Module-V

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Diffusion

- Diffusion is the process by which molecules, ions, or other small particles spontaneously mix, moving from regions of relatively high concentration into regions of lower concentration.
- This process can be analyzed in two ways.
- First, it can be described with Fick's law and
- a diffusion coefficient,

First law of diffusion (Steady state Law)

- Adolf Fick (1955) first described the molecular diffusion in an isothermal, isobaric binary system of components A and B. According to his idea of molecular diffusion, the molar flux of a species relative to an observer moving with molar average velocity is proportional to the concentration gradient in a certain direction.

$$J_A \propto \frac{dC_A}{dZ}$$

Or

$$J_A = -D_{AB} \frac{dC_A}{dZ}$$

- Where, J_A is the molar flux of component A in the Z direction.
- C_A is the concentration of A and Z is the distance of diffusion.
- The proportionality constant, D_{AB} is the diffusion coefficient of the molecule A in B.
- This is valid only at steady state condition of diffusion

$$\frac{\partial C_A}{\partial t} = D_{AB}\frac{\partial^2 C_A}{\partial Z^2}$$

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Both the diffusive and non-diffusive constituents affect the rate of unsteady state diffusion. The diffusivity at unsteady state condition can be expressed in terms of activation energy and the temperature as

$$D_{AB} = D_0 \exp\left(-\frac{E_D}{RT}\right)$$

- The activation energy (E_D) for the diffusion decreases the rate of diffusion whereas temperature increases the diffusion rate

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- Steady state diffusion through a stagnant gas film Assume steady state diffusion in the Z direction without any chemical reaction in a binary gaseous mixture of species A and B. For one dimensional diffusion of species A, the Equation of molar flux can be written as

$$N_A = -CD_{AB}\frac{dy_A}{dZ} + y_A(N_A + N_B)$$

$$\frac{-dy_A}{N_A - y_A(N_A + N_B)} = \frac{dZ}{CD_{AB}}$$

Mass transfer coefficient

- mass transfer refers to mass in transit due to a species concentration gradient in a mixture, and mass convection is one of the mechanisms for this transit.
- Mass transfer by convection involves the transport of material between a boundary surface (such as solid or liquid surface) and a moving fluid or between two relatively immiscible, moving fluids.
- Convective mass transfer is really *diffusion* (the random movement of molecules) in combination with *advection* (molecules being carried along with the motion of the fluid).

Convective Mass Transfer Definition of convective mass transfer: The transport of material between a boundary surface and a moving fluid or between two immiscible moving fluids separated by a mobile interface Convection is divided into two types:

1. Forced convection
2. 2. Natural convection Compare between forced and natural convection mass transfer?

- Forced convection: In this type the fluid moves under the influence of an external force (pressure difference) as in the case of transfer of liquids by pumps and gases by compressors.
- Natural convection: Natural convection currents develop if there is any variation in density within the fluid phase.
- The density variation may be due to temperature differences or to relatively large concentration differences.

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- The rate equation:
- The rate equation for convective mass transfer (either forced or natural) is: $N_A = k_c \Delta c_A$
- N_A is the molar-mass flux of species A, measured relative to fixed spatial coordinates
- kc is the convective mass-transfer coefficient
- Δc_A is the concentration difference between the boundary surface concentration and the average concentration of the diffusing species in the moving fluid stream

What is the mass transfer coefficient $\boldsymbol{kc}$?

- From the rate equation (NA = $kc\Delta cA$) the mass transfer coefficient is the rate of mass transfer per unit area per unit driving force.
- It gives an indication to how fast is the mass transfer by convection.

What are the factors affecting $\boldsymbol{kc}$?

- The mass-transfer coefficient is related to:
- (1).The properties of the fluid,
- (2).The dynamic characteristics of the flowing fluid, and
- (3).The geometry of the specific system of interest

Evaluation of the mass transfer coefficient

- There are four methods of evaluating convective mass-transfer coefficients.
- They are: (1). dimensional analysis coupled with experiment
- (2). analogy between momentum, energy, and mass transfer
- (3). exact laminar boundary-layer analysis
- (4). approximate boundary-layer analysis

Significant parameters in convective mass transfer

A. Forced convection

Dimensionless parameters are often used to correlate convective transfer data. In momentum transfer Reynolds number and friction factor play a major role. In the correlation of convective heat transfer data, Prandtl (Pr) and Nusselt (Nu) numbers are important. Some of the same parameters, along with some newly defined dimensionless numbers, will be useful in the correlation of convective mass-transfer data.

The molecular diffusivities of the three transport process (momentum, heat and mass) have been defined as:

Momentum diffusivity	$\nu = \frac{\mu}{\rho}$
Thermal diffusivity	$\alpha = \frac{k}{\rho c_p}$
Mass diffusivity	D_{AB}

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- It can be shown that each of the diffusivities has the dimensions of (L 2 T) hence; a ratio of any of the two of these must be dimensionless. ?
- The ratio of the momentum diffusivity to the thermal diffusivity is designated as the
- Prandtl Number Pr = $Momentum\ diffusivity$ /$Thermal\ diffusivity$ = ν/ α = μcp /k
- The analogous number in mass transfer is Schmidt number given as which represents the ratio of the momentum diffusivity to mass diffusivity.

