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# Lecture 1

## Diffusion in dilute solutions

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# Mass transfer

- Convection
  - Free convection and forced convection
- Diffusion
  - diffusion is caused by random molecular motion that leads to complete mixing.
    - in gases, diffusion progresses at a rate of about 10 cm/min;
    - in liquid, its rate is about 0.05 cm/min;
    - in solids, its rate may be only about 0.00001 cm/min
  - less sensitive to temperature than other phenomena

# Diffusion

- When it is the slowest step in the sequence, it limits the overall rate of the process:
  - commercial distillations
  - rate of reactions using porous catalysts
  - speed with which the human intestine absorbs nutrients
  - the growth of microorganisms producing penicillin
  - rate of the corrosion of steel
  - the release of flavor from food
- Dispersion (different from diffusion)
  - the dispersal of pollutants

# Understand diffusion?

- What is Diffusion?
  - process by which molecules, ions, or other small particles spontaneously mix, moving from regions of relatively high concentration into regions of lower concentration
- How to study diffusion?
  - Scientific description: By Fick's law and a diffusion coefficient
  - Engineering description: By a mass transfer coefficient

# Models for diffusion

- Mass transfer: define the flux

$$\text{carbon dioxide flux} = \frac{\text{amount of gas removed}}{(\text{time})(\text{unit area})}$$

- Two models (from assumptions!)
  - Fick's law

$$\text{carbon dioxide flux} = D \frac{\text{carbon dioxide concentration difference}}{\text{capillary length}}$$

- Mass transfer coefficient model

$$\text{carbon dioxide flux} = k \text{ carbon dioxide concentration difference}$$

# Models

- The choice between the mass transfer and diffusion models is often a question of taste rather than precision.
- The diffusion model
  - more fundamental and is appropriate when concentrations are measured or needed versus both position and time
- The mass transfer model
  - simpler and more approximate and is especially useful when only average concentrations are involved.

# Diffusion in dilute solutions

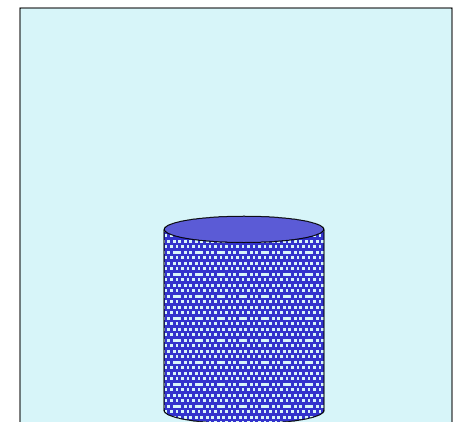
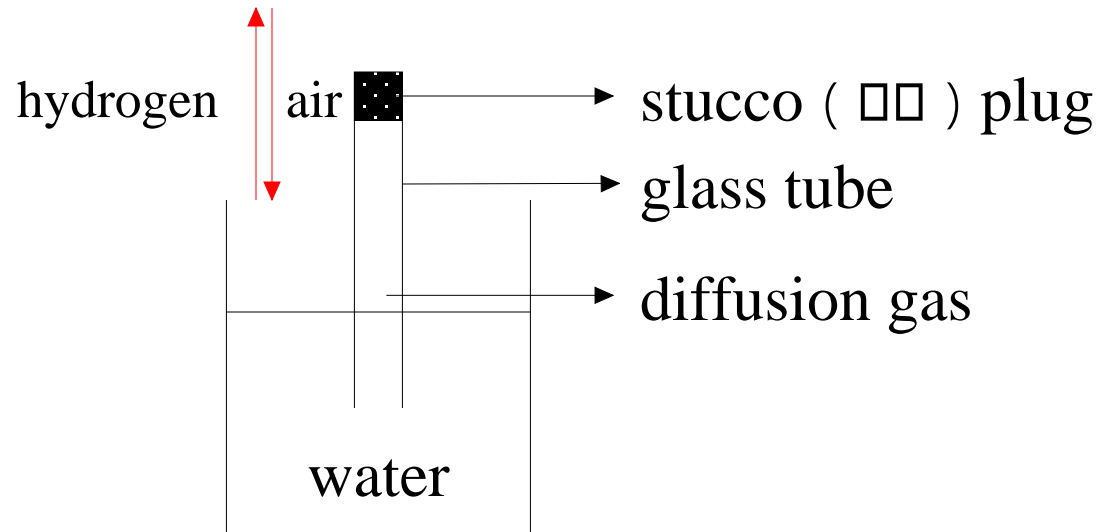
# Diffusion in dilute solutions

- Diffusion in dilute solutions are frequently encountered
  - diffusion in living tissue almost always involves the transport of small amounts of solutes like salts, antibodies, enzymes, or steroids.
- Two cases are studied
  - steady-state diffusion across a thin film
    - basic to membrane transport
  - unsteady-state diffusion into a infinite slab
    - the strength of welds
    - the decay of teeth



# Early work in diffusion

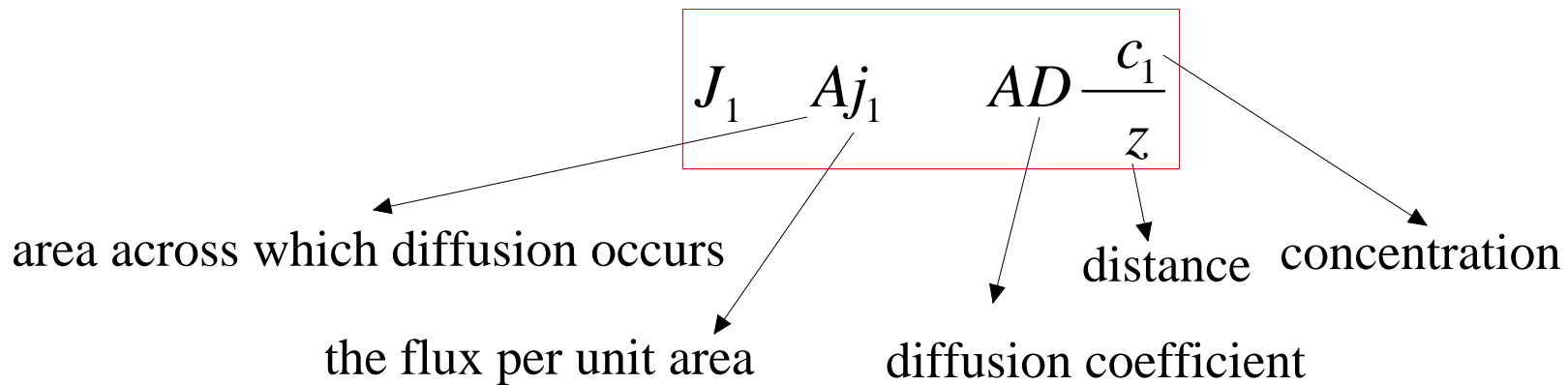
- Thomas Graham (University of Glasgow)
  - diffusion of gases (1828 ~ 1833); constant pressure
  - The flux by diffusion is proportional to the concentration difference of the salt



