energy flux / projected area

$r_{12} >> D_1, D_2$ ∴ treat r_{12} = cst

For a sphere, $dA_1 = \frac{1}{4} D_1^2 \sin\theta_1 \, d\phi_1 \, d\theta_1$

$$\left(\frac{dQ_{\vec{12}}}{\cos\theta_2 \, dA_2} \right) = \frac{\sigma T_1^4}{\pi} \frac{D_1^2}{4 r_{12}^2} \int_0^{2\pi} \int_0^{\frac{\pi}{2}} \sin\theta_1 \cos\theta_1 \, d\theta_1 \, d\phi_1$$

$$= \frac{\sigma T_1^4}{\pi} \frac{D_1^2}{4 r_{12}^2} \pi = \frac{\sigma T_1^4 D_1^2}{4 r_{12}^2}$$

$$= q_{b1} \frac{1}{r_{12}^2} \cdot \frac{1}{\pi} \cdot \frac{\pi D_1^2}{4}$$

$\frac{\pi D_1^2}{4}$ ← projected area of sun (disk)

$\frac{1}{\pi}$ factor in Lambert's law

$\frac{1}{r_{12}^2}$ ↑ inverse square of dist.

Alt; for this problem may look at total flux over surface $r = r_{12}$:

Total E/time = $q_{b1} \pi D_1^2$

area of $r = r_{12}$ surface = $4\pi r_{12}^2$

$$\therefore \frac{dQ_{\vec{12}}}{\cos\theta_2 \, dA_2} = \frac{q_{b1} D_1^2}{4 r_{12}^2} = 430 \ \frac{Btu}{hr \, ft^2}$$

Note: if E dia is $D_2 = 8 \times 10^3$ mi, then

$$F_{12} = \frac{\frac{1}{4}\pi D_2^2}{4\pi r_{12}^2} = 0.45 \times 10^{-9}$$ ← projected area

or ½ of 1 billion of sun's power!

How do we obtain F_{12} in more complex geometries?

Either (1) Brute force integration (messy)

(2) Break up into smaller problems & use tables

(3) Configuration factor algebra

look at last:

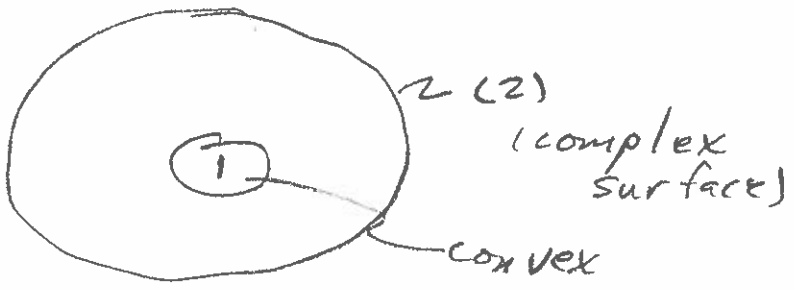
If surface (1) is enclosed <u>completely</u> by N surfaces (including self if concave) then

$$\sum_{i=1}^{N} F_{1i} = 1$$ as radiation must go <u>somewhere</u>

As well as $A_1 F_{1i} = A_i F_{i1}$

If (1) is <u>convex</u> then $F_{11} = 0$ (i.e., does not absorb own radiation)

Ex:



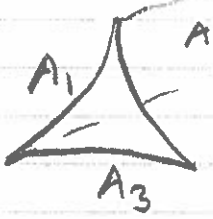
Now $F_{11} + F_{12} = 1$ but $F_{11} = 0 \therefore F_{12} = 1$

Thus $A_2 F_{21} = A_1 F_{12} = A_1$ or $F_{21} = \frac{A_1}{A_2}$

and $F_{22} = 1 - \frac{A_1}{A_2}$; if $A_1 = 0$ then $F_{22} = 1$

Now look at a more complex system:

3 non-concave surfaces forming an enclosure:



→ would be very messy integration!

Have equations:

$$F_{12} + F_{13} = 1$$
$$F_{21} + F_{23} = 1$$
$$F_{31} + F_{32} = 1$$
$$A_1 F_{12} = A_2 F_{21}$$
$$A_1 F_{13} = A_3 F_{31}$$
$$A_2 F_{23} = A_3 F_{32}$$

6 eq'n, 6 unknowns!

Note: if $F_{11}, F_{22}, F_{33} \neq 0$ we have 3 more unknown & system is no longer closed

Obtain $F_{12} = \dfrac{A_1 + A_2 - A_3}{2A_1}$

$$F_{23} = \frac{A_2 + A_3 - A_1}{2A_2}$$

$$F_{31} = \frac{A_3 + A_1 - A_2}{2A_3}$$

N D!!0

Can readily extend to arbitrary N => reduces integral problem to simple algebra.

End lec. 28

Thus far, have dealt w/ black bodies. Now look at N isothermal gray surfaces forming an enclosure.

