

Steady-state diffusion in multicomponent mixtures

Diffusion in multicomponent system is very complicated, but they can frequently be handled by using an effective diffusivity.

Where the effective diffusivity of a component can be synthesized from its binary diffusivities with each of other constituents.

Thus in equation $N_A + N_B$ is replaced by $\sum_{i=A}^n N_i$, where N_i is positive if diffusion is in the same direction as that of A and negative if in the opposite direction and D_{AB} is replaced by the effective $D_{A,M}$.

$$D_{A,M} = \frac{N_A - y_A \sum_{i=A}^n N_i}{\sum_{i=A}^n \frac{1}{D_{Ai}} (y_i N_A - y_A N_i)}$$

Where D_{Ai} are the binary diffusivities.

$D_{A,M}$ may vary considerably from one end of the diffusion path to the other, but a linear variation with distance can be assumed. For this situation, assume all but one component is stagnant, then equation becomes,

$$D_{A,M} = \frac{1 - y_A}{\sum_{i=B}^n y_i / D_{Ai}} = \frac{1}{\sum_{i=B}^n y_i / D_{Ai}}$$

Where y_i is the mole fraction of component i on an A-free basis.

Diffusivity prediction in gases

Diffusion coefficient is a significant parameter which depends upon temperature, pressure and composition of the components (Advanced kinetic theory predicts that in the binary system effect of composition is very small). Diffusivity can be determined experimentally and their dimension is $\text{length}^2/\text{time}$.

Hirschfelder-Bird-Spottz developed an empirical relation to determine the diffusivity for mixtures of non-polar or a polar with non-polar gas.

$$D_{AB} = \frac{\left[10^{-4} \left(1.084 - 0.249 \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \right) T^{3/2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \right]}{\left[P_t (r_{AB})^2 f \left(\frac{KT}{\epsilon_{AB}} \right) \right]}$$

where

D_{AB} is the diffusivity, m^2/s

T is the absolute temperature, K

M_A, M_B is the molecular weight of A and B respectively, kg/kmol

P_t is the absolute pressure, N/m^2

r_{AB} is the molecular separation at collision = $\frac{r_A + r_B}{2}$, nm

ϵ_{AB} is the energy of molecular attraction = $\sqrt{\epsilon_A \epsilon_B}$

K is the Boltzmann's constant

$f\left(\frac{KT}{\epsilon_{AB}}\right)$ is the collision function

The value of r and ϵ such as those listed in Table can be calculated from other properties of gases such as viscosity. They can also be estimated empirically by

$$r = 1.18 v^{1/3}$$

$$\epsilon/K = 1.21 T_b$$

Where v is the molal volume of liquid at normal boiling point, $m^3/kmol$ and T_b is the normal boiling point, K.

