CHEN3001-TP
Mass Transport - 3

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Outline

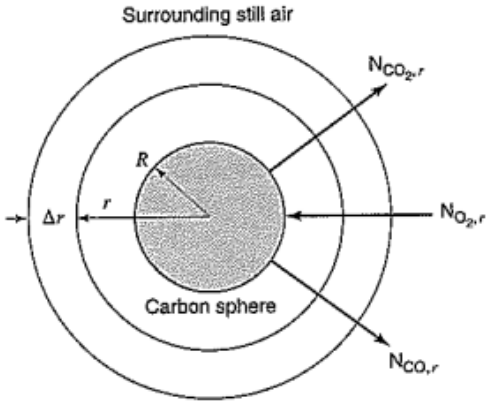
- Unsteady-state diffusion mass transfer
  - Pseudo steady state analysis
    - Case study-1: coal particle burning
  - In finite medium
    - Equations and boundary conditions
    - Application of Heisler charts
    - Classroom example-1
  - In semi-infinite medium
    - Equations and boundary conditions
    - Case study-2: chemical vapour deposition

Pseudo steady state analysis

- Case study-1: coal particle burning
  - Oxygen diffuses to the surface of a coal particle.
  - At the surface, O_2 reacts instantaneously with carbon

$$3\ C(s) + 2.5\ O_2(g) \rightarrow 2\ CO_2(g) + CO(g)$$

  - No homogeneous reaction along the diffusion path
  - Size of particle with time?
    - Assume steady state condition first to analyse diffusion – reaction
    - Use quasi-steady analysis to analyse coal particle



Pseudo steady state analysis

- Case study-1: coal particle burning

Let us write the continuity equation for component-A (oxygen – O_2)in the spherical coordinate system:

$$\frac{\partial c_A}{\partial t} = -\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 N_{Ar}\right) + \frac{1}{r\sin\theta}\frac{\partial}{\partial \theta}\left(N_{A\theta}\sin\theta\right) + \frac{1}{r\sin\theta}\frac{\partial N_{A\phi}}{\partial \phi} \right) + R_A$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 N_{Ar}\right) = 0 \quad \Rightarrow \quad \boxed{\frac{\partial}{\partial r}\left(r^2 N_{O_2 r}\right) = 0}$$

$(A = O_2)$

$r^2 N_{O2r}$ is constant along the diffusion path in the r-direction. Therefore,

$$r^2 N_{O_2 r}\Big|_r = R^2 N_{O_2 r}\Big|_R$$

Pseudo steady state analysis

- Case study-1: coal particle burning

Mass transfer flux of component-A: $N_{Ar} = -cD_{AB}\frac{dx_A}{dr} + x_A \sum N_r$

3 C(s) + 2.5 O_2(g) → 2 CO_2(g) + CO(g) ⇒ *Need to consider 4 species! O_2; CO_2; CO; N_2*

$N_{N_2} = 0$ *(stagnant & non-reactive)*

$N_{CO_2} = -(2/2.5)N_{O_2}$

$N_{CO} = -(1/2.5)N_{O_2}$

(from stoichiometry)

So, total molar flux around the coal particle:

$$\sum N_r = N_{O_2} + N_{CO_2} + N_{CO} + N_{N_2}$$
$$= N_{O_2} - \frac{2}{2.5}N_{O_2} - \frac{1}{2.5}N_{O_2} + (0)$$
$$= -0.2N_{O_2}$$

Pseudo steady state analysis

- Case study-1: coal particle burning

Mass transfer flux of component-A: $N_{Ar} = -cD_{AB}\frac{dx_A}{dr} + x_A \sum N_r$

$$N_{O_2 r} = -cD_{O_2-mix}\frac{dx_{O_2}}{dr} - 0.2x_{O_2}N_{O_2 r} \quad \Leftrightarrow \quad N_{O_2 r} = -\frac{cD_{O_2-mix}}{1+0.2x_{O_2}}\frac{dx_{O_2}}{dr}$$

As we're dealing with spherical coordinates → Need to multiply both sides with r^2

$$r^2 N_{O_2 r} = -\frac{cD_{O_2-mix}r^2}{1+0.2x_{O_2}}\frac{dx_{O_2}}{dr}$$

B.C. 1: $r = R,\ x_{O_2} = 0$ *(instantaneous reaction at particle surface)*

B.C. 2: $r = \infty,\ x_{O_2} = 0.21$ *(molar fraction of O_2 in stagnant air)*

Pseudo steady state analysis

- Case study-1: coal particle burning
- Key points:
  - Do steady state analysis to get the molar flux of oxygen (N_{O2})
  - Use stoichiometry to relate N_{O2} to the molecular consumption of carbon, i.e. (3/2.5) (N_{02}) (surface area)
  - Use material/molecular balance to determine the rate of consumption of carbon.

Unsteady-state diffusion – Finite Medium

- Let us consider the continuity equation for component-A
- 1-D, stationary medium, no reaction, transient

Rectangular: $C_i = C_i(x, y, z, t)$

$$\frac{\partial C_i}{\partial t} + v_x \frac{\partial C_i}{\partial x} + v_y \frac{\partial C_i}{\partial y} + v_z \frac{\partial C_i}{\partial z} = D_i \left[\frac{\partial^2 C_i}{\partial x^2} + \frac{\partial^2 C_i}{\partial y^2} + \frac{\partial^2 C_i}{\partial z^2} \right] + R_i$$

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

Assumptions:

- Mass transfer driven by 1-D diffusion only
- No bulk motion contribution
- No chemical reaction

Examples:

- Diffusion in solids, in stationary liquids, or in systems with equimolar counter-diffusion
- Slow diffusion in dilute solutions

Unsteady-state diffusion – Finite Medium

- 1-D, stationary medium, no reaction, transient

Let $\Theta = (C_A - C_{As})/(C_{A0} - C_{AS})$

$$\frac{\partial C_A}{\partial t} = D_{AB}\frac{\partial^2 C_A}{\partial x^2} \longrightarrow \frac{\partial \Theta}{\partial t} = D_{AB}\frac{\partial^2 \Theta}{\partial x^2}$$

I.C.:	t=0,	$C_A(x, 0) = C_{A0}$	$\Theta(x, 0) = 1,$	for all $0 \le x \le L$
B.C.1:	x=0,	$C_A(0, t) = C_{as}$	$\Theta(0, t) = 0,$	for all $t > 0$
B.C.2:	x=L,	$C_A(L, t) = C_{As}$	$\Theta(\infty, t) = 0,$	for all $t > 0$