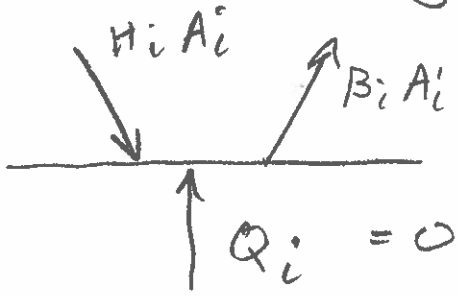
To solve for energy transp., assume radiation incident on any given surface is uniform (spatially anyway) ⇒ not nec. good assumption as we are interested in case where surfaces are at different temp.

Define radiosity $B_i \equiv$ net energy leaving / time · area (includes emitted & reflected)

$$B_i = \varepsilon_i \sigma T_i^4 + \rho_i H_i$$

H_i ← incident radiation

ρ_i = reflectivity $= 1 - \varepsilon_i$ for opaque bodies



$Q_i = 0$ if everything is at same temp

$$Q_i = B_i A_i - H_i A_i = \frac{\varepsilon_i A_i (\sigma T_i^4 - B_i)}{1 - \varepsilon_i}$$

Let's compute H_i: energy incident surface i ⇒

energy leaving $j = B_j A_j$

of this, $B_j A_j F_{ji}$ reaches surface i

$$\therefore \quad H_i A_i = \sum_{j=1}^{N} B_j A_j F_{ji} = \sum_{j=1}^{N} B_j A_i F_{ij}$$

$$= A_i \sum_{j=1}^{N} B_j F_{ij}$$

End lect. 28

Hence

$$Q_i = B_i A_i - H_i A_i$$

$$= B_i A_i \left(\sum_{j=1}^{N} F_{ij} \right) - A_i \sum_{j=1}^{N} B_j F_{ij}$$

$\sum_{j=1}^{N} F_{ij} = 1$ for an enclosure!

$$\therefore Q_i = \sum_{j=1}^{N} (B_i - B_j) A_i F_{ij}$$

$$\text{i.e. } Q_i \equiv \frac{e_i A_i (\sigma T_i^4 - B_i)}{1 - e_i} = \sum_{j=1}^{N} (B_i - B_j) A_i F_{ij}$$

$$\text{or } \frac{(\sigma T_i^4 - B_i)}{\frac{1 - e_i}{e_i A_i}} + \sum_{j=1}^{N} \frac{(B_j - B_i)}{\frac{1}{A_i F_{ij}}} = 0$$

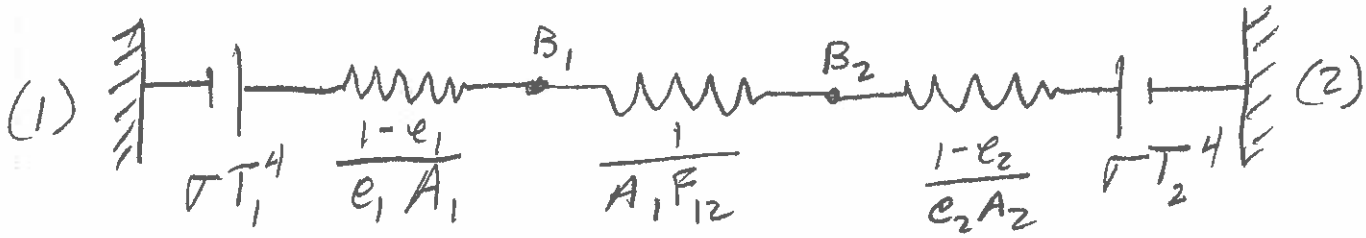
If T_i known, get N eq'n for B_i's !
(assuming F_{ij} known as well)

For $N = 2$: ~~$A_1 F_{12} = A_2 F_{21}$ ⇒ Assume convex~~

$$\frac{\sigma T_1^4 - B_1}{\frac{1 - e_1}{e_1 A_1}} + \frac{B_2 - B_1}{\frac{1}{A_1 F_{12}}} = 0 \qquad i = 1$$

$$\frac{\sigma T_2^4 - B_2}{\frac{1 - e_2}{A_2 e_2}} + \frac{B_1 - B_2}{\frac{1}{A_2 F_{21}}} = 0 \qquad i = 2$$

What does this mean physically? Use analogy to electric circuit:



Energy flows from 1 to 2 & from 2 to 1 through resistances

surface (1): $\dfrac{1-\epsilon_1}{\epsilon_1 A_1}$

View factor: $\dfrac{1}{A_1 F_{12}} = \dfrac{1}{A_2 F_{21}}$

surface (2): $\dfrac{1-\epsilon_2}{\epsilon_2 A_2}$

Thus

$$Q_{12} = \frac{\sigma (T_1^4 - T_2^4)}{\sum \text{Resis}}$$

where $\sum \text{Resis} = \dfrac{1-\epsilon_1}{\epsilon_1 A_1} + \dfrac{1-\epsilon_2}{\epsilon_2 A_2} + \dfrac{1}{A_1 F_{12}}$!

