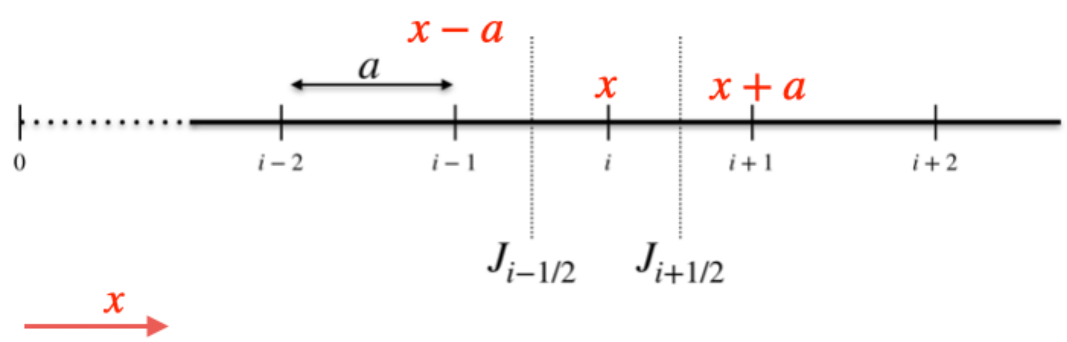
ChE-402: Diffusion and Mass Transfer

Lecture 2

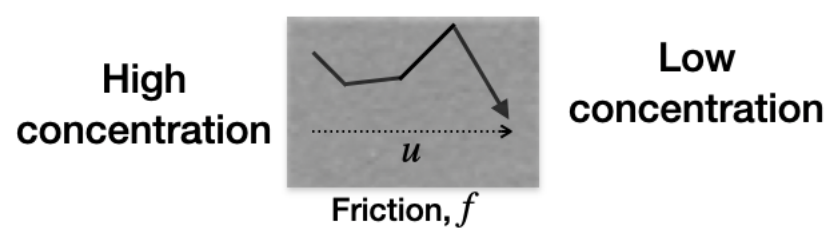
Intended Learning Outcomes

To apply mass balance using Fick's law to predict time-independent (steady-state) and time-dependent (unsteady state or transient) evolution of concentration profile.

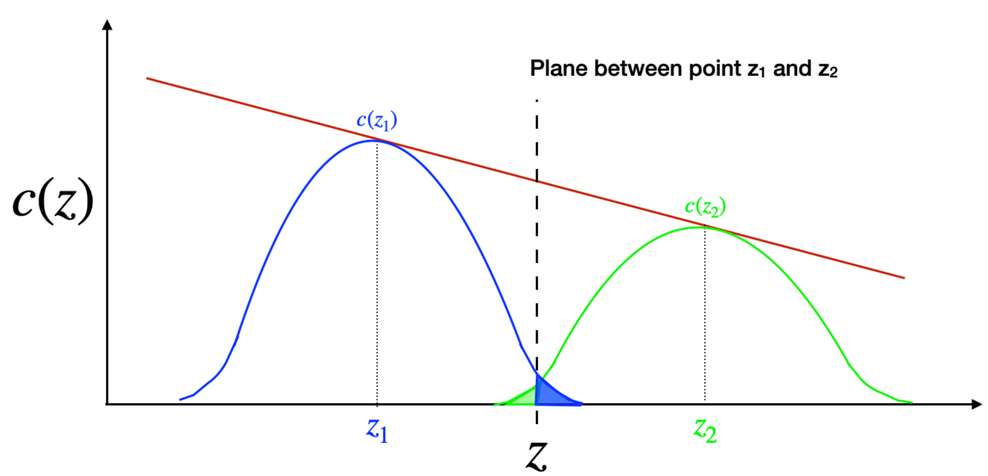
Three interpretation on origin of diffusion



$$D = \frac{\Gamma a^2}{2}$$



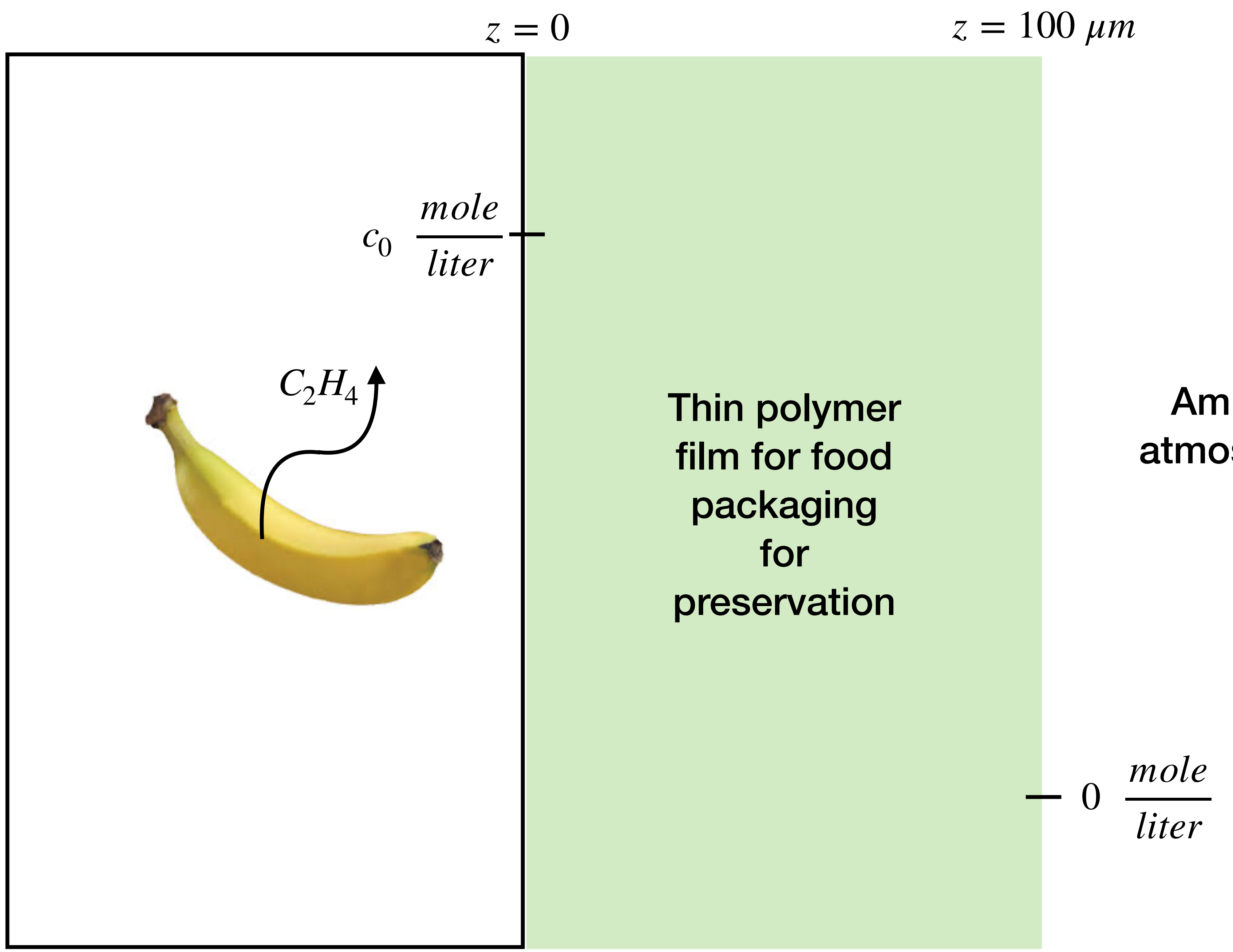
$$D_o = \frac{k_B T}{f}$$



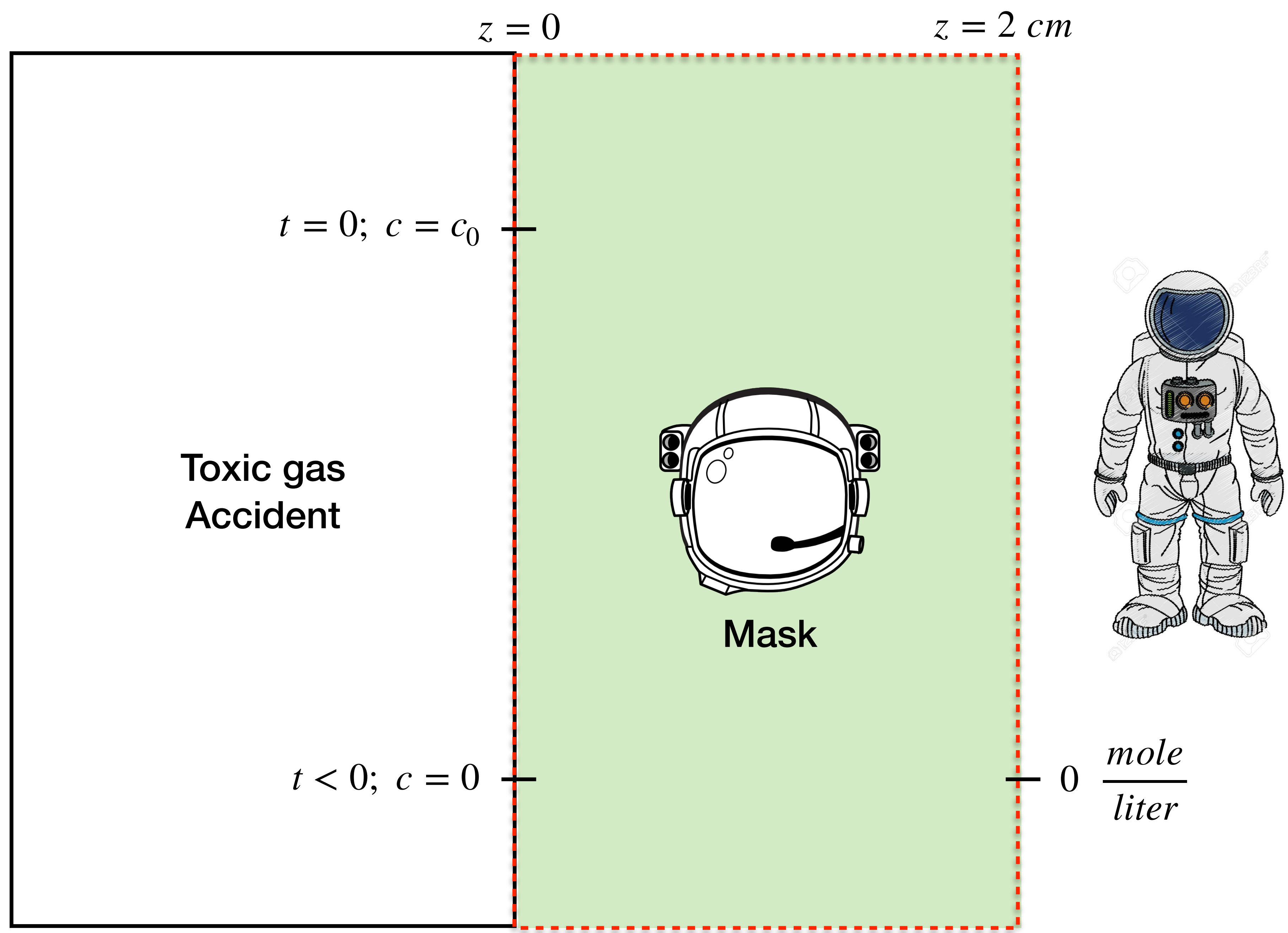
$$N(z,t) = \frac{N_o(t=0, z_0)}{\sqrt{4\pi D_o t}} \exp\left(\frac{-z^2}{4D_o t}\right)$$