Unsteady-state diffusion – Finite Medium

- 1-D, stationary medium, no reaction, transient

$$\frac{C_A - C_{A0}}{C_{A0} - C_{As}} = \frac{4}{\pi}\sum_{n=1}^{n=\infty}\frac{1}{n}\sin\left(\frac{n\pi x}{L}\right)e^{-(n\pi x/2)^2(4D_{AB}t/L^2)}$$

$n = 1, 3, 5, \ldots$

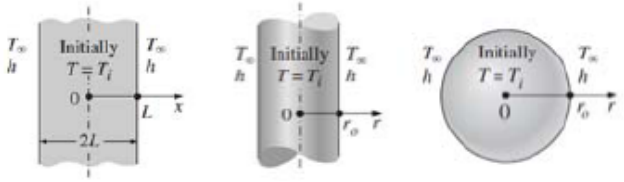
The diffusion flux at any position in the medium:

$$N''_{Ax} = J^*_{Ax} = -D_{AB}\frac{\partial C_A}{\partial x} = \frac{4D_{AB}}{L}(C_{AS} - C_{A0})\sum_{n=1}^{n=\infty}\cos\left(\frac{n\pi x}{L}\right)e^{-(n\pi x/2)^2(4D_{AB}t/L^2)}$$

$n = 1, 3, 5, \ldots$

$$N''_A\Big|_{x=L/2} = 0 \qquad \frac{\partial C_A}{\partial x}\Big|_{x=L/2} = 0$$

Symmetry condition at the centre point/line



Unsteady-state diffusion – Finite Medium

- 1-D, stationary medium, no reaction, transient

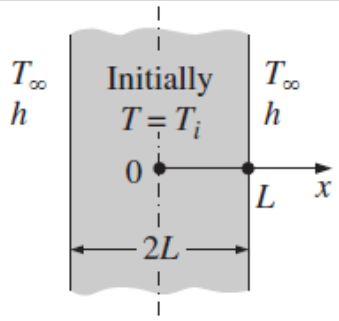
Analogy between the quantities that appear in the formulation and solution of transient heat conduction and transient mass diffusion in a stationary medium

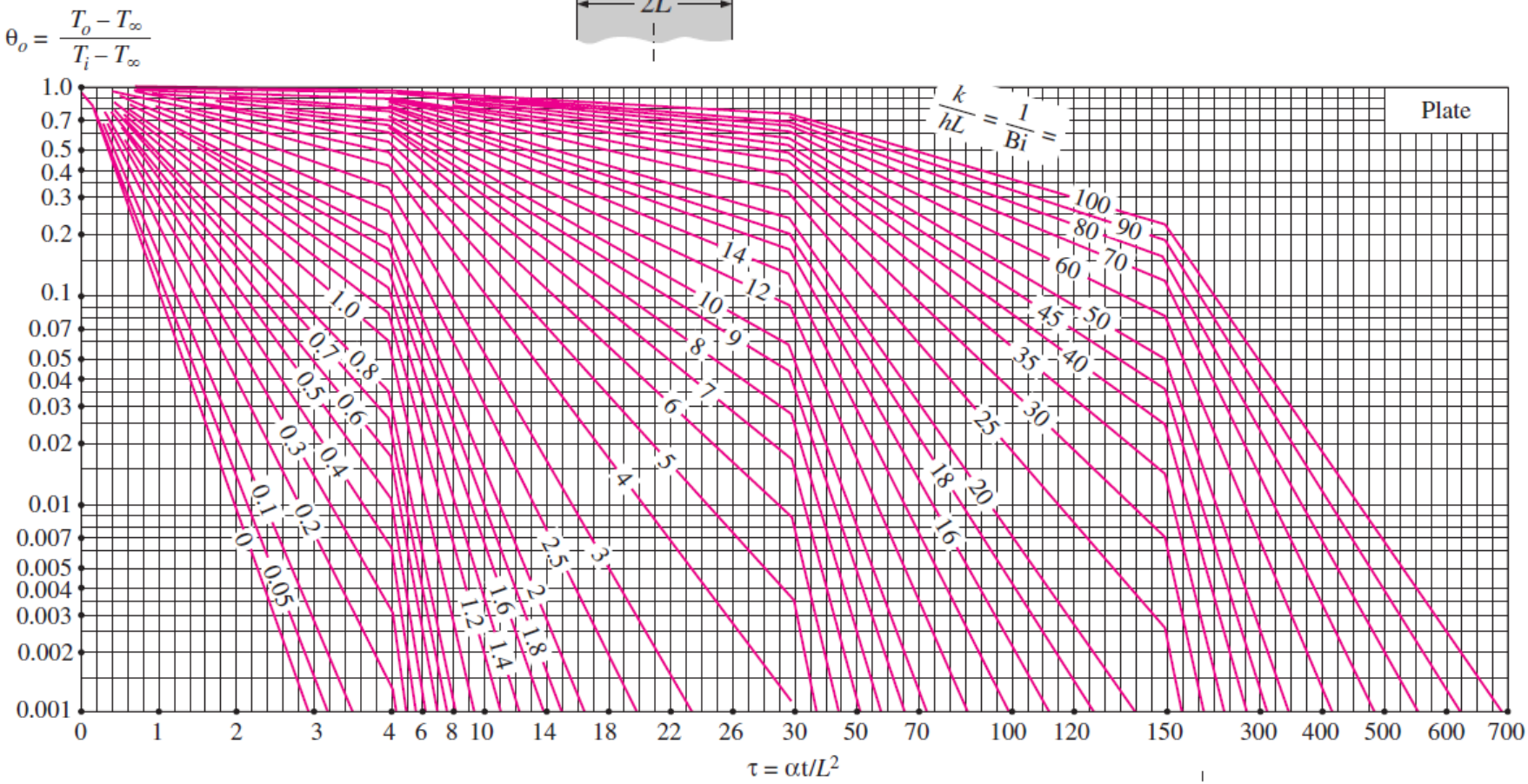
Heat Conduction	Mass Diffusion
T	C, y, ρ or w
α	D_{AB}
$\theta = \dfrac{T(x,t) - T_\infty}{T_i - T_\infty}$, $\dfrac{T(x,t) - T_s}{T_i - T_s}$	$\theta_{mass} = \dfrac{w_A(x,t) - w_{A,\infty}^*}{w_{A,i} - w_{A,\infty}}$, $\dfrac{w_A(x,t) - w_A}{w_{A,i} - w_A}$
$\xi = \dfrac{x}{2\sqrt{\alpha t}}$	$\xi_{mass} = \dfrac{x}{2\sqrt{D_{AB} t}}$
$\mathrm{Bi} = \dfrac{h_{conv} L}{k}$	$\mathrm{Bi}_{mass} = \dfrac{h_{mass} L}{D_{AB}}$
$\tau = \dfrac{\alpha t}{L^2}$	$\tau = \dfrac{D_{AB} t}{L^2}$

$$\frac{C_A(x,t) - C_{A,i}}{C_{A,s} - C_{A,i}} = \frac{\rho_A(x,t) - \rho_{A,i}}{\rho_{A,s} - \rho_{A,i}} = \frac{w_A(x,t) - w_{A,i}}{w_{A,s} - w_{A,i}} = \frac{y_A(x,t) - y_{A,i}}{y_{A,s} - y_{A,i}}$$

