically possible but which occur at a very slow rate because of their chemical kinetics. Since heterogeneous catalysis is a surface “interface phenomenon”, the catalysts need a large surface area often expressed in $m^2.g^{-1}$ to provide a sufficiently high activity. The highly porous structures of zeolites, containing a three dimensional network of channels, make them ideal as industrial catalysts, especially as it is possible to modify their porosities and activities to selectivity minimize as much as possible the formation of by-products. Therefore, this kind of catalyst is utilized to realize a maximum conversion of the feedstock by increasing the rate of reaction. In addition, the catalyst must has a good thermal stability (i.e. temperature at which it decomposes upon heating at a constant rate) and is highly resistance to chemical agents during catalysis.

Moreover, zeolite catalyst has a high diffusivity – an important physical property required for a commercially successful operation, which characterizes the ability of fluids to diffuse throughout the zeolite structure. As such, the mass transfer of the reactants to the active sites is increased, making possible the use of higher space velocities of hydrocarbons often expressed in $time^{-1}$ and lower residence times in the reactor chamber. Additionally, most recent zeolitic or molecular sieve catalysts, as they are also known, have a good hardness and are able to resist attrition and abrasion, meaning that each catalyst particle is able to hold its shape. The choice of catalyst for any specific purpose is depending on the operating conditions, feedstock, product demands and the cost of process.

Catalytic properties of zeolites:

Zeolites can operate both as ion-exchange materials and also reversible adsorption systems for water or small organic molecules, with a potential capacity of more than 25% of the framework weight; however the two most significant properties for zeolites are acidity and porosity. The acidity of a zeolite is usually responsible for the catalytic activity of catalysts, whilst the porosity is responsible for the catalytic selectivity during the reactions. These catalytic properties can be modified to provide enhanced flexibility across a range of applications.

A- Catalytic activity of zeolites:

Zeolites are mostly employed as acid catalysts, with the catalytic activities of zeolites attributed to the generation of strong acidic sites on their surfaces. Electron pair acceptors or Lewis acid sites (L) and proton donor or Brönsted acid sites (B), are both found in zeolites with the former resulting from the rupturing of hydroxyl bridges between aluminium and silicon atoms in the framework, and the latter resulting from the hydroxyl bridge that forms as shown in Figure 5. The Brönsted acid site is formed when the negatively chared aluminium framework is counter-balanced by proton (H^+), such that it is necessary to replace the cations present in the freshly synthesized zeolite with protons, for instance by substitution of sodium ion (Na^+) with an ammonium ion (NH^+_4). A high temperature calcining process is then required to drive off the ammonia and leave a protonated form of the zeolite. In other circumstances where the zeolite is not protonated, a trigonally coordinated Al-atom possessing a vacant orbital is produced that can accept an electron pair and acts as a Lewis acid site.

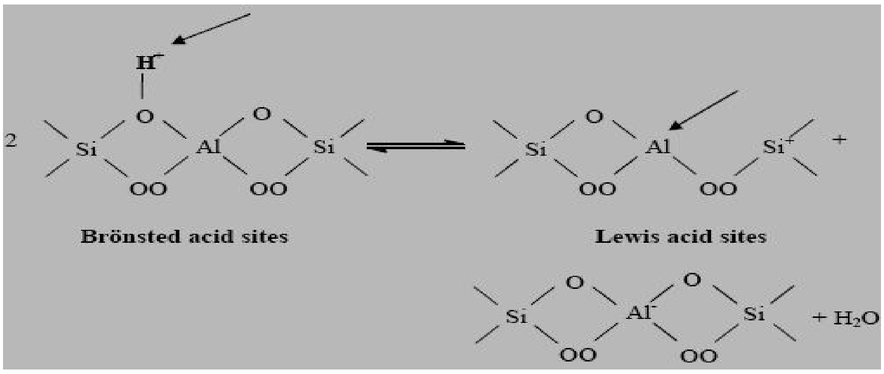


Figure 5 Reversible formations of the classical Lewis and Brönsted acid sites.

The activity of a zeolite catalyst may be defined by: (a) the strength of acidity, (b) the acid sites density, and (c) the accessibility of the bridging hydroxyl groups, which act as Brönsted acid sites. Undoubtedly, a decrease in the number of Al-atoms in the framework “high Si/Al ratio” causes a decrease in the density of Brönsted acidity of a zeolite, but may also increase the single acid site “proton donor” strength. By decreasing the Al content, the charge density of anions “hydroxyl groups within the framework” decreases and leads to less intense interaction of OH-groups whitin the framework, thereby increasing the ease of proton transfer from the surface site to the adsorbed base. Thus, the overall catalytic activity of a zeolite can be enhanced.

B- Catalytic selectivity of zeolites:

A catalyzed chemical reaction frequently takes place within the zeolite pores, internal channels or cavities, and therefore there are size restrictions on the reactants, products, or transition states intermediates. The maximum free pore diameters (Ø) must thus significantly influence the shape-selectivity phenomenon.

Usually, shape selective catalysis is applied either to increase yields of a preferred product or to hinder undesirable reactions, and the desire for precise control over selectivity means that the heterogeneous catalysis is more favourable than the homogeneous one for cracking reactions, since the pore size depends on the type of cation present within the zeolite framework – e.g. a monovalent cation such as potassium or sodium reduces the actual pore size of zeolite-A to below 0.4 nm. However, the pores enlarge slightly at higher temperatures, which can then allow the diffusion of molecules into or out-of the channel systems throughout the reaction. Whilst there are many factors impacting shape selectivity, the zeolite frameworks may be modified for specific applications.

Weisz and Csiscery have shown that zeolite shape-selectivity can be divided into three main categories, described with mechanisms shown in Figure 6 A, B and C:

A- Reactant selectivity: This arises when some of the reactant molecules are too large to enter the zeolite channel system and products are only formed from those molecules that are able to diffuse through the catalyst pores.

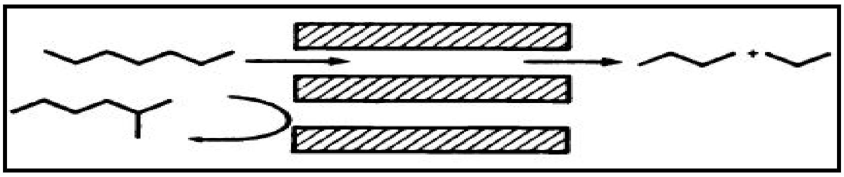


Figure 6 **(A)** Reactant selectivity.

B- Product selectivity: This arises when some of the product molecules created inside the channel systems are too large to transport out of the zeolite structure. They either deactivate the catalyst or are converted by cracking to less bulky molecules, which then escape from catalyst pores.

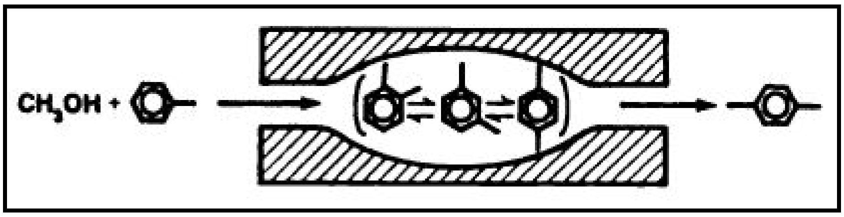


Figure 6 **(B)** Product selectivity.

C- Restricted transition-state selectivity: This arises when some transition state molecules are too large to form in the zeolite channels or cavities because those molecules would require more space than available. Both reactant and product molecules are prevented from dispersing through the pores and only the possible product molecules from the transition states are produced in the void space.

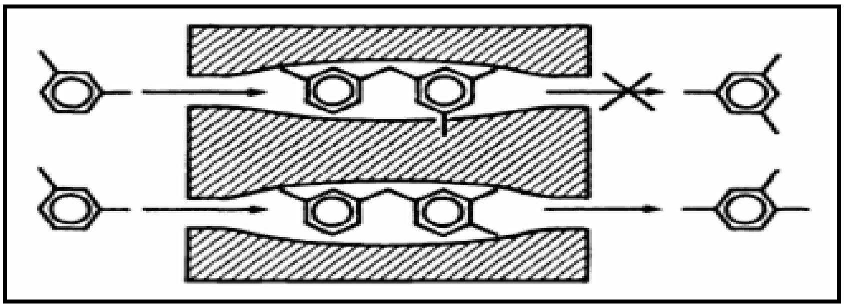


Figure 6 **(C)** Restricted transition-state selectivity.

Surface area of solid catalysts:

BET-surface area measurements are generally based on the phenomenon of gas adsorption-desorption isotherm. The two processes are based on the same principle, but one is reversed to the other. The adsorption takes place when the gas molecules contact the surface of the solid material and a film of the adsorbate is formed. The gas atoms are taken up by the solid surface e.g. the accumulation of N_2-gas molecules on the zeolite surface – adsorption is different to absorption, in which molecules diffuse into a liquid or solid to form a solution and that's why, it refers to a volume rather than a surface. In essence, the process simultaneously encompasses both adsorption and absorption is called sorption.

Irving Langmuir in 1920 published a theory to develop the sorption data, which is known as a Langmuir-isotherm. The theory assumed that the adsorbed gas at a fixed temperature and gas pressure could be adsorbed from only one layer of adsorbate on the solid surface. Few years later around 1938, three scientists, Brunauer, Emmett and Teller modified and optimized Langmuir's theory by using the hypothesis of multilayer gas adsorption. Thus, a new theory was evolved, which was called BET-isotherm. The pore structure and the total surface area, which includes all the internal structure of solid catalyst, can be calculated using BET-method.

Brunauer, Deming, Deming and Teller also classified the isothermal adsorption into five different types as exposed in Figure 7. The Van der Waals adsorption isotherm type-I is the category that commonly expresses the crystalline microporous materials such as zeolite, while the other exhibited types are relevant examples of the adsorption isotherm for other porous materials. The shape of the adsorption or desorption branch may be mechanistically attributed to the pore structure of a solid. Such that the analysis of the adsorption-desorption hysteresis loop is essential in order to get a complete picture about the main structure of the pores in the sample. The formation of mesopores, less of micropores, within the structure normally gives rise to adsorption-desorption hysteresis loops. Generally, a total pore volume of solid "adsorbent surface" can easily be found, if the density of gas "adsorbate" is known.

According to the international union of pure and applied chemistry (IUPAC), the classification is as follows; Micropores: $d_p \leq 2$ nm, Mesopores: 2 nm, $< d_p \leq 50$ nm and Macropores: $d_p > 50$ nm, with d_p being the pore diameter. In these pores, the dissolved organic molecules with appropriate sizes to fit into the catalyst pores are adsorbed during the reaction.

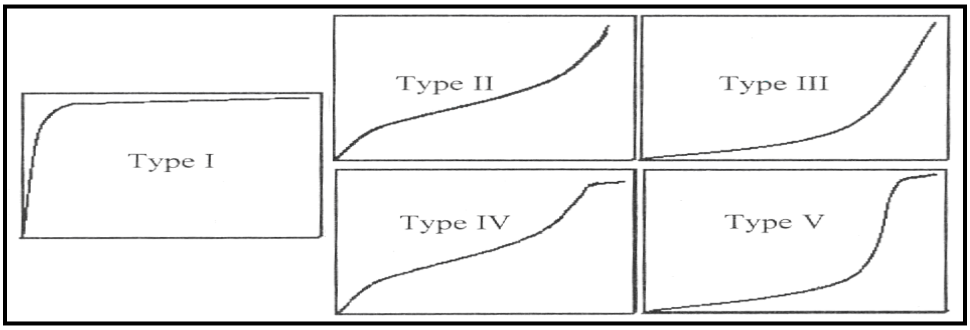


Figure 7 The adsorption isotherm curves according to BDDT-classification.

Determination of surface area of catalyst:

Langmuir treatment of adsorption was assumed that all the surface of the catalyst has the same activity for adsorption under the same mechanism and there is no interaction between the adsorbed molecules. In addition, the adsorption is limited (less than one) to complete coverage by a monomolecular layer – as such the catalyst surface may be divided into two parts:

1- ϴ: is the fraction covered by the adsorbed molecules, and
2- 1 - ϴ: is the fraction of bare surface (uncovered part of the surface).

Since, the rate of adsorption per unit of total surface is equal to;

$$r_a = kp(1-\theta)$$

Where; k is a constant, and p is a gas pressure (equilibrium adsorbate pressure)

And the rate of desorption is equal to;

$$r_d = k'\theta$$

The langmuir isotherm can then be obtained at the equilibrium (at $r_a = r_d$) as follows;

$$\theta = \frac{kp}{k' + kp} = \frac{Kp}{1 + Kp}$$

Where; $K = k/k'$ is the adsorption equilibrium constant, expressed in units of $(\text{pressure})^{-1}$. In addition, this langmuir equation can also be regarded as a relationship between the pressure of the gas and the volume adsorbed as follows;

$$\theta = \frac{v}{v_m} = \frac{Kp}{1 + Kp}$$

Where,

v_m = Volume of the adsorbed gas in the monomolecular layer ($cm^3.g^{-1}$), and

v = Volume of gas adsorbed at the equilibrium adsorbate pressure, and at the temperature of adsorption (liquid nitrogen boiling point = 77 K).

Langmuir isotherm can also be rearranged to the following form:

$$\frac{p}{v} = \frac{1}{Kv_m} + \frac{p}{v_m}$$

The gas adsorption measurement is the most commonly used technique for characterization of the volume of gas required for the formation of a monolayer on the surface of the sample. By applying the following equation for multilayer adsorption, a straight-line relationship may be derived for the BET-isotherm data:

$$\frac{p/p\circ}{v\left(1-p/p\circ\right)}=\frac{p}{v(p\circ-p)}=\frac{1}{v_m\cdot C}+\left[\frac{C-1}{v_m\cdot C}\right]\times\frac{p}{p\circ}$$

By plotting the appropriate left-hand side of above equation versus ($p\,/\,p^{\circ}$), this gives a reasonable straight line with following slop and intercept.

So, $Slope(S)=\left[\frac{C-1}{v_m\cdot C}\right]$ and $Intercept(I)=\left[\frac{1}{v_m\cdot C}\right]$

Thus, $C=\left[\frac{slope}{Intercept}\right]+1$ and $v_m=\left[\frac{1}{Slope+Intercept}\right]$

Where,

C = BET-constant for the particular temperature and gas-solid system, which is an indication to the interaction between the adsorbent and adsorbate, as it is exponentially attributed to the energy of adsorption in the first adsorbed layer.

By solving the above equations algebraically, the values of both v_m and C could be obtained.

The nitrogen adsorption curve can be obtained typically by plotting the volume of gas adsorbed ($cm^3.g^{-1}$) versus the relative pressure (p/p◦). Indeed, when the equilibrium adsorbate pressure (p) in the sample tube becomes close to the saturated vapor pressure of gas (p◦), the opening pores of the solid catalyst have to fully fill with adsorbate. This means that at saturation pressure of gas (i.e. the pressure at which the adsorbate gas liquefies) an infinite number of adsorbate layers must build up on the solid surface and to fulfil this limitation by BET-method, the (p/p◦) should be unity when (p) approaches (p◦). Since a specified relative pressure (p/p◦) range between 0.05 and 0.25 had been chosen from the data to get the linear mathematical form. In this narrow range of validity, the infinite adsorbate layers cannot be condensed on a given surface during the BET-isotherm for many porous materials. A theoretical value for the total surface area (S_g) for the sample in ($m^2.g^{-1}$) (if v_m is based on a 1 g sample) could thence be calculated from the following expression:

$$S_g = \left[\frac{v_m \times N_a}{V}\right]\alpha$$

Where, N_a = Avogadro's number (6.022×10^{23} molecules / mol)

V = Molecular volume of the adsorbate molecules (22414 ml.mol^{-1}), and

The term in brackets represents the number of molecules adsorbed.

α = The projected area of a molecule on the surface or area of an adsorbed molecule of gas. The proposed equation to calculate such area is:

$$\alpha = 1.09\left[\frac{M}{N_a \rho}\right]^{2/3}$$

Where M is molecular weight and ρ is the density of the adsorbed molecules.

The term in brackets represents the volume of one adsorbed molecule.

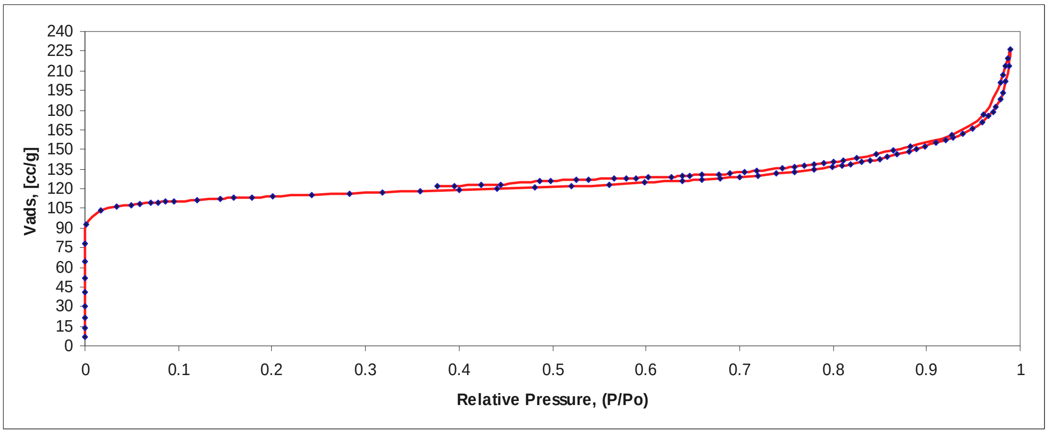
The value of BET-surface area (m^2) per gram of solid adsorbent could finally be represented in the following general form:

$$S_g = \left[v_m \times (4.35)\right]$$

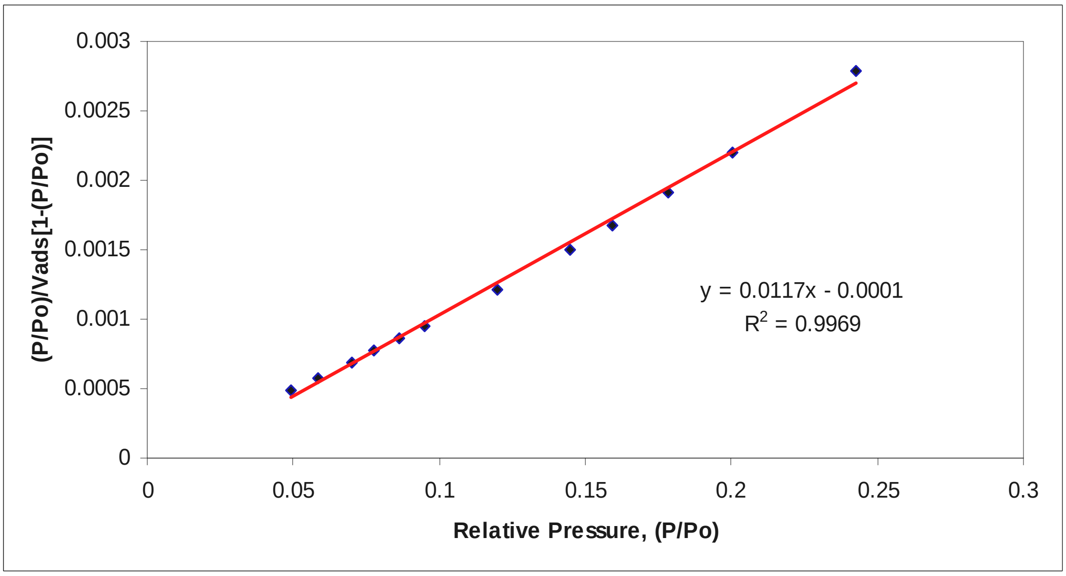
Example: Illustrate both the BET-profile and the BET-equation plots and then estimate both the BET-constant and the BET-surface area per gram of the zeolite catalyst by using the following experimental data of adsorption of nitrogen at equilibrium at the normal boiling point of (– 195.8°C), which is obtained from a Micromeritics-Coulter SA-3100 instrument.

Solution:

P/P^o	**v_{ads} cc/g**	**1-(p/p^o)**	**v(1-(p/p^o)**	**(P/P^o) / v(1-(p/p^o))**
0.0494	**107.662**	0.9506	102.3434972	0.000482688
0.0587	**108.449**	0.9413	102.0830437	0.000575022
0.0702	**109.245**	0.9298	101.576001	0.000691108
0.0777	**109.573**	0.9223	101.0591779	0.000768856
0.0862	**110.074**	0.9138	100.5856212	0.000856981
0.0947	**110.522**	0.9053	100.0555666	0.000946474
0.1196	**111.541**	0.8804	98.2006964	0.001217914
0.1445	**112.309**	0.8555	96.0803495	0.00150395
0.1593	**112.748**	0.8407	94.7872436	0.001680606
0.1786	**113.338**	0.8214	93.0958332	0.001918453
0.2005	**113.977**	0.7995	91.1246115	0.002200284
0.2429	**115.038**	0.7571	87.0952698	0.0027889



1- BET-profile



2- BET-equation plots

$$S = 0.012 = \left[\frac{y_2 - y_1}{x_2 - x_1}\right] = \left[\frac{0.003 - 0.0005}{0.25 - 0.05}\right]$$

I = - 0.0001

$$v_m = \left[\frac{1}{0.012 + (-0.0001)}\right] = 84.034 \text{ cm}^3/\text{ g}_{\text{-zeolite catalyst}} \qquad C = \left[\frac{0.012}{-0.0001}\right] + 1 = -119$$

$$S_g = \left[v_m \times (4.35)\right]$$

Thus, S_g = 365.55 seq m/g$_{\text{-cat}}$.

Catalyst density:

Volume and density of variety of powders, solids and slurries can usually be measured by using a gas displacement technique. Density may be considered in three distinct types. The first type is the *absolute or skeletal density*, which is obtained when only the solid volume of sample is measured – "excluding the open pores and void spaces between particles". The second type is the *envelope density*, which is obtained when only the solid volume and the pore spaces are measured. Finally the *bulk or tap density*, which is obtained when the solid volume, pore and void spaces are measured. Thus, the total porosity is determined by the difference between the absolute and envelope densities for the same sample material.

The density of the solid catalyst sample (ρ_s) in g.cm^{-3} can usually be derived if both the mass and the volume of the catalyst are known.

Pore volume, solid density and porosity:

The helium-mercury method is the procedure that typically used for these purposes, which is based on a gas displacement hypothesis. In this test both the volumes of displaced helium and mercury are measured successively. In view of the fact that the helium gas can fully fill the pores of most solid catalysts at atmospheric pressure, while the mercury can not. Therefore, the difference in volumes gives the volume occupied by the pores of catalyst (volumes of void only). In addition, the volume of helium displaced is a measure of the volume occupied by the solid catalyst. Thus, dividing the weight of the catalyst sample on this volume (volume of solid catalyst) gives the density (ρ_s) of the solid phase. Moreover, the void fraction (porosity) of the particle (ε_p, dimensionless) can also be calculated by dividing the pore volume of particle on the total volume of particle as follows:

$$\varepsilon_p = \frac{m_p.v_g}{m_p.v_g + m_p\left({}^{1}\!\big/_{\rho_s}\right)} = \frac{v_g.\rho_s}{v_g.\rho_s + 1}$$

Where; m_p is the mass of the particle, and v_g is the pore volume per gram of particles.

On the other hand, dividing the weight of the catalyst particles on the displaced mercury volume gives the density (ρ_p) of the porous particles. The following expression may also be used to calculate the porosity: $\varepsilon_p \frac{v_g}{{}^{1}\!\big/_{\rho_p}} = \rho_p.v_g$

Usually, during a packed-bed catalytic reactor about 30% of the volume is pore space, 30% is solid catalyst and 40% is void space between catalyst particles. In fact, the catalyst particles are pelleted or agglomerated when they are used in the packed-bed reactors, in order to avoid excessive pressure drop during the reaction – (it is usually referred to the pressure exerted on a moving fluid by obstructions against its direction of flow as backpressure).

The pellets are usually cylindrical or granular and such kind of agglomeration of porous particles gives a pellet containing two space regions: small spaces within the individual particles are termed as *micropores* (pore space), and larger spaces between particles are called *macropores* (void space). Both the macro- and micro-pore volumes and porosities for such bi-disperse pore systems could be calculated using the same as mentioned equations for the mono-disperse pore systems.

Example: The following data were found from a helium-mercury displacement experiment to determine the pore volume and catalyst particle porosity of activated silica sample, which is granulated between 4 to 12 mesh sizes:
Mass of activated silica sample placed in the chamber is 101.5 g.
Volume of helium displaced by catalyst sample is 45.1 cm^3.
Volume of mercury displaced by catalyst sample is 82.7 cm^3.
Calculate these required properties?

Solution:

Pore volume = [Volume of mercury displaced – Volume of helium displaced] / Mass

$$v_g = \frac{82.7 - 45.1}{101.5} = 0.371 cm^3.g^{-1}.$$

The density of the solid phase in the silica catalyst could be obtained as follows:

$$\rho_s = \frac{101.5}{45.1} = 2.25 g.cm^{-3}$$

The density of the porous particles in the silica catalyst could be acquired as follows:

$$\rho_p = \frac{101.5}{82.7} = 1.23 g.cm^{-3}$$

Either (ρ_s) or (ρ_p) may be applied to calculate the porosity of the silica gel particles:

$$\varepsilon_p = \frac{0.371 \times 2.25}{(0.371 \times 2.25) + 1} = 0.455 \qquad \text{Or} \qquad \varepsilon_p = 1.23 \times 0.371 = 0.455$$

Calculations of pressure drop in a fixed bed reactor:

The Ergun equation for gas-phase reactions is commonly employed to calculate the pressure drop in a packed porous bed of catalyst inside the reactor, which is given by the following expression:

$$\frac{dP}{dZ} = -\frac{G}{\rho . g_c . D_p} . \frac{\left(1-\varepsilon_p\right)}{\varepsilon_p^3}\left[\frac{150.\mu.\left(1-\varepsilon_p\right)}{D_p} + 1.75G\right]$$

Where:

P = pressure, (lb / ft^2).