$$J = -D\frac{\partial c(x,t)}{\partial x}$$

How can we describe the flux of C_2H_4 from the food packaging film to make sure food is not wasted?

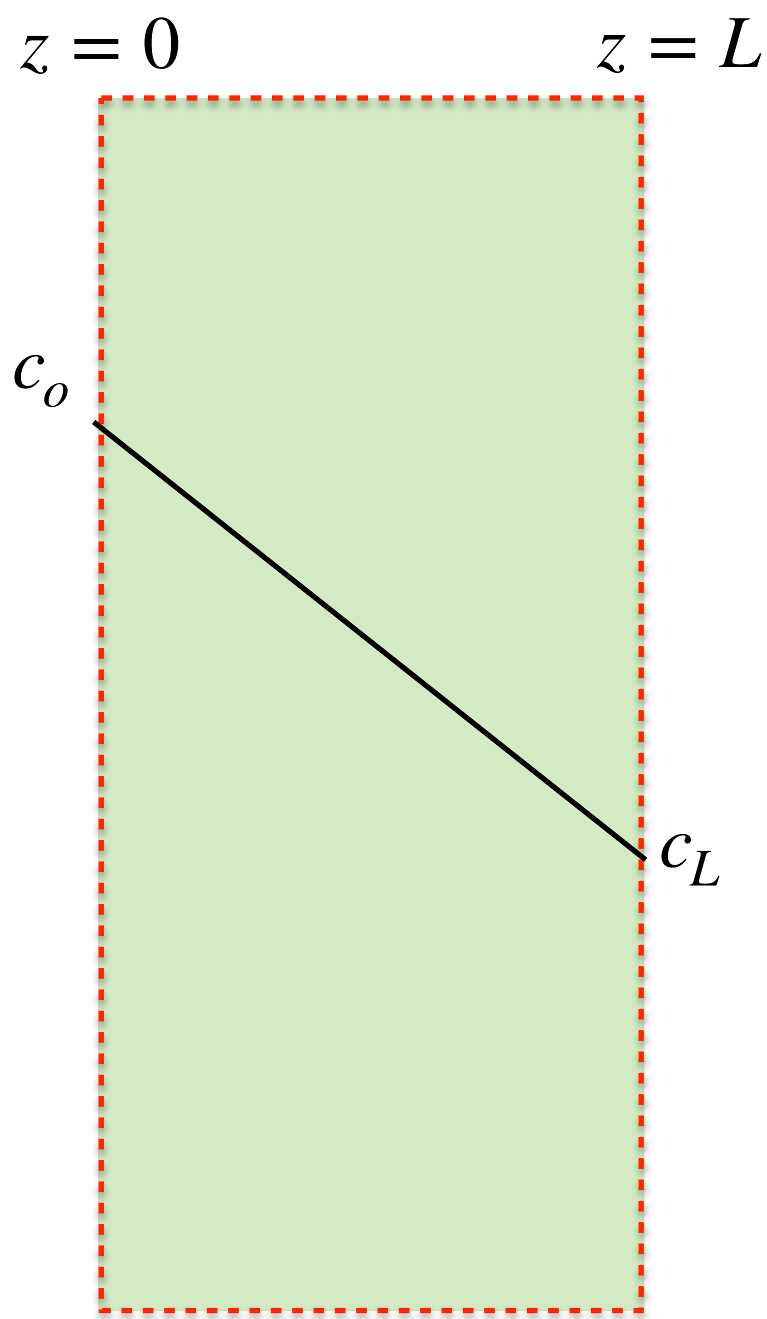


How can we calculate the time that an astronaut has to fix the accident before toxic gas reaches critical concentration, c_{toxic} inside the mask ?