Unsteady-state diffusion – Finite Medium

Heisler chart (Plane wall)

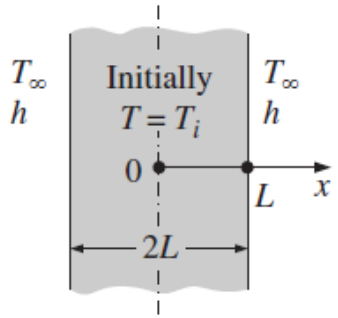


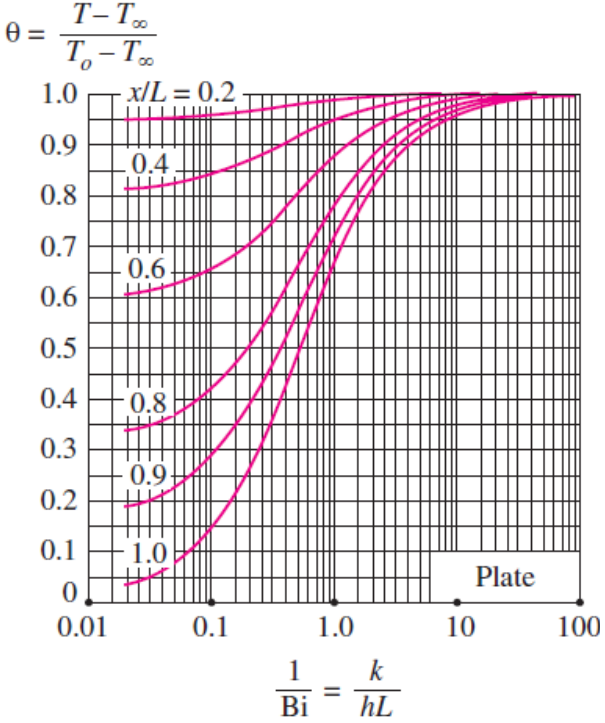


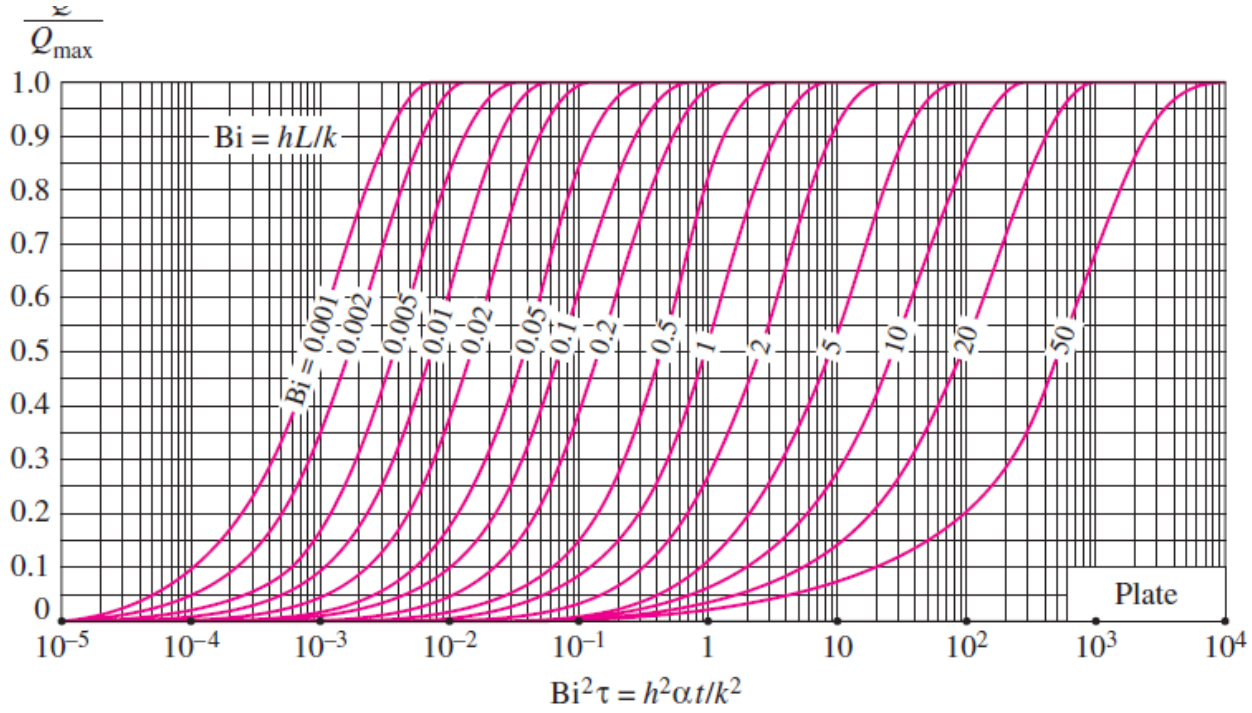
taken from Cengel, 2006

Unsteady-state diffusion – Finite Medium

Heisler chart (Plane wall)