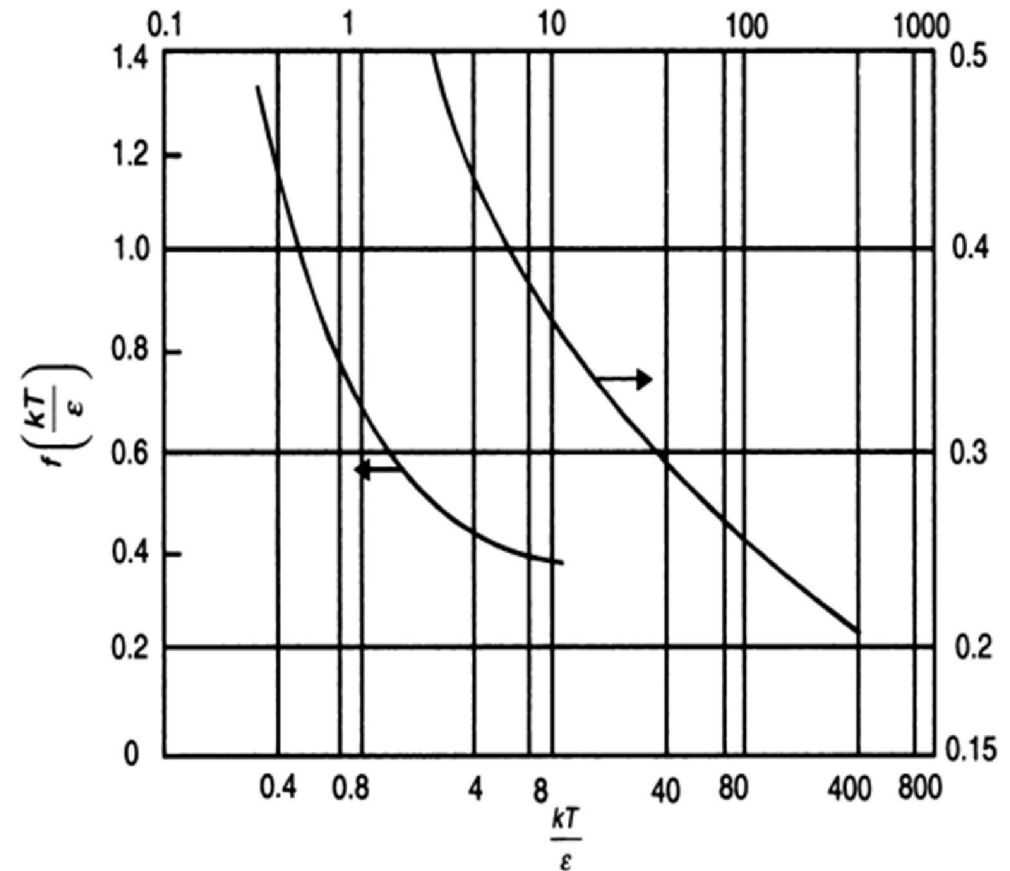


Table Force constants of gases as determined from viscosity data

<i>Gas</i>	$\epsilon/K, K$	<i>r, nm</i>
Air	78.6	0.3711
CCl ₄	322.7	0.5947
CH ₃ OH	481.8	0.3626
CH ₄	148.6	0.3758
CO	91.7	0.3690
CO ₂	195.2	0.3941
CS ₂	467	0.4483
C ₂ H ₆	215.7	0.4443
C ₃ H ₈	237.1	0.5118
C ₆ H ₆	412.3	0.5349
Cl ₂	316	0.4217
HCl	344.7	0.3339
He	10.22	0.2551
H ₂	59.7	0.2827
H ₂ O	809.1	0.2641
H ₂ S	301.1	0.3623
NH ₃	558.3	0.2900
NO	116.7	0.3492
N ₂	71.6	0.3798
N ₂ O	232.4	0.3828
O ₂	106.7	0.3467
SO ₂	335.4	0.4112

Molecular diffusion in Liquids

In the case of diffusion in liquids, C and D_{AB} may vary considerably with respect to process conditions. Hence equation can be modified to

$$N_A = \left(\frac{N_A}{N_A + N_B} \right) \left(\frac{D_{AB}}{Z} \right) \left(\frac{\rho}{M} \right)_{av} \ln \left[\frac{\frac{N_A}{N_A + N_B} - x_{A2}}{\left(\frac{N_A}{N_A + N_B} \right) - x_{A1}} \right]$$

Where ρ is solution density and M is solution molecular weight.

Case 1- Diffusion of liquid A through a stagnant liquid B

In this case, $N_B = 0$ and $N_A = \text{constant}$. Hence

$$N_A = \left(\frac{D_{AB}}{Z x_{B,M}} \right) \left(\frac{\rho}{M} \right)_{av} (x_{A1} - x_{A2}) \quad \text{where} \quad x_{B,M} = \left[\frac{x_{B2} - x_{B1}}{\ln \left(\frac{x_{B2}}{x_{B1}} \right)} \right]$$
$$N_A = \left(\frac{D_{AB}}{Z} \right) \left(\frac{\rho}{M} \right)_{av} \ln \left[\frac{1 - x_{A2}}{1 - x_{A1}} \right]$$

Case 2 – Equimolar counter-diffusion

In the case $N_A = -N_B$

Hence,

$$N_A = \left(\frac{D_{AB}}{Z} \right) (C_{A1} - C_{A2}) = \left(\frac{D_{AB}}{Z} \right) \left(\frac{\rho}{M} \right)_{av} (x_{A1} - x_{A2})$$

