CHAPTER 27: UNSTEADY STATE MOLECULAR DIFFUSION

27.1 Unsteady-State (USS) Molecular Diffusion and Fick's Second Law

Introduction & Definitions

Recall from topic 25.2 & 25.3:

Differential Equation of Mass Transfer
(Fick's Second Law of Diffusion)

$$D_{AB}\frac{\partial^2 C_A(z,t)}{\partial z^2} = \frac{\partial C_A(z,t)}{\partial t}$$

- The box is the system boundary
- 1-D diffusion along z
- Unsteady state diffusion process
- Constant D_{AB}
- No generation or consumption of A ($R_A = 0$)

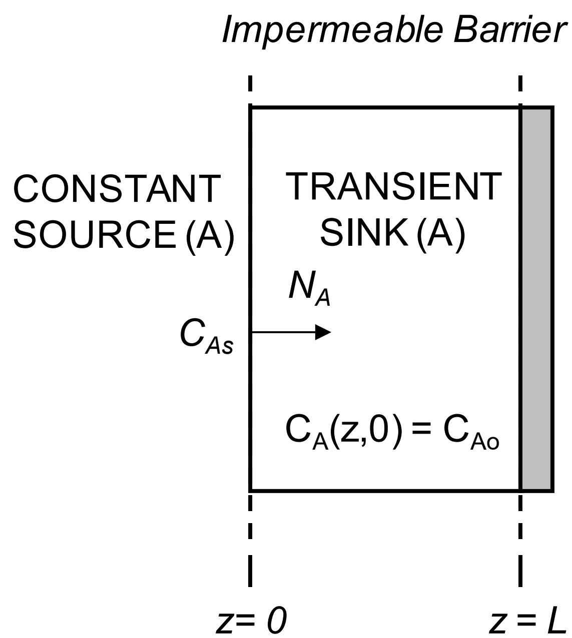
Boundary & Initial Conditions:

$t = 0$, all z $\quad C_A(z,0) = C_{Ao}$

$z = 0$ for all $t>0$ (surface) $C_A(0,t) = C_{As}$

$z = L$ for all $t>0$ (symmetry or impermeable barrier), no flux of A

$$N_A(L,t) = \partial C_A(L,t)/\partial z = 0$$



For an UNSTEADY STATE Diffusion process

- The Control Volume of the System itself serves as a TRANSIENT SOURCE or a TRANSIENT SINK for thermal energy

- The concentration of species A (C_A) within the System Control Volume will vary with *position* and *time* (t) until STEADY STATE or EQUILBRIUM is achieved

What are the various forms of Fick's Second Law?

Recall the Differential Equation for Mass Transfer

$$-\nabla N_A + R_A = \frac{\partial C_A}{\partial t}$$

Under these simplifications:

- no homogeneous chemical reaction ($R_A = 0$)
- binary mixture of species "A" and "B" (A is the diffusing species, B is the medium for diffusion)
- EMCD or dilute UMD molecular diffusion ($N_A = -D_{AB}\nabla C_A$)
- Uniform initial concentration within the control volume at time t = 0
- Boundary conditions which do not change with time
- Constant D_{AB}, constant total molar concentration C

Differential Equation for Mass Transfer simplifies to *Fick's Second Law*:

$$-\nabla N_A = -\nabla(-D_{AB}\nabla C_A) = \nabla^2 C_A = \frac{\partial C_A}{\partial t}$$

One-dimensional flux in rectangular (slab), cylindrical, and spherical geometry

$$slab: \quad D_{AB}\frac{\partial^2 C_A(z,t)}{\partial z^2} = \frac{\partial C_A(z,t)}{\partial t}$$

$$cylinder: \quad D_{AB}\left[\frac{\partial^2 C_A(r,t)}{\partial r^2} + \frac{1}{r}\frac{\partial C_A(r,t)}{\partial r}\right] = \frac{\partial C_A(r,t)}{\partial t}$$

$$sphere: \quad D_{AB}\left[\frac{\partial^2 C_A(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C_A(r,t)}{\partial r}\right] = \frac{\partial C_A(r,t)}{\partial t}$$

Analytical solutions for C_A as a function of position and time are available in two forms:

1. Semi-infinite medium: "Error Function" type solution by the Method of Combination of Variables (semi-infinite boundary conditions)
2. Finite-dimensional medium: "Convergent Infinite Series" solution by Method of Separation of Variables (finite boundary conditions)

What Makes a Diffusion Process Unsteady State?

If the process is *unsteady state*, then:

- The numerical values of the terms
  $\nabla N_A \quad and \quad \frac{\partial C_A}{\partial t}$ are comparable
- The concentration profile C_A and flux N_A change with time under *Equilibrium* or *Steady State* is achieved

- The control volume itself serves as a SOURCE or a SINK for mass transfer

  Move from USS Condition to Equilibrium Condition:
  If the Control Volume serves as the only SOURCE, then
  · Concentration C_A is highest at line of symmetry (or impermeable barrier)
  · Concentration profile will decrease toward a single equilibrium value uniform with the boundary
  · Flux $N_A\,(z,t)$ at all positions will go to zero at long times

  If the Control Volume serves as the only SINK, then
  · Concentration C_A is lowest at line of symmetry (or impermeable barrier)
  · Concentration profile will increase toward a single equilibrium value uniform with the boundary
  · Flux $N_A\,(z,t)$ at all positions will go to zero at long times

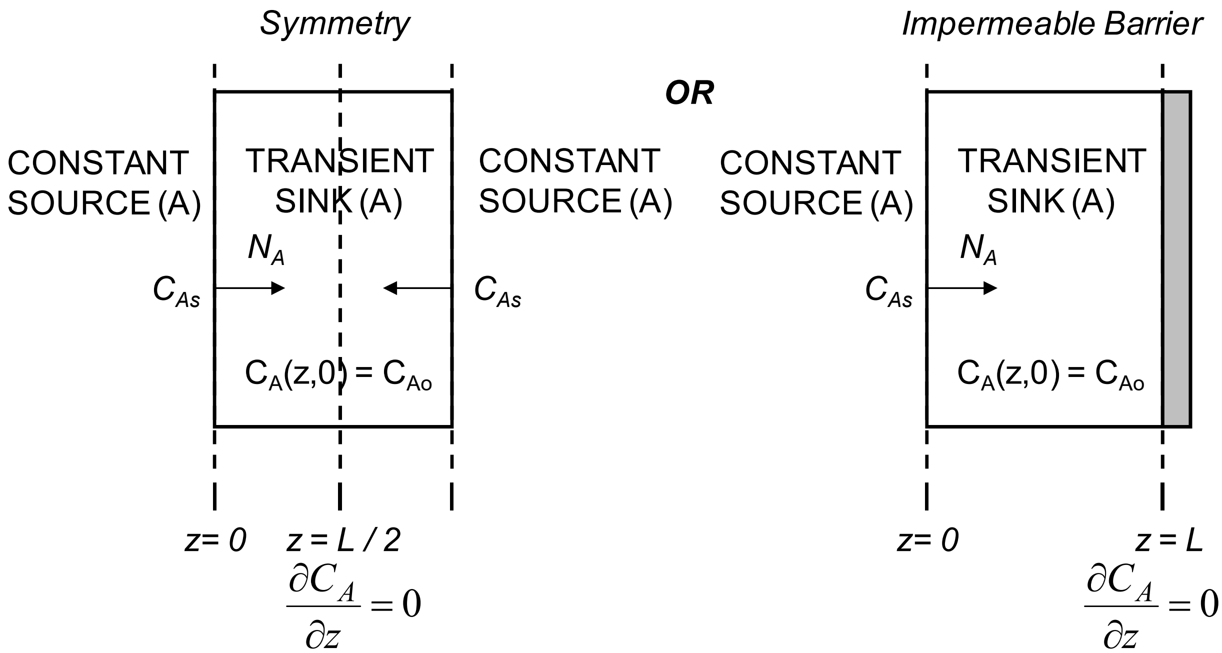
  Move from USS Condition to Steady-State Condition:
  If the Boundary serves as a CONSTANT SOURCE and the Control Volume also serves as a TRANSIENT SOURCE or a SINK, then
  · The concentration profile is asymmetric
  · Uniform concentration profile (the steady-state concentration profile) is established within the control volume
  · Flux N_A at a given position approaches steady-state at long times

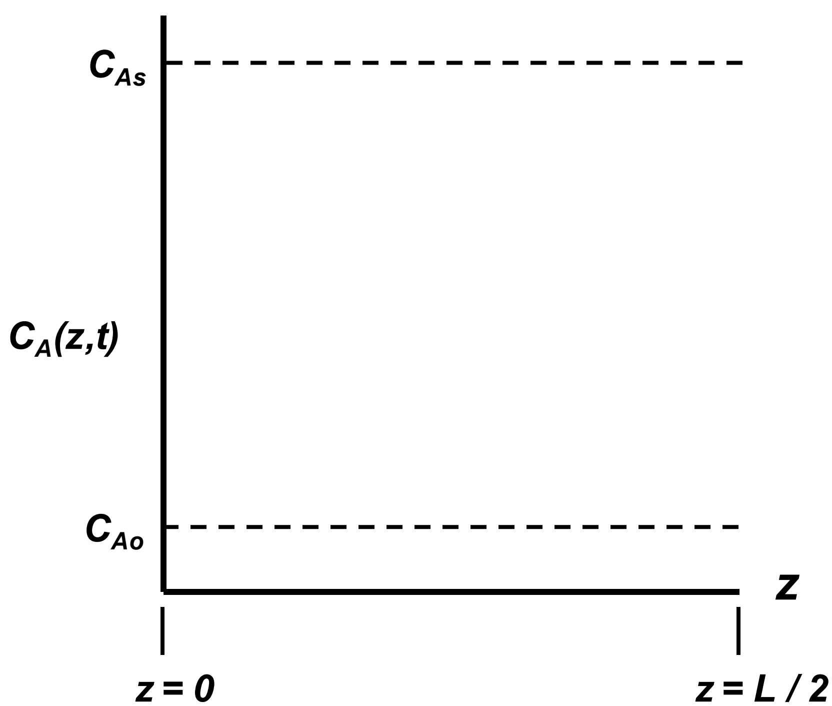
- In real systems, USS diffusion processes usually involve solid material which physically defines the shape of the control volume, e.g.
  · A fluid mixture (gaseous or liquid) diffusing within a porous solid (very common, especially for heterogeneous catalysts)
  · A solute diffusing within a solid material or "semi-solid" pseudo homogeneous material (e.g. gel, water-saturated soil, biological tissue)

27.1a USS Diffusion to Equilibrium (Finite Dimensional System)

Constant SOURCE for "A" at System Boundary

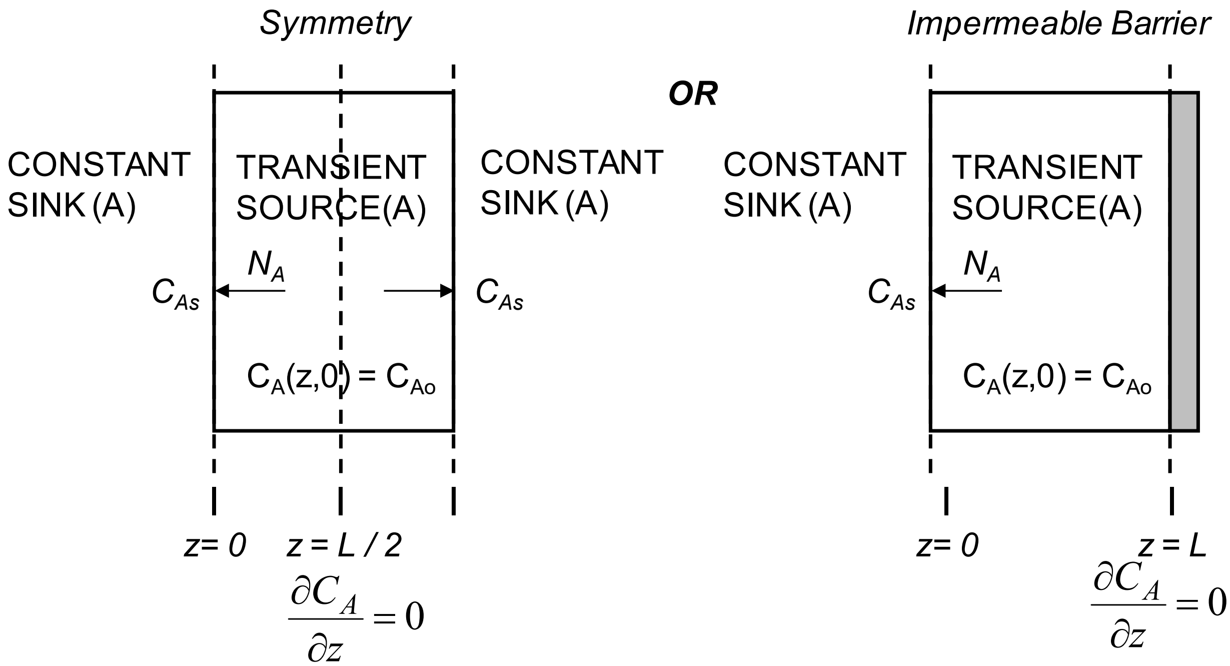
- System Control Volume = TRANSIENT SINK for A, $C_A(x,0) = C_{Ao} < C_{As}$
- Surroundings = CONSTANT SOURCE for A (maintained at C_{As})
- Symmetry at $z = L/2$ or impermeable barrier at $z = L$
- At time $t \rightarrow \infty$, $C_A(z,t) \rightarrow C_{As}$ (equilibrium condition)