Apparatus for liquids

- Adolf Eugen Fick (~1855)

- Diffusion can be described on the same mathematical basis as Fourier's law for heat conduction or Ohm's law for electrical conduction
- One dimensional flux:



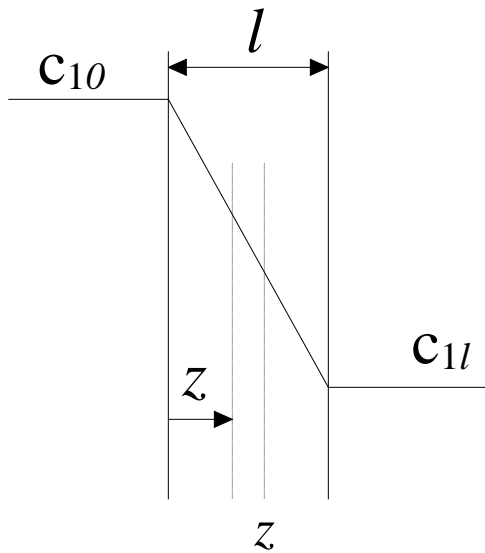
- Paralleled Fourier's conservation equation

$$\frac{c_1}{t} = D \frac{d^2 c_1}{dz^2} = \frac{1}{A} \frac{d}{dz} \left( \frac{A}{z} \frac{dc_1}{dz} \right)$$

Fick's second law:  
one-dimensional unsteady-state diffusion

# Steady diffusion across a thin film

- On each side of the film is a well-mixed solution of one solute,  $c_{10} > c_{1l}$



Mass balance in the layer  $z$

$$\left( \begin{array}{c} \text{Solute} \\ \text{accumulation} \end{array} \right) = \left( \begin{array}{c} \text{rate of} \\ \text{diffusion into} \\ \text{the layer at } z \end{array} \right) - \left( \begin{array}{c} \text{rate of diffusion} \\ \text{out of the layer} \\ \text{at } z + z \end{array} \right)$$

S.S.

$$0 = A \left( j_1 \Big|_z - j_1 \Big|_{z+z} \right)$$

$$0 \quad A \quad j_1|_z \quad j_1|_z \quad z$$

Dividing A z

$$0 \quad \frac{j_1|_z \quad z \quad j_1|_z}{(z \quad z) \quad z}$$

z 0

$$0 \quad \frac{d}{dz} j_1$$

$$j_1 \quad D \frac{c_1}{z}$$

$$0 \quad D \frac{d^2 c_1}{dz^2}$$

$$0 \quad D \frac{d^2 c_1}{dz^2}$$

B.C.

$$z = 0, c_1 = c_{10}$$

$$z = l, c_1 = c_{1l}$$

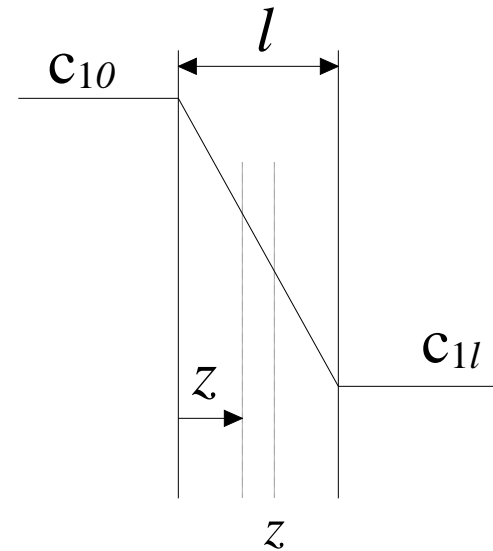
$$c_1 \quad c_{10} \quad (c_{1l} \quad c_{10}) \frac{z}{l}$$

*linear concentration profile*

$$j_1 \quad D \frac{c_1}{z}$$

$$j_1 \quad \frac{D}{l} c_{10} \quad c_{1l}$$

*Since the system is in s.s., the flux is a constant.*



Derive the concentration profile and the flux for a single solute diffusing across a thin membrane. The membrane is chemically different from the solutions.

Similar to the previous slide, a steady-state mass balance gives:

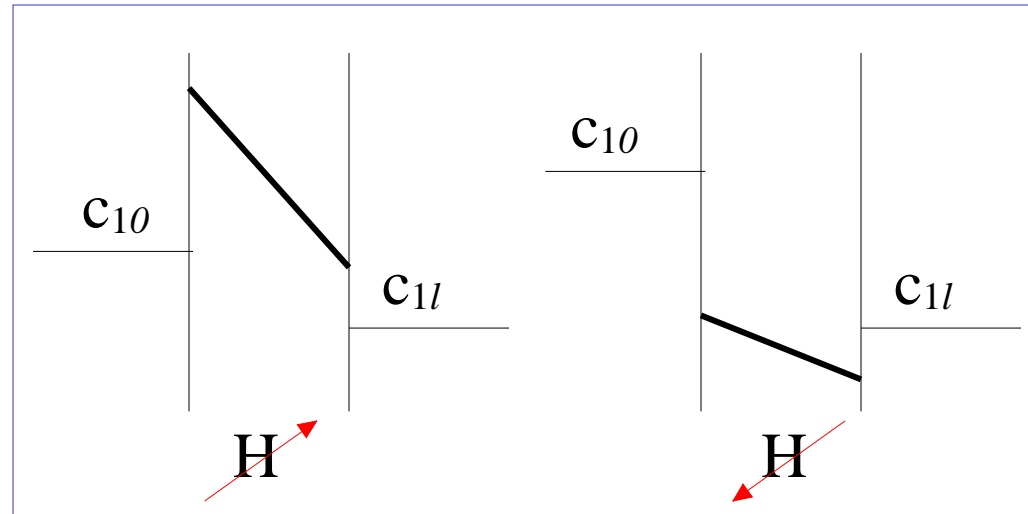
$$0 = D \frac{d^2 c_1}{dz^2}$$

B.C.