Z = length down (depth) the packed bed of pipe, (ft).

ε_p = porosity (interparticle void fraction) = (volume of void) / (total bed volume).

$1 - \varepsilon_p$ = (volume of solid) / (total bed volume).

(As a general rule, values of ε_p are of the order of 0.5, indicating that the particle is about half void space and half solid material).

g_c = gravitational constant (conversion factor) = 4.17×10^8 (lb$_m$·ft / h^2·lb$_f$)

= 32.174 (lb$_m$·ft / s^2·lb$_f$).

D_p = effective particle diameter in the bed, (ft).

ρ = gas density, (lb / ft^3).

μ = viscosity of gas passing through the bed, (lb$_m$ / ft·h).

Either, $G = \rho . u$ = superficial mass velocity, (lb$_m$ / ft^2·h).

$u = \frac{Q}{A_c}$ = superficial velocity, (ft / h).

Q = volumetric flow rate of gas, (ft^3 / h).

A_c = cross sectional area of tubular reactor, (ft^2).

Or, $G = \frac{m}{A_c}$ where m = mass flow rate of gas, (lb$_m$ / h).

In order to express the pressure in term of reactor length (Z), the following relationship may be used:

$$\frac{P}{P_0} = \left(1 - \frac{2\beta_0.Z}{P_0}\right)^{1/2}$$

Where, P_o = entering pressure, and thus: $\Delta P = P_o - P$

β_o = right-hand side of Ergun equation = $\frac{G}{\rho.g_c.D_p}.\frac{(1-\varepsilon_p)}{\varepsilon_p^3}\left[\frac{150.\mu.(1-\varepsilon_p)}{D_p} + 1.75G\right]$

At the end of the reactor $Z = L$, where L is the whole length of the tubular reactor.

Therefore; $$\frac{P}{P_0} = \left(1 - \frac{2\beta_0.L}{P_0}\right)^{1/2}$$

Pore volume distribution:

It is difficult to determine the pore volume distribution according to the size of the pore, as such void spaces are usually non-uniform in size, shape, and length. In most cases, one of the following two established methods is utilized in order to measure the distribution of pore volumes within the catalyst particles:

1- The mercury – penetration methods: In this method the pressure required to force the mercury (Hg) to pass through into the pores is depended on the pore radius, because the mercury has a significant surface tension and does not wet (make contact with) most of the catalytic surfaces. Ritter and Drake obtained the following relation due to this fact:

$$\pi.a^2.P = -2.\pi.a.\sigma.\cos\theta \qquad \text{Thus, } a = \frac{-2.\sigma.\cos\theta}{P}$$

Where, σ = mercury surface tension.

Θ = contact angle between the Hg and pore wall (the average value of such angle can be taken as 140^o).

a = radius of a cylindrical pore.

P = pressure required to fill the catalyst pores with mercury.

The relationship between the radius and the pressure is; $a = \frac{8.75\times10^5}{P}$

Where, (a) in (Å) and (p) in (lb / in^2).

2- The nitrogen – desorption method: In this method the (surface area measurement) the nitrogen pressure (p) approaches the saturation pressure (p^o) value (1 atm at the normal boiling point 77 K), and the obtained data can be plotted as volume desorbed vs. pore radius. Thus, such procedure also gives the distribution of pore volumes. According to the corrected version of Kelvin relationship, the pore radius is related to the saturation pressure ratio (relative pressure) (p/p°). as shown in by the following expression:

$$a-\delta=\frac{-2.\sigma.V_1.\cos\theta}{R_g.T.\ln\left(p/p^0\right)}$$

Where: V_1 = molar volume of the condensed liquid nitrogen.

σ = nitrogen surface tension.

Θ = contact angle between surface and condensate. Condensation will be complete as (p/p°) becomes near from one.

T = temperature, and R_g = gas constant.

δ = thickness of the adsorbed layers, which depends on (p/p°) and can be found in angstroms (Å) from Wheeler equation:

$$\delta=9.52\left(\log\frac{p^0}{p}\right)^{-1/n}$$

Since nitrogen completely wets the surface covered with adsorbed nitrogen, the value of Θ becomes (0^o) and cos Θ = 1. For nitrogen at normal boiling point the equation becomes:

$$a-\delta=9.52\left(\log\frac{p^0}{p}\right)^{-1}$$

Promoters and inhibitors:

A carrier, which is sported on the catalyst, can be divided into: promoter and inhibitors. Promoter is defined as a small amount of substance added during the preparation of a catalyst in order to improve its activity or selectivity or stability to help in prolonging the catalyst life. Chlorides are sometimes added as promoters to hydrogenation and isomerization catalysts, and sulfiding usually improves hydro-desulfurization (Co-Mo) catalysts, Inhibitor is defined as the opposite of the promoter, therefore adding small amounts from inhibitor during catalyst manufacture leads to the reduction of its activity or selectivity or stability to help in reducing an undesirable side reaction. It has been found that adding halogen compounds to the catalyst inhibits the complete oxidation and results in satisfactory selectivity.

Catalyst deactivation (poisoning):

Because of the activity of a catalyst decreases with time during the reaction, the life of the catalyst is a major economic consideration. Poisons may be defined as substances, either in the reactants stream or produced by the reaction, which lower the activity of the catalyst. Catalyst poisoning is a problem in all reactions, but the generation of coke as a by-product is the most significant problem. The deposition of coke by occupying active catalytic sites leads to reduce catalyst activity, thereby reducing the products yield with deactivation occurring in two discrete ways:

A) Pore blockage which prevents the access of reactant molecules to the whole segments of catalyst pores. This poisoning (fouling) occurs rapidly and caused by physically depositing a substance, which blocks the active sites of the catalyst.

B) Site coverage caused by poisoning the catalyst acid sites. This slow decrease in the catalyst activity is due to chemisorption of reactants, products, or impurities.

It is possible to increase the catalyst life by means of decreasing its sensitivity to the effects of coking, however a proper regeneration treatment is required to burn off all the coke in an oxygen rich dry atmosphere. In fact, the deactivation can also be caused by a sintering (i.e. change in the surface structure of the catalyst as a result of elevating the reaction temperature). In general, classification the poisons according to the way in which they operate as follows;

1- Deposited poisons: such as carbon deposition on the catalysts that used in the petroleum industry. This kind of de-activated catalyst can simply be re-activated using the heterogeneous regeneration process (a gas-solid non-catalytic reaction).

2- Chemisorbed poisons: such as the sulfur compounds or other materials are chemisorbed on nickel, copper, or platinum catalysts.

3- Selectivity poisons: In this way some materials in the reactant stream will adsorb on the surface and then catalyze other undesirable reactions, which usually leads to the lowering of catalyst selectivity. The small quantities of nickel, vanadium, iron in petroleum stocks can act as poisons in this way.

4- Stability poisons: such as a decrease in oxidation activity when water vapor is present in the sulfur dioxide-air mixture supplied to a platinum-alumina catalyst. Because such water vapor may change the structure of the alumina carrier. Sintering and localized melting another examples on this way of poisoning.

5- Diffusion poisons: such as blocking the pore mouths, which prevents the reactants from diffusing into the inner surface of catalyst. The formation of solid residue due to react the feed with the catalyst can cause this way of poisoning.

Calculations the rate of reaction & the activation energy in a fixed bed reactor:

Fixed (or packed) bed reactors refer to two-phase systems in which the reacting fluid flow through a tube filled with stationary catalyst particles or pellets. By assuming that the plug-flow tubular reactor (PFTR) awards both a constant concentration and a stable density system, the following equations can be commonly utilized to describe the irreversible reaction kinetics of the reactant substance:

$$A_{react.} \Rightarrow products$$

$$R_{re} = k.C_A = -\frac{dC_A}{d\tau} \qquad \text{(a)}$$

By integrating Equation a;

$$-\int \frac{dC_A}{C_A} = k \int d\tau$$

$$\Longrightarrow \qquad \ln C_A = -k.\tau + b \qquad \text{(b)}$$

Where, $A_{react.}$ = Reactant substance.

R_{re} = Overall rate of reaction (i.e. speed of reaction), (mol.cm^{-3}.min^{-1})

k = Rate constant (min^{-1}), which has a positive relation with R_{re}

C_A = Concentration of the reactant ($A_{react.}$), (mol.cm^{-3})
τ = Reaction time (min), and
b = Constant of integration

At the beginning of the cracking reaction ($\tau = 0$).

Thus, $b = \ln C_{A\circ}$ (c)

Where, $C_{A\circ}$ = Initial concentration of reactant substance (mol.cm^{-3}).

By substituting Equation c in Equation b;

$$\ln C_A = -k.\tau + \ln C_{A\circ} \tag{d}$$

Rewriting Equation d gives,

$$\ln\left(\frac{C_A}{C_{A\circ}}\right) = -k.\tau$$

$$\Rightarrow \quad \frac{C_A}{C_{A\circ}} = e^{-k\tau} \tag{e}$$

Since the concentration of reactant substance at any time during the reaction can be given by means of fractional conversion of reactant (X_A), as shown by the following expression:

$$X_A = \frac{C_{A\circ} - C_A}{C_{A\circ}}$$

$$\Rightarrow \quad \frac{C_A}{C_{A\circ}} = (1 - X_A) \tag{f}$$

By combining Equation f and Equation e;

$$(1 - X_A) = \exp(-k\tau) \tag{g}$$

Where, "k" has a unit of (time^{-1}) and "$exp\ (-k\tau)$" is a possibility that any given collision will result in a reaction. Equation g can be rewritten as follows;

$$\ln(1 - X_A) = -k.\tau \tag{h}$$

Equation h can also be written as an experimental form of the integrated rate equation;

$$-\ln(1-X_A)=k.\left(\frac{W}{F}\right) \qquad \text{(i)}$$

Where, F (mol.h^{-1}) is the molar flow rate of the feed, W (g) is the weight of the catalyst, therefore W/F (g·h.mol^{-1}) is referred to the residence time (i.e. contact time between the feed and catalyst). k (mol.g^{-1}·h^{-1}) is represented as the rate constant of chemical reaction.

The term contact time can be calculated, if the catalyst weight and the feed flow rate are known. The rate constant (k) in Equation i can be determined from the slope by plotting [$-\ln(1-X_A)$] versus [W/F].

In addition, the classical exponential law of Arrhenius, as given in Equation j, can be applied to estimate the kinetic parameters of reaction, assuming the (k) values at different reaction temperatures are identified.

$$k = A.\exp\left(-E_a/RT\right) \qquad \text{(j)}$$

Indeed, the required energy to break down the molecules bond over the -catalysts can be calculated from the slope by plotting the left-hand side of the following operative equation against [$1/T$].

$$\ln(k)=\left(-E_a/R\right).1/T+\ln(A) \qquad \text{(k)}$$

Where; k, E_a, R, T, and A have already been defined in page 1.

Example: The catalysts were shaped by pelleting the powder and then sieving the particles (125 – 425 µm pellets). Two ultra stabilized (US) zeolite type Y catalysts with different silicon / aluminum (Si/Al) ratio were successively loaded into a cylindrical Pyrex micro-reactor of 4 mm ID and 400 mm length. About 100 mg from each USY catalyst was employed in the catalytic cracking experiment. At inlet feed temperature of 110 °C and 1.013 bar, a range of flow rates (75, 56 and 37.5 ml/min) of nitrogen / n-heptane mixtures (mole of nC_7 in the feed = 3 %) was introduced to the reaction zone in order to obtain different contact times. Each kinetic test was achieved at two different temperatures (375 and 425 °C) with constant backpressure of 0.04 bar throughout the packed bed reactor. In the end of the experiments, the following data was obtained:

Zeolite catalyst	USY- catalyst No. 1		USY- catalyst No. 2	
Reaction temperature	375 °C	425 °C	375 °C	425 °C
Flow rate \ Conversion	Mol (% *X*)	Mol (% *X*)	Mol (% *X*)	Mol (% *X*)
75 ml/min	0.962	5.601	4.409	12.852
50 ml/min	2.369	8.162	6.394	18.982
37.5 ml/min	8.828	17.163	17.422	34.013

In terms of activity and stability, which of these two USY-catalysts could you recommended to use in this catalytic cracking reaction? (R = 83.14 bar.cm^3.K^{-1}.mol^{-1}) and (Mwt of nC$_7$ = 100.20592).

Solution: Summarization of the contact time (W/F) calculations:

Parameters	Values		
Pressure (P), bar	1.013	1.013	1.013
Backpressure (∆P), bar	0.04	0.04	0.04
Total pressure (*P* = P+∆P), bar	1.053	1.053	1.053
Inlet temperature (T), K	383.15	383.15	383.15
Total flow rate of feed (Q), ml.min^{-1}	**37.5**	**56**	**75**
Gas constant (R), bar.cm^3.K^{-1}.mol^{-1}	83.14	83.14	83.14
Total inlet mole (n = *P*F/RT), mol.min^{-1}	0.001239598	0.001851133	0.002479196
Flow rate of nC$_7$ only (F), mol.min^{-1}	3.71879E-05	5.5534E-05	7.43759E-05
Flow rate of nC$_7$ only (F), g.min^{-1}	0.003726451	0.005564834	0.007452902
Catalyst weight (W), g	0.1	0.1	0.1
Contact time (W/F), g.min.mol^{-1}	2689.044297	1800.699306	1344.522148
Contact time (W/F), g.h.mol^{-1}	44.81740495 **44** ≈	30.0116551 **30** ≈	22.40870247 **22** ≈

Catalyst No. 1:

T = 375 ^{0}C	**W/F**	**Conv. Mol(%X)**	**(X / 100)**	**(1 - X)**	**Function: - ln(1-X)**
75	22.41	0.962006201	0.009620062	0.990379938	0.009666634
50	30.01	2.368960004	0.0236896	0.9763104	0.02397471
37.5	44.81	8.827728348	0.088277283	0.911722717	0.092419374

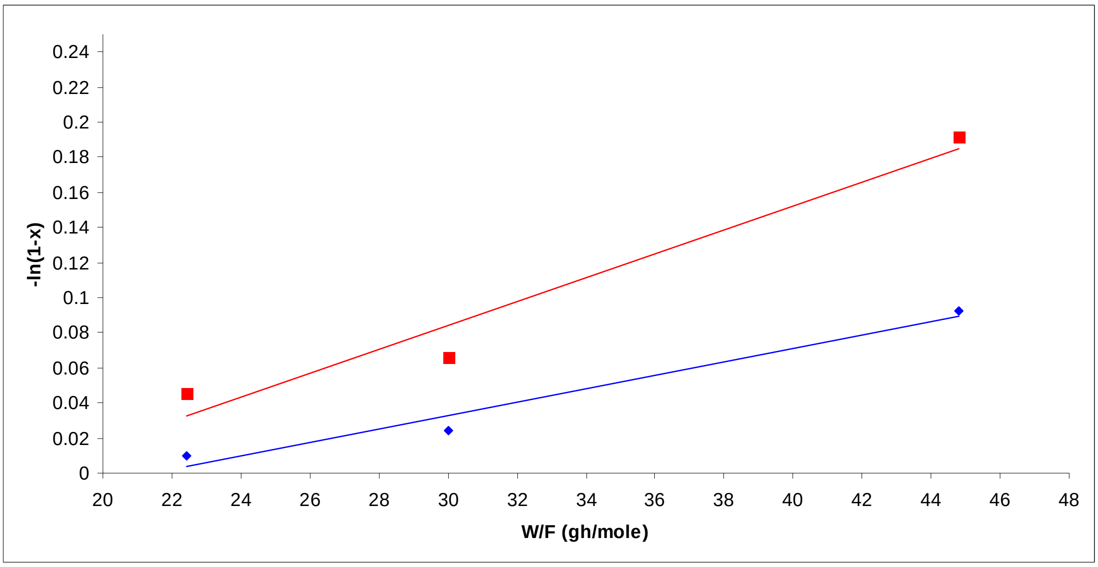
T = 425 ^{0}C	**W/F**	**Conv. Mol(%X)**	**(X / 100)**	**(1 - X)**	**Function: - ln(1-X)**
75	22.41	5.600562391	0.056005624	0.943994376	0.05763507
50	30.01	8.161698619	0.081616986	0.918383014	0.085140749
37.5	44.81	17.16326834	0.171632683	0.828367317	0.188298604

Catalyst No. 2:

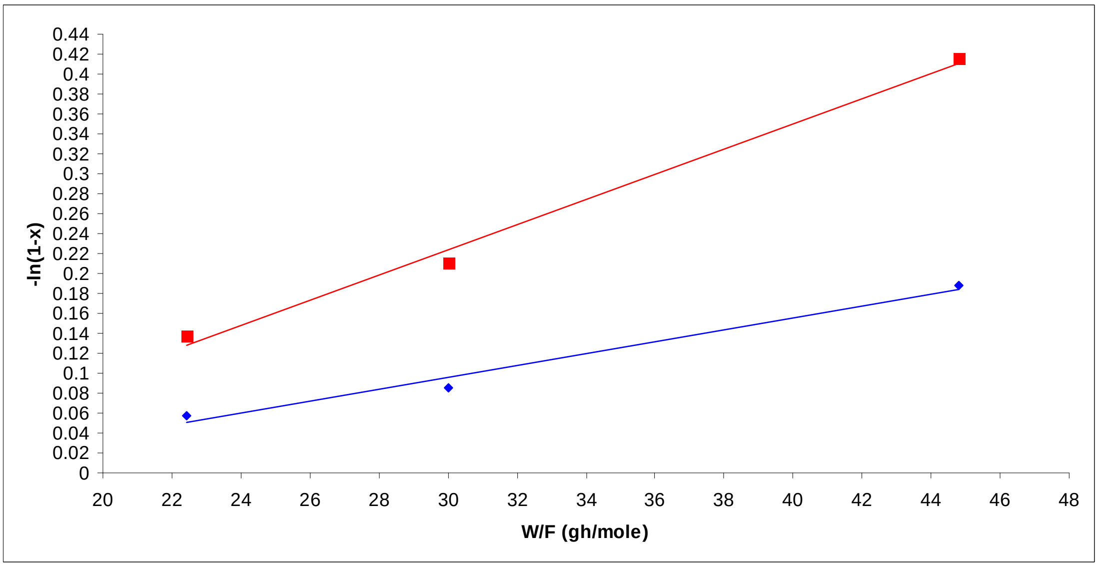
T = 375 ^{0}C	**W/F**	**Conv. Mol(%X)**	**(X / 100)**	**(1 - X)**	**Function: - ln(1-X)**
75	22.41	4.408643425	0.044086434	0.955913566	0.045087782
50	30.01	6.394083153	0.063940832	0.936059168	0.06607659
37.5	44.81	17.42164577	0.174216458	0.825783542	0.191422595

T = 425 ^{0}C	**W/F**	**Conv. Mol(%X)**	**(X / 100)**	**(1 - X)**	**Function: - ln(1-X)**
75	22.41	12.85221715	0.128522171	0.871477829	0.137564855
50	30.01	18.98209419	0.189820942	0.810179058	0.210499996
37.5	44.81	34.01256085	0.340125608	0.659874392	0.415705778

At **T = 375 ^{0}C**, the following First-order plots for n-heptane cracking reactions over USY-zeolite catalysts were obtained;



At **T = 425 ^{0}C**, the following First-order plots for n-heptane cracking reactions over USY-zeolite catalysts were obtained;



Using equation (i): $-\ln(1-X_A)=k.\left(\frac{W}{F}\right)$

The rate constant (k) of reaction over each catalyst can be determined from the slope:

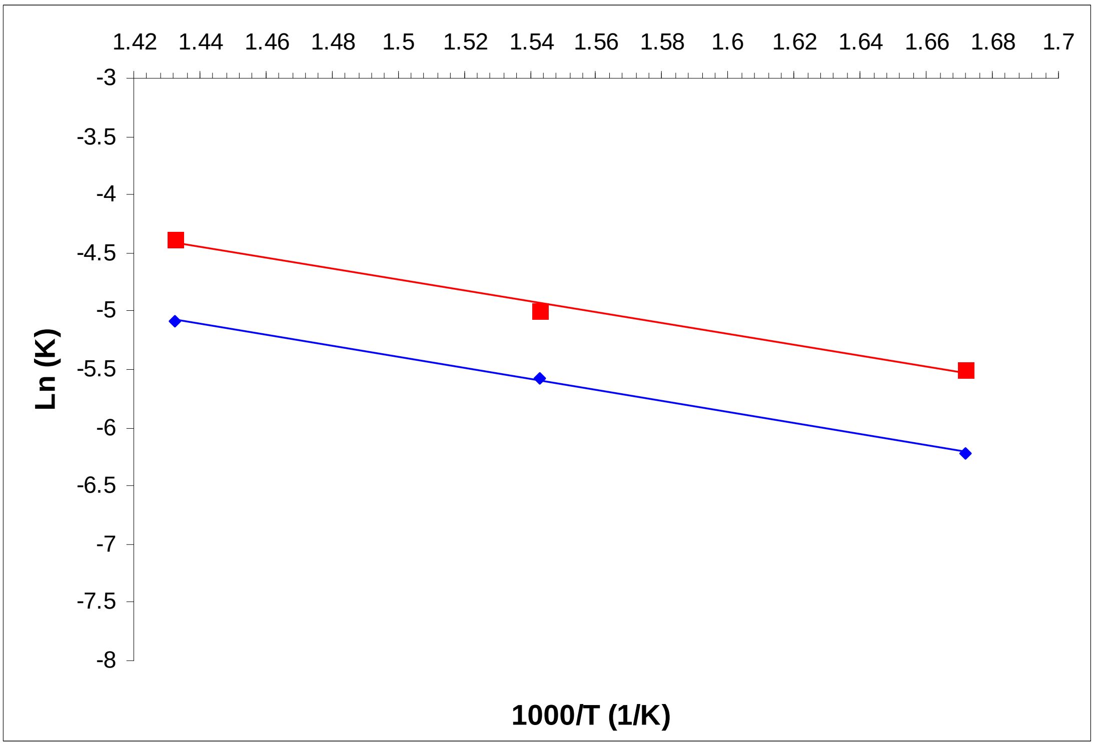
USY-Catalyst	Rate at **375 ^{0}C**	Rate at **425 ^{0}C**
Catalyst No. 1	0.0038 mol.g^{-1}·h^{-1}	0.0062 mol.g^{-1}·h^{-1}
Catalyst No. 2	0.0068 mol.g^{-1}·h^{-1}	0.0126 mol.g^{-1}·h^{-1}

Using equation (j): $k = A.\exp\left(-E_a/RT\right)$ where R = 8.314× 10^{-3} kJ.mol^{-1}·K^{-1}, both the value of E_a and A could be found.

Or by plotting equation (k): $\ln(k)=\left(-E_a/R\right).1/T+\ln(A)$

^{0}C	K	1000/T
375	648.15	1.542852735
425	698.15	1.432356943

Where;
R = 8.314 kJ.mol^{-1}·K^{-1}, from the slope: E_a over each catalyst could be found.

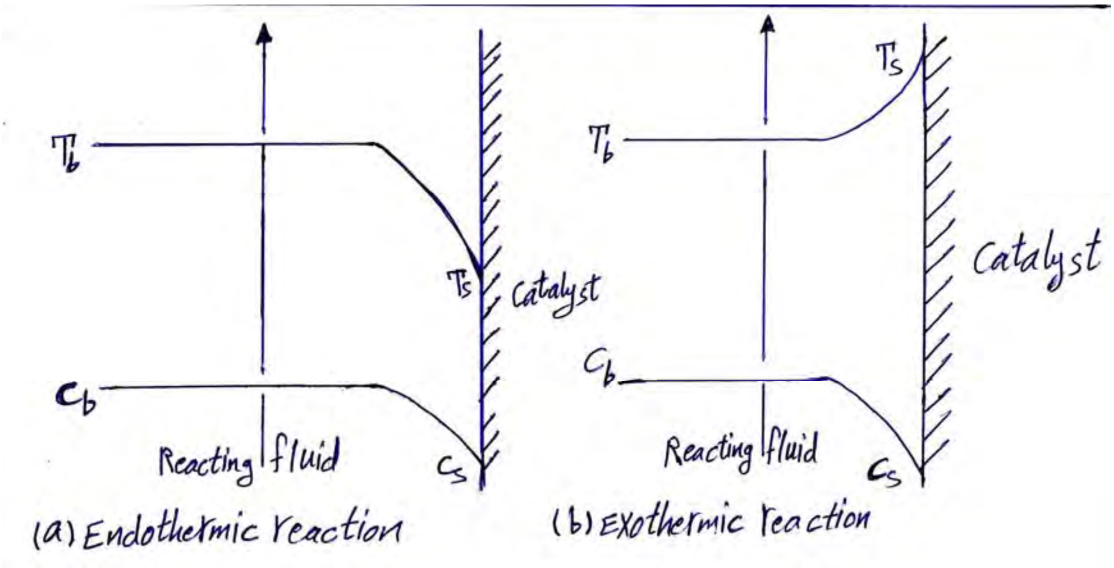


The value of activation energy of cracking is decreased with increasing in proportion rate constant value over more active and stabile USY-catalyst.