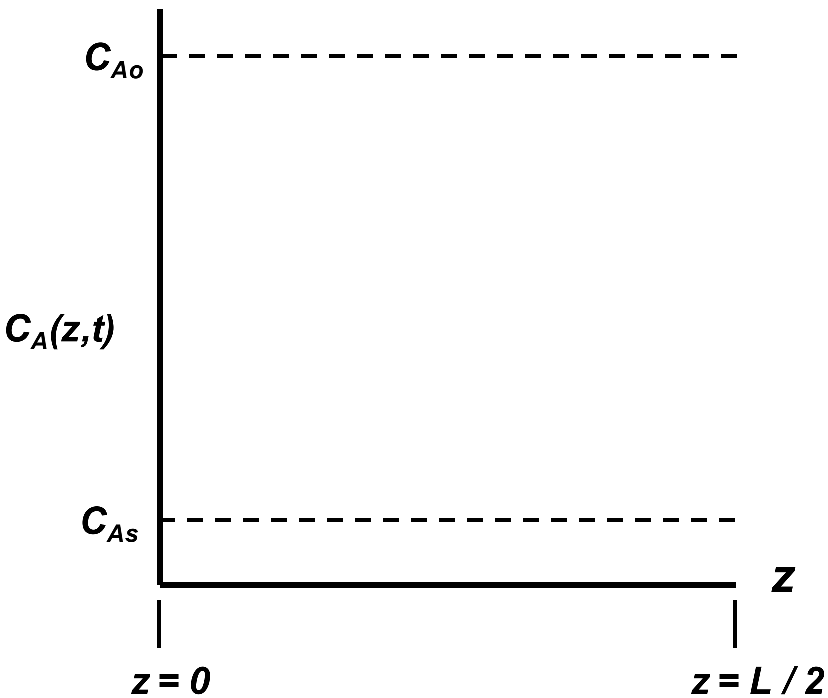




Constant SINK for "A" at System Boundary

- System Control Volume = TRANSIENT SOURCE for A $C_A(x,0) = C_{Ao} > C_{As}$
- Surroundings = CONSTANT SINK for A (maintained at C_{As})
- Symmetry at $z = L/2$ or impermeable barrier at $z = L$
- At time $t \rightarrow \infty$, $CA(z,t) \rightarrow C_{As}$ (equilibrium condition)

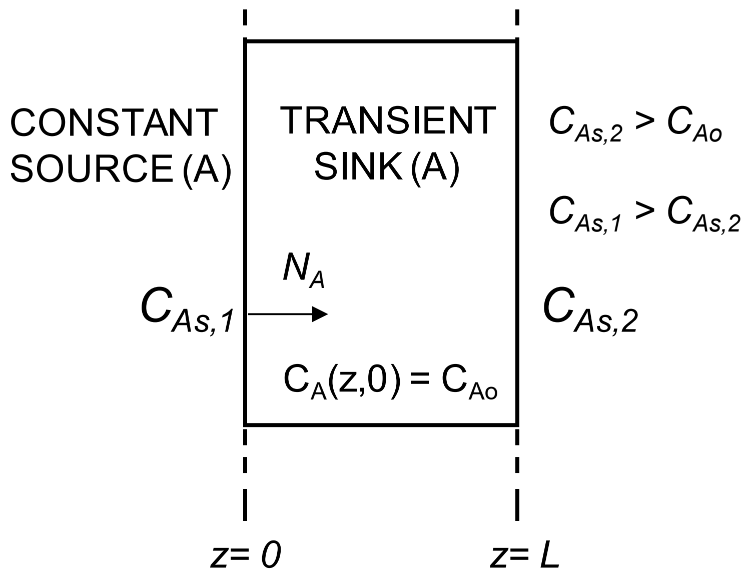


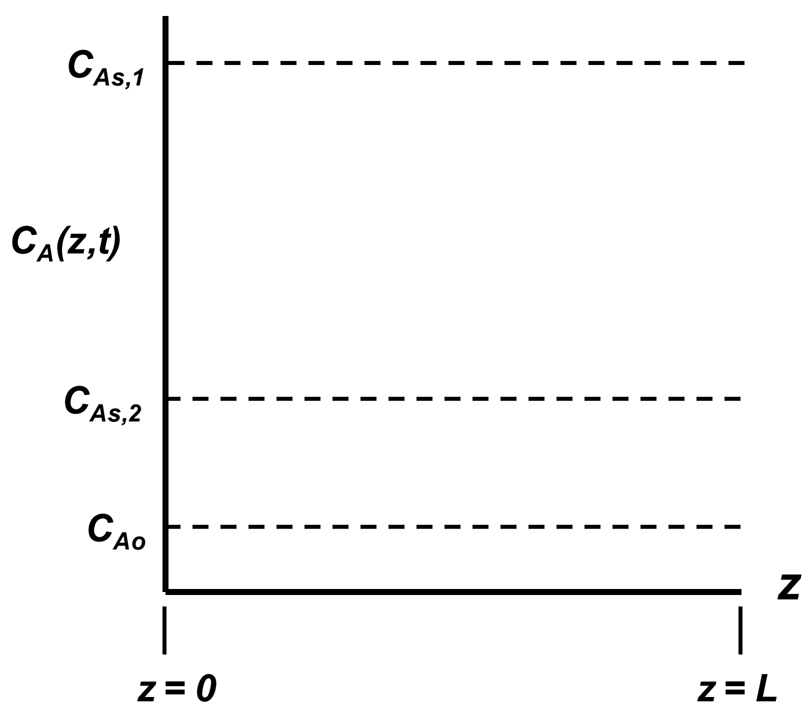


27.1b USS Diffusion to Steady State (Finite Dimensional System cont.)

Example: Constant SOURCE for "A" at Boundary z=0, Steady-State SINK for A at Boundary z = L

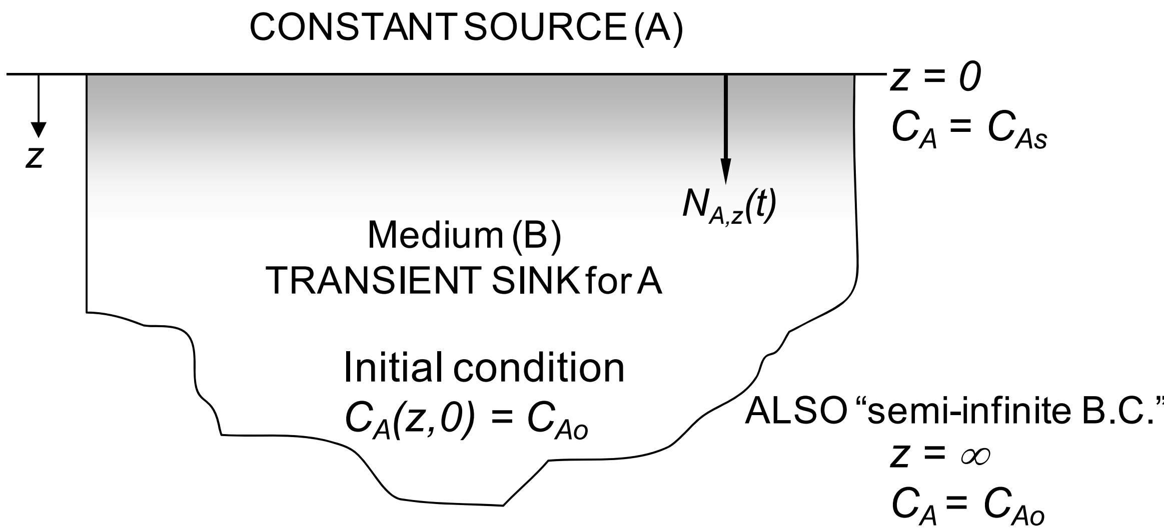
- System Control Volume = TRANSIENT SINK $C_A(x,0) = C_{Ao} < C_{As,2} < C_{As,1}$
- At $z = 0$, CONSTANT SOURCE for A (maintained at $C_{As,1}$)
- At $z = L$, SINK for A *after* steady state is achieved (maintained at $C_{As,2}$)
- At time $t \rightarrow \infty$, $C_A(z,t) \rightarrow C_A(z)$ ***steady state temperature profile***





27.2 Transient Diffusion into a Semi-infinite Medium

"Semi-Infinite" medium



In practical terms, if the concentration profile $C_A(z,t)$ does not penetrate very far into the "medium", then the medium can be considered "semi-infinite" even though in reality it will always be finite. This occurs for

- Short times or really thick slab
- Small D_{AB} value (e.g. in solute A in solid medium B)

Hense, solute "A" never "sees" a possible line of symmetry or impermeable barrier

Differential Equation of Mass Transfer

$$D_{AB}\frac{\partial^2 C_A(z,t)}{\partial z^2} = \frac{\partial C_A(z,t)}{\partial t}$$

Initial Condition (I.C.):

t = 0, all z $\quad$ $C_A(z,0) = C_{Ao}$

Boundary Conditions (B.C.):

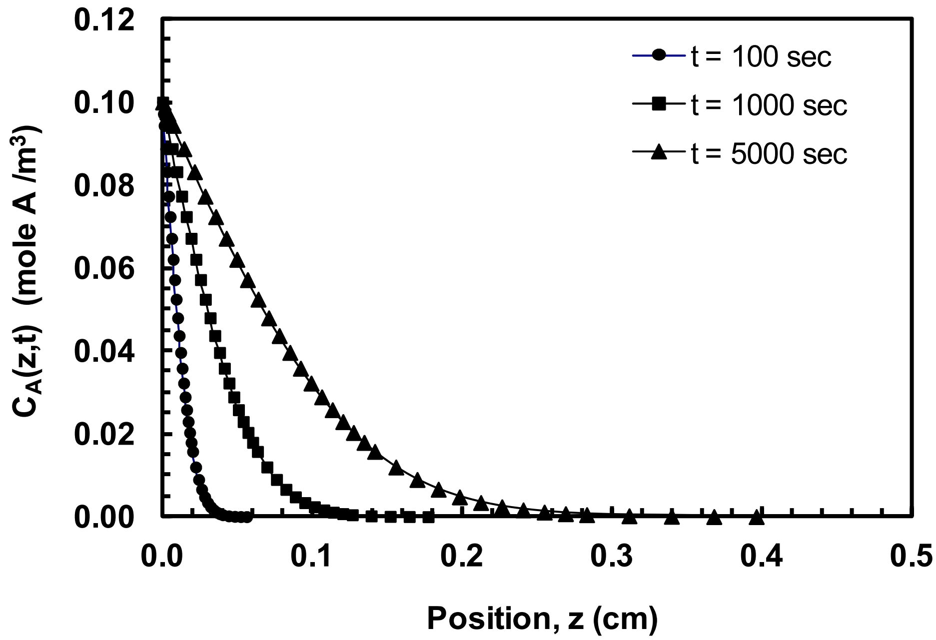
z = 0, all t > 0 $\quad$ $C_A(0,t) = C_{As}$

z = ∞, all t > 0 $\quad$ $C_A(\infty,t) = C_{Ao}$

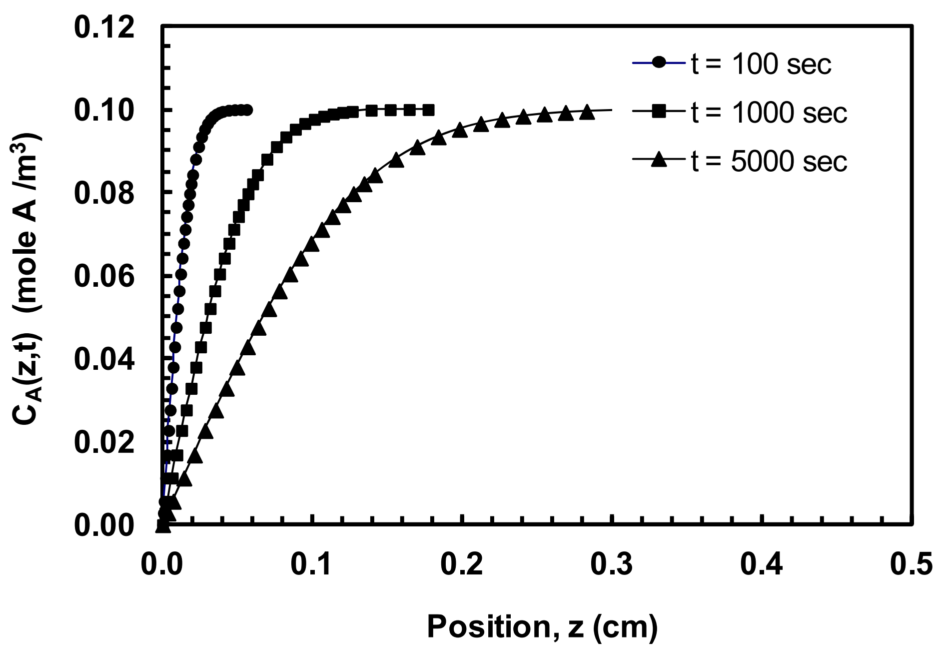
Analytical Solution of Partial Differential Equation for $C_A(x,t)$**,** given I.C. & B.C.

$$\frac{C_{As} - C_A(z,t)}{C_{As} - C_{Ao}} = erf\left(\frac{z}{2\sqrt{D_{AB}\,t}}\right) = erf(\phi)$$

D_{AB} = 1.0 x 10^{-6} cm^2/sec, C_{As} = 0.1 mol A/m^3, C_{Ao} = 0 mol A/m^3
(semi-infinite medium is the Transient SINK)



D_{AB} = 1.0 x 10^{-6} cm^2/sec, C_{As} = 0 mol A/m^3, C_{Ao} = 0.10 mol A/m^3
(semi-infinite medium is the Transient SOURCE)



Mathematical Description of USS Diffusion in Semi-Infinite Medium

Differential Equation for Mass Transfer:

$$D_{AB}\frac{\partial^2 C_A(z,t)}{\partial z^2} = \frac{\partial C_A(z,t)}{\partial t}$$

Initial Condition:

$t = 0$ $\qquad$ $C_A(z,0) = C_{Ao}$ for all z

Boundary Conditions:

$z = 0$ *(surface)* $\qquad$ $C_A(0,t) = C_{As}$ for $t > 0$

$z = \infty$ *(semi-infinite medium)* $\qquad$ $C_A(\infty,t) = C_{Ao}$ for all t

Analytical Solution of the Partial Differential Equation for $C_A(z,t)$

(e.g. by Laplace Transform, or Method of Combination of Variables)

$$\frac{C_A(z,t) - C_{Ao}}{C_{As} - C_{Ao}} = erfc\left(\frac{z}{2\sqrt{D_{AB}\,t}}\right) = 1 - erf\left(\frac{z}{2\sqrt{D_{AB}\,t}}\right)$$

or

$$\frac{C_{As} - C_A(z,t)}{C_{As} - C_{Ao}} = erf\left(\frac{z}{2\sqrt{D_{AB}\,t}}\right) = erf(\phi)$$

Valid for $L > \sqrt{D_{AB}\,t}$

where "***L***" is the actual thickness of the semi-infinite slab

Error Function erf (ϕ)