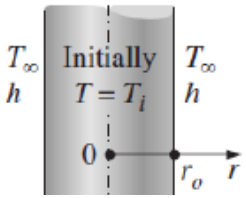


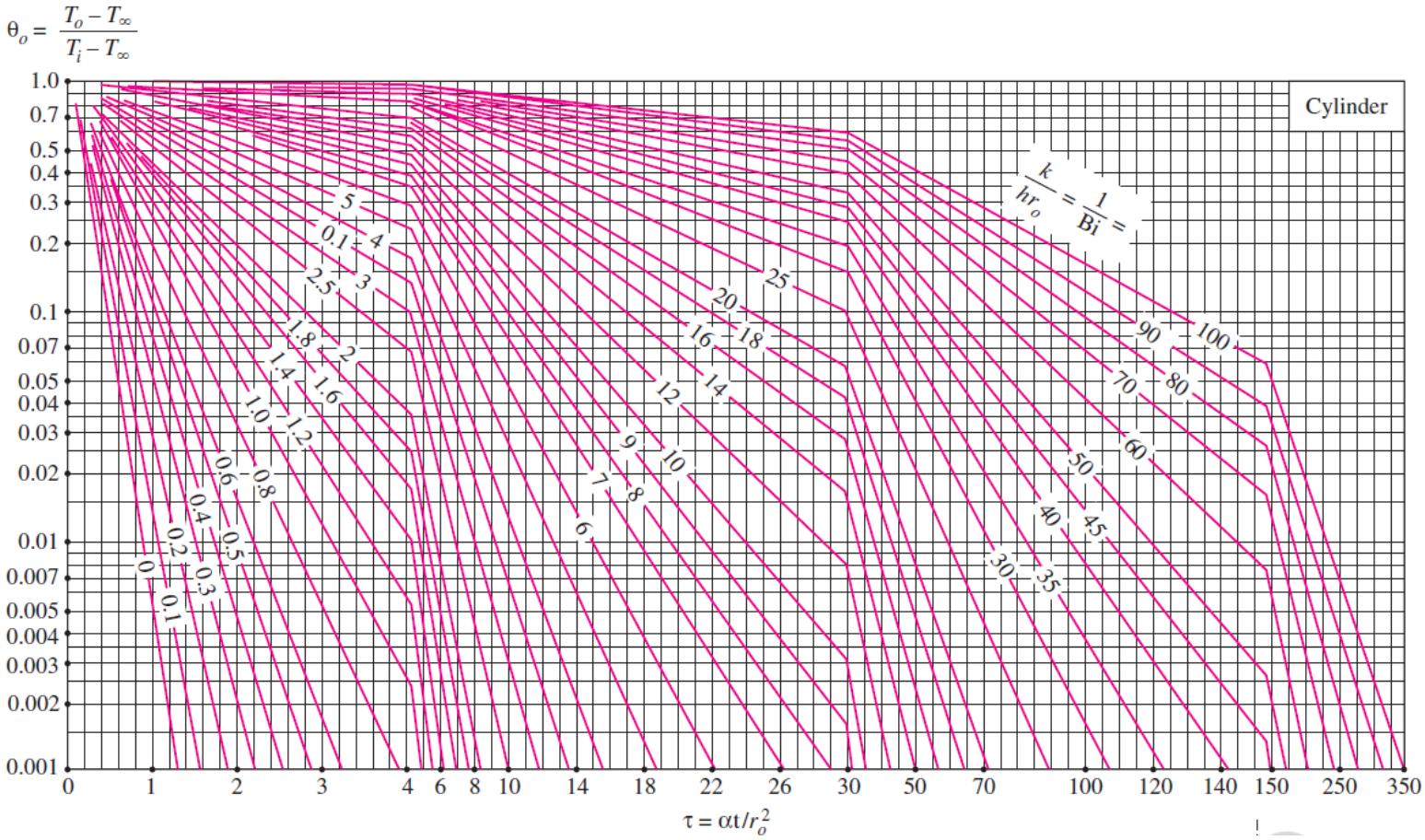


taken from Cengel, 2006

Unsteady-state diffusion – Finite Medium

Heisler chart (cylinder)