I- External transport processes in heterogeneous reactions

In case of mass transfer, the transfer of reactant from the bulk fluid to the outer surface of the catalyst particle requires a driving force (Concentration difference between bulk fluid and particle surface, which usually depends on: 1) the velocity pattern in the fluid near the catalyst surface, 2) the physical properties of the fluid, and 3) the intrinsic rate of the chemical reactions at the catalyst, in other words: it depends on the mass transfer coefficient between fluid and surface and the rate constant for the catalytic reaction).

In case of heat transfer, the same reasoning suggests that there will be a temperature difference between bulk fluid and catalyst, which depends on: 1) the heat transfer coefficient between fluid and catalyst surface, 2) the reaction rate constant, and 3) the heat of the reaction (If the reaction is exothermic, the temperature of the catalyst surface will be greater than that of the fluid. If the reaction is endothermic, the temperature of the catalyst surface will be less than that in the bulk fluid).



The objective from this study is to understand quantitatively how these external physical processes affect the global rate, which is the rate that we need in order to design heterogeneous reactors. For porous catalysts both reaction and heat and mass transfer occur at the same internal location within the catalyst pellet, and the effect of such internal physical processes will be considered in the next section of this study (Internal transport processes-reaction and diffusion in porous catalysts).

A- Fixed-bed reactors:

In such reactors there will be regions near the outer surface of the particles where the fluid velocity is very low. In these region (near from the points of contact between catalyst particles), the mass and the heat (energy) transfer between bulk fluid and pellet surface will be primarily by conduction. The transport rates between bulk fluid and pellet surface are normally defined in terms of an (average heat (h) or mass (k_m) transfer coefficient). It will be assumed that the average coefficient can be applied to all the outer surface coefficient.

The study of the effect of the physical processes on the rates of reaction in this case can be achieved by using an irreversible gaseous reaction with order (n) on a solid catalyst pellet. At steady state the rate of the reaction may be written either in terms of the diffusion rate from the bulk gas to the surface or in terms of the rate on the surface as follows:

$r_p = k_m a_m (C_b - C_s)$ Therefore, $r_p = k.C_s^n$

Where, C = reactant concentration, C_b and C_s are the concentration in the bulk gas and the catalyst surface, respectively. k_m = the mass-transfer coefficient between bulk gas and solid surface, a_m = the external surface area per unit mass of the pellet (mass-transfer area), and k = the reaction-rate constant.

When both diffusion and reaction resistance are significant, and for first order reaction the above equations can be easily solved to obtain an expression for the rate in terms of the bulk concentration C_b:

$$C_s = \frac{k_m.a_m}{k + k_m.a_m} C_b \qquad \text{Therefore, } r_p = k_0.C_b = \frac{1}{1/k + 1/k_m.a_m} C_b$$

Where; $\frac{1}{k_0} = \frac{1}{k} + \frac{1}{k_m.a_m}$

It can be seen in this intermediate case that the observed rates can be used to calculate the overall rate constant k_0.

From Arrhenius equation the term $A.e^{-E/R.T}$ can be substituted for the rate constant k of the surface step. Thus,

$$\frac{1}{k_0} = \frac{e^{E/RT}}{A} + \frac{1}{k_m.a_m} \qquad \text{Therefore, } k_0 = \frac{k_m.a_m.A.e^{-E/RT}}{k_m.a_m + A.e^{-E/RT}}$$

Here E is the true activation energy of the surface reaction.

The external mass-transfer resistances [$r_p = k.C_s^n$] have been based on isothermal conditions with n = 1. Temperature difference due to external heat-transfer resistance can also be important. The corresponding energy (heat, Q_R) evolved by reaction can be given as:

$$Q_R = (-\Delta H)r_p = (-\Delta H).A\left(e^{-E/RT_s}\right).C_s$$

Where the second equality is obtained by expressing k in terms of the Arrhenius function of temperature.

For non-isothermal behavior at steady state the heat loss, Q_L, from a catalyst (heat-transfer per unit mass of catalyst) is equal to the Q_R, as given by the following equation for a first order reaction:

$$h.a_m.(T_s - T_b) = (-\Delta H)r_p = (-\Delta H).A\left(e^{-E/RT_s}\right).C_s$$

Where: $r_p = k_m a_m (C_b - C_s)$, and

$Q_L = h.a_m.(T_s - T_b)$, in this equation the heat-transfer coefficient (h) was defined in terms of the temperature difference ($T_s - T_b$), and the particle surface (heat- transfer area).

In a design problem, A, E, ΔH, h, k_m, and a_m would be known. The global rate (r_p) is to be calculated for a given bulk concentration (C_s) and bulk temperature (T_s).

Where; $k_m.a_m.(C_b - C_s) = r_p = A\left(e^{-E/RT_s}\right).C_s$

The relationship between the temperature and concentration differences between fluid and pellet surface be established by combining the correlations for h and k_m. The energy balance on the catalyst pellet for steady state gives:

$$h.a_m.(T_s - T_b) = k_m.a_m(C_b - C_s)(-\Delta H) \qquad \text{OR,} \qquad (T_s - T_b) = \frac{r_p(-\Delta H)}{h.a_m}$$

Mass and heat-transfer coefficients (fluid-particle) in packed beds:

Average transport coefficients between the bulk stream and particle surface can be correlated in terms of dimensionless groups, which characterize the flow conditions.

In the case of mass transfer, the Sherwood number; $\frac{k_m.\rho}{G}$ is an empirical function of the Reynolds number; $\frac{D_p.G}{\mu}$ and the Schmidt number; $\frac{\mu}{\rho.D}$. It is usually used to correlate the experimental date in terms of *j-factors*, which are defined as the following function of the Sherwood (Sh) & Schmidt (Sc) numbers:

$$j_D = \frac{k_m.\rho}{G}\left(\frac{a_m}{a_t}\right).\left(\frac{\mu}{\rho.D}\right)^{2/3}$$

The ratio (a_m/a_t) allows for the possibility that the effective mass-transfer area, a_m, may be less than the total external area, a_t, of the particles.

For Reynolds numbers (*Re.*) greater than 10, the following relationship between j_D and *Re* could be used to represent the experimental data:

$$j_D = \frac{0.458}{\varepsilon_p}\left(\frac{D_p.G}{\mu}\right)^{-0.407} .$$

Where; G = mass velocity (superficial) based upon cross-sectional area (A_c) of empty reactor (See page 17).

D_p = diameter of catalyst particle for sphere {for other shapes, an approximate value of D_p is that of a sphere with the same external area as the non-spherical particle}.

μ = viscosity.

ρ = density.

D = molecular diffusivity of component being transferred (cm^2/s or ft^2/h).

ε_p = void fraction of the interparticle space = (void fraction of the bed).

In the case of heat transfer between a fluid and particle surface in a packed bed occurs by the same molecular and convective processes as describe mass transfer, the experimental date can be correlated in terms of *j-factors*, which are defined as the following function of the Prandtl $[\frac{C_p.\mu}{k_f}]$ and the Stanton $[\frac{h}{C_p.G}]$ numbers:

$$j_H = \frac{h}{C_p.G}\left(\frac{a_m}{a_t}\right).\left(\frac{C_p.\mu}{k_f}\right)^{2/3}$$

Where; Stanton (*St*) = Nusselt ($Nu = \frac{h.D_p}{k_f}$) / [Reynolds (*Re*) × Prandtl (*Pr*)].

C_p = specific heat, (kJ/kg.K or Btu/lb.°F).

k_f = thermal conductivity, (kJ/s.cm.K or (Watt/cm.K) or Btu/h.ft.°F).

The validity of the difference between j_D and j_H is uncertain in the absence of radiation, therefore; $j_H = j_D = \frac{0.458}{\varepsilon_p}\left(\frac{D_p.G}{\mu}\right)^{-0.407}$.

In addition using both j_D and j_H equations for the mass-transfer coefficient (k_m) and heat transfer coefficient (h) yields;

$$(T_s - T_b) = (C_b - C_s)\frac{(-\Delta H)}{C_p.\rho}.\left(\frac{C_p.\mu/k_f}{\mu/\rho.D}\right)^{2/3}.\left(\frac{j_D}{j_H}\right)$$

The expression can be used to evaluate the temperature difference from ($C_b - C_s$). For many gases the Lewis number (Le), which is the ratio of the Prandtl and Schemidt numbers is about one : $Le = \frac{pr}{Sc} = \left(\frac{C_p.\mu/k_f}{\mu/\rho.D}\right) = 1.0$, and also $j_D \sim j_H$. Hence, the above equation can be reduced approximately to the following form:

$$(T_s - T_b) = \frac{-\Delta H}{C_p.\rho}(C_b - C_s).$$

B- Fluidized-bed reactors:

In the *fixed-bed reactor* the catalyst particles are relatively large and stationary. In contrast, in a fluidized-bed reactor, the small particles (50 to 250 microns) move dependent on the velocity of the reacting fluid. In most *fluidized-bed catalytic reactors*, the fluid is a gas and the normal operating condition is in the bubbling regime. In this condition the gas moves through the reactor in two ways: as bubbles containing relatively few solid particles and moving at above the average velocity, and as a continuous dense or emulsion phase where the concentration of particle is high.

Particle-fluid mass and heat transfer:

In the fluidized beds, the very high mass- and heat-transfer areas, per unit mass of catalyst, are associated with the small moving particles. As a result, external concentration and temperature effects are not very significant in design of fluidized bed reactors (i.e. both concentration and temperature differences between fluid and particle surface are usually negligible.

Kunii and Levenspiel have summarized available mass- and heat-transfer data in the form of graphs of Sherwood and Nusselt numbers vs. Reynolds number. Typical results may be expressed in terms of *j-factors* as:

$$j_H \ \& \ j_D = 1.77\left(\frac{D_p.G}{\mu\left(1-\varepsilon_p\right)}\right)^{-0.44} \quad .$$

For the range $30 < [D_p.G / \mu\ (1 - \varepsilon_p)] < 5000$. Here j_D and J_H are as defined in the previously equations. This correlation is based on data for both liquid-solid and gas-solid beds.

Example: Estimate the ratio of mass-transfer rates, per unit volume, for fixed-bed and fluidized-bed reactors at reasonable operating conditions. Suppose these conditions are:

Properties	Fluidized bed	Fixed bed
Particle size, D_p, cm	0.0063 (250 mesh)	0.635
Void fraction of the bed, ε_p	0.90	0.40
Fluid mass velocity, G g/cm^2.s	0.02	0.10

Solution:

The mass-transfer rates, per unit volume of reactor is:

$$r_v = \rho_p\left(1-\varepsilon_p\right)r_p = \rho_p\left(1-\varepsilon_p\right)k_m a_m (C_b - C_s)$$

For spherical particles of diameter D_p, the external area per unit mass, $a_m = 6 / D_p.\rho_p$.

$$r_v = \frac{6\left(1-\varepsilon_p\right)}{D_p} k_m (C_b - C_s)$$

By substituting the values of k_m and then dividing the results to obtain the ratio of mass-transfer rates for the same fluid (same physical properties in both fixed- and fluidized-bed reactors) and also the same concentration difference.

$$\frac{r_{fluid}}{r_{fixed}} = \frac{\left[\left(1-\varepsilon_p\right)\big/ D_p\right]_{fluid} .\left(G.J_D\right)_{fluid}}{\left[\left(1-\varepsilon_p\right)\big/ D_p\right]_{fixed} .\left(G.J_D\right)_{fixed}}$$

Substituting the values of j_D-*factors* in both fixed- and fluidized-bed reactors as already have been given in the following equations:

$$j_D = \frac{0.458}{\varepsilon_p}\left(\frac{D_p.G}{\mu}\right)^{-0.407} . \qquad \& \qquad j_D = 1.77\left(\frac{D_p.G}{\mu\left(1-\varepsilon_p\right)}\right)^{-0.44} .$$

Therefore, $$\frac{r_{fluid}}{r_{fixed}} = \frac{\left[1.77\left(1-\varepsilon_p\right)^{1.44}.G^{0.56}.d_p^{-1.44}\right]_{fluid} .}{\left[\left(0.458/\varepsilon_p\right)\left(1-\varepsilon_p\right).G^{0.593}.d_p^{-1.407}\right]_{fixed}}$$

Numerical solution gives: $\dfrac{r_{fluid}}{r_{fixed}} = 32$

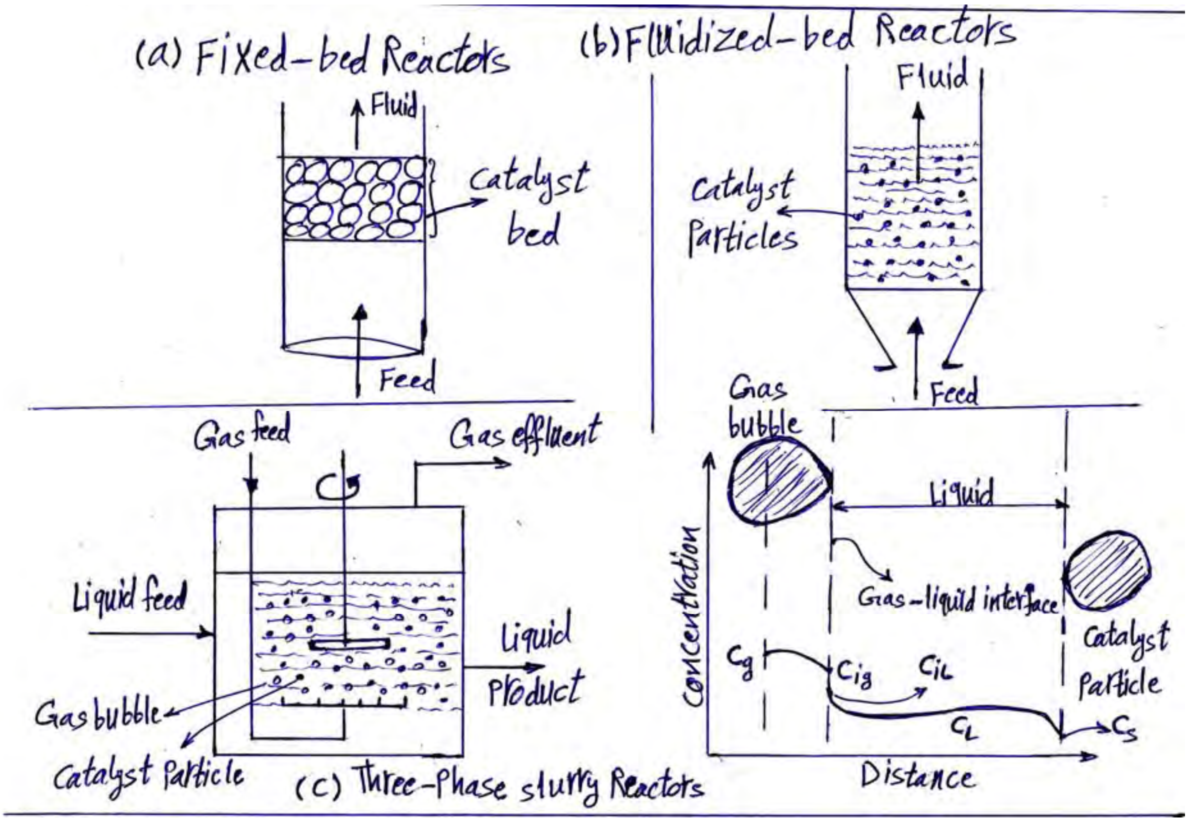
As a result, the mass-transfer rate between particle and fluid for a fluidized bed can be an order of magnitude greater than that for a fixed bed even though the mass- and heat-transfer coefficients in fluidized beds are less than those in fixed beds. It is evident that $(C_b - C_s)$, will be negligible for fluid for a fluidized bed. A similar result applies for external temperature differences $(T_s - T_b)$.

C- Slurry reactors:

In both fixed- and fluidized-bed reactors, the external transport has been analyzed for two-phase systems (fluid and solid catalyst). When there are both volatile and non-volatile reactants, or when a liquid solvent is necessary with all gaseous reactants, three phase reactors are needed. Example is hydrogenation of oils with a nickel catalyst, where a gaseous reactant must be transferred from gas to liquid and then from liquid to solid catalyst before reaction occurs.

The two common forms of three-phase reactors are the slurry and trickle-bed, as shown in the figure. In three-phase system bubbles of gas rise through the agitated slurry and the particles tend to move with liquid. The external temperature differences can normally be neglected in slurry reactors. It is reasonable to assume that the liquid and catalyst particles in a slurry reactor are well mixed, as in a stirred-tank, and the gas bubbles are raised through the liquid. Thus, the concentration of gaseous reactant in bubble will change with position. At one position, the overall reaction consists of the following processes in series as shown in the figure:

1- Mass transfer from the bulk concentration in the gas bubble to the bubble-liquid interface.
2- Mass transfer from the bubble interface to the bulk-liquid phase.
3- Mixing and diffusion in the bulk liquid.
4- Mass transfer to the external surface of the catalyst particles.
5- Reaction at the catalyst surface.



The rates of all the steps will be identical at steady state. If we make the assumption of a first-order irreversible catalytic reaction, the rate per unit volume of bubble-free slurry (r_v) may be written:

$$r_v = k.a_c.C_s \qquad \text{(Step 5: reaction at the catalyst surface)} \qquad (1)$$

Where a_c = external area of catalyst particles per unit volume of liquid (bubble free).
k = first-order rate constant.
C_s = concentration of reactant (hydrogen) at the outer surface of the catalyst particle.

The rates of the three mass-transfer processes may be expressed as: (Note that the resistance of Step 3 can be neglected, as the rise of the bubbles through the liquid, along with the mechanical agitation is as a general rule sufficient to achieve uniform condition in the bulk liquid).

$r_v = k_g.a_g.(C_g - C_{ig})$ (Step 1: bulk gas to bubble interface) (2)

$r_v = k_L.a_g.(C_{iL} - C_L)$ (Step 2: bubble interface to bulk liquid) (3)

$r_v = k_c.a_c.(C_L - C_s)$ (Step 4: bulk liquid to catalyst surface) (4)

Where a_g is the gas bubble-liquid interfacial area per unit volume of bubble-free liquid and k_g, k_L, and k_c are the appropriate mass-transfer coefficients.

If equilibrium exists at the bubble-liquid interface, C_{ig} and C_{iL} are related by Henry's law:

$C_{ig} = HC_{iL}$ (Equilibrium: where H is the Henry's constant) (5)

{Note that Henry's law for solubility can also be expressed as: [$P_g = H_p C_{iL}$], where the concentration C_{iL} at the bubble-liquid interface will be that in equilibrium with the pressure P_g in the bulk gas of the bubble, and H_p is the solubility constant (atm.cm^3/g mol) or (kPa.m^3/kg mol)}.

These five equations can be combined to eliminate C_{ig}, C_{iL}, C_L, *and* C_s. Then the global rate can be expressed in terms of the concentration of reactant in the gas:

$$r_v = k_\circ.a_c.C_g$$

Where: $\frac{1}{k_\circ} = \frac{a_c}{a_g}.\frac{1}{k_g} + \frac{a_c}{a_g}.\frac{H}{k_L} + H.\left(\frac{1}{k_c} + \frac{1}{k}\right)$

The global mass-transfer coefficient (k_o) is a function of three mass-transfer coefficients (k_g, k_L, and k_c), the specific reaction rate k, and the area ratio a_c/a_g (Note that the rate will increase as this ratio falls). The constant k is sensitive to temperature and should be associated with the temperature of the catalyst particle (or liquid temperature, as the external temperature differences between catalyst particle and the bulk liquid are not important in slurry reactors).

In fact, there is no resistance to diffusion from bulk gas (in the bubble) to bubble-liquid interface, and the resistance to mass transfer on the liquid side of the interface is predominant. For these conditions ($C_g = C_{ig}$) and last equation becomes:

$$\frac{1}{k_\circ.H} = \frac{a_c}{a_g}.\frac{1}{k_L} + .\left(\frac{1}{k_c} + \frac{1}{k}\right)$$

The global rate (r_v) can sometime be defined in terms of the liquid-phase concentration $(C_L)_{\text{eq.}}$ in equilibrium with (C_g).

Since $C_g = C_{ig} = H(C_L)_{\text{eq.}}$, the rate [$r_v = k_\circ.a_c.C_g$] can be given as:

$$r_v = k_\circ.H.a_c.(C_L)_{eq.}$$

Where $k_\text{o}.H$ can be calculated from the same equation: { $\frac{1}{k_\circ.H} = \frac{a_c}{a_g}.\frac{1}{k_L} + .\left(\frac{1}{k_c} + \frac{1}{k}\right)$ }.

C-1 Mass-transfer coefficients: Gas bubble to Liquid (k_L):

Even when the bubble is a gas mixture, the major resistance to transport for slightly soluble gases is in the liquid. Therefore, k_L is usually the important coefficient in gas bubble-to-liquid mass transfer. Several experimental studies and correlation for k_L are available. In one correlation it is defined in the following dimensional equation:

$$k_L = 0.592.D_A^{0.5}.\left(\sigma / v\right)^{0.25}$$

The energy dissipation rate (σ) per unit mass of liquid (erg/s.g) is given by:

$$\sigma = \frac{N_p.\rho_L.N^3.D_1^5}{W}.\phi$$

Where: D_1 = impeller diameter, cm.

D_A = molecular diffusivity of reactant in liquid, cm^2/s.

υ = kinematic viscosity in (cm^2/s), Note: The kinematic viscosity (υ) is given in Stokes (S) = cm^2/s or C.S = 0.01 Stoke, and the dynamic viscosity (μ) is given in Poise (P) = g/cm.s or C.P = 0.01 Poise. Where: $\upsilon = \frac{\mu}{\rho}$, ($\rho$ is the density, g/cm^3). In addition, the thermo viscosity = $15 + 148.5.\upsilon$.

k_L = liquid-side mass-transfer coefficient, cm/s.

N = impeller speed in rps.

W = mass of liquid in the slurry, g.

ρ_L = density of liquid phase, g/cm^3.

ϕ = a correction factor ($0 < \phi < 1$) to account for the decrease in energy dissipation rate due to gas bubbles. For $Q/N.D_1^3 < 0.035$, Calderbank gives the following relationship: $\phi = 1 - 12.6.\left(Q/ND_1^3\right)$, where Q is the gas flow rate, (cm^3/s).

N_p = power number, defined by the following expression:

$$N_p = \frac{P_W}{\rho_L.N^3 D_1^5}$$

This number depends upon the design (number and size) of baffles, and vessel, but frequently is about 10. P_w is the power input, erg/s.

This method of correlation to obtain the mass-transfer coefficient (k_L), requires a measurement of the energy dissipation rate by determining the torque of the agitator.

In the absence of mechanical agitation and for bubbles whose diameter is less than 2.5 mm (the usual size range for slurry reactors), the following correlation is available using the Schmidt number, $Sc = \frac{\mu}{\rho.D}$:

$$k_L.\left(\frac{\mu_L}{\rho_L.D}\right)^{2/3} = 0.31.\left(\frac{\Delta\rho.\mu_L.g}{\rho_L^2}\right)^{1/3}$$

Where: k_L = mass-transfer coefficient, cm/s.

$\Delta\rho$ = difference in density between liquid phase and gas bubbles, g/cm^3.

μ_L = viscosity of liquid phase, g/cm.s.

g = acceleration of gravity, g/s^2.

ρ_L = density of liquid phase, g/cm^3.

This correlation is for bubbles rising through the liquid phase because of gravitational force. In the absence of such gravitational force, mass transfer from a stagnant bubble would be by molecular diffusion through the surrounding stagnant liquid.

The Sherwood number is $Sh = \dfrac{k_1.\rho}{G} = \dfrac{k_1}{u} = \dfrac{k_1}{D/D_p} = \dfrac{k_1.D_p}{D} = 2$, where D_p is the diameter of the bubble. D is the diffusivity, and k_1 is the mass-transfer coefficient.

C-2 Mass-transfer coefficients: Liquid to catalyst particle (k_c):

The velocity between the particle and the liquid determines the extent to which convection increases the Sherwood number above that for stagnant conditions, i.e. above 2. The basis for correlating k_c as a function of agitation speed and particle size is Kolmogoroffs theory of isotropic turbulence. According to this theory the Reynolds number (*Re*) is defined in terms of the energy dissipation rate (σ). If the eddy size (ζ) is greater than the particle diameter (D_p):

$$R.e = \left(\frac{\sigma.D_p^4}{\upsilon^3}\right)^{1/2} \qquad \zeta > D_p$$

Or otherwise:

$$R.e = \left(\frac{\sigma.D_p^4}{\upsilon^3}\right)^{1/3} \qquad \zeta < D_p$$

Where: (ζ) is a function of (σ) and the kinematic viscosity (υ).