For two inf. parallel plates $F_{12} = 1$ and $A_1 = A_2 = A$

$$\therefore Q_{12} = A \frac{\sigma (T_1^4 - T_2^4)}{\frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} - 1}$$ as obtained before!

(see opposite)

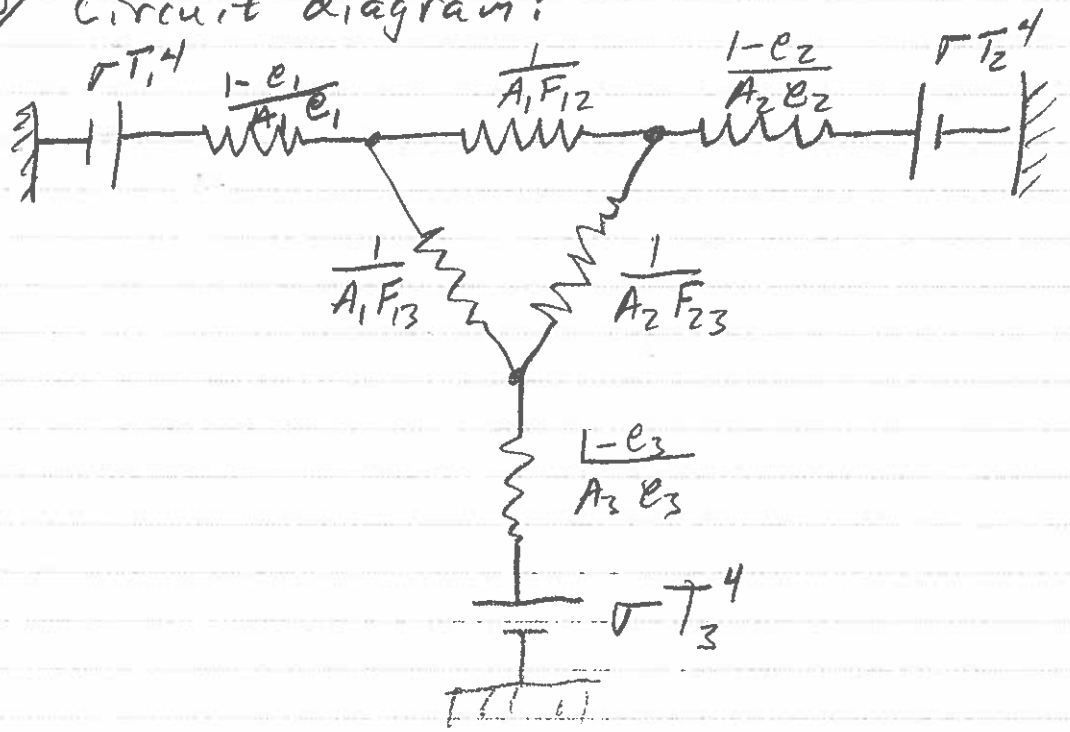
For $N=3$ we have the more complex system:

$$i=1 \quad \frac{\sigma T_1^4 - B_1}{\frac{1-e_1}{e_1 A_1}} + 0 + \frac{B_2 - B_1}{\frac{1}{A_1 F_{12}}} + \frac{B_3 - B_1}{\frac{1}{A_1 F_{13}}} = 0$$

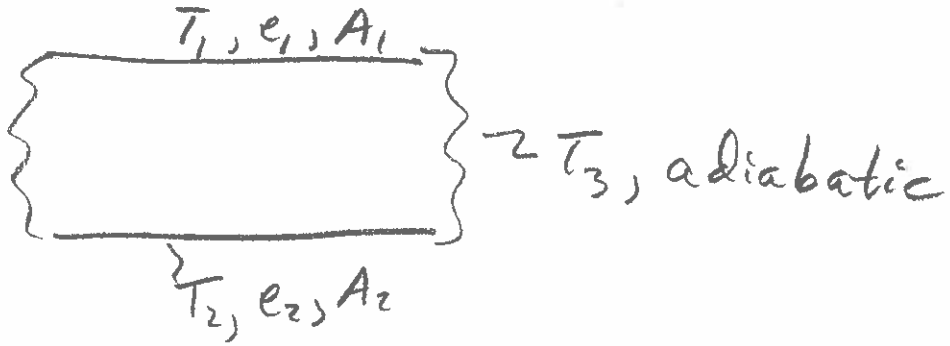
$$i=2 \quad \frac{\sigma T_2^4 - B_2}{\frac{1-e_2}{e_2 A_2}} + \frac{B_1 - B_2}{\frac{1}{A_2 F_{21}}} + 0 + \frac{B_3 - B_2}{\frac{1}{A_2 F_{23}}} = 0$$

$$i=3 \quad \frac{\sigma T_3^4 - B_3}{\frac{1-e_3}{e_3 A_3}} + \frac{B_1 - B_3}{\frac{1}{A_3 F_{31}}} + \frac{B_2 - B_3}{\frac{1}{A_{32} F_{32}}} + 0 = 0$$

w/ circuit diagram:

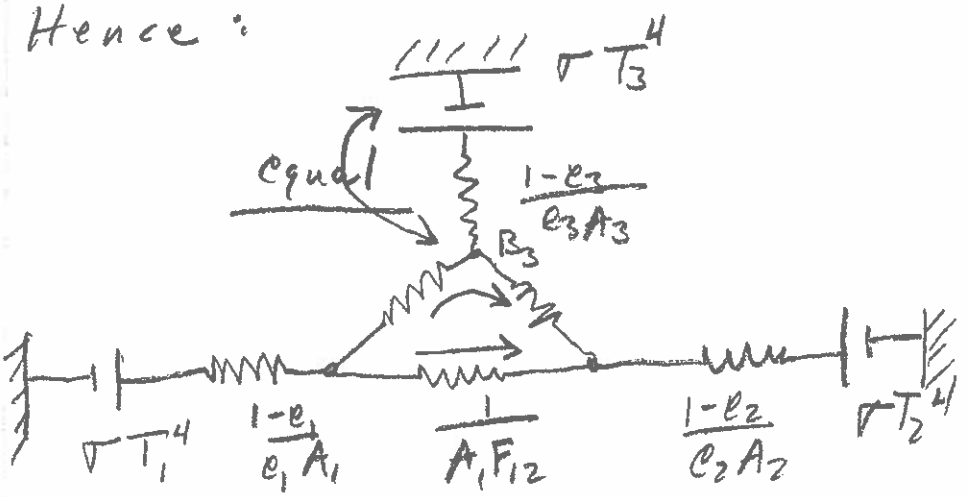


An example of this type of system is rad. exchange between 2 surfaces w/ outer walls that are adiabatic, i.e.:



If T_3 = adiabatic, $Q_3 = 0$ $\therefore B_3 = \sigma T_3^4$

Hence:



$$Q_{12} = \frac{\sigma (T_1^4 - T_2^4)}{\frac{1-e_2}{e_2 A_2} + \frac{1-e_1}{e_1 A_1} + \frac{1}{A_1 F_{12}}}$$

Where $$\frac{1}{A_1 \overline{F}_{12}} = \left\{ \left(\frac{1}{A_1 F_{13}} + \frac{1}{A_2 F_{23}} \right)^{-1} + \left(\frac{1}{A_1 F_{12}} \right)^{-1} \right\}^{-1}$$

If $A_1 = A_2 = A$, obtain result

$$Q_{12} = \frac{\sigma (T_1^4 - T_2^4) A}{\left(\frac{1}{e_1} - 1\right) + \left(\frac{1}{e_2} - 1\right) + \frac{F_{23} + F_{13}}{F_{13} F_{23} + F_{12} F_{13} + F_{12} F_{23}}}$$

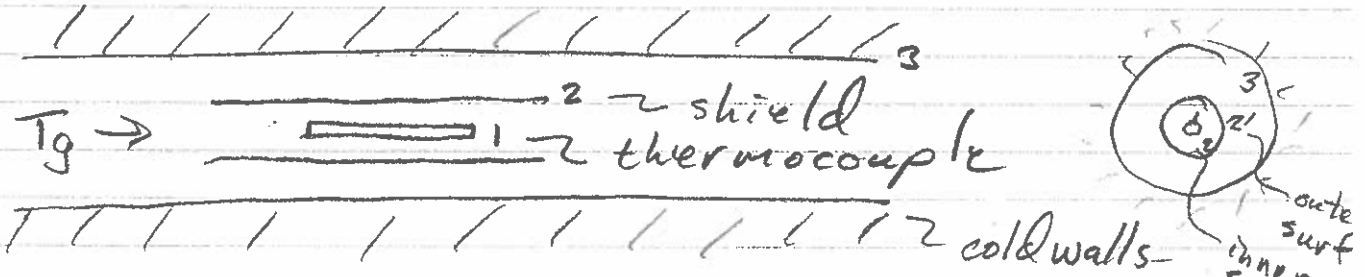
or $Q_{12} = A_1 \overline{F}_{12} \sigma (T_1^4 - T_2^4)$

Where $\overline{\mathcal{F}}_{12} \equiv \frac{1}{A_1 \overline{F}_{12}} + \frac{1}{A_1}\left(\frac{1}{e_1} - 1\right) + \frac{1}{A_2}\left(\frac{1}{e_2} - 1\right)$

↑ geom. resis ↑ surf (1) resis ↑ surf (2) resis.

Which is approximately correct for any enclosu
where only two surfaces are non-adiabatic

Let's solve a practical problem: shielded thermocouple (error due to radiation)



wish to meas. temp. of gas. What is error due to radiation?

have conv. & cond. energy interchange between thermocouple & gas & radiative energy exchange between thermocouple & surrounding surfaces

Say we meas. $T_1 = 800°K$, & $T_3 = 600°K$

ht transf. coeff between gas & thermocouple.

$$h = 56.7 \frac{W}{m^2 °K}$$

Also $e_1 = 0.5$, $e_2 = 0.4$

and $A_2 = 3A_1$

What are T_2 & T_g?