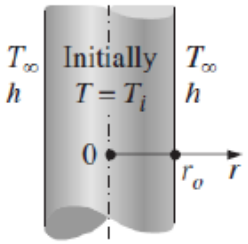


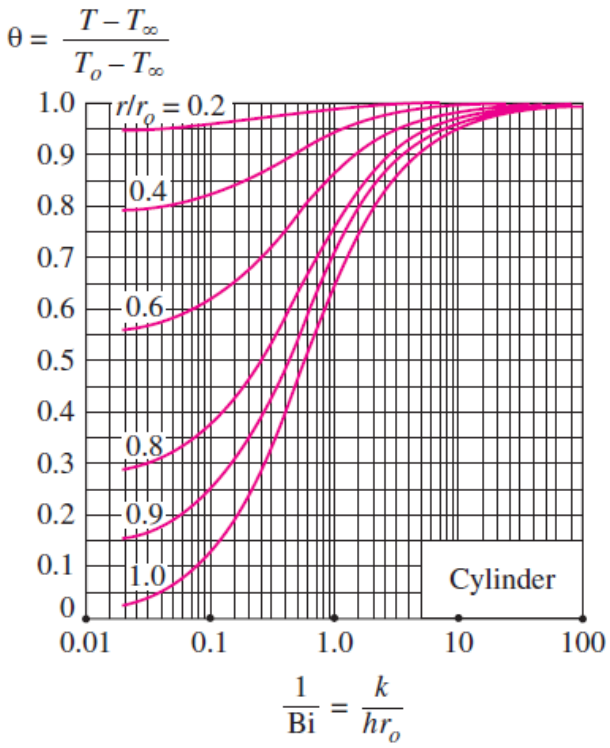


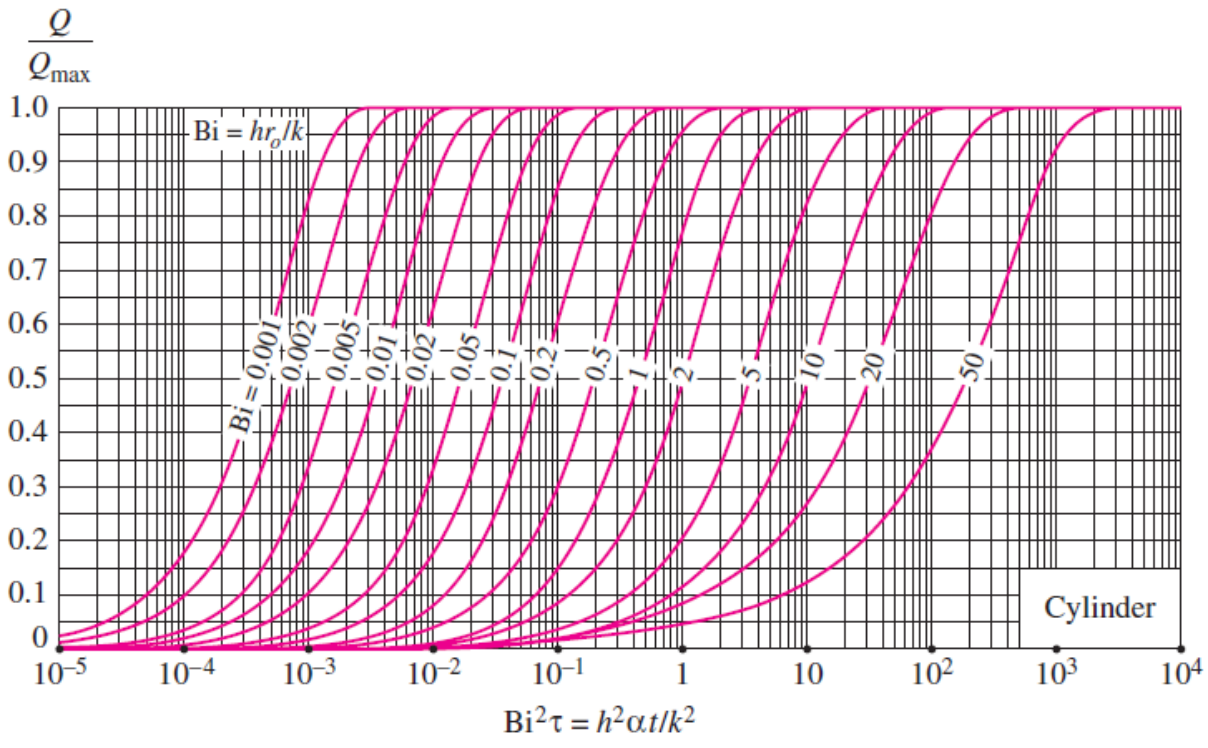
taken from Cengel, 2006

Unsteady-state diffusion – Finite Medium

Heisler chart (Cylinder)



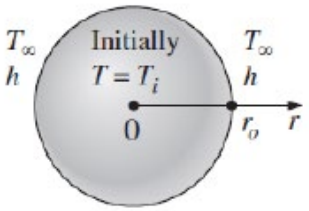


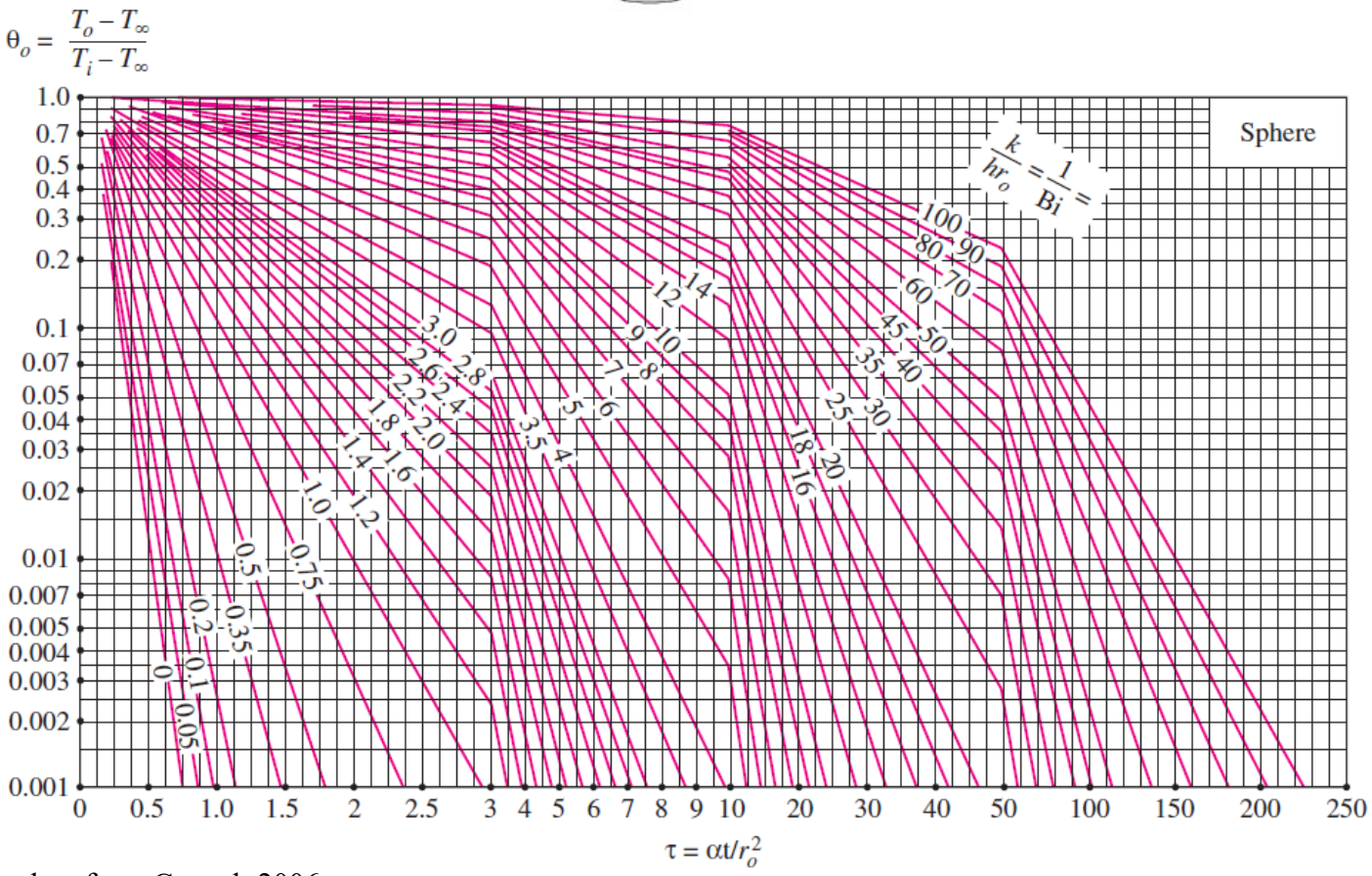


taken from Cengel, 2006

Unsteady-state diffusion – Finite Medium

Heisler chart (Sphere)