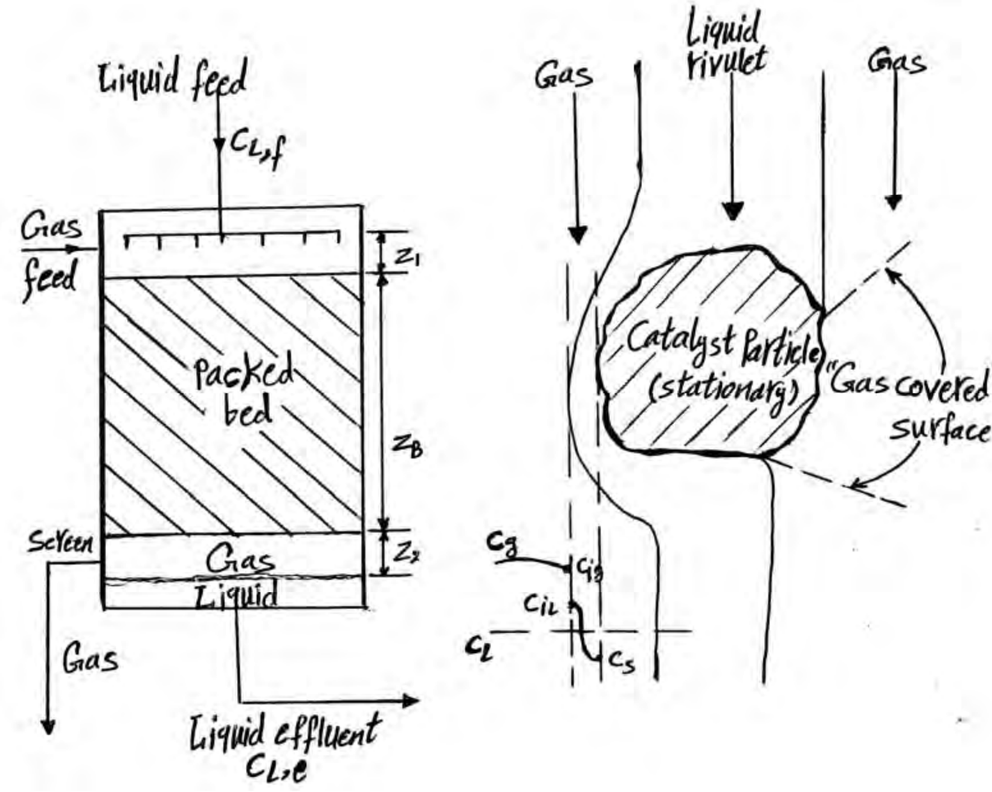
Thus, $$\zeta = \left(\frac{\upsilon^3}{\sigma}\right)^{1/4}$$

Where, the energy dissipation rate (σ) (erg/s.g) is given by: $\sigma = \dfrac{N_p.\rho_L.N^3.D_1^5}{W}.\phi$

In such three-phase slurries, both bubble-liquid and liquid-particle mass transfer can influence the global rate.

D- Trickle-bed reactors:

In this down-flow of liquid and gas over a fixed-bed of catalyst particles as shown in the below figure, the nature of the flow depends on both the liquid and the gas flow rates. Amongst the boundaries of the different flow regimes, the trickle-flow regime would be discussed here. In such regime and at low liquid and gas mass velocities, the gas phase is continuous and the liquid falls in rivulets from one particle to the next. For this type of flow the concentration profile for a reactant in the gas phase is sketched in the following figure.



This profile is similar to that for a slurry reactor. However and as shown in the above figure, a small part of the particle (labeled gas-covered) is exhibited without a liquid rivulet. In fact, such surfaces exist at low liquid rates, and on this surface there would be much less mass-transfer resistance for a gaseous reactant.

In trickle beds the external mass-transfer limitations are determined by the two volumetric coefficients: gas-to-liquid, $k_L.a_g$, and liquid-to-particle, $k_c.a_c$. The areas a_g, a_c refer to the effective mass-transfer surface per unit volume of empty reactor.

D-1 Mass-transfer coefficients: Gas to Liquid ($k_L a_g$):

In trickle beds the gas phase is often either a nearly pure component such as the hydrogenations or a slightly soluble gas as in the oxidations. Therefore, the most important coefficient for gas-liquid transport is the liquid side value $k_L.a_g$.

Two type of correlations have been used for $k_L.a_g$: one relates $k_L.a_g$ to the pressure drop for two-phase flow in the reactor, and the other is in terms of the flow velocities, which can be given in the following dimensional equation:

$$\frac{k_{L.}a_g}{D} = \alpha_L \cdot \left(\frac{G_L}{\mu_L}\right)^{\eta_L} \cdot \left(\frac{\mu_L}{\rho_L.D}\right)^{1/2}$$

Schmidt number = $\dfrac{\mu_L}{\rho_L.D}$, Where: μ_L = liquid viscosity (g/cm.s), ρ_L = liquid density (g/cm^3), and D = molecular diffusivity of the diffusing component (cm^2/s).

$k_L.a_g$ = volumetric liquid-side mass-transfer coefficient (gas-liquid) (s^{-1})

G_L = superficial mass velocity of the liquid (g/ cm^2.s).

α_L is about 7 (cm)$^{\eta L-2}$, and η_L = 0.40 for granular catalyst particles (0.054 and 0.29 cm in diameter).

<u>Note:</u> The above equation does note involve the gas rate $k_g.a_g$, and this correlation applies for the trickle-flow regime.

D-2 Mass-transfer coefficients: Liquid to Particle ($k_c a_c$):

A correlation for the mass transfer between fluid and particle for the trickle-flow regime that includes much of the data can be expressed as follows:

$$j_D = 1.64\left(\frac{D_p.G_L}{\mu_L}\right)^{-0.331} \qquad [\text{for } 0.2 < (Re_L = D_p\, u_L\, \rho_L / \mu_L) < 2400]$$

Where:

$$k_c a_c = j_{D.}(u_L.a_t)\left(\frac{\mu_L}{\rho_L.D}\right)^{-2/3}$$

And u_L = superficial velocity of liquid = $G_L/\rho_L = Q_L/A_c$.

a_t = total external area of particles per unit volume of reactor.

$K_c.a_c$ = volumetric bulk liquid to catalyst mass-transfer coefficient (liquid-solid) (s^{-1}).

D-3 Calculation of global rate:

The global rate is obtained by equating, at steady state, the rate of mass transfer of reactant from the liquid to the catalyst particle (k_c) to the rate of reaction (k). For a unit volume of reactor the equality may be written:

$$r_v = k_c . a_c . (C_L - C_s) = \rho_B . r(C_s,T_s)$$

Where: C_L is the bulk concentration in the liquid, ρ_B is the bulk density of the catalyst bed, and $r(C_s,T_s)$ is the intrinsic rate per unit mass of catalyst, which evaluated at the reactant concentration and temperature at the catalysts surface {for first-order kinetics, $r(C_s,T_s) = k.T_s.C_s$}. When the temperature T_s is known (or when T_b is known and there is no heat-transfer resistance so that $T_s = T_b$) as well as C_L can be solved for C_s (i.e. the concentration in the catalyst surface). Then this result, substituted in the function $r(C_s,T_s)$, gives the global rate corresponding to the bulk values C_L and T_b. Note that the global rate is obtained without considering the gas phase. This is because the assumption is made that the liquid completely covers the outer surface of the particle. No reaction can occur without transfer of reactant from liquid to particle. In order to evaluate the transfer rate of a gaseous reactant from gas to liquid, the mass-transfer coefficient ($k_L.a_g$) would be necessary.

II- Internal transport processes – reaction and diffusion in porous catalysts

The reaction that occurs within the pellet consumes reactant and evolves (or absorbs) the heat of reaction. At steady state the average rate for the whole pellet will be equal to the global rate at the location of the pellet in the reactor. The concentration and temperature of the bulk fluid at this location may not be equal to the values at the outer surface of the pellet. Also, it should be remembered that all intra-pellet transport effects will become less important as the pellet size decreases. For fluidized-bed and slurry reactors intra-particle transport processes can usually be neglected.

Intrapellet mass transfer:

Diffusivity or **diffusion coefficient,** is a proportionality constant between the molar flux due to molecular diffusion and the gradient in the concentration of the species (or the driving force for diffusion). Diffusivity is encountered in Flick's law and numerous other equations of physical chemistry. It is generally prescribed for a given pair of species. For a multi-component system, it is prescribed for each pair of species in the system. The higher the diffusivity (of one substance with respect to another), the faster they diffuse into each other.

Knudsen diffusion, is a means of diffusion that occurs in a long pore with a narrow (or very small) diameter (2–50 nm) because molecules frequently collide with the pore wall. Consider the diffusion of gas molecules through very small capillary pores. If the diameter is smaller than the mean free path of the diffusing gas molecules and the density of the gas is low, the gas molecules collide with the pore walls more frequently than with each other. This process is known as Knudsen flow or Knudsen diffusion. In fact, both Knudsen diffusion and bulk diffusion (it means the collisions, especially in the large pore radius, will occur between bulk molecules rather than molecules and pore wall) are important.

A: **Gaseous diffusion in single cylindrical pores:**

In a porous solid with interconnected pathways, a gas molecule may collide with another molecule or with the pore walls. When the gas pressure is high, molecule-molecule collisions dominate and the system is said to be in the normal or Fickian regime. At low pressure, collisions are dominantly between molecules and the walls, and the free path is restricted by the geometry of the void space. In this regime, termed Knudsen diffusion, the presence of other gases no longer affects the transport, and the flux depends only on the density gradient of the species of interest .

Basic equations, for many catalysts and reaction conditions (especially pressure) both bulk and Knudsen diffusion contribute to the mass-transport rate within the pore volume. For some years the proper combination of the two mechanisms was in doubt. About 1961 three independent investigations proposed identical equation for the rate of diffusion (in a binary gaseous mixture of *A* and *B*) in terms of the bulk diffusivity D_{AB} and Knudsen diffusivity D_K. If N_A is the molar flux of *A*, it is convenient to represent the result as:

$$N_A = -\frac{p_t}{R_g T} D \frac{dy_A}{dx} \tag{1}$$

Where; y_A is the mole fraction of *A*, *x* is the coordinate in the direction of diffusion, and *D* is a combined diffusivity given by:

$$D = \frac{1}{(1-\alpha . y_A)/D_{AB} + 1/(D_K)_A} \tag{2}$$

The quantity α is related to the ratio of the diffusion rates of *A* and *B* by:

$$\alpha = 1 + \frac{N_B}{N_A} \tag{3}$$

For reactions at steady state, α is determined by the stoichiometry of the reaction. For example, for the reaction $A \longrightarrow B$, reaction and diffusion in a pore would require equimolar counterdiffusion; that is, $N_B = -N_A$. Then $\alpha = 0$, and the effective diffusivity is:

$$D = \frac{1}{1/D_{AB} + 1/(D_K)_A} \tag{4}$$

When the pore radius is large, the combined diffusivity equation (Eqn. 2) reduce to the conventional constant-pressure form for bulk diffusion. For this condition:
$(D_K)_A \longrightarrow \infty$. The combining Eqns. (1) to (3) gives:

$$N_A = -\frac{p_t}{R_g T} D_{AB} \frac{dy_A}{dx} + y_A (N_A + N_B) \tag{5}$$

If, in addition, the diffusion is equimolar, $N_B = -N_A$, Eqn. (5) may be written:

$$N_A = -\frac{p_t}{R_g T} D_{AB} \frac{dy_A}{dx} \tag{6}$$

If the pore radius is very small, collisions will occur primarily between gas molecules and pore wall, rather than between molecules. Then the Knudsen diffusivity becomes very low, and the combined diffusivity equation (Eqn. 2) reduce to:

$$N_A = -\frac{p_t}{R_g T} (D_K)_A \frac{dy_A}{dx} \tag{7}$$

This equation is the usual one expressing Knudsen diffusion in a long capillary.

Effective diffusivities in porous catalysts are usually measured under conditions where the pressure is maintained constant. Under this condition, and for a binary counter-diffusing system, the ratio N_B / N_A is the same regardless of the extent of Knudsen and bulk diffusion . Evans *et. al.* have shown this constant ratio to be (at constant pressure):

$$\frac{N_B}{N_A} = -\sqrt{\frac{M_A}{M_B}} \tag{8}$$

$$\alpha = 1 - \sqrt{\frac{M_A}{M_B}}$$

Where *M* represents the molecular weight. Eqn. (8) applies for non-reacting conditions. When reaction occurs, stoichiometry determines α.

Calculation of Diffusivities:

In analyzing Knudsen (kə′nüd·sən) and bulk diffusivities, the important parameter is the size of the pore with reference to the mean free path. The bulk diffusivity is a function of the molecular velocity and the mean free path; that is, it is a function of temperature and pressure. The Knudsen diffusivity depends on the molecular velocity $\bar{\upsilon}$ and the pore radius *a*. In terms of simple kinetic theory, these two diffusivities may be described by the equations:

$$D_{AB} = \frac{1}{3}\bar{v}.\lambda \qquad \lambda \propto \frac{1}{p}$$

$$\left(D_K\right)_A = \frac{2}{3}\bar{v}.a$$

Where λ is the mean free path. Since λ is of the order of 1000 Å for gases at atmospheric pressure, diffusion in ***micro-pores*** of a catalyst pellet will be predominantly by the Knudsen mechanism. This would be the case for a material such as silica gel, where the mean pore radius is from 15 to 100 Å. For a pelleted catalyst of alumina, the mean ***macro-pore*** radius is about 8000 Å. At atmospheric pressure bulk diffusion would prevail in these pores. Since the mean free path is inversely proportional to pressure (See the above equation), bulk diffusivity becomes more important as the pressure increases.

For more accurate calculations the Chapman-Enskog formula has been found suitable for evaluating the bulk diffusivity at moderate temperature and pressures. The equation is (for the binary gas mixture *A*, *B*):

$$D_{AB} = 0.0018583\frac{T^{3/2}\left(1/M_A + 1/M_B \right)^{1/2}}{p_t.\sigma_{AB}^2\Omega_{AB}}$$

Where; D_{AB} = bulk diffusivity, cm^2/s.

T = temperature, K.

M_A, M_B = molecular weights of gases *A* and *B*.

p_t = total pressure of the gas mixture, atm.

σ_{AB}, ε_{AB} = constants in the Lennard-Jones potential-energy function for the molecular pair *AB*; σ_{AB} is in Å.

Ω_{AB} = collision integral, which would be unity if the molecules were rigid spheres and is a function of ($k_B\, T$ / ε_{AB}) for real gases, (k_B = Boltzmann's constant "See page 1").

Since the Lennard-Jones potential-energy function is used, the equation is strictly valid only for non-polar gases. The Lennard-Jones constants for the unlike molecular pair *AB* can be estimated from the constants for like pairs *AA* and *BB*:

$$\sigma_{AB} = \frac{1}{2}\left(\sigma_A + \sigma_B\right)$$

$$\varepsilon_{AB} = \left(\varepsilon_A . \varepsilon_B\right)^{1/2}$$

The force constant for many gases are given in the literature and are summarized in the following Table:

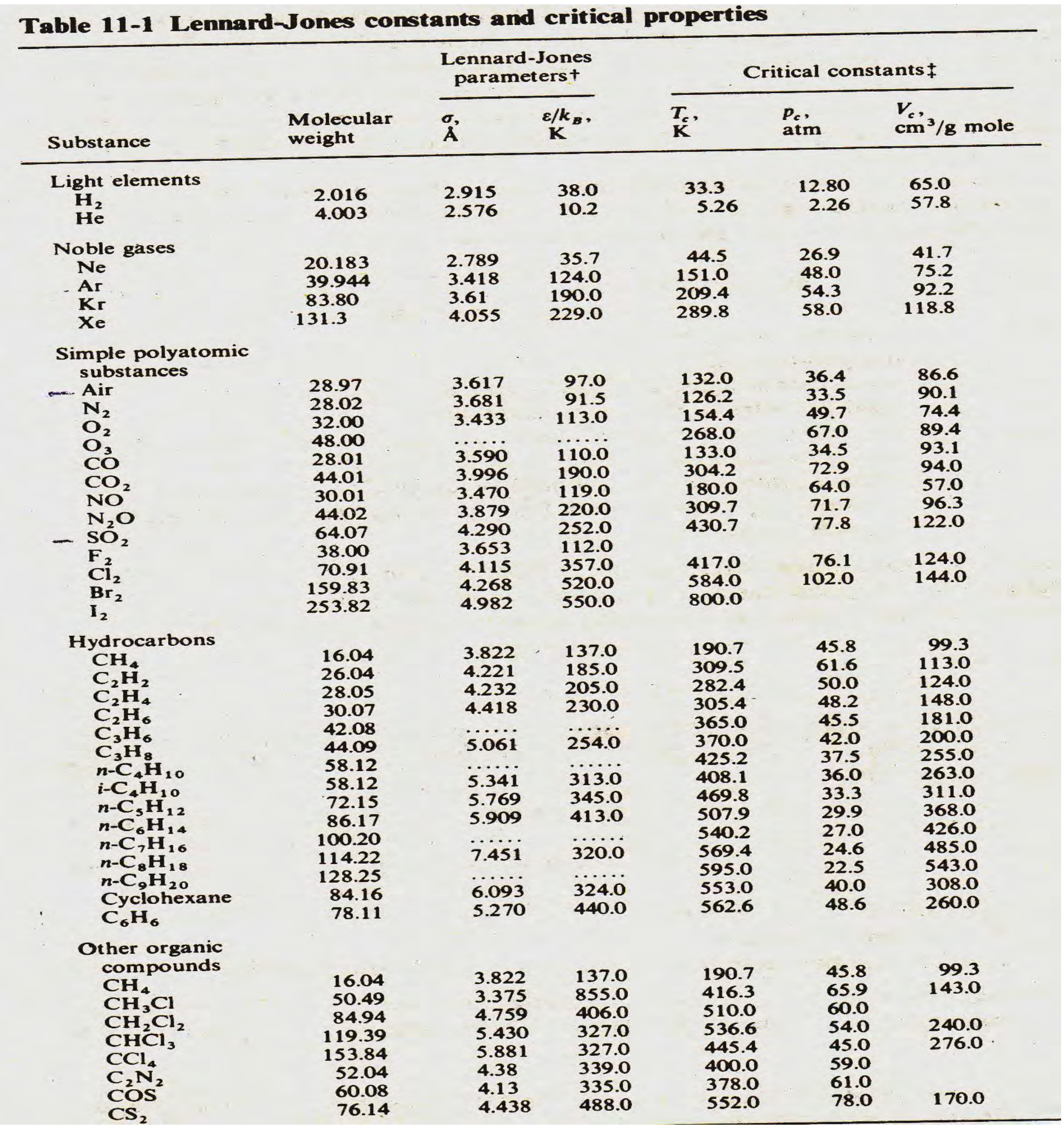


Table 11-1 Lennard-Jones constants and critical properties

Substance	Molecular weight	Lennard-Jones parameters† σ, Å	ε/k_B, K	Critical constants‡ T_c, K	p_c, atm	V_c, cm^3/g mole
Light elements						
H_2	2.016	2.915	38.0	33.3	12.80	65.0
He	4.003	2.576	10.2	5.26	2.26	57.8
Noble gases						
Ne	20.183	2.789	35.7	44.5	26.9	41.7
Ar	39.944	3.418	124.0	151.0	48.0	75.2
Kr	83.80	3.61	190.0	209.4	54.3	92.2
Xe	131.3	4.055	229.0	289.8	58.0	118.8
Simple polyatomic substances						
Air	28.97	3.617	97.0	132.0	36.4	86.6
N_2	28.02	3.681	91.5	126.2	33.5	90.1
O_2	32.00	3.433	113.0	154.4	49.7	74.4
O_3	48.00	......	......	268.0	67.0	89.4
CO	28.01	3.590	110.0	133.0	34.5	93.1
CO_2	44.01	3.996	190.0	304.2	72.9	94.0
NO	30.01	3.470	119.0	180.0	64.0	57.0
N_2O	44.02	3.879	220.0	309.7	71.7	96.3
SO_2	64.07	4.290	252.0	430.7	77.8	122.0
F_2	38.00	3.653	112.0			
Cl_2	70.91	4.115	357.0	417.0	76.1	124.0
Br_2	159.83	4.268	520.0	584.0	102.0	144.0
I_2	253.82	4.982	550.0	800.0		
Hydrocarbons						
CH_4	16.04	3.822	137.0	190.7	45.8	99.3
C_2H_2	26.04	4.221	185.0	309.5	61.6	113.0
C_2H_4	28.05	4.232	205.0	282.4	50.0	124.0
C_2H_6	30.07	4.418	230.0	305.4	48.2	148.0
C_3H_6	42.08	......	......	365.0	45.5	181.0
C_3H_8	44.09	5.061	254.0	370.0	42.0	200.0
n-C_4H_{10}	58.12	......	......	425.2	37.5	255.0
i-C_4H_{10}	58.12	5.341	313.0	408.1	36.0	263.0
n-C_5H_{12}	72.15	5.769	345.0	469.8	33.3	311.0
n-C_6H_{14}	86.17	5.909	413.0	507.9	29.9	368.0
n-C_7H_{16}	100.20	......	......	540.2	27.0	426.0
n-C_8H_{18}	114.22	7.451	320.0	569.4	24.6	485.0
n-C_9H_{20}	128.25	......	......	595.0	22.5	543.0
Cyclohexane	84.16	6.093	324.0	553.0	40.0	308.0
C_6H_6	78.11	5.270	440.0	562.6	48.6	260.0
Other organic compounds						
CH_4	16.04	3.822	137.0	190.7	45.8	99.3
CH_3Cl	50.49	3.375	855.0	416.3	65.9	143.0
CH_2Cl_2	84.94	4.759	406.0	510.0	60.0	
$CHCl_3$	119.39	5.430	327.0	536.6	54.0	240.0
CCl_4	153.84	5.881	327.0	445.4	45.0	276.0
C_2N_2	52.04	4.38	339.0	400.0	59.0	
COS	60.08	4.13	335.0	378.0	61.0	
CS_2	76.14	4.438	488.0	552.0	78.0	170.0

Those are not available otherwise may be approximated by the expressions:

$$\sigma = 1.18 . V_b^{1/3}$$

$$\frac{k_B T}{\varepsilon} = 1.30 \frac{T}{T_c}$$

Where; k_B = Boltzmann's constant.

T_c = critical temperature.

V_b = volume per mole (cm^3/g mole) at normal boiling point.

If necessary, V_b may be estimated by adding the increments of volume for the atoms making up the molecule (Kopp's law). Such increments are given in the following Table:

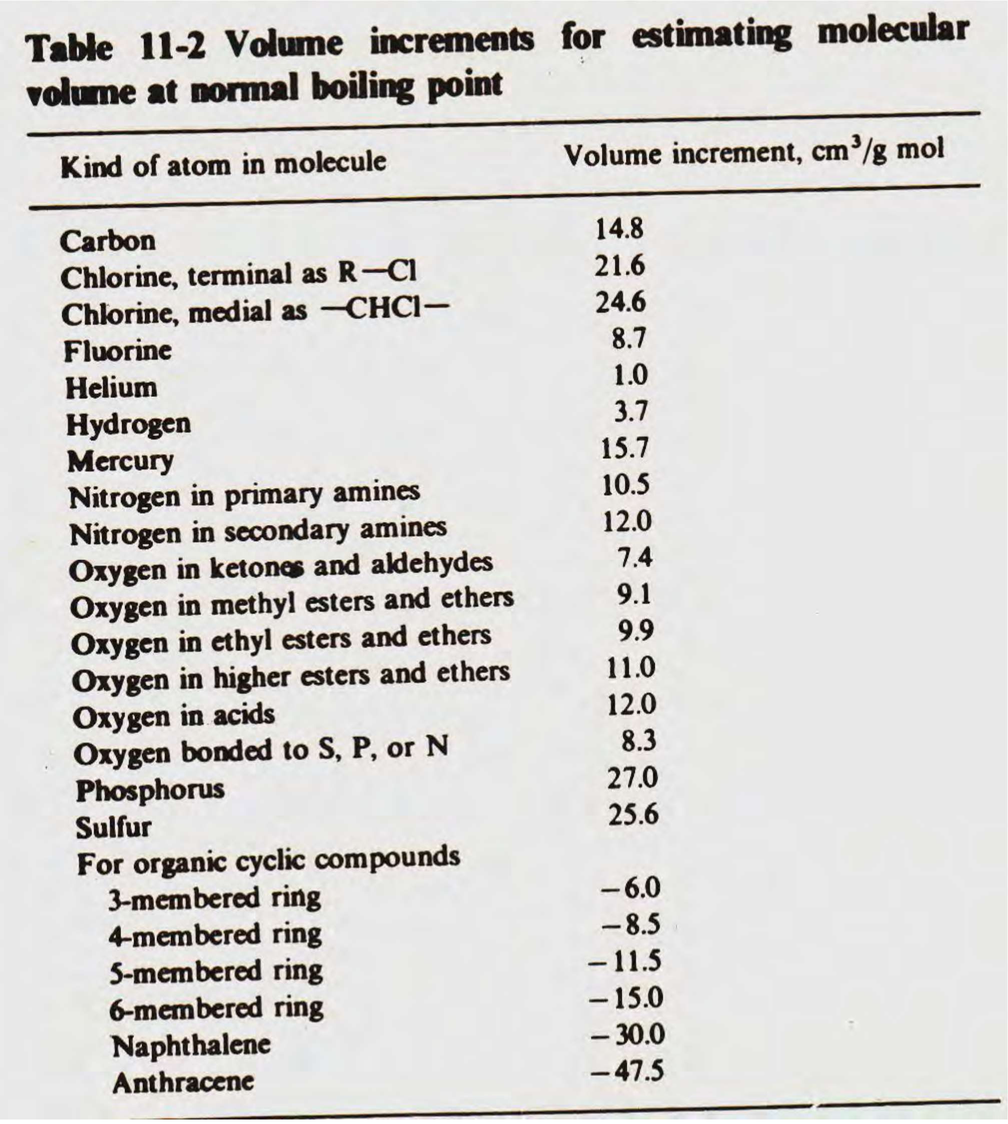


Table 11-2 Volume increments for estimating molecular volume at normal boiling point

Kind of atom in molecule	Volume increment, cm^3/g mol
Carbon	14.8
Chlorine, terminal as R—Cl	21.6
Chlorine, medial as —CHCl—	24.6
Fluorine	8.7
Helium	1.0
Hydrogen	3.7
Mercury	15.7
Nitrogen in primary amines	10.5
Nitrogen in secondary amines	12.0
Oxygen in ketones and aldehydes	7.4
Oxygen in methyl esters and ethers	9.1
Oxygen in ethyl esters and ethers	9.9
Oxygen in higher esters and ethers	11.0
Oxygen in acids	12.0
Oxygen bonded to S, P, or N	8.3
Phosphorus	27.0
Sulfur	25.6
For organic cyclic compounds	
3-membered ring	−6.0
4-membered ring	−8.5
5-membered ring	−11.5
6-membered ring	−15.0
Naphthalene	−30.0
Anthracene	−47.5