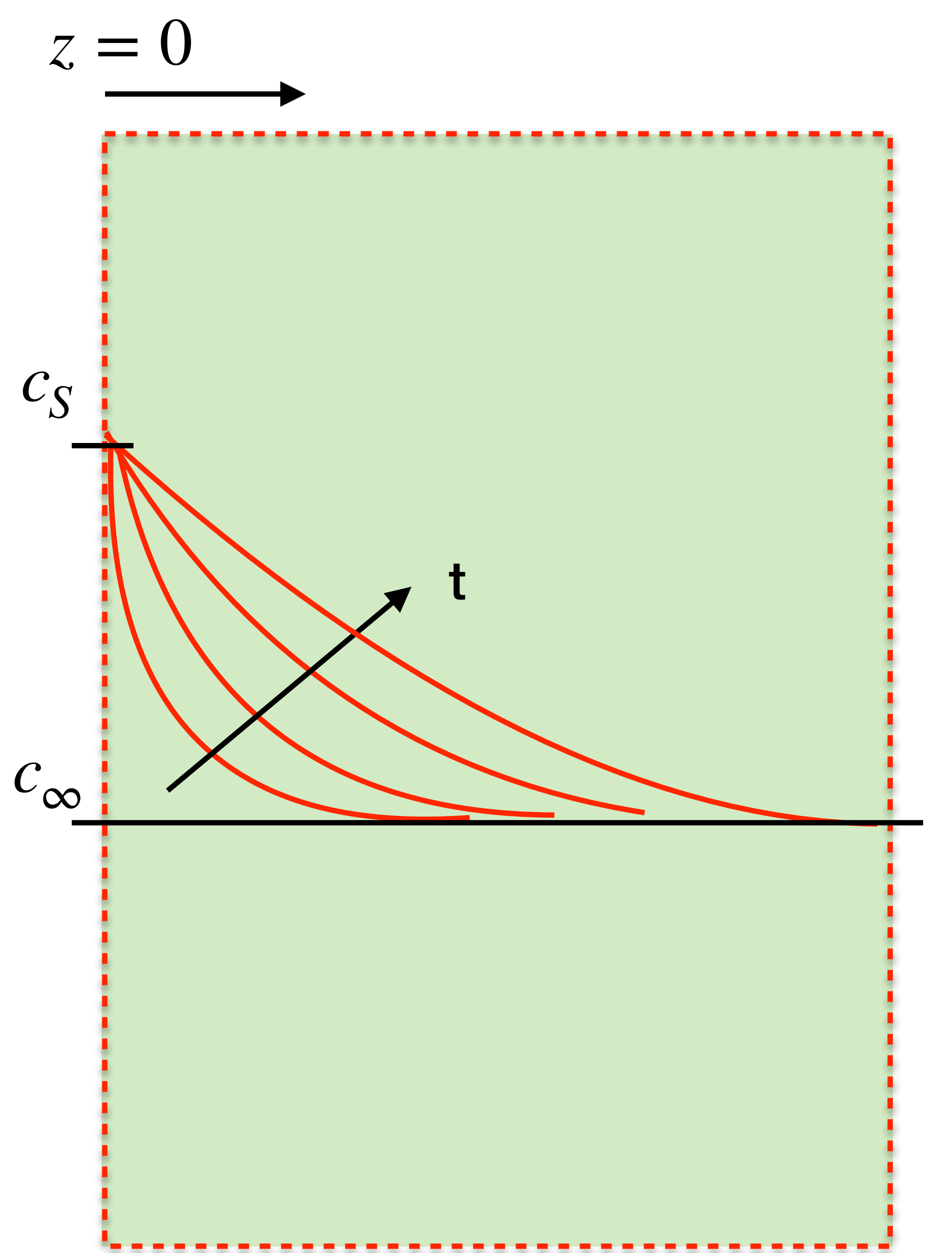
EPFL

Steady-state diffusion across a thin film



- Sensors
- Catalytic films
- Membranes
- Electrochemistry
- Barriers

Transient diffusion across a semi-infinite slab



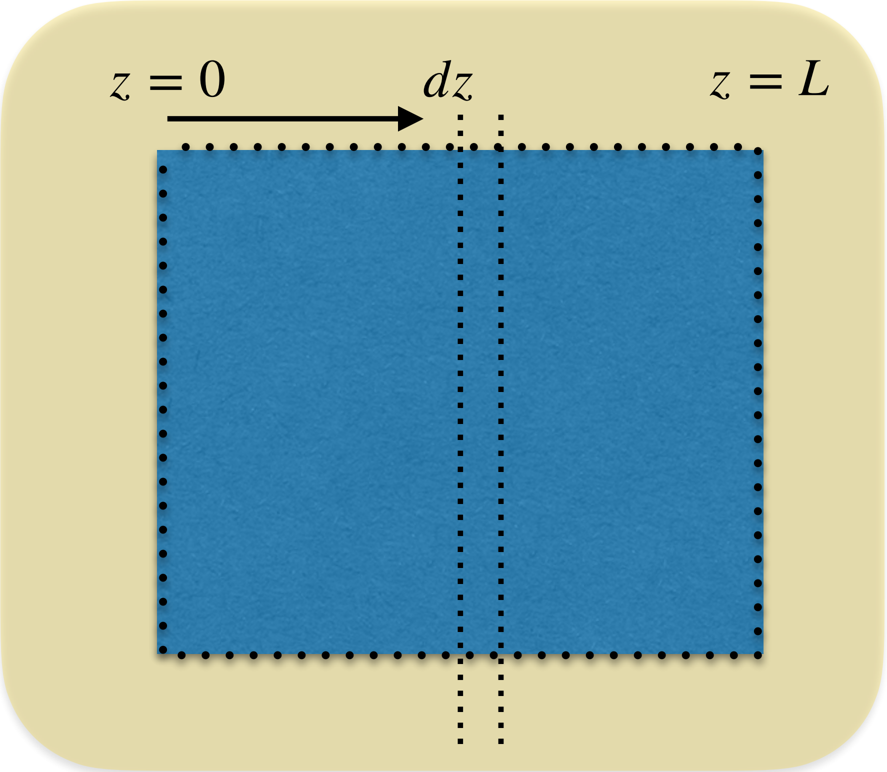
$$\zeta = \frac{z}{\sqrt{4Dt}}$$

EPFL

Approach to solve diffusion problems

1. Define your system.
2. Identify boundary and initial conditions.
3. Choose an element with volume, dV, where you will do mass balance
4. Apply mass balance on the element.
5. Apply transport, reaction and thermodynamic laws in the mass balance.
6. Apply boundary and initial condition.

Diffusion across the blue box



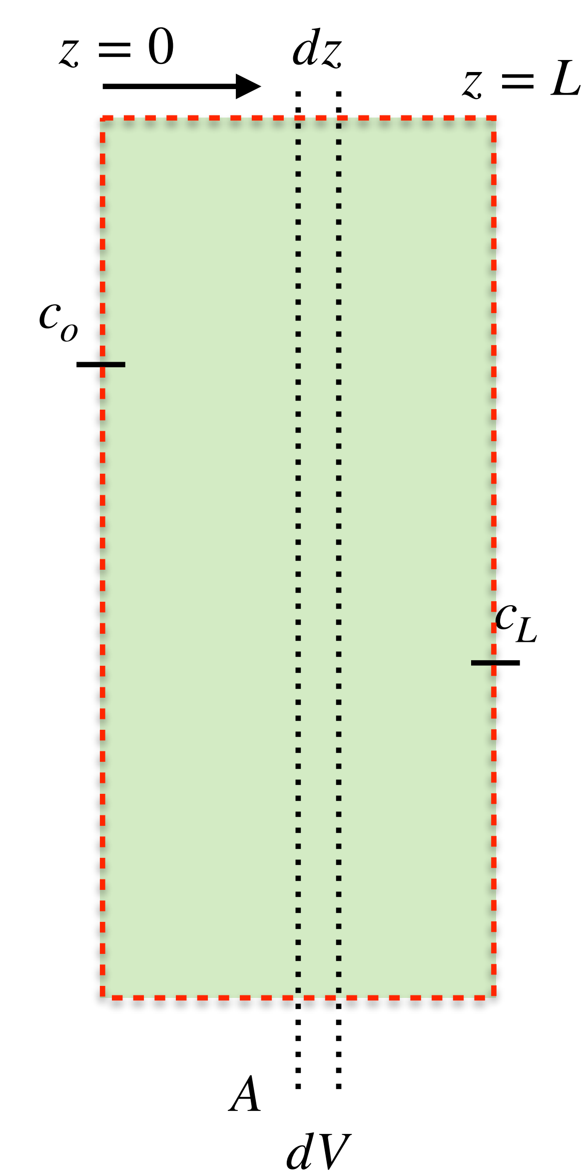
Steady-state diffusion across a thin film - generic case

Define your system: the thin film

2 boundary conditions: $c = c_0 \ at \ z = 0$ $\quad$ $c = c_L \ at \ z = L$

Choose an element with volume, dV, to do mass balance

$$\overset{o}{Accumulation} * dV = \overset{o}{Flux} |_{in} * A - \overset{o}{Flux} |_{out} * A + \overset{o}{Generation} * dV - \overset{o}{Consumption} * dV$$



Concentration is uniform along the width of the film

Cross$-$sectional area = A

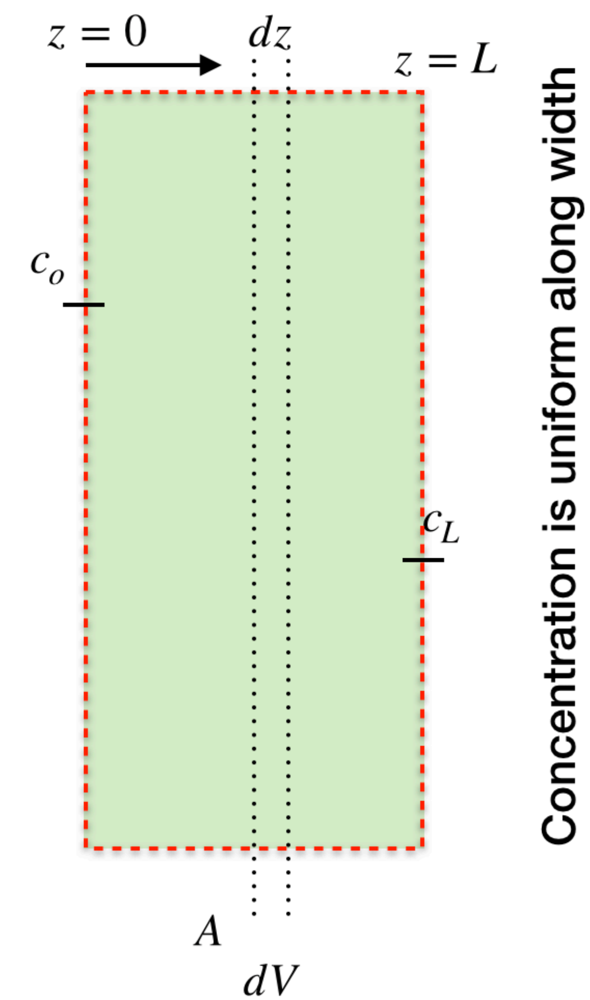
Steady-state diffusion across a thin film - generic case

$$0 = \frac{J\,|_z - J\,|_{z+dz}}{dz}$$

$$0 = -\left(\frac{J\,|_{z+dz} - J\,|_z}{(z+dz) - z}\right) \qquad\qquad 0 = -\frac{d}{dz}J$$

Apply transport law; we can use Fick's law here with constant D

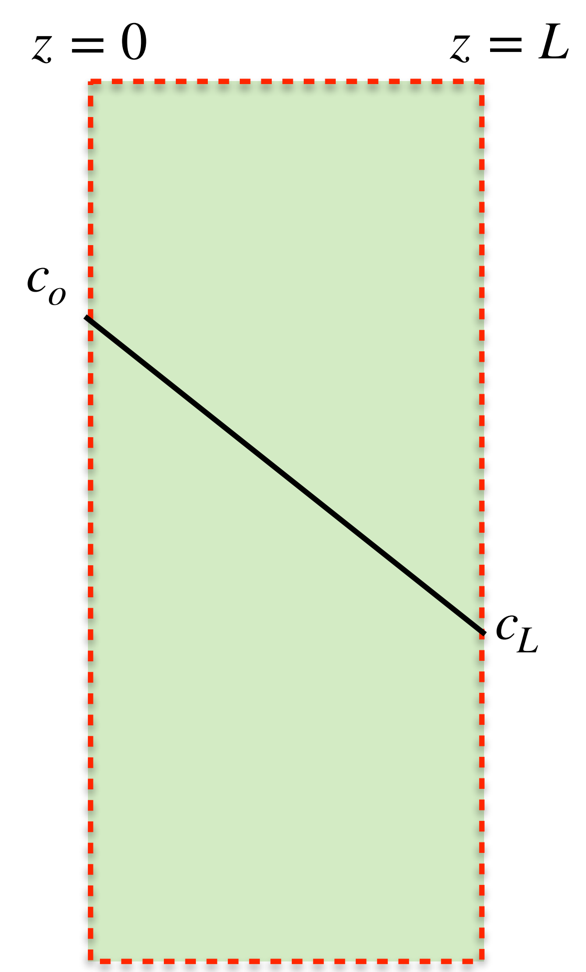
Solve using the 2 boundary conditions $c = c_0\ at\ z = 0$ $\qquad c = c_L\ at\ z = L$



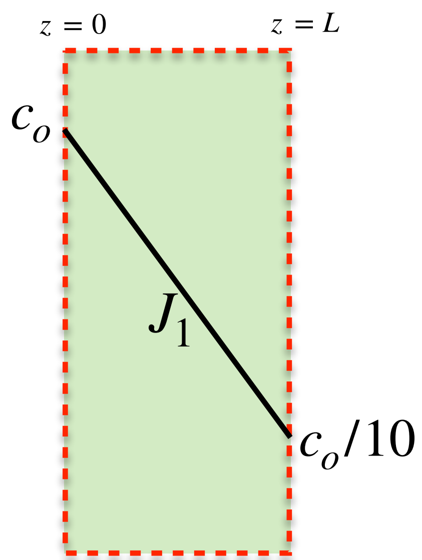
Steady-state diffusion across a thin film - generic case

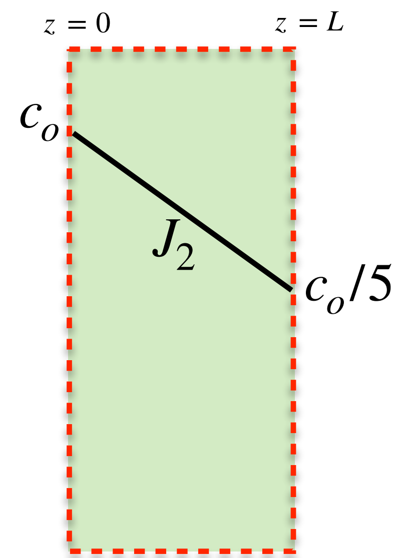
$$c = c_0 + (c_L - c_0)\frac{z}{L}$$

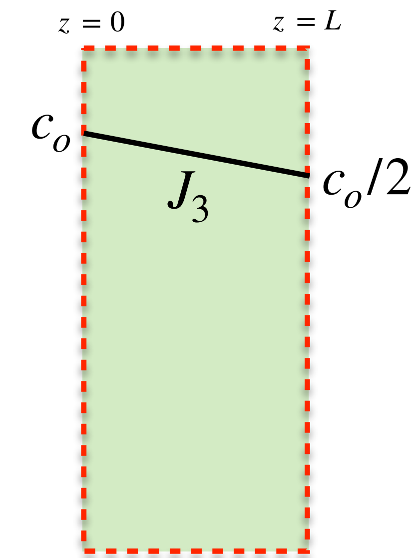
Can you calculate flux, J ?