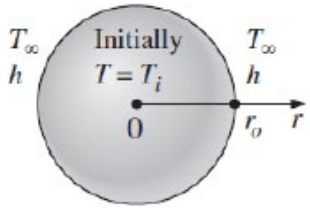


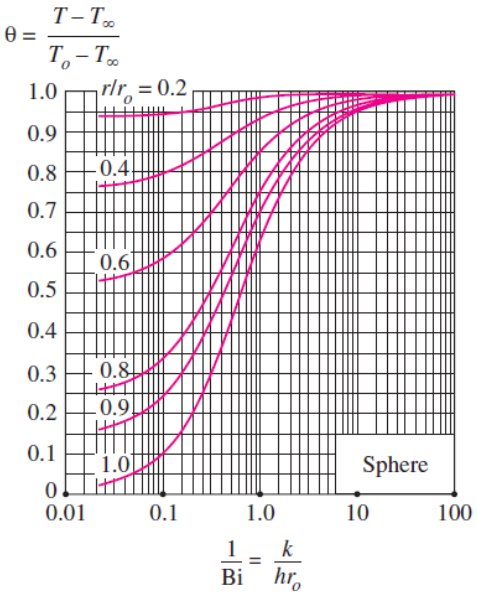


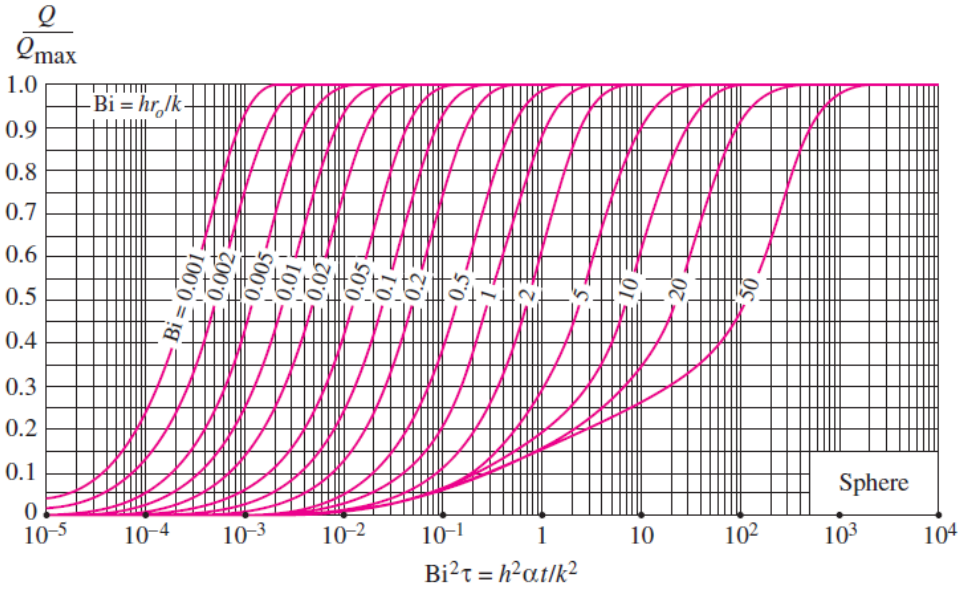
taken from Cengel, 2006

Unsteady-state diffusion – Finite Medium

Heisler chart (Sphere)







taken from Cengel, 2006

Unsteady-state diffusion – Finite Medium

Classroom example:

A spherical drug capsule (0.652 cm diameter) has an initial concentration of 68.9 mg/cm^3 Dramamine.

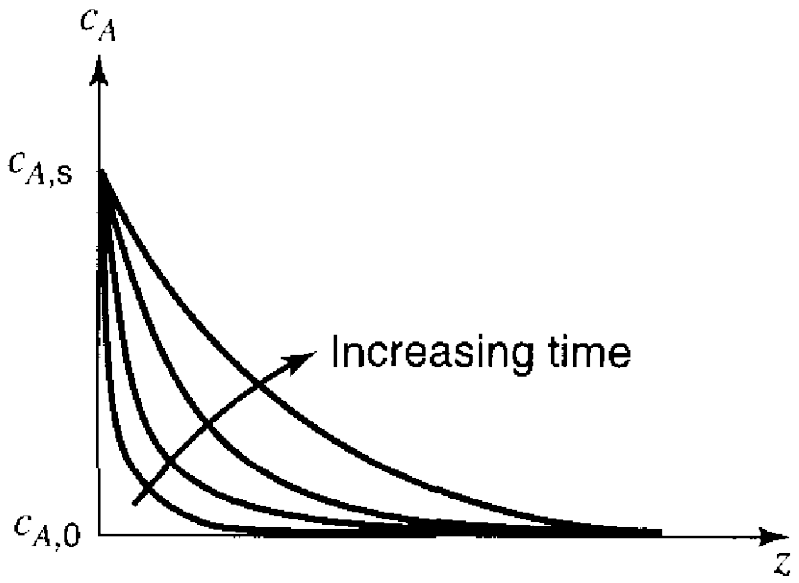
- What is the residual concentration of Dramamine at the centre of the spherical bead after 48 hours?

  - *Capsule is to be ingested into the human body and settle in the gastrointestinal system.*
  - *The capsule is made of a nontoxic gelatinous material, through which the drug is gradually dissolved.*
  - *Drug loaded within the bead → source of mass transfer*
  - *Fluid surrounding the bead → sink of mass transfer*

Data: D_{AB} (Dramamine in the gel matrix of the capsule) = 3×10^{-7} cm^2/s at body temperature of 37°C.

Unsteady-state diffusion – Semi-infinite Medium

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



Initial condition: t=0, $C_A(x, 0) = C_{Ai}$ (for all x)

B.C.1: x=0, $C_A(0, t) = C_{as}$ (for all t>0)

B.C.2 $x \rightarrow \infty$, $C_A(\infty, t) = C_{Ai}$ (for all t>0)

Unsteady-state diffusion – Semi-infinite Medium

Let $\theta = c_A - c_{Ai}$,

$$\frac{\partial C_A}{\partial t} = D_{AB}\frac{\partial^2 C_A}{\partial x^2} \longrightarrow \frac{\partial \theta}{\partial t} = D_{AB}\frac{\partial^2 \theta}{\partial x^2}$$

Initial condition:	$t = 0,\ c_A(x,0) = c_{Ai}$	$\theta(x,0) = 0$	(for all x)
B.C. 1:	$x = 0, c_A(0,t) = c_{As}$	$\theta(0,t) = c_{As} - c_{Ai}$	(for all t > 0)
B.C. 2:	$x \to \infty, c_A(\infty,t) = c_{Ai}$	$\theta(\infty,t) = 0$	(for all t > 0)

$$\frac{C_A - C_{Ai}}{C_{As} - C_{Ai}} = 1 - erf\left(\frac{x}{2\sqrt{D_{AB}t}}\right) = 1 - erf(\varphi)$$

$$erf(\phi) = \frac{2}{\sqrt{\pi}}\int_0^{\phi}\exp(-\phi^2)d\phi$$

$$\phi = \frac{x}{2\sqrt{D_{AB}t}}$$

Unsteady-state diffusion – Semi-infinite Medium

ϕ	erf ϕ	ϕ	erf ϕ
0	0.0	0.85	0.7707
0.025	0.0282	0.90	0.7970
0.05	0.0564	0.95	0.8209
0.10	0.1125	1.0	0.8427
0.15	0.1680	1.1	0.8802
0.20	0.2227	1.2	0.9103
0.25	0.2763	1.3	0.9340
0.30	0.3286	1.4	0.9523
0.35	0.3794	1.5	0.9661
0.40	0.4284	1.6	0.9763
0.45	0.4755	1.7	0.9838
0.50	0.5205	1.8	0.9891
0.55	0.5633	1.9	0.9928
0.60	0.6039	2.0	0.9953
0.65	0.6420	2.2	0.9981
0.70	0.6778	2.4	0.9993
0.75	0.7112	2.6	0.9998
0.80	0.7421	2.8	0.9999