The collision integral Ω_{AB} is given as a function of ($k_B\, T / \varepsilon_{AB}$) in the following Table:

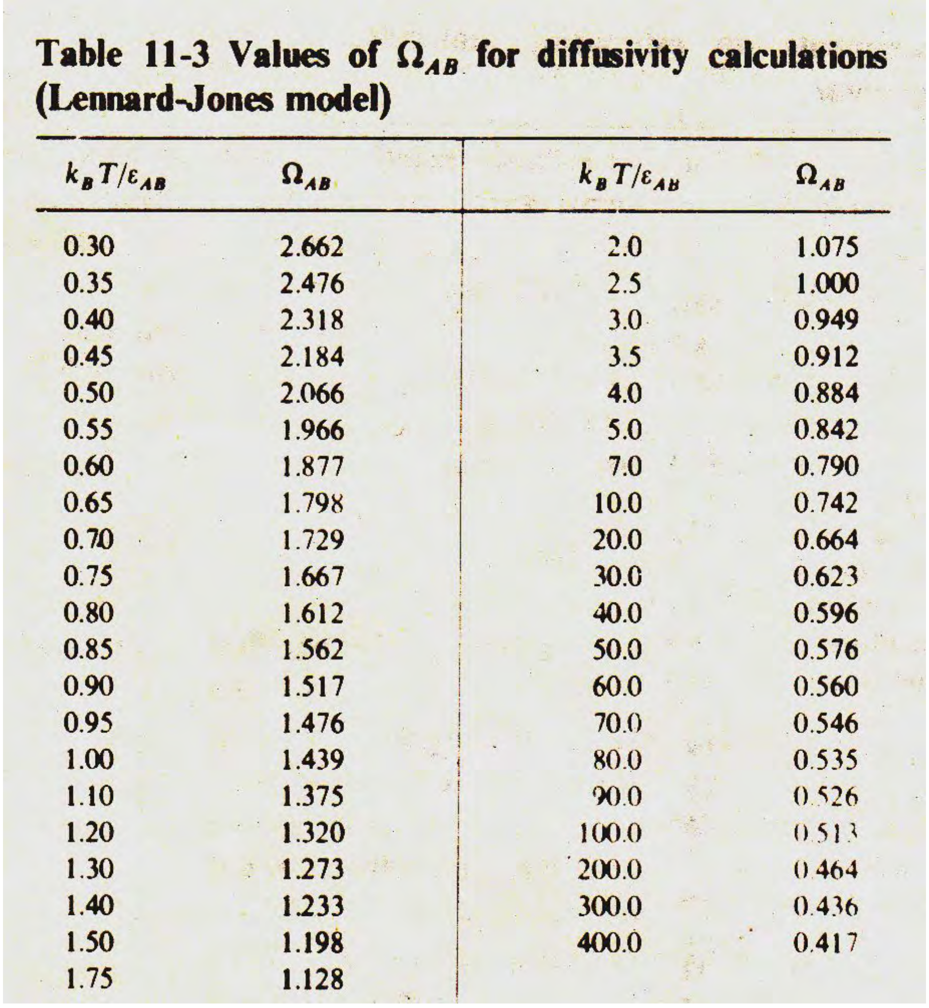


Table 11-3 Values of Ω_{AB} for diffusivity calculations (Lennard-Jones model)

$k_B T/\varepsilon_{AB}$	Ω_{AB}	$k_B T/\varepsilon_{AB}$	Ω_{AB}
0.30	2.662	2.0	1.075
0.35	2.476	2.5	1.000
0.40	2.318	3.0	0.949
0.45	2.184	3.5	0.912
0.50	2.066	4.0	0.884
0.55	1.966	5.0	0.842
0.60	1.877	7.0	0.790
0.65	1.798	10.0	0.742
0.70	1.729	20.0	0.664
0.75	1.667	30.0	0.623
0.80	1.612	40.0	0.596
0.85	1.562	50.0	0.576
0.90	1.517	60.0	0.560
0.95	1.476	70.0	0.546
1.00	1.439	80.0	0.535
1.10	1.375	90.0	0.526
1.20	1.320	100.0	0.513
1.30	1.273	200.0	0.464
1.40	1.233	300.0	0.436
1.50	1.198	400.0	0.417
1.75	1.128		

From these data and the equations, binary diffusivities may be estimated for any gas. For evaluating the Knudsen diffusivity we may use the following equation for the average molecular velocity ῡ for a component of gas in a mixture:

$$\bar{v}_A = \left(\frac{8R_g.T}{\pi.M_A}\right)^{1/2}$$

Combining this with equation: $(D_K)_A = \frac{2}{3}\bar{v}.a$ gives a working expression for $(D_K)_A$ in a circular pore of radius a.

$$(D_K)_A = 9.70\times10^3.a\left(\frac{T}{M_A}\right)^{1/2}$$

Where; $(D_K)_A$ is in square centimeters per second, a is in centimeters, and T is in degrees Kelvin.

B: Diffusion in liquids:

The mean free path in liquids is so small that Knudsen diffusion is not significant. Thus the diffusion rate is unaffected by the pore diameter and pressure (in the absence of surface diffusion). The effective diffusivity is determined by the molecular diffusivity and the pore structure of the catalyst pellet. Since the molecules in liquids are close together, the diffusion of one component is strongly affected by the force fields of nearby molecules and at the pore wall. As a result, diffusivities are concentration dependent and difficult to predict. As an approximation, we may express the diffusion flux of component *A* in a single cylindrical pore as:

$$N_A = -D_{AB} \frac{dC_A}{dx}$$

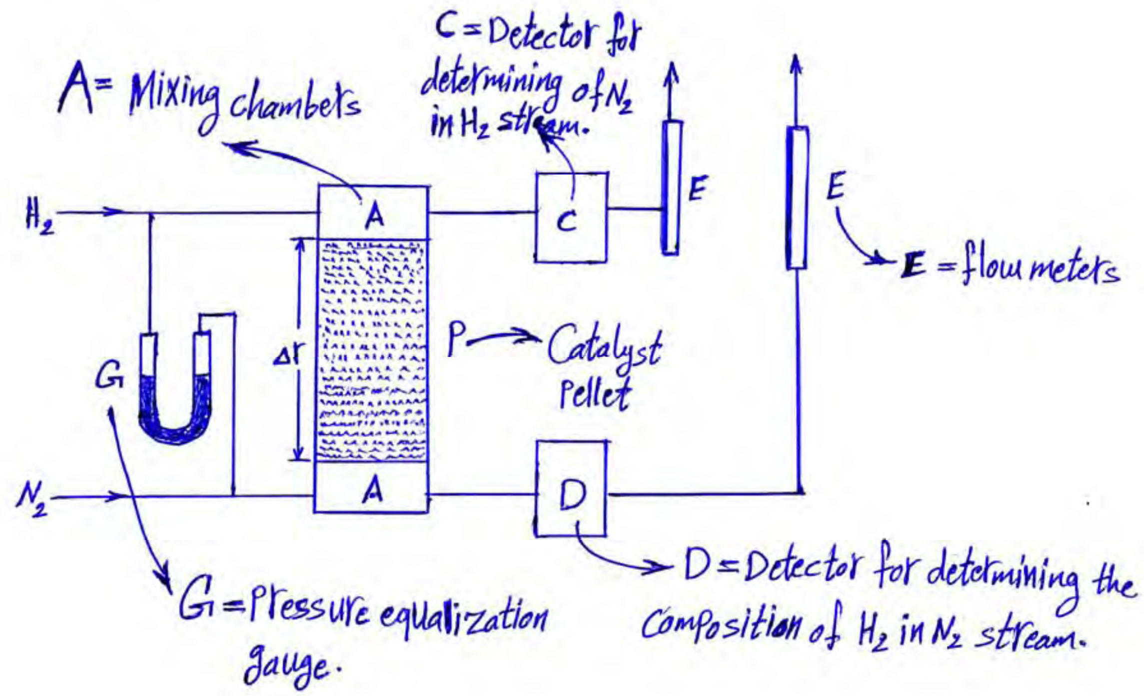
Where; D_{AB} is the molecular diffusivity of liquid *A* in a solution of *A* and *B*, and dC_A / dx is the concentration gradient in the direction of diffusion.

Values of D_{AB} are much less than those for gases and are, in general, of the order of 1×10^{-5} cm^2/s.

The major need for liquid-phase diffusivities is in problems involving slurry or trickle-bed reactors. Even though a gas phase is present, the wetting of the catalyst particles by the liquid means that the pores will be essentially filled with liquid. Since diffusivities in liquids are lower than those in gases, internal transport resistances can have a larger effect on the global rate for trickle-bed reactors than for gas-solid (two-phase), fixed-bed reactors.

Diffusion in porous catalysts:

Considerable experimental data has already been accumulated for effective diffusivities in gas-filled pores. Since reactors normally are operated at steady state and nearly constant pressure, diffusivities have also been measured under these restraints. The usual apparatus is of the steady-flow type, illustrated in the following figure for studying diffusion rates of H_2 and N_2 . The effective diffusivity is defined in terms of such rates (per unit of total cross-sectional area) by the equation:



$$(N_A)_e = -D_e \frac{dC_A}{dr} = -\frac{p_t}{R_g T} D_e \frac{dy_A}{dr}$$

Where the subscript *e* on N_A emphasizes that this is a diffusion flux in a porous catalyst rather than for a single pore, as given by Eqn. (1). If we use the concentration-independent diffusivity *D* given by Eqn. (4), D_e for a porous pellet will also be constant. Then the last equation can be integrated to give:

$$(N_A)_e = -\frac{p_t}{R_g T} D_e \frac{(y_A)_2 - (y_A)_1}{\Delta r}$$

Where Δr is the length of the pellet. If the flow rates and concentrations are measured for the experiment pictured in the above figure, $(N_A)_e$ can be calculated. Then this flux and the measured concentration and pellet length are substituted in this equation to obtain an experimental effective diffusivity.

In the absence of experimental data, it is necessary to estimate D_e from the physical properties of the catalyst. In this case the first step is to evaluate the diffusivity for a single cylindrical pore. That is, to evaluate *D* from Eqn. (4). Then a geometric model of the pore system is used to convert *D* to D_e for the porous pellet.

A model is necessary because of the complexity of the geometry of the void spaces. The optimum model is a realistic representation of the geometry of the voids (with tractable mathematics) that can be described in terms of easily measurable physical properties of the catalyst pellet. These properties are the surface area and pore volume per gram, the density of the solid phase, and the distribution of void volume according to pore size.

1- The parallel-pore model :

Wheeler proposed a model, based on the first three of these properties, to represent the mono-disperse pore-size distribution in a catalyst pellet. From ρ_s and V_g the porosity ε_p is obtained from the equation: $\varepsilon_p = \frac{v_g \cdot \rho_s}{v_g \cdot \rho_s + 1}$. Then a mean pore radius $\bar{a}$ is evaluated by writing equations for the total pore volume and total pore surface in a pellet. The result, developed as shown in the following equation: $\bar{a} = \frac{2V_g}{S_g}$

By using V_g, S_g, and ρ_s, Wheeler replaced the complex porous pellet with an assembly (having a porosity ε_p) of cylindrical pores of radius $\bar{a}$. To predict D_e from the model the only other property necessary is the length x_L of the diffusion path. If we assume that, on the average, the pore makes an angle of 45^o with the coordinate r in the resultant direction of diffusion (for example, the radial direction in a spherical pellet), $x_L = \sqrt{2r}$.

Owing to pore interconnections and non-cylindrical shape, this value of x_L is not very satisfactory. Hence, it is customary to define x_L in terms of an adjustable parameter, the tortuosity factor δ, as follows: $x_L = \delta r$.

An effective diffusivity can now be predicted by combining Eqn. (1): [$N_A = -\frac{p_t}{R_g T} D \frac{dy_A}{dx}$], for a single pore with this parallel-pore mode.

To convert D, which is based on the cross-sectional area of the pore, to a diffusivity based upon the total area perpendicular to the direction of diffusion, D should be multiplied by the porosity. Thus, the diffusivity is: $D = \varepsilon.D$. In Eqn. (1), x is the length of a single, straight cylindrical pore.

To convert this length to the diffusion path in a porous pellet, x_L from equation $x_L = \delta r$ should be substituted for x. Therefore, $1/dx_L = 1/\delta\, dr$. With these modifications the diffusive flux in the porous pellet will be:

$$(N_A)_e = -\frac{p_t}{R_g T} \cdot \frac{\varepsilon D}{\delta} \cdot \frac{dy_A}{dr}$$

Comparison with diffusivity equation in porous catalysts: $(N_A)_e = -\frac{p_t}{R_g T} D_e \frac{dy_A}{dr}$,

shows that the effective diffusivity here is: $D_e = {\varepsilon D}/{\delta}$.

Where D is given by Eqn. (4): $D = \dfrac{1}{1/D_{AB} + 1/(D_K)_A}$.

The use of these equations to predict D_e is somewhat limited because of the uncertainty about δ. Comparison of D_e from the last equation with values obtained from experimental data for various catalysts shows that δ varies from less than unity to more than 6.

2- The random- pore model:

This model was originally developed for pellets containing a bidisperse pore system, such as the alumina. It is supposed that the pellet consists of an assembly of small particles. When the particles themselves contain pores (micro-pores), there exists both a macro and a micro void-volume distribution. The voids are not imagined as capillaries, but more as an assembly of short void regions surrounding and between individual particles.

The nature of the interconnection of macro and micro void regions is the essence of the model. Transport in the pellet is assumed to occur by a combination of diffusion through the macro regions (of void fraction ε_M), the micro regions (of void fraction ε_μ), and a series contribution involving both regions. It is supposed that both micro and macro regions can be represented as straight, short cylindrical pores of average radii $\bar{a}_M$ and $\bar{a}_\mu$. The magnitude of the individual contributions is dependent on their effective cross-sectional areas (perpendicular to the direction of diffusion).

The details of the development are given elsewhere, but in general these areas are evaluated from the probability of pore interconnections. The resultant expression for D_e may be written:

$$D_e = \overline{D}_{M.}\varepsilon_M^2 + \frac{\varepsilon_\mu^2(1+3\varepsilon_M)}{1-\varepsilon_M}\overline{D}_\mu$$

Here $\overline{D}_{M.}$ and $\overline{D}_\mu$ are obtained by applying Eqn.(4) to macro and micro regions. Thus;

$$\frac{1}{\overline{D}_M} = \frac{1}{D_{AB}} + \frac{1}{(\overline{D}_K)_M}$$

$$\frac{1}{\overline{D}_\mu} = \frac{1}{D_{AB}} + \frac{1}{(\overline{D}_K)_\mu}$$

No tortuosity factor is involved in this model. The actual path length is equal to the distance coordinate in the direction of diffusion. To apply D_e-equation requires void fractions and mean pore radii for both macro and micro regions. The mean pore radii can be evaluated for the micro region by applying $\bar{a} = \frac{2V_g}{S_g}$ to this region.

However, $\bar{a}_M$ must be obtained from the pore-volume distribution, as described. The mean pore radii are necessary in order to calculate $(\overline{D}_{K.})_M$ and $(\overline{D}_K)_\mu$ from the above equations.

The random-pore model can also be applied to monodisperse systems. For a pellet containing only macro-pores, $\varepsilon_\mu = 0$ and D_e-equation becomes:

$$D_e = \overline{D}_{M.}\varepsilon_M^2$$

Similarly, for a material such as silica gel, where $\varepsilon_M = 0$, the effective diffusivity is:

$$D_e = \overline{D}_\mu.\varepsilon_\mu^2$$

Comparison of these last two equations with $D_e = {}^{\varepsilon D}\!/_{\delta}$ indicates that $\delta = 1/\varepsilon$.

The significance of the random-pore model is that the effective diffusivity is proportional to the square of the porosity.

Example: Calculate the pressure drop in a 60 ft length of $1\frac{1}{2}$ in. schedule 40 pipe packed with catalyst pellets $\underline{1/4}$ in diameter when $104.4 \frac{Lb}{h}$ of gas is passing through the bed. the temperature is constant along the length of pipe at 260°C. The void fraction is 45% and the properties of the gas are similar to those of air at this temperature The entering pressure is 10 atm?

Solution) At the end of the reactor $Z = L \Rightarrow \frac{P}{P_0} = \left[1 - \frac{2\beta_0 L}{P_0}\right]^{1/2}$

$$\beta_0 = \frac{G(1-\mathcal{E}_P)}{g_c\, \rho\, D_P\, \mathcal{E}_P^3}\left[\frac{150(1-\mathcal{E}_P)\mu}{D_P} + 1.75G\right]$$

For $1\frac{1}{2}$ in $\Rightarrow$ schedule 40 pipe, $A_c = 0.01414\ ft^2$

$$G = \frac{\text{mass flow rate}}{A_c} = \frac{104.4\ Lb/h}{0.01414\ ft^2} = 7383.3\ \frac{Lb}{h \cdot ft^2}$$

For air at 260°C and 10 atm.

$\mu = 0.0673\ Lb/ft \cdot h$

$\rho = 0.413\ Lb/ft^3$

From the problem statement, $D_P = \frac{1}{4}\ in = 0.0208 ft$

$g_c = 4.17 \times 10^8\ \frac{Lbm \cdot ft}{Lb_f \cdot h^2}$

$$\beta_0 = \left[\frac{7383.3\ Lbm/ft^2 \cdot h\,(1-0.45)}{(4.17\times10^8\ Lb_m \cdot ft/Lb_f\, h^2)(0.413\ Lb_m/ft^3)(0.0208 ft)(0.45)^3}\right] \times$$

$$\left[\frac{150(1-0.45)(0.0673\ Lbm/ft \cdot h)}{0.0208\ ft} + 1.75(7383.3)\frac{Lbm}{ft^2 \cdot h}\right]$$

$$= 0.01244 \frac{\text{lbf}\cdot\text{h}}{\text{ft}\cdot\text{lbm}} (266.9 + 12{,}920.8) \frac{\text{lbm}}{\text{ft}^2\text{-h}} = 164.1 \frac{\text{lbf}}{\text{ft}^3}$$

$$\beta_0 = 164.1 \frac{\text{lbf}}{\text{ft}^3} \times \frac{1\,\text{ft}^2}{144\,\text{in}^2} \times \frac{1\,\text{atm}}{14.7\,\text{lb}_f/\text{in}^2} = 0.0775 \frac{\text{atm}}{\text{ft}} = 25.8 \frac{\text{kPa}}{\text{m}}$$

$$\frac{P}{P_0} = \left[1 - \frac{2 \times 0.0775\,\text{atm}/\text{ft} \times 60\,\text{ft}}{10\,\text{atm}}\right]^{1/2}$$

$$\Rightarrow P = 0.265\,P_0 = 2.65\,\text{atm}.$$

$$\Delta P = P_0 - P = 10 - 2.65 = 7.35\,\text{atm}.$$

Example: A hydrogenation catalyst is prepared by soaking alumina particles (100 to 150 mesh size) in aqueous $NiNO_3$ solution. After drying and reduction, the particles contain about 7 wt% NiO. This catalyst is then made into large cylindrical pellets for rate studies. The gross measurements for one pellet are:

Mass = 3.15 g, Diameter = 1.00 in, Thickness = $\frac{1}{4}$ in, volume = 3.22 cm^3

The Al_2O_3 particles cotain micropores, and the pelleting process introduces macropores surrounding the particles. From the experimental methods already described, the macropore volume of the pellet is 0.645 cm^3 and the micropore volume is 0.40 cm^3/g of particles. From this information calculate:

(a) The density of the pellet.

(b) The macropore volume in cubic centimeters per gram.

(c) The macropore void fraction in the pellet.

(d) The micropore void fraction in the pellet.

(e) The solid fraction.

(f) The density of the particles.

(g) The density of the solid phase.

(h) The void fraction of the particles.

Solution)

(a) $$\underset{\text{Pellet}}{\rho_p} = \frac{3.15}{3.22} = 0.978 \ g/cm^3$$

(b) $$(V_g)_{Macr.} = \frac{0.645}{3.15} = 0.205 \ cm^3/g$$

(c) $$\varepsilon_{Macr.} = \frac{\text{macropore volume}}{\text{total volume}} = \frac{(V_g)_M}{1/\rho_p} = \frac{0.205}{1/0.978} = 0.200 \doteq 20\%$$

(d) $$(V_g)_{Micr.} = 0.40 \ cm^3/g$$

then $$\varepsilon_{micr.} = \frac{(V_g)_{micr}}{1/\rho_p} = \frac{0.40}{1/0.978} = 0.391 \cong 40\%$$

(e) The solids fraction ε_s : $1 = \%100 = \varepsilon_M + \varepsilon_\mu + \varepsilon_s$

$$\Rightarrow \varepsilon_s = 1 - 0.200 - 0.391 = 0.409 \cong 40\%$$

(f) $$\underset{\text{Particles}}{\rho_{Part.}} = \frac{3.15}{3.22 - 0.645} = 1.22 \ g/cm^3$$

or $$\rho_{Part.} = \frac{1}{1/\rho_p - (V_g)_{macr}} = \frac{\rho_p}{1 - (V_g)_M \cdot \rho_p} = \frac{0.978}{1 - 0.205(0.978)} = 1.22 \ g/cm^3$$

(g) The solid phase density (ρ_s): $$\rho_s = \frac{\text{mass of Pellet}}{(\text{volume of Pellet})\varepsilon_s} = \frac{\rho_{Pellet}}{\varepsilon_s} = \frac{0.978}{0.409} = 2.39 \ g/cm^3$$

(h) $$\varepsilon_{Part.} = \frac{(V_g)_\mu}{1/\rho_p} = \rho_p (V_g)_{Micr} = 1.22(0.40) = 0.49$$ & 0.409 is solid

For this pellet a fraction equal to $\varepsilon_M + \varepsilon_\mu = 0.591$ is void

EX.1) Rates of oxidation of SO_2 with air have been measured in a differential fixed-bed reactor. Experimental global rates are given in the following Table for two levels of conversion of SO_2 to SO_3.

Mean conversion of SO_2	r_P, gmoles SO_2/(h).(g-catalyst)	P_b, atm SO_2	SO_3	O_2
0.1	0.0956	0.0603	0.0067	0.201
0.6	0.0189	0.0273	0.0409	0.187

The Platinum catalyst was deposited only in the outer surface of the $\frac{1}{8}$ in x $\frac{1}{8}$ in Cylindrical Al_2O_3 Pellets so that intraparticle transport effects were negligible. Bulk gas compositions entering and then leaving the reactor and flow rate were measured. The gas properties are those of air (At 480°C, the viscosity is about 0.09 Lb/h.ft, the density is 0.0304 Lb/ft³, the molecular diffusivity of SO_2-air is 2.44 ft²/h). The objective of the study was to determine the significance of external diffusion resistance by calculating the concentration difference for SO_2 between bulk gas and pellet surface with neglecting possible temperature differences. The gases passed through the reactor at a superficial mass velocity of 147 Lb/h.ft², and at a pressure of 790 mmHg. The temperature of the catalyst pellets was 480°C, and the feed gas contained 6.42 mole% SO_2, and 93.58 mole% air. The external area of the catalyst pellets was 5.12 ft²/(Lb of pellets), and the void fraction of the bed was 43%?

Solution) $SO_2 + \frac{1}{2} O_2 \xrightarrow{753K} SO_3$

$$J_D = \frac{k_m \rho}{G} \left(\frac{a_m}{a_t}\right)\left(\frac{\mu}{\rho D}\right)^{2/3}$$

$r_p = k_m a_m (C_b - C_s)$, where: $C_b - C_s$ = concentration differ.

$$\Rightarrow C_b - C_s = \frac{r_p (\mu/\rho D)^{2/3}}{a_t \cdot (G/\rho) \cdot J_D}$$

The particle diameter to employ is the diameter of the sphere with the same area as that of the cylindrical pellets. Thus, (πD_p^2) will equal the sum of the areas of the الجانبي lateral and end surfaces of the cylinder:

$$\pi D_p^2 = \pi \cdot d \cdot L + 2\frac{\pi}{4}d^2 \quad \text{, where } d = \frac{1}{8}\text{ in} = \frac{1}{96}\text{ ft},\ L = \frac{1}{8}\text{ in} = \frac{1}{96}\text{ ft}$$

$$= \pi\frac{1}{96}\left(\frac{1}{96}\right) + \frac{2\pi}{4}\left(\frac{1}{96}\right)^2 \qquad (1\text{ m} = 100\text{ cm} = 3.28\text{ ft} = 39.37\text{ in}) \;\&\; (1\text{ ft} = 12\text{ in})$$

$$\Rightarrow D_p^2 = \frac{3}{2}\left(\frac{1}{96}\right)^2 \Longrightarrow D_p = 0.0128\text{ ft or } 0.0039\text{ m}.$$

The Reynolds number is: $\frac{D_p G}{\mu} = \frac{0.0128(147)}{0.09} = 21$

The Re value is greater than 10.