Assume (1) cannot see (3) directly

$$Q_{12} = \frac{\sigma (T_1^4 - T_2^4) A_1}{\frac{1}{e_1} + \frac{A_1}{A_2}\left(\frac{1}{e_2} - 1\right)} = h A_1 (T_g - T_1)$$

(energy balance on thermocouple)

$$Q_{2'3} = e_2 A_2 \sigma (T_2^4 - T_3^4)$$ } radiative int. between 2 & 3

∴ energy balance on shield gives:

$$e_2 A_2 \sigma (T_2^4 - T_3^4) + \frac{\sigma A_1 (T_2^4 - T_1^4)}{\frac{1}{e_1} + \frac{A_1}{A_2}\left(\frac{1}{e_2} - 1\right)} = h \cdot 2A_2 (T_g - T_2$$

↑ energy transf. from inside & outside of shield.

∴ have 2 eq'n & 2 unknowns: solve for T_g & T_2

Obtain $T_g = 817°K$, $T_2 = 778°K$

i.e., meas temp 17°K lower than T_g due to rad. losses to cold walls

If no rad. shielding, same problem yields:

$$Q_{13} = e_1 \sigma (T_1^4 - T_3^4) A_1 = h A_1 (T_g - T_1)$$

$$\therefore T_g = T_1 + \frac{e_1 \sigma (T_1^4 - T_3^4)}{h} \approx 940°K \rightarrow$$

off by 140°K!

End lec. 30

Radiant Energy Transp. in Absorbing Medium

Have so far considered only cases where media either transparent or opaque → now examine case where absorbs as well as transmits.

Recall, in absence rad. have eq'n for int. E:

$$\frac{\partial}{\partial t}\rho\hat{u} = -\underset{\sim}{\nabla}\cdot(\rho\hat{u}\underset{\sim}{V}) - \underset{\sim}{\nabla}\cdot\underset{\sim}{\underset{\sim}{\tau}} - p\underset{\sim}{\nabla}\cdot\underset{\sim}{V} - \underset{\sim}{\underset{\sim}{\tau}}:\underset{\sim}{\nabla}\underset{\sim}{V}$$

- $\frac{\partial}{\partial t}\rho\hat{u}$: int. E change
- $-\underset{\sim}{\nabla}\cdot(\rho\hat{u}\underset{\sim}{V})$: convection
- $-\underset{\sim}{\nabla}\cdot\underset{\sim}{\underset{\sim}{\tau}}$: conduction
- $-p\underset{\sim}{\nabla}\cdot\underset{\sim}{V}$: compression (adiabdic)
- $-\underset{\sim}{\underset{\sim}{\tau}}:\underset{\sim}{\nabla}\underset{\sim}{V}$: visc diss.

May generalize this to include ~~ephases~~ radiation: consider 2 phases: material phase & radiation phase.

For material phase:

$$\frac{\partial\rho\hat{u}}{\partial t} = -\underset{\sim}{\nabla}\cdot(\rho\hat{u}\underset{\sim}{V}) - \underset{\sim}{\nabla}\cdot\underset{\sim}{\underset{\sim}{\tau}} - \rho\underset{\sim}{\nabla}\cdot\underset{\sim}{V} - \underset{\sim}{\underset{\sim}{\tau}}:\underset{\sim}{\nabla}\underset{\sim}{V} - (E-A)$$

- Absorption
- Emissivity per unit volume

Last term is source-sink term due to radiative transport.

For radiation phase:

$$\frac{\partial u^{(r)}}{\partial t} = -\underset{\sim}{\nabla}\cdot\underset{\sim}{\underset{\sim}{\tau}}^{r} + (E-A)$$

- $u^{(r)}$: radiant energy density
- $\underset{\sim}{\underset{\sim}{\tau}}^{r}$: radiant energy flux.

No convective term as radiation moves independently of medium. (cannot carry radiation with it)

. Not at all unreasonable to look at radiation as a phase ⇒ in very early universe, total mass (energy) bound up in radiation >> than that in matter ⇒ was radiation dominated, now live in matter dominated due to expansion of universe.

To solve equations, need relationship for E & A

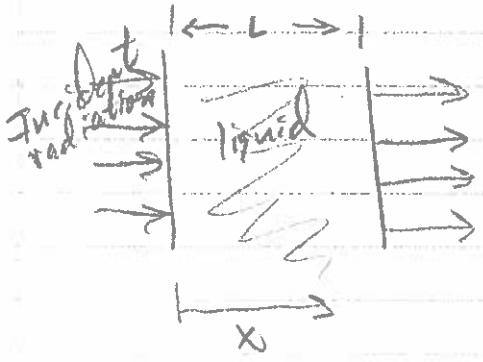
Consider simplified case: $\underset{\sim}{q}^{(r)} \equiv q_x^{(r)}$, $E = 0$

would be poor for case of energy transp. in solar atm., but good approx. for light shining on mat'l at room temp.