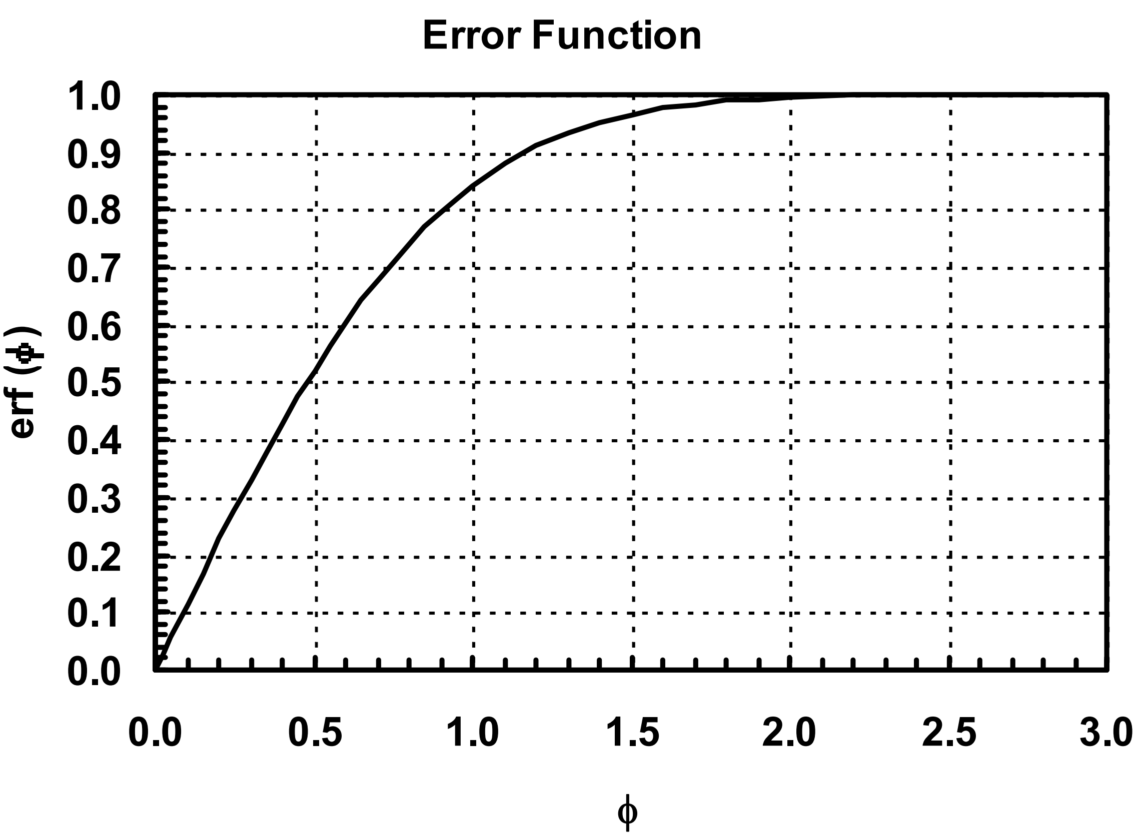
The *Argument* of the Error function ϕ is dimensionless (show in your notes)

$$\phi = \left(\frac{z}{2\sqrt{D_{AB}\, t}} \right)$$

Analytical Approximations to ***erf (ϕ)***

$$erf\,(\phi) \approx \frac{2}{\sqrt{\pi}} \left[\phi - \frac{\phi^3}{3} \right] \quad if \quad \phi \le 0.5$$

$$erf\,(\phi) \approx 1 - \frac{1}{\phi\sqrt{\pi}}\, e^{-\phi^2} \quad if \quad \phi > 1$$



Model Extensions with Error function (USS Diffusion Semi-Infinite Medium)

The *Error function* is mathematically defined as

$$erf(\phi) = \frac{2}{\sqrt{\pi}} \int_o^{\phi} e^{-\xi^2} d\xi \qquad \xi \text{ is a dummy variable for integration}$$

with $erf(0) = 0$ and $erf(\infty) = 1$; $erf(\phi)$ has the analytical approximations

$$erf(\phi) \approx \frac{2}{\sqrt{\pi}} \left[\phi - \frac{\phi^3}{3} \right] \quad if \quad \phi \le 0.5 \qquad\qquad erf(\phi) \approx 1 - \frac{1}{\phi\sqrt{\pi}} e^{-\phi^2} \quad if \quad \phi > 1$$

ϕ vs. $erf(\phi)$ is tabulated in Appendix L. For USS diffusion in semi-infinite medium

$$\phi = \frac{z}{2\sqrt{D_{AB}\, t}} \qquad \text{and} \qquad \frac{C_{A\,s} - C_A(z,t)}{C_{A\,s} - C_{A\,o}} = erf\left(\frac{z}{2\sqrt{D_{AB}\, t}} \right) = erf(\phi)$$

Flux of "A" at surface with time (differentiate concentration profile at surface)

One-dimensional diffusion flux N_A into the semi-infinite medium at surface (z= 0)

$$N_A\big|_{z=0} = -D_{AB} \frac{dC_A}{dz}\Big|_{z=0} \quad (N_{A,z} \text{ is NOT constant along z})$$

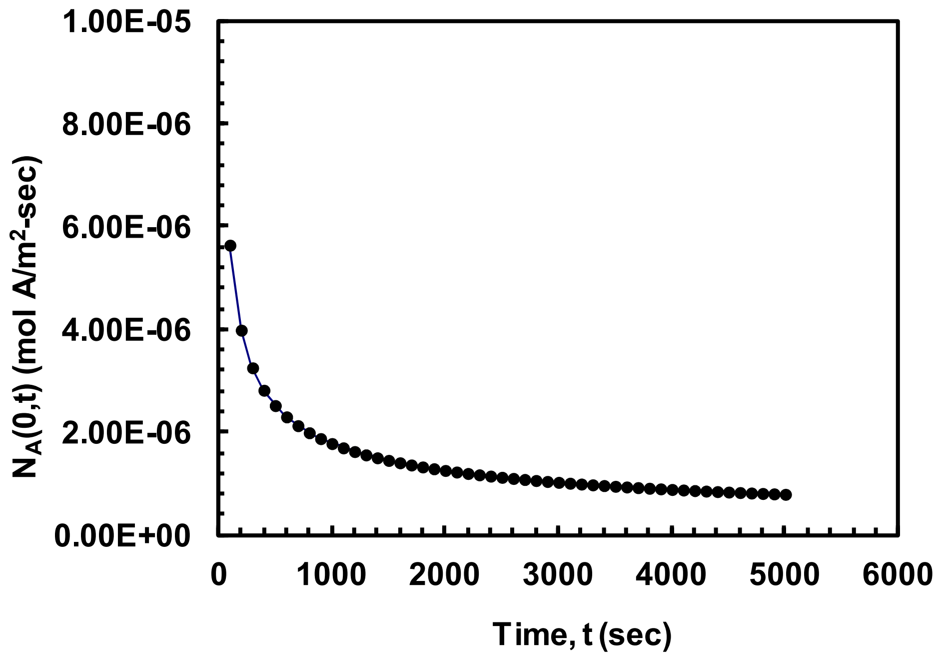
With little math, it can be shown that $\displaystyle \frac{dC_A}{dz}\Big|_{z=0} = -\frac{(C_{A\,s} - C_{A\,o})}{\sqrt{\pi\, D_{AB}\, t}}$

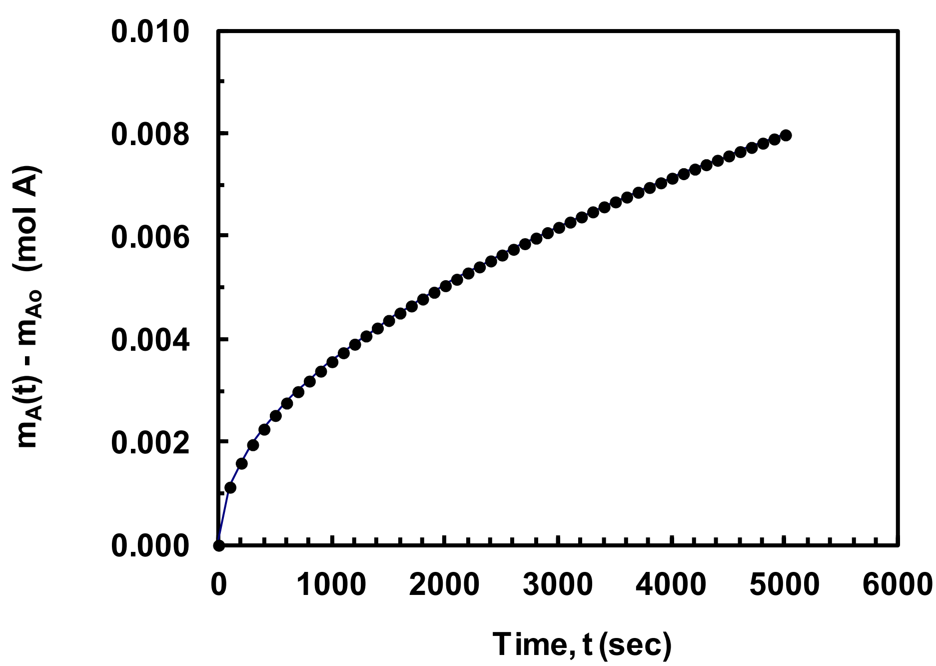
$$N_{A,\,z}\big|_{z=0} = \sqrt{\frac{D_{AB}}{\pi\, t}} \left(C_{A\,s} - C_{A\,o} \right) \quad \text{for } t > 0,\ N_A \text{ decreases with increasing time}$$

Total Amount of "A" transferred with time (integrate flux over time)

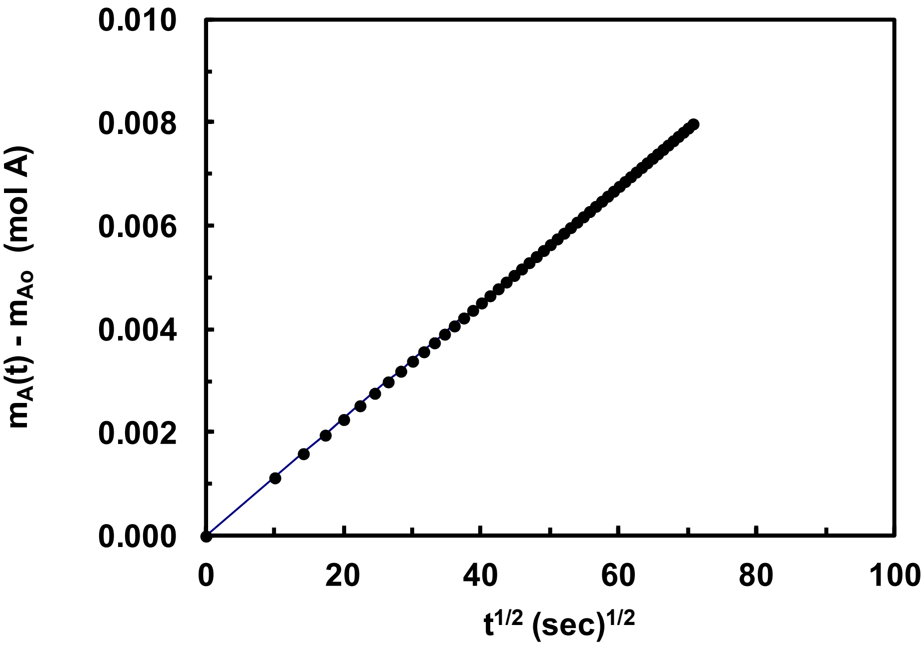
$$m_A(t) - m_{Ao} = S\int_0^t N_{A,\,z}\big|_{z=0} dt = S\int_0^t \sqrt{\frac{D_{AB}}{\pi\, t}} \left(C_{A\,s} - C_{A\,o} \right) dt = S\sqrt{\frac{4D_{AB}\, t}{\pi}} \left(C_{A\,s} - C_{A\,o} \right)$$

$\boldsymbol{D_{AB}}$ = 1.0 x 10^{-6} cm^2/sec, $\boldsymbol{C_{Ao}}$ = 0.1 mol A/m^3, $\boldsymbol{C_{As}}$ = 0 mol A/m^3
(semi-infinite medium is the Transient SINK)



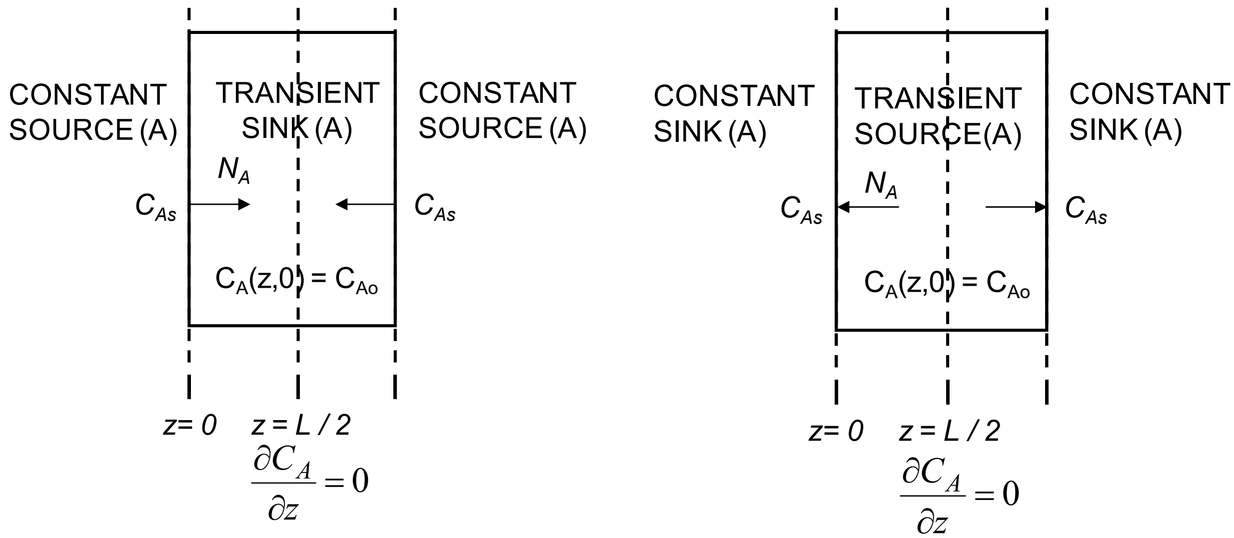


$\boldsymbol{D_{AB}}$ = 1.0 x 10^{-6} cm^2/sec, $\boldsymbol{C_{Ao}}$ = 0.1 mol A/m^3, $\boldsymbol{C_{As}}$ = 0 mol A/m^3
(semi-infinite medium is the Transient SINK)



27.3 Transient Diffusion in a Finite-Dimensional Medium Under Conditions of Negligible Surface Resistance

A Finite-Dimensional Medium has discrete boundary conditions. Recall the "rectangular" slab with USS diffusion to equilibrium, e.g.