Therefore: $J_D = \frac{0.458}{\varepsilon_p}\left(\frac{D_p G}{\mu}\right)^{-0.407} = \frac{0.458}{0.43}(21)^{-0.407} = 0.31$

The Schmidt group is $\frac{\mu}{\rho D} = \frac{0.09}{0.0304(2.44)} = 1.21$

For 10% conversion $r_p = 0.0956$ gmol/(h)(g) , a_m = mass-transfer area

a_t = total external area of the catalyst pellets $= 5.12\,\frac{\text{ft}^2}{\text{lb-pellet}}$

$$C_b - C_s = \frac{0.0956 \times (1.21)^{2/3}}{5.12 \times (147/0.0304) \times 0.31}$$

$$= 1.40 \times 10^{-5}\text{ lbmol/ft}^3 \text{ or } 16.0\text{ kgmol/m}^3.$$

This calculation can be converted to partial pressures. In atmospheres, the difference between bulk and surface pressures of sulfur dioxide is:

$$PV = nRT \Rightarrow P = RT\cdot\left(\frac{n}{V}\right) \quad \text{where } c = \frac{n}{V}$$

$$(P_b - P_s) = RT(C_b - C_s) = 0.73\,[1.8(480+273)](1.40 \times 10^{-5})$$

$$= 0.0139\text{ atm.} \quad , P_b = 0.0603\text{ atm (from the Table)}$$

$$\& \; P_s = 0.0603 - 0.0139 = 0.0464\text{ atm or } 4.7 \times 10^3\text{ Pa}.$$

Thus P_s is about 23% less than P_b.

The same can be done with 60% conversion.

EX $\underline{\underline{2}}$) The temperature reported in Example ($\underline{1}$) was measured by inserting thermocouples in the catalyst pellets, thus giving $T_s = 480^\circ C$. Calculate the temperature difference $T_s - T_b$ for the conditions of Ex. $\underline{\underline{1}}$. The heat of reaction for: $SO_2 + \frac{1}{2} O_2 \longrightarrow SO_3$ is approximately $(-23000 \frac{cal}{gmol})$ at $480^\circ c$, and the activation energy may be taken as 20000 cal/gmol?

$C_p = 0.26\ Btu/lb^\circ F$

$K_f = 0.03343 \frac{Btu}{h.ft^\circ F}$

$G = \rho u = 147 \frac{Lb}{h.ft^2}$.

solution) $$J_H = \frac{h}{C_p G}\left(\frac{a_m}{a_t}\right)\left(\frac{C_p . \mu}{k_f}\right)^{2/3}$$

$$h . a_m (T_s - T_b) = r_p(-\Delta H)$$

$$\Rightarrow T_s - T_b = \frac{r_p (-\Delta H)\left(C_p . \mu / k_f\right)^{2/3}}{a_t \cdot J_H \cdot C_p \cdot G}$$

$$\text{Prandtl number} = \frac{C_p \mu}{k_f} = \frac{0.26 \times 0.09}{0.03343} = 0.6999 \simeq 0.7$$

The Reynolds number is $\frac{D_p G}{\mu} = 21$ greater than 10

Thus, $J_H = J_D = 0.31$.

$(-\Delta H) = 23000 \frac{cal}{g\,mol}$, C_p in $\frac{Btu}{lb\,\Delta^\circ F}$ or $\frac{cal}{g\,\Delta^\circ C}$ where:

$\Delta^\circ C = 1.8\,\Delta^\circ F$

$\Delta K = 1.8\,\Delta^\circ R$

$\Delta K = \Delta^\circ C$

$\Delta^\circ R = \Delta^\circ F$

$$T_s - T_b = \frac{(0.0956)(23000)(1.8)(0.7)}{(5.12)(0.31)(0.26)(147)} = 51^\circ F \text{ or } \underset{\frac{51}{1.8}''}{28^\circ C}$$

$$\underset{\underline{\underline{T}}}{^\circ F} = 1.8\,\underset{\underline{\underline{T}}}{^\circ C} + 32$$

$$T_b = T_s - 28 \Rightarrow T_b = 480 - 28 = 452^\circ C.$$

The temperature difference could also have been obtained from the concentration difference by using the energy balance.

$$T_s - T_b = (C_b - C_s)\frac{(-\Delta H)}{C_p . \rho}\left(\frac{C_p \mu / k_f}{\mu / \rho D}\right)^{2/3}\left(\frac{J_D}{J_H}\right)$$

$$T_s - T_b = 1.40 \times 10^{-5}\left(\frac{23000\,(1.8)}{0.26\,(0.0304)}\right)\left(\frac{0.70}{1.21}\right)^{2/3} . \left(\frac{0.31}{0.31}\right) = 51^\circ F \text{ or } 28^\circ C$$

Thus, with an $E_a = 20000 \frac{cal}{gmol}$, a $28^\circ c$ temperature drop would cause a 40% decrease in rate at $480^\circ c$.

Example -1- one method of determining the gas bubble -to- liquid mass transfer cofficients, k_L, is to introduce a step function of transferable component A, in the gas stream fed to the slurry reactor. If no catalyst particles are present, so that the gas bubbles, whose average diameter was 1.8 mm, rise through only the liquid. Calculate the mass-transfer coefficient and the superficial mass velocity by using the following data: vertical bubble velocity = 22.5 cm/s viscosity of liquid phase = 0.01 g/cm.s, acceleration of gravity = 980 g/s². molecular diffusivity for bubbles rising through the liquid phase because of gravitational force is about 2×10^{-5} cm²/s. Take the density of liquid phase (1 g/cm³), and the gas bubbles density (0.22 g/cm³)?

solution) $1.8\ mm = d_b < 2.5\ mm$.

$$\Rightarrow k_L\left(\frac{\mu_L}{\rho_L D}\right)^{2/3} = 0.31\left(\frac{\Delta\rho\cdot\mu_L\cdot g}{\rho_L^2}\right)^{1/3}$$

$$\Rightarrow k_L = (0.31)\left[\frac{(\Delta\rho\cdot\mu_L\cdot g/\rho_L^2)^{1/3}}{(\mu_L/\rho_L\cdot D)^{2/3}}\right]$$

$$\Delta\rho = 1 - 0.22 = 0.78\ g/cm^3.$$

$$\Rightarrow k_L = (0.31)\left[\frac{[0.78(0.01)(980)/(1)^2]^{1/3}}{[(0.01)/(1)(2\times10^{-5})]^{2/3}}\right] = ?\ cm/s.$$

$$G = V_B\cdot\rho_{gas\ bubbles} = 22.5\times0.22 = ?\ g/cm^2.s.$$

Note: The diameter of the gas bubbles formed over a porous plate →

→ Can be calculate from koide relationship as follows:

$$d_b = (1.35) \times \left\{ \frac{(U/g) \cdot \delta_P}{(\delta_P U^2 \cdot \rho_L / \sigma_L)^{1/2}} \right\} \left(\frac{\sigma_L \cdot \delta_P}{g \cdot \rho_L} \right)^{1/3}$$

where: d_b = bubble diameter, cm.

U = gas velocity through the porous plate.

δ_P = Pore diameter of porous plate.

σ_L = surface tension of liquid.

ρ_L = density of liquid.

g = acceleration of gravity,

Example -2- The reaction: $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(aq)}$ is catalyzed by activated carbon. Hence, it provides a means of studying mass transfer in a three-phase aqueous slurry of carbon particles. During the steady-state period and when the equilibrium exists at the bubble-liquid interface, Henry's law constant for oxygen in water at $25^\circ C$ is $H = 35.4\ [g\,mol/(cm^3\ of\ gas)]/[g\,mol/cm^3\ of\ liquid)]$. In order to evalute the liquid-to-particle coefficient, k_c, the following relationship may be applied: $\frac{1}{k_c} = \frac{a_c\, C_g}{H}\left(\frac{1}{r_{O_2}} - \frac{1}{r_{O_2,b}}\right)$ with the density of the carbon particles ($\rho_p = 0.80\ g/cm^3$). The gas feeds containing 1.2 to 2.3% SO_2 & 21% O_2 in helium at $25^\circ C$ and 1 atm. Since oxygen is slightly soluble in water, it was the limiting reactant. The results showed that at these conditions the rate was first-order in oxygen bubbles and zero order in SO_2. Rates of SO_2 oxidation (rates of disappearance of oxygen) in aqueous slurries of activated carbon at $25^\circ C$ are given in the Table for several concentration (m_s) of carbon particles. The gas bubble size was about 3 mm. The gas hold-up (V_B) measurements (measuring the increase in volume when gas is bubbled through the slurry) gave $V_B = 0.070\ cm^3\ gas/cm^3\ of\ liquid$. Rates were also measured by enclosing the carbon particles in stationary baskets made from stainless-steel screen. For $m_s = 0.0333\ g/(cm^3\ of\ water)$, and for $d_p = 0.542\ mm$, the rates without and with particles held in the baskets were:

$r_{O_2} = 5.05 \times 10^{-9}\ g\,mol/s\cdot(cm^3\ of\ water)$: (no baskets)

$r_{O_2,b} = 6.08 \times 10^{-9}\ g\,mol/s\cdot(cm^3\ of\ water)$: (particles in baskets)

Carbon particle size, d_p, mm	Particle concentration, m_s g/(cm³ of water)	Rate, $r_{O_2} \times 10^9$ mol/s(cm³ of liquid)
0.03	0.037	21.0
0.03	0.0111	10.4
0.03	0.0056	7.44
0.03	0.00278	4.11
0.03	0.00139	2.33

For constant $(C_L)_{eq}$ & d_p, the above data gives straight line with an intercept equal to 3.6×10^7. Calculate the mass-transfer coefficients. K_L, k_c, and the reaction resistance, k?

Solution) $$\frac{1}{k_o H} = \frac{a_c}{a_g} \cdot \frac{1}{K_L} + \frac{1}{k_c} + \frac{1}{k} \quad \text{---} ①$$

$$r_v = r_{O_2} = k_o H a_c (C_L)_{eq} \Rightarrow k_o H = \frac{r_{O_2}}{a_c \cdot (C_L)_{eq}}$$

$$\Rightarrow \frac{1}{k_o H} = \frac{a_c \cdot (C_L)_{eq}}{r_{O_2}} \quad \text{---} ②$$

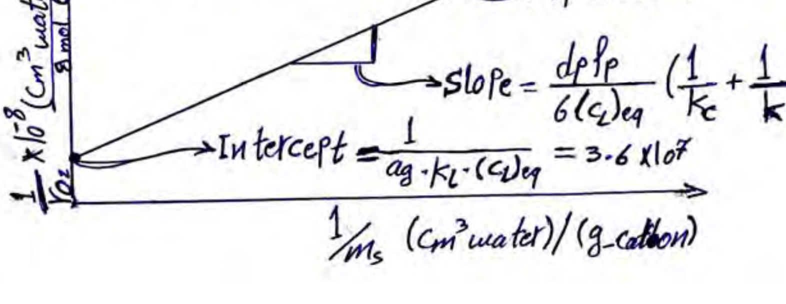
Substituting Eq② in Eq① gives:

$$\frac{(C_L)_{eq}}{r_{O_2}} = \frac{1}{a_g \cdot K_L} + \frac{1}{a_c}\left(\frac{1}{k_c} + \frac{1}{k}\right) \quad \text{---} ③$$

For spherical particles: $a_c = \frac{\pi d_p^2}{\pi d_p^3/6}\left(\frac{1}{\rho_p}\right) m_s = \frac{6 \cdot m_s}{d_p \rho_p}$

$$\frac{1}{a_c} = \frac{d_p \cdot \rho_p}{6 m_s} \Rightarrow \frac{(C_L)_{eq}}{r_{O_2}} = \frac{1}{a_g \cdot K_L} + \frac{d_p \rho_p}{6 m_s}\left(\frac{1}{k_c} + \frac{1}{k}\right) \quad \text{---} ④$$

$$\Rightarrow \frac{1}{r_{O_2}} = \frac{1}{a_g \cdot K_L \cdot (C_L)_{eq}} + \frac{d_p \rho_p}{6 (C_L)_{eq}}\left(\frac{1}{k_c} + \frac{1}{k}\right) \cdot \frac{1}{m_s}$$



$$\text{slope} = \frac{d_p \rho_p}{6 (C_L)_{eq}}\left(\frac{1}{k_c} + \frac{1}{k}\right)$$

$$\text{Intercept} = \frac{1}{a_g \cdot K_L \cdot (C_L)_{eq}} = 3.6 \times 10^7$$

$$\Rightarrow \frac{1}{a_g \cdot k_L \cdot (C_L)_{eq}} = 3.6 \times 10^{7} \quad ---⑤$$

For spherical bubbles of diameter d_b : $a_g = \frac{\pi d_b^2}{\pi d_b^3/6} V_B = \frac{6}{d_b} V_B$

$$\Rightarrow a_g = \frac{6}{\underset{3\,mm = 0.3\,cm}{0.3}} (\underset{\frac{cm^3}{cm^3}}{0.07}) = 1.4\,cm^{-1}.$$

$$C_g = H\,(C_L)_{eq} \Rightarrow (C_L)_{eq} = \frac{C_g}{H} \quad ---⑥$$

$$PV = nRT \Rightarrow \frac{n_g}{V_g} = C_g = \frac{P}{RT}\%O_2 \Rightarrow \frac{1}{(\underset{R}{82})(\underset{T}{25+273})(\underset{H}{35.4})}(\underset{\%O_2}{0.21}) = \left(\frac{C_g}{H}\right)_{O_2}$$

$$\Rightarrow (C_L)_{eq} = \left(\frac{C_g}{H}\right)_{O_2} = 2.43 \times 10^{-7}\,g_{mol}/cm^3$$

substituting in Eqn ⑤ : $k_L = (3.6 \times 10^{7})(2.43 \times 10^{-7})(1.4) = 0.08\,cm/s$.

using the relationship : $\frac{1}{k_c} = \frac{a_c\,C_g}{H}\left(\frac{1}{r_{O_2}} - \frac{1}{r_{O_2,b}}\right) \quad ---⑦$

substituting Eq⑥ in Eq ⑦ gives : $\frac{1}{k_c} = \frac{6\,m_s}{d_p \rho_p}(C_L)_{eq} \cdot \left(\frac{1}{r_{O_2}} - \frac{1}{r_{O_2,b}}\right)$

where : $a_c = \frac{6\,m_s}{d_p \rho_p}$

$$\Rightarrow \frac{1}{k_c} = \frac{6(0.0333)(2.43 \times 10^{-7})}{0.0542(0.80)}\left(\frac{1}{5.05 \times 10^{-9}} - \frac{1}{6.08 \times 10^{-9}}\right)$$

$$= 37\,s/cm \Rightarrow k_c = 0.027\,cm/s$$

using either the slope or eqn ④ to find the value of k.

$$\frac{(C_L)_{eq}}{r_{O_2}} = \frac{1}{a_g \cdot k_L} + \frac{d_p \rho_p}{6 m_s}\left(\frac{1}{k_c} + \frac{1}{k}\right).$$

$$\Rightarrow \frac{d_p \rho_p}{6 m_s}\left(\frac{1}{k}\right) = \frac{(C_L)_{eq}}{r_{O_2}} - \frac{1}{a_g k_L} - \frac{d_p \rho_p}{6 m_s}\left(\frac{1}{k_c}\right) \quad ---⑧$$

$$\left.\begin{aligned} \frac{1}{a_g k_L} &= \frac{1}{1.4(0.08)} = 8.9(s) \\ \frac{d_p \rho_p}{6 m_s}\left(\frac{1}{k_c}\right) &= \frac{0.0542(0.80)}{6(0.0333)}\left(\frac{1}{0.027}\right) = 8.0\,(s) \end{aligned}\right\} \Rightarrow \frac{d_p \rho_p}{6 m_s}\left(\frac{1}{k}\right) = \frac{2.43 \times 10^{-7}}{5.05 \times 10^{-9}} - 8.9 - 8.0$$

$$\Rightarrow \frac{d_p \rho_p}{6 m_s}\left(\frac{1}{k}\right) = 31.2\,(s)$$

$$\Rightarrow k = 0.696 \times 10^{-2}$$

Example: The oxidation of dilute aqueous solutions of acetic acid was studied in a trickle-bed reactor using a commercial, iron oxide catalyst. Air and solutions of acetic acid saturated with oxygen (by bubbling air through the solution at atmospheric pressure) flowed at 252°C and 26[illegible] atm downward over 0.0541 cm catalyst particles (packed to a depth of 2.2 cm) in a 2.54 cm ID reactor. The flow rates are $Q_L = 0.66$ cm³/s and $Q_g = 3.5$ cm³/s. At the reactor entrance the concentration $C_{L_0 O_2}$ of oxygen in the liquid is 2.40×10^{-7} gmol/cm³, that for acetic acid is $C_{L_0 HA} = 33.7 \times 10^{-7}$ gmol/cm³, and the gas is air, saturated with water at 252°C. The bulk density of the catalyst bed is $\rho_B = 1.17$ g/cm³, while the particle density is, $\rho_p = 2.05$ g/cm³. For the reaction,

$$CH_3COOH_{(aq)} + 2O_{2(aq)} \longrightarrow 2CO_{2(aq)} + 2H_2O$$

the intrinsic rate for the disappearance of oxygen is given by:

$$r_{O_2}\,(\text{gmol}/(\text{g catalyst})(\text{s})) = \frac{9.9 \times 10^{9}\left[\exp(-21{,}000/R_g T)\right] C_{s,HA}\, C_{s,O_2}^{1/2}}{1 + 7.2 \times 10^{5}\, C_{s,HA}} \;\text{--}\, *$$

where the concentrations are those at the outer surface of the catalyst particle and T is given in degrees Kelvin. Henry's law constant for oxygen in liquid water at 252°C is 0.89 [gmol/(cm³ gas at 25°C, 1 atm)]/[gmol/cm³ liquid]. Other physical properties at 252°C and 67 atm for liquid water are estimated to be:

$\rho_L = 0.81$ g/cm³, $\mu_L = 1.18 \times 10^{-3}$ g/cm.s, $(D_{O_2}) = 2.1 \times 10^{-4}$ cm²/s, $(D_{HA})_L = 1.2 \times 10^{-4}$ cm²/s.

A - From this information calculate the global rate at the reactor entrance?

B - Also calculate the rate of mass transfer of oxygen from the gas to the liquid?

Solution: $CH_3COOH_{(aq)} + 2O_{2\,(aq)} \longrightarrow 2CO_{2\,(aq)} + 2H_2O$ ②

The reaction occurs by oxygen and acetic acid in the liquid diffusing to the catalyst particles and reacting, and oxygen is transferred from the air stream to replenish the oxygen in the liquid. The rate of oxygen transfer, per unit volume to reactor, from gas to liquid is: $r_v = k_L a_g (C_{iL} - C_L)$, where: $H = \frac{C_{ig}}{C_{iL}}$

$$\Rightarrow N_{O_2}\left[\frac{g\,mol}{(s)(cm)^3}\right] = (k_L a_g)_{O_2}\left(C_{g,O_2}/H - C_{L,O_2}\right) \text{ --- } ①$$

Similarly, the rate of oxygen and acetic acid transfer from liquid to particle are given by the expressions:

$$(r_v)_{O_2} = (k_c a_c)_{O_2}\,(C_{L,O_2} - C_{S,O_2})$$

$$(r_v)_{HA} = (k_c a_c)_{HA}\,(C_{L,HA} - C_{S,HA})$$

A - At steady state the rates of mass transfer from liquid to particle are equal to the rates of reaction. Therfore:-

$$r_{O_2} = (k_c a_c)_{O_2}(C_{L,O_2} - C_{S,O_2}) = \left(\frac{9.9\times10^9\,[\exp(-21{,}000/R_gT)]\,C_{S,HA}\,C_{S,O_2}^{1/2}}{1 + 7.2\times10^5\,C_{S,HA}}\right)(\rho_B) \text{ --- } ②$$

$$r_{HA} = (k_c a_c)_{HA}(C_{L,HA} - C_{S,HA}) = \left(\frac{9.9\times10^9\,[\exp(-21{,}000/R_gT)]\,C_{S,HA}\,C_{O_2}^{1/2}}{1 + 7.2\times10^5\,C_{S,HA}}\right)\left(\tfrac{1}{2}\rho_B\right) \text{ - } ③$$

$$G_L = \frac{Q_L \cdot \rho_L}{A_c} = \frac{0.66\,(0.81)}{\frac{\pi}{4}\,(2.54)^2} = 0.11\ g/cm^2.s.$$

$$U_L = \frac{Q_L}{A_c} = \frac{0.66}{\frac{\pi}{4}\,(2.54)^2} = 0.13\ cm/s.$$

$$Re_L = \frac{d_p U_L \rho_L}{\mu_L} = \frac{0.0541\,(0.13)(0.81)}{1.18\times10^{-3}} = 4.8 \Rightarrow \underline{\underline{(0.2 < Re_L < 2400)}}$$

$$\frac{\mu_L}{\rho_L D_{O_2}} = \frac{1.18\times10^{-3}}{0.81\,(2.1\times10^{-4})} = 6.9 \quad \& \quad \frac{\mu_L}{\rho_L D_{HA}} = \frac{1.18\times10^{-3}}{0.81\,(1.2\times10^{-4})} = 42.1$$

For spherical particles, $a_t = \frac{\pi d_p^2\,\rho_B}{(\pi d_p^3/6)\,\rho_p} = \frac{6}{0.0541}\left(\frac{1.17}{2.05}\right) = 63\ cm^2/cm^3$

substituting these values in the following equations:

$$J_D = 1.64\,Re_L^{-0.331} \Rightarrow J_D = 1.64(4.8)^{-0.331} \Rightarrow J_D \cong 0.97$$

$$(k_c a_c)_{O_2,\,HA} = J_D\,(U_L a_t)\left(\frac{\mu_L}{\rho_L D_{O_2}}\right)^{-2/3} \Rightarrow \begin{cases}(k_c a_c)_{O_2} = 0.97(0.13)(0.28) = 2.2\ s^{-1}.\\ (k_c a_c)_{HA} = 0.97(0.13)(0.19) = 1.5\ s^{-1}.\end{cases}$$

With these mass-transfer coefficients, $T = 252 + 273 = 525\,k$.

$C_{L,O_2} = 2.4\times10^{-7}$ gmol/cm³ & $C_{L,HA} = 33.7\times10^{-7}$ gmol/cm³.

All quantities in equations ② & ③ are known except C_{S,O_2} & $C_{S,HA}$.

Thus, numericall solution yields:

$$C_{S,O_2} = 33.6\times10^{-7}\ \text{gmol/cm}^3.$$
$$C_{S,HA} = 2.35\times10^{-7}\ \text{gmol/cm}^3.$$

Substituting these values in equation ✱ to obtain the global rate:

$$r_{O_2} = \frac{9.9\times10^{9}\left[\exp(-21{,}000/525R)\right](33.6\times10^{-7})^{1/2}(2.35\times10^{-7})}{1+7.2\times10^{5}(2.35\times10^{-7})} \simeq 8.4\times10^{-9}\ \text{gmol/(s)(g catalyst)}$$

B- The coefficient $(k_L\cdot a_g)_{O_2}$ can be determined as follows:-

$$(k_L\cdot a_g)_{O_2} = \mathcal{D}_{O_2}\cdot\alpha\left(\frac{G_L}{\mu_L}\right)^{n}\left(\frac{\mu_L}{\rho_L\mathcal{D}_{O_2}}\right)^{1/2}$$

$$\Rightarrow (k_L\cdot a_g)_{O_2} = (2.1)\times(10^{-4})(7)\left(\frac{0.11}{1.18\times10^{-3}}\right)^{0.40}(6.9)^{1/2} = 0.024\ s^{-1}.$$

The concentration of oxygen in the gas at 67 atm and 252°C is:

$$P = CRT \Rightarrow C_g = \frac{P_{O_2}}{R_g T} = \frac{0.21(26.2)}{82(525)},\quad \text{Air}\begin{Bmatrix}21\%\ O_2\\ 79\%\ N_2\end{Bmatrix}\rightarrow \begin{matrix}0.21(67)=\\ 0.79(67)=\end{matrix}$$

$$\Rightarrow C_g = 1.3\times10^{-4}\ \text{gmol/cm}^3$$

Henry's law constant is $H_{O_2} = 0.89$ at 25°C & 1 atm.

$$P_{O_2} = 0.21\,(26.2) = 5.50\ \text{atm at } t = 252^\circ C.$$

$$H_{O_2} = (0.89)\left(\frac{5.5}{1}\right)\left(\frac{\overset{\rightarrow 25+273}{298}}{252+273}\right)$$

$$\Rightarrow H_{O_2} = 2.78\ \frac{\text{gmol/(cm}^3\text{ gas at 5.5 atm, 252°C)}}{\text{gmol/cm}^3\text{ of liquid}}$$

substituting in equation (1) gives:

$$N_{O_2} = (0.024)\left[\frac{1.3\times10^{-4}}{2.78} - 2.4\times10^{-7}\right] = 0.024(4.59-0.02)\times10^{-5}$$
$$= 1.1\times10^{-6}\ \text{gmol/(s)(cm)}^3.$$

Per unit mass of catalyst this is: $(1.1\times10^{-6})/\rho_B = 9.4\times10^{-7}$ gmol/(s)(g catalyst)

Example: Rates of oxidation of SO_2 with air have been measured in a differential, fixed-bed reactor. The gases passed through the reactor at a pressure of 790 mmHg, or 105×10^3 Pa. The temperature of the catalyst pellets was 480°C (753 K). The gas composition is about 94% air, with the remainder SO_2 and SO_3. Estimate the diffusivity of SO_2?