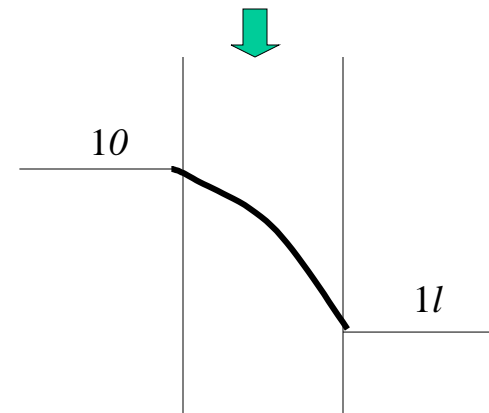
$$z = 0, c_1 = H C_{10}$$

$$z = l, c_1 = H C_{1l}$$

$$c_1 = H C_{10} + H(C_{1l} - C_{10}) \frac{z}{l}$$



Different boundary conditions are used; where H is a partition coefficient. This implies that equilibrium exists across the membrane surface. Solute diffuses from the solution into the membrane.



chemical potential: driving force

$$c_1 \quad HC_{10} \quad H(C_{1l} - C_{10}) \frac{z}{l}$$

$$j_1 \quad D \frac{c_1}{z}$$

$$j_1 \quad \frac{[DH]}{l} (C_{10} - C_{1l})$$

[DH] is called the permeability. The partition coefficient H is found to vary more widely than the diffusion coefficient D, so differences in diffusion tend to be less important than the difference in solubility.

Derive the concentration profile and the flux for a single solute diffusing across a micro-porous layer.

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Micro-porous layer



No longer one-dimensional



Effective diffusion coefficient is used

$$j_1 = \frac{[DH]}{l} (C_{10} - C_{1l})$$

Homogeneous membrane



$$j_1 = \frac{[D_{eff}H]}{l} (C_{10} - C_{1l})$$

Micro-porous layer

$$D_{eff} = f(\text{solute, solvent, local geometry})$$

# Membrane diffusion with fast reaction

A solute is diffusing steadily across a thin membrane, it can rapidly and reversibly react with other immobile solutes fixed with the membrane. Derive the solute's flux.

A mass balance for reactant 1 gives:

$$\left( \begin{array}{c} \text{Solute} \\ \text{accumulation} \end{array} \right) = \left( \begin{array}{c} \text{rate of} \\ \text{diffusion into} \\ \text{the layer at } z \end{array} \right) - \left( \begin{array}{c} \text{rate of diffusion} \\ \text{out of the layer} \\ \text{at } z + \Delta z \end{array} \right) - \left( \begin{array}{c} \text{rate of} \\ \text{consumption} \\ \text{by reaction} \end{array} \right)$$

S.S

$$\boxed{0 \quad A \quad j_1|_z \quad j_1|_{z+\Delta z} \quad r_1 A \quad \Delta z} \longrightarrow \boxed{0 \quad \frac{d}{dz} j_1 \quad r_1}$$

A mass balance for (immobile) product 2 gives:

$$\boxed{0 \quad r_1 A \quad \Delta z} \longrightarrow \boxed{0 \quad r_1}$$

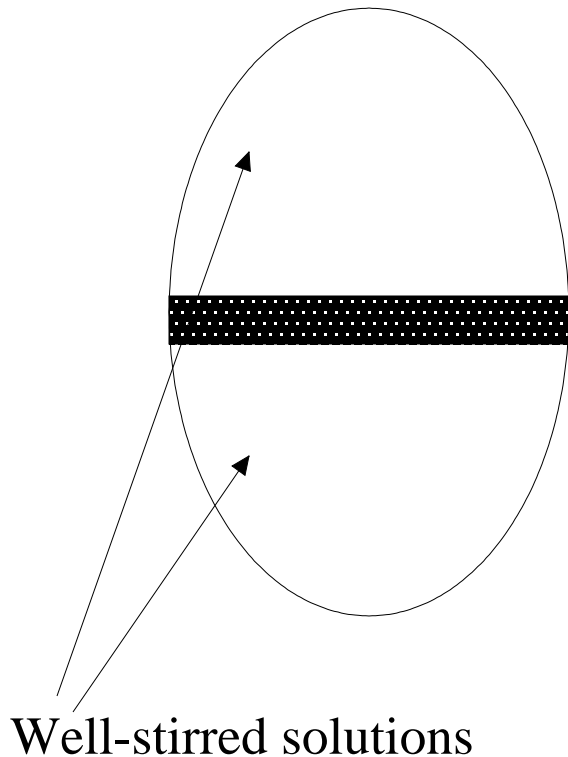
$$\boxed{0 \quad \frac{d}{dz} j_1}$$

The reaction has no effect.



# Diaphragm ( $\square\square$ ) cell

- Two well-stirred volumes separated by a thin porous barrier or diaphragm.
- The diaphragm is often a sintered glass frit/ a piece of filter paper.
- Calculate the diffusion coefficient when the concentrations of the two volumes as a function of time are known.



Assuming the flux across the diaphragm quickly reaches its steady-state value, although the concentrations in the upper and lower compartments are changing with time:

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Pseudo steady-state for membrane diffusion

$$j_1 = \frac{[DH]}{l} (C_{1,lower} - C_{1,upper})$$

$H$  includes the fraction of the diaphragm's area that is available for diffusion.

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Overall mass balance on the adjacent compartments

$$\left[ \begin{array}{l} V_{lower} \frac{dC_{1,lower}}{dt} \\ V_{upper} \frac{dC_{1,upper}}{dt} \end{array} \right] - A j_1 = \frac{d}{dt} \left[ C_{1,lower} - C_{1,upper} \right] A j_1 \left[ \frac{1}{V_{lower}} - \frac{1}{V_{upper}} \right]$$

$A$  is the diaphragm's area

$$\frac{d}{dt} \begin{pmatrix} C_{1,lower} \\ C_{1,upper} \end{pmatrix} = A j_1 \begin{pmatrix} 1 \\ V_{lower} \\ 1 \\ V_{upper} \end{pmatrix}$$

$$j_1 \frac{[DH]}{l} \begin{pmatrix} C_{1,lower} \\ C_{1,upper} \end{pmatrix}$$

$$\frac{d}{dt} \begin{pmatrix} C_{1,lower} \\ C_{1,upper} \end{pmatrix} = A \frac{[DH]}{l} \begin{pmatrix} C_{1,lower} \\ C_{1,upper} \end{pmatrix} \begin{pmatrix} 1 \\ V_{lower} \\ 1 \\ V_{upper} \end{pmatrix}$$

$$A \frac{[H]}{l} \begin{pmatrix} 1 \\ V_{lower} \\ 1 \\ V_{upper} \end{pmatrix}$$