Rank the flux when the diffusivity is same in all cases.







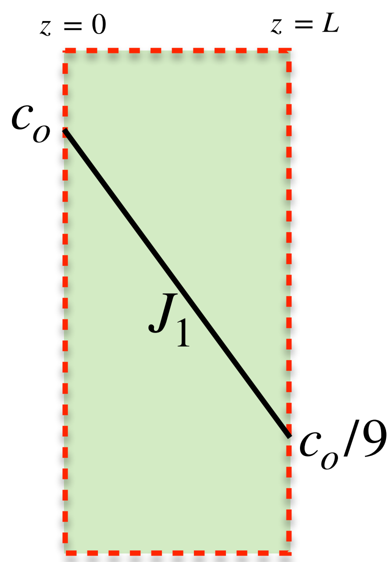
A) $J_1 = J_2 = J_3$

B) $J_1 > J_2 > J_3$

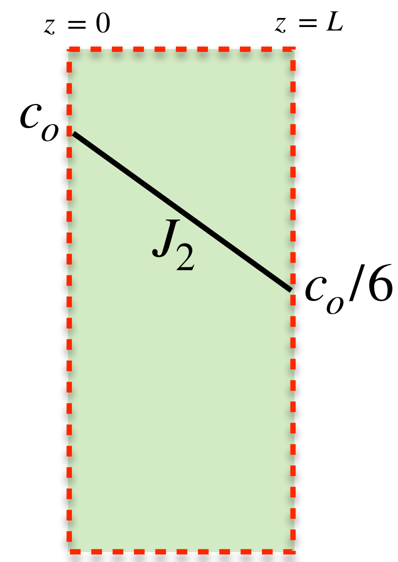
C) $J_1 < J_2 < J_3$

D) Not sufficient evidence

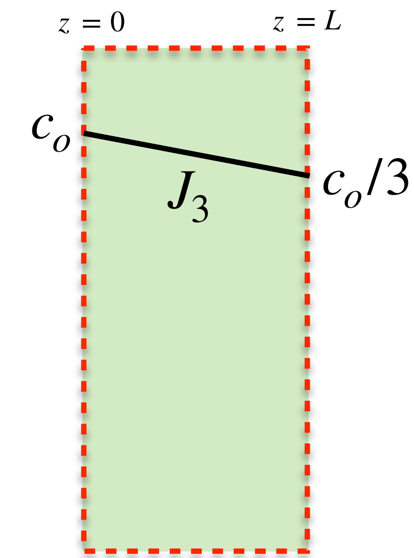
Rank the flux when the diffusivity is not same in all cases.



$D = \frac{1}{8} D_o$



$D = \frac{2}{15} D_o$



$D = \frac{1}{6} D_o$

A) $J_1 = J_2 = J_3$

B) $J_1 > J_2 > J_3$

C) $J_1 < J_2 < J_3$

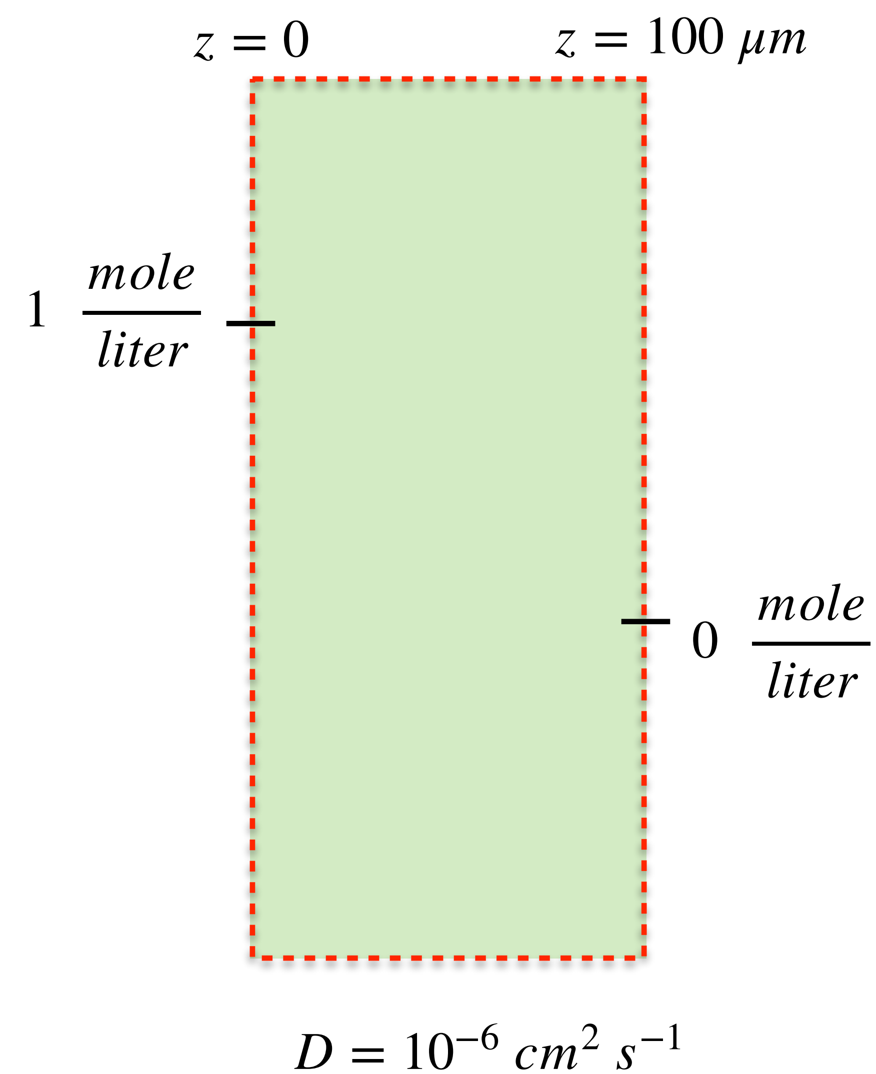
D) Not sufficient evidence

Steady-state diffusion across a thin film - generic case

For the following case, calculate

1) **Concentration at z = 30 and 70 μm**
2) **Flux at z = 30 and z = 70 μm**

$D = 10^{-6}\ cm^2\ s^{-1}$



Steady-state diffusion across a thin membrane

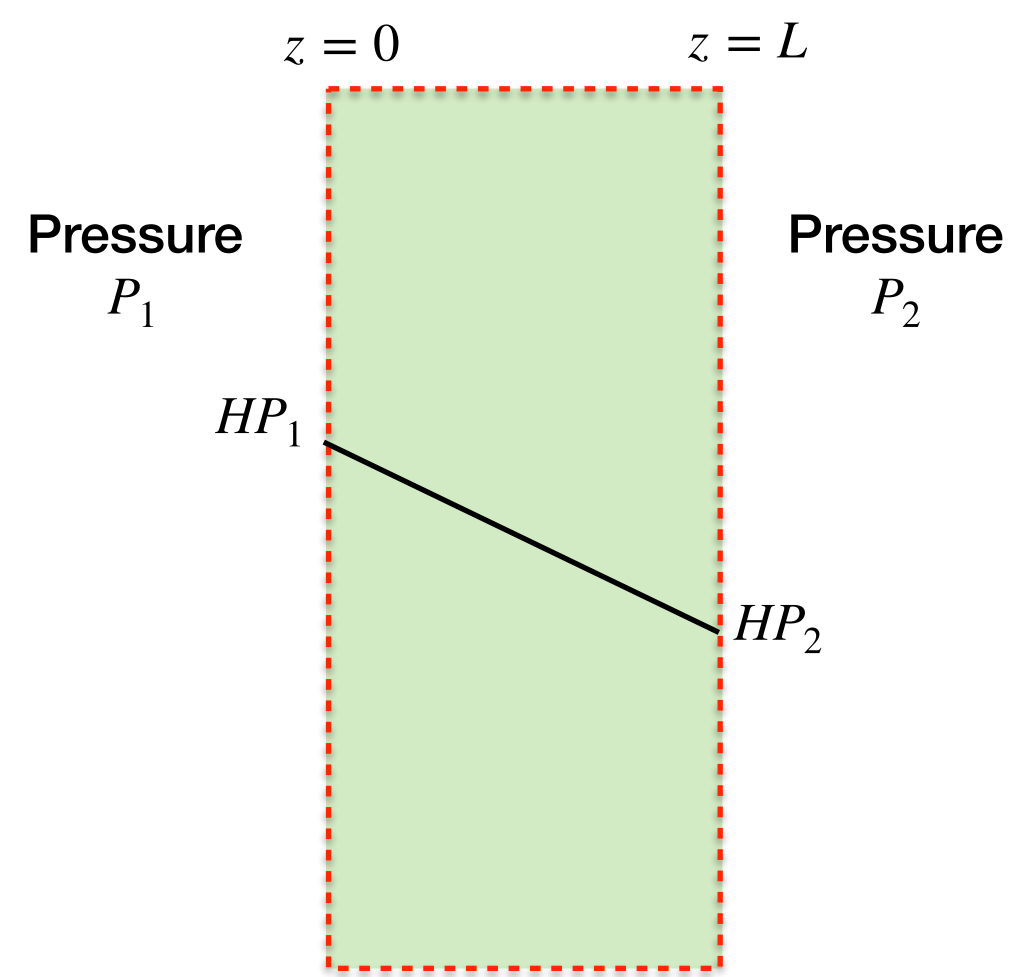
Additional considerations here:
What is the difference with the previous case ?