Solution: A satisfactory simplification is to consider the system as a binary mixture of air and SO_2. $(K_B = 1.38066 \times 10^{-23}\ J/k)$ & $\left\{ \begin{matrix} M_{wt\,air} = 28.9 \\ M_{wt\,SO_2} = 64.1 \end{matrix} \right\}$

From Table 11-1, for air $\Rightarrow \frac{\varepsilon}{K_B} = 97°k$

& $\sigma = 3.617 \mathring{A}$ or $3.617 \times 10^{-10}\, m$ or 0.3617 nano-meters.

and for $SO_2 \Rightarrow \frac{\overset{J \xleftarrow{\text{الوحدات}}}{\varepsilon}}{\underset{J/k \xleftarrow{\text{الوحدات}}}{K_B}} = 252°k$ & $\sigma = 4.290\ \mathring{A}$ or $(0.429\, nm)$.

$$\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B) \Rightarrow \sigma_{AB} = \frac{1}{2}(3.617 + 4.290) = 3.953 \mathring{A}$$
$$= 0.3953\, nm.$$

$$\varepsilon_{AB} = (\varepsilon_A \cdot \varepsilon_B)^{1/2} \Rightarrow \varepsilon_{AB} = K_B\,(97(252))^{1/2}$$

At the temperature of 480°C.

$$\frac{K_B T}{\varepsilon_{AB}} = \frac{K_B\,(753)}{K_B\,[97(252)]^{1/2}} = 4.8$$

From Table 11-3, at $K_B T/\varepsilon_{AB} = 4.8 \Rightarrow \Omega_{AB} = 0.85$

substituting all these values in the following equation gives:

$$D_{AB} = 0.0018583 \left(\frac{T^{3/2}\,(1/M_A + 1/M_B)}{P_t\, \sigma_{AB}^2\, \Omega_{AB}} \right)^{1/2}$$

$$D_{SO_2-air} = 0.0018583 \left(\frac{\overbrace{(753)}^{T}{}^{3/2}\,(1/\overbrace{64.1}^{M_A} + 1/\overbrace{28.9}^{M_B})^{1/2}}{\underbrace{(790/760)}_{P_t}\underbrace{(3.953)}_{\sigma_{AB}}{}^2\,\underbrace{(0.85)}_{\Omega_{AB}}} \right)$$

$$= 0.629\ cm^2/s \text{ or } (0.629 \times 10^{-4}\ m^2/s).$$

Example: A nickel catalyst for the hydrogenation of ethylene has a mean pore radius of 50Å. Calculate the bulk and Knudsen diffusivities of hydrogen for this catalyst at 100°C, and 1 and 10 atm pressures, in a hydrogen-ethane mixture?

solution: From Table 11-1, for $H_2 \Rightarrow \frac{\varepsilon}{k_B} = 38\,K$ & $\sigma = 2.915\,Å$

And for $C_2H_6 \Rightarrow \frac{\varepsilon}{k_B} = 230\,K$ & $\sigma = 4.418\,Å$

For the mixture :- $\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B) = \frac{1}{2}(2.915 + 4.418) = 3.67\,Å$

$$\varepsilon_{AB} = (\varepsilon_A \cdot \varepsilon_B)^{1/2} = k_B\,[38(230)]^{1/2}$$

$$\text{or} \Rightarrow \frac{\varepsilon_{AB}}{1.38066\times10^{-23}} = [38(230)]^{1/2} \Rightarrow \frac{k_B T}{\varepsilon_{AB}} = \frac{\cancel{k_B}(273+100)}{\cancel{k_B}[(38(230)]^{1/2}} = 4.00$$

From Table 11-3, for $\frac{k_B T}{\varepsilon_{AB}} = 4 \Rightarrow \Omega_{AB} = 0.884$.

Substituting these values in the Chapman-Enskog equation gives the bulk diffusivity: $\mathcal{D}_{AB} = 0.0018583\left(\frac{T^{3/2}\left(1/M_A + 1/M_B\right)^{1/2}}{P_t \cdot \sigma_{AB}^2 \cdot \Omega_{AB}}\right)$

$$\Rightarrow \mathcal{D}_{H_2,C_2H_4} = 0.0018583\,\frac{\overset{100+273\leftarrow}{(373)^{3/2}}\left(1/2.016 + 1/30.05\right)^{1/2}}{P_t \cdot (3.67)^2 \cdot (0.884)} = \frac{0.86}{P_t}$$

⇒ This gives $(0.86\,\frac{cm^2}{s})$ at 1atm, or $(0.086\,\frac{cm^2}{s})$ at 10 atm.

The Knudsen diffusivity, which is independent of pressure, is obtained as follows :- $(\mathcal{D}_K)_A = 9.70\times10^3 \cdot a \cdot \left(\frac{T}{M_A}\right)^{1/2}$

$$\Rightarrow (\mathcal{D}_K)_{H_2} = 9.70\times10^3 \cdot (50\times10^{-8})\left(\frac{373}{2.016}\right)^{1/2} = 0.065\,\frac{cm^2}{s}.$$

These results show that 1 atm pressure the Knudsen diffusivity is much less than the bulk value. At 10 atm both bulk and Knudsen diffusivities are important.

Example:- **(a)** Calculate the combined diffusivity of hydrogen in a mixture of ethane, ethylene, and hydrogen in a pore of radius 50 Å (5.0 nm) at two total pressures, corresponding to 1 and 10 atm. Suppose that the pore is closed at one end, and that the open end is exposed to a mixture of ethylene and hydrogen. The pore wall is a catalyst for the reaction: $C_2H_4 + H_2 \longrightarrow C_2H_6$

The temperature is 100°C.

(b) For comparison calculate the combined diffusivity of hydrogen for diffusion through a noncatalytic capillary of radius 50 Å (5.0 nm). Hydrogen is supplied at one end and ethane at the other. The pressure is maintained the same at both ends of the capillary. Make the calculations for two compositions, $y_{H_2} =$ 0.5 and 0.8?

Solution: (a) Assume that the binary $H_2 - C_2H_6$ will be satisfactory for representing the diffusion of hydrogen in the three-component system.

under <u>reaction conditions</u> in a catalyst pore: From the reaction stoichiometry, the molar diffusion rates of H_2 and C_2H_6 will be equal and in opposite directions:

$$N_{H_2} = -N_{C_2H_6} \Rightarrow \alpha = 0 \Rightarrow D = \frac{1}{1/D_{AB} + 1/(D_K)A}$$

$$D = \begin{cases} \dfrac{1}{1/0.86 + 1/0.065} = 0.060\ cm^2/s \text{ at 1atm} \\[2ex] \dfrac{1}{1/0.086 + 1/0.065} = 0.037\ \frac{cm^2}{s} \text{ at 10 atm} \end{cases}$$

ملاحظة/ قيم الإنتشارية إي (0.86) و(0.086) و(0.065) تم حسابها كما في المثال السابق وعند نفس درجة الحرارة والضغط ...!!

(b) For constant-pressure diffusion, and for <u>non-reacting systems</u>:-

$$\alpha = 1 + \frac{N_{C_2H_6}}{N_{H_2}} = 1 - \sqrt{\frac{M_{H_2}}{M_{C_2H_6}}} = 1 - \sqrt{\frac{2.016}{30.05}} = 0.741$$

Then at $y_{H_2} = 0.5$; $D = \dfrac{1}{(1-\alpha y_A)/D_{AB} + 1/(D_K)A}$

$$D = \frac{1}{[1-\underbrace{0.741}_{\alpha}\underbrace{(0.5)}_{y_A}]/D_{H_2-C_2H_6} + 1/(D_K)_{H_2}}$$

$$\Rightarrow D = \frac{1}{0.630/D_{H_2-C_2H_6} + 1/(D_K)_{H_2}}$$

For the two pressures this expression gives:

$$D = \begin{cases} \dfrac{1}{0.630/0.86 + 1/0.065} = 0.062\ \frac{cm^2}{s} \text{ or } (0.062\times10^{-4}\ \frac{m^2}{s}) \text{ at 1atm.} \\[2ex] \dfrac{1}{0.630/0.086 + 1/0.065} = 0.044\ \frac{cm^2}{s} \text{ or } (0.044\times10^{-4}\ \frac{m^2}{s}) \text{ at 10 atm.} \end{cases}$$

At $Y_{H_2} = 0.8$ the two results are:-

$$D = \frac{1}{[1-\underbrace{0.741}_{\alpha}\underbrace{(0.8)}_{y_A}]/D_{H_2-C_2H_6} + 1/(D_K)_{H_2}}$$

ملاحظة: بأستخدام نفس الطريقة
اعلاه نستطيع الحصول على قيم
الأنتشارية الموضحة :-

$$D = \begin{cases} 0.063\ \frac{cm^2}{s} \text{ or } (0.063\times10^{-4}\ \frac{m^2}{s}) \text{ at 1atm.} \\ 0.050\ \frac{cm^2}{s} \text{ or } (0.050\times10^{-4}\ \frac{m^2}{s}) \text{ at 10atm.} \end{cases}$$

Note :- when bulk diffusion is significant, the effect is a function of α. For equimolar counterdiffusion, $\alpha = 0$, and y_A has no influence on D. In our example where $\alpha = 0.741$, and at 10 atm pressure, D increased only from 0.044 to 0.050 $\frac{cm^2}{s}$ as Y_{H_2} increased from 0.5 to 0.8.

①

Example: Rothfeld has measured diffusion rates for isobutane, in the isobutane-helium system, through a $\frac{1}{8}$ in long pelleted cylinder of alumina (diameter $\frac{1}{8}$ in). The measurements were at 750 mmHg total pressure and 25°C, and the diffusion direction was throgh the pellet parallel to the central axis. The following data are available:

$S_g = 76\ m^2/g$, $\varepsilon_M = 0.18$, $\varepsilon_\mu = 0.34$, $\bar{a}_M = 4800 Å$, and $\bar{a}_\mu = 84 Å$.

The mole fraction of isobutane is 1.0 on one face of the pellet and zero on the other face. The experimental results gave: $\frac{(N_A)_e R_g T \Delta r}{D_{AB} P_t (y_2 - y_1)} = -0.023$

where N_A is the diffusion flux of isobutane and D_{AB} is the bulk diffusivity in the Isobutane-helium system. (a) Calculate the experimental value of D_e. (b) What macropore tortuosity factor is indicated by the data? What is δ_M predicted by the random pore model?

Solution: (a) The chapman Enskog equation can be used to get the bulk diffusivity in the isobutane-helium system at 750 mmHg pressure and 25°C: $D_{AB} = 0.313\ cm^2/s$.

Thus, the measured diffusion flux of isobutane is: $(N_A)_e = \frac{(-0.023) D_{AB} P_t (y_2 - y_1)}{R_g T \Delta r}$

$$\Rightarrow (N_A)_e = \frac{(-0.023)(0.313)(\frac{750}{760})(0-1.0)}{82(25+273)(\frac{1}{8})(2.54)} = 9.1 \times 10^{-7}\ g\,mol/s.cm^2.$$

This value of $(N_A)_e$ can be used to calculate the experimental D_e:

$$(N_A)_e = -D_e \left(\frac{P}{R_g T}\right) \cdot \left(\frac{y_{A_2} - y_{A_1}}{\Delta r}\right) \Rightarrow D_e = -\frac{(N_A)_e R_g T \Delta r}{P(y_2 - y_1)}$$

$$\Rightarrow D_e = \frac{-9.1 \times 10^{-7}(82)(298)(\frac{1}{8})(2.54)}{(\frac{750}{760})(0-1.0)} = 0.0072\ cm^2/s.$$

(b) The parallel-pore model is designed for a monodisperse pore system. Since the macropores are much larger than the micropores, an approximate approach is to neglect the contribution of the micropores to the mass transport.

$$\mathcal{D}_e = \bar{D}_M \varepsilon_M^2 + \frac{\varepsilon_\mu^2 (1+3\varepsilon_M)}{1-\varepsilon_M} \overset{\to 0 \text{ (neglect)}}{\cancel{\bar{D}_\mu}}$$

$$\Rightarrow \mathcal{D}_e = \bar{D}_M \varepsilon_M^2 \quad , \delta = \frac{1}{\varepsilon} \quad \Rightarrow \mathcal{D}_e = \bar{D}_M \left(\frac{1}{\delta}\right) \varepsilon_M$$

$$\Rightarrow \mathcal{D}_e = \frac{\varepsilon_M \bar{D}_M}{\delta_M} \Rightarrow 0.0072 = \frac{0.18 \bar{D}_M}{\delta_M} \Rightarrow \delta_M = \frac{0.18\ \bar{D}_M}{0.0072}$$

$$\frac{1}{\bar{D}_M} = \frac{1}{\underset{0.313 \frac{cm^2}{s}}{\overset{}{\mathcal{D}_{AB}}}} + \frac{1}{(\bar{D}_K)_M} \qquad (\bar{\mathcal{D}}_K)_M = 9.70 \times 10^3 \bar{a}_M \left(\frac{T}{M_A}\right)^{1/2}$$

$$\Rightarrow (\bar{D}_K)_M = 9.7 \times 10^3 (4800 \times 10^{-8}) \left(\frac{298}{58.1}\right)^{1/2}$$

$$= 1.10 \ \frac{cm^2}{s}. \quad \text{Å} \Rightarrow cm$$

$$\Rightarrow \frac{1}{\bar{D}_M} = \frac{1}{0.313} + \frac{1}{1.10} \Rightarrow \bar{D}_M = 0.243 \ \frac{cm^2}{s}.$$

Then the tortuosity factor (δ) suggested by the data is:

$$\delta_M = \frac{0.18(0.243)}{0.0072} \Rightarrow \delta_M = 6.1$$

OR for the random-pore model: $\delta_M = \frac{1}{\varepsilon_M}$ $\Big\{$ assume that all the diffusion is in the macropores.

$$\Rightarrow \delta_M = \frac{1}{0.18} = 5.5 .$$

In reasonable agreement with the experimental result. Actually, this pellet is relatively dense (low ε_M) and probably was prepared with a high pelleting pressure. Hence, the diffusion likely is affected by the micropores.

Example:- Vycor (Porous silica) appears to have a Pore system with fewer inter-connections than alumina. The Pore system Is mono-disperse, with the somewhat unusual combination of a small mean Pore radius (45A) and a low Porosity 0.31. Vycor may be much closer to an assembly of individual voids than to an assembly of Particles surrounded by void spaces. Since the random-Pore model is based on the assembly-of-Particles concept, it is instructive to see how it applies to Vycor. Rao and Smith measured an effective diffusivity for hydrogen of 0.0029 cm^2/s in Vycor. The data were obtained using an H_2-N_2 System at 25°C and 1atm. Predict the effective diffusivity by the random-Pore model?

Solution:- only micropores are Present, and so D_e should be Predicted by means of $D_e = \bar{D}_\mu \varepsilon_\mu^2$. The mass transport in the small Pores will be Predominately by Knudsen diffusion. Hence, $\bar{D}_\mu = (\bar{D}_K)_\mu$.

Note: when the Pore radius is large $\Rightarrow (D_K)_A \rightarrow \infty$ (macro-Pore)

when the Pore radius is very small $\Rightarrow D_{AB} \rightarrow \infty$ (micro-Pore)

$$\Rightarrow D_e = (\bar{D}_K)_\mu \, \varepsilon_\mu^2 \Rightarrow D_e = 0.053\,(0.31)^2 \Rightarrow D_e = 0.005\ \frac{cm^2}{s}$$

$$\downarrow$$

$$(\bar{D}_K)_\mu = 9.7\times10^3\,(\underbrace{45\times10^{-8}}_{\bar{a}_\mu})\,\Big(\underbrace{\frac{298}{2.02}}_{M_A}\Big)^{1/2} \Rightarrow (\bar{D}_K)_\mu = 0.053\ \frac{cm^2}{s}$$

This value is very greater than the experimental result. Thus, the random-Pore model is not very suitable for Vycor.

$$\delta = \frac{\varepsilon_\mu \bar{D}_\mu}{D_e} = \frac{0.31\,(\bar{D}_K)_\mu}{D_e} = \frac{0.31\,(0.053)}{0.0029} = 5.6$$

In contrast, the tortuosity Predicted by the random-Pore model would be $\frac{1}{\varepsilon} = 3.2$

Characterisation Techniques

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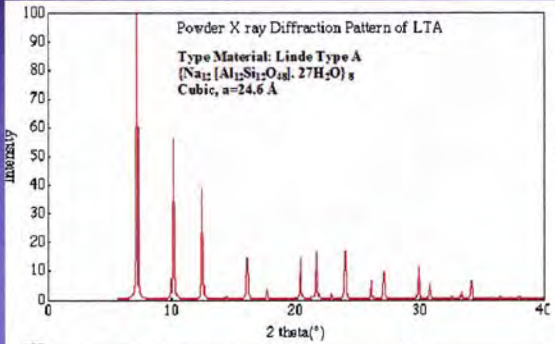
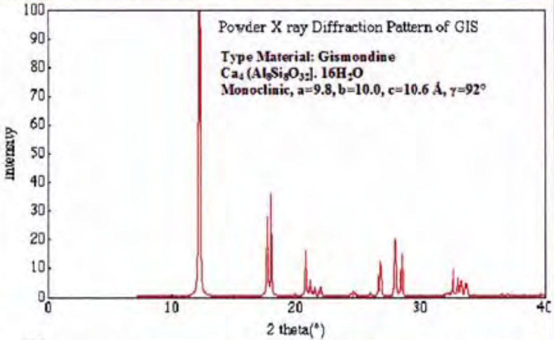
University of Technology-Baghdad

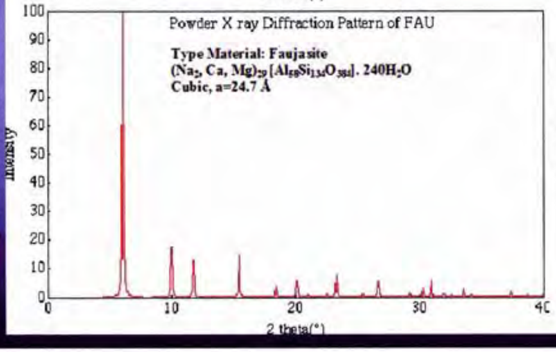
- **Characterisation Techniques**

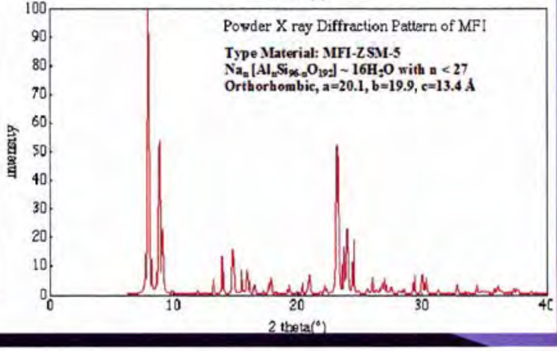
1- X-ray diffraction (XRD) analysis:

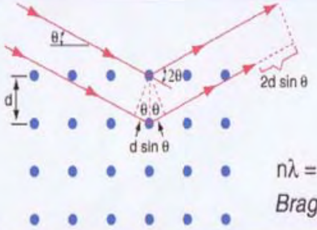
XRD is used to determine the degree of crystallinity of the zeolite samples by measuring the diffraction pattern, and may also be used to provide information about the electronic distribution of atoms throughout the zeolite structure. This can be achieved as soon as the X-ray beam collides to the atoms of the zeolite specimen and then deflects into another direction inside the XRD-machine. Each type of crystalline solid such as zeolite having unique characteristic X-ray diffraction pattern, which is typically utilized as a "fingerprint" for its identification and classification.









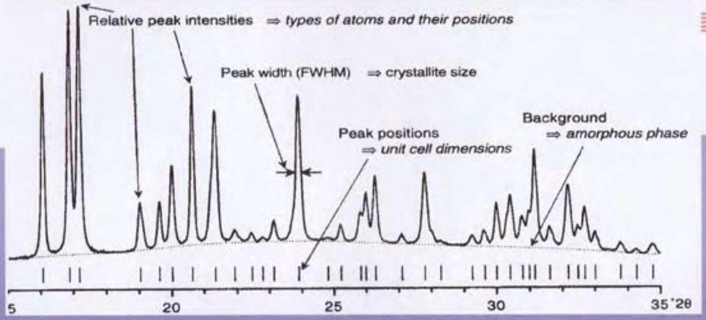


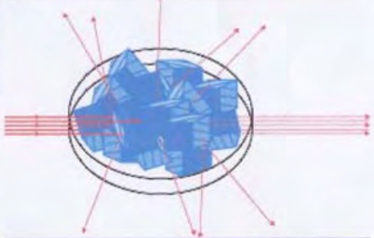
$n\lambda = 2d \sin \theta$

Bragg's Law

$$\theta_{hkl} = arcSin\left(\lambda / 2d_{hkl} \right)$$

$$a_{\circ} = \lambda \sqrt{h^2 + k^2 + l^2} \Big/ 2Sin(\theta_{hkl})$$





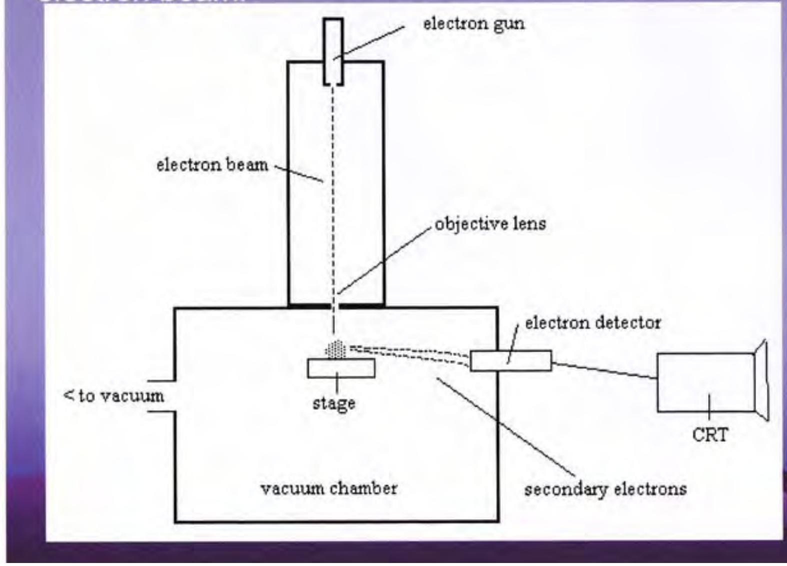
$$N_{Al} = 101.202\left[\left(a_{\circ} / \Phi \right) - 24.2115\right]$$

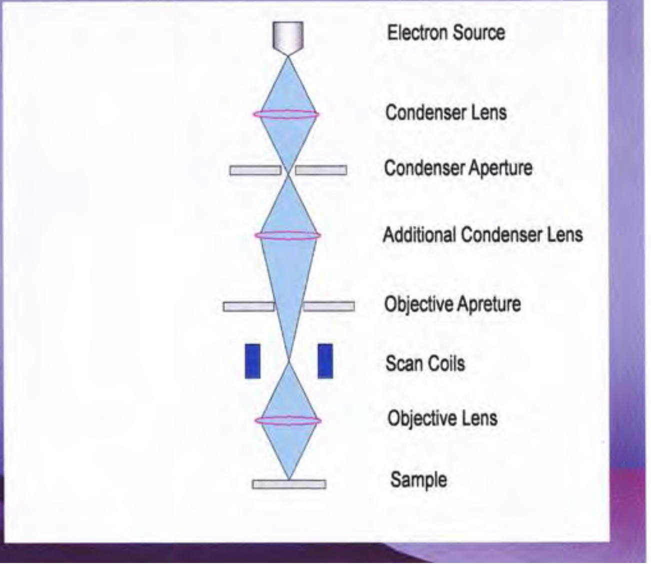
$$\left(Si / Al \right) = \left[\left(192 / N_{Al} \right) - 1\right]$$

2- Environmental scanning electron microscopy (ESEM) analysis:

An important instrument for the biological sciences and morphological observations of materials that have dimensions in the micrometer (μ m) to nanometer. The microscope column in this tool consists of three chambers; the electron gun chamber, the electron beam condenser chamber and finally the sample chamber. The detector is utilized to transfer the secondary electrons to the cathode ray tube (CRT), which can be converted into a voltage and then transformed into an image displaying the topography of the sample on an SEM screen that can be typically showed. Magnification of the image is achieved by decreasing the width of the electron beam, as the width of the CRT is fixed. This relation is expressed: $Mag = {}^{W_c}\!/\!_{w_e}$

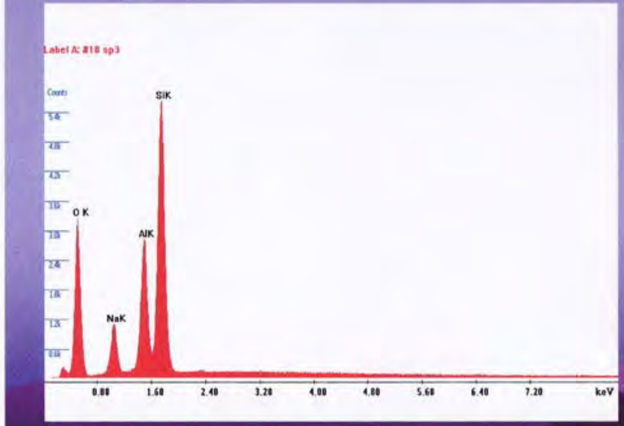
Where (*Mag*) is the magnification, (*Wc*) is the width of the CRT, and (*we*) is the width of the electron beam.