Mathematical Description of USS Diffusion in Finite Medium: Approach to Equilibrium

Differential Equation for Mass Transfer

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

Uniform Initial Condition: $C_A(z,0) = C_{Ao}$ for t = 0, $0<z<L$ (not at boundary)

Constant Boundary Conditions:

surface: $z = 0$ or $z = L$ $C_A(0,t) = C_{As}$ for $t \geq 0$

center: $z = L/2$ $\frac{\partial C_A}{\partial z} = 0$ for $t \geq 0$

Analytical Solution of the Partial Differential Equation for $C_A(z,t)$

(by Method of Separation of Variables with Two Independent Variables z & t)

$$Y(z,t) = \frac{C_A(z,t) - C_{As}}{C_{Ao} - C_{As}} = \frac{4}{\pi}\sum_{n=1}^{\infty} \frac{1}{n}\sin\left(\frac{n\pi z}{L}\right) e^{-(n\pi/2)^2 X_D} \qquad n = 1, 3, 5\ldots\infty$$

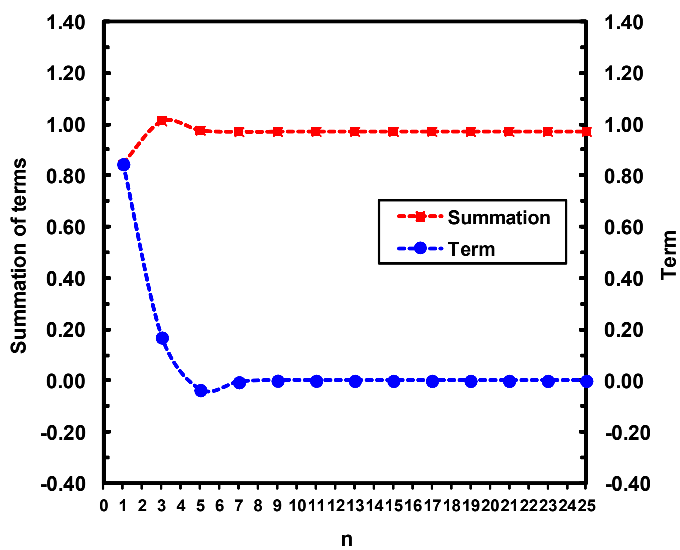
| periodic function| |exponential decay function|
(position) (time)

with $X_D = \dfrac{D_{AB}\,t}{x_1^2}$ (dimensionless) where $x_1 = \dfrac{L}{2}$ (symmetry)

Concentration of A within a Slab

D_{AB} =	3.00E-07	cm^2/sec
C_{As} =	0.0	mol/m^3
C_{Ao} =	10.00	mol/m^3
t =	21600	sec
t =	6.000	hr
x_1 = L/2 =	0.500	cm
z =	0.250	cm
$C_A(z,t)$ =	9.72	mol/m^3
X_D =	0.025920	

n	Term	Summation	% Change
1	8.45E-01	8.445E-01	
3	1.69E-01	1.013E+00	16.655
5	-3.64E-02	9.769E-01	3.726
7	-5.60E-03	9.713E-01	0.577
9	5.63E-04	9.719E-01	0.058
11	3.57E-05	9.719E-01	0.004
13	-1.40E-06	9.719E-01	0.000
15	-3.38E-08	9.719E-01	0.000
17	4.98E-10	9.719E-01	0.000
19	4.45E-12	9.719E-01	0.000
21	-2.42E-14	9.719E-01	0.000
23	-7.93E-17	9.719E-01	0.000
25	1.57E-19	9.719E-01	0.000
27	1.88E-22	9.719E-01	0.000
29	-1.36E-25	9.719E-01	0.000
31	-5.90E-29	9.719E-01	0.000
33	1.54E-32	9.719E-01	0.000
35	2.43E-36	9.719E-01	0.000
37	-2.30E-40	9.719E-01	0.000



- The "infinite series" (*n* is a counter) converges to a finite value, and so typically only a few terms of the series need to be calculated. Convergence of the series is accelerated as X_D increases.
- For a given value of x, t, X_D, you will get a number on the right hand side. If C_{Ao} and C_{As} are also known, then you can get $C_A(z,t)$. An Excel spreadsheet might help to get the calculation done.

At $t = 0$ $\quad Y(z,0) = \dfrac{C_{Ao} - C_{As}}{C_{Ao} - C_{As}} = 1 \;\; (0<z<1)$ $\quad C_A(z,0) = C_{Ao}$

At $t \rightarrow \infty$ $\quad Y(z,\infty) = \dfrac{C_{As} - C_{As}}{C_{Ao} - C_{As}} = 0$ $\quad C_A(z,\infty) = C_{As}$

Flux of "A" (differentiate concentration profile)

$N_{Az} = -D_{AB}\dfrac{\partial C_A}{\partial z}$ for *EMCD* or dilute *UMD* ($N_{A,z}$ is NOT constant along z)

$$\frac{\partial C_A}{\partial z} = (C_{Ao} - C_{As})\frac{\partial Y}{\partial z} = (C_{Ao} - C_{As})\frac{4}{\pi}\sum_{n=1}^{\infty}\left(\frac{1}{n}\frac{n\pi}{L}\right)\cos\left(\frac{n\pi z}{L}\right) e^{-(n\pi/2)^2 X_D}$$

$$N_{Az}(z,t) = \frac{4D_{AB}}{L}(C_{As} - C_{Ao})\sum_{n=1}^{\infty}\cos\left(\frac{n\pi z}{L}\right)e^{-(n\pi/2)^2 X_D} \qquad n = 1, 3, 5\ldots\infty$$

At surface ($z = 0$)

$$N_{Az}(0,t) = \frac{4D_{AB}}{L}(C_{As} - C_{Ao})\sum_{n=1}^{\infty} e^{-(n\pi/2)^2 X_D}$$

Total Amount of "A" transferred with time (integrate flux *into* slab over time)

For slab, define

$m_{Ao} = C_{Ao} \cdot S \cdot L$ initial amount (moles A) loaded within slab at t = 0

$m_{A\infty} = C_{As} \cdot S \cdot L$ final (equilibrium) amount of loaded within slab at $t \rightarrow \infty$

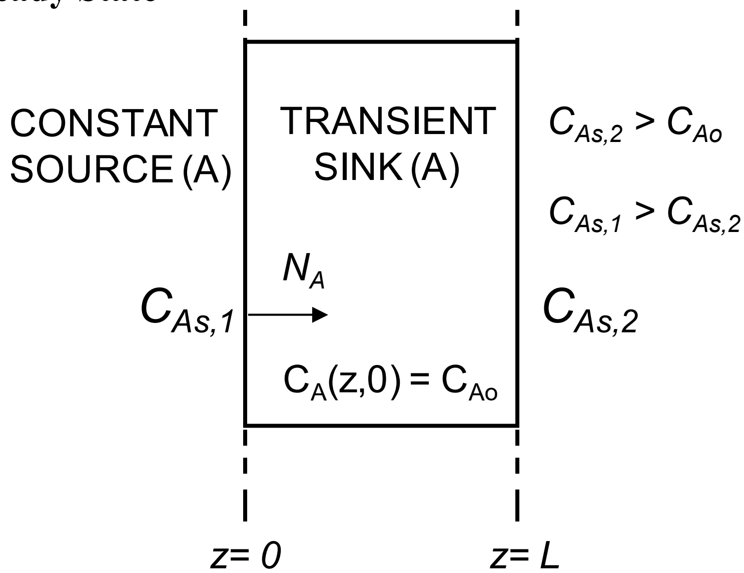
Flux is into both sides of the slab of thickness L

$$m_A(t) - m_{Ao} = 2S\int_0^t N_{Az}(0,t)dt = 2S\int_0^t \frac{4D_{AB}}{L}(C_{As} - C_{Ao})\sum_{n=1}^{\infty} e^{-\left[(n\pi/2)^2\frac{D_{AB}t}{x_1^2}\right]}dt$$

After a little math and some manipulation of infinite series identities

$$\frac{m_{A\infty} - m_A(t)}{m_{A\infty} - m_{Ao}} = \frac{8}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp^{-\left[\frac{n^2\pi^2 D_{AB}\,t}{L^2}\right]} \qquad n = 1, 3, 5\ldots\infty$$

Mathematical Description of USS Diffusion in Finite Medium: Approach to Steady State



Differential Equation for Mass Transfer

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

Uniform Initial Condition: $C_A(z,0) = C_{Ao} = 0$ for t = 0
$0 < z < L$ (not at boundary)

Constant Boundary Conditions:

surface: $z = 0$ $C_A(0,t) = C_{As,1} = C_{As}$ for $t \geq 0$

surface: $z = L$ $C_A(L,t) = C_{As,2} = 0$ for $t \geq 0$

Analytical Solution for $C_A(z,t)$

$$\frac{C_A(z,t)}{C_{As}} = 1 - \frac{z}{L} - \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\sin\left(\frac{n\pi z}{L}\right)e^{-n^2\pi^2 D_{AB}t/L^2}$$

note $t \rightarrow \infty$ $\quad \dfrac{C_A(z)}{C_{As}} = 1 - \dfrac{z}{L}$ steady-state linear concentration profile

27.4 Transient Diffusion in a Finite-Dimensional Medium: Concentration Time Charts for Simple Geometries (Slab, Cylinder, Sphere)

The analytical solution for local concentration $C_A(x,t)$ at position "x" and time "t" is tabulated graphically in the form of the ***Concentration-Time Charts,*** which are provided in *Appendix F* of W^3-R.

Dimensionless parameters used in the Concentration-Time Charts:

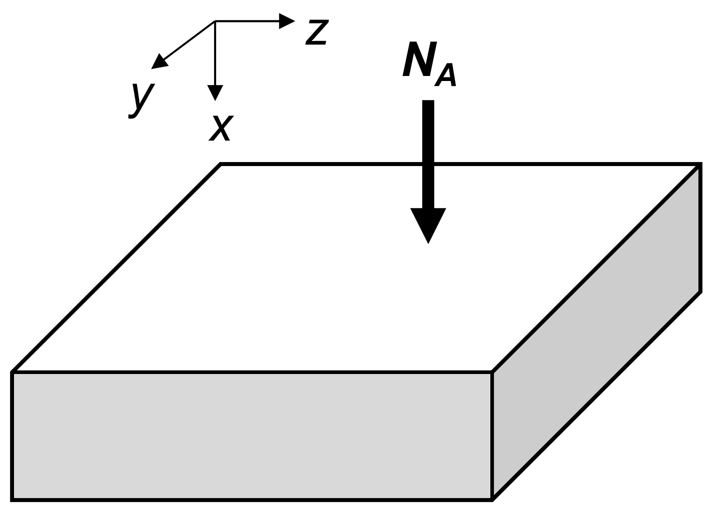
$$Y = \frac{C_{A,1} - C_A(x,t)}{C_{A,1} - C_{Ao}}$$ Unaccomplished concentration change

$$X_D = \frac{D_{AB} \cdot t}{x_1^2}$$ Relative time

$$n = \frac{x}{x_1}$$ Relative position

For *1-D* diffusion, $x_1 = L$ (slab), $x_1 = R$ (cylinder)

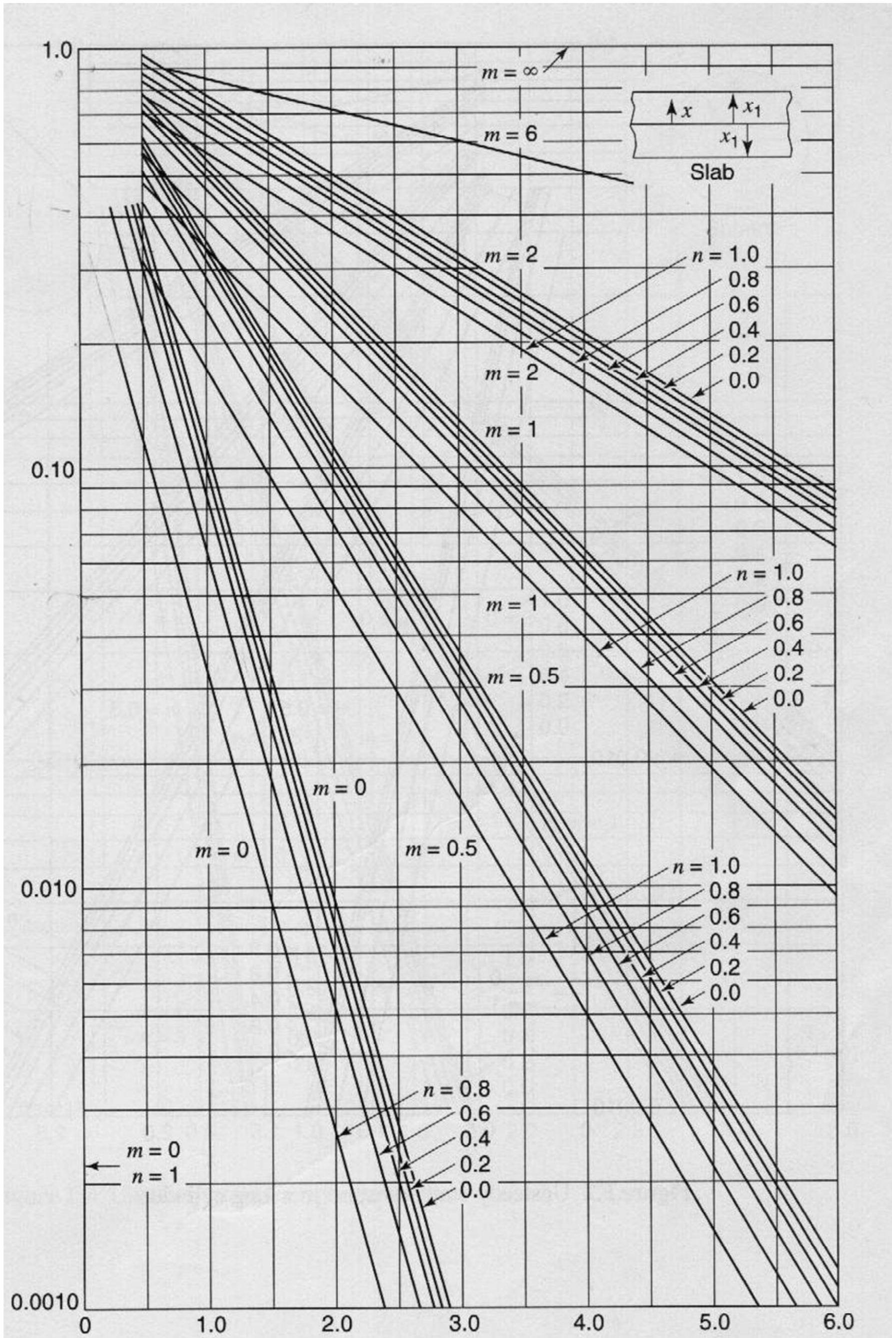
$$m = \frac{D_{A-B}}{k_c \cdot x_1}$$ Convective mass transfer "resistance"



sealed edges
(no flux through *x-y* & *x-z* planes)

For example, *Figure F.1* for one-dimensional USS diffusion in a slab:

$$Y = \frac{C_{A,1} - C_A(x,t)}{C_{A,1} - C_{Ao}}$$



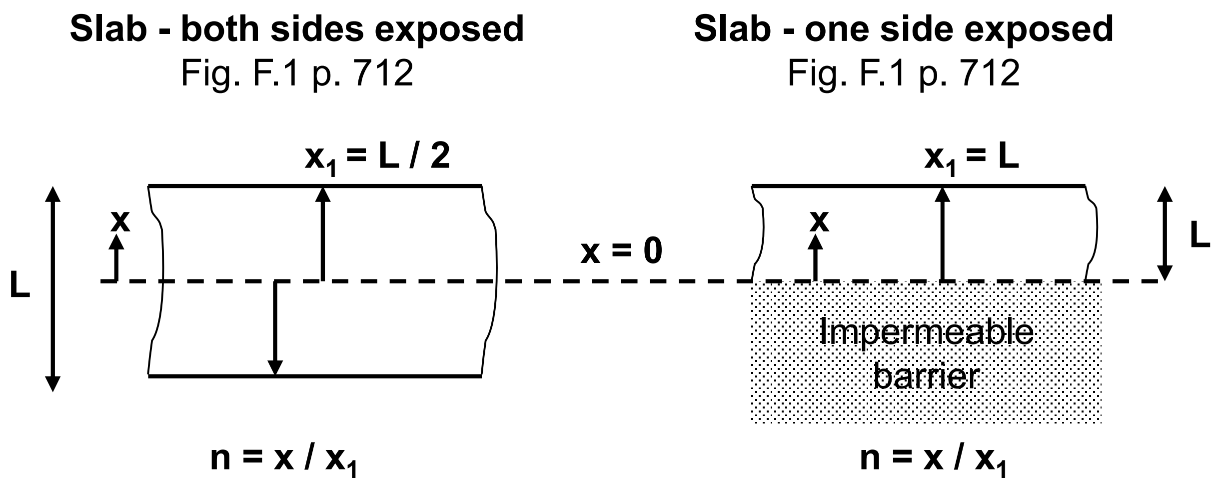
$$X_D = \frac{D_{AB} \cdot t}{x_1^2}$$

Note for gases that

$$Y = \frac{C_{As} - C_A(x,t)}{C_{As} - C_{Ao}} = \frac{y_{As} - y_A(x,t)}{y_{As} - y_{Ao}} = \frac{P_{As} - P_A(x,t)}{P_{As} - P_{Ao}}$$

One-Dimensional Diffusion – Slab (edges are sealed)

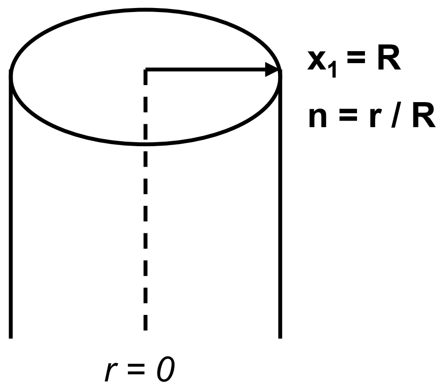
$$Y = \frac{C_{As} - C_A(x,t)}{C_{As} - C_{Ao}} \text{ and } X_D = \frac{D_{AB}}{x_1^{\,2}} t$$



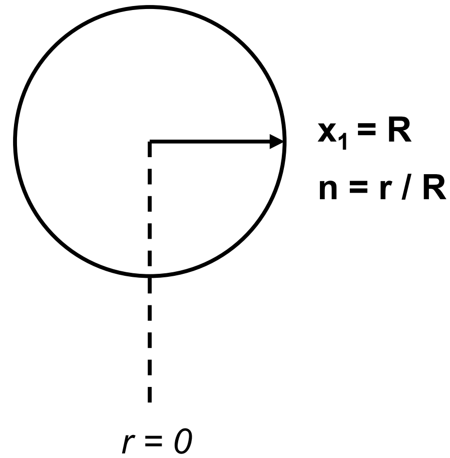
One-Dimensional Diffusion – Cylinder (sealed ends) & Sphere

$$Y = \frac{C_{As} - C_A(r,t)}{C_{As} - C_{Ao}} \text{ and } X_D = \frac{D_{AB}}{R^2} t$$

Long Cylinder
cylindrical surface exposed (ignore ends)
Fig. F.2 p. 713



Sphere
Fig. F.3 p. 714



Topic 27.4 cont.

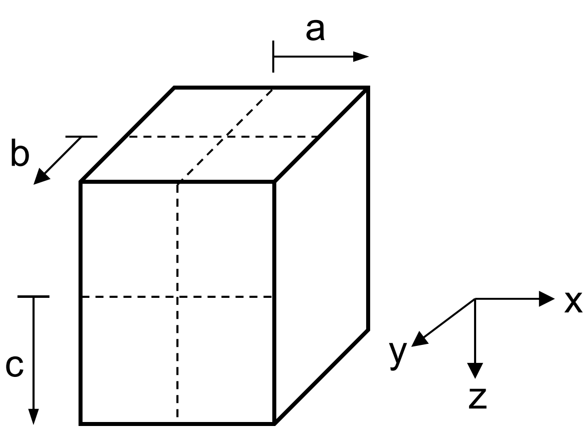
Rules for Extension of the Concentration-Time Charts to Multiple Dimensions

Rectangular Bar

$$Y = \frac{C_{As} - C_A(x, y, z, t)}{C_{As} - C_{Ao}} = Y_a Y_b\, Y_c$$

a = width / 2, b = thickness / 2, c = depth / 2 (measured from center point of bar)

$$X_{D,a} = \frac{D_{AB}}{a^2} t\,,\ X_{D,b} = \frac{D_{AB}}{b^2} t\,,\ X_{D,c} = \frac{D_{AB}}{c^2} t$$

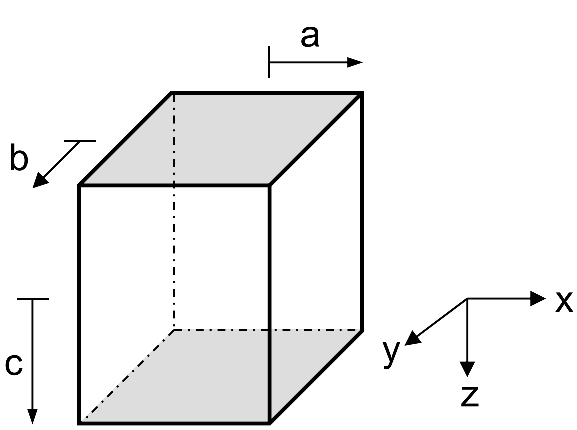


3-D flux Along *x, y, z*
(no sealed ends)

$n_a = x / a$, $n_b = y / b$, $n_c = z / c$

Rectangular Bar with Sealed Ends

$$Y = \frac{C_{As} - C_A(x, y, t)}{C_{As} - C_{Ao}} = Y_a Y_b$$



2-D flux Along *x, y*
(sealed ends, no flux along z)

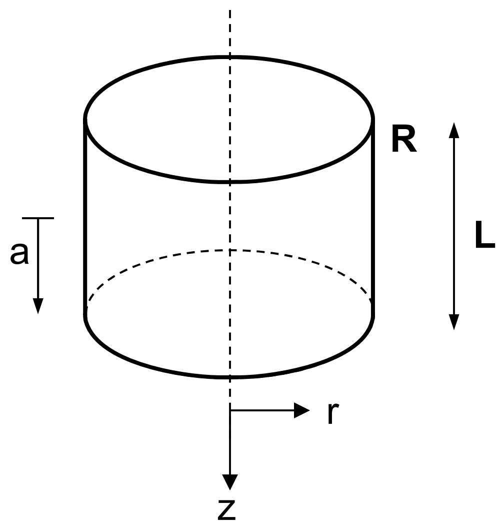
$n_a = x / a$, $n_b = y / b$

Topic 27.4 cont.

Cylinder with Exposed Ends

a = L/2 length of the cylinder (measured from center point of cylinder)

$$Y = \frac{C_{As} - C_A(r,z,t)}{C_{As} - C_{Ao}} = Y_a Y_{cylinder} \qquad X_{D,a} = \frac{D_{AB}}{a^2}t\,,\; X_{D,cylinder} = \frac{D_{AB}}{R^2}t$$



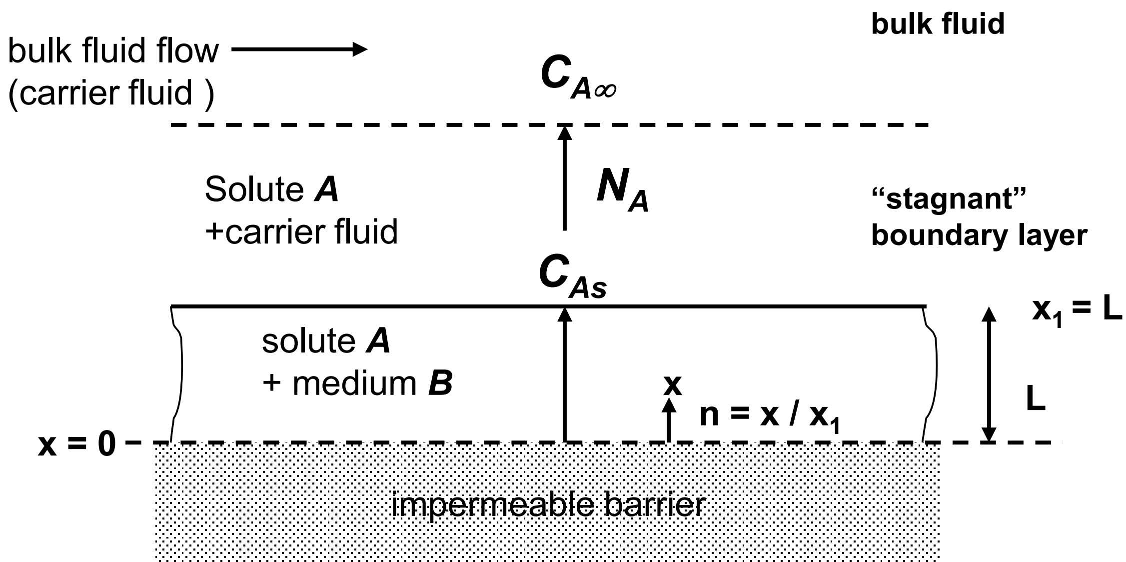
2-D flux Along *r, z*
(no sealed ends)

$n_a = z / a$ ($a = L / 2$)

$n_{cyl} = r / R$

Topic 27.4 cont.

What is "m" in the Concentration-Time Charts?



$$m = \frac{D_{A-B}}{k_c \cdot x_1} \qquad Y = \frac{C_{A,1} - C_A(x,t)}{C_{A,1} - C_{Ao}}$$

$m \approx 0$	**$m > 0$**
no convection resistance	**convection resistance**
$x = L$, $C_{A,1} = C_{As} = C_{A\infty}$	***$x = L$, $C_{A,1} = C_{A\infty}$***

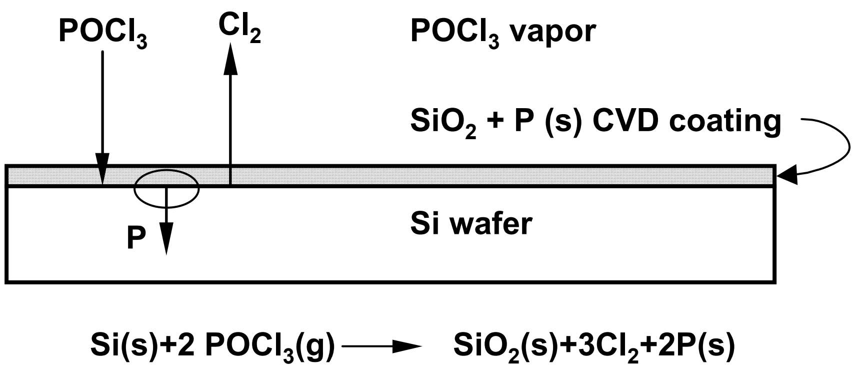
$$N_A(L,t) = -D_{AB}\frac{\partial C_A}{\partial x}\Big|_{x=L} = k_c(C_{As} - C_{A\infty})$$

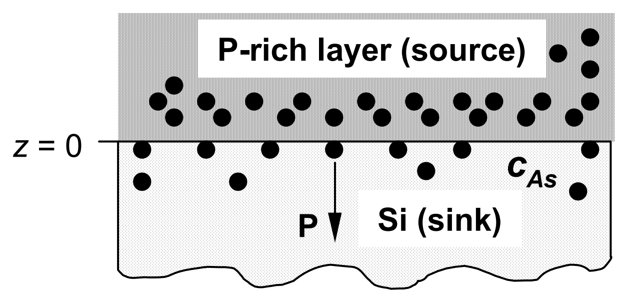
OR $$N_A(L,t) = -D_{AB}\frac{\partial C_A(L,t)}{\partial x} = k_c(C_A(L,t) - C_{A\infty})$$

k_c = convective mass transfer coefficient (cm/sec)