How would you solve this problem?

Apply thermodynamics to calculate boundary conditions

For dilute case, one can use Henry's law of adsorption

$$c\,|_{z=0} = HP_1 \qquad\qquad c\,|_{z=L} = HP_2$$



Can you derive the rest??

$$c = c_0 + (c_L - c_0)\frac{z}{L} = HP_1 + H(P_2 - P_1)\frac{z}{L}$$

$$J = -D\frac{dc}{dz} = D\frac{(c_0 - c_L)}{L} = D\frac{(HP_1 - HP_2)}{L} = constant$$

EPFL

Calculate c_i at the steady–state

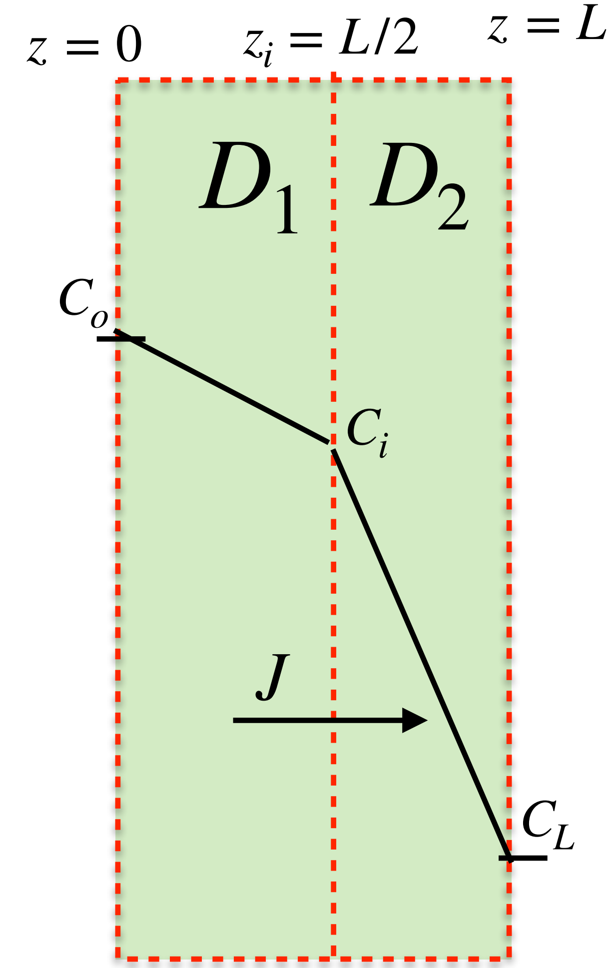
$$J = J_{left} = J_{right}$$

$$-D_1 \frac{(c_0 - c_i)}{z_i} = - D_2 \frac{(c_i - c_L)}{z_L - z_i}$$

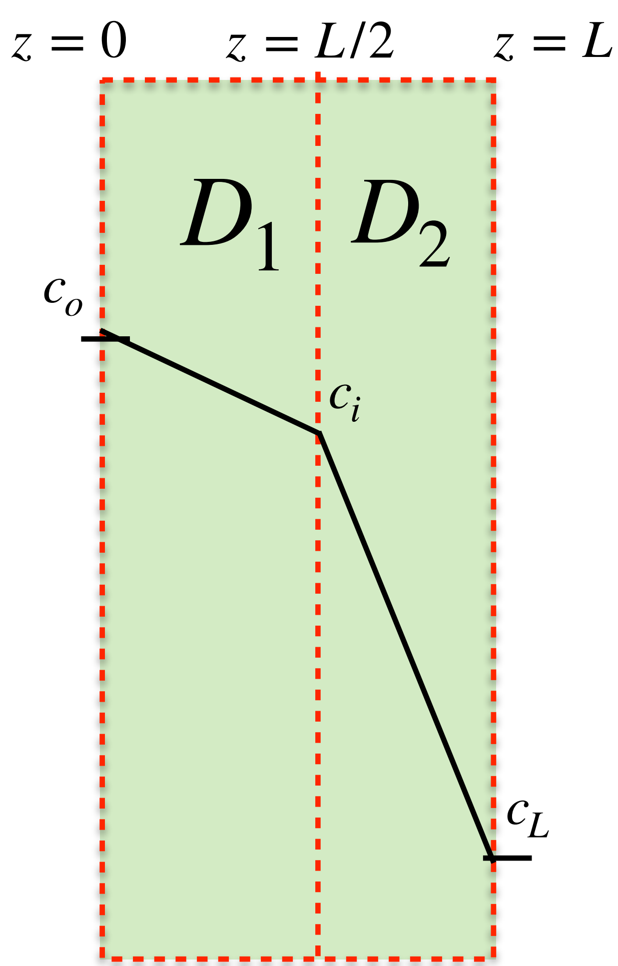
$$\Rightarrow c_0 - c_i = (c_i - c_L)\left(\frac{D_2}{D_1} \; \frac{z_i}{z_L - z_i}\right)$$

$$= (c_i - c_L)\left(\frac{D_2}{D_1}\right)$$

$$\Rightarrow c_i = \frac{c_o + c_L\left(\frac{D_2}{D_1}\right)}{1 + \left(\frac{D_2}{D_1}\right)}$$



What is the relation between D_1 and D_2 at the steady state?



A) $D_1 = D_2$

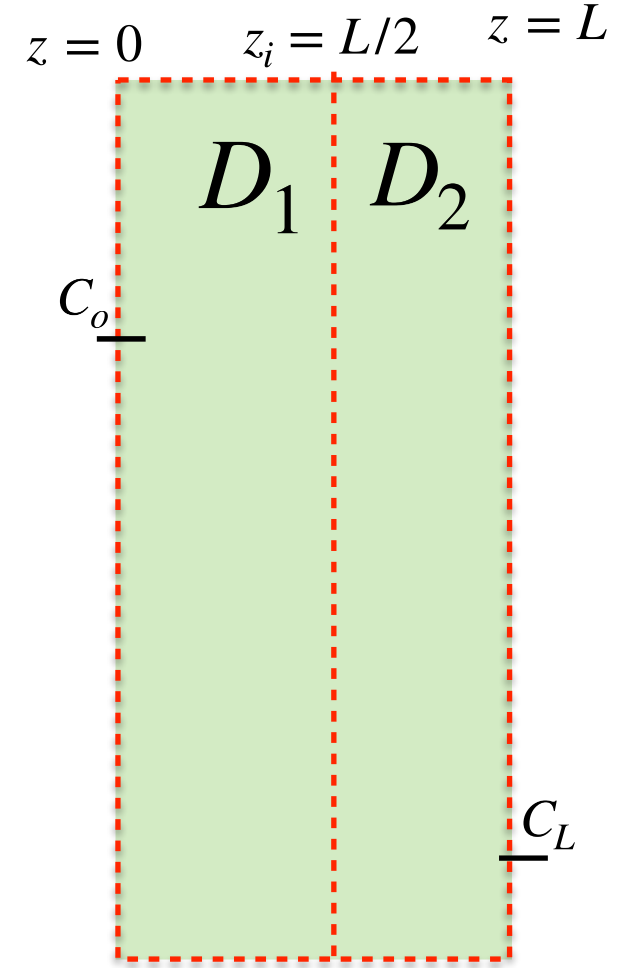
B) $D_1 > D_2$

C) $D_1 < D_2$

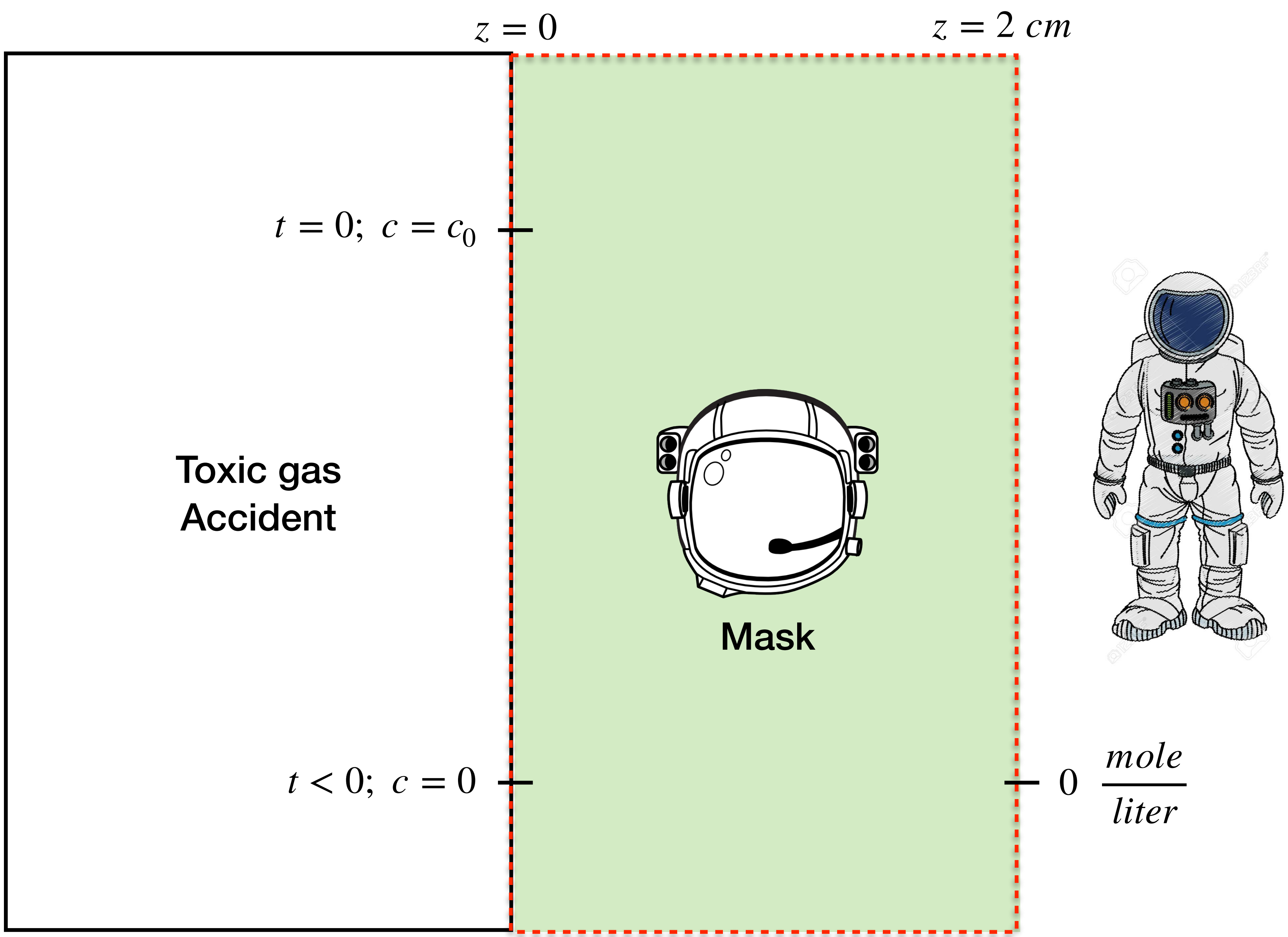
D) Not sufficient evidence

Draw concentration profiles at steady-state:

$$D_1 = 0.05\ \mathrm{cm^2/s},\ \ D_2 = \infty$$



How can we calculate the time that an astronaut has to fix the issue before toxic gas reaches toxic concentration, c_{toxic}



Transient diffusion across a semi-infinite slab

Initial condition: $t = 0, \; c = c_\infty$

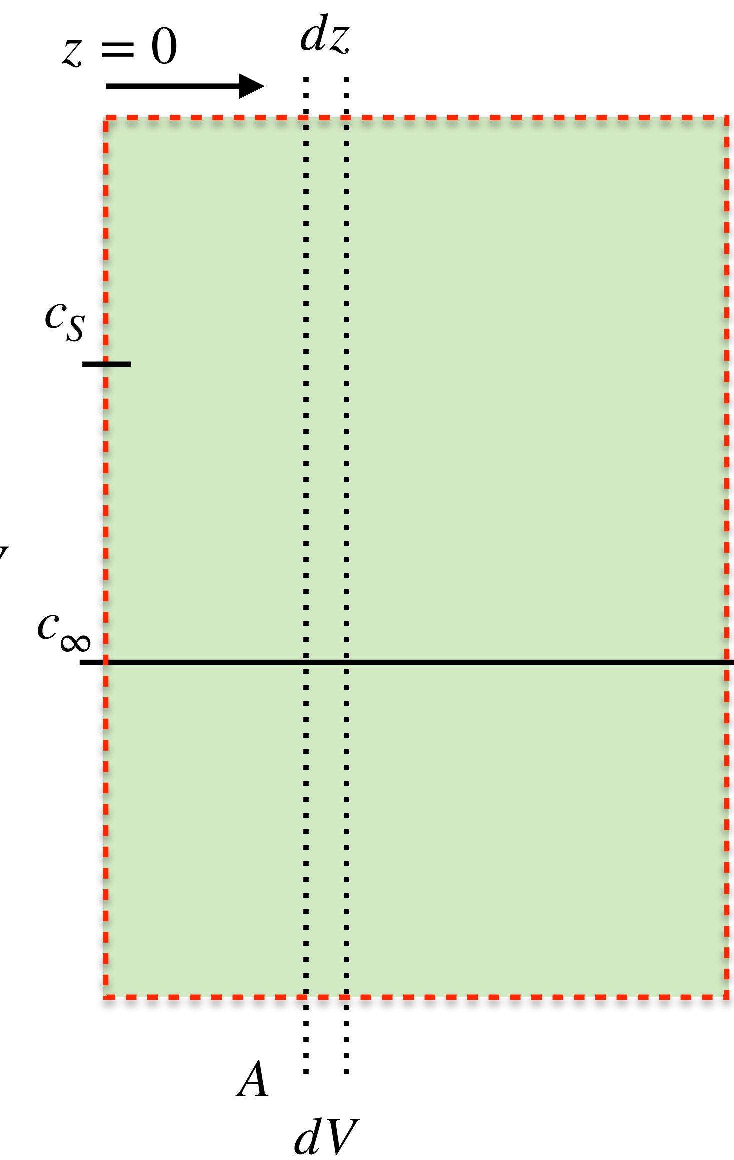
The concentration at left face (z= 0) is suddenly raised to C_s at t=0

Define your system: The slab

Define an elemental volume to do mass balance: dV = Adz

Apply mass balance

$$\overset{o}{Accumulation} * dV = \overset{o}{Flux}\,|_{in} * A - \overset{o}{Flux}\,|_{out} * A + \overset{o}{Generation} * dV - \overset{o}{Consumption} * dV$$



Boundary conditions:

Transient diffusion across a semi-infinite slab

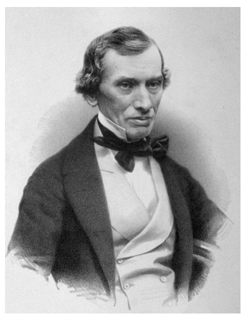
$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2}$$

Initial condition: $t = 0, \; c = c_\infty$

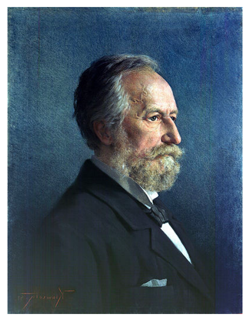
Boundary conditions: $t > 0 \quad c\,|_{z=0} = c_S; \; c\,|_{z=\infty} = c_\infty$

Search of solution:

Fourier



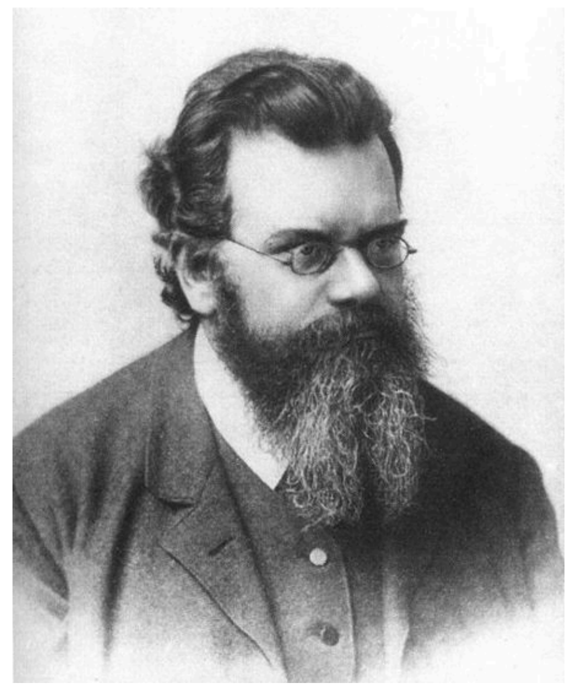
Graham



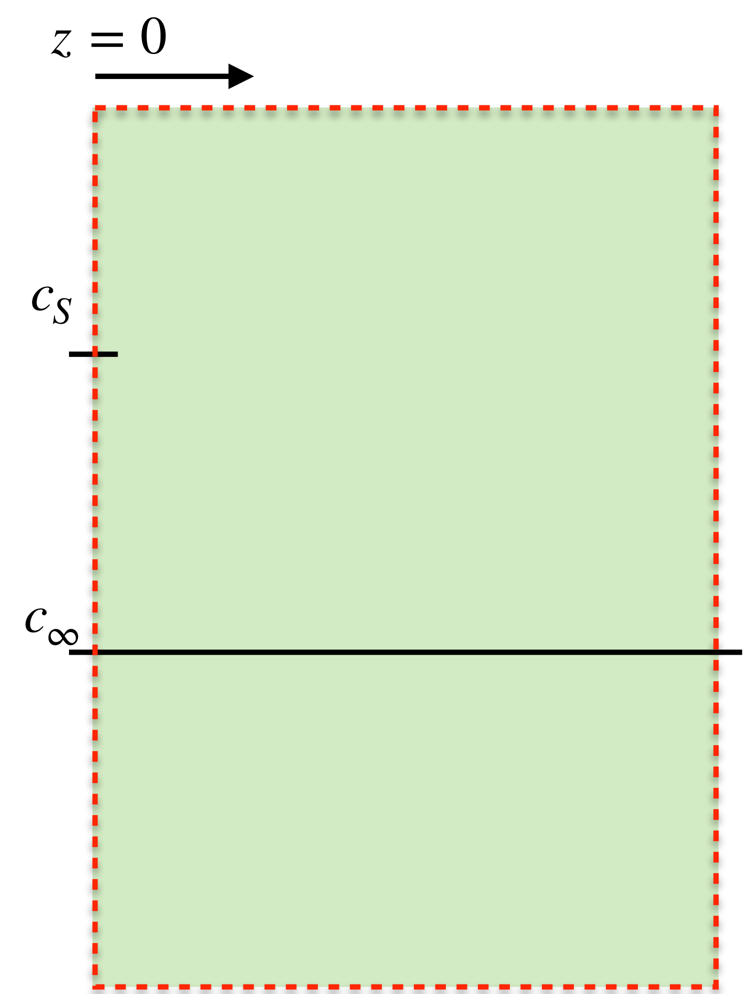
Fick

$$\zeta = \frac{z}{\sqrt{4Dt}} \qquad c = c(\zeta)$$

$$\Rightarrow \frac{dc}{d\zeta}\left(\frac{\partial \zeta}{\partial t}\right) = D\frac{d^2c}{d\zeta^2}\left(\frac{\partial \zeta}{\partial z}\right)^2$$



Ludwig Boltzmann
using combination of variable



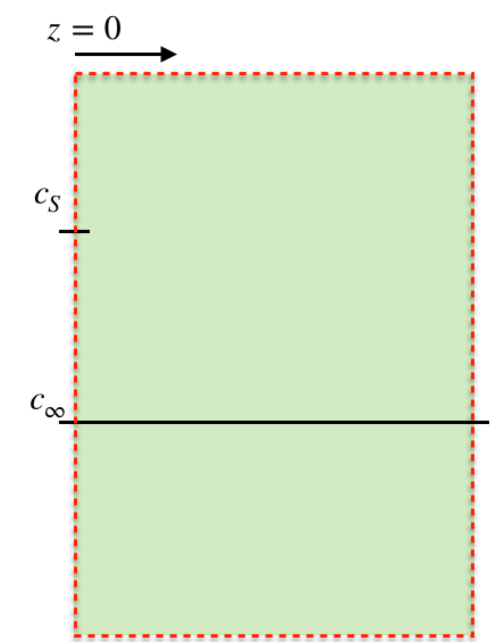
$$\Rightarrow \frac{dc}{d\zeta}\left(\frac{z}{-2t\sqrt{4Dt}}\right) = D\frac{d^2c}{d\zeta^2}\left(\frac{1}{\sqrt{4Dt}}\right)^2$$

$$\Rightarrow \frac{d^2c}{d\zeta^2} + 2\zeta\frac{dc}{d\zeta} = 0$$

EPFL

Transient diffusion across a semi-infinite slab

$$\frac{d^2c}{d\zeta^2} + 2\zeta\frac{dc}{d\zeta} = 0 \qquad\qquad \zeta = \frac{z}{\sqrt{4Dt}}$$



Boundary conditions: $t > 0$

$$c\,|_{z=0} = c_S \qquad\qquad c\,|_{\zeta=0} = c_S;$$

$$c\,|_{z=\infty} = c_\infty \qquad\qquad c\,|_{\zeta=\infty} = c_\infty$$

First Integration

assume $\dfrac{\mathrm{dc}}{\mathrm{d}\zeta} = \mathrm{Q}$ $\quad \Rightarrow \dfrac{dQ}{d\zeta} + 2\zeta Q = 0 \quad \Rightarrow \displaystyle\int \frac{dQ}{Q} = -2\int \zeta d\zeta \quad \Rightarrow \ln Q = -\zeta^2 + \text{constant}$

$$\Rightarrow Q = W\exp(-\zeta^2)$$

2nd Integration

$$\int dc = \int Q d\zeta \qquad \Rightarrow \int dc = \int W\exp(-\zeta^2)d\zeta \qquad \Rightarrow c = \frac{\sqrt{\pi}}{2}W \operatorname{erf}\zeta + \bar{\mathrm{W}}$$

$$\text{where,}\ \operatorname{erf}\zeta = \frac{2}{\sqrt{\pi}}\int_0^\zeta \exp(-\mathrm{r}^2)\mathrm{dr}$$

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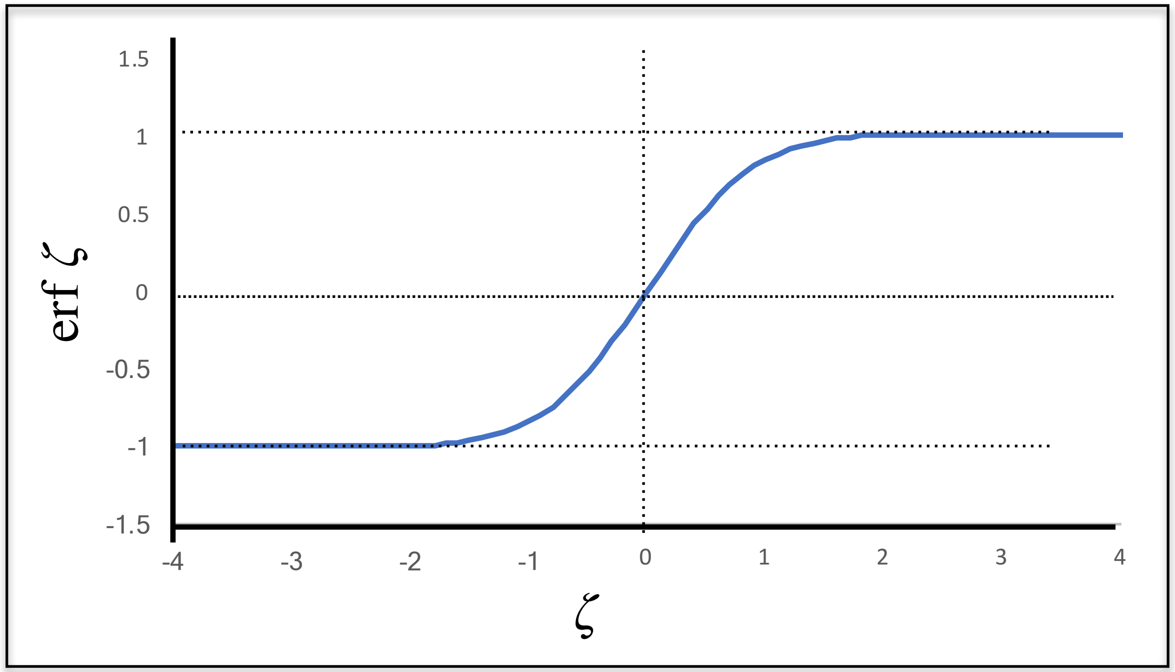
Transient diffusion across a semi-infinite slab

$$c = \frac{\sqrt{\pi}}{2} W \,\mathrm{erf}\,\zeta \;+\; \bar{W}$$

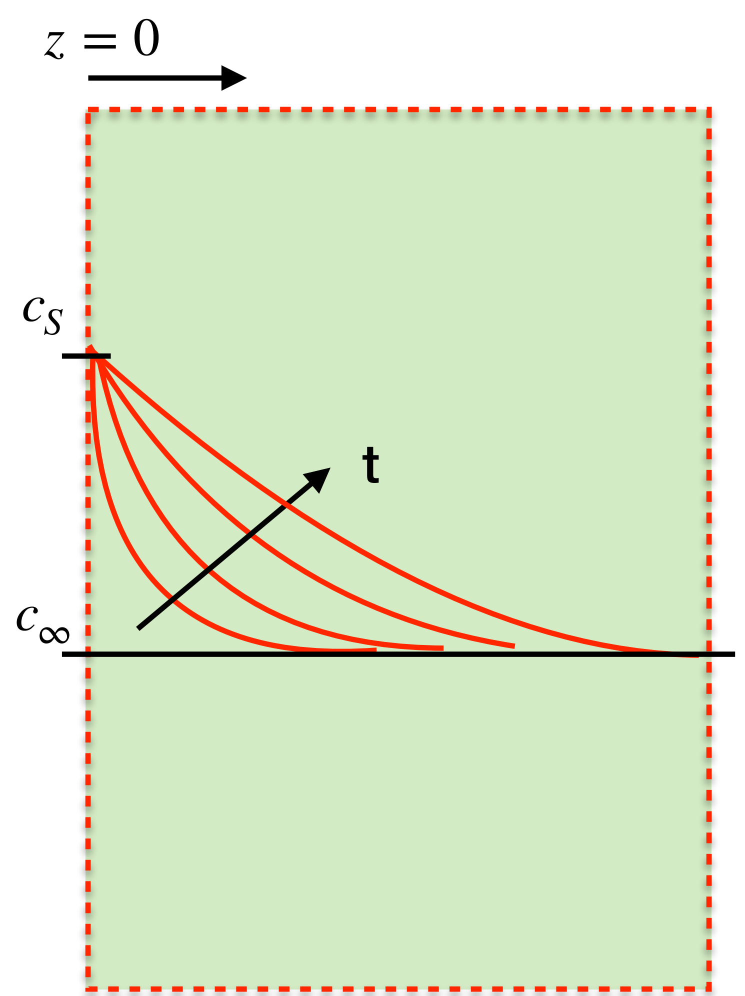
$$erf\,\zeta \;=\; \frac{2}{\sqrt{\pi}} \int_0^{\zeta} \exp(-r^2)dr$$



Boundary conditions:

$$c\;|_{\zeta=0} = \;c_S;$$

$$c\;|_{\zeta=\infty} = \;c_\infty$$



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

Applying boundary conditions

$$\bar{W} = \;c_S$$

$$W \;=\; \frac{2}{\sqrt{\pi}}(c_\infty \;-\; c_S)$$

$$\frac{c(z,t) - c_S}{c_\infty - c_S} = erf\,\zeta \;=\; \frac{2}{\sqrt{\pi}} \int_0^{\zeta} \exp(-r^2)dr$$

$$\frac{c_1 - c_{10}}{c_{1\infty} - c_{10}} \;=\; \mathrm{erf}\,\zeta$$

Calculation of flux for transient diffusion

$$\frac{c(z,t)-c_S}{c_\infty - c_S} = erf\,\zeta = \frac{2}{\sqrt{\pi}}\int_0^\zeta \exp(-r^2)dr$$

$$J = -D\frac{\partial c}{\partial z}$$

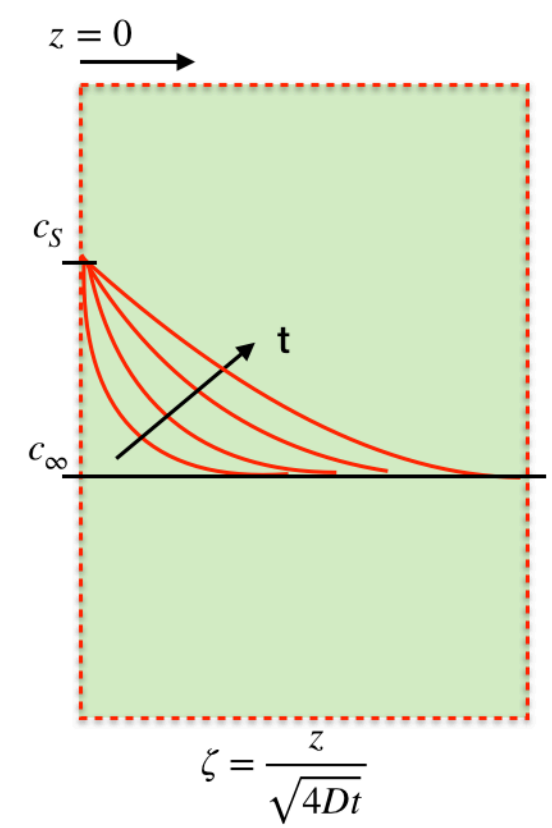
$$\frac{\partial c}{\partial z} = \left(\frac{dc}{d\zeta}\right)\left(\frac{\partial \zeta}{\partial z}\right)$$

$$\frac{dc}{d\zeta} = (c_\infty - c_S)d(erf\,\zeta) = (c_\infty - c_S)\frac{2}{\sqrt{\pi}}\exp\left(-\frac{z^2}{4Dt}\right)$$

$$\zeta = \frac{z}{\sqrt{4Dt}} \qquad \Rightarrow \left(\frac{\partial \zeta}{\partial z}\right) = \frac{1}{\sqrt{4Dt}}$$

$$\Rightarrow \frac{\partial c}{\partial z} = (c_\infty - c_S)\frac{1}{\sqrt{\pi D t}}\exp\left(-\frac{z^2}{4Dt}\right)$$

$$\boxed{\Rightarrow J = -D\frac{\partial c}{\partial z} = -\sqrt{\frac{D}{\pi t}}\,(c_\infty - c_S)\exp\left(-\frac{z^2}{4Dt}\right)}$$



$$J_{z=0} = -\sqrt{\frac{D}{\pi t}}\,(c_\infty - c_S)$$

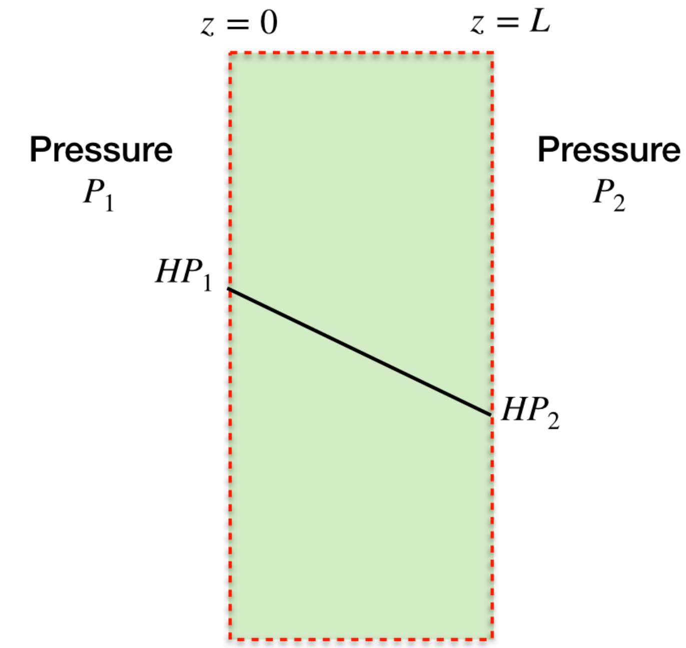
EPFL

Exercise 1: steady-state diffusion across a thin membrane

A plastic bag is designed to increase the shelf life of bananas. It works by removing ethylene responsible for ripening bananas. The bag is made of 1 µm thick polymer film. Assuming that the concentration of ethylene outside the bag (in the room) is zero, and inside the bag is 1 mole%, calculate grams of ethylene that would be removed in 1 day from a bag made of 1 m^2 material. The pressure inside and outside the bag is 1 bar.

$$H = 0.1 \ \frac{mol}{liter\ bar}$$

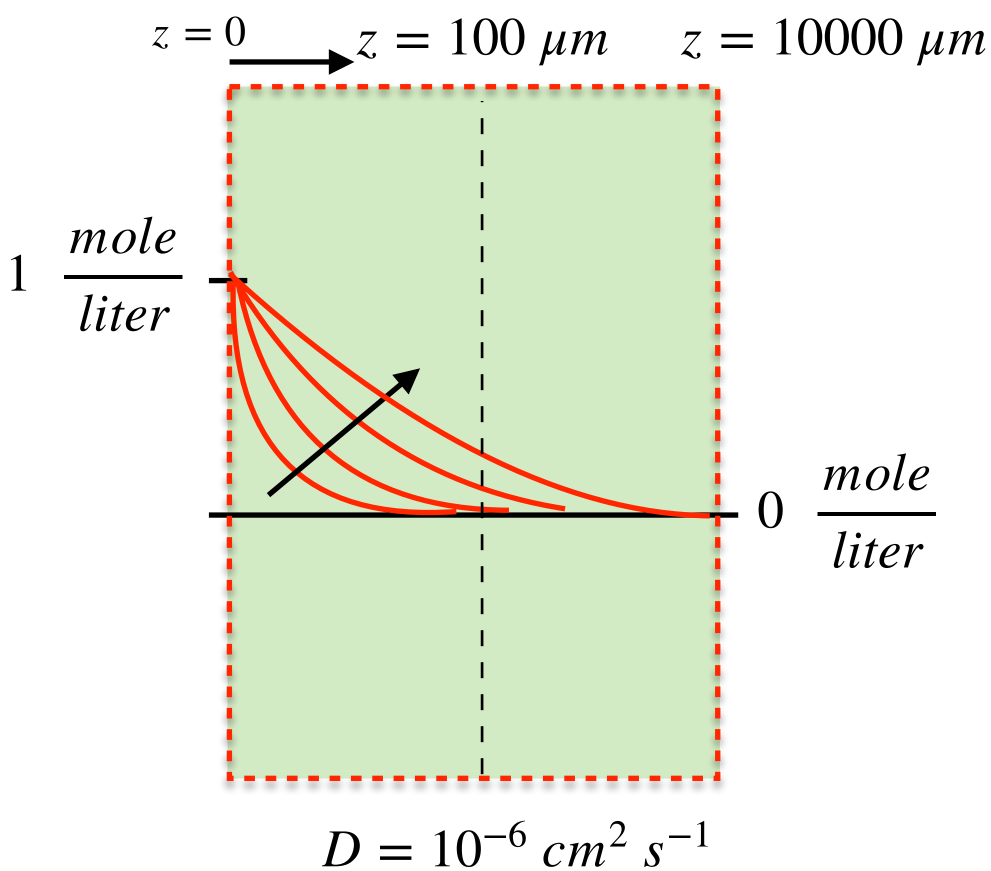
$$D = 10^{-6}\ cm^2\ s^{-1}$$

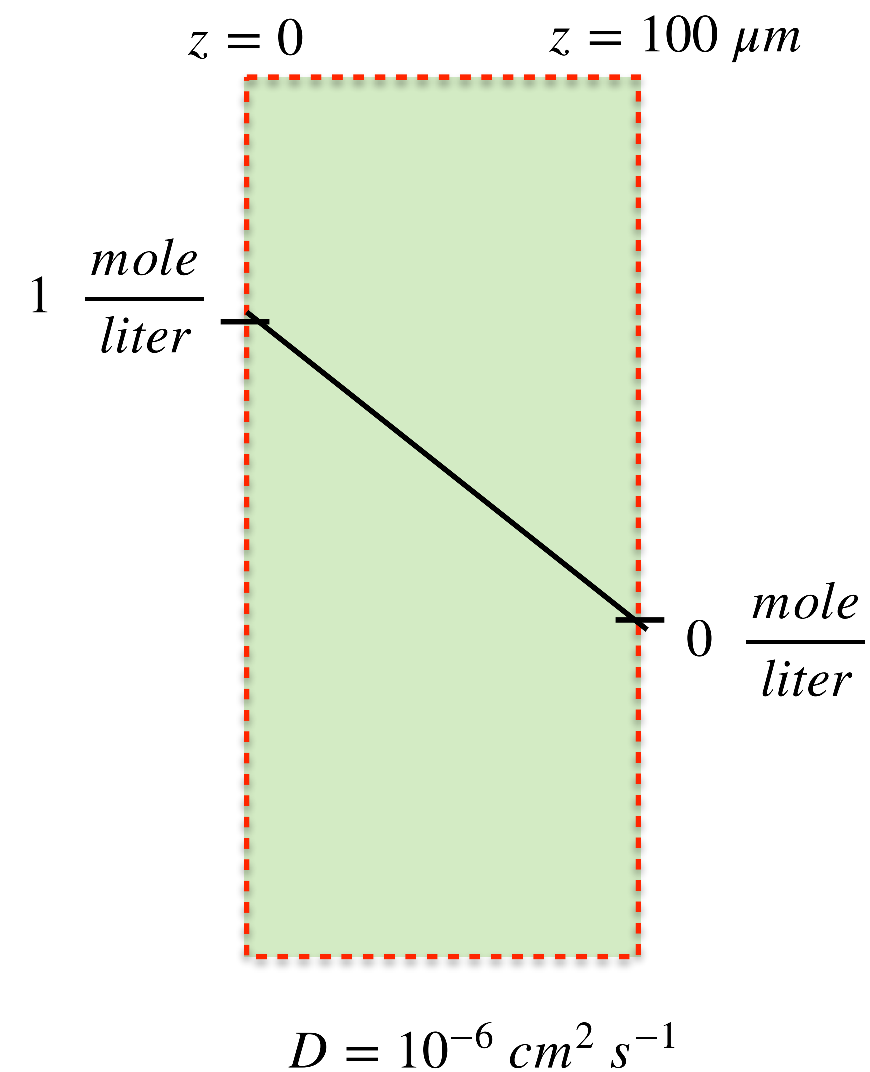


Exercise 2: Compare the flux in transient vs. steady-state case

Calculate flux at z = 100 µm at t = 1 min in the case of transient and steady-state.

$$J = -D\frac{\partial c}{\partial z} = -\sqrt{\frac{D}{\pi t}}\,(c_\infty - c_S)\,\exp\left(-\frac{z^2}{4Dt}\right)$$





Exercise 3

Calculate c_i at the steady–state if $D_2 = 6D_1$

$c_o = 10$ mole/L $c_L = 0$

Draw the concentration profile