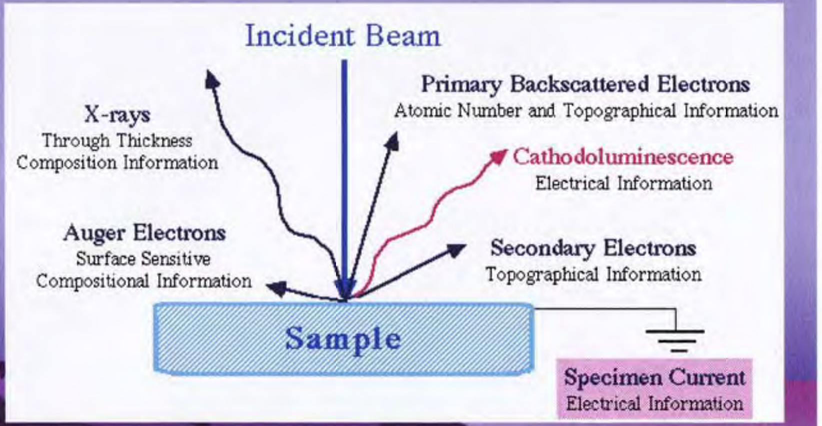




3- Energy dispersive X-ray (EDX) analysis:

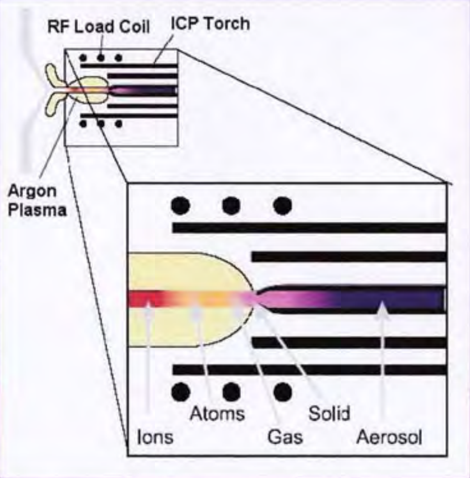
(EDX) can be used to identify the compositions of the elements on the surface of a specimen, because each element has a unique atomic structure. Therefore, the percentages by weight of different elements can be measured by EDX analysis. Usually the EDX system was used in conjunction with the SEM-Iinstrument. In general, the EDX consists of four primary components: the beam source, the X-ray detector "spectrometer", the pulse processor and the analyzer. It works when an electron beam strikes the surface of the sample and a number of reactions occur. The number and energy of X-rays emitted from each element present within the specimen can therefore be caught and determined by an energy dispersive spectrometer. The EDX spectrum just displays peaks corresponding to the energy levels and each of these peaks are unique to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen. It is also sufficient enough to utilize for estimating the indicative Si/Al average ratio for the bulk of the zeolite sample.

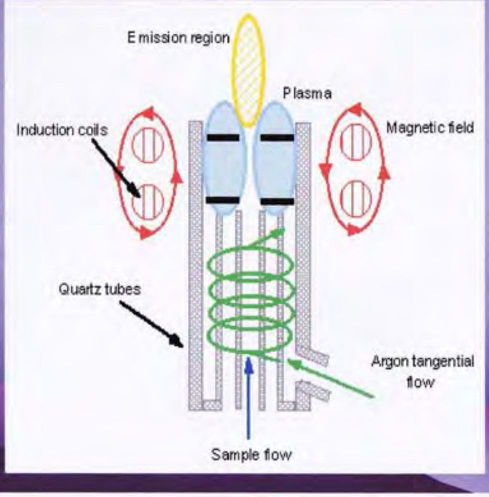




4- Inductively coupled plasma (ICP) analysis:

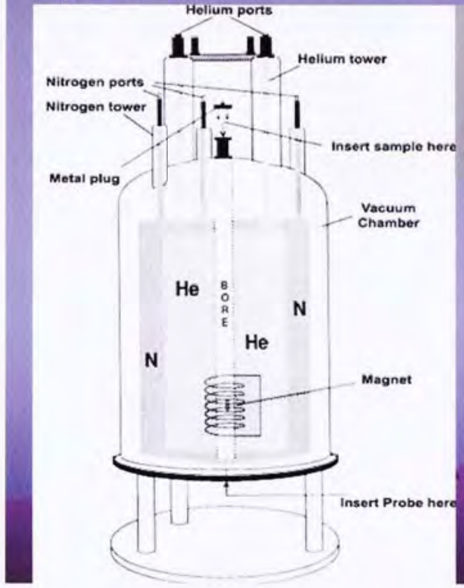
It is fundamentally a type of emission spectroscopy widely employed to detect the traces of metals within the sample, which can identify each element from the wavelength of its electro-magnetic radiation. The ionization of argon gas consequently leads to generate stable, high temperature plasma, and the liquid sample is nebulized into an aerosol and then introduced into the centre of the plasma. When the sample atoms are dissolved, vaporized, and atomized in the excitation region, light is emitted simultaneously. Afterward from this emitted light, the intensities of characteristic wavelengths are detected and compared to intensities for known standards to provide quantitative results. Since the minerals like zeolites are not easy soluble, the used sample in this work was treated by acid digestion to destroy its structure and release the metal into solution – a mixture of sulphuric acid "H2SO4", perchloric acid "HClO4", nitric acid "HNO3" and/or hydrofluoric acid "HF".



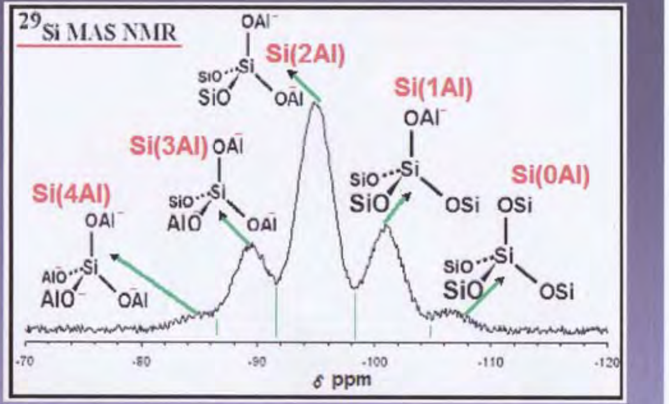


5- Magic angle spinning nuclear magnetic resonance (MAS NMR) analysis:

High resolution solid-state NMR, principally 29Si NMR and 27Al NMR, have been employed to investigate the framework Si/Al ratio of zeolites. NMR-technique is used in zeolite science to provide information about the structural environment (i.e. chemical surrounding) of an atomic nucleus present within the zeolite framework and/or non-framework, which cannot be obtained by using X-ray diffraction. In summary, this scientific technique is based on the principle that nuclei in a magnetic field absorb energy from electromagnetic (EM) pulses and then radiate this energy at a specific resonance frequency, which is collected as signals. Thus specific quantum mechanical magnetic properties of an atomic nucleus can be obtained, and given by NMR-spectrum.



Coordination	Notation	Chemical shift (ppm)
$Si(OSi)_4$	Si(0 Al)	(−101.5) - (−116.5)
$Si(OSi)_3(OAl)$	Si(1 Al)	(−97.5) - (−107)
$Si(OSi)_2(OAl)_2$	Si(2 Al)	(−93) - (−102)
$Si(OSi)(OAl)_3$	Si(3 Al)	(−88) - (−97)
$Si(OAl)_4$	Si(4 Al)	(−86) - (−90.5)



The ^{29}Si NMR equation, which is traditionally applied to determine the quantitative molar ratio of framework tetrahedral Si and Al in zeolite, is:

$$\left[{}^{Si}\!/_{Al}\right] = \frac{\sum_{n=0}^{n=4} \mathrm{I}Si(nAl)}{\sum_{n=0}^{n=4} \frac{n}{4}\,\mathrm{I}Si(nAl)} \qquad \text{Or,} \qquad \left[{}^{Si}\!/_{Al}\right] = \frac{\mathrm{I}_4 + \mathrm{I}_3 + \mathrm{I}_2 + \mathrm{I}_1 + \mathrm{I}_0}{\mathrm{I}_4 + (0.75)\mathrm{I}_3 + (0.5)\mathrm{I}_2 + (0.25)\mathrm{I}_1}$$

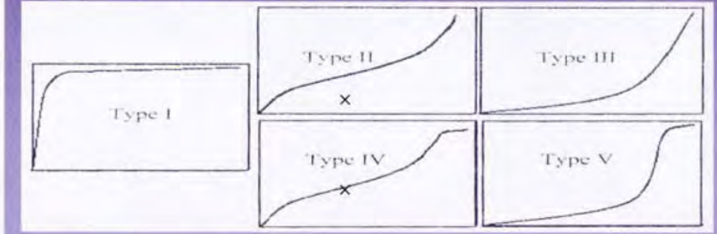
Where, "I" is the intensity of Si-peak in the NMR-spectrum, which is accordingly referred to the Si(nAl) building units, and n = 0, 1, 2, 3 and 4 – the number of coordinated Al-atoms for the given peak.

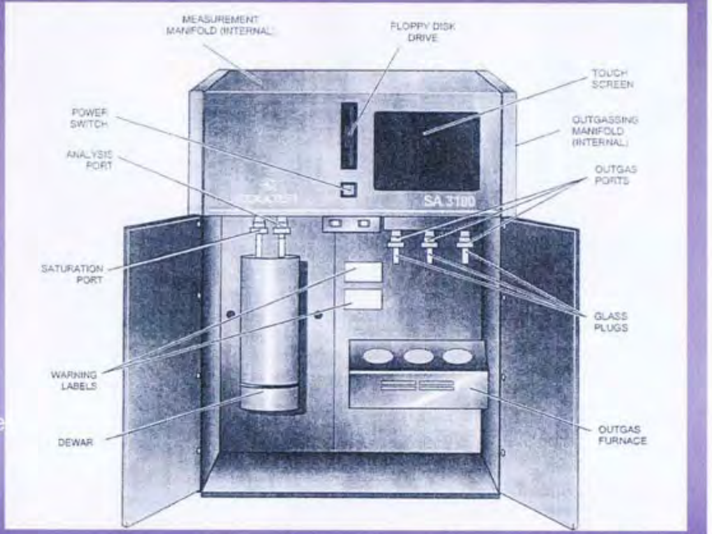
The intensities of the Al-peaks (i.e. I_{60} and I_0) in association with bulk molar ratio from the chemical analysis $(Si/Al)_{tot}$ can be used to predict the framework molar ratio $(Si/Al)_{fr}$ of zeolite. The 27Al MAS NMR-spectra of zeolite-Y materials e.g. NaY, and NH4Y are shown a sharp signal at about 60 ppm, corresponding to the four-coordinated tetrahedral framework aluminum species, Al(OSi)4. Hydrothermal de-alumination process consists of hydrolysis of Al-O bonds and creates the neutral and cationic non-framework Al-species. It is therefore possible to appear two further resonance signals in the NMR-spectra of USY at 30 and 0 ppm due to the five-coordinated pentahedral (Al(H2O)5)3+ and six-coordinated octahedral (Al(H2O)6)3+, respectively:

$$\left[{}^{Si}\!/_{Al}\right]_{fr} = \left[{}^{Si}\!/_{Al}\right]_{tot} \left[\mathrm{I}_{60} + \mathrm{I}_0\right] \Big/ \mathrm{I}_{60}$$

6- Gas adsorption measurement using nitrogen – BET isotherm analysis:

BET-surface area measurements are generally based on the phenomenon of gas adsorption-desorption isotherm. The two processes are based on the same principle, but one is reversed to the other. The shape of the adsorption or desorption branch may be mechanistically attributed to the pore structure of a solid as shown in the figure. The Van der Waals adsorption isotherm type-I is the category that commonly expresses the crystalline microporous materials such as zeolite, while the other exhibited types are relevant examples of the adsorption isotherm for other porous materials.





$$\frac{p/p\circ}{Va\left(1-p/p\circ\right)}=\frac{p}{Va(p\circ-p)}=\frac{1}{Vm\cdot C}+\left[\frac{C-1}{Vm\cdot C}\right]\times\frac{p}{p\circ}$$

Vm = Volume of the adsorbed gas in the monolayer (cm3.g-1),
Va = Volume of gas adsorbed at the equilibrium adsorbate pressure and at the temperature of adsorption (liquid nitrogen boiling point = 77 K)

$$S_{BET}=\left[\frac{Vm\times Na\times Am}{Mv}\right]$$

Na = Avogadro's number (6.022 x 1023 mol-1), and *Mv* = Molecular volume of the adsorbate molecules (22414 ml.mol-1).

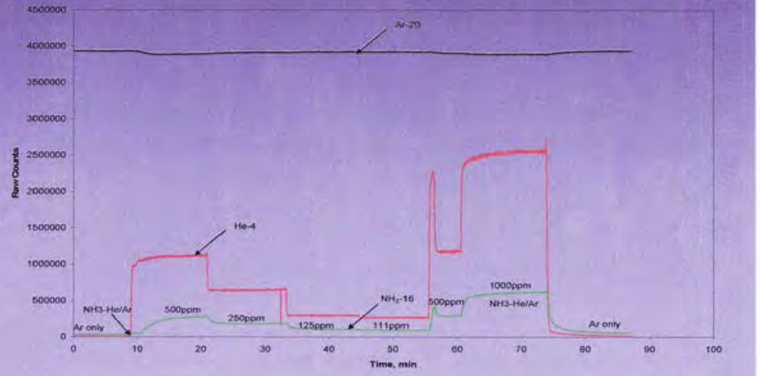
Am = Cross-sectional area of the adsorbate molecule (16.2 x 10-20 m2).

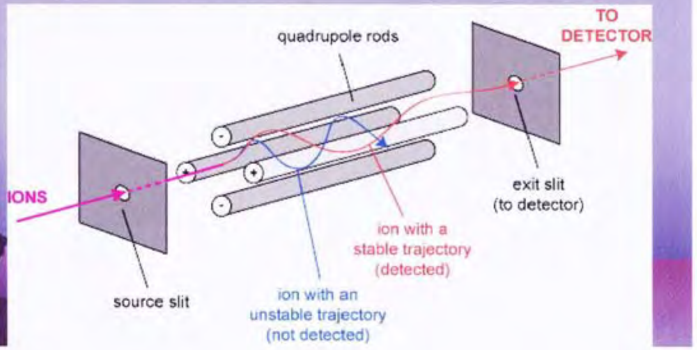
7- Temperature programmed desorption of ammonia (NH3-TPD) analysis:

TPD-method was employed to determine the number of acid sites in the catalyst. Principally, this test is one of the several techniques that can be utilized to characterize the total acidity of zeolite catalysts, and typically a quadrupole mass spectrometer (MS) is used to provide data for each ion fragment present during the TPD-process. The TPD-curve consists of the following two peaks:

1- A low temperature peak (LT) can be used to represent the desorption of ammonia from the weak acid sites (i.e. physisorbed ammonia).

2- A high temperature peak (HT) can be used to represent the desorption of ammonia molecules from the strong acid sites (i.e. protonic acidity or chemisorbed ammonia).

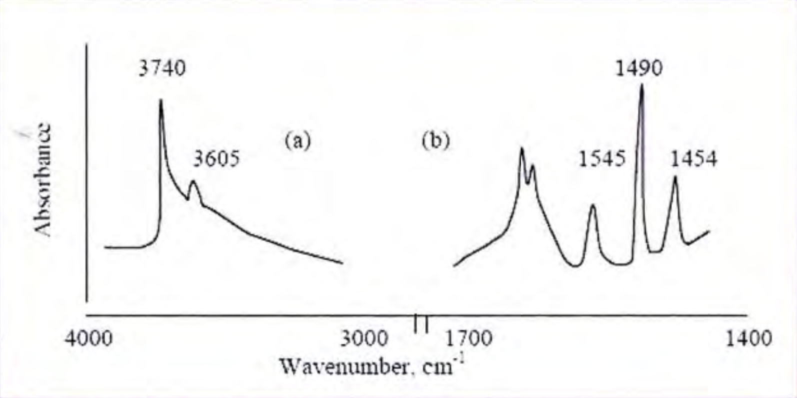


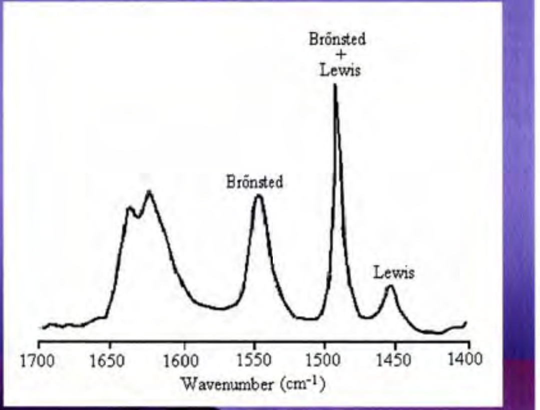


8- Pyridine Adsorption for Fourier Transform Infrared Spectroscopy (Py-FTIR):

TPD-technique cannot differentiate between Brönsted and Lewis acid sites, however FTIR of the adsorption of pyridine (C5H5N) can be used to determinate the Brönsted/Lewis acid sites ratios. The infrared is an electromagnetic radiation. The characteristic absorption bands at 1545, 1454 and 1490 cm-1 were assigned to the pyridine adsorbed on the Brönsted acid sites (B), the Lewis acid sites (L) and on both acid sites (B, L) respectively, as shown in Figure. The formation of these bands is due to the vibration of pyridine (ring deformation mode) which interacts differently with these two adsorption sites.

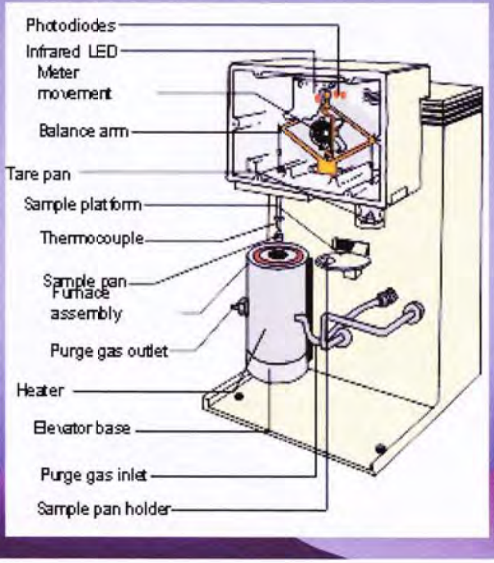
For determination of the type of hydroxyl groups, sample was dehydrated at elevated temperature under vacuum pressure. Two types of hydroxyl groups which are commonly present in zeolites such as zeolite Y. Hydroxyl silanol (Si-OH) groups was observed at 3740 cm-1 and bridging hydroxyl (Si-OH-Al) groups was observed around 3605 cm-1.





9- Thermo-gravimetric (TG) analysis:

TGA is a type of high sensitive testing commonly employed in research, which is performed on samples to determine changes in weight as a function of temperature and/or time. Because of the ability to automatically switch gases within TG system, it is widely applied to measure the total amount of accumulated coke on the catalysts. TG is also utilized to determine the decomposition kinetics, residual solvent levels, and polymer degradation temperatures. The weight loss curve from the TG instrument can be used to characterize the exact point at which weight loss occurs. Simultaneous TGA/"DTG: derivative therm-ogravimetric analysis" analyzer is useful to study the stability of structures, as the rate of weight loss can be obtained from the derivative weight loss curve.



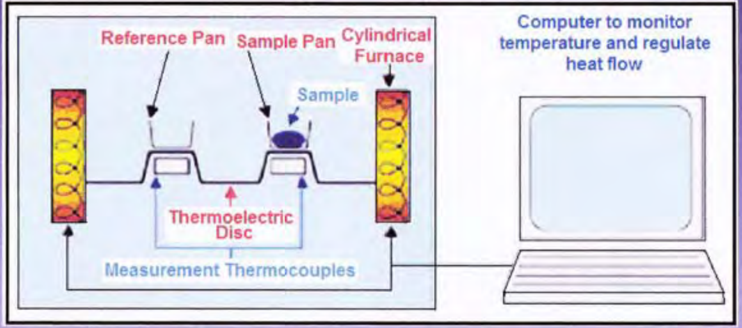
10- Differential scanning calorimetry (DSC) analyses:

DSC is used to investigate the enthalpies of transitions during the calcination step. The DSC-instrument can mostly be utilized to investigate the thermo-physical properties of polymers and to study oxidation or other chemical reactions, and it is also used extensively in the pharmaceutical and food science research.

$$\Delta H = K.A$$

$$\frac{q/t}{\Delta T/t} = \frac{q}{\Delta T} = Cp \Rightarrow \int dq = \int Cp.dT = \Delta H$$

K is the calorimetric constant, which is actually varies from instrument to instrument and can be determined by analyzing a well-characterized sample with known enthalpies of transition (i.e. well-defined heat capacity over the range of temperatures). Indium (In), a very soft metal as a reference with a value of *K* about 1.0780 was used for this purpose



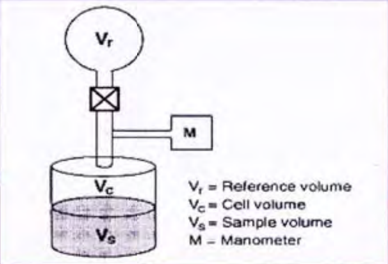
11- He-Pycnometer for density analysis:

Pycnometer is a fully automatic gas displacement pycnometer and the computer is programmed the device and displayed the results. The precision of analysis results can be increased by reporting data from more than five consecutive runs.

Pycnometer is usually applied to measure the sample volume, and the density (ρ) can also be derived automatically if the sample mass (w) is known.

$$V_{SAMP} = V_{CELL} - \frac{V_{EXP}}{\frac{P_{1g}}{P_{2g}} - 1}$$

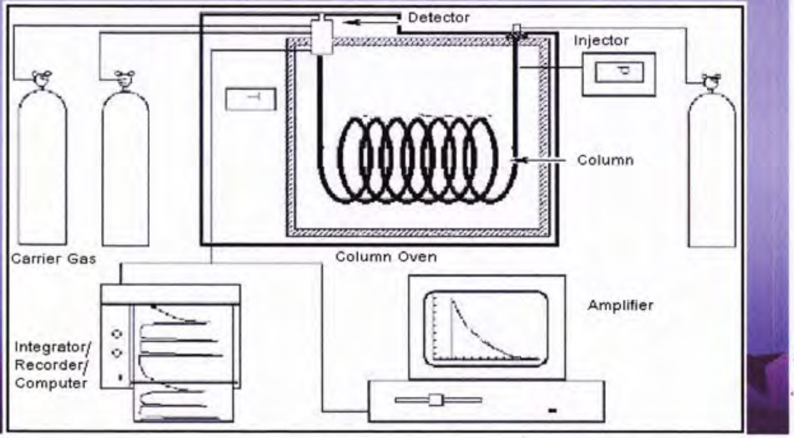
$$\rho = \frac{w}{V_{SAMP}}$$

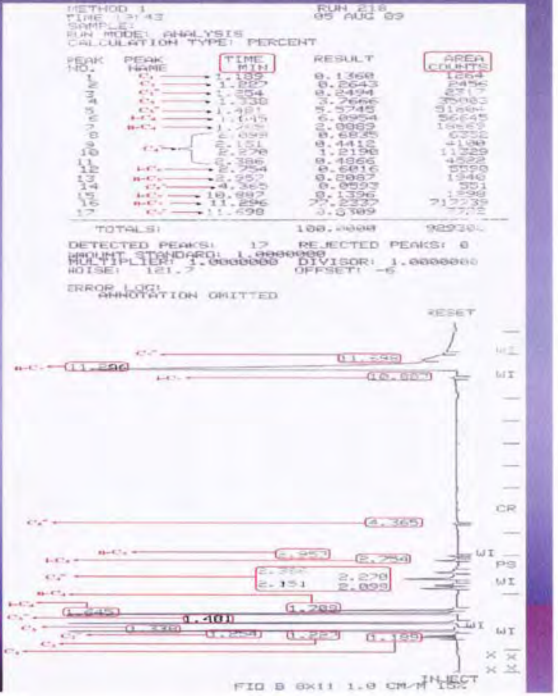


12- Gas chromatography (GC) analysis:

The chromatography analysis is a useful technique used in the separation of a mixture into individual components, based on the interactions between the flowing sample compounds in a carrier gas as a moving phase "mobile phase" and a stationary phase "immobilized phase" in a GC-column. The carrier medium is an inert gas such as N2, He, or Ar and it has no interaction with the analytes. The stationary phase is usually a thin layer of a high boiling point organic liquid and immiscible with the sample, which is accurately coated onto the inner wall of the GC-column.

The combustion of H2 and air leads to the formation of a sensitive flame that can ionize the hydrocarbons electrically in the detector . A collector converts the liberated electrons into a current, which is proportional to the quantity of hydrocarbons in the analyte. GC-paper or GC-trace is represented as a series of peaks, which actually refer to the components present in the sample.





```
METHOD 1                                    RUN 218
TIME 12:43                                  05 AUG 09
SAMPLE:
RUN MODE: ANALYSIS
CALCULATION TYPE: PERCENT

PEAK   PEAK      TIME        RESULT        AREA
NO.    NAME       MIN                      COUNTS
 1     C1    -> 1.189       0.1360         1264
 2     C2    -> 1.227       0.2643         2456
 3     C2=   -> 1.254       0.2494         2317
 4     C3    -> 1.330       3.7666        35003
 5     C3=   -> 1.481       5.5745        51804
 6     i-C4  -> 1.645       6.0954        56645
 7     n-C4  -> 1.745       2.0089        18663
 8           ┌  2.099       0.6835         6352
 9     C4= --┤  2.151       0.4412         4100
10           │  2.270       1.2190        11329
11           └  2.386       0.4866         4522
12     i-C5  -> 2.754       0.6016         5590
13     n-C5  -> 2.957       0.2087         1940
14     C5=   -> 4.365       0.0593          551
15     i-C[illegible] -> 10.887  0.1396    1298
16     n-C[illegible] -> 11.296  77.2337 712239
17     C[illegible]=  -> 11.698  3.5309    7722
      TOTALS:                 100.0000      929304

DETECTED PEAKS:    17     REJECTED PEAKS: 0
AMOUNT STANDARD: 1.0000000
MULTIPLIER: 1.0000000    DIVISOR: 1.0000000
NOISE:   121.7           OFFSET: -6

ERROR LOG:
   ANNOTATION OMITTED
```

(13)