Topic 27.2 Example: Phosphorous Doping of a Silicon Wafer

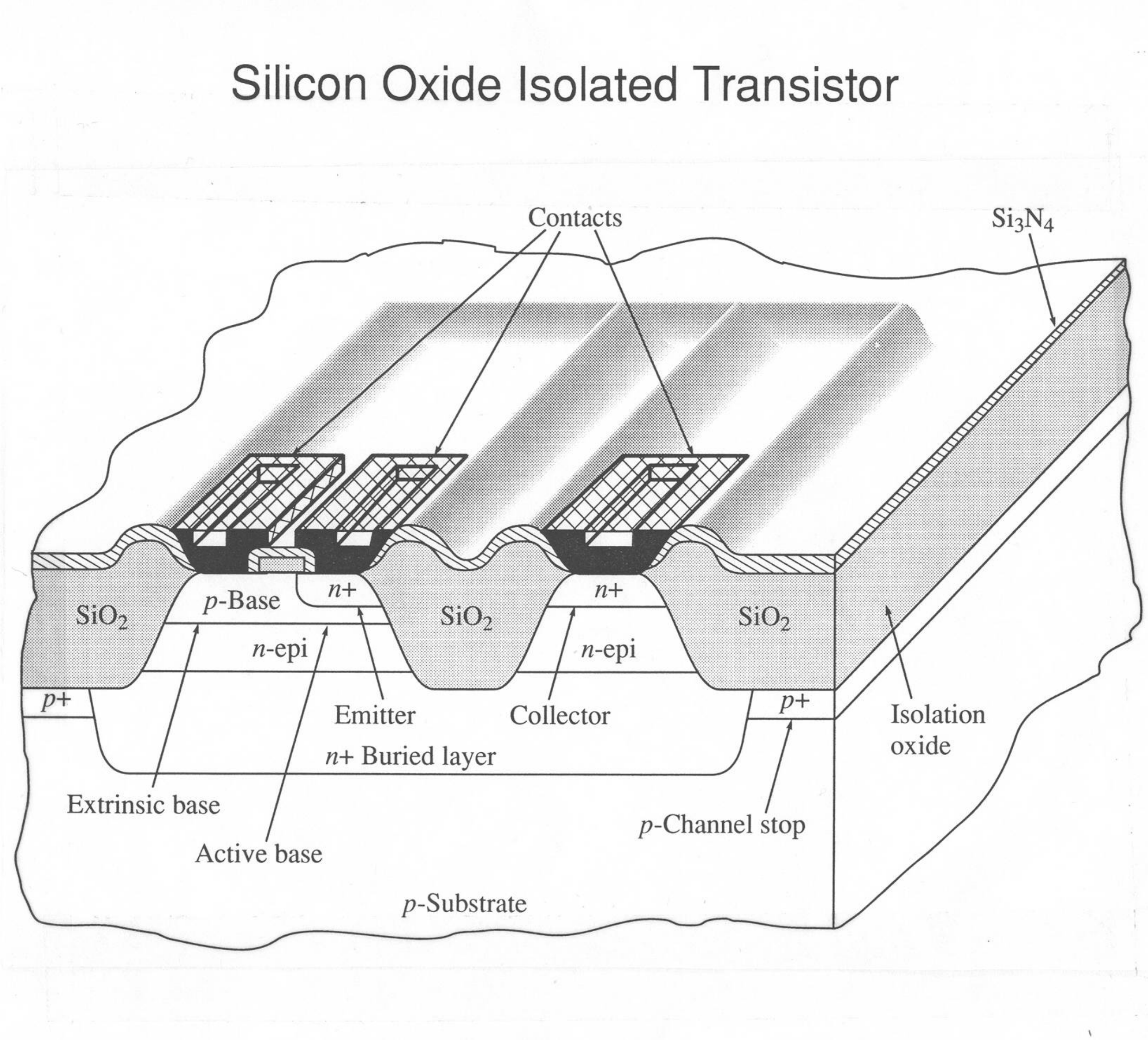
Some interesting facts. In the fabrication of solid-state microelectronic devices, semi-conducting thin films can be made by impregnating either phosphorous or boron into a silicon wafer. This process is called doping. The doping of phosphorous atoms into crystalline silicon makes a *n-type* semiconductor, whereas the doping of boron atoms into crystalline silicon makes a *p-type* semiconductor. The formation of the semi-conducting thin film is controlled by the molecular diffusion of the dopant atoms through crystalline silicon matrix.





Doping as a diffusion process. Prior to doping, a coating rich in molecular phosphorous (P) is formed over the crystalline silicon surface. The molecular phosphorous then diffuses through the crystalline silicon to form the Si-P thin film. The coating is the source for mass transfer of phosphorous, and the silicon wafer is the sink for mass transfer of phosphorous. Consider a simplified case where the P atom concentration is constant at the interface. Since the diffusion coefficient of P atoms in crystalline silicon is very small, and only a thin film of Si-P is desired, phosphorous atoms to not penetrate very far into the silicon, i.e. the Si solid serves as a semi-infinite sink for the diffusion process.

Aside: simplified diffusion steps in fabrication of a thin film MOSFET (Metal Oxide Semiconductor Field Effect Transistor)

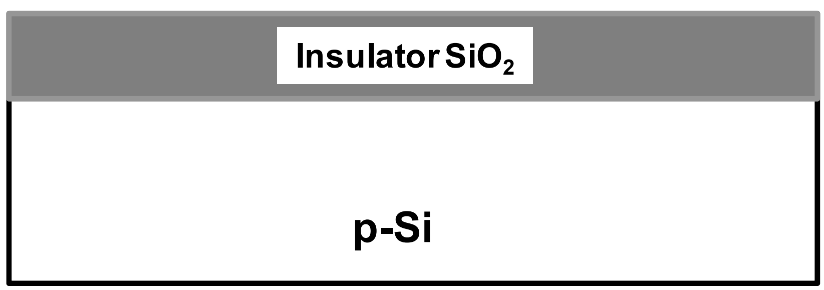


Ref:: Middleman, S., Hochberg, A.K. *Process Engineering Analysis in Semiconductor Device Fabrication*, McGraw-Hill, 1993. Fig. 2-20.

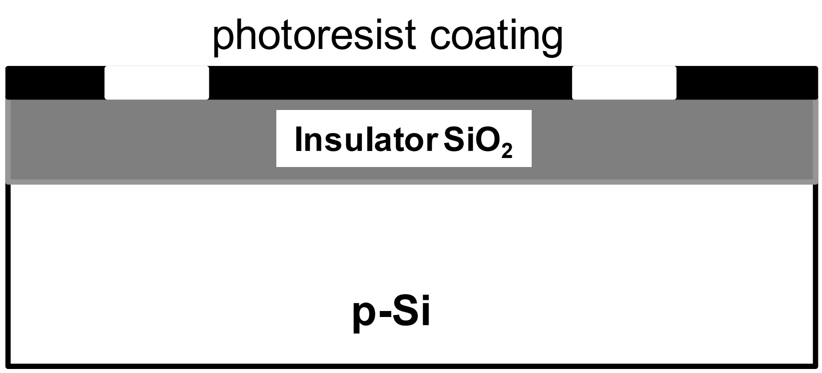
Aside: simplified diffusion steps in fabrication of a thin film transistor (cont.)

Step 1: diffuse boron into silicon

Step 2: diffuse and react O_2 (g) with Si to make SiO_2 layer

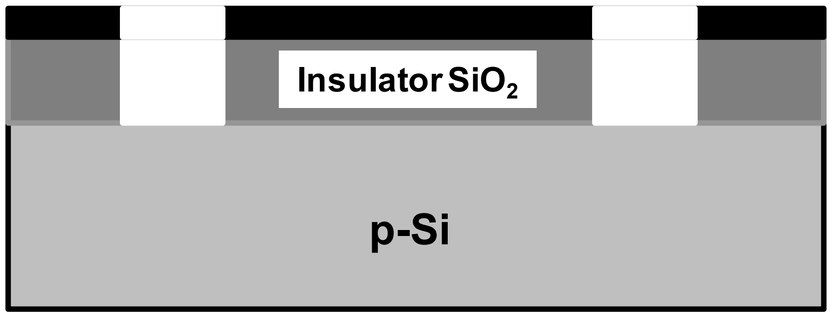


Step 3: make a pattern (photolithography)

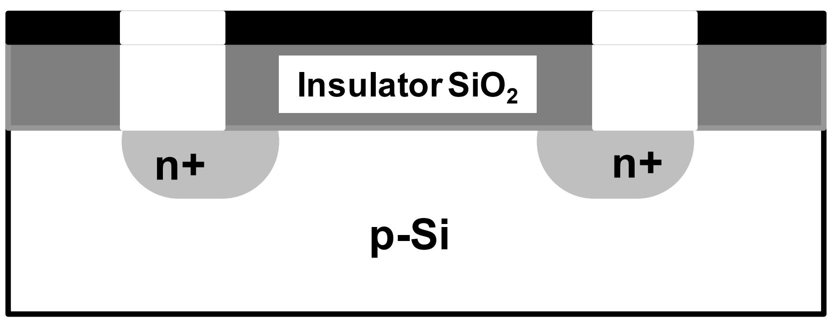


Aside: simplified diffusion steps in fabrication of a thin film transistor (cont.)

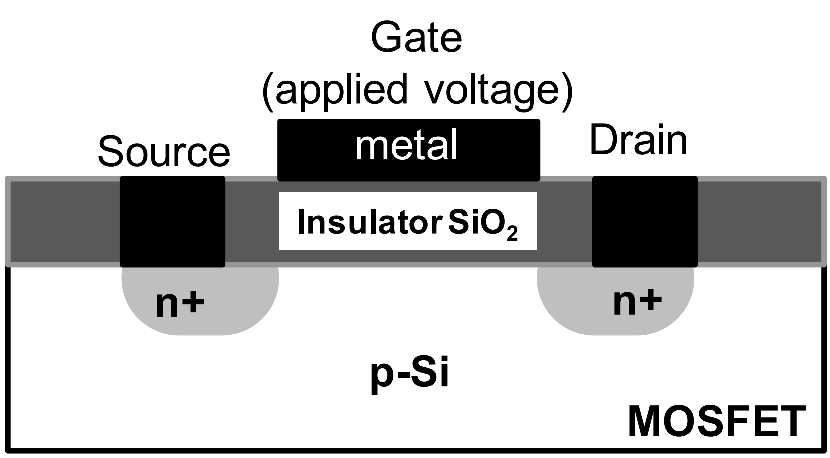
Step 4: chemically etch pattern in SiO_2 layer



Step 5: diffuse in phosphorous dopant to p-Si (n+ region)

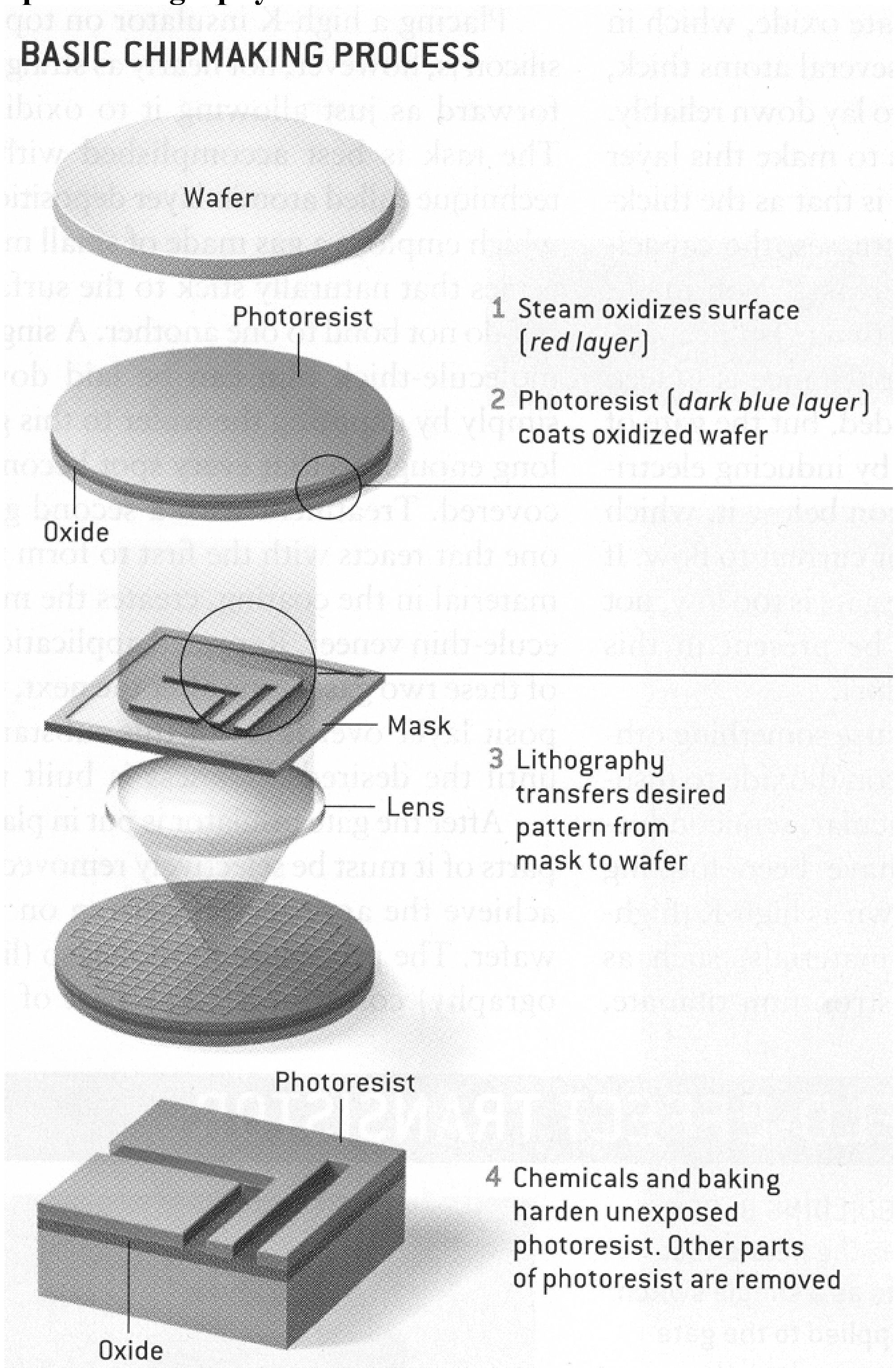


Step 6: metallization (requires several steps)



n+ = phosphorous-doped silicon
p-Si = boron-doped silicon

Aside: simplified diffusion steps in fabrication of a thin film transistor, more detail on photolithography



Credit: *Scientific American, April 2004, p. 80 (*used without permission)

Topic 27.2 Example: Phosphorous Doping of a Silicon Wafer (continued)

Problem statement. The phosphorous doping of crystalline silicon occurs at 1100 °C, a temperature high enough to promote phosphorous diffusion. The surface concentration of phosphorous (c_{As}) in the silicon is $2.5 \cdot 10^{20}$ atoms P / cm^3 solid Si, which relatively dilute, since pure solid silicon is $5 \cdot 10^{22}$ atoms Si/cm^3 solid. The "junction gap" for semi-conductor performance is the distance into the Si thin film where the P atom concentration is at least 1% of the surface value (2.5 10^{18} atoms P/cm^3 solid Si).

(a) Predict the depth of the Si-P thin film after 1.0 hour if the target concentration is 1% of the surface value (2.5 10^{18} atoms P/cm^3 solid Si), and the concentration profile of P atoms after one hour.

(b) What is the implantation rate (flux) of P atoms into the surface of the wafer at one hour? What is the cumulative amount of P atoms in the wafer after one hour?

(c) What is the P concentration 0.5 μm into the film after one hour?

(d) Predict the doping time required to fabricate a "junction gap" of 1.0 μm.

Topic 27.2 Example: Phosphorous Doping of a Silicon Wafer (continued)

Solution

part (a)

Differential equation for Mass Transfer for USS concentration profile $C_A(z,t)$
one-dimensional, phosphorous (species A*) in solid silicon (species* B*)*

$$D_{AB}\frac{\partial^2 c_A}{\partial z^2} = \frac{\partial c_A}{\partial t}$$

Semi-infinite medium IC/BC

IC: $t = 0$, $c_A(z,0) = c_{Ao} = 0$ for all z
BC: $z = 0$, $c_A(0,t) = c_{As} = 2.5 \cdot 10^{20}$ atoms P/cm^3 solid Si, for $t > 0$
BC: $z = \infty$, $c_A(\infty,t) = c_{Ao} = 0$ for all t

Analytical solution

$$\frac{C_{As} - C_A}{C_{As} - C_{Ao}} = erf\left(\frac{z}{2\sqrt{D_{AB}\,t}}\right) = erf(\phi)$$

$$\frac{C_{As} - C_A}{C_{As} - C_{Ao}} = \frac{2.5\ \cdot 10^{20}\,atoms\,P/cm^3 - 2.5\cdot 10^{18}\,atoms\,P/cm^3}{2.5\ \cdot 10^{20}\,atoms\,P/cm^3 - 0} = 0.990$$

Therefore $\quad 0.990 = erf(\varphi)$

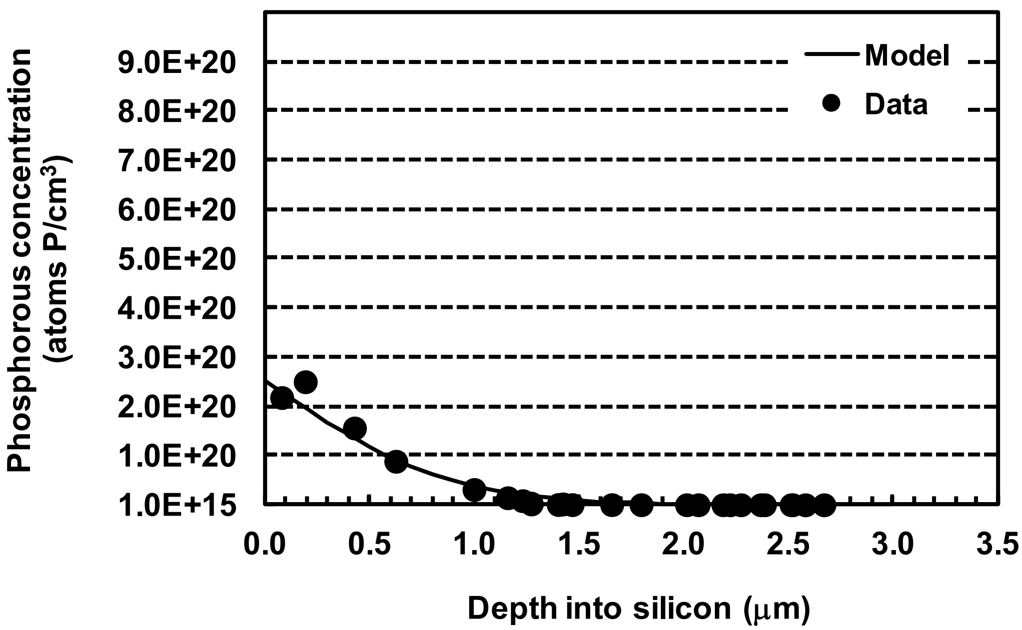
From Appendix Table L, at $erf(\phi) = 0.990$, $\phi = 1.82$.

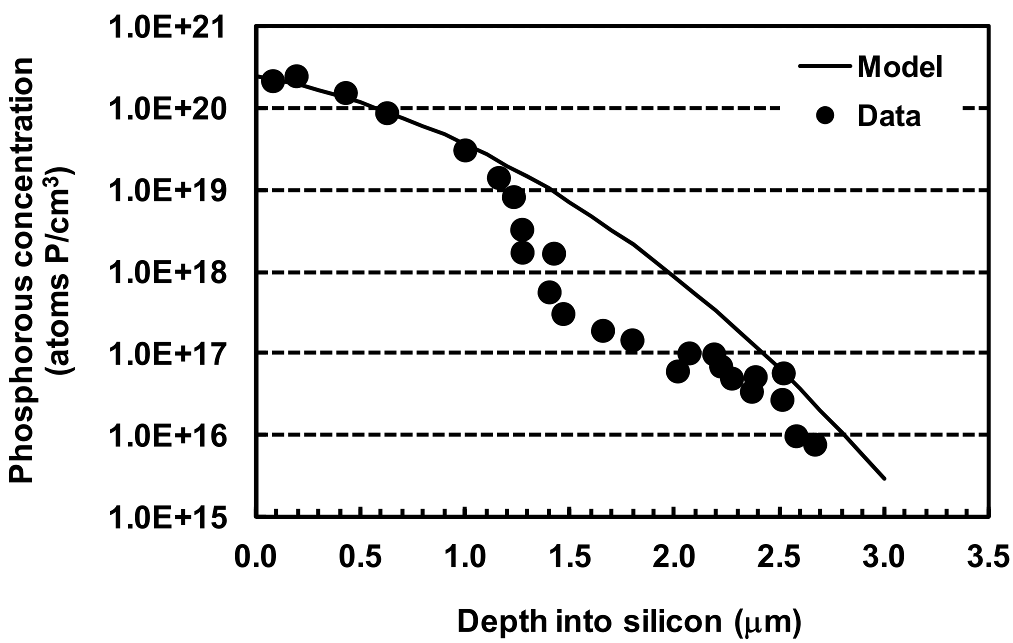
From Topic 24.2, the solid diffusion coefficient of P atoms (species *A*) in crystalline silicon (species *B*) is $6.5 \cdot 10^{-13}$ cm^2/s at 1100 °C (1373 K).

Back out depth z from ϕ

$$z = \phi \cdot 2\sqrt{D_{AB}t} = 1.82 \cdot 2 \cdot \sqrt{\left(6.5 \cdot 10^{-13}\,\frac{cm^2}{s}\cdot\frac{10^8\,\mu m^2}{1\ cm^2}\right)\left(1.0\,h \cdot \frac{3600\,s}{1\ h}\right)} = 1.76\,\mu m$$

Phosphorous Doping of a Silicon Wafer (continued) – concentration profiles in Silicon (1100 °C, t = 1.0 hr)



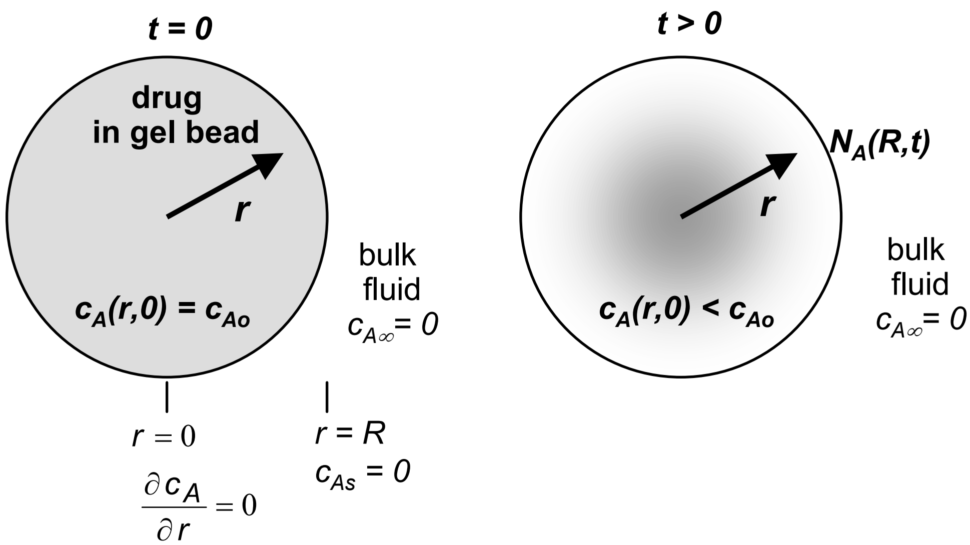


Ref. for Data: Middleman, S., Hochberg, A.K. Process Engineering Analysis in Semiconductor Device Fabrication, McGraw-Hill, 1993. Fig. 10-6.

Topic 27.3 Example: Timed Release Drug Dosage in a Spherical Capsule

Some interesting facts. One way to deliver a timed dosage of a drug with the human body is to ingest a capsule and allow it to settle in the gastrointestinal system. Once inside the body, the capsule slowly releases the drug by a diffusion-limited process. A suitable drug carrier is a spherical bead of a non-toxic gelatinous material that can pass through the gastrointestinal system without disintegrating. A water-soluble drug (solute A) is uniformly dissolved within the gel, and has an initial concentration C_{Ao}. The drug loaded within the bead is the transient source for mass transfer, whereas the fluid surrounding the bead is the constant sink for mass transfer.

Consider a limiting case where the drug is immediately consumed or swept away once it reaches the surrounding solution so that in essence the surrounding fluid is an infinite sink, i.e. $r = R,\ C_{As} = 0$.



Problem statement. It is desired to design a spherical capsule for the timed release of the drug dimenhydrinate, commonly called Dramamine, which is used to treat motion sickness. A conservative total dosage for one capsule is 10 mg, where 50% of the drug must be released to the body within 3 hours. Determine the size of the bead and the initial concentration of Dramamine in the bead necessary to achieve this dosage. The diffusion coefficient of Dramamine (species A) in the gel matrix (species B) is $3.0 \cdot 10^{-7}$ cm^2/s at a body temperature of 37 ^{o}C. The solubility limit of Dramamine in the gel is 100 mg/cm^3, whereas the solubility of Dramamine in water is only 3 mg/cm^3.

Topic 27.3 Example (Timed Release Drug Dosage cont.)

Model Development & Analysis

Assumptions and Conditions

SYSTEM: Spherical gel bead bearing the drug (solute A)
SOURCE of A: A initially loaded into bead (finite, transient source)
SINK forf A: Fluid surrounding bead (constant infinite sink)

KEY ASSUMPTIONS

- Unsteady state
- Radial symmetry with 1-D flux along r
- dilute solution of the drug dissolved in the gel matrix (UMD approximates EMCD flux equation)
- No degradation of the drug inside the bead ($R_A = 0$)
- $C_{As} = 0$ at $r = R$ (limiting case)
- Constant bead radius R

Differential Equation for Mass Transfer

$$D_{AB}\left(\frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r}\frac{\partial C_A}{\partial r}\right) = \frac{\partial C_A}{\partial t}$$

Uniform Initial Condition: $t = 0, C_A = C_{Ao}, 0 < r < R$

Constant Boundary conditions:

center $r = 0, \dfrac{\partial C_A(0,t)}{\partial r} = 0, t \geq 0$

surface $r = R, C_A(R,t) = C_{As} = 0, t \geq 0$

Analytical solution to Model Equations for $C_A(r,t)$

$$Y = \frac{C_A(r,t) - C_{Ao}}{C_{As} - C_{Ao}} = 1 + \frac{2R}{\pi r}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin\left(\frac{n\pi r}{R}\right)e^{-D_{AB}\,n^2\pi^2 t/R^2} \quad r \neq 0, n = 1,2,3...$$

At $r = 0$

$$Y = \frac{C_A(0,t) - C_{Ao}}{C_{As} - C_{Ao}} = 1 + 2\sum_{n=1}^{\infty} \left(-1\right)^n \, e^{-D_{AB}\, n^2 \pi^2 t / R^2} \qquad r = 0,\, n = 1,2,3\ldots$$

Rate of drug release W_A (moles A/time) at the surface of the bead (r = R)

$$W_A(t) = 4\pi R^2 N_{Ar} = 4\pi R^2 \left(-D_{AB} \frac{\partial C_A(R,t)}{\partial r} \right)$$

Take a "math moment" to show that

$$W_A(t) = 8\pi R C_{Ao} D_{AB} \sum_{n=1}^{\infty} e^{-D_{AB}\, n^2 \pi^2 t / R^2} \qquad \mathrm{W_A}(t) \to 0 \ \text{ as } \ \mathrm{t} \to \infty$$

Cumulative amount of drug released from the bead

Initially: $m_{Ao} = c_{Ao} V = c_{Ao} \frac{4}{3} \pi \; R^3$

Finally: $m_{A\infty} = c_{A\infty} V = c_{A\infty} \frac{4}{3} \pi \; R^3 = 0$ (no drug left if $C_{A\infty} = C_{As} = 0$)

$$\frac{\mathrm{m_A(t)}}{\mathrm{m_{Ao}}} = \frac{\text{amount of A remaining}}{\text{initial amount of A loaded}}$$

Integrate $W_A(t)$ over time to get $m_A(t)$

$$m_{Ao} - m_A(t) = \int_0^t W_A(t) dt$$

Take a "math moment" to show that

$$\frac{m_A(t)}{m_{Ao}} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-D_{AB}\, n^2 \pi^2 t / R^2}$$

Fractional release = $1 - \frac{m_A(t)}{m_{Ao}}$

Predictions for $C_A(r,t)$ and $m_A(t)$ follow. The dimensionless parameter $D_{AB}\, t\, /\, R^2$ is controls the convergence of the infinite series solution. Note how variables R and C_{Ao} can be manipulated set the drug release profile.

