

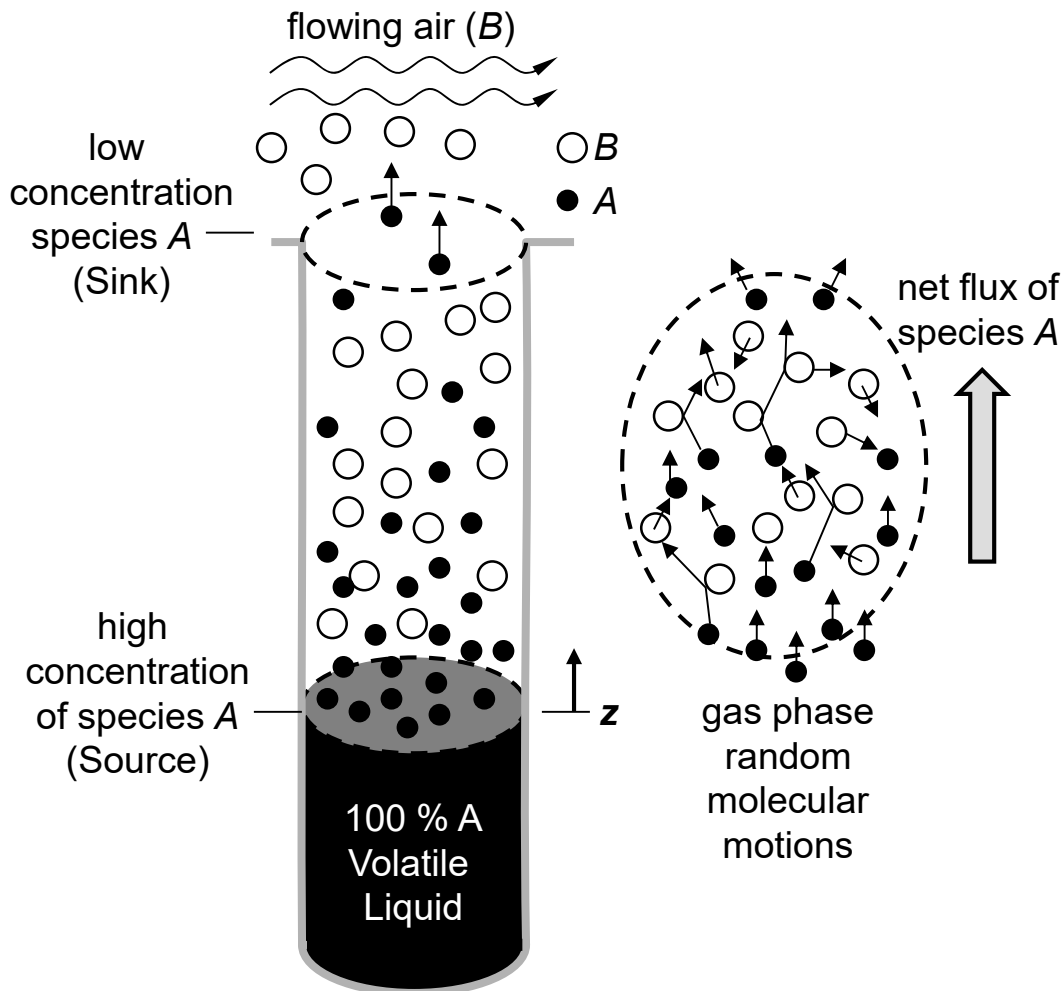
## CHAPTER 24: FUNDAMENTALS OF MASS TRANSFER

### 24.1 Molecular Mass Transfer

#### 24.1a Definitions of Mass Transfer

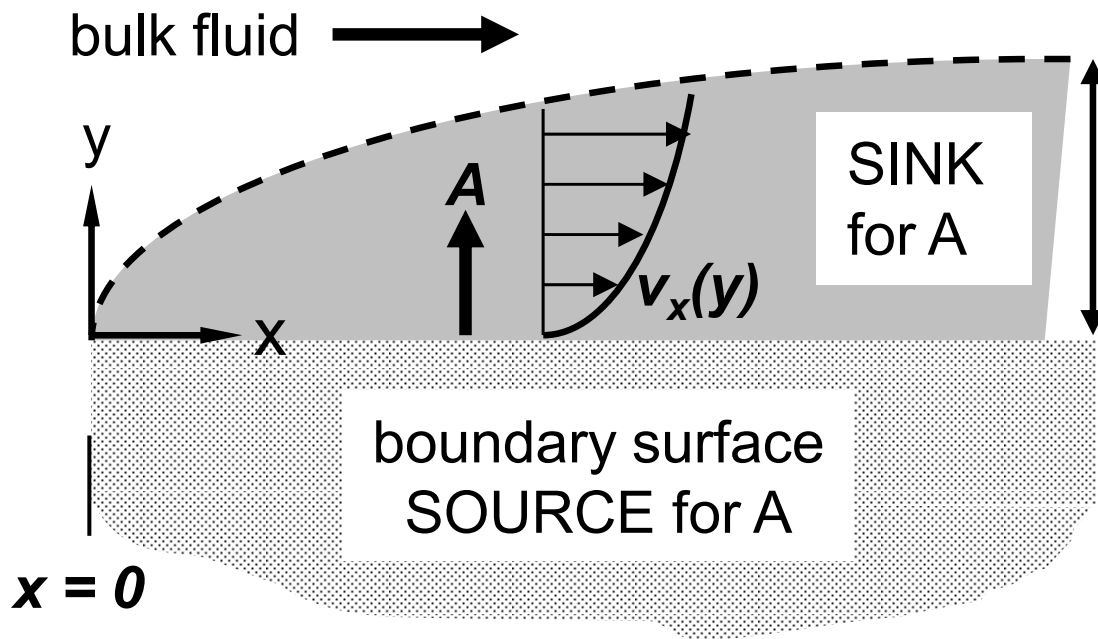
*Mass Transfer:* natural tendency to transfer a given component in a mixture from a region of high concentration (the SOURCE) to a region of low concentration (the SINK) in an effort to bring about uniform, equilibrium conditions. Mass Transfer has three requirements: 1) mass transfer only occurs in mixtures; 2) a given substance within the mixture moves from a defined SOURCE to a defined SINK; 3) the rate of mass transfer, i.e. the “flux” of a given substance, is determined by the concentration gradient defined by the SOURCE and SINK for that substance. If these three requirements are not met, mass transfer will not occur.

*Molecular Mass Transfer (Diffusion):* mass transfer through a quiescent medium (fluid or solid).



*Convective Mass Transfer:* mass transfer promoted by fluid flow, usually across a boundary layer between two distinct phases.

## Convective Mass Transfer – Flow over a Flat Plate

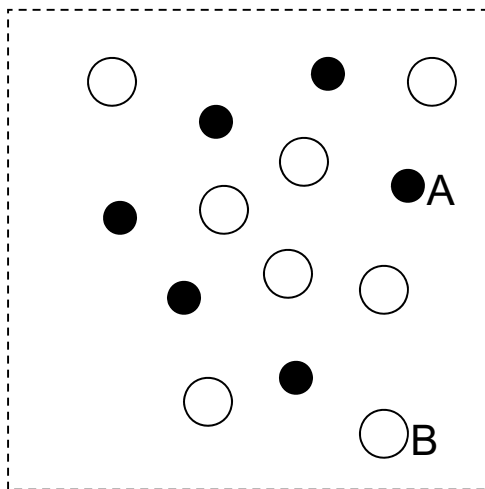


*Binary Mixture:* two chemical components, species *A* and species *B*, are present in the mixture; either one or both species may be undergoing mass transfer. Only unimolecular or bimolecular interaction processes of these two species take place in a homogeneous fluid mixture. However, for mass transfer of this binary fluid mixture in porous solid medium, additional interactions between the species in the mixture and the pore walls take place.

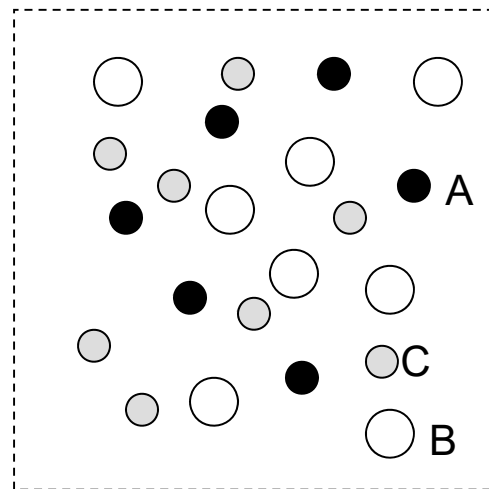
*Pseudo Binary Mixture:* there may be three or more components in the mixture, but one component is present in very high concentration (called the "solvent" for liquids or the "carrier gas" for gases), whereas the remaining components (the solutes) are present in very low concentrations. In this case, mass transfer process of a given low-concentration solute (species *A*) in the solvent medium (species *n*) as treated as a "pseudo binary mixture" of species *A* in species *n*. All remaining low concentration solutes can be also treated as a pseudo binary mixture of species *B* in species *n*, species *C* in species *n*, etc.

*Multicomponent Mixture:* three or more components are in the mixture, but no one component dominates. Therefore the fluxes of all components interact with one another to set the total net flux of all species within the system.