Diffusivity Prediction in Liquids

The dimensions for diffusivity in liquids are the same as those for gases. However, the diffusivity varies appreciably with concentration. For dilute solutions of nonelectrolytes, Wilke and Chang given the empirical correlation.

$$D_{AB}^{\circ} = \frac{(117.3 \times 10^{-18})(\varphi M_B)^{0.5} T}{\mu \nu_A^{0.6}}$$

where

D_{AB}° is the diffusivity of A in very dilute solution in solvent B, m^2/s

M_B is the molecular weight of solvent, kg/kmol.

T is the absolute temperature, K

μ is the solution viscosity, kg/m-s

ν_A is the solute molal volume at normal boiling point, $m^3/kmol$.

= 0.0756 for water as solute.

ϕ is the association factor for solvent.

= 2.26 for water as solvent

= 1.90 for methanol as solvent

= 1.50 for ethanol as solvent

= 1.00 for unassociated solvents, e.g. benzene and ethyl ether.

The value of v_A may be true value or, if necessary, estimated from the data of Table, except when water is the diffusing solute

Table Atomic and molecular volumes

Atomic volume, $\text{m}^3/1000 \text{ atoms} \times 10^3$		Molecular volume, $\text{m}^3/\text{kmol} \times 10^3$		Atomic volume, $\text{m}^3/1000 \text{ atoms} \times 10^3$		Molecular volume, $\text{m}^3/\text{kmol} \times 10^3$	
Carbon	14.8	H ₂	14.3	Oxygen	7.4	NH ₃	25.8
Hydrogen	3.7	O ₂	25.6	In methyl esters	9.1	H ₂ O	18.9
Chlorine	24.6	N ₂	31.2	In higher esters	11.0	H ₂ S	32.9
Bromine	27.0	Air	29.9	In acids	12.0	COS	51.5
Iodine	37.0	CO	30.7	In methyl ethers	9.9	Cl ₂	48.4
Sulfur	25.6	CO ₂	34.0	In higher ethers	11.0	Br ₂	53.2
Nitrogen	15.6	SO ₂	44.8	Benzene ring: subtract	15	I ₂	71.5
In primary amines	10.5	NO	23.6	Naphthalene ring: subtract	30		
In secondary amines	12.0	N ₂ O	36.4				

The diffusivity in concentrated solutions differs from that in dilute solutions because of changes in viscosity with concentration and also because of changes in the degree of nonideality of the solution

$$D_{A\mu} = (D_{BA}^0 \mu_A)^{x_A} (D_{AB}^0 \mu_B)^{x_B} \left(1 + \frac{d \log \gamma_A}{d \log x_A} \right)$$

Where D_{AB}^0 is the diffusivity of A at infinite dilution in B
 D_{BA}^0 is the diffusivity of B at infinite dilution in A
 γ_A activity coefficient (obtained from vapor-liquid equilibrium data as the ratio (at ordinary pressure) of the real to ideal partial pressures of A in the vapor in equilibrium with a liquid of concentration x_A)

$$\gamma_A = \frac{\bar{p}_A}{x_A p_A} = \frac{y_A p_i}{x_A p_A}$$

And the derivative $(d \log \gamma_A)/(d \log x_A)$ can be obtained graphically as the slope of graph of $\log \gamma_A$ vs. $\log x_A$.