- $Sc = Momentum\ diffusivity / Mass\ diffusivity = \nu / D_{AB} = \mu / \rho D_{AB}$
- The ratio of the diffusivity of heat to the diffusivity of mass is designated the Lewis number,
- and is given by $Le = Thermal\ diffusivity / Mass\ diffusivity = \alpha / D_{AB} = k / \rho c_p D_{AB}$
- Note: Lewis number is encountered in processes involving simultaneous convective transfer of mass and energy

- The ratio of molecular mass transport resistance to the convective mass transport resistance of the fluid. This ratio is generally known as the Sherwood number, Sh and analogous to the Nusselt number Nu, in heat transfer.
- $Sh = molecular\ mass\ transport\ resistance / \ convective\ mass\ transport\ resistance = kcL/\ D_{AB}$
- Note: L is the characteristic length (it depends on the geometry)

Mass, heat and momentum transfer analogy

- Analogies among mass, heat and momentum transfer have their origin either in the mathematical description of the effects or in the physical parameters used for quantitative description.
- To explore those analogies, it could be understood that the diffusion of mass and conduction of heat obey very similar equations.

- In particular, diffusion in one dimension is described by the Fick's Law as $J_A = -D_{AB}(dcA\ /dz\ )$
- Similarly, heat conduction is described by
- Fourier's law as $q = -k\ dT\ /dz$
- where k is the thermal conductivity.
- The similar equation describing momentum transfer as given by Newton's law is $\tau = -\mu\ du\ /dz$
- where τ is the momentum flux (or shear stress) and μ is the viscosity of fluid. At this point it has become conventional to draw an analogy among mass, heat and momentum transfer. Each process uses a simple law combined with a mass or energy or momentum balance

Newton's law of cooling for mass transfer

$$\dot{N}_A = h_m\, A\, (c_{A,s} - c_{A,\infty})$$

Hence, the driving potential for convective mass transfer is $c_{A,s} - c_{A,\infty}$

n the above equations,

Variable	Definition	Typical units
$\dot{N}_{A,x}$	moles of species A transferred per unit time from the surface to the bulk fluid far from the surface	$\mathrm{mol}\,/\mathrm{s}$
h_m	the mass transfer coefficient	$\mathrm{m/s}$
A	the area (cross section) through which transfer occurs	m^2
$c_{A,s} - c_{A,\infty}$	the difference in concentration between the surface and bulk fluid	$\mathrm{mol}\,/\mathrm{m}^3$

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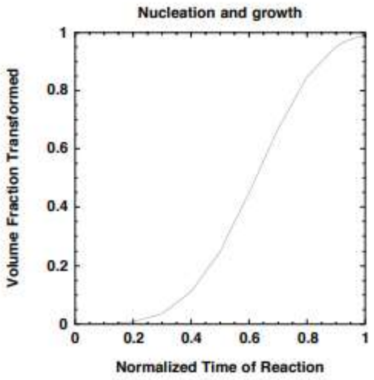
Nucleation,growth and bubble formation

Nucleation and Growth

- Important for:
  - Phase transitions, precipitation, crystallization of glasses
  - Many other phenomena
- Nucleation has thermodynamic barrier
- Initially, large compositional change
  - Small in size
- Volume transformations
  - α to β phase transformation
  - Avrami equation
    - V^β is the volume of second phase
    - V is system volume
    - I_v is the nucleation rate
    - u is the growth rate
    - t is time
  - Sigmoidal transformation curves
- Infinitesimal changes raise system free energy

$$\frac{V^\beta}{V} = \frac{\pi}{3} I_v u^3 t^4$$



Volume Energy

- ΔG_v is ΔG_{rxn} (energy/volume) times the new phase volume
- Spherical clusters have the minimum surface area/volume ratio
- So: the volume term can be:

$$(\text{volume})\Delta G_v \quad \text{or}$$

$$\frac{4}{3}\pi r^3 \Delta G_v$$

Surface Energy

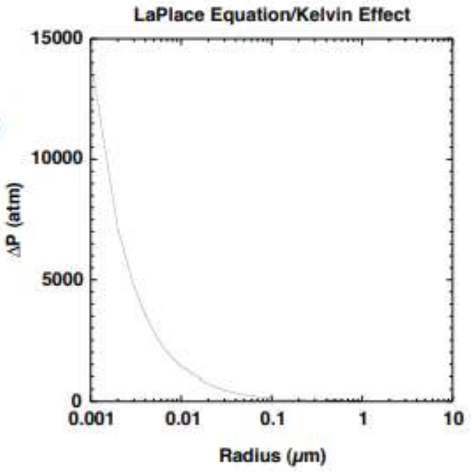
- The LaPlace equation shows the importance of surface energy

$$\Delta P = \frac{2\gamma}{r}$$

Where: ΔP is the pressure drop across a curved surface
γ is the surface energy
r is particle radius