$$erf(\phi) = \frac{2}{\sqrt{\pi}} \int_0^{\phi} \exp(-\phi^2) d\phi$$

$$erf(\phi) \approx \frac{2}{\sqrt{\pi}} \left(\phi - \frac{\phi^3}{3} \right) \qquad for\ \phi \leq 0.5$$

$$erf(\phi) \approx \left(1 - \frac{1}{\sqrt{\pi}} e^{-\phi^2} \right) \left(\frac{1}{\phi} \right) \qquad for\ \phi \geq 1$$

Unsteady-state diffusion – Semi-infinite Medium

The complementary error function

ξ	erfc (ξ)	ξ	erfc (ξ)	ξ	erfc (ξ)	ξ	erfc (ξ)	ξ	erfc (ξ)	ξ	erfc (ξ)
0.00	1.00000	0.38	0.5910	0.76	0.2825	1.14	0.1069	1.52	0.03159	1.90	0.00721
0.02	0.9774	0.40	0.5716	0.78	0.2700	1.16	0.10090	1.54	0.02941	1.92	0.00662
0.04	0.9549	0.42	0.5525	0.80	0.2579	1.18	0.09516	1.56	0.02737	1.94	0.00608
0.06	0.9324	0.44	0.5338	0.82	0.2462	1.20	0.08969	1.58	0.02545	1.96	0.00557
0.08	0.9099	0.46	0.5153	0.84	0.2349	1.22	0.08447	1.60	0.02365	1.98	0.00511
0.10	0.8875	0.48	0.4973	0.86	0.2239	1.24	0.07950	1.62	0.02196	2.00	0.00468
0.12	0.8652	0.50	0.4795	0.88	0.2133	1.26	0.07476	1.64	0.02038	2.10	0.00298
0.14	0.8431	0.52	0.4621	0.90	0.2031	1.28	0.07027	1.66	0.01890	2.20	0.00186
0.16	0.8210	0.54	0.4451	0.92	0.1932	1.30	0.06599	1.68	0.01751	2.30	0.00114
0.18	0.7991	0.56	0.4284	0.94	0.1837	1.32	0.06194	1.70	0.01612	2.40	0.00069
0.20	0.7773	0.58	0.4121	0.96	0.1746	1.34	0.05809	1.72	0.01500	2.50	0.00041
0.22	0.7557	0.60	0.3961	0.98	0.1658	1.36	0.05444	1.74	0.01387	2.60	0.00024
0.24	0.7343	0.62	0.3806	1.00	0.1573	1.38	0.05098	1.76	0.01281	2.70	0.00013
0.26	0.7131	0.64	0.3654	1.02	0.1492	1.40	0.04772	1.78	0.01183	2.80	0.00008
0.28	0.6921	0.66	0.3506	1.04	0.1413	1.42	0.04462	1.80	0.01091	2.90	0.00004
0.30	0.6714	0.68	0.3362	1.06	0.1339	1.44	0.04170	1.82	0.01006	3.00	0.00002
0.32	0.6509	0.70	0.3222	1.08	0.1267	1.46	0.03895	1.84	0.00926	3.20	0.00001
0.34	0.6306	0.72	0.3086	1.10	0.1198	1.48	0.03635	1.86	0.00853	3.40	0.00000
0.36	0.6107	0.74	0.2953	1.12	0.1132	1.50	0.03390	1.88	0.00784	3.60	0.00000

Notes:

- Concentration at the surface is considered constant → assumption of *negligible* surface resistance (or very high convection coefficient, k_c)
- Concentration away from the surface ($x \rightarrow \infty$) is assumed equal to initial concentration → within the time frame of the calculation, concentration away from the surface is not expected to change considerably, i.e. diffusion path is much shorter than the thickness of the geometry!

Examples: (i) absorption of oxygen gas into a deep tank of still water, (ii) case-hardening of mild steel within a carburizing atmosphere, (iii) "doping" of phosphorous atoms into a silicon wafer.

Unsteady-state diffusion – Semi-infinite Medium

Case study – 2 – Chemical Vapour deposition

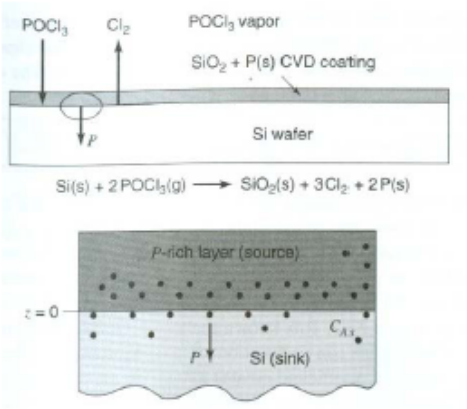
- 'Doping' process in the fabrication of solid-state microelectronics

Case study 2

Unsteady state mass transfer in a semi-infinite medium

Chemical vapour deposition (cont.)

- The CVD process forms a SiO_2 coating rich in molecular phosphorous (P) over the crystalline-silicon surface.
- Phosphorous atoms then diffuses through the crystalline silicon to form the Si-P thin film.
  - Coating becomes the source for mass transfer of phosphorous
  - Silicon wafer is the sink for mass transfer of phosphorous



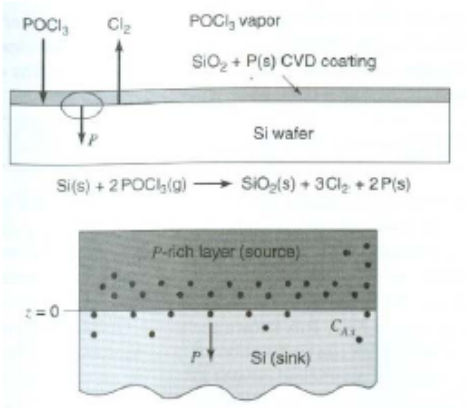
Welty et al. (2001)

Unsteady-state diffusion – Semi-infinite Medium

Case study – 2 – Chemical Vapour deposition

Chemical vapour deposition (cont.)