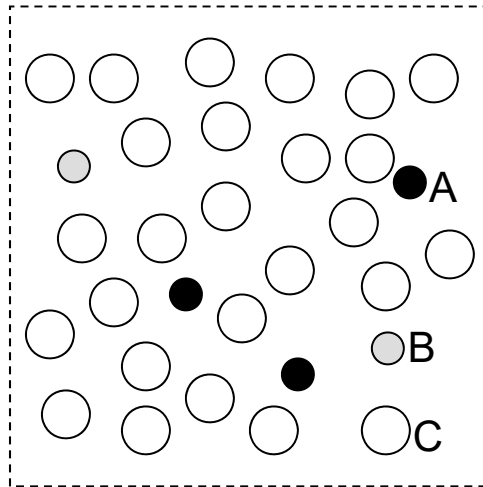
### *Mixtures*



**Binary Mixture**  
**A + B**



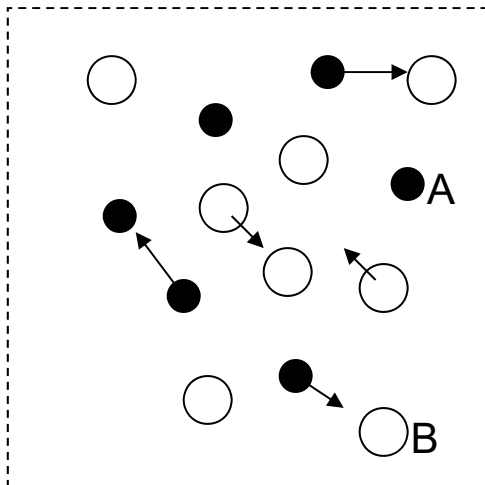
**Multi-component Mixture**  
3 or more components  
e.g. A+B+C



### Pseudo-Binary Mixture

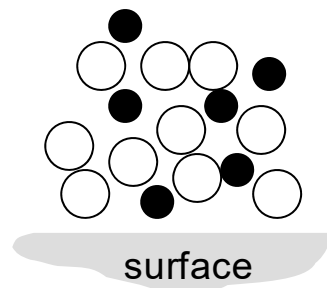
3 or more components,  
but one component dominates  
treat as  $A+C$ ,  $B+C$

*Binary Mixtures in a Continuous Phase (molecules  $A + B$ )*



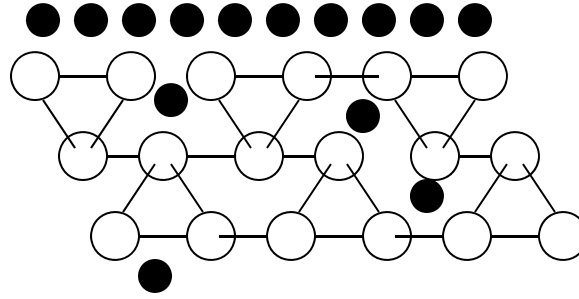
### Gas

molecules are separated  
but collide frequently



### Liquid

molecules touch  
but are still mobile



### **Solid**

some molecules are connected  
and immobile

24.1a cont.

*Driving Forces in Transport Phenomena*

<b>Transport Phenomena</b>	<b>Driving Force</b>
Momentum	Velocity gradient (Newton's Law of Viscosity)
Heat (Energy)	Temperature gradient (Fourier's Law of Heat Conduction)
Mass	Concentration gradient (in a mixture) (Fick's Laws of Diffusion)

24.1a cont.

***Definitions of Concentration, Velocity, and Flux Terms used in Diffusion***

$C_A$	molar concentration of species "A" in a mixture, gas, liquid, or solid (kgmole A/m <sup>3</sup> ); also referred to as $c_A$
$C$	total molar concentration of all species in a mixture (gas, liquid, solid) (kgmole/m <sup>3</sup> ); also referred to as “ $c$ ”
$J_A$	diffusion flux of species "A" relative to the molar average velocity (kgmole A/m <sup>2</sup> -sec)
$j_A$	diffusion flux of species "A" relative to the mass average velocity (kg A/m <sup>2</sup> -sec)
$M_A$	molecular weight of species "A" (kg A / kgmole A)
$N_A$	molar flux of species "A" relative to fixed coordinates (kgmole A/m <sup>2</sup> -sec)
$v_A$	velocity of species "A" (m/sec)
$v$	<i>mass average</i> velocity of all species in a mixture with respect to fixed coordinates (m/sec)
$V$	<i>molar average</i> velocity of all species in a mixture with respect to fixed coordinates (m/sec); not to be confused with volume, which is also “V”
$w_A$	mass fraction of species "A" in mixture, gas, liquid, or solid (mass of A/total mass of all species in mixture)
$x_A$	mole fraction of species "A" in a liquid or solid phase (moles of A/total moles of all species in mixture)
$y_A$	mole fraction of species "A" in the gas phase (moles of A/total moles of all species in mixture)
$\rho_A$	mass concentration of species "A" in a mixture, gas, liquid, solid (kg A/m <sup>3</sup> )
$\rho$	total mass concentration of all species in a mixture (kg/m <sup>3</sup> )

***Interconversions of Concentration, Velocity, and Flux Terms used in Diffusion***

The “concentration” of species A in a mixture is

$$C_A = \frac{\text{moles of species A in mixture}}{\text{unit volume of mixture in a given phase}} = \frac{\text{kgmole A}}{m^3}$$

$$\rho_A = \frac{\text{mass of species A in mixture}}{\text{unit volume of mixture in a given phase}} = \frac{\text{kg A}}{m^3}$$

Component concentrations in the mixture sum up to the total concentration

$$\sum_i C_i = C \quad \sum_i \rho_i = \rho$$

The molar and mass fractions of species A in a mixture are

$$x_A \text{ or } y_A = \frac{\text{moles of species A in mixture}}{\text{total moles of mixture in a given phase}}$$

$$w_A = \frac{\text{mass of species A in mixture}}{\text{total mass of mixture in a given phase}}$$

Component mole and mass fractions sum up to 1.0

$$\sum_i x_i = 1.0 \quad \sum_i y_i = 1.0 \quad \sum_i w_i = 1.0$$

Concentration conversions

$$C_A = \frac{\rho_A}{M_A} \quad C_A = y_A C \text{ (gas)} \quad C_A = x_A C \text{ (liq)}$$

$$\rho_A = C_A M_A \quad y_A = C_A / C \text{ (gas)} \quad x_A = C_A / C \text{ (liq)}$$



### CHE 333: Fundamentals of Mass Transfer

Ideal Gas Law (partial pressure  $p_A$ , total system pressure  $P$ , absolute temperature  $T$ )

$$C_A = \frac{p_A}{RT} \quad C = \frac{P}{RT}$$

Dalton's Law of Partial Pressure

$$p_A = y_A P \quad \sum_i p_i = P$$

Dilute liquids (mostly solvent B)

$$C \approx \frac{\rho_B}{M_B}$$

Mole/mass fraction conversions

$$w_A = \frac{\rho_A}{\rho} = \frac{y_A M_A}{\sum_i y_i M_i} \quad w_A = \frac{\rho_A}{\rho} = \frac{x_A M_A}{\sum_i x_i M_i}$$

$$y_A = \frac{C_A}{C} = \frac{\frac{w_A}{M_A}}{\sum_i \frac{w_i}{M_i}} \quad x_A = \frac{C_A}{C} = \frac{\frac{w_A}{M_A}}{\sum_i \frac{w_i}{M_i}}$$

Mass Average Velocity

$$v = \frac{1}{\rho} \sum_i \rho_i v_i = \sum_i w_i v_i$$

Molar Average Velocity

$$V = \frac{1}{C} \sum_i C_i v_i = \sum_i y_i v_i$$

## 24.1b Molecular Mass Transfer: The General Flux Equation

$$\left( \begin{array}{c} \text{Molar Flux} \\ \text{of } A \\ \text{in mixture} \end{array} \right) = \frac{(\text{moles of species } A \text{ transferred})}{(\text{cross-sectional area for flux})(\text{time})} = \frac{\text{kgmoles } A}{\text{m}^2 \cdot \text{sec}}$$

Diffusion Flux of Species "A" (moving coordinates, relative to average velocity)

$$J_A = C_A(v_A - V) \quad \text{molar units, relative to molar average velocity}$$

$$j_A = \rho_A(v_A - v) \quad \text{mass units, relative to mass average velocity}$$

Molar Flux of Species "A" (fixed coordinates)

$$N_A = C_A v_A$$

Now consider

$$\left[ \frac{\text{total mass}}{\text{transported}} \right] = \left[ \frac{\text{mass transported}}{\text{by diffusion}} \right] + \left[ \frac{\text{mass transported}}{\text{bulk motion of fluid}} \right]$$

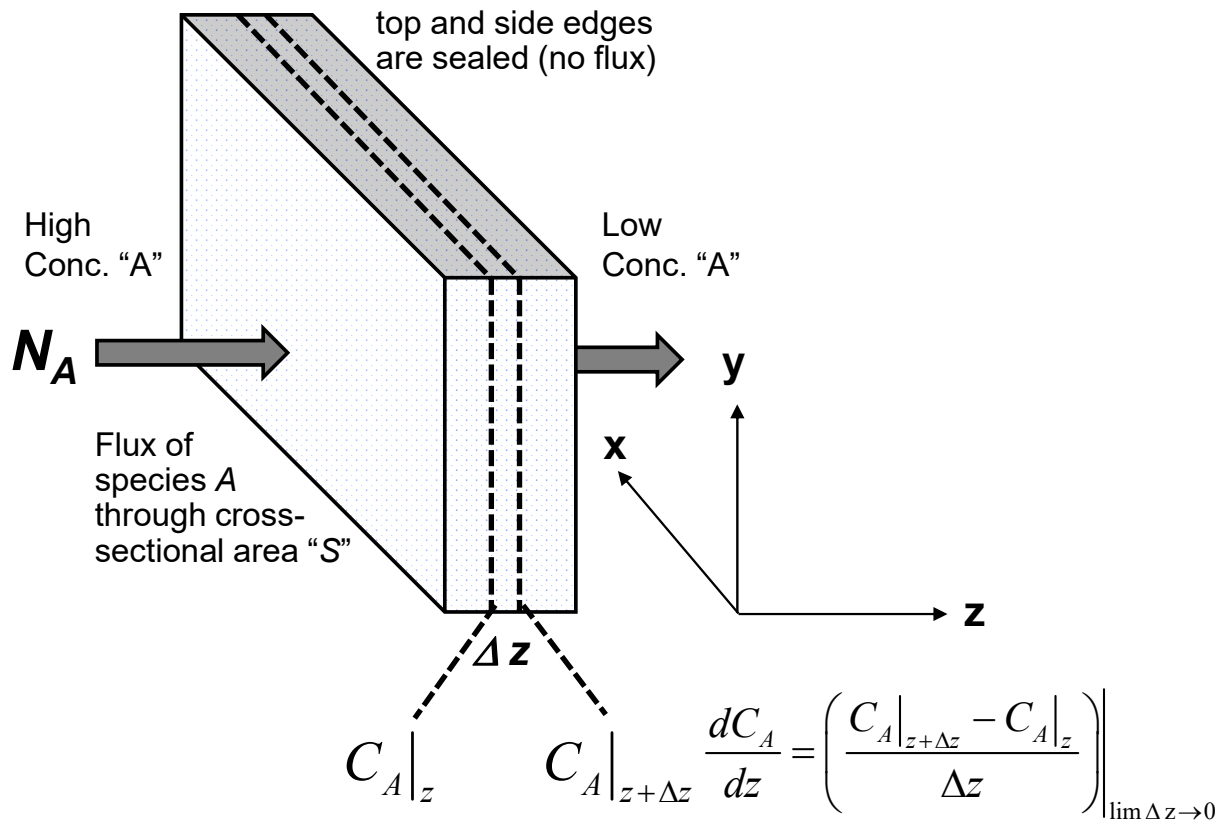
$$N_A = J_A + C_A V \quad (\text{units} = \frac{\text{kgmole}}{\text{m}^2 \text{ sec}})$$

Define **Fick's First Law** for one-dimensional flux along coordinate "z", binary mixture of A and B

$$\left( \begin{array}{c} \text{Diffusion Flux} \\ \text{of } A \end{array} \right) = \left( \begin{array}{c} \text{Diffusion} \\ \text{Coefficient} \end{array} \right) \left( \begin{array}{c} \text{Concentration} \\ \text{Gradient of } A \end{array} \right)$$

$$J_{A,z} = -D_{AB} \frac{dC_A}{dz}$$

The negative “-“ sign sets the direction of flux along positive z, because the concentration gradient of species A is negative as it moves from high concentration to low concentration along increasing z



### CHE 333: Fundamentals of Mass Transfer

Now recall

$$J_{A,z} = C_A (v_{A,z} - V_z)$$

$$\therefore C_A (v_{A,z} - V_z) = -D_{AB} \frac{dC_A}{dz}$$

We need to relate the velocity terms to terms involving flux. Recall

$$V_z = \frac{1}{C} \sum_i C_i v_{i,z}$$

For a binary mixture of A and B

$$C_A v_{A,z} - \frac{C_A}{C} (C_A v_{A,z} + C_B v_{B,z}) = -D_{AB} \frac{dC_A}{dz}$$

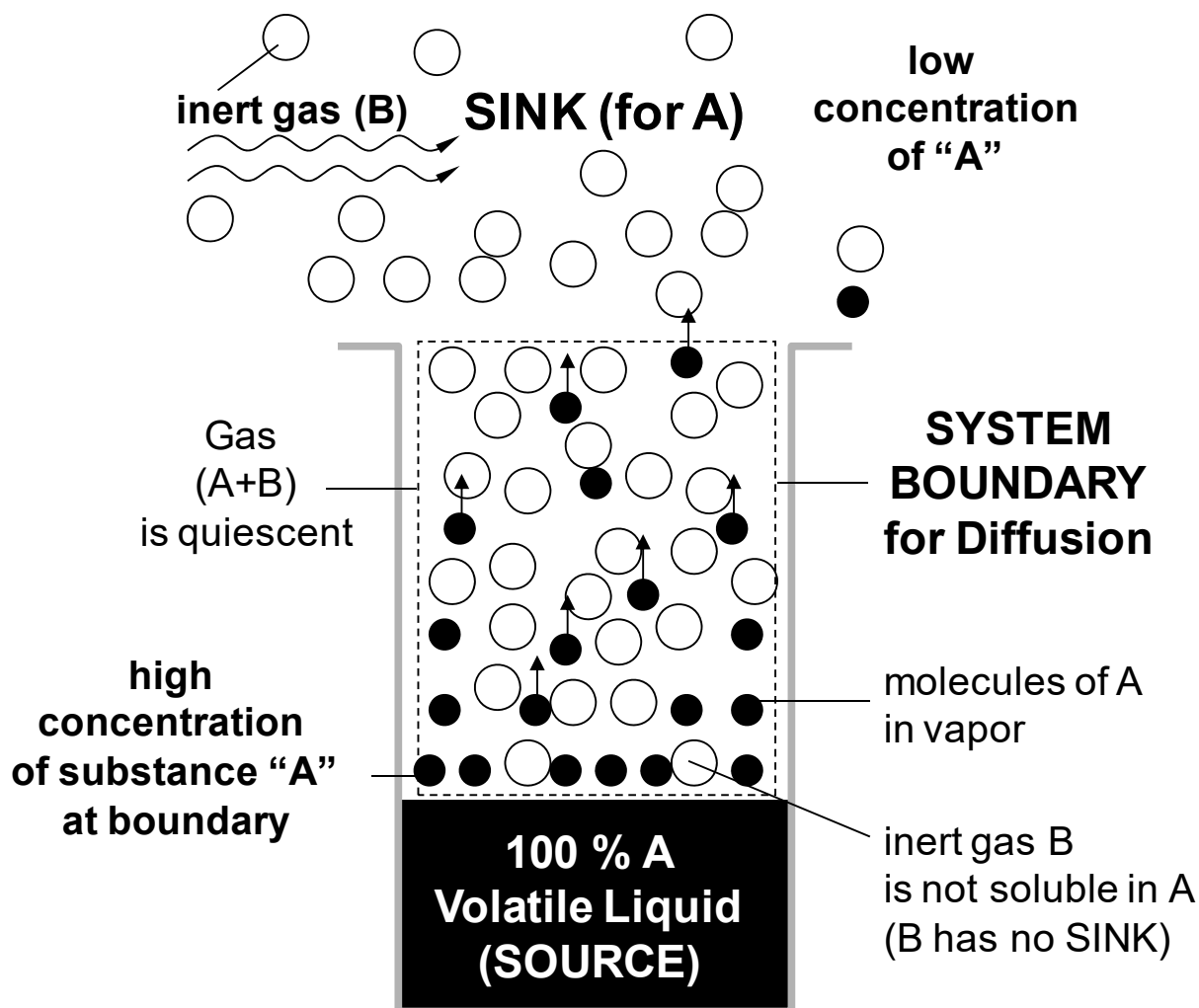
Recall

$$N_{A,z} = C_A v_{A,z} \quad \text{and} \quad N_{B,z} = C_B v_{B,z}$$

$$\therefore N_{A,z} = -D_{AB} \frac{dC_A}{dz} + \frac{C_A}{C} (N_{A,z} + N_{B,z})$$

24.1b Molecular Mass Transfer: The General Flux Equation (cont.)

**Simple Example of Flux of “A”  
from a SOURCE to a SINK**



## 24.2 The Diffusion Coefficient

*Summary of Estimation Methods for Homogeneous Binary Diffusion Coefficients  $D_{AB}$* 

Gas State	Liquid State
Kinetic Theory of Gases $D_{AB} = \frac{2}{3} \left( \frac{\kappa}{\pi} \right)^{3/2} N^{1/2} \frac{T^{3/2} \left( \frac{1}{2M_A} + \frac{1}{2M_B} \right)^{1/2}}{P \left( \frac{\sigma_A + \sigma_B}{2} \right)^2}$	Stokes-Einstein $D_{AB} = \frac{\kappa T}{6 \pi \mu_B r_A}$
Hirschfelder $D_{AB} = \frac{0.001858 T^{3/2} \left[ \frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2}}{P \sigma_{AB}^2 \Omega_D}$	Wilke-Chang $\frac{D_{AB} \mu_B}{T} = \frac{7.4 \times 10^{-8} [\phi M_B]^{1/2}}{V_A^{0.6}}$
Fuller-Schettler-Giddings $D_{AB} = \frac{0.001 T^{1.75} \left[ \frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2}}{P \left[ (\sum V_i)_A^{1/3} + (\sum V_i)_B^{1/3} \right]^2}$	Scheibel $\frac{D_{AB} \mu_B}{T} = \frac{K}{V_A^{1/3}}$ $K = (8.2 \times 10^{-8}) \left[ 1 + \left( \frac{3V_B}{V_A} \right)^{2/3} \right]$ <p style="text-align: center;"><i>except</i></p> <ol style="list-style-type: none"> <li>1. For benzene as solvent, if <math>V_A &lt; 2V_B</math>, <math>K = 18.9 \cdot 10^{-8}</math></li> <li>2. For other organic solvents, if <math>V_A &lt; 2.5V_B</math>, <math>K = 17.5 \cdot 10^{-8}</math></li> </ol>
Hirschfelder Extrapolation $D_{AB}(T_2, P_2) = D_{AB}(T_1, P_1) \left( \frac{P_1}{P_2} \right) \left( \frac{T_2}{T_1} \right)^{3/2} \frac{\Omega_D _{T_1}}{\Omega_D _{T_2}}$	

## 24.2 The Diffusion Coefficient

### *Introductory Comments*

The proportionality constant in Fick's First Law is the Diffusion Coefficient,  $D_{AB}$

$$D_{AB} = \frac{\text{diffusion flux}}{\text{conc. gradient}} = \frac{J_{A,z}}{-dC_A/dz} = \frac{\frac{\text{mole}}{\text{cm}^2 \text{ sec}}}{\frac{\text{mole}}{\text{cm}^3 \text{ cm}}} = \frac{\text{cm}^2}{\text{sec}}$$

For *binary mixtures*,  $D_{AB}$  refers to the diffusion coefficient of species A in a mixture of species A and B.

For *dilute multicomponent mixtures*,  $D_{AB}$  refers to the diffusion coefficient of species A in the medium which contains all the dilute species in an inert carrier medium (species B), e.g. dissolved solutes in a solvent carrier medium such as water. This type of system is often called a pseudo binary system.

The diffusion coefficient of species "i" in a multi-component mixture is represented by " $D_{i-m}$ " which is function of all binary  $D_{i-j}$  diffusion coefficients and the composition of those species.

Magnitude of Diffusion Coefficients (ambient temperature and pressure)

<i>Gases</i>	0.1 cm <sup>2</sup> /sec	
<i>Liquids</i>	1 x 10 <sup>-5</sup> cm <sup>2</sup> /sec	(dissolved solute in solvent)
<i>Solids</i>	1 x 10 <sup>-10</sup> cm <sup>2</sup> /sec	(dissolved solute in solid matrix)

## 24.2a Gas Phase Binary Diffusion Coefficients

The term "*Homogeneous*" refers to a single phase of material (gas, liquid, solid)

Consider molecules in a gaseous state. In the simplest model of gas dynamics, the molecules are regarded as rigid spheres that exert no molecular forces. Bi-molecular collisions between these rigid spheres are considered to be completely elastic. With these assumptions, a simplified model for an ideal gas mixture of species "A" diffusing through its isotope "A\*" yields an equation for the self-diffusion coefficient, defined as

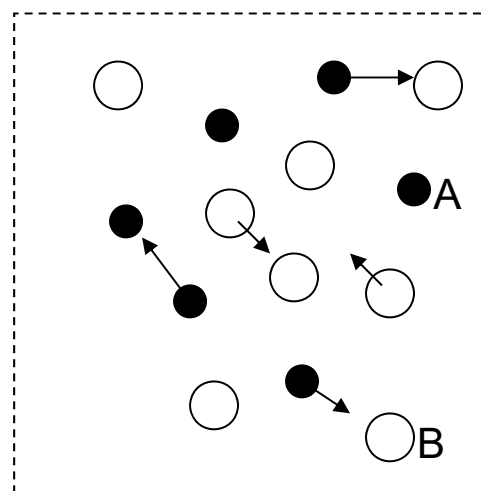
$$D_{AA^*} = \frac{1}{3} \lambda u$$

$u$  = average molecular speed of molecular of species A, given by

$$u = \sqrt{\frac{8 \kappa N T}{\pi M_A}}$$

$\lambda$  = mean free path length for species 1 between bi-molecular collisions, given by

$$\lambda = \frac{\kappa T}{\sqrt{2} \pi \sigma_A^2 P}$$



**Gas**

molecules are separated but collide frequently

Therefore, the self-diffusion coefficient becomes

$$D_{AA^*} = \frac{2}{3} \left( \frac{\kappa}{\pi} \right)^{3/2} N^{1/2} \frac{T^{3/2} \left( \frac{1}{M_A} \right)^{1/2}}{P \sigma_A^2}$$

$\kappa$  = Boltzmann's constant,  $1.38 \times 10^{-16}$  erg/K

$N$  = Avogadro's number,  $6.022 \times 10^{23}$  molecules/mole

$M_A$  = molecular weight of species A

$\sigma_A$  = collision diameter of species A (similar to molecular diameter)

$P$  = absolute system pressure

$T$  = absolute system temperature



## CHE 333: Fundamentals of Mass Transfer

Now consider a binary mixture of species A and B. For rigid spheres of unequal diameter, the gas phase diffusion coefficient is

$$D_{AB} = \frac{2}{3} \left( \frac{\kappa}{\pi} \right)^{3/2} N^{1/2} \frac{T^{3/2} \left( \frac{1}{2M_A} + \frac{1}{2M_B} \right)^{1/2}}{P \left( \frac{\sigma_A + \sigma_B}{2} \right)^2}$$

Show in your notes that the units for  $D_{AB}$  ultimately yield  $\text{cm}^2/\text{sec}$ .

Most experimentally-derived correlations use the above theoretical result as a template.

### *Observations:*

1. For diffusion in gases (not liquids)

$$D_{AB} = D_{BA}$$

2. As temperature  $T$  increases, the molecules move faster, so that

$$D_{AB} \propto T^{3/2}$$

3. As total system pressure  $P$  increases, molecular collisions become more frequent, so that

$$D_{AB} \propto \frac{1}{P}$$

4. As molecular size increases, molecules move slower, and are harder to “knock out of the way”, so that

$$D_{AB} \propto \left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2} \quad \text{and} \quad D_{AB} \propto \frac{1}{\sigma_{AB}^2}$$

## 24.2a Gas Phase Binary Diffusion Coefficients (cont.)

*Hirschfelder Correlation*

$$D_{AB} = \frac{0.001858 T^{3/2} \left[ \frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2}}{P \sigma_{AB}^2 \Omega_D}$$

$D_{AB}$	=	the diffusion coefficient of species A in a binary mixture of species A and B (cm <sup>2</sup> /sec)
$M_A, M_B$	=	molecular weight of species A, molecular weight of species B (g/gmole)
$P$	=	total system pressure (atm)
$T$	=	absolute temperature (K)
$\sigma_{AB}$	=	collision diameter (Å), where $\sigma_{AB} = (\sigma_A + \sigma_B)/2$ Appendix K, Table K.2 W <sup>3</sup> -R
$\Omega_D$	=	collision integral (dimensionless), estimated from $\kappa T / \varepsilon_{AB}$ where $\varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B}$ Appendix K, Table K.1

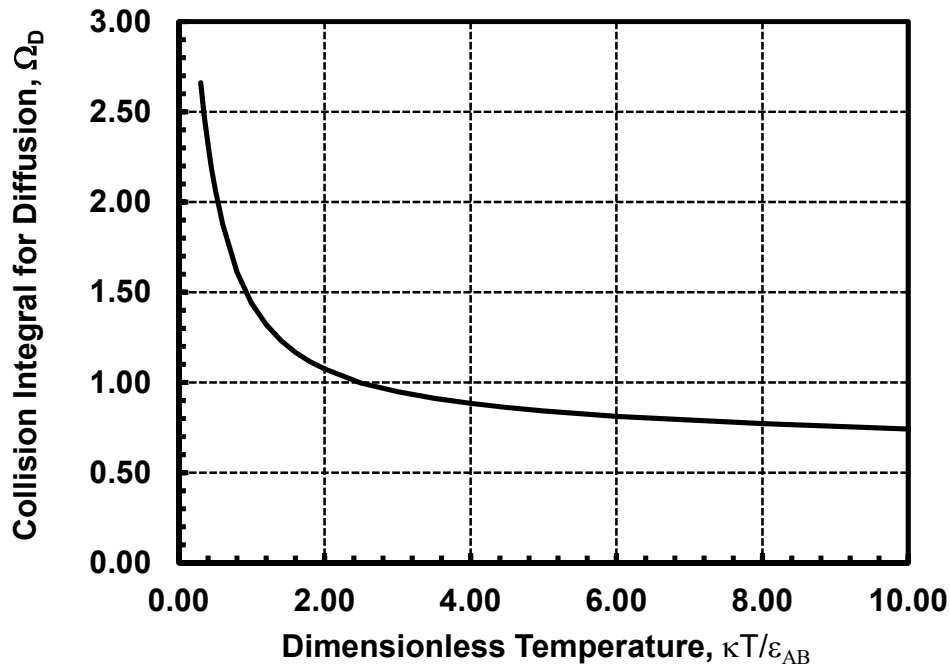
If the Lennard-Jones (L-J) parameters are not available, then estimate collision diameter  $\sigma_A$  (Å) and energy of molecular interaction  $\varepsilon_A$  (ergs) for a given species using the following correlations

$$\sigma_A = 1.18 (V_b)_A^{1/3} \quad \text{or} \quad \sigma_A = 0.841 (V_c)_A^{1/3} \quad \text{or} \quad \sigma_A = 2.44 (T_c/P_c)_A^{1/3}$$

$$\varepsilon_A/\kappa = 0.77 (T_c)_A \quad \text{or} \quad \varepsilon_A/\kappa = 1.15 (T_b)_A$$

where  $V_c$ ,  $P_c$ , and  $T_c$  and the critical volume (cm<sup>3</sup>/gmole), pressure (atm), and temperature (K) of a given pure component respectively,  $V_b$  is the molal volume at the normal boiling point (cm<sup>3</sup>/gmole),  $T_b$  is the normal boiling point (K), and  $\kappa$  is the Boltzmann constant ( $\kappa = 1.38 \times 10^{-16}$  ergs/K).

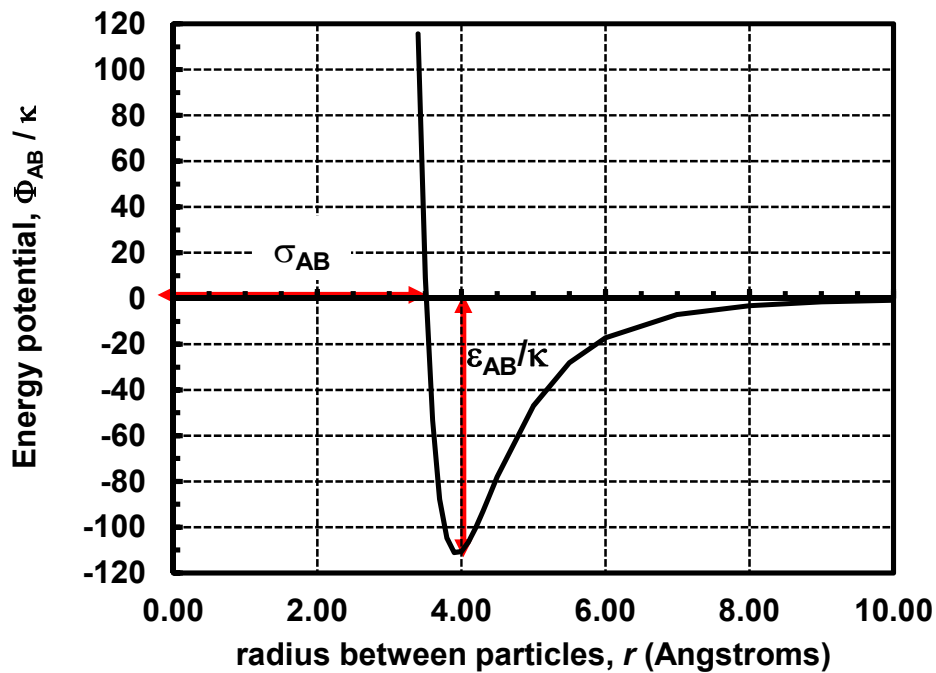
## 24.2a Gas Phase Binary Diffusion Coefficients (cont.)



Lennard-Jones potential ( $\Phi_{AB}$ ) between molecules A and B:

$$\Phi_{AB} = 4\epsilon_{AB} \left[ \left( \frac{\sigma_{AB}}{r} \right)^{12} - \left( \frac{\sigma_{AB}}{r} \right)^6 \right]$$

Example: A = CO, B = O<sub>2</sub>,  $\sigma_{AB} = 3.512 \text{ \AA}$ ,  $\epsilon_{AB}/\kappa = 111.5 \text{ K}$



## 24.2a Gas Phase Binary Diffusion Coefficients (cont.)

*Fuller-Schettler-Giddings Correlation*

$$D_{AB} = \frac{0.001 T^{1.75} \left[ \frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2}}{P \left[ (\sum V_i)_A^{1/3} + (\sum V_i)_B^{1/3} \right]^2}$$

The term  $(\sum V_i)_A$  is the atomic diffusion volume of species A, computed by adding volume increments  $V_i$  for each atom within a molecule of species A (group contribution approach). Values for  $V_i$  are given in Table 24.3 of W3-R.

- $D_{AB}$  = gas-phase binary diffusion coefficient of species A in a mixture of species A and B, cm<sup>2</sup>/sec  
 $P$  = total system pressure, atm  
 $T$  = system temperature, K (degrees Kelvin)

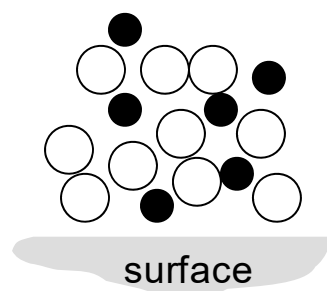
Atomic and Structure Diffusion Volume Increments $V_i$					
C	16.5	Cl	19.5		
H	1.98	S	17.0		
O	5.48	Aromatic Ring	-20.2		
N	5.69	Heterocyclic Ring	-20.2		
Atomic Diffusion Volumes for Simple Molecules					
H <sub>2</sub>	7.07	Ar	16.1	H <sub>2</sub> O	12.7
D <sub>2</sub>	6.70	Kr	22.8	CHClF <sub>2</sub>	114.8
He	2.88	CO	18.9	SF <sub>6</sub>	69.7
N <sub>2</sub>	17.9	CO <sub>2</sub>	26.9	Cl <sub>2</sub>	37.7
O <sub>2</sub>	16.6	N <sub>2</sub> O	35.9	Br <sub>2</sub>	67.2
Air	20.1	NH <sub>3</sub>	14.9	SO <sub>2</sub>	41.1

## 24.2b Liquid Phase Binary Diffusion Coefficients

Consider a solute (species A, dark spheres) dissolved in a liquid solvent (species B, open spheres). The solute is "infinitely dilute" in the mixture. The Stokes-Einstein model proposes that the solute "flows" through the solvent as a hard sphere, with a molecular drag force coefficient defined as the diffusion coefficient of the form:

$$D_{AB} = \frac{\kappa T}{6 \pi \mu_B r_A}$$

$\mu_B$  = viscosity of the solvent (g/cm-sec)  
 $r_A$  = radius of the solute molecule (cm)



Show in your notes that the units for  $D_{AB}$  ultimately yield  $\text{cm}^2/\text{sec}$ .

*Observations:*

1. For diffusion in liquids

$$D_{AB} \neq D_{BA}$$

2. As temperature  $T$  increases, the molecules move faster, so that

$$D_{AB} \propto T$$

3. As solvent viscosity  $\mu_B$  increases, the cohesiveness of the diffusion medium increases, and impedes molecular transport so that

$$D_{AB} \propto \frac{1}{\mu_B}$$

But remember, solvent viscosity is also a function of  $T$ .

4. As the molecular radius  $r_A$  increases, the "drag force" on the molecule increases, so that

$$D_{AB} \propto \frac{1}{r_A}$$

**Liquid**  
 molecules touch  
 but are still mobile

**24.2b Liquid Phase Binary Diffusion Coefficients (cont.)**

Most correlations for liquid-phase solute-solvent binary diffusion coefficients use the following template

$$\frac{D_{AB} \mu_B}{T} = f(V)$$

where  $V$  is the molar volume of the diffusing solute.

**Wilke-Chang Correlation**

For non-electrolyte solutes at *infinite dilution* (A = solute, B = solvent)

$$\frac{D_{AB} \mu_B}{T} = \frac{7.4 \times 10^{-8} [\phi M_B]^{1/2}}{V_A^{0.6}}$$

$D_{AB}$  = the diffusion coefficient of solute A in solvent B at infinite dilution of A (cm<sup>2</sup>/sec)

$M_B$  = molecular weight of the solvent

$T$  = absolute temperature (K)

$V_A$  = molar volume of solute at its normal boiling point (cm<sup>3</sup>/gmole)

$\mu_B$  = viscosity of solvent (centipoise, note 1.0 kg/m-sec = 1000 cP)

$\phi$  = association factor for the solvent (dimensionless)

<i>Solvent</i>	$\phi$
nonassociated solvents	1.0
ethanol	1.5
methanol	1.9
water	2.6

If data for computing  $V_A$  is not available, then estimate from the Tyn & Calus Correlation

$$V_A = 0.285 V_C^{1.048}$$

where  $V_C$  = critical volume of species A (cm<sup>3</sup>/gmole)

***Hayduk and Laudie Correlation***

For nonelectrolyte solutes in water solvent at *infinite dilution*

$$D_{AB} = 13.26 \times 10^{-5} \mu_B^{-1.14} \cdot V_A^{-0.589}$$

All units are consistent with the Wilke-Chang Correlation above. The temperature  $T$  is implicitly lumped into the correlation through the physical property terms.

Notes on  $D_{AB}$  for liquid phase systems:

1.  $D_{AB}$  for species A and B in the liquid phase are typically  $10^{-4}$  to  $10^{-5}$  times smaller than  $D_{AB}$  of the same components in the gas phase.

Example: for Ethanol (A) - H<sub>2</sub>O (B) in the *gas phase*,

$$D_{AB} = 0.128 \text{ cm}^2/\text{sec at } 25^\circ\text{C and } 1 \text{ atm}$$

for Ethanol (A) - H<sub>2</sub>O (B) in the *liquid phase*,

$$D_{AB} = 0.84 \times 10^{-5} \text{ cm}^2/\text{sec at } 25^\circ\text{C}$$

2. Correlations for  $D_{AB}$  assume infinite dilution of the solute in the solvent.
3. For very dilute mixtures of multi-component solutes, simply compute each solute diffusion coefficient separately, i.e.  $D_{1-B}$ ,  $D_{2-B}$  etc. for solutes 1, 2,.. in solvent  $B$ .
4.  $D_{AB} \neq D_{BA}$

Example: Ethanol (1) - H<sub>2</sub>O (2) in the *liquid phase*

$$D_{AB} = 0.84 \times 10^{-5} \text{ cm}^2/\text{sec at } 25^\circ\text{C infinite dilution of ethanol in water}$$

$$D_{AB} = 1.24 \times 10^{-5} \text{ cm}^2/\text{sec at } 25^\circ\text{C infinite dilution of water in ethanol}$$

**Liquid phase binary diffusion coefficients for ionic solutes**

To maintain charge neutrality, both the cation and the anion of the ionic salt must diffuse through water as an ionic pair

***Nernst-Haskell equation for univalent salt in dilute solutions***

$$D_{AB} = \frac{2RT}{\left(1/\lambda_+^0 + 1/\lambda_-^0\right)(\mathcal{F})^2}$$

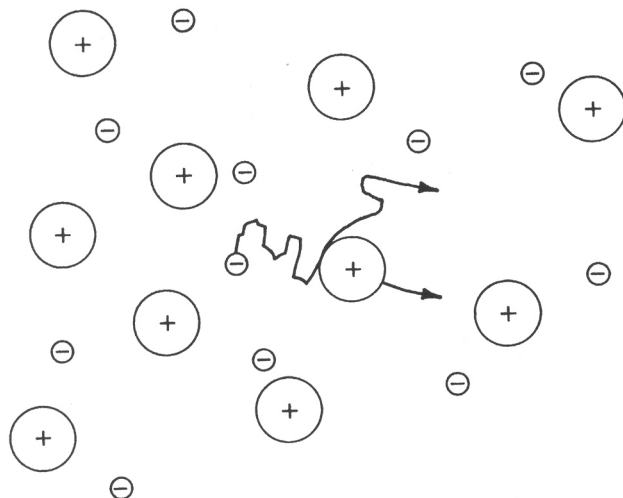
$D_{AB}$  = diffusion coefficient of the ion pair (cation+anion) in solvent B at infinite dilution

$R$  = thermodynamic gas constant (8.316 J/gmole·K)

$T$  = absolute temperature (K)

$\lambda_+^0, \lambda_-^0$  = limiting (zero concentration) ionic conductances of the cation and anion respectively in the ion pair (A·cm<sup>2</sup>/V·gmole)

$\mathcal{F}$  = Faraday's constant (96,500 C/gmole), note 1 C = 1 A·s and 1 J/s = 1 A·V

***Extended Nernst-Haskell equation for polyvalent ions***

$$D_{AB} = \frac{\left(1/n^+ + 1/n^-\right)RT}{\left(1/\lambda_+^0 + 1/\lambda_-^0\right)(\mathcal{F})^2}$$

$n^+$  and  $n^-$  are the valences of the cation and anion

Selected limiting ionic conductances in water at 25 °C (A·cm<sup>2</sup>/V·gmole)

<u>Cation</u>	$\lambda_+^0$	Anion	$\lambda_-^0$
H <sup>+</sup>	349.8	OH <sup>-</sup>	197.6
Li <sup>+</sup>	38.7	Cl <sup>-</sup>	76.3
Na <sup>+</sup>	50.1	Br <sup>-</sup>	78.3
K <sup>+</sup>	73.5	I <sup>-</sup>	76.8
NH <sub>4</sub> <sup>+</sup>	73.4	NO <sub>3</sub> <sup>-</sup>	71.4
Ag <sup>+</sup>	61.9	HCO <sub>3</sub> <sup>-</sup>	44.5
Mg <sup>+2</sup>	106.2	SO <sub>4</sub> <sup>-2</sup>	160
Ca <sup>+2</sup>	119		
Cu <sup>+2</sup>	108		
Zn <sup>+2</sup>	106		

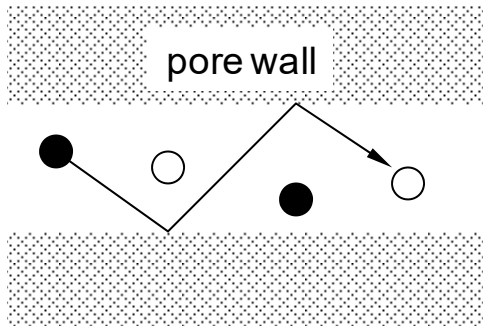


### 24.2c Diffusion Coefficients - Pore Diffusion

“Pore Diffusion” involves the diffusion of a binary mixture of species A and B within the pores of a “porous” solid medium.

#### *Knudsen Diffusion (Gases in a Porous Solid)*

For gas-filled straight cylindrical pores in parallel array, consider the following:



diffusing molecule hits pore wall more frequently than other molecules within the gas space inside the pore

Define the Knudsen Number,  $Kn$

$$Kn = \frac{\lambda}{d_{pore}} = \frac{\text{mean free path length of the diffusing species}}{\text{pore diameter}}$$

where

$$\lambda = \frac{\kappa T}{\sqrt{2} \pi \sigma_A^2 P}$$

Recall from the Kinetic Theory of Gases

$$D_{AA^*} = \frac{1}{3} \lambda u = \frac{1}{3} \lambda \sqrt{\frac{8 \kappa N T}{\pi M_A}}$$

Replace path length  $\lambda$  with pore diameter  $d$ , as species A is now more likely to collide with the pore wall as opposed to another molecule

$$D_{KA} = \frac{d_{pore}}{3} u = \frac{d_{pore}}{3} \sqrt{\frac{8 \kappa N T}{\pi M_A}}$$

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$$D_{KA} = \frac{d_{pore}}{3} \sqrt{\frac{8 \kappa N T}{\pi M_A}} = \frac{d_{pore}}{3} \sqrt{\frac{8 \cdot \left( 1.38 \cdot 10^{-16} \frac{g \cdot cm^2}{sec^2 K} \right) \cdot \left( 6.023 \cdot 10^{23} \frac{molecules}{mole} \right)}{\pi}} \sqrt{\frac{T}{M_A}} = 4850 \cdot d_{pore} \sqrt{\frac{T}{M_A}}$$

units:  $d$  (cm),  $T$  (K),  $D_{KA}$  (cm<sup>2</sup>/sec)

Notes:

1.  $D_{KA}$  is only a function of species A parameters and absolute temperature  $T$ ; it is not a function of absolute pressure  $P$  (however,  $Kn \propto 1/P$ ).
2. In practice,  $D_{KA}$  is only for gases since  $\lambda$  for liquids is near the molecular diameter of the molecule itself.
3. Generally, Knudsen diffusion is significant only at low system pressure and small pore diameter.
4.  $D_{KA} \propto T^{1/2}$  vs.  $D_{AB} \propto T^{3/2}$  for molecular diffusion coefficients.

**Knudsen Diffusion (Gases in a Porous Solid) cont.**

What happens if both Knudsen Diffusion ( $D_{KA}$ ) and Molecular Diffusion ( $D_{AB}$ ) are important? Consider a "Resistances in Series" approach where it can be shown that

$$\frac{l}{D_{Ae}} = \frac{l - \alpha y_A}{D_{AB}} + \frac{l}{D_{KA}}$$

with

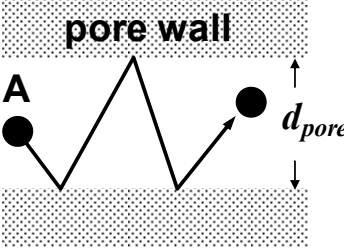
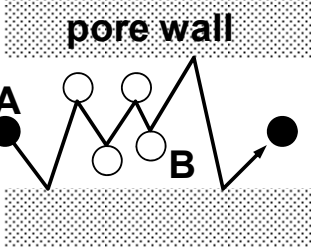
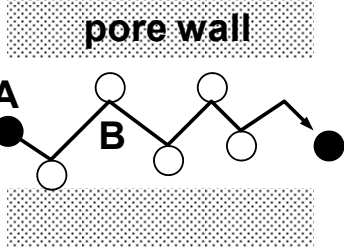
$$\alpha = l + \frac{N_B}{N_A}$$

Notes:

1. If  $\alpha = 0$  ( e.g.  $N_A = -N_B$  ) or  $y_A$  is close to zero ( $y_A \ll 1$ )

$$\frac{l}{D_{Ae}} \cong \frac{l}{D_{AB}} + \frac{l}{D_{KA}}$$

2. As  $d_{pore}$  increases,  $D_{Ae}$  approaches  $D_{AB}$

Pure Knudsen Diffusion	Knudsen + Molecular Diffusion	Pure Molecular Diffusion
		
$D_{KA} = \frac{d_{pore}}{3} \sqrt{\frac{8 \kappa N T}{\pi M_A}}$	$\frac{l}{D_{Ae}} \cong \frac{l}{D_{AB}} + \frac{l}{D_{KA}}$	$D_{AB} = \frac{0.001858 T^{3/2} \left[ \frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2}}{P \sigma_{AB}^2 \Omega_D}$

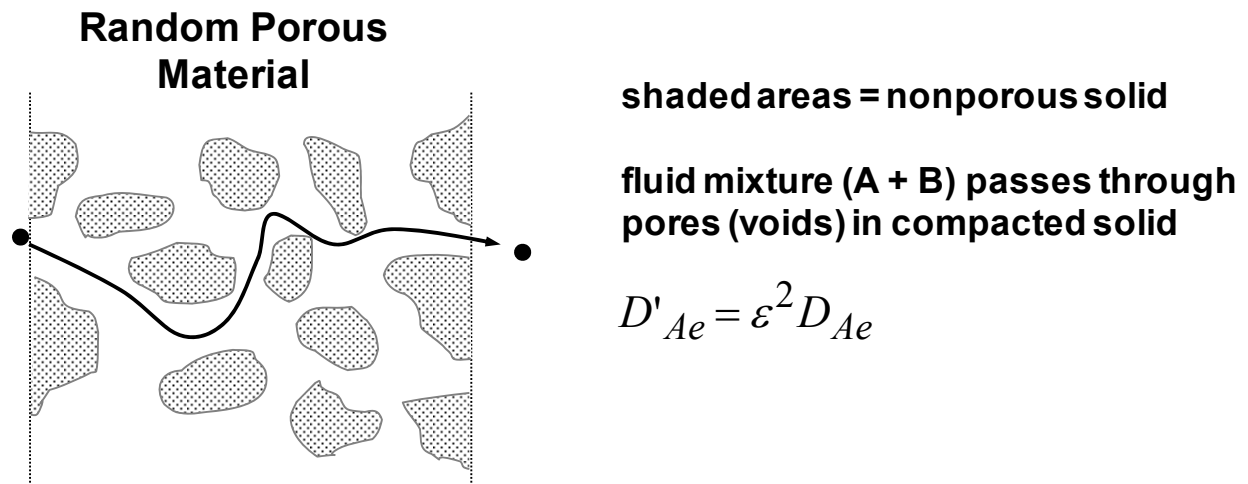
***Effective Diffusion Coefficients in “Real” Porous Materials***

- Pores of various diameters are twisted and interconnected with one another
- The path for diffusion of the gas molecule within these pores is “tortuous”
- Estimate  $D_{Ae}$  based on an average pore diameter
- Correct  $D_{Ae}$  for the random nature of the pores by

$$D'_{Ae} = \varepsilon^2 D_{Ae}$$

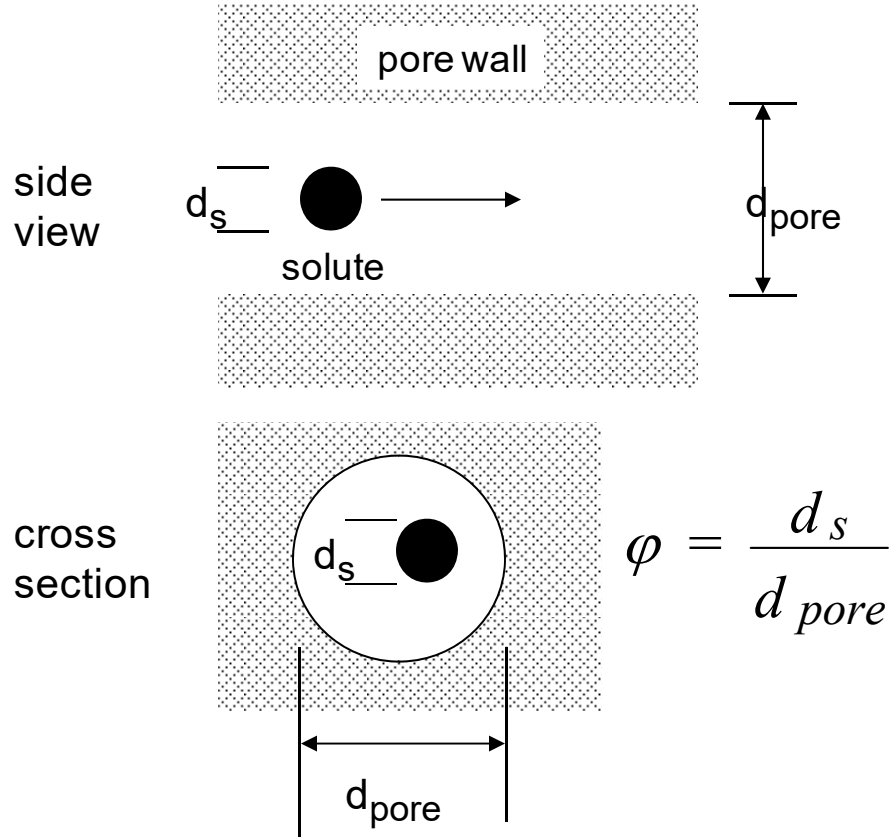
$$\varepsilon = \frac{\text{volume occupied by pores within the porous solid}}{\text{total volume of porous solid(solid + pores)}} \quad \text{with } 0 < \varepsilon < 1$$

The “void fraction”  $\varepsilon$  is usually experimentally determined for a given material.



24.2c Diffusion Coefficients - Pore Diffusion (cont.)

*Solute Diffusion in Solvent-Filled Pores (Liquid in Porous Solid)*



Define *reduced pore diameter*  $\phi$

$$\phi = \frac{d_s}{d_{pore}} = \frac{\text{solute molecular diameter}}{\text{pore diameter}}$$

General model for "hindered diffusion" of solutes in solvent-filled pores (A = dissolved solute, B = solvent, infinite dilution of solute) is

$$D_{Ae} = D_{AB}^0 F_1(\phi) F_2(\phi)$$

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Two correction factors on  $D^o_{AB}$

Stearic partition factor  $F_1(\varphi)$  ( $0 \leq F_1(\varphi) \leq 1$ )

$$F_1(\varphi) = \frac{\text{flux area available to solute}}{\text{total flux area}} = \frac{\pi (d_{\text{pore}} - d_s)^2}{\pi d_{\text{pore}}^2} = (1 - \varphi)^2$$

if  $\varphi \geq 1$ , then solute A is “excluded” from the pore and  $D_{Ae} = 0$ .

Hydrodynamic hindrance factor  $F_2(\varphi)$  (Renkin Equation)

$$F_2(\varphi) = 1 - 2.104 \varphi + 2.09 \varphi^3 - 0.95 \varphi^5$$

- $F_2(\varphi) < 1$
- rigid spherical solutes in straight cylindrical pore
- valid  $0 \leq \varphi \leq 0.6$
- based on complicated hydrodynamic calculations involving the hindered Brownian motion of the solute within the solvent-filled pores
- ignores electrostatic or other energetic solute-solvent-pore wall interactions

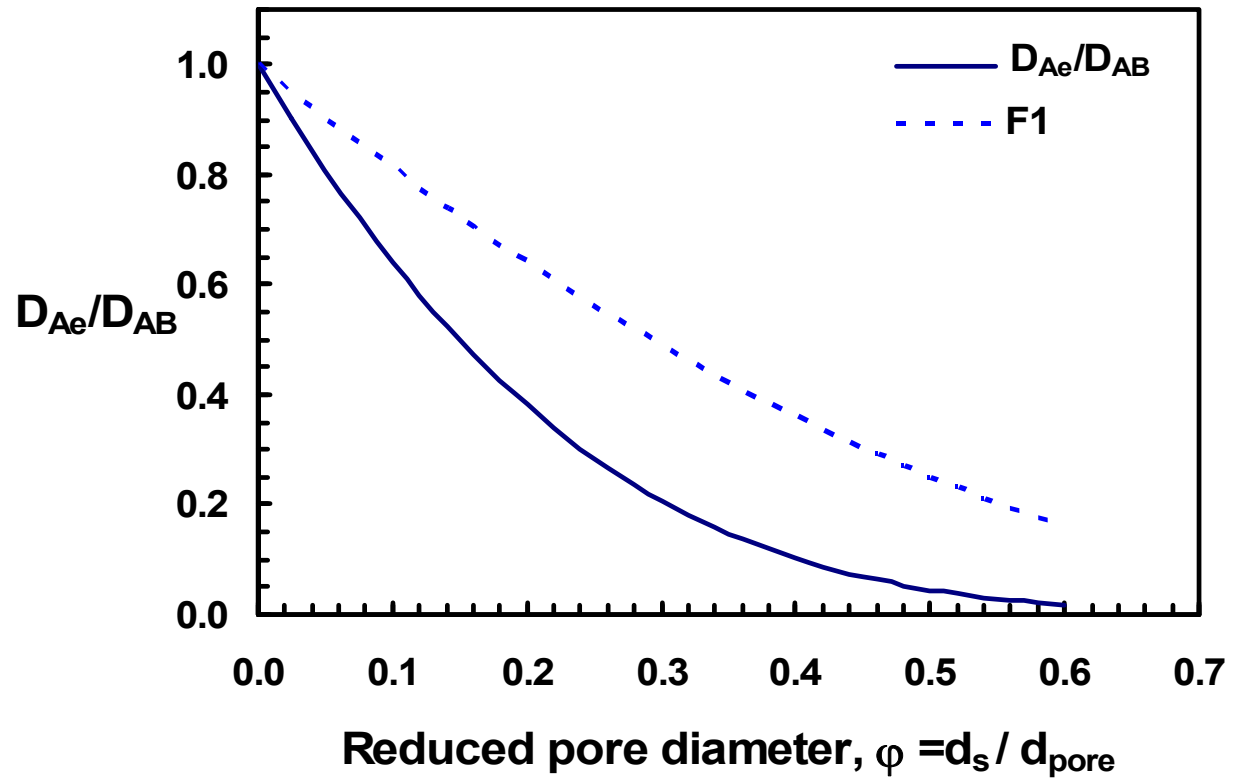
$$D_{Ae} = D_{AB}^o F_1(\varphi) F_2(\varphi)$$

Stearic partition factor  $F_1(\varphi)$  ( $0 \leq F_1(\varphi) \leq 1$ )

$$F_1(\varphi) = \frac{\text{flux area available to solute}}{\text{total flux area}} = \frac{\pi (d_{\text{pore}} - d_s)^2}{\pi d_{\text{pore}}^2} = (1 - \varphi)^2$$

Hydrodynamic hindrance factor  $F_2(\varphi)$  (Renkin Equation)

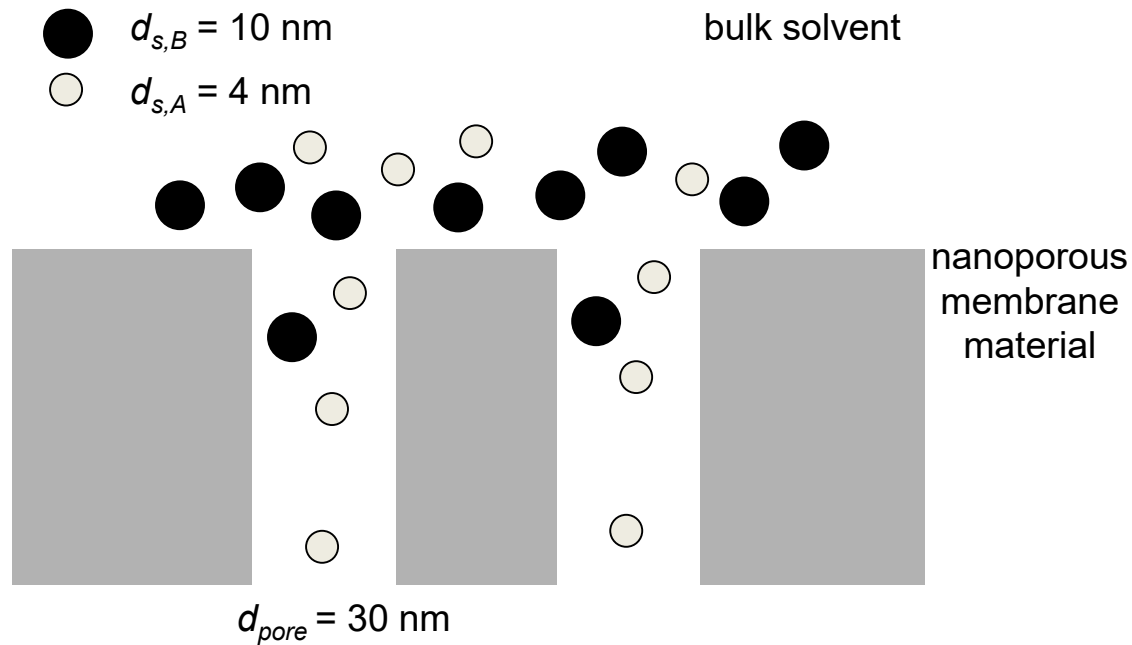
$$F_2(\varphi) = 1 - 2.104 \varphi + 2.09 \varphi^3 - 0.95 \varphi^5$$



## 24.2c Diffusion Coefficients - Pore Diffusion (cont.)

### *Solute Diffusion in Solvent-Filled Pores (Liquid in Porous Solid)*

Molecular Sieve based separation of solutes *A* and *B* in bulk solvent *C*



$$D_{Ae} = D_{AC}^o F_1(\phi_A) F_2(\phi_A)$$

$$D_{Be} = D_{BC}^o F_1(\phi_B) F_2(\phi_B)$$

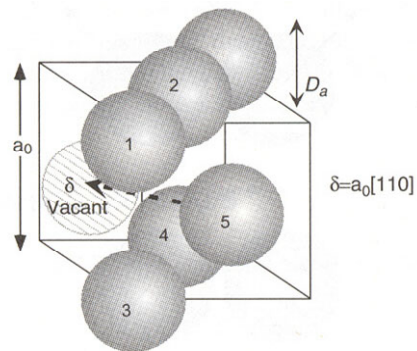
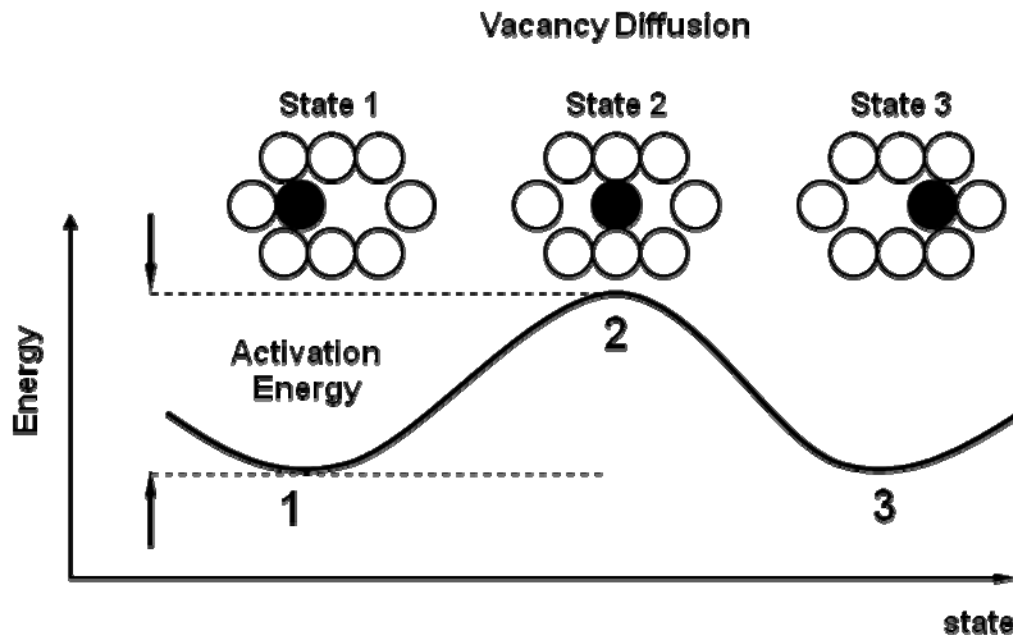
Separation Factor ( $\alpha$ )

$$\alpha = \frac{D_{Ae}}{D_{Be}}$$

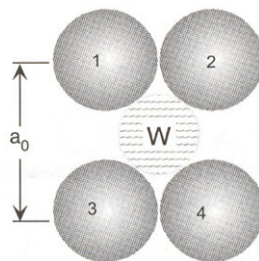


## 24.2d Solid-Phase Diffusion Coefficients

Two modes for diffusion of solute A “dissolved” in solid medium B

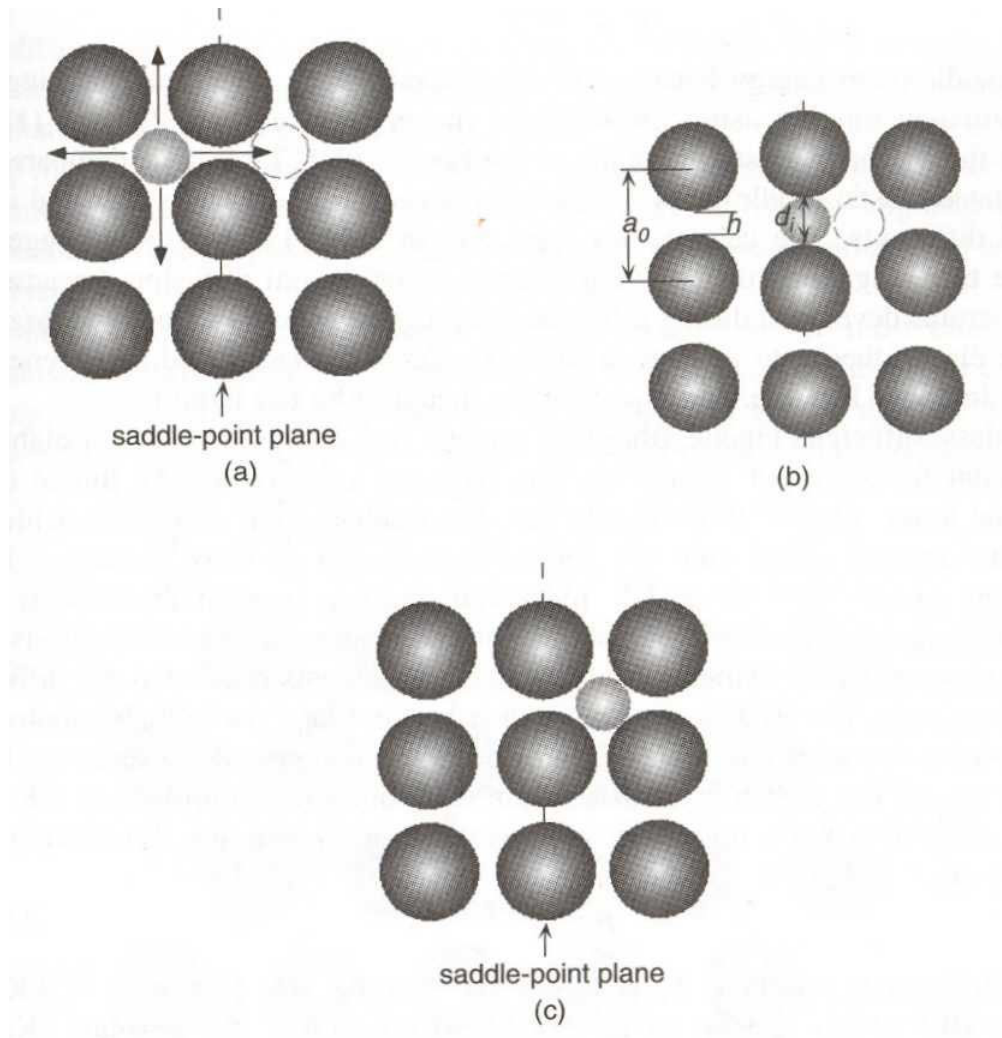
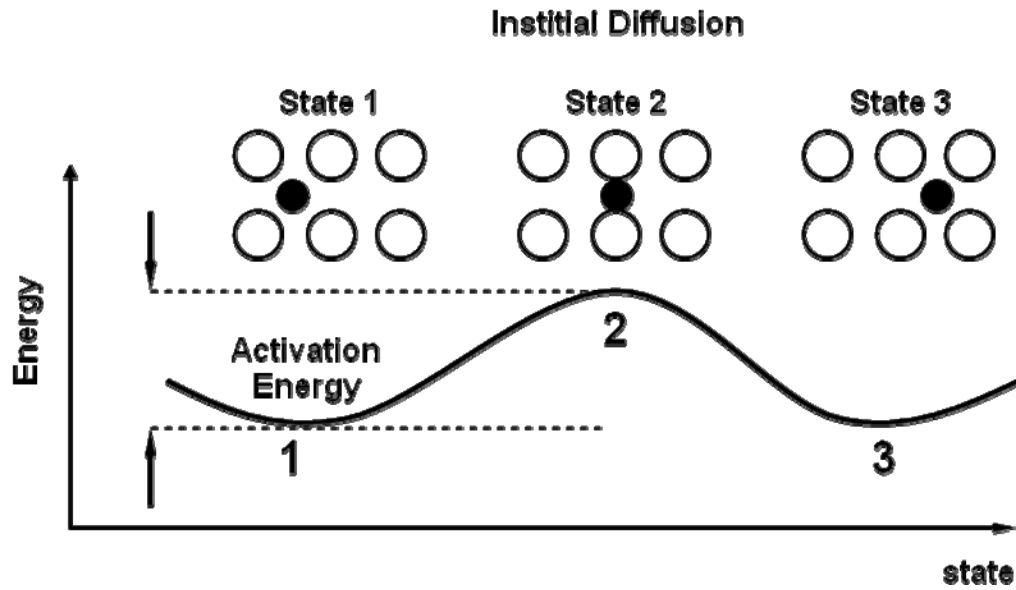


(a)



(b)

Ref: Glickman, M.E. *Diffusion in Solids*, Wiley Press (2000).



Ref: Glickman, M.E. *Diffusion in Solids*, Wiley Press (2000).

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Diffusion coefficients of solute A “dissolved” in solid medium B are often an exponential function of temperature:

$$D_{AB} = D_o e^{-Q/RT}$$

In linear form,  $Q$  and  $D_o$  are determined from slope and intercept

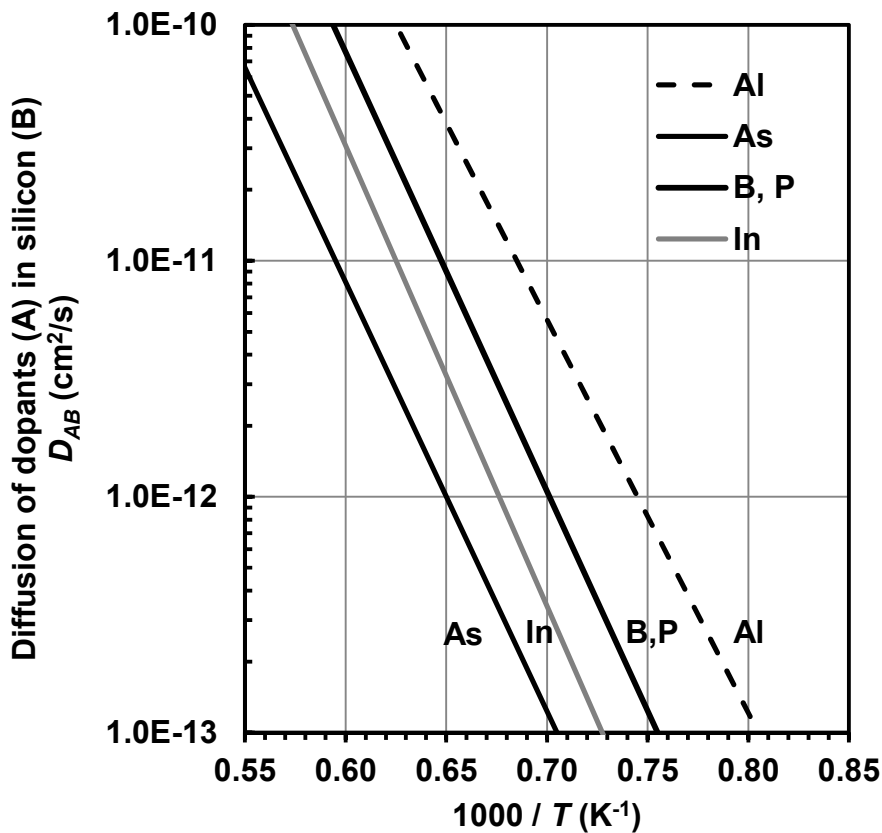
$$\ln(D_{AB}) = -\frac{Q}{R} \frac{1}{T} + \ln(D_o)$$

$Q$  = activation energy for solid diffusion of A (J/mole)

$R$  = thermodynamic constant (8.314 J/mole-K)

$D_o$  = proportionality constant (cm<sup>2</sup>/sec)

Example Data: Solid Diffusion Coefficients vs. Temperature common elemental dopants in solid silicon.

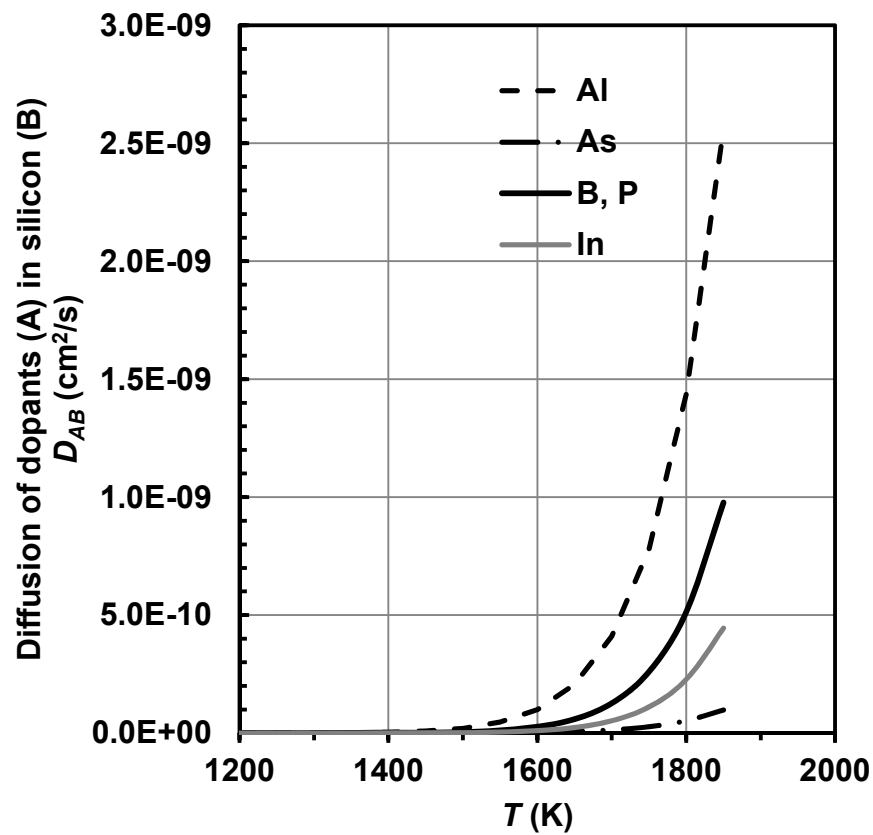


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Diffusion parameters common substitutional dopants in polycrystalline silicon, using data obtained from Ghandhi (1983)

Dopant	$D_0$ (cm <sup>2</sup> /s)	$Q$ (kJ/gmole)
Al	2.61	319.1
As	0.658	348.1
B, P	11.1	356.2
Ga	0.494	312.6
In	15.7	373.5

S. K. Ghandhi, *VLSI Fabrication Principles*, John Wiley & Sons, New York, 1983.



## 2.4e Diffusion Coefficients for Ideal Gases in Multi-component Mixtures

Diffusion coefficients are fundamentally defined only for two given species, i.e. a binary pair. In a true multi-component mixture, the “mixture based diffusion coefficient” for species A in the multi-component mixture,  $D_{A-m}$ , is based on the assembling the individual diffusion coefficients for all binary pairs, using principles derived from the Stefan-Maxwell relationships.

Consider:

- Ternary mixture of A, B, and C
- No composition of A, B, or C dominates (true multi-component mixture)
- Component “A” has a SOURCE and a SINK for mass transfer
- Components “B” and “C” are “spectators” which may not have a defined source and sink, i.e. diffusion of A is through a stagnant mixture of A, B, and C
- Gas phase mixture is an ideal gas

Under these conditions, the  $D_{A-m}$  for species A in a mixture of A, B, and C is

$$\frac{1}{D_{A-m}} = \frac{y'_B}{D_{AB}} + \frac{y'_C}{D_{AC}} \quad \text{or} \quad \frac{1-y_A}{D_{A-m}} = \frac{y_B}{D_{AB}} + \frac{y_C}{D_{AC}}$$

where  $y'_B$  and  $y'_C$  are defined on a “A” free basis with

$$y'_B + y'_C = 1.0 \quad \text{and} \quad y'_B = \frac{y_B}{1-y_A}, \quad y'_C = \frac{y_C}{1-y_A}$$

$$\text{and} \quad y_A + y_B + y_C = 1.0$$

Extending the above to species “1” in the an “n” component mixture is

$$\frac{1}{D_{1-m}} = \sum_{j=2}^n \frac{y'_j}{D_{1-j}} \quad \text{or} \quad \frac{1-y_1}{D_{1-m}} = \sum_{j=2}^n \frac{y_j}{D_{1-j}}$$