Pseudo Steady State Diffusion

In many mass transfer operations, one of the boundaries between the fluids may move with time. If the length of the diffusion path changes over a period of time, a pseudo steady state develops. Here, the molar flux is related to the amount of A leaving the liquid by,

Flux = rate of change of liquid level \times molar concentration of A in liquid phase

$$N_{AZ} = \frac{dZ}{dt} \times C_{A,L}$$

$$N_{AZ} = \left(\frac{C D_{AB}}{Z x_{B,M}} \right) \times (x_{B2} - x_{B1}) = \left(\frac{dZ}{dt} \right) C_{A,L}$$

Integrating the equation between $t = 0, Z = Z_{t0}$ and $t = t, Z = Z_t$

$$\int_{Z_{t0}}^{Z_t} z dz = \left[\frac{C D_{AB} (x_{B2} - x_{B1})}{x_{B,M} C_{A,L}} \right] \int_0^t dt$$

After integration and simplification ,

$$\frac{t}{Z_t - Z_{t0}} = \frac{x_{B,M} C_{A,L} (Z_t + Z_{t0})}{2 C D_{AB} (x_{A1} - x_{A2})}$$

$$\text{i.e } \frac{t}{Z_t - Z_{t0}} = \frac{x_{B,M} C_{A,L} (Z_t + Z_{t0} + Z_{t0} - Z_{t0})}{2 C D_{AB} (x_{A1} - x_{A2})}$$

$$\text{i.e } \frac{t}{Z_t - Z_{t0}} = \frac{x_{B,M} C_{A,L} (Z_t - Z_{t0})}{2 C D_{AB} (x_{A1} - x_{A2})} + \frac{2 Z_{t0} x_{B,M} C_{A,L}}{2 C D_{AB} (x_{A1} - x_{A2})}$$

Equation is the form of

$$y = mx + C$$

$$\text{where } y = \frac{t}{Z_t - Z_{t0}} \text{ and } x = (Z_t - Z_{t0})$$

$$\text{Slope, } m = \frac{x_{B,M} C_{A,L}}{2 C D_{AB} (x_{A1} - x_{A2})}$$

and

$$\text{Constant } C = \frac{Z_{t0} x_{B,M} C_{A,L}}{C D_{AB} (x_{A1} - x_{A2})}$$

Since equation is linear, by plotting $t/(Z_t - Z_{t0})$ against $(Z_t - Z_{t0})$, from the slope of Line, D_{AB} can be calculated, as other parameter of equation are all known. This equation is called as Winkelmann's relation.

Diffusion through a varying cross-sectional area

In the case so far at steady state we have considered N_A and J_A as constant in the integrations. In these cases the cross-sectional area A m² through which the diffusion occurs has been constant with varying distance Z .

In some situations the area A may vary. Then it is convenient to define N_A as

$$N_A = \frac{\check{N}_A}{A}$$

Where \check{N}_A is kg moles of A diffusing per seconds or kg moles/s. At steady state, \check{N}_A will be constant but area will be vary.

- **Diffusion from sphere**

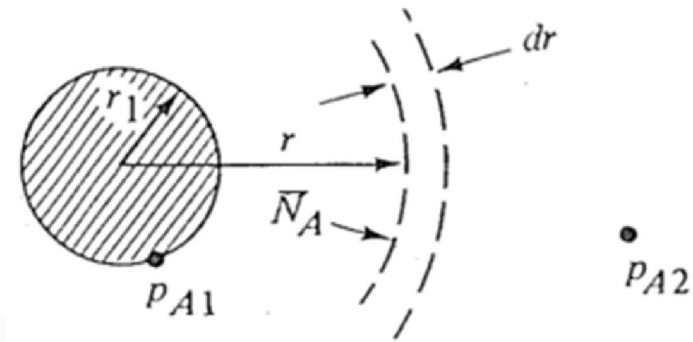
Diffusion from sphere in a gas will be considered. This situation appears often in such case as the evaporation of a drop of liquid, the evaporation of a ball of naphthalene, and the diffusion of nutrients to a spherical like microorganism in a liquid.

In figure shown a sphere of fixed radius r_1 m in an infinite gas medium. Component (A) at partial pressure p_{A1} at the surface is diffusing into the surrounding stagnant medium (B), where $p_{A2} = 0$ at some large distance away. Steady state diffusion will be assumed.