Have relation for $A = \alpha_a q_x$ (absorptivity related to flux density ⇒ exp'tl provided radiation intensity is low)

→ spectrophotometer cell

For a stagnant fluid, obtain:



$$0 = -\frac{dq_x}{dx} + A \quad \Leftarrow \text{energy (thermal) balance}$$

And $0 = -\frac{\partial}{\partial x} q_x^{(r)} - A$

$$= -\frac{\partial q_x^{(r)}}{\partial x} - m_a q_x^{(r)}$$

$$\therefore \quad \frac{\partial q_x}{\partial x} = m_a q_x^{(r)} \quad ; \quad \frac{\partial q_x^{(r)}}{\partial x} = -m_a q_x^{(r)}$$

latter has solution

$$q_x^{(r)} = q_x\Big|_{x=0} e^{-m_a x}$$) Lambert's Law

decreases exponentially, length scale inverse of extinction coeff.

Can obtain q_x as well:

$$\frac{\partial q_x}{\partial x} = m_a q_x^{(r)}\Big|_{x=0} e^{-m_a x}$$

$$\therefore q_x = -q_x^{(r)}\Big|_{x=0} e^{-m_a x} + \text{Const.}$$

latter result may be used to obtain temp. distrib. in absorbing media.

Total absorptivity useful in turbidity meters where related to conc. of suspended particles (often depends on scattering as well, though). For spectrophotometry, interested

in effect of spectrum. May differentiate eq'n of rad. energy w.r.t. freq:

$$\frac{\partial u_\nu^{(r)}}{\partial t} = -\nabla \cdot \underset{\sim}{q}_\nu^{(r)} + (E_\nu - A_\nu)$$

...where now just at freq. ν

sim., have $A_\nu = m a_\nu \left| \underset{\sim}{q}_\nu^{(r)} \right|$ for isotropic material. $m a_\nu$ dependence on ν is specific function of material, thus det of $m a_\nu$ for unknown substance may lead to identification.

Recall: Spectral effects in thermal radiation: let q be total rad. energy flux from surface, and $q_\lambda d\lambda$ be energy flux in wavelength range $[\lambda, \lambda + d\lambda]$. Thus,

$$q \equiv \int_0^\infty q_\lambda \, d\lambda$$

We have for a black body q_b & $q_{b\lambda}^{(2)}$, where from Plank's distrib. law:

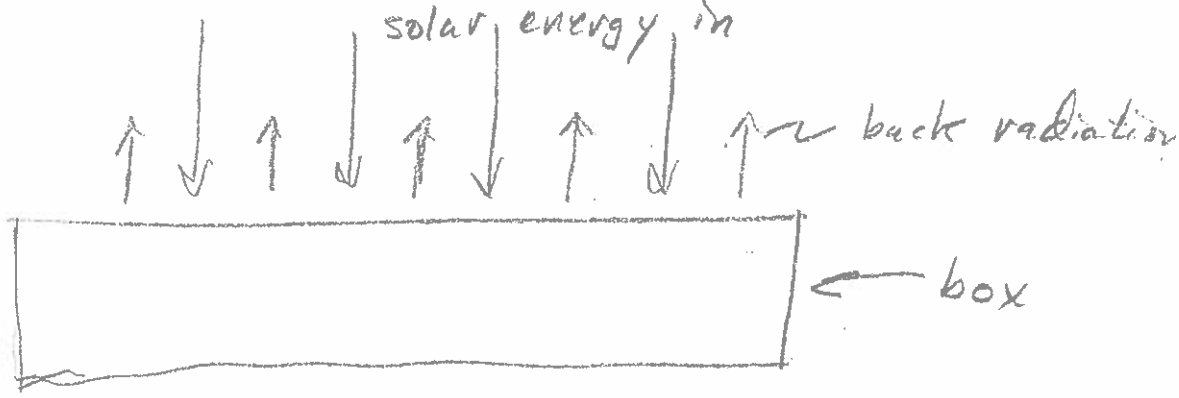
$$q_{b\lambda} = \frac{2\pi c^2 h}{\lambda^5} \frac{1}{e^{ch/\lambda KT} - 1}$$

and define spectral emissivity

$$\varepsilon_\lambda = \frac{q_\lambda}{q_{b\lambda}} = f^n(\lambda, T)$$

for a gray body, $\varepsilon_\lambda \neq f^n(\lambda)$

For non-gray body this will not be true. Has important implications in solar energy applications. Consider solar collector:



wish to minimize back radiation, while maximizing absorption.

Coating surface w/ low ϵ gray mat'l would lower emissivity, but also absorptivity $\Rightarrow$ not very efficient.

Recognize that energy in is at diff. temp. from ~~one~~ box.