Topic 27.3 Example (Timed Release Drug Dosage cont.) – spreadsheet calculations for cumulative drug release

EXCEL SPREADSHEET FOR DRUG RELEASE PROFILE										
m_{Ao} =		10.0	mg							
D_{AB} =		3.00E-07	cm^2/s							
R =		0.326	cm							
c_{Ao} =		68.9	mg/cm^3							
Time, t (s)	0.0	18	180	1800	3600	7200	10800	14400	18000	21600
Time, t (h)	0.0	0.005	0.05	0.50	1.00	2.00	3.00	4.00	5.00	6.00
$m_A(t) / m_{Ao}$	1.0	0.964	0.925	0.774	0.689	0.578	0.500	0.439	0.389	0.347
$1 - m_A(t) / m_{Ao}$	0.0	0.036	0.075	0.226	0.311	0.422	0.500	0.561	0.611	0.653
Series Term n =	1	9.99E-01	9.95E-01	9.51E-01	9.05E-01	8.18E-01	7.40E-01	6.70E-01	6.06E-01	5.48E-01
	2	2.49E-01	2.45E-01	2.05E-01	1.67E-01	1.12E-01	7.50E-02	5.02E-02	3.36E-02	2.25E-02
	3	1.11E-01	1.06E-01	7.08E-02	4.51E-02	1.83E-02	7.41E-03	3.00E-03	1.22E-03	4.94E-04
	4	6.20E-02	5.77E-02	2.80E-02	1.26E-02	2.52E-03	5.07E-04	1.02E-04	2.05E-05	4.11E-06
	5	3.95E-02	3.53E-02	1.14E-02	3.26E-03	2.66E-04	2.16E-05	1.76E-06	1.44E-07	1.17E-08
	6	2.73E-02	2.32E-02	4.57E-03	7.51E-04	2.03E-05	5.49E-07	1.48E-08	4.01E-10	1.08E-11
	7	1.99E-02	1.60E-02	1.75E-03	1.50E-04	1.10E-06	8.07E-09	5.92E-11	4.34E-13	3.19E-15
	8	1.51E-02	1.13E-02	6.31E-04	2.55E-05	4.15E-08	6.77E-11	1.10E-13	1.80E-16	2.93E-19
	9	1.19E-02	8.22E-03	2.13E-04	3.66E-06	1.08E-09	3.21E-13	9.52E-17	2.82E-20	8.36E-24
	10	9.51E-03	6.06E-03	6.64E-05	4.41E-07	1.94E-11	8.56E-16	3.77E-20	1.66E-24	7.33E-29
	11	7.78E-03	4.50E-03	1.91E-05	4.43E-08	2.38E-13	1.27E-18	6.84E-24	3.67E-29	1.97E-34
	12	6.46E-03	3.37E-03	5.07E-06	3.71E-09	1.98E-15	1.06E-21	5.65E-28	3.02E-34	1.61E-40
	13	5.44E-03	2.54E-03	1.23E-06	2.57E-10	1.12E-17	4.87E-25	2.12E-32	9.23E-40	4.02E-47
	14	4.62E-03	1.91E-03	2.75E-07	1.48E-11	4.29E-20	1.25E-28	3.61E-37	1.05E-45	3.04E-54
	15	3.97E-03	1.44E-03	5.59E-08	7.03E-13	1.11E-22	1.76E-32	2.79E-42	4.41E-52	6.98E-62
	16	3.44E-03	1.08E-03	1.04E-08	2.76E-14	1.95E-25	1.38E-36	9.72E-48	6.87E-59	4.85E-70
	17	2.99E-03	8.12E-04	1.76E-09	8.93E-16	2.30E-28	5.94E-41	1.53E-53	3.95E-66	1.02E-78
	18	2.62E-03	6.08E-04	2.71E-10	2.38E-17	1.83E-31	1.41E-45	1.09E-59	8.41E-74	6.48E-88
	19	2.31E-03	4.53E-04	3.80E-11	5.22E-19	9.85E-35	1.86E-50	3.50E-66	6.60E-82	1.24E-97
Series Term n =	20	2.05E-03	3.36E-04	4.86E-12	9.43E-21	3.56E-38	1.34E-55	5.06E-73	1.91E-90	7.20E-108

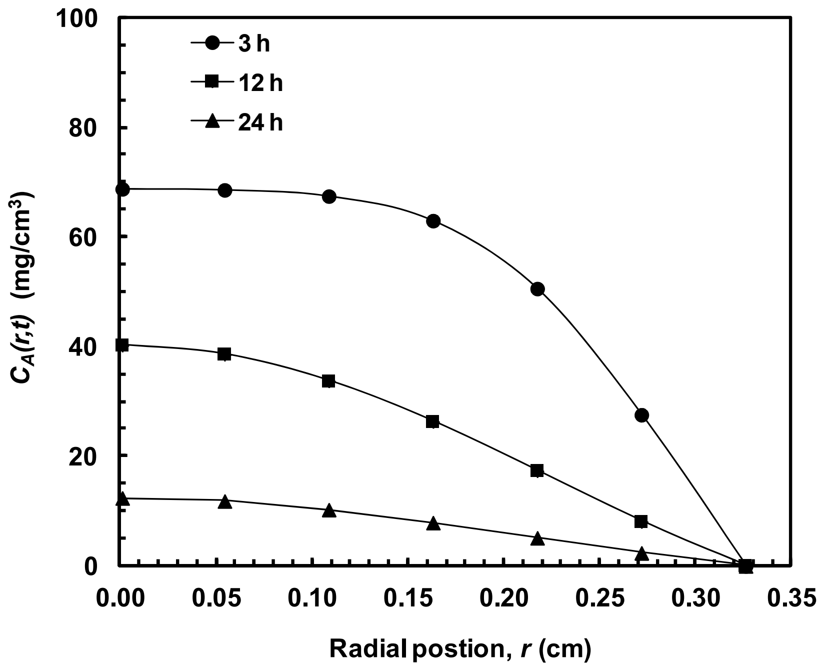
Topic 27.3 Example (Timed Release Drug Dosage cont.) – Sample Predictions

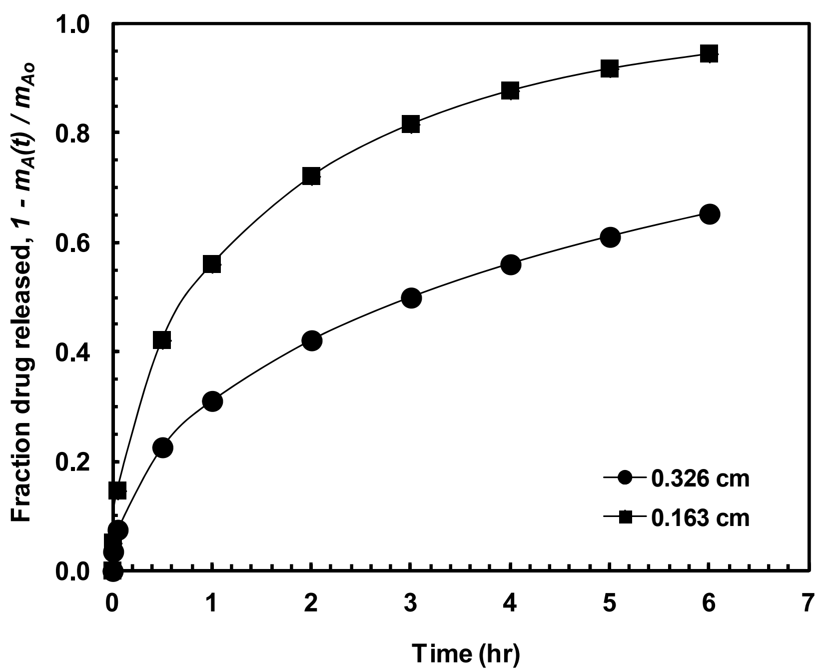
D_{AB} = 3.00E-07 cm^2/s

R = 0.326 cm

C_{Ao} = 68.91 mg/cm^3

C_{As} = 0.0 mg/cm^3



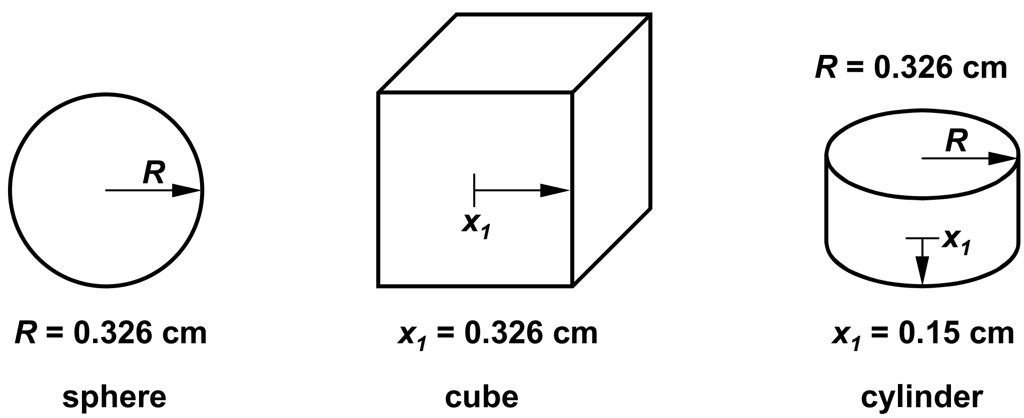


Topic 27.4 Example: Timed Release Drug Dosage with *Concentration-Time Charts*

(a) The present drug capsule consists of a 0.652 cm diameter spherical bead (radius of 0.326 cm) containing a uniform initial concentration of 68.9 mg/cm^3 Dramamine. What is the residual concentration of Dramamine at the center of the spherical bead after 48 hours?

(b) The capsule is now a cube 0.652 cm on a side. Recalculate part (a) above.

(c) The capsule is now a cylindrical tablet of diameter 0.652 cm and thickness 0.3 cm. Recalculate part (a) above. The diffusion coefficient of Dramamine (species *A*) in the gel matrix (species *B*) is $3.0 \cdot 10^{-7}$ cm^2/s at a body temperature of 37 °C. The three capsules are presented below.



Solution

(a) $C_A(0,t)$ *(center) of spherical capsule of* R = *0.326 cm at t = 48 h*

$$X_D = \frac{D_{AB}\,t}{R^2} = \frac{\left(3.0\cdot 10^{-7}\,\frac{cm^2}{s}\right)\left(48\,h\,\frac{3600\,s}{1\,h}\right)}{(0.326\;cm)^2} = 0.488$$

$$n = \frac{r}{R} = \frac{0\;\;cm}{0.326\;\;cm} = 0.0\quad\text{(center of sphere)}$$

$$m = \frac{D_{AB}}{k_c\,R} \approx 0\quad (c_{As} = 0)$$

From Appendix Figure F.3 or Figure 18.3

$$Y = 0.018 = \frac{C_{As} - C_A}{C_{As} - C_{Ao}} = \frac{0 - c_A}{0 - 68.9\;mg/cm^3}$$

C_A = 1.24 mg/cm^3 at t = 48 h

b) $C_A(0,t)$ *(center)* of cube-shaped capsule 0.652 cm on a side at t = 48 hr

Orthogonal distance from the midpoint of the cube to any of the six faces is
x_1 = 0.652 cm / 2 = 0.326 cm

$$X_D = \frac{D_{AB}\,t}{{x_1}^2} = \frac{\left(3.0\cdot 10^{-7}\,\frac{cm^2}{s}\right)\left(48\,h\,\frac{3600\,s}{1\,h}\right)}{(0.326\;cm)^2} = 0.488$$

Values for n and m are unchanged, $n = 0$ and $m = 0$

All of the faces of the cube are of equal dimension: $Y = Y_a Y_b Y_c = {Y_a}^3$

From Appendix Figure F.4, Y_a = 0.4 for $x_1 = a$ = 0.326 cm.

$$Y = {Y_a}^3 = (0.4)^3 = 0.064$$

$$Y = 0.064 = \frac{C_{As} - C_A}{C_{As} - C_{Ao}} = \frac{0 - C_A}{0 - 68.9\;mg/cm^3}$$

C_A = 4.41 mg / cm^3 at t = 48 hr

(c) Cylindrical capsule. For a cylinder with exposed ends, R = 0.652 cm / 2 for the radial coordinate, and $x_1 = a$ = 0.3 cm /2 for the axial coordinate. The relative times are

$$X_D = \frac{D_{AB}\, t}{R^2} = \frac{\left(3.0 \cdot 10^{-7}\, \frac{cm^2}{s}\right)\left(48\, h\, \frac{3600\, s}{1\, h}\right)}{(0.326\ cm)^2} = 0.488$$

for the cylindrical dimension and

$$X_D = \frac{D_{AB}\, t}{x_1{}^2} = \frac{3.0 \cdot 10^{-7}\, \frac{cm^2}{s}\, 48\, h\, \frac{3600\, s}{1\, h}}{(0.15\ cm)^2} = 2.30$$

for the axial dimension. Values for n and m are unchanged, with $n = 0$ and $m = 0$. From Figures F.2 and F.1 respectively, $Y_{cylinder} = 0.1$ for the cylindrical dimension, and $Y_a = 0.006$ for the axial dimension. Therefore

$$Y = Y_{cylinder}\, Y_a = (0.1)(0.006) = 0.0006$$

and finally

$$Y = 0.006 = \frac{c_{As} - c_A}{c_{As} - c_{Ao}} = \frac{0 - c_A}{0 - 68.9\ mg / cm^3}$$

with c_A = 0.413 mg / cm^3 after 48 hours. Since $Y_a << Y_{cylinder}$, the flux directed out of the exposed ends of the cylindrical tablet along the axial dimension dominates.