The flux N_A can be represented by equation, where A is the cross-sectional area $4\pi r^2$ at point r distance from the center of the sphere, Also \bar{N}_A is a constant at steady state.

$$N_A = \frac{\bar{N}_A}{4\pi r^2}$$

Since this is a case of A diffusing through stagnant, nondiffusing B. Equation will be used in its differential form and N_A will be equated



$$N_A = \frac{\bar{N}_A}{4\pi r^2} = -\frac{D_{AB}}{RT} \frac{dp_A}{(1 - p_A/P) dr}$$

dr was substituted for dz . Rearranging and integrating between r_1 and some point r_2 a large distance away,

$$\frac{\bar{N}_A}{4\pi} \int_{r_1}^{r_2} \frac{dr}{r^2} = -\frac{D_{AB}}{RT} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{(1 - p_A/P)}$$

$$\frac{\bar{N}_A}{4\pi} \left(\frac{1}{r_1} - \frac{1}{r_2} \right) = \frac{D_{AB} P}{RT} \ln \frac{P - p_{A2}}{P - p_{A1}}$$

Since $r_2 \gg r_1$, $1/r_2 \equiv 0$. Substituting p_{BM} from equation

$$\frac{\bar{N}_A}{4\pi r_1^2} = N_{A1} = \frac{D_{AB} P}{RT r_1} \frac{p_{A1} - p_{A2}}{p_{BM}}$$

This equation can be simplified further. If p_{A1} is small compared to P (a dilute gas phase), $p_{BM} \equiv P$. Also, setting $2r_1 = D_1$, diameter, and $c_{A1} = p_{A1}/RT$, we obtain

$$N_{A1} = \frac{2D_{AB}}{D_1} (c_{A1} - c_{A2})$$

This equation can also be used for liquids, where D_{AB} is the diffusivity of A in the liquid.

Case:

If the sphere is evaporating, the radius r of the sphere decreases slowly with time. The equation for the time for the sphere to evaporate completely can be derived by assuming pseudo-steady state and by equating the diffusion flux equation to the moles of solid A evaporated per dt time and per unit area as calculated from material balance.

Let us consider an evaporating drop that has radius r_s at any instant t . Imagine a thin spherical shell of inner radius r and thickness Δr around the drop as shown in figure. This is binary system involving diffusion of water vapor (A) through air (B). Then

Rate of input of A into the thin shell (at $r = r$)

$$(4\pi r^2)N_A|_r$$

Rate of output of A from the thin shell (at $r = r + \Delta r$)

$$(4\pi r^2)N_A|_{r+\Delta r}$$

By steady state mass balance

$$(4\pi r^2)N_A|_r - (4\pi r^2)N_A|_{r+\Delta r} = 0$$

Input Output Accumulation

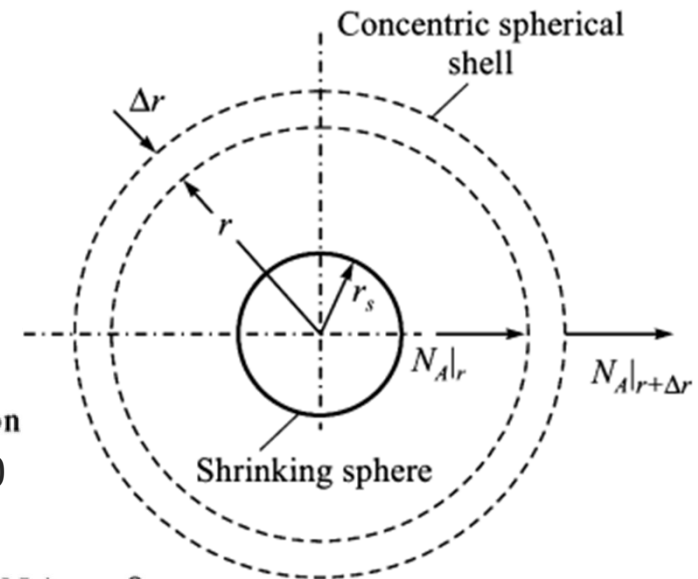
Dividing both side by Δr and taking the limit $\Delta r \rightarrow 0$

$$\lim_{\Delta r \rightarrow 0} \frac{(4\pi r^2)N_A|_r - (4\pi r^2)N_A|_{r+\Delta r}}{\Delta r} = 0 \Rightarrow -\frac{d}{dr}(4\pi r^2 N_A) = 0$$

$$4\pi r^2 N_A = \text{constant} = W \text{ (say)}$$

Equation is very important result for steady state diffusion through a variable area and can be generalized as

$$(\text{Area})(\text{flux}) = \text{constant}$$



In this case water vapor diffuse out, but air does not diffuse because it is not soluble in water. So the case corresponds to diffusion of A through non-diffusing B. since diffusion occur in radial direction, we replace z by r in equ.