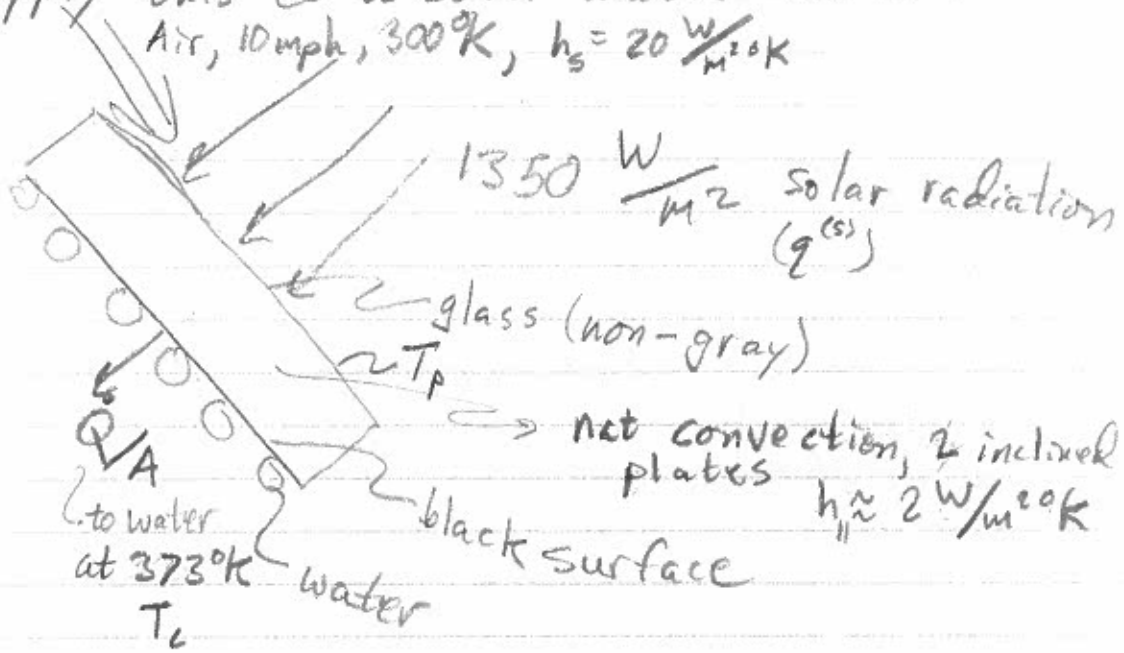
Sun approx. black body at 5800°K, e_λ max at $\sim \lambda = 0.5\,\mu m$.

Over 99% of energy in range $\lambda < 4\,\mu m$

Sim. for body at temp $T \approx 300°K$, $\lambda_{max} \approx 10\,\mu m$ and > 99% energy for $\lambda > 4\,\mu m$.

Thus, may optimize solar gain if box absorbs short wavelength rad., but low ϵ for $\lambda > 4\mu m$ (thermal rad'). (e:1)

Now apply this to a solar water heater:



What is $\dot{Q}$?

First, assume the glass plate has the following properties:

transmittivity

$0 < \lambda < 2.5 \mu m$; $t \approx 1$, $e, a = 0$ | Note: $a + t + r = 1$ (together)

$\lambda \geq 2.5 \mu m$; $e = a = 1$, $t = 0$

∴ black body to thermal radiation, transparent to light ⇒ essentially just a radiation shield (blacke)

Performing energy balance:

Energy balance on collector:

$$\dot{Q} = \overset{\text{Btm}}{A} \cdot q^{(s)} + A e \sigma T_p^4 - A(1-\rho)\sigma T_c^4 - h_{\parallel} A (T_c - T_p)$$

Btm by rad. top plate; Emit by rad. to top plate; reflectivity of plate; Emit by conv.

Energy balance on plate:

$$0 = \varepsilon\sigma T_c^4 - 2\varepsilon\sigma T_p^4 + \varepsilon\sigma T_a^4 - h_s(T_p - T_a) + h_{11}(T_c - T_p$$

(back radiation from atm; energy in from collector, rad; energy out by radiation (both sides); energy out by convection; conv. in from colle)

for thermal radiation, $\varepsilon = 1$ $\therefore$ may solve:

$$T_p = 323°K \qquad \dot{Q}/A = 770\ W/m^2$$

Now, we may reduce ε at $\lambda > 2.5\mu m$ by coating glass w/ Fe_2O_3: "low ε" glass

Assume $\varepsilon = 1$ for $0 < \lambda < 2.5\mu m$,

$t = 0$, $\varepsilon = a = 0.25$ $\lambda > 2.5\mu m$ (reflected)

$$\therefore \frac{\dot{Q}}{A} = q^{(s)} + 0.25\sigma T_p^4 + (1 - 0.75)\sigma T_c^4 - h_{11}(T_c - T_p)$$

$$0 = 0.25\sigma\left((T_c^4 - T_p^4) - (T_p^4 - T_a^4)\right) - h_s(T_p - T_a) + h_{11}(T_c - T_a)$$

$\therefore$ $T_p = 312°K$ $\dot{Q}/A = 1090\ W/m^2$

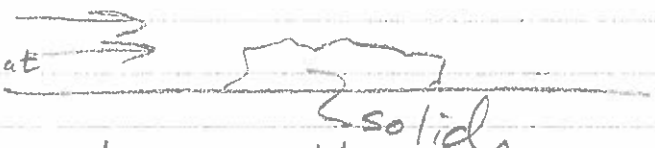
↳ increase of nearly 50%!