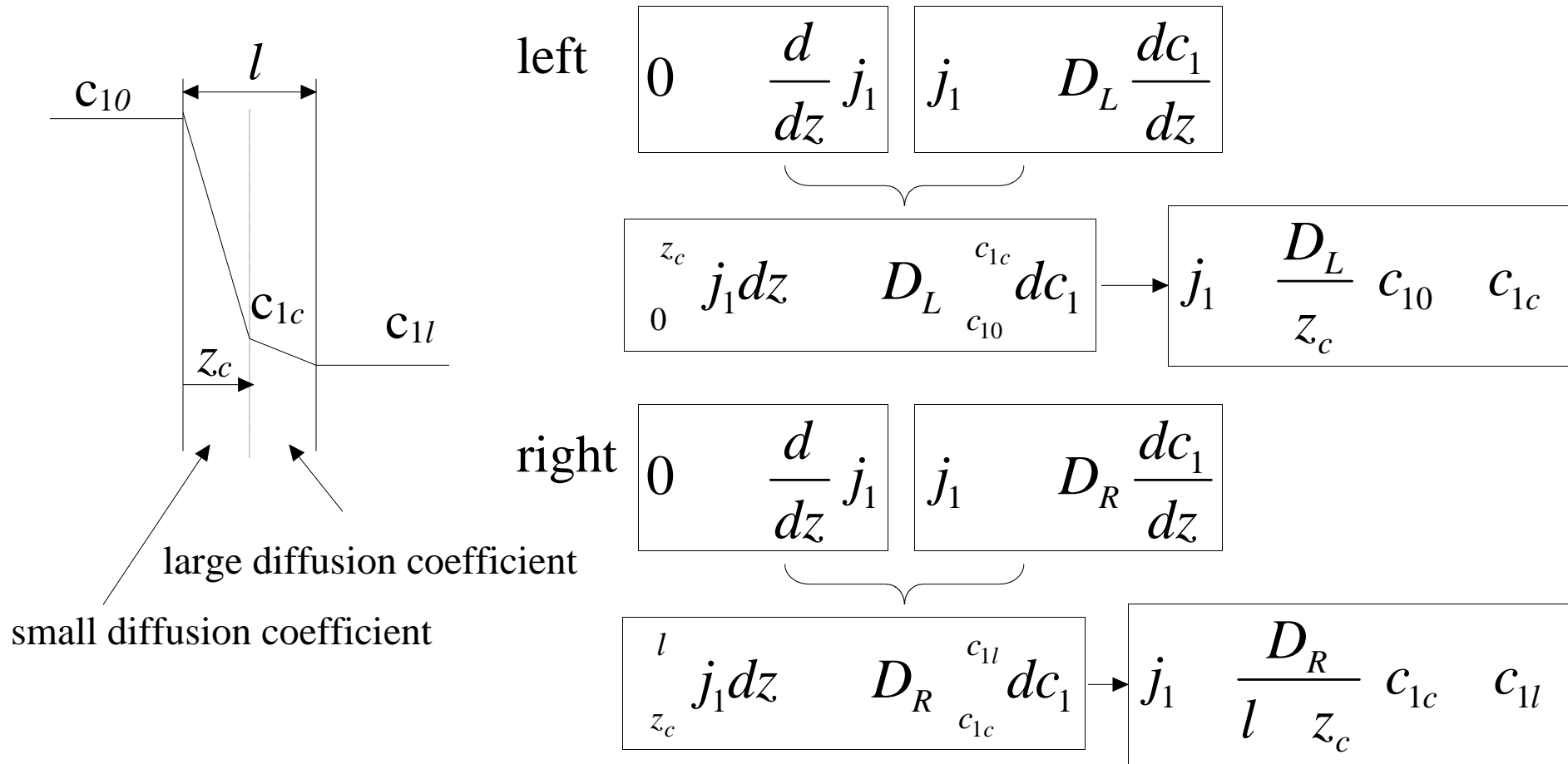
$$\frac{d}{dt} \begin{pmatrix} C_{1,lower} \\ C_{1,upper} \end{pmatrix} = D \begin{pmatrix} C_{1,lower} \\ C_{1,upper} \end{pmatrix}$$

$$C_1^* = \frac{\begin{pmatrix} C_{1,lower} \\ C_{1,upper} \end{pmatrix}}{\begin{pmatrix} C_{1,lower}^0 \\ C_{1,upper}^0 \end{pmatrix}}$$

$$\frac{d}{dt} C_1^* = D C_1^*$$

$$D \frac{1}{t} \ln C_1^*$$

Find the flux across a thin film in which diffusion varies sharply (i.e., the diffusion coefficient is not a constant). Assume that below some critical concentration  $c_{1c}$ , diffusion is fast, but above this concentration it is suddenly much slower.

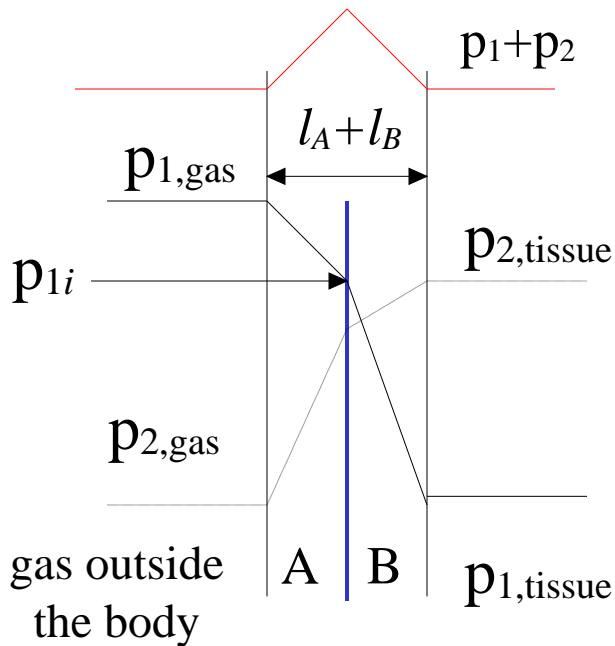


➡ The flux is the same across both films:

$$j_1 = \frac{D_L (c_{10} - c_{1c}) + D_R (c_{1c} - c_{1l})}{l}$$

# Skin diffusion

Skin behaves as if it consists of two layers, each of which has a different gas permeability. Explain how these two layers can lead to the rashes observed.



Assuming that the gas pressure is in equilibrium with the local concentration:

concentration  $\longrightarrow$  gas pressure

For layer A,

$$p_1 - p_{1,gas} = \frac{z}{l_A} (p_{1,i} - p_{1,gas})$$

For layer B,

$$p_1 - p_{1,i} = \frac{z}{l_B} (p_{1,tissue} - p_{1,i})$$

The flux through layer A equals that through layer B :

$$j_1 = \frac{[D_A H_A]}{l_A} (p_{1,gas} - p_{1,i}) = \frac{[D_B H_B]}{l_B} (p_{1,i} - p_{1,tissue})$$

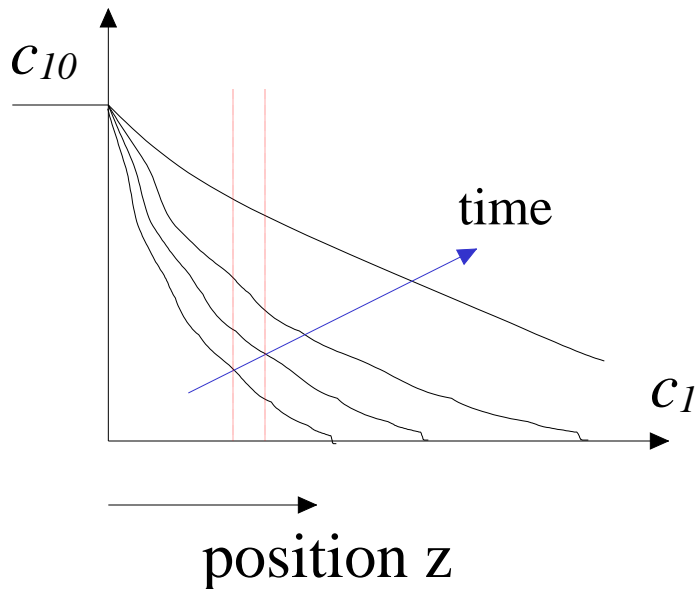


$$p_{1,i} = \frac{\frac{D_A H_A}{l_A} p_{1,gas} - \frac{D_B H_B}{l_B} p_{1,tissue}}{\frac{D_A H_A}{l_A} + \frac{D_B H_B}{l_B}}$$

# Unsteady diffusion in a semiinfinite slab - free diffusion

- Any diffusion problem will behave as if the slab is infinitely thick at short enough times.

At time zero, the concentration at  $z = 0$  suddenly increases to  $c_{10}$



Mass balance on the thin layer  $A \Delta z$

$$\left( \text{Solute accumulation} \right) = \left( \text{rate of diffusion into the layer at } z \right) - \left( \text{rate of diffusion out of the layer at } z + \Delta z \right)$$

$$\frac{d}{dt} A \Delta z c_1 = A j_1|_z - j_1|_{z + \Delta z}$$

$$\frac{1}{t} A z c_1 \quad A j_1|_z \quad j_1|_z \quad z$$

Dividing A z

$$\frac{1}{t} c_1 \quad \frac{j_1|_z \quad j_1|_z}{(z \quad z) \quad z}$$

z 0

$$\frac{c_1}{t} \quad \frac{j_1}{z}$$

$$j_1 \quad D \frac{c_1}{z}$$

$$\frac{c_1}{t} \quad D \frac{c_1^2}{z^2}$$

Fick's second law

$$\frac{c_1}{t} \quad D \frac{c_1^2}{z^2}$$

Boundary conditions

$$\begin{aligned} c_1 &= c_1 \quad \text{at } t = 0, \text{ for all } z \\ c_1 &= c_{10} \quad \text{at } t = 0, z = 0 \\ c_1 &= c_1 \quad \text{at } t = 0, z \end{aligned}$$

$$\frac{z}{\sqrt{4Dt}}$$

$$\frac{c_1 - c_{10}}{c_1 - c_{10}} \quad \text{erf}$$

$$\text{erf} \quad \frac{2}{\sqrt{\quad}} \int_0^{s^2} e^{-s^2} ds$$

$$j_1 \quad D \frac{c_1}{z}$$

$$j_1 \quad D \frac{c_1}{z} \quad \sqrt{\frac{D}{t}} e^{-\frac{z^2}{4Dt}} \quad c_{10} \quad c_1$$

$$j_1|_{z=0} \quad \sqrt{\frac{D}{t}} \quad c_{10} \quad c_1$$

# Free diffusion with fast reaction

A solute is diffusing steadily across a semiinfinite slab, it can rapidly and reversibly react with other immobile solutes fixed within the slab. Derive the solute's flux.

A mass balance for reactant 1 gives:

$$\left( \text{Solute accumulation} \right) = \left( \text{rate of diffusion into the layer at } z \right) - \left( \text{rate of diffusion out of the layer at } z + \Delta z \right) + \left( \text{rate of generation by reaction} \right)$$

$$\frac{\Delta c_1}{\Delta t} \Delta V = A j_1|_z - A j_1|_{z+\Delta z} + r_1 A \Delta z \quad \rightarrow \quad \frac{c_1}{t} D \frac{\partial^2 c_1}{\partial z^2} + r_1$$

For a first-order reaction

$$r_1 = kc_1$$

$$\frac{c_1}{t} D \frac{\partial^2 c_1}{\partial z^2} + kc_1$$

Use  $\frac{D}{1+k}$  to replace D

$$\frac{c_1}{t} \frac{D}{1+k} \frac{\partial^2 c_1}{\partial z^2}$$

The reaction has left the mathematical form of the answer unchanged, but it has altered the diffusion coefficient.



If the same B.C.s are used:

Without reaction

$$\frac{c_1}{t} = D \frac{c_1}{z^2}$$

With first-order fast reaction

$$\frac{c_1}{t} = \frac{D}{1+k} \frac{c_1}{z^2}$$

$$\frac{c_1 - c_{10}}{c_1 - c_{10}} \operatorname{erf} \left( \frac{z}{\sqrt{4Dt}} \right) = \operatorname{erf} \left( \frac{z}{\sqrt{4Dt}} \right) + \frac{2}{\sqrt{\pi}} \int_0^{s^2} e^{-s^2} ds$$

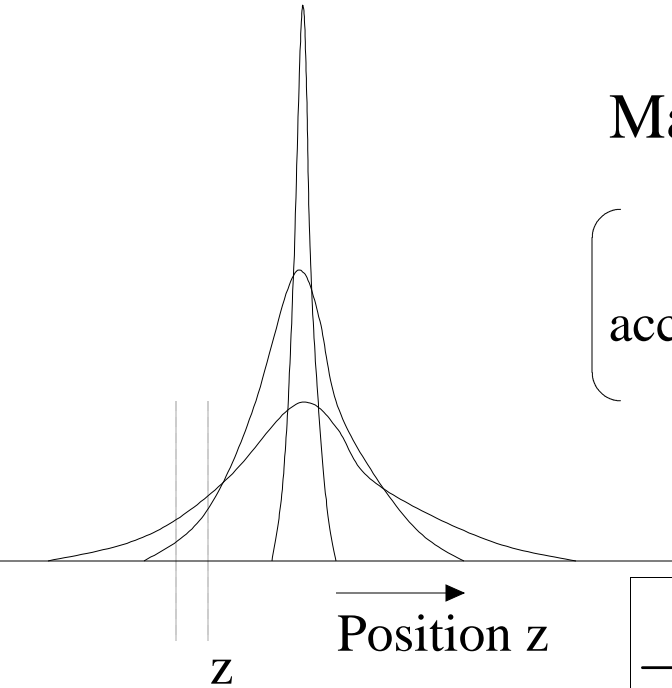
$$\frac{c_1 - c_{10}}{c_1 - c_{10}} \operatorname{erf} \left( \frac{z}{\sqrt{4 \frac{D}{1+k} t}} \right) = \operatorname{erf} \left( \frac{z}{\sqrt{4 \frac{D}{1+k} t}} \right) + \frac{2}{\sqrt{\pi}} \int_0^{s^2} e^{-s^2} ds$$

$$j_1|_{z=0} = \sqrt{\frac{D}{t}} (c_{10} - c_1)$$

$$j_1|_{z=0} = \sqrt{\frac{D}{1+k} t} (c_{10} - c_1)$$

# A sharp pulse of solute

The initial sharp concentration gradient relaxes by diffusion in the z direction into the smooth curves. Calculate the shape of these curves.



Mass balance on the differential volume  $A \, z$

$$\left( \begin{array}{c} \text{Solute} \\ \text{accumulation} \\ \text{in } A \, z \end{array} \right) = \left( \begin{array}{c} \text{rate of} \\ \text{diffusion into} \\ \text{this volume} \end{array} \right) - \left( \begin{array}{c} \text{rate of diffusion} \\ \text{out of this volume} \end{array} \right)$$



$$\frac{d}{dt} (A \, z c_1) = A j_1 \Big|_z - A j_1 \Big|_{z+z}$$

Dividing  $A \, z$

$$\frac{dc_1}{dt} = - \frac{j_1}{z}$$

$$j_1 = -D \frac{dc_1}{dz}$$

$$\frac{dc_1}{dt} = D \frac{d^2 c_1}{dz^2}$$

# Boundary conditions

$$\begin{array}{l}
 t = 0, \quad z \rightarrow \infty, \quad c_1 = 0 \\
 t = 0, \quad z = 0, \quad \frac{c_1}{z} = 0 \\
 t = 0, \quad z = 0, \quad c_1 = \frac{M}{A} \delta(z)
 \end{array}$$

far from the pulse, the solute concentration is zero

at  $z = 0$ , the flux has the same magnitude in the positive and negative directions

all the solute is initially located at  $z = 0$

A: the cross-sectional area over which diffusion is occurring

M: the total amount of solute in the system

$\delta(z)$ : the Dirac function  $(\text{length})^{-1}$

$$c_1 A dz = \frac{M}{A} \delta(z) A dz = M$$

Apply Laplace Transform to solve

$$\frac{c_1}{t} \quad D \frac{c_1}{z^2}$$

$$\wedge \quad \frac{c_1}{t} \quad \overline{sc_1(s)} \quad \text{and} \quad \wedge \quad \frac{c_1}{z^2} \quad \frac{d^2 \overline{c_1(s)}}{dz^2}$$

$z$  and  $c_1$  are independent variables

$$\frac{c_1}{t} \quad D \frac{c_1}{z^2} \xrightarrow{\text{Laplace transform}} \overline{sc_1(s)} \quad D \frac{d^2 \overline{c_1(s)}}{dz^2}$$

Second order linear O.D.E.

$$D \overline{c_1} \quad \overline{sc_1} \quad 0 \xrightarrow{s \text{ regards as constant}} \overline{c_1} \quad Ae^{\sqrt{\frac{s}{D}}z} \quad Be^{\sqrt{\frac{s}{D}}z}$$

The boundary condition:

$$t = 0, \quad z = 0, \quad c_1 = \frac{M}{A}(z)$$

Laplace transform

$$\frac{d\bar{c}_1}{dz} = \frac{M}{A} \frac{1}{2D} \text{ at } z = 0$$

$$t = 0, \quad z = \infty, \quad c_1 = 0$$

Laplace transform

$$\bar{c}_1 = 0 \text{ at } z = \infty$$

$$\bar{c}_1 = A e^{-\sqrt{\frac{s}{D}}z} + B e^{\sqrt{\frac{s}{D}}z}$$

$$\bar{c}_1 = 0 \text{ at } z = \infty$$

$$\frac{d\bar{c}_1}{dz} = \frac{M}{A} \frac{1}{2D} \text{ at } z = 0$$



$$\bar{c}_1 = \frac{M}{A} \frac{1}{2D} \sqrt{\frac{D}{s}} e^{-\sqrt{\frac{s}{D}}z}$$

inverse transform

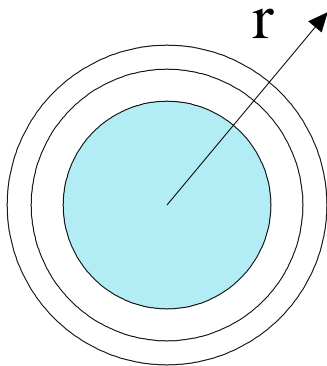
$$c_1 = \frac{M}{A} \frac{1}{\sqrt{4Dt}} e^{-\frac{z^2}{4Dt}}$$

Gaussian curve

# The steady dissolution of a spherical particle

The sphere is of a sparingly soluble material, so that the sphere's size does not change much. However, the material quickly dissolves in the surrounding solvent, so that solute's concentration at the sphere's surface is saturated. The sphere is immersed in a very large fluid volume, the concentration far from the sphere is zero. Find the dissolution rate and the concentration profile around the sphere.

Mass balance on a spherical shell of thickness  $\Delta r$  located at  $r$  from the sphere:



$$\left( \begin{array}{c} \text{Solute} \\ \text{accumulation} \\ \text{within the shell} \end{array} \right) = \left( \begin{array}{c} \text{rate of} \\ \text{diffusion into} \\ \text{the shell} \end{array} \right) - \left( \begin{array}{c} \text{rate of diffusion} \\ \text{out of the shell} \end{array} \right)$$



$$\frac{d}{dt} (4\pi r^2 \Delta r c_1) = 4\pi r^2 j_1|_r - 4\pi (r + \Delta r)^2 j_1|_{r + \Delta r}$$

S.S

$$0 \quad 4 r^2 j_1 \Big|_r \quad 4 r^2 j_1 \Big|_r \quad r$$

Dividing  $4 r^2 r$   
 $r \quad 0$

$$0 \quad \frac{1}{r^2} \frac{d}{dr} r^2 j_1$$

$$j_1 \quad D \frac{c_1}{r}$$

$$0 \quad \frac{D}{r^2} \frac{d}{dr} r^2 \frac{dc_1}{dr}$$

## Boundary conditions

$$r \quad R_0, \quad c_1 \quad c_1(sat)$$

$$r \quad , \quad c_1 \quad 0$$

$$c_1 \quad c_1(sat) \frac{R_0}{r}$$

$$j_1 \quad D \frac{c_1}{r}$$

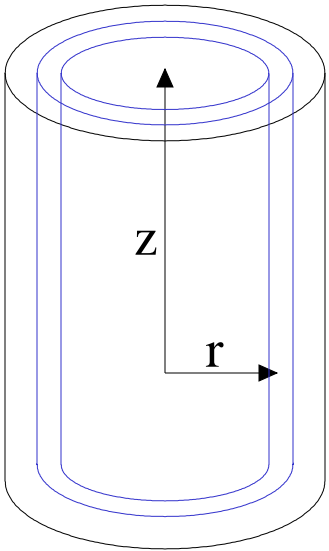
$$j_1 \quad D \frac{R_0}{r^2} c_1(sat)$$

Example:

The growth of fog droplets and the dissolution of drugs

## The diffusion of a solute into the cylinder

The cylinder initially contains no solute. At time zero, it is suddenly immersed in a well-stirred solution that is of such enormous volume that its solute concentration is constant. The solute diffuses into the cylinder symmetrically. Find the solute's concentration in this cylinder as a function of time and location.



Mass balance on a cylindrical shell of thickness  $\Delta r$  located at  $r$  from the central axis:

$$\left( \begin{array}{c} \text{Solute} \\ \text{accumulation} \\ \text{within the shell} \end{array} \right) = \left( \begin{array}{c} \text{rate of} \\ \text{diffusion into} \\ \text{the shell} \end{array} \right) - \left( \begin{array}{c} \text{rate of diffusion} \\ \text{out of the shell} \end{array} \right)$$

$$\frac{\Delta}{\Delta t} 2 \pi r L \Delta r c_1 = 2 \pi r L j_1|_r - 2 \pi r L j_1|_{r+\Delta r}$$



$$\frac{1}{t} \frac{\partial}{\partial t} (2 r L r c_1) = \frac{1}{r} \frac{\partial}{\partial r} (2 r L j_1|_r) - \frac{1}{r} \frac{\partial}{\partial r} (2 r L j_1|_r)$$

Dividing by  $2 r L r$

$$\frac{1}{t} \frac{\partial c_1}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} (r j_1)$$

$$j_1 = D \frac{\partial c_1}{\partial r}$$

$$\frac{\partial c_1}{\partial t} = \frac{D}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c_1}{\partial r} \right)$$

## Boundary conditions

$$\begin{aligned} t = 0, \text{ all } r, c_1 &= 0 \\ t = 0, r = R_0, c_1 &= c_1(\text{surface}) \\ t = 0, r = 0, \frac{\partial c_1}{\partial r} &= 0 \end{aligned}$$

$$\frac{c_1}{t} \frac{D}{r} \frac{c_1}{r} r \frac{c_1}{r}$$

Dimensionless:

$$1 \frac{c_1}{c_1(\text{surface})}$$

$$\frac{r}{R_0}$$

$$\frac{Dt}{R_0^2}$$

$$\frac{1}{\frac{c_1}{c_1(\text{surface})} \frac{r}{R_0} \frac{Dt}{R_0^2}}$$

$$t = 0, \text{ all } r, c_1 = 0$$

$$t = 0, r = R_0, c_1 = c_1(\text{surface})$$

$$t = 0, r = 0, \frac{c_1}{r} = 0$$

$$0, \text{ all } r, 1$$

$$0, 1, 0$$

$$0, 0, \frac{c_1}{r} = 0$$

$$\frac{1}{\dots}$$

$$\begin{matrix} 0, & \text{all} & , & 1 \\ 0, & 1, & & 0 \\ 0, & 0, & \text{---} & 0 \end{matrix}$$

**Assume:**  $g = f(\dots)$  Using the method of “Separation of variables”

...

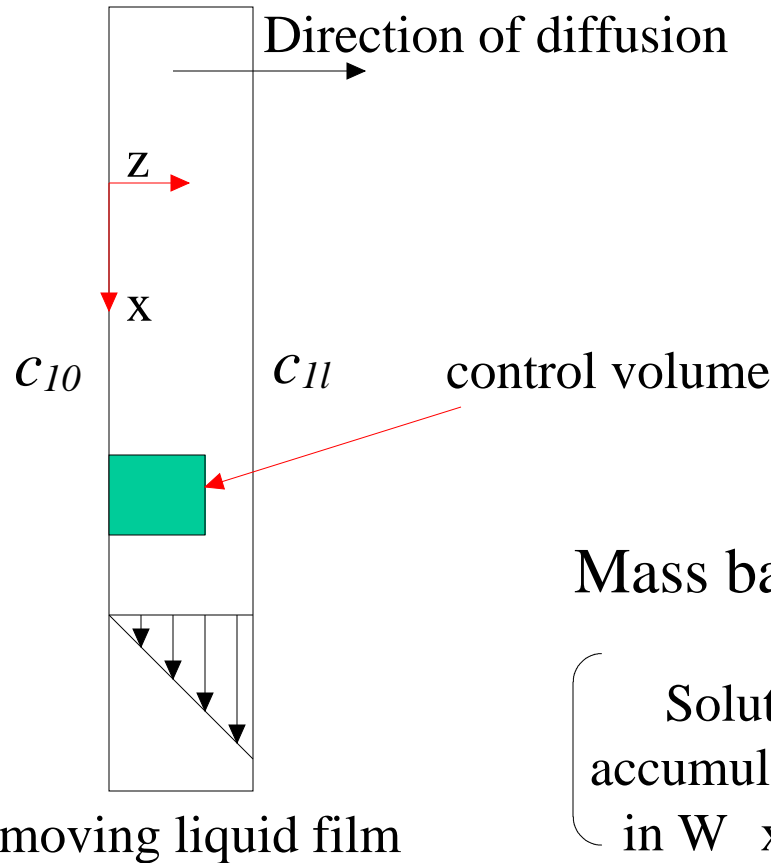
Please refer to my lecture note number 8 for the “applied mathematics”.

$$\frac{2}{J_1(\alpha_n)} J_0(\alpha_n r/R_0) e^{-\alpha_n^2 t/R_0^2}$$

$$\frac{c_1}{c_1(\text{surface})} \sum_{n=1}^{\infty} \frac{J_0(\alpha_n r/R_0) e^{-\alpha_n^2 t/R_0^2}}{J_1(\alpha_n r/R_0)}$$

# Diffusion across a thin, moving liquid film

The concentrations on both sides of this film are fixed by electrochemical reactions, but the film itself is moving steadily.