- The CVD process forms a SiO_2 coating rich in molecular phosphorous (P) over the crystalline-silicon surface.
- Phosphorous atoms then diffuses through the crystalline silicon to form the Si-P thin film.
  - Coating becomes the source for mass transfer of phosphorous
  - Silicon wafer is the sink for mass transfer of phosphorous



To analyse:

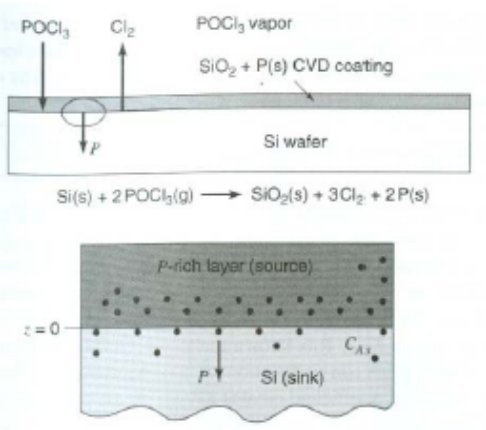
- (Assumption) P-atom concentration is constant at the interface.
- Diffusion coefficient of P atoms in crystalline silicon is very low and only a thin film of Si-P is desired
  - P-atoms do not penetrate very far into the silicon, i.e. the P-atoms cannot "see" through the entire thickness of the wafer
  - Si solid serves as a semi-infinite sink for the diffusion process.
- Predict the properties of the Si-P thin film as a function of the doping conditions

Unsteady-state diffusion – Semi-infinite Medium

Case study – 2 – Chemical Vapour deposition

Chemical vapour deposition (cont.)

- CVD operation at 1100°C
  - This temperature is high enough to promote phosphorous diffusion
- The surface concentration of phosphorous (C_{AS}) in the silicon is 2.5 x 10^{20} atoms P/cm^3 solid Si
  - This conc. is relatively dilute (pure solid silicon is 5x10^{22} atoms Si/cm^3 solid)
- The phosphorous-rich coating is considered as an infinite source relative to the amount of P atoms transferred → C_{AS} is constant.
- Predict the depth of the Si-P thin film after 1 hour, if the target concentration is 1% of the surface value (2.5x10^{18} atoms P/cm^3 solid Si)
- Predict the concentration profile of P atoms after 1 hour.



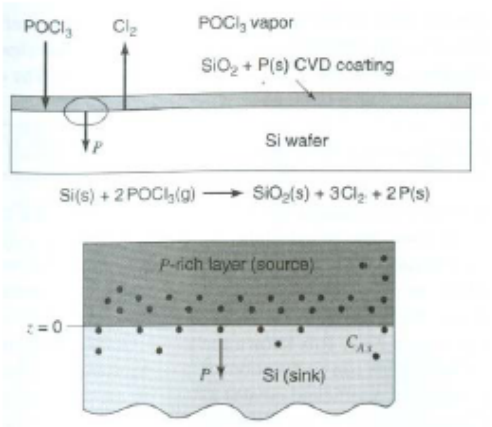
Unsteady-state diffusion – Semi-infinite Medium

Case study – 2 – Chemical Vapour deposition

Chemical vapour deposition (cont.)

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

$C_A(x,t)$ → Concentration of phosphorous (species A) in solid silicon (species B)



Relevant IC and BCs:

I.C.:	t=0,	$C_A(x, 0) = C_{A0}=0$,	for all x
B.C.-1:	x=0,	$C_A(0, t) = C_{As}=2.5\times10^{20}$ atoms P/cm^3,	for all t>0
B.C.-1:	$x\rightarrow\infty$,	$C_A(\infty, t) = C_{A0}=0$,	for all t>0

Unsteady-state diffusion – Semi-infinite Medium

Case study – 2 – Chemical Vapour deposition

Chemical vapour deposition (cont.)

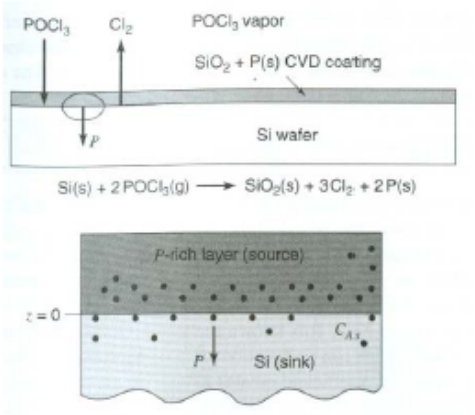
(Assumption) D_{AB} is constant
→ Analytical solution:

$$\frac{C_{AS}-C_A}{C_{AS}-C_{A0}} = erf\left(\frac{x}{\sqrt{4D_{AB}t}}\right) = erf(\phi)$$

$$\Leftrightarrow \frac{C_{AS}-C_A}{C_{AS}-C_{A0}} = \frac{2.5x10^{20}-2.5x10^{18}}{2.5x10^{20}} = 0.99 = erf(\phi)$$

$$\Leftrightarrow erf(\phi) = 0.99 \quad \text{where} \quad \phi = 1.82 = x/\sqrt{4D_{AB}t}$$

$$x = \phi * \sqrt{4D_{AB}t} = 1.82 * \sqrt{4 * 6.5x10^{-13}[cm^2/s] * 3600[s]} = 1.76x10^{-4} cm$$



Welty et al. (2001)

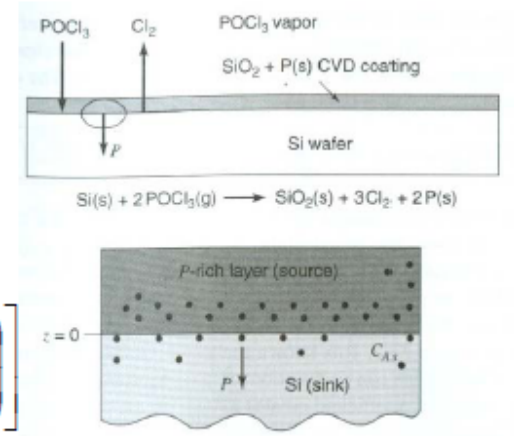
Unsteady-state diffusion – Semi-infinite Medium

Case study – 2 – Chemical Vapour deposition

Chemical vapour deposition (cont.)

Concentration profile after 1 hour:

$$\frac{C_{AS}-C_A}{C_{AS}-C_{A0}} = erf\left(\frac{x}{\sqrt{4D_{AB}t}}\right)$$



$$\Leftrightarrow C_A = (2.5x10^{20})\left[1-erf\left(\frac{x}{\sqrt{4(6.5x10^{-13}\,cm^2/s)(3600s)}}\right)\right]$$

Concentration profile after 1 hour:

