University Of Jordan

Faculty of Engineering and Technology

Department of Chemical Engineering

Transport Phenomena II

Lec 1: Fundamentals of Mass Transfer

Content

Mode of mass transfer, Molecular diffusion, Convection Mass Transfer, General Flux Equation, Diffusivity

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Content

- Introduction
- Mode of Mass Transfer
  - Molecular Diffusion
  - Convection Mass Transfer
- The General Flux Equation
- Diffusivity

Introduction

- Three fundamental transfer processes:
  - ***i)*** ***Momentum transfer*** occurs in unit operations as fluid flow, mixing,. sedimentation, and filtration.
  - ***ii)*** ***Heat transfer*** occurs in conductive and convective transfer of heat, evaporation, distillation, and drying
  - ***iii)*** ***Mass transfer*** occurs in distillation, absorption, drying, liquid-liquid extraction, adsorption, and membrane processes.

- All three of the molecular transport processes of momentum, heat, and mass are characterized by the same general type of equation: **General molecular transport equation:**

$$Rate\ of\ a\ trasnfer\ process = \frac{driving\ force}{resistance}$$

Introduction Cont.

- This can be written as follows for molecular diffusion of the property momentum, heat, and mass:

$$\psi_z = -\delta \frac{d\Gamma}{dz}$$

Name	Process	Flux	Gradient
1. Fick's law	Diffusion	$N / A = -D \frac{dC}{dx}$	Concentration
2. Fourier's law	Conduction	$q / A = -k \frac{dT}{dx}$	Temperature
3. Alternative formulation		$q / A = -\alpha \frac{d(\rho CpT)}{dx}$	Energy concentration
4. Newton's viscosity law	Molecular momentum transport	$F_x / A = \tau_{qx} = -\mu \frac{dv_x}{dy}$	Velocity
5. Alternative formulation		$F_x / A = \tau_{yx} - \nu \frac{d(\rho v_x)}{dy}$	Momentum concentration

Mass Transfer

- When a system contains two or more components whose concentrations vary from point to point, there is a natural tendency for mass to be transferred, minimizing the concentration differences within a system.
- The transport of one constituent from a region of higher concentration to that of a lower concentration is called mass transfer.

Mass transfer occurs when a component in a mixture transfers in the same phase or from phase to phase because of a difference in concentration between two points.

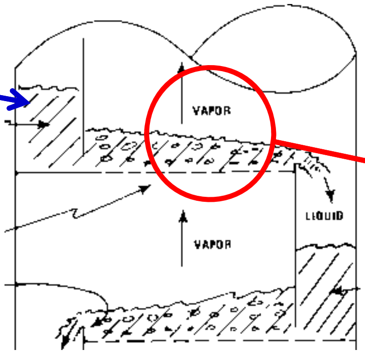
Mass Transfer

- The transfer of mass within a fluid mixture or across a phase boundary is a process that plays a major role in many industrial processes.
- Mass transfer may occur in a gas mixture, a liquid solution or solid.
- Examples of such processes are:
  - Dispersion of gases from stacks

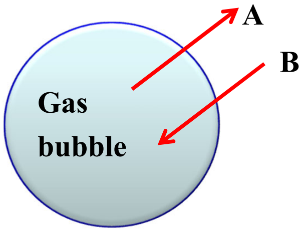
Examples of Mass Transfer Processes

Distillation columns

e.g., in petroleum refinery



Species exchange between gas-liquid around the trays



This mass transfer enriches species (A) in the liquid, and species (B) in the gas

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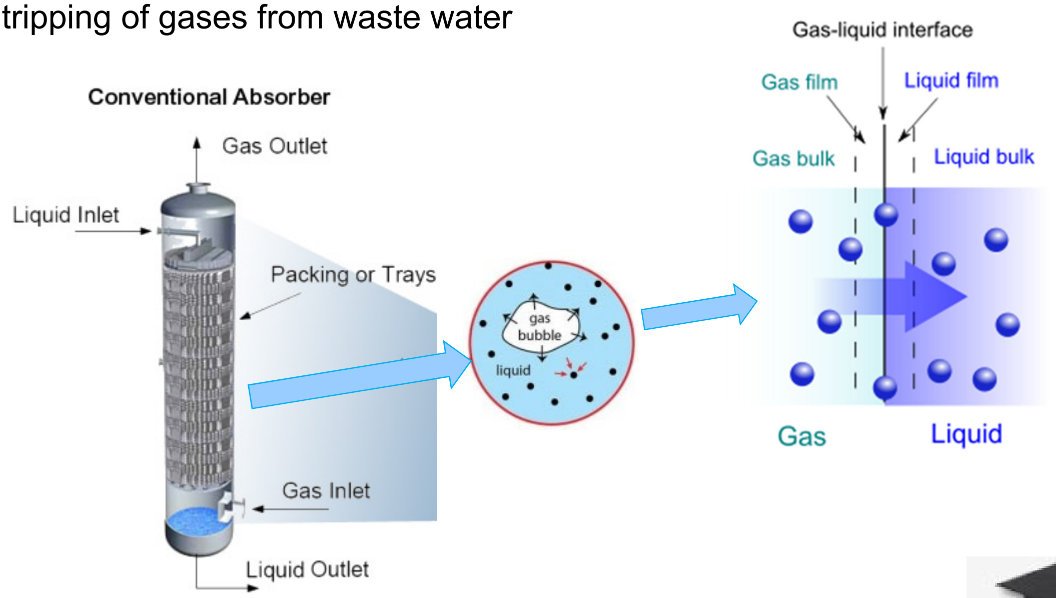
Examples of Mass Transfer Processes

- Removal of pollutants from plant discharge streams by absorption (for example, absorption of CO_2 by water)
- Stripping of gases from waste water

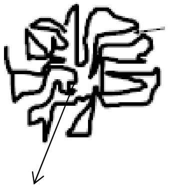


Examples of Mass Transfer Processes

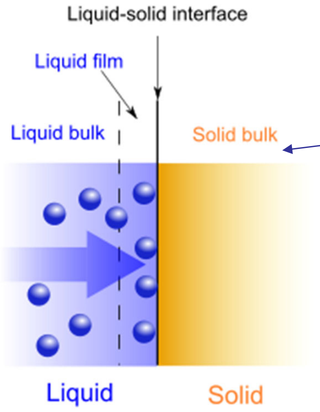
- Adsorption of liquid or gas to a solid surface

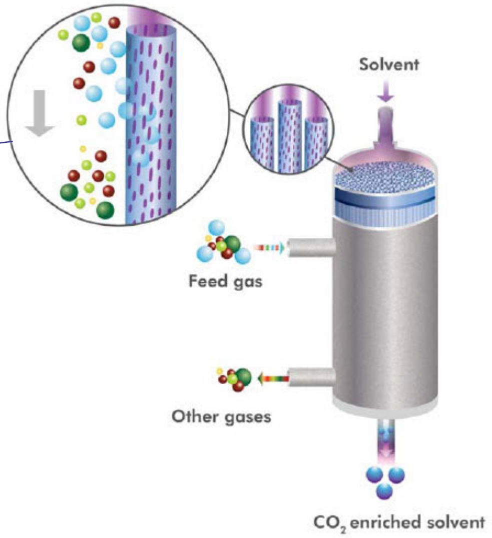
Reaction in porous catalyst

$C_2H_6 \rightarrow C_2H_4 + H_2$



Reactants or products diffuse in or out of porous catalysts pellet

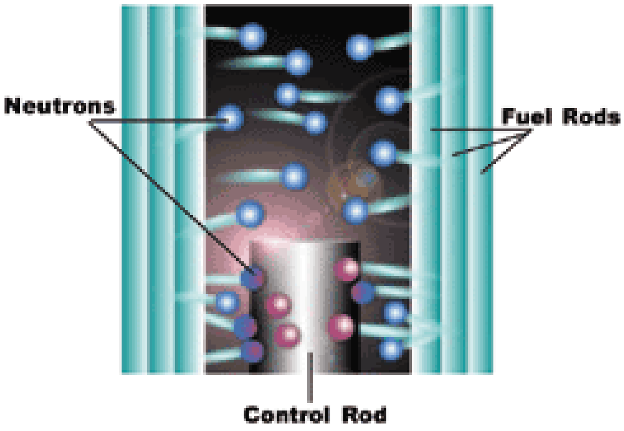




Examples of Mass Transfer Processes

- Neutron diffusion within nuclear reactors

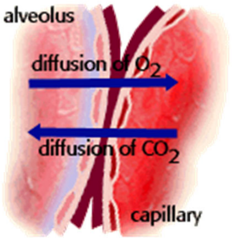
- Control rods are made of a material that absorbs excess neutrons (usually Boron or Cadmium).
- By controlling the number of neutrons, we can control the rate of fissions

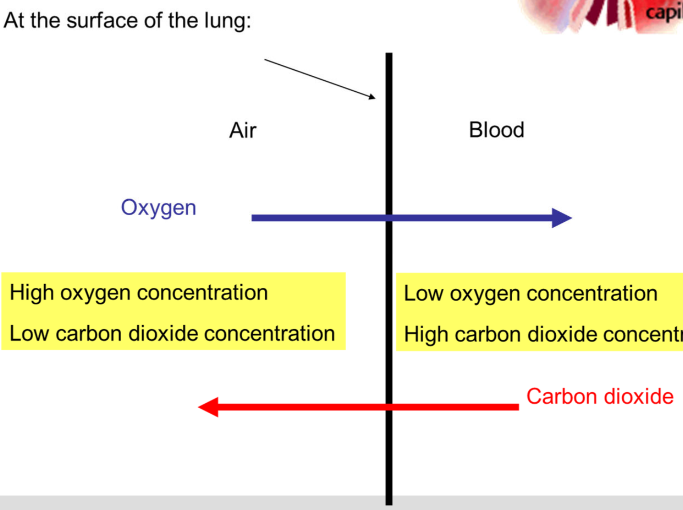


Examples of Mass Transfer Processes

Breathing

Inhaling of O_2 and exhale of CO_2 as gas exchange between lungs and blood capillaries




At the surface of the lung:

Air

Blood

Oxygen

High oxygen concentration

Low carbon dioxide concentration

Low oxygen concentration

High carbon dioxide concentration

Carbon dioxide

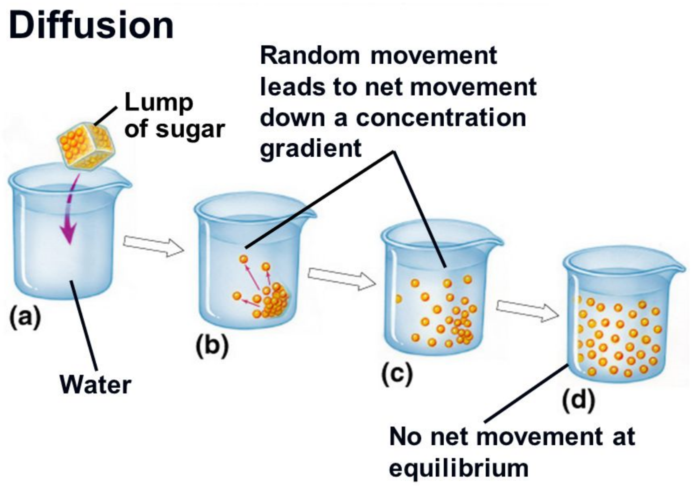
Why Mass Transfer is important?

- There are many reasons for wanting pure substances. Some of these reasons include:
  - Need for pure material in engineering application (semiconductors)
  - Preparation of raw materials into their components
  - Need for pure material for materials processing
  - Need to remove toxins or inactive components from solution (drugs)
  - Need for ultrapure samples for testing
  - Need for analysis of the components of the mixture (DNA testing)
  - Based on these motivations for separations, we can divide separations up into three main areas:

- Note: 50 to 90 percent of capital investment in chemical plant is for separations equipment.

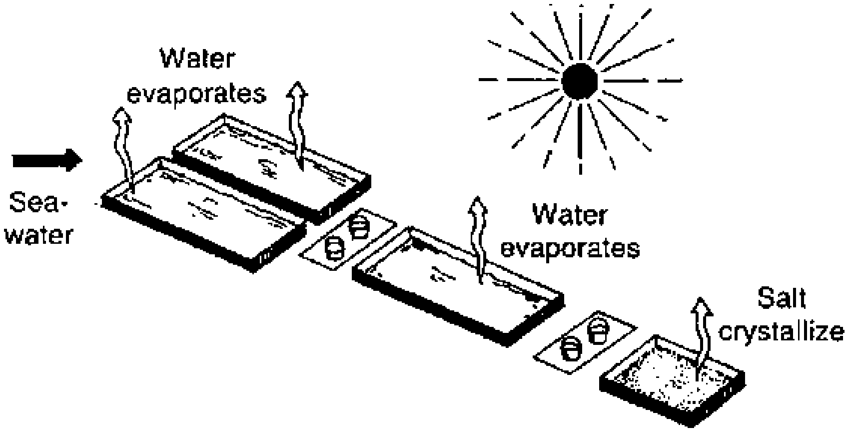
Examples of Mass Transfer Processes

- Many of day-by-day experiences also involve mass transfer, for example:
  - A lump of sugar added to a cup of coffee eventually dissolves and then eventually diffuses from high concentration region to low concentration region to make the concentration uniform.



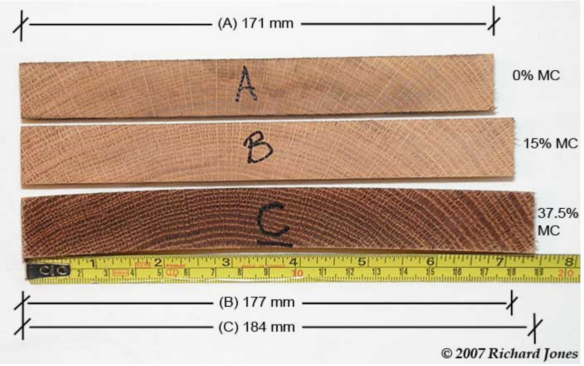
Examples of Mass Transfer Processes

- Water evaporates from ponds to increase the humidity of passing-air-stream or to separate a solid substance that has dissolved in water



Examples of Mass Transfer Processes

- When newly cut and moist green timber is exposed to the atmosphere, the wood will dry partially when water in the timber diffuses through the wood, to the surface, and then to the atmosphere.



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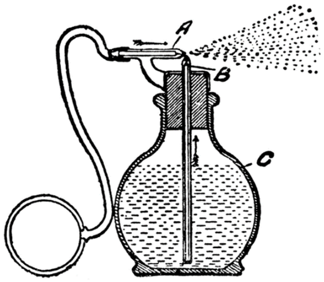
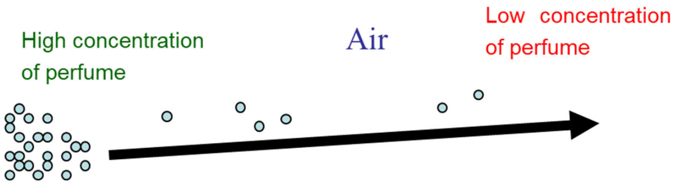
- The mass-transfer operations are characterized by transfer of a substance through another on a molecular scale.

Examples of Mass Transfer Processes

- Perfumes presents a pleasant fragrance which is imparted throughout the surrounding atmosphere.





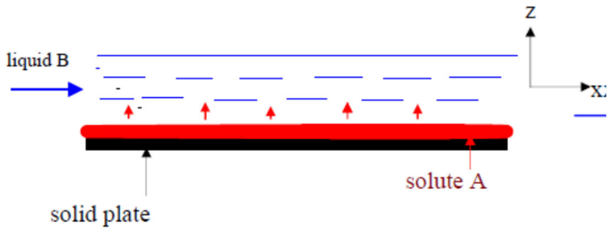
- The mass-transfer operations are characterized by transfer of a substance through another on a molecular scale.

Modes of Mass Transfer: Molecular Diffusion

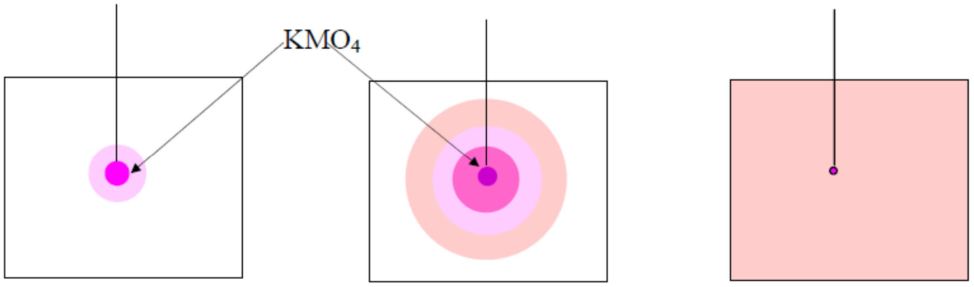
- Mass transfer could occur by the following three ways:

i. **Diffusion** is the net transport of substances **in a stationary solid or** in stagnant fluids or in fluids which are moving only in laminar flow, due to a **concentration gradient**

- It may also always present even in highly developed turbulent flow but near the solid surface .



Molecular Diffusion

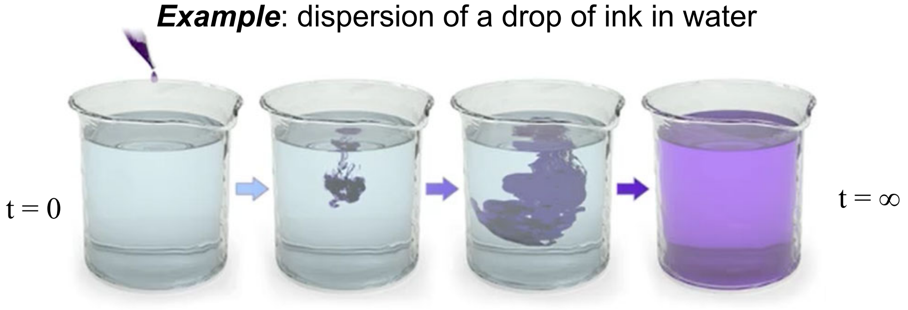


Dissolution of KMO$_4$ crystal and mass transfer by molecular diffusion

Molecular Diffusion

- ➢ If a drop of colored ink is placed in a bottle filled with water, the color will slowly spread through the bottle.

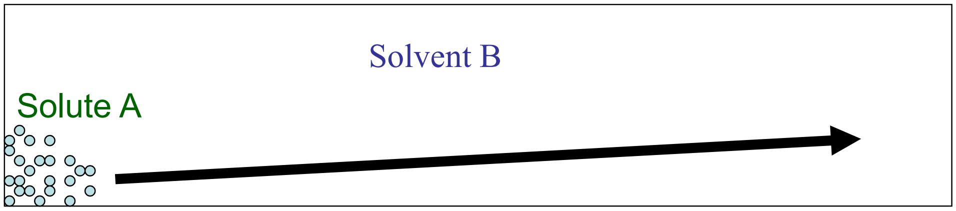
Example: dispersion of a drop of ink in water



- The process responsible for movement of colored ink is called **diffusion**.
- **Diffusion** is caused by random molecular motion that leads to complete mixing.
- **Diffusion** takes place in mixtures (≥ 2 components). Heat and momentum transfer need one-component phases.

Molecular Diffusion

- ➢ Molecular diffusion or molecular transport can be defined as the transfer or movement of individual molecules through a fluid by means of the random, individual movements of the molecules



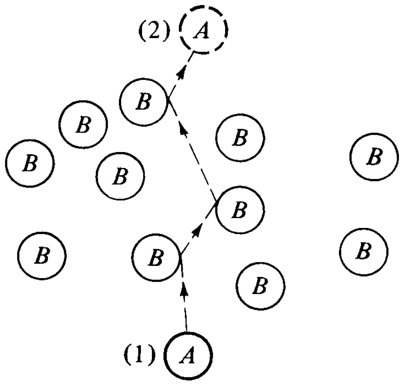
concentration of A is high

concentration of A is

Solute transport is from the left to the right;
movement of the solutes is due to the concentratior
gradient (dC/dx).

- ➢ The molecules travel in a random path, molecular diffusion is often called *a random-walk process.*

Molecular Diffusion

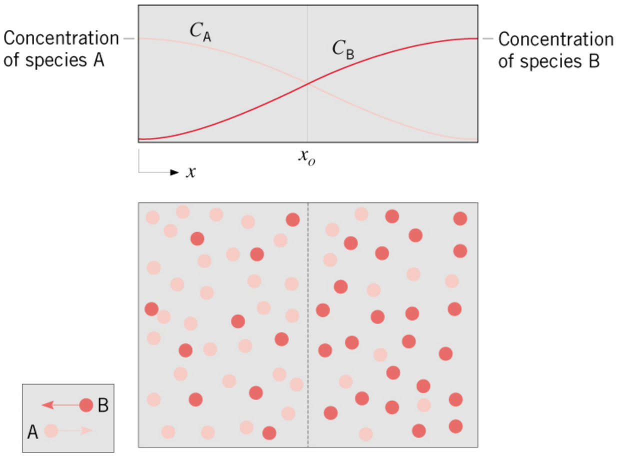


A random path that molecule *A* might take in diffusing through *B* molecules from point (1) to (2)

- If there are a greater number of *A* molecules near point (1) than at (2), then, since molecules diffuse randomly in both directions, more *A* molecules will diffuse from (1) to (2) than from (2) to (1).
- The net diffusion of *A* is from high- to low-concentration regions.

Molecular Diffusion

- Consider two species A and B at the same *T* and *p*, but initially separated by a partition.
  - Diffusion in the direction of decreasing concentration dictates net transport of A molecules to the right and B molecules to the left.
  - In time, uniform concentrations of A and B are achieved.



t = ∞

Molecular Diffusion Flux

- ***Fluxes*** The mass (or molar) flux of a given species is a vector quantity denoting the amount of the particular species, in either mass or molar units, that passes per given increment of time through a unit area normal to the vector.
- The flux may be defined with reference to coordinates that are fixed in space, coordinates that are moving with the mass average velocity, or coordinates that are moving with the molar-average velocity.
- The dimensions of molar flux are given below:

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

Fick's Law for Molecular Diffusion

- An <u>empirical relation</u> for this molar flux, first postulated by Fick (accordingly often referred to as Fick's first law), can be written as follows for an isothermal, isobaric **binary mixture of *A* and *B*** ***in stagnant media or laminar flow regimes***:

$$J^*_{AZ} = -c_T D_{AB} \frac{dx_A}{dz} \qquad \text{(1a)}$$

J^*_A is the **molar flux** of component A in the z direction relative to the molar-average velocity in kmol A/s.m^2 (fluxes of molecules)

D_{AB} is the molecular diffusivity of the molecule A in B in m^2/s

c_T is the total concentration in kmol (A +B) /m^3.

z is the distance of diffusion in m

x_A is mole fraction of A in the mixture of A and B

Fick's Law for Molecular Diffusion

- If a concentration gradient exists for the other component B of the mixture, similar equation for this component is written as:

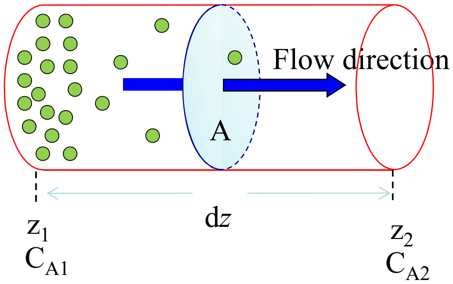
$$J^{*}_{BZ} = -c_T D_{BA} \frac{dx_B}{dz}$$

Rate of molecular diffusion, $\bar{J}_{Az}$ (k-molA/s) can be related to the diffusional flux, J_{Az} by :

$$J_{Az} = \frac{\bar{J}_{Az}}{A_m}$$

where, A_m (m^2) is the mass transfer area which is normal to the transfer direction.

Fick's Law for Molecular Diffusion

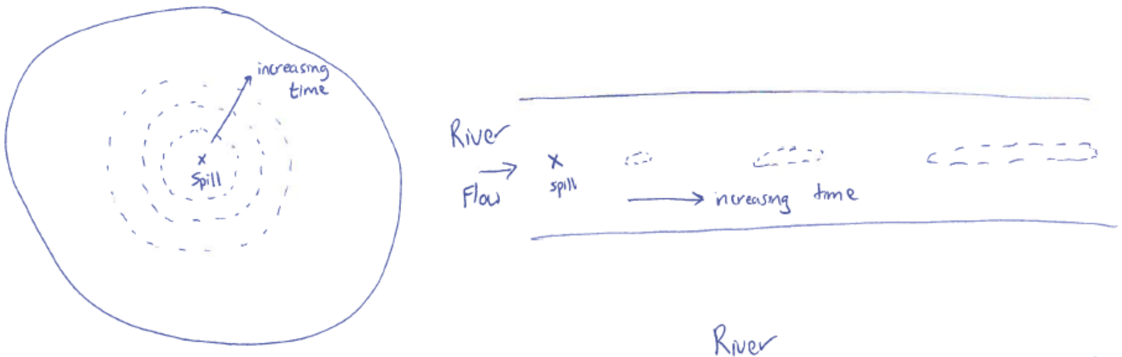


$$J_{A,z} = \frac{dn_A}{dt}\frac{1}{A} = -D_{AB}\frac{dc_A}{dz}$$

1. Mass transfer by ordinary molecular diffusion in a binary mixture occurs because of a concentration gradient; that is, a species diffuses in the direction of decreasing concentration.
2. The mass-transfer rate is proportional to the area normal to the direction of mass transfer. Thus, the rate can be expressed as a flux.
3. Net transfer stops when concentrations are uniform.

- Fick's law allows us to calculate ta flux due to diffusion (J_{Az}) but not the flux due to bulk flow (N_{Az})

Fick's Law for Molecular Diffusion



Stagnant Lake

- spill spreads by random molecular motion ⇒ DIFFUSION

River

- spill spreads by both macroscopic fluid motion and diffusion

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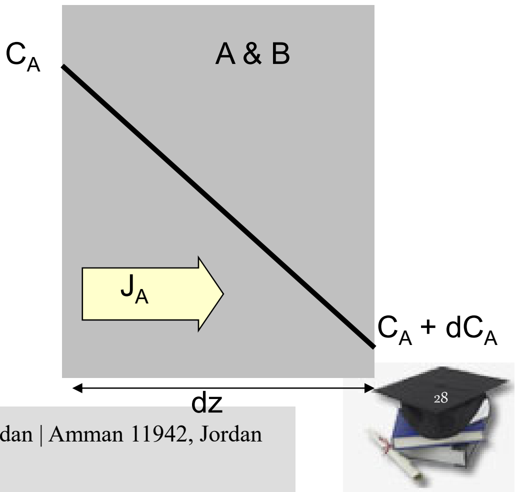
Fick's Law for Molecular Diffusion

- The negative sign emphasizes that **diffusion is in occurs in the direction of a drop in concentration.**
- The diffusivity is a characteristic of a constituent and its environment (temperature, pressure, concentration, whether in liquid, gas, or solid solution, and the nature of the other constituents).
  - For dissolved matter in water: $D \approx 10^{-5}$ cm^2/s
  - For gases in air at 1 atm and at room temperature: $D \approx 0.1$ to 0.01 cm^2/s

If c is constant, then since $c_A = cx_A$

$$c\,dx_A = d(cx_A) = dc_A$$

➡ $$J^*_{AZ} = -D_{AB}\frac{dc_A}{dz} \qquad (1b)$$



Example

A mixture of He and N_2 gas is contained in a pipe at 298 K and 1 atm total pressure which is constant throughout. At one end of the pipe at point 1 the partial pressure p_{A1} of He is 0.6 atm and at the other end 0.2 m $p_{A2} = 0.2$ atm. Calculate the flux of He at steady state if D_{AB} of the He-N_2 mixture is 0.687×10^{-4} m^2/s.

Example cont.

Example cont.

Molecular Diffusion in Gases

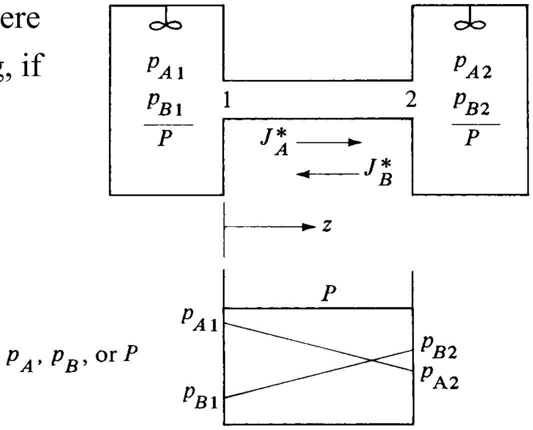
Equimolar Counter diffusion in Gases

- For two gases A and B at constant total pressure P in two large chambers connected by a tube where molecular diffusion at steady state is occurring, if

  $P_{A1} > P_{A2}$ and $P_{B2} > P_{B1}$

  - Molecules of A diffuse to the right and B to the left.
  - Since the total pressure P is constant throughout, the net moles of A diffusing to the right must equal the net moles of B to the left.

$$J^*_{AZ} = -J^*_{BZ}$$



Equimolar Counter diffusion in Gases

$$J^*_{BZ} = -D_{BA}\frac{dc_B}{dz}$$

Since $P = P_A + P_B = Cons.$ then $c = c_A + c_B = cons.$

Also, $dc = dc_A + dc_B = 0 \quad \Rightarrow \quad dc_A = -dc_B$

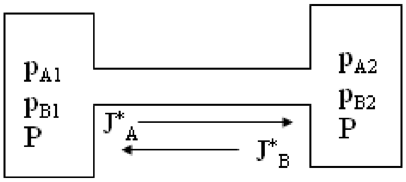
Hence, $J^*_{AZ} = -D_{AB}\frac{dc_A}{dz} = -J^*_{BZ} = -(-D_{BA}\frac{dc_B}{dz})$

$$\Rightarrow \quad D_{AB} = D_{BA}$$

Example

Ammonia gas *(A)* is diffusing through a uniform tube 0.10 m long containing N_2 gas *(B)* at 1.0132 x 10^5 Pa press and 298 K. At point 1, P_{A1} = 1.013x10^4 Pa and at point 2, P_{A2} = *0.507* x10^4 Pa. The diffusivity D_{AB} = 0.230x10^{-4} m²/s.

1. Calculate the J^*_{AZ} of A at steady state.
2. Repeated for J^*_{BZ}



Example cont.

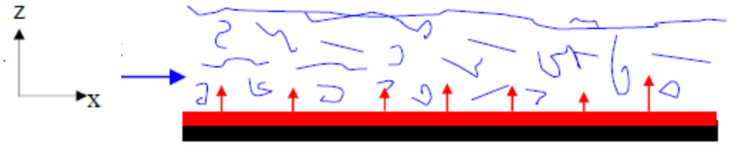
Modes of Mass Transfer: Convection

- At some cases, the mixture itself moves in the diffusion direction of the components, which is known as

ii. **Advection** is the net transport of substances by the **moving fluid**, and so cannot happen in solids. It does not include transport of substances by simple diffusion.

iii. **Convection** is the net transport of substances caused by both advective transport and diffusive transport in fluids.

  - Mass transfer takes place between a moving fluid and a surface or between immiscible moving fluids separated by a mobile interface, for example in a gas/liquid or liquid/liquid contactor),



Convection Mass Transfer

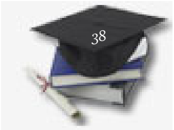
- The transfer always going from a higher to a lower concentration of the species being transferred.
- Convective transfer depends on both the transport properties and the dynamic characteristics of the moving fluid.
- The rate equation for convective mass transfer, generalized in a manner analogous to Newton's "law" of cooling, equation

$$\mathrm{N}_{\mathrm{AZ}} = k_C \Delta C_A$$

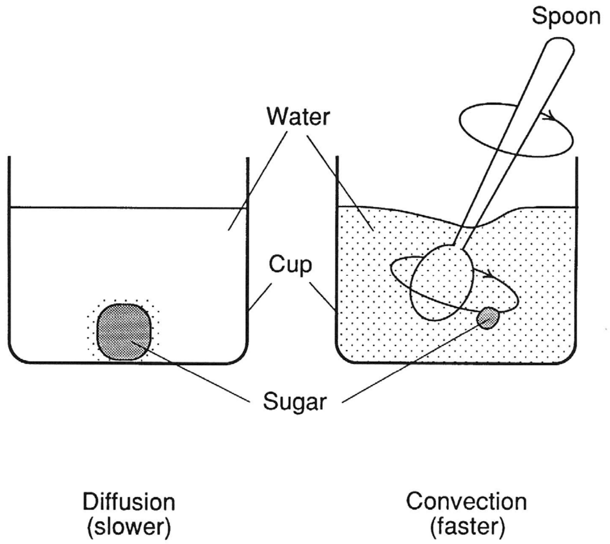
Where N_A is the molar mass transfer of species A measured relative to fixed spatial coordinates, Δc_A is the concentration difference between the boundary surface concentration and the average concentration of the fluid stream of the diffusing species A, and k_c is the convective mass-transfer coefficient, which has SI units of m/s.

Convection Mass Transfer

- For example, a drop of blue liquid dye or a sugar cube is added to a cup of water.
  - The dye (sugar) molecules will diffuse slowly by molecular diffusion to all parts of the water.
  - To increase this rate of mixing of the dye (sugar), the liquid can be mechanically agitated by a spoon and ***convective mass transfer*** will occur.
  - The blue color (or sugar) in time becomes everywhere uniform, and no subsequent change occurs.



Convection Mass Transfer



- Stirring the water with a spoon creates forced convection.
- That helps the sugar molecules to transfer to the bulk water much faster.

Summary

Molecular Diffusion	Convective Mass Transfer
▪ Caused by random microscopic movement of individual molecules in gas/liq/solid as a result of thermal motion. ▪ Extremely slow ▪ Occurs in solids and fluids that are stagnant or in laminar flow. ▪ Mass transfer under turbulent-flow but across an interface or near solid surface, the conditions near surface can be assumed laminar. ▪ Mathematically described by Fick's law: $J^*_{AZ} = -D_{AB}\frac{dc_A}{dz}$	▪ Caused by random macroscopic fluid bulk motion (dynamic characteristics). ▪ *Orders of magnitude* faster than molecular diffusion. ▪ Involves transport of materials at the interface between moving fluids (liq-gas) or at interface between a moving fluid and a solid surface (liq-solid, gas-solid). ▪ Mathematically described in a manner analogous to Newton's law : $\mathrm{N}_{\mathrm{AZ}} = k_C \Delta C_A$

The General Flux Equation

General Flux Equation

- In reality, when a concentration gradient exists for one component of a binary mixture in any direction, there must be a concentration difference for the other component of the mixture in the opposite direction.
- As a result of these concentration differences, both components of the mixture diffuse in the opposite directions.
- If the rates of these diffusions are not equal in molar units, then the mixture it self drifts in the direction of the component whose molar diffusional rate is greater.
- So, it is obvious that total molar flux of each component for a fixed observer will be different than the diffusional fluxes of the components.

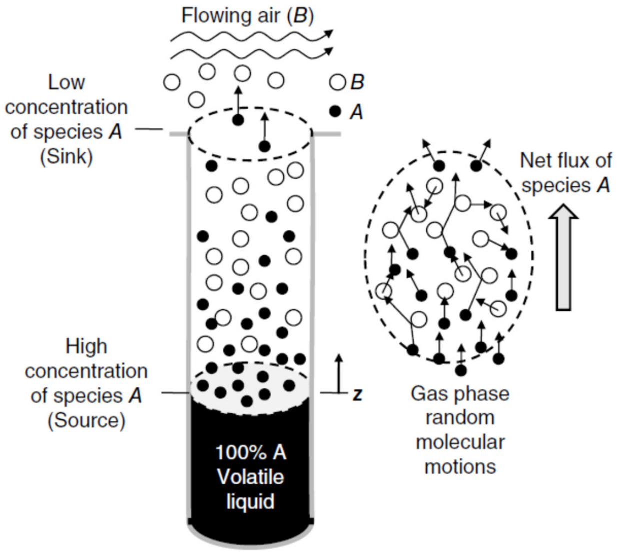
General Flux Equation

- Initial experimental investigations of molecular diffusion were unable to verify Fick’s law of diffusion.
- This was apparently because mass is often transferred simultaneously by two possible means:
  1. As a result of the concentration differences as postulated by Fick, and
  2. By convection differences induced by the density differences that resulted from the concentration variation.
- Stefan (1872) and Maxwell (1877), using the kinetic theory of gases, proved that the mass flux relative to a fixed coordinate was a result of two contributions: the concentration gradient contribution and the bulk motion contribution;

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

General Flux Equation

- The mechanism of mass transfer usually involves both molecular diffusion and convection, i.e. both mechanisms may act simultaneously
- The two modes of heat transfer, conduction and convective heat transfer, are analogous to molecular diffusion and convective mass transfer.



Arnold diffusion cell (to analyze mass-transfer processes)

General Flux Equation

Velocities

- The molar diffusive flux of A in B (binary mixture) is given by:

$$J^*_{AZ} = -D_{AB}\frac{dc_A}{dz} \qquad (1b)$$

- Then, the velocity of the diffusive flux of A in B (diffusion velocity of A) can be given by

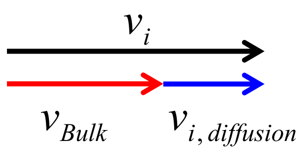
$$v_{A,diffusion}(m/s) = \frac{J^*_A(mol/m^2.s)}{c_A(mol/m^3)} \qquad (2)$$

- In a multicomponent system, the various species will normally move at different velocities.
- Accordingly, an evaluation of a velocity for the gas mixture requires the averaging of the velocities of each species present.

General Flux Equation

- The molar-average velocity (bulk velocity relative to stationary coordinates) for a multicomponent mixture is defined in terms of the molar concentrations of all components by

$$v_{bulk} = \frac{\sum_{i=1}^{n} c_i v_i}{\sum_{i=1}^{n} c_i} = \frac{\sum_{i=1}^{n} c_i v_i}{c}$$



Where v_i is the velocities of each type of molecules in the specified direction,

- The velocity of a particular species relative to the molar-average velocity is termed a *diffusion velocity*

$$v_{i,\,diffusion} = v_i - v_{Bulk} \qquad (3)$$

General Flux Equation

- For binary mixture of A and B;

$$v_{Bulk}\,(m/s) = \frac{(c_A v_A + c_B v_B)(mol/m^2.s)}{c_T\,(mol/m^3)} \qquad (4a)$$

Where c_T is the total concentration

- Also, the total molar flux of components A and B relative to the fixed coordinates are

$$N_A = c_A v_A \quad \text{and} \quad N_B = c_B v_B \qquad (5)$$

$$\Longrightarrow \quad v_{Bulk}\,(m/s) = \frac{(N_A + N_B)(mol/m^2.s)}{c_T\,(mol/m^3)} \qquad (4b)$$

General Flux Equation

Where $N_i\,(mol/m^2.s)$ denotes to the total molar flux of species *i* by **convection** (which is diffusion plus advection) with respect to a stationary observer

$$N_i\,(mol/m^2.s) = \frac{\overline{N_i}\,(mol/s)}{A(m^2)} \qquad (6)$$

- Hence, the velocity of the net flux of A in B (relative to stationary coordinates) can be given by

$$v_A\,(m/s) = \frac{N_A\,(mol/m^2.s)}{c_A\,(mol/m^3)} \qquad (5b)$$

General Flux Equation

- Hence, for species A,

$$v_A = v_{A,\,diffusion} + v_{Bulk} \qquad (3)$$

- Multiplying the above by C_A, we get

$$c_A v_A = \underbrace{c_A v_{A,diffusion}}_{\text{Molecular Diffusion}} + \underbrace{c_A v_{Bulk}}_{\text{Bulk Flow Flux}} \qquad (6)$$

→ $$N_A = J_A^* + c_A \frac{(N_A + N_B)}{c_T}$$

General Flux Equation

(7a)

General Flux Equation

Substituting J_A^* from (1b), we get

$$N_A = \underbrace{-D_{AB}\frac{dc_A}{dz}}_{\text{Molecular Diffusion of A}} + \underbrace{\frac{c_A}{c_T}(N_A + N_B)}_{\text{Bulk Flow Flux of A}} \qquad (7b)$$

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

- If the concentration of A is too small (the mixture is dilute in A), then the bulk flow term can be ignored, thus

$$N_A = J_A^* = -D_{AB}\frac{dc_A}{dz}$$

General Flux Equation

Let us introduce partial pressure p_A into as follows:

$$c_A = \frac{n_A}{V} = \frac{p_A}{RT}$$

$$c_T = \frac{n_T}{V} = \frac{P}{RT}$$

Total pressure

Total number of moles

Hence,

$$N_A = -\frac{D_{AB}}{RT}\frac{dp_A}{dz} + \frac{p_A}{P}(N_A + N_B) \qquad \text{(7c)}$$

General Flux Equation

since $$x_A = \frac{p_A}{P} = \frac{N_A}{N_A + N_B} = \frac{c_A}{c_T}$$

➡ $$N_A = -c_T D_{AB}\frac{dx_A}{dz} + x_A(N_A + N_B) \qquad \text{(7d)}$$

- Similarly for species B:

➡ $$N_B = -c_T D_{AB}\frac{dx_B}{dz} + x_B(N_A + N_B) \qquad \text{(7e)}$$

$$N_B = -D_{AB}\frac{dc_B}{dz} + \frac{c_B}{c_T}(N_A + N_B)$$

Molecular Diffusion of B

Bulk Flow Flux of B

Diffusivity

$$D_{AB} = \frac{-J_{A,z}}{dc_A/dz} = \left(\frac{M}{L^2 t}\right)\left(\frac{1}{M/L^3 1/L}\right) = \frac{L^2}{t}$$

Diffusivity

- Fick's law proportionality, D_{AB}, is known as mass diffusivity (simply as diffusivity) or as the diffusion coefficient.
- D_{AB} has the dimension of L^2/t, identical to the fundamental dimensions of the other transport properties: Kinematic viscosity, $\nu = (\mu/\rho)$ in momentum transfer, and thermal diffusivity, α ($= k/\rho C_\rho$) in heat transfer.
- Diffusivity is normally reported in cm^2/sec; the SI unit being m^2/sec.
- Diffusivity depends on pressure, temperature, and composition of the system.
- General range of values of diffusivity:

Gases :	5×10^{-6}	-------------	1×10^{-5}	m^2 / sec.
Liquids :	10^{-6}	-------------	10^{-9}	m^2 / sec.
Solids :	5×10^{-14}	-------------	1×10^{-10}	m^2 / sec.

Diffusivity

- Diffusivities of gases at low density are almost composition independent, increase with the temperature and vary inversely with pressure.
- Liquid and solid diffusivities are strongly concentration dependent and increase with temperature
- In the absence of experimental data, semi-theoretical expressions have been developed (the empirical equations) which give approximation, sometimes as valid as experimental values, due to the difficulties encountered in experimental measurements

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Diffusivity in Gases

- Pressure dependence of diffusivity is given by

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

(for moderate ranges of pressures, up to 25 atm).

- And temperature dependency is according to

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

- The diffusion coefficient at any temperature and at any pressure below 25 atm can be predicted from a known experimental value by the Hirschfelder extrapolation, given by

$$D_{AB}(T_2, P_2) = D_{AB}(T_1, P_1)\left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right)^{3/2} \tag{8}$$

Diffusivity in Gases

- Diffusivity of a component in a mixture of components can be calculated using the diffusivities for the various binary pairs involved in the mixture. The relation given by Wilke is

$$D_{1-mixture} = \frac{1}{\frac{x'_2}{D_{1-2}} + \frac{x'_3}{D_{1-3}} + ... + \frac{x'_n}{D_{1-n}}}$$

Where

$D_{1\text{-mixture}}$ is the diffusivity for component 1 in the gas mixture;

$D_{1\text{-n}}$ is the diffusivity for the binary pair, component 1 diffusing through component n; and

x'_n is the mole fraction of component n in the gas mixture evaluated on a component –1 – free basis, that is

$$x'_n = \frac{x_2}{x_2 + x_3 + ...x_n} \qquad (9)$$

Diffusivity in Gases

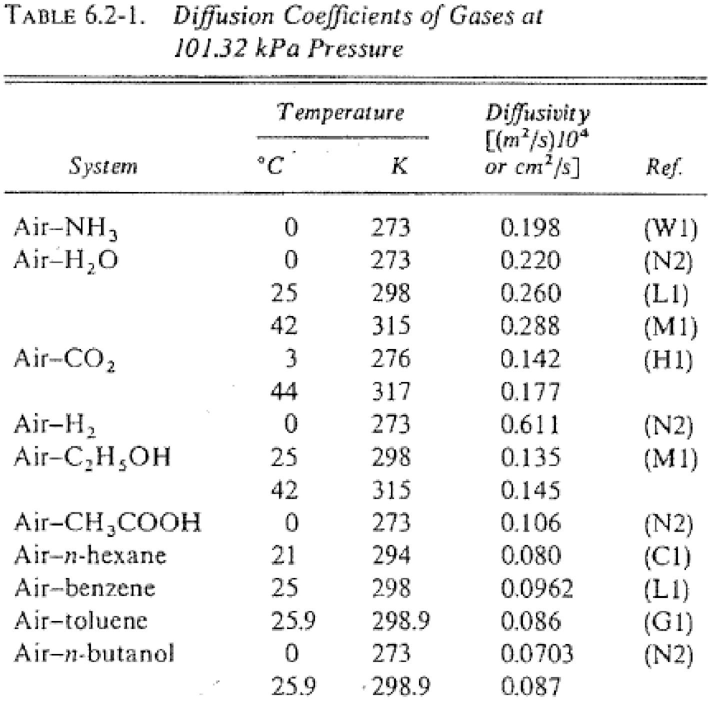
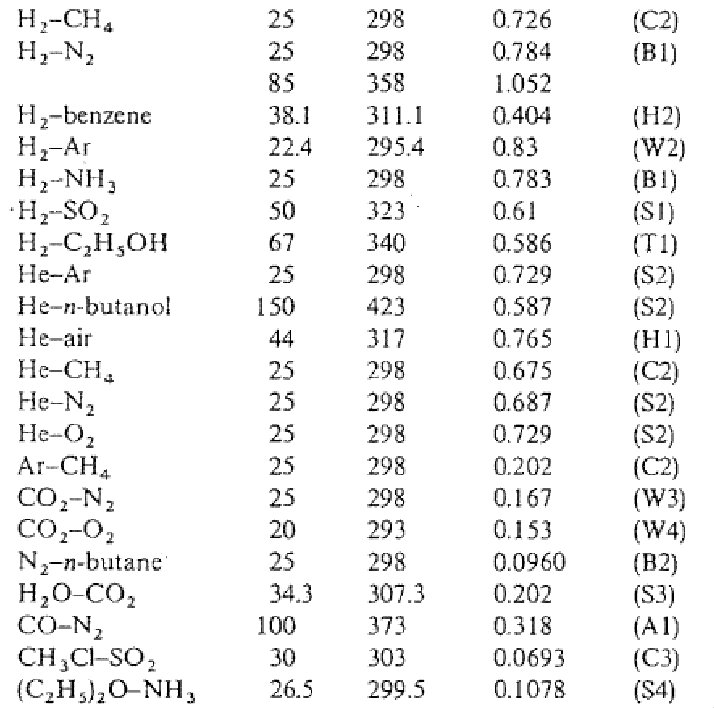


TABLE 6.2-1. *Diffusion Coefficients of Gases at 101.32 kPa Pressure*

System	*Temperature* °C	K	*Diffusivity* [$(m^2/s)10^4$ or cm^2/s]	*Ref.*
Air–NH_3	0	273	0.198	(W1)
Air–H_2O	0	273	0.220	(N2)
	25	298	0.260	(L1)
	42	315	0.288	(M1)
Air–CO_2	3	276	0.142	(H1)
	44	317	0.177	
Air–H_2	0	273	0.611	(N2)
Air–C_2H_5OH	25	298	0.135	(M1)
	42	315	0.145	
Air–CH_3COOH	0	273	0.106	(N2)
Air–*n*-hexane	21	294	0.080	(C1)
Air–benzene	25	298	0.0962	(L1)
Air–toluene	25.9	298.9	0.086	(G1)
Air–*n*-butanol	0	273	0.0703	(N2)
	25.9	298.9	0.087	

Diffusivity in Gases



H_2–CH_4	25	298	0.726	(C2)
H_2–N_2	25	298	0.784	(B1)
	85	358	1.052	
H_2–benzene	38.1	311.1	0.404	(H2)
H_2–Ar	22.4	295.4	0.83	(W2)
H_2–NH_3	25	298	0.783	(B1)
H_2–SO_2	50	323	0.61	(S1)
H_2–C_2H_5OH	67	340	0.586	(T1)
He–Ar	25	298	0.729	(S2)
He–*n*-butanol	150	423	0.587	(S2)
He–air	44	317	0.765	(H1)
He–CH_4	25	298	0.675	(C2)
He–N_2	25	298	0.687	(S2)
He–O_2	25	298	0.729	(S2)
Ar–CH_4	25	298	0.202	(C2)
CO_2–N_2	25	298	0.167	(W3)
CO_2–O_2	20	293	0.153	(W4)
N_2–*n*-butane	25	298	0.0960	(B2)
H_2O–CO_2	34.3	307.3	0.202	(S3)
CO–N_2	100	373	0.318	(A1)
CH_3Cl–SO_2	30	303	0.0693	(C3)
$(C_2H_5)_2O$–NH_3	26.5	299.5	0.1078	(S4)

Binary Gas Diffusivity

- To predict the diffusivity of a binary gas pair of *A* and *B* molecules

$$D_{AB} = \frac{10^{-3} T^{1.75} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}}}{P \left[\left(\sum V_A \right)^{\frac{1}{3}} + \left(\sum V_B \right)^{\frac{1}{3}} \right]^2} \qquad (10)$$

D_{AB} - diffusivity in cm^2/s
P - absolute pressure in atm
M_i - molecular weight
T - temperature in K
V_i - sum of the diffusion volume for component i

D_{AB} is proportional to 1/P and $T^{1.75}$

Binary Gas Diffusivity

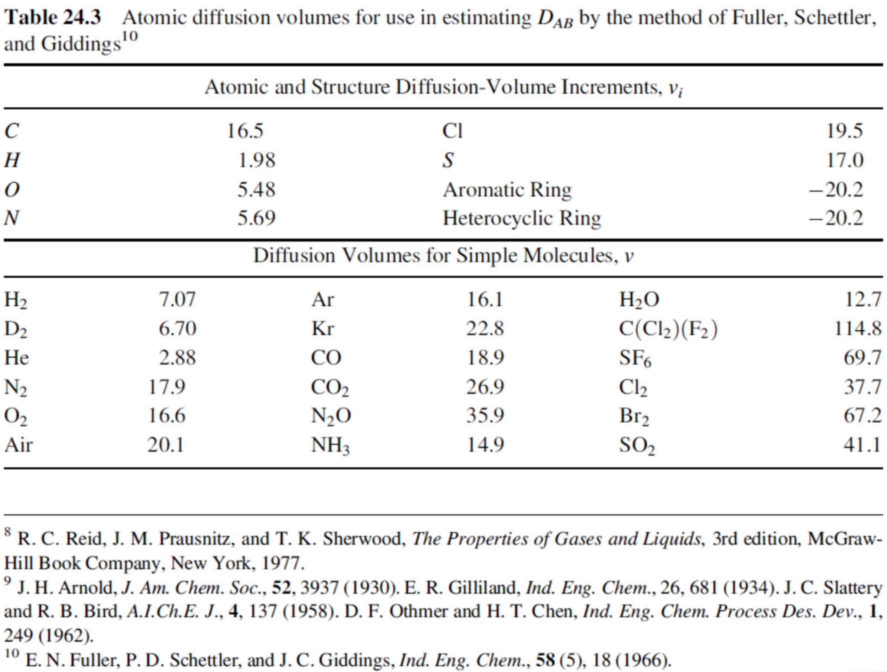


Table 24.3 Atomic diffusion volumes for use in estimating D_{AB} by the method of Fuller, Schettler, and Giddings[10]

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

Diffusion Volumes for Simple Molecules, v					
H_2	7.07	Ar	16.1	H_2O	12.7
D_2	6.70	Kr	22.8	$C(Cl_2)(F_2)$	114.8
He	2.88	CO	18.9	SF_6	69.7
N_2	17.9	CO_2	26.9	Cl_2	37.7
O_2	16.6	N_2O	35.9	Br_2	67.2
Air	20.1	NH_3	14.9	SO_2	41.1

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[8] R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, 3rd edition, McGraw-Hill Book Company, New York, 1977.

[9] J. H. Arnold, *J. Am. Chem. Soc.*, **52**, 3937 (1930). E. R. Gilliland, *Ind. Eng. Chem.*, 26, 681 (1934). J. C. Slattery and R. B. Bird, *A.I.Ch.E. J.*, **4**, 137 (1958). D. F. Othmer and H. T. Chen, *Ind. Eng. Chem. Process Des. Dev.*, **1**, 249 (1962).

[10] E. N. Fuller, P. D. Schettler, and J. C. Giddings, *Ind. Eng. Chem.*, **58** (5), 18 (1966).

Example

Normal butanol (*A*) is diffusing through air (*B*) at 1 atm abs. Using the Fuller et al. method, estimate the diffusivity D_{AB} for the following temperatures with the experimental data:

(a) For 0 °C.

(b) For 25.9 °C.

(c) For 0 °C and 2.0 atm abs.

Example cont.

Diffusivity in liquids

- Diffusivity in liquid are about ten thousand times shower than those in dilute gases.
- Most of these values are nearer to 10^{-5} cm^2/sec (10^{-9} m^2/sec)
- This characteristic of liquid diffusion often limits the overall rate of processes accruing in liquids (such as reaction between two components in liquids).
- In chemistry, diffusivity limits the rate of acid-base reactions; in the chemical industry, diffusion is responsible for the rates of liquid-liquid extraction.
- Diffusion in liquids is important because it is slow.
- Certain molecules diffuse as molecules, while others which are designated as electrolytes ionize in solutions and diffuse as ions.
- For example, sodium chloride (NaCl), diffuses in water as ions Na^+ and Cl^-.

Diffusivity in liquids

- Though each ions has a different mobility, the electrical neutrality of the solution indicates the ions must diffuse at the same rate; accordingly it is possible to speak of a diffusion coefficient for molecular electrolytes such as NaCl.
- However, if several ions are present, the diffusion rates of the individual cations and anions must be considered, and molecular diffusion coefficients have no meaning.
- Diffusivity varies inversely with viscosity when the ratio of solute to solvent ratio exceeds five.
- In extremely high viscosity materials, diffusion becomes independent of viscosity.

Diffusivity in liquids

- For very large spherical dilute solute molecules (A) of 1000 molecular weight or greater diffusing in a liquid solvent (B) of small molecules:

$$D_{AB} = \frac{9.96 \times 10^{-12}\, T}{\mu\, V_A^{1/3}} \qquad (11)$$

applicable for biological solutes such as proteins

D_{AB} - diffusivity in cm^2/s
T - temperature in K
μ - viscosity of solution in kg/m s
V_A - solute molar volume at its normal boiling point in m^3/kmol

D_{AB} is proportional to 1/μ and T →

$$\left(\frac{D_{AB}\,\mu}{T}\right)_{T2} = \left(\frac{D_{AB}\,\mu}{T}\right)_{T1} \qquad (12)$$

Diffusivity in liquids

- For smaller molecules (A) diffusing in a dilute liquid solution of solvent (B):

$$D_{AB} = \frac{7.4 \times 10^{-8} (\Phi M_B)^{1/2} T}{\mu_B V_A^{0.6}} \qquad (13)$$

applicable for biological solutes

D_{AB} - diffusivity in cm^2/s

M_B - molecular weight of solvent B

T - temperature in K

μ - viscosity of solvent B in cp

V_A - solute molar volume at its normal boiling point in cm^3/mol (table 24.5)

Φ - association parameter of the solvent, which 2.6 for water, 1.9 for methanol, 1.5 for ethanol, and 1.0 for nonpolar solvents

D_{AB} is proportional to $1/\mu_B$ and T

Diffusivity in liquids

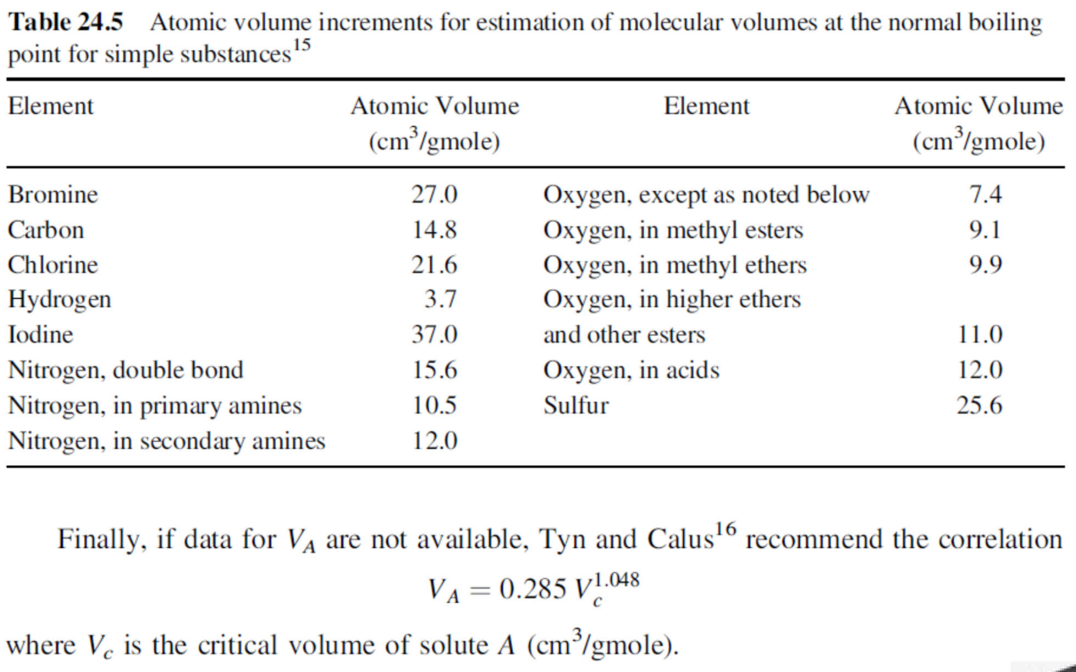


Table 24.5 Atomic volume increments for estimation of molecular volumes at the normal boiling point for simple substances[15]

Element	Atomic Volume (cm^3/gmole)	Element	Atomic Volume (cm^3/gmole)
Bromine	27.0	Oxygen, except as noted below	7.4
Carbon	14.8	Oxygen, in methyl esters	9.1
Chlorine	21.6	Oxygen, in methyl ethers	9.9
Hydrogen	3.7	Oxygen, in higher ethers and other esters	11.0
Iodine	37.0	Oxygen, in acids	12.0
Nitrogen, double bond	15.6	Sulfur	25.6
Nitrogen, in primary amines	10.5		
Nitrogen, in secondary amines	12.0		

Finally, if data for V_A are not available, Tyn and Calus[16] recommend the correlation

$$V_A = 0.285\, V_c^{1.048}$$

where V_c is the critical volume of solute A (cm^3/gmole).

Diffusivity of Electrolytes in Liquids

- For smaller molecules (A) diffusing in a dilute liquid solution of solvent (B):

$$D^{o}_{AB} = \frac{8.928 \times 10^{-10}\, T\, (1/n_{+} + 1/n_{-})}{(1/\lambda_{+} + 1/\lambda_{-})} \qquad (14)$$

D^{o}_{AB} is diffusivity in cm^2/s

n_{+} is the valence of cation

n_{-} is the valence of anion

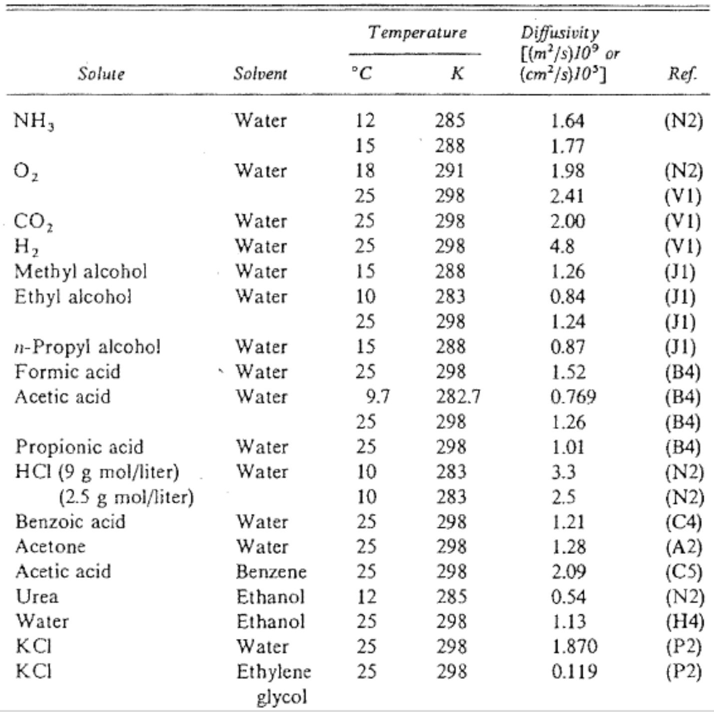
λ_{+} and λ_{-} are the limiting ionic conductance in very dilute solutions

T is 298.2 when using the above at 25°C

D_{AB} is proportional to T

Diffusion Coefficients for Dilute Liquid Solutions

TABLE 6.3-1.



Solute	Solvent	Temperature °C	Temperature K	Diffusivity [$(m^2/s)10^9$ or $(cm^2/s)10^5$]	Ref.
NH_3	Water	12	285	1.64	(N2)
		15	288	1.77	
O_2	Water	18	291	1.98	(N2)
		25	298	2.41	(V1)
CO_2	Water	25	298	2.00	(V1)
H_2	Water	25	298	4.8	(V1)
Methyl alcohol	Water	15	288	1.26	(J1)
Ethyl alcohol	Water	10	283	0.84	(J1)
		25	298	1.24	(J1)
n-Propyl alcohol	Water	15	288	0.87	(J1)
Formic acid	Water	25	298	1.52	(B4)
Acetic acid	Water	9.7	282.7	0.769	(B4)
		25	298	1.26	(B4)
Propionic acid	Water	25	298	1.01	(B4)
HCl (9 g mol/liter)	Water	10	283	3.3	(N2)
(2.5 g mol/liter)		10	283	2.5	(N2)
Benzoic acid	Water	25	298	1.21	(C4)
Acetone	Water	25	298	1.28	(A2)
Acetic acid	Benzene	25	298	2.09	(C5)
Urea	Ethanol	12	285	0.54	(N2)
Water	Ethanol	25	298	1.13	(H4)
KCl	Water	25	298	1.870	(P2)
KCl	Ethylene glycol	25	298	0.119	(P2)

Diffusivity in Solids

- Typical values for diffusivity in solids are ranged between $5x10^{-14}$ and $1x10^{-10}$.
- One outstanding characteristic of these values is their small size, usually thousands of time less than those in a liquid, which are in turn 10,000 times less than those in a gas.
- Diffusion plays a major role in catalysis and is important to the chemical engineer. For metallurgists, diffusion of atoms within the solids is of more importance.
- Examples:
  - Leaching of metal ores
  - Drying of timber, and foods
  - Diffusion and catalytic reaction in solid catalysts
  - Separation of fluids by membranes
  - Treatment of metal at high temperature by gases.