## Assumptions:

- the liquid is dilute
- the liquid is the only resistance to mass transfer
- diffusion in the z direction
- convection in the x direction

Mass balance on a control volume  $W \times x \times z$ :

$$\left( \begin{array}{c} \text{Solute} \\ \text{accumulation} \\ \text{in } W \times x \times z \end{array} \right) = \left( \begin{array}{c} \text{rate of} \\ \text{diffusion in} \\ \text{the z direction} \end{array} \right) + \left( \begin{array}{c} \text{rate of} \\ \text{diffusion in} \\ \text{the x direction} \end{array} \right)$$

$$\frac{d}{dt} c_1 W \times x \times z = j_1 W \times x \Big|_z - j_1 W \times x \Big|_{z+z} - c_1 v_x W \times z \Big|_x + c_1 v_x W \times z \Big|_{x+x}$$

$$\frac{1}{t} c_1 W x z \quad j_1 W x|_z \quad j_1 W x|_z z \quad c_1 v_x W z|x \quad c_1 v_x W z|x x$$

S.S.

Dividing  $W x z$

$$\begin{matrix} x & 0 \\ z & 0 \end{matrix}$$

Neither  $c_l$  nor  $v_x$  change with  $x$

$$0 \quad \frac{dj_1}{dz}$$

$$j_1 \quad D \frac{dc_1}{dz}$$

$$0 \quad D \frac{d^2 c_1}{dz^2}$$

B.C.

$$\begin{matrix} z & 0, & c_1 & c_{10} \\ z & l, & c_1 & c_{1l} \end{matrix}$$

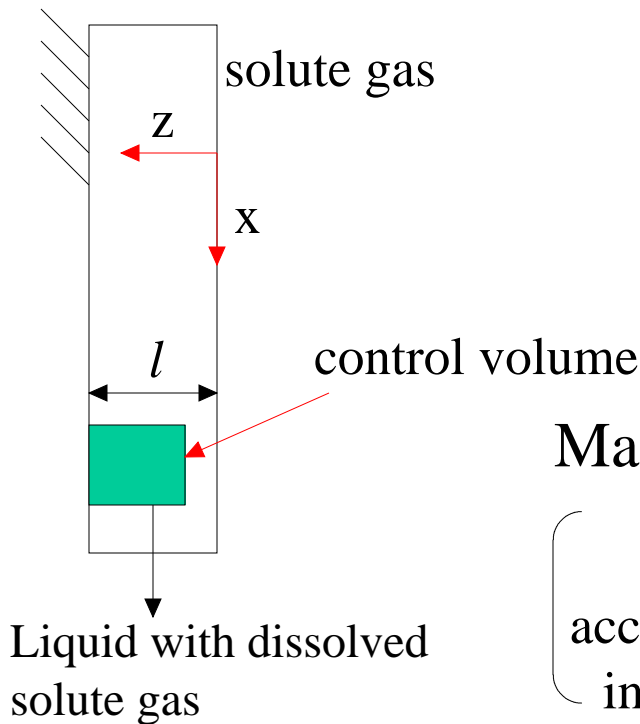
$$c_1 \quad c_{10} \quad (c_{1l} \quad c_{10}) \frac{z}{l}$$

$$j_1 \quad \frac{D}{l} c_{10} \quad c_{1l}$$

The flow has no effect!

# Diffusion into a falling film

A thin liquid film flows slowly and without ripples down a flat surface. One side of this film wets the surface; the other side is in contact with a gas, which is sparingly soluble in the liquid. Find how much gas dissolve in the liquid.



## Assumptions:

- the liquid is dilute
- the contact between gas and liquid is short
- diffusion in the z direction
- convection in the x direction

Mass balance on a control volume  $W \times z$ :

$$\left( \begin{array}{c} \text{Solute} \\ \text{accumulation} \\ \text{in } W \times z \end{array} \right) = \left( \begin{array}{c} \text{rate of} \\ \text{diffusion in} \\ \text{the } z \text{ direction} \end{array} \right) + \left( \begin{array}{c} \text{rate of} \\ \text{diffusion in} \\ \text{the } x \text{ direction} \end{array} \right)$$

$$\frac{d}{dt} c_1 W \times z = j_1 W \times z \Big|_z - j_1 W \times z \Big|_z - c_1 v_x W \times z \Big|_x + c_1 v_x W \times z \Big|_x$$

$$\frac{1}{t} c_1 W \quad x \quad z \quad j_1 W \quad x|_z \quad j_1 W \quad x|_z \quad z \quad c_1 v_x W \quad z|x \quad c_1 v_x W \quad z|x \quad x$$

S.S.

Dividing  $W \quad x \quad z$

$$\begin{matrix} x & 0 \\ z & 0 \end{matrix}$$

$$0 \quad \frac{j_1}{z} \quad \frac{1}{x} c_1 v_x$$

$v_x \sim \text{constant}$

$$j_1 \quad D \frac{dc_1}{dz}$$

$$\frac{c_1}{x/v_x} \quad D \frac{c_1^2}{z^2}$$

B.C.

$$\frac{c_1}{c_1(\text{sat})} \quad 1 \quad \text{erf} \frac{z}{\sqrt{4Dx/v_x}}$$

$$\begin{matrix} x=0, & \text{all } z, & c_1=0 \\ x=0, & z=0, & c_1=c_1(\text{sat}) \\ x=0, & z=l, & c_1=0 \end{matrix}$$

$$j_1|_{z=0} = \sqrt{D \frac{v_x}{x}} c_1(\text{sat})$$

What we have done are:

1. We write a mass balance as a differential equation
  2. Combine this with Fick's law
  3. Integrate this to find the desired result
- 

$$j_1 = \frac{D}{l} c_1 \quad \text{For thin film}$$

$$j_1 = \sqrt{\frac{D}{t}} c_1 \quad \text{For thick slab}$$

---

## Fourier Number

$$\frac{(\text{length})^2}{(D)(\text{time})}$$

Much larger than unity ..... Assume a semiinfinite slab

Much less than unity ..... Assume a steady state or an equilibrium

Approximately unity ..... Used to estimate the process



### Example:

Hydrogen has penetrated about 0.1 cm into nickel,  $D = 10^{-8} \text{ cm}^2/\text{sec}$ , estimate the operation time of the process.

$$\frac{(length)^2}{(D)(time)} = 1 \quad \rightarrow \quad \frac{(10^{-1} \text{ cm})^2}{(10^{-8} \text{ cm}^2 / \text{sec})(time)} = 1$$



Approximately 10 days.