- Surface energy is important for small particles
- Nuclei are on the order of 100 molecules
- More generally, surface energy is given by:

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,P,\text{composition}}$$



Nucleation

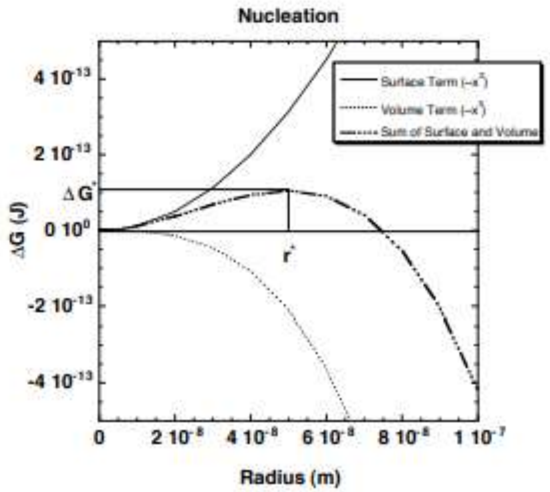
- Consider the nucleation of a new phase at a temperature T
  The transition temperature (T) is below that predicted by thermodynamics when surface or volume are not considered

- We can estimate the free energy change as a function of the radius of the nuclei from the volume and surface terms

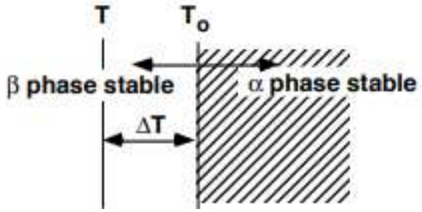
- When r is small, surface dominates

- When r is large, volume dominates

- r^* is the inflection point



$$\Delta T = T_0 - T$$



Nucleation

- r^* is the critical size nucleus and inflection point on the curve

  At r*: $$\frac{\partial(\Delta G_r)}{\partial r} = 0$$

- We can use this to calculate r* and ΔG_r*

$$r^* = -\frac{2\gamma}{\Delta G_v} \quad \Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2}$$

Critical Nuclei

- The number of molecules in the critical nucleus, n*, can be calculated by equating the volume of the critical nucleus, $4/3\pi(r^*)^3$, with the volume of each molecule, V, times the number of molecules per nucleus

$$\frac{4}{3}\pi(r^*)^3 = n^* V$$

- Substituting the previous equations and solving gives

$$n^* = -\frac{32\pi\gamma^3}{3V(\Delta G_v)^3}$$

Nucleus Formation

- The number of nuclei can be calculated using statistical entropy

$$\Delta G_n = N_r \Delta G_r + kT\left[\left(\frac{N_r}{N+N_r}\right)\ln\left(\frac{N_r}{N+N_r}\right)+\left(\frac{N}{N+N_r}\right)\ln\left(\frac{N}{N+N_r}\right)\right]$$

Where: ΔG_n is the free energy for cluster formation
N_r is the number of clusters of radius r per unit volume
N is the number of molecules per unit volume

- At equilibrium, $N_r \ll N$ so the previous equation simplifies to:

$$N_{r^*} = N\exp\left(-\frac{\Delta G^*}{kT}\right)$$

Quiz

- 1. A stream of air at 100 kPa pressure and 300 K is flowing on the top surface of a thin flat sheet of solid naphthalene of length 0.2 m with a velocity of 20 m/sec. The other data are: Mass diffusivity of naphthalene vapor in air = 6 × 10−6 $m2\ /s$ Kinematic viscosity of air = 1.5 × 10−5 $m2\ /s$ Concentration of naphthalene at the air-solid naphthalene interface = 1 × 10−5$kmol/m$3 For heat transfer over a flat plate, convective heat transfer coefficient for laminar flow can be calculated by the equation: Nu = 0.664 ReL 0.5Pr0.33

- In applying dimensional analysis to explain mass-transfer coefficient, one must consider the geometry involved, a variable to explain the flow characteristics of the moving stream, and the properties of the moving stream. Predict the variables that are necessary to explain the mass-transfer coefficient for a gas stream flowing over a flat plate and arrange these variables into dimensionless groups.

- In a mass transfer spray column, a liquid is sprayed into a gas stream, and mass is transferred between the liquid and gas phases. The mass of the drops that are formed from a spray nozzle is considered a function of the nozzle diameter, acceleration of gravity, and surface tension of the liquid against the gas, fluid density, fluid viscosity, fluid velocity, and the viscosity and density of the gas medium. Arrange these variables in dimensionless groups. Should any other variables have been included?