$$N_A = (N_A + N_B) \frac{p_A}{P} - \frac{D_{AB}}{RT} \frac{dp_A}{dr}$$

Putting $N_B = 0$ and rearranging

$$N_A = - \frac{D_{AB}P}{RT(P - p_A)} \frac{dp_A}{dr}$$

Putting N_A value and rearranging

$$- \frac{dp_A}{P - p_A} = \frac{WRT}{4\pi D_{AB}P} \frac{dr}{r^2}$$

The above equation can be integrated from $r = r_s$ (i.e. the surface of the drop) to $r = \infty$ (i.e. far away from the drop) where $p_A = p_{A\infty}$. Here p_{As} is the vapor pressure of water at the temperature of the drop and $p_{A\infty}$ is the partial pressure of water vapor in the 'bulk air'.

$$- \int_{p_{As}}^{p_{A\infty}} \frac{dp_A}{P - p_A} = \frac{WRT}{4\pi D_{AB}P} \int_{r_s}^{\infty} \frac{dr}{r^2} \quad \Rightarrow \quad \ln \frac{P - p_{A\infty}}{P - p_{As}} = \frac{WRT}{4\pi D_{AB}P} \frac{1}{r_s}$$

$$W = \frac{4\pi D_{AB}P r_s}{RT} \ln \frac{P - p_{A\infty}}{P - p_{As}}$$

Since W is the constant molar rate of mass transfer, it is equal to the rate of vaporization of the drop at any instant. This rate can be related to the change in the drop radius by the following equation.

$$W = -\frac{d}{dt} \left(\frac{4}{3} \pi r_s^3 \frac{\rho_A}{M_A} \right) = -4\pi \frac{\rho_A}{M_A} r_s^2 \frac{dr_s}{dt}$$

The negative sign is incorporated because the size of the drop decreases with time. Equating the equations

$$-4\pi \frac{\rho_A}{M_A} r_s^2 \frac{dr_s}{dt} = \frac{4\pi D_{AB} P r_s}{RT} \ln \frac{P - p_{A\infty}}{P - p_{As}}$$

According to pseudo steady state assumption drop size changes so slowly that the diffusion of water vapor through the surrounding air occurs virtually at steady state at all time. The change in drop size over a considerable period of time can be determined by integrating the above equation. If at time $t = 0$, the radius of the drop is r_{s0} and at time t' is r'_s ,

$$-\int_{r_{s0}}^{r'_s} r_s dr_s = \frac{D_{AB} P M_A}{RT \rho_A} \ln \frac{P - p_{A\infty}}{P - p_{As}} \int_0^{t'} dt \Rightarrow r_{s0}^2 - r_s'^2 = \frac{2 D_{AB} P M_A t'}{RT \rho_A} \ln \frac{P - p_{A\infty}}{P - p_{As}}$$

Time for complete evaporation $r'_s = 0$

$$t' = \frac{RT \rho_A r_{s0}^2}{2 D_{AB} P M_A \ln [(P - p_{A\infty}) / (P - p_{As})]}$$

- **Diffusion through a conduit of nonuniform cross-sectional area**

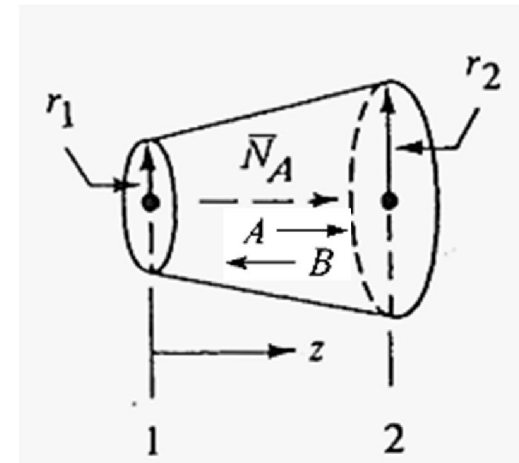
Diffusion of component A at steady state through a circular conduit which is tapered uniformly. At point 1 the radius is r_1 and at point 2 it is r_2 . At position z in the conduit, for A diffusion through stagnant, nondiffusing B,

$$N_A = \frac{\bar{N}_A}{\pi r^2} = - \frac{D_{AB}}{RT} \frac{dp_A}{(1 - p_A/P) dz}$$

Using the geometry shown, the variable radius r can be related to position z in the path as follows:

$$r = \left(\frac{r_2 - r_1}{z_2 - z_1} \right) z + r_1$$

This value of r is substituted into equation to eliminate r and the equation integrated.



$$\frac{\bar{N}_A}{\pi} \int_{z_1}^{z_2} \frac{dz}{\left[\left(\frac{r_2 - r_1}{z_2 - z_1} \right) z + r_1 \right]^2} = - \frac{D_{AB}}{RT} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{1 - p_A/P}$$

Knudsen Diffusion, Surface Diffusion and self diffusion

The kind of diffusion phenomena discussed so far relate to transport in the presence of a concentration gradient in a continuum.

These are other important diffusional phenomena occur in solids shown in figures.

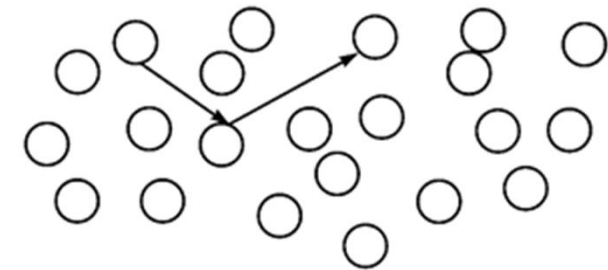
Knudsen Diffusion

The movement of molecules in a mixture is governed by molecular velocity as well as collision with other molecules.

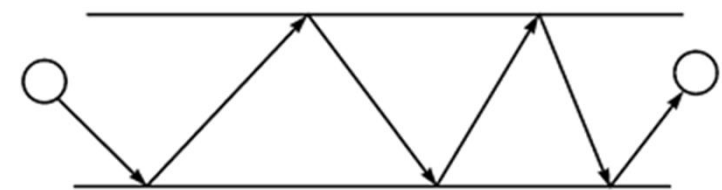
Collision of the diffusing molecules with others present in the mixture offers the resistance to diffusion.

If gas diffusion occur in very fine pore, particularly at a low pressure, the mean free path of the molecules may be larger than the diameter of the passage.

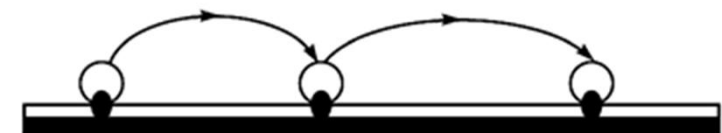
Then collision with wall becomes much more frequent than collision with other molecules.



(a) diffusion in a continuum,



(b) Knudsen diffusion,



(c) surface diffusion.

● An active site

○ An adsorbed molecule

The rate of diffusional transport of species is now governed by its molecular velocity, the diameter of the passage and the gradient of concentration or partial pressure. This is called 'Knudsen Diffusion' and become important if the pore size is normally below 50 nm.

Such a situation commonly occurs for intra-particle transport in a catalyst containing fine pores.

A few model have been proposed to describe and quantify Knudsen Diffusion. A simple approach based on the Kinetic theory of gases yields the following expression for Knudsen diffusivity.

$$D_K = \left(\frac{2}{3}\right)r_p v_T$$

where

r_p = radius of the passage or capillary T = temperature, in K M = molecular weight.

$v_T = \left(\frac{8RT}{\pi M}\right)^{1/2}$ = average velocity of the molecules by virtue of their thermal energy