$\Rightarrow$ $T_p \approx 307°K$, $\dot{Q}/A \approx 1220\ W/m^2$ for $\varepsilon = 0$

End lec. 30

Mass Transport

When investigating mass transport, primarily interested in relative transport of mat'l due to conc. gradients:



interesting problem

If no solid present & c is uniform, result is uninteresting: may be treated as a uniform material

In diffusing mixture, velocities of different components are different. Can talk of average local velocities in several ways, some more convenient than others. Look at some definitions:

Follow Bird ch 16

Can either define local concentration, velocity on a mass basis or molar basis. For gases use molar basis as, in ideal gas, one mole occupies fixed vol. @ indep. of molecular wt.

Vol basis for MW

For liquids & solids, usually more convenient to work w/ mass-based units.

All are equivalent!

Mass

Mass conc: ρ_i

$$\rho_i = \frac{\text{mass spec. } (i) \text{ in a vol } \Delta V \text{ at a pt.}}{\text{Vol } \Delta V}$$

Mass fraction ω_i:

$$\omega_i = \frac{\text{mass of } i \text{ in } \Delta V}{\text{total mass in } \Delta V}$$

$$= \frac{\rho_i}{\sum \rho_i} = \frac{\rho_i}{\rho}$$

ρ → density

Molar

Molar Conc.: c_i

$$c_i = \frac{\text{moles species } (i) \text{ in a vol } \Delta V \text{ at a pt.}}{\text{Vol } (\Delta V)}$$

Note: $c_i = \rho_i / M_i$ → mol. wt. of i

Mole fraction x_i:

$$x_i = \frac{\text{moles of } (i) \text{ in } \Delta V}{\text{total moles in } \Delta V}$$

$$= \frac{c_i}{\sum c_i} = \frac{c_i}{c}$$

c → molar density

Velocities

Mass average velocity $\underset{\sim}{v}$:

$$\underset{\sim}{v} = \frac{\sum \rho_i \underset{\sim}{v}_i}{\sum \rho_i} = \sum \omega_i \underset{\sim}{v}_i$$

$\rho \underset{\sim}{v}$ ≡ total mass flux across unit area

molar average velocity: $\underset{\sim}{v}^*$

$$\underset{\sim}{v}^* = \frac{\sum c_i \underset{\sim}{v}_i}{\sum c_i} = \sum x_i \underset{\sim}{v}_i$$

$c \underset{\sim}{v}^*$ ≡ total moles/sec flowing across unit area

Mass	Molar
Diffusion velocities:	
$\underset{\sim}{v}_i - \underset{\sim}{v}$ = velocity of (i) relative to $\underset{\sim}{v}$	$\underset{\sim}{V}_i - \underset{\sim}{V}^*$ = molar diff. velocity
Fluxes (w.r.t. stationary coord. system)	
mass flux of i: $\underset{\sim}{n}_i = \rho_i \underset{\sim}{v}_i$	molar flux $\underset{\sim}{N}_i = c_i \underset{\sim}{V}_i$ ↳ moles of (i) moving across unit area/sec.
Relative fluxes	
$\underset{\sim}{j}_i = \rho_i (\underset{\sim}{v}_i - \underset{\sim}{v})$	$\underset{\sim}{J}_i^* = c_i (\underset{\sim}{V}_i - \underset{\sim}{V}^*)$
$\sum \underset{\sim}{j}_i = \sum \rho_i \underset{\sim}{v}_i - \rho \underset{\sim}{v}$	$\sum \underset{\sim}{J}_i = \sum c_i \underset{\sim}{V}_i - c \underset{\sim}{V}^*$
$= 0$	$= 0$
$\underset{\sim}{n}_i = \rho_i \underset{\sim}{v} + \underset{\sim}{j}_i$	$\underset{\sim}{N}_i = c_i \underset{\sim}{V}^* + \underset{\sim}{J}_i^*$

Need constitutive relation between flux & conc. gradient to solve eq'ns:

Fick's Law (from exp't)

In binary system $\mathcal{D}_{AB} = \mathcal{D}_{BA}$ → units L^2/t

$\equiv \underset{\sim}{J}_A^* = -c\,\mathcal{D}_{AB}\,\underset{\sim}{\nabla} x_A$,

Sim. $\underset{\sim}{j}_A = -\rho\,\mathcal{D}_{AB}\,\underset{\sim}{\nabla}\omega_A$ } equivalent

$\underset{\sim}{J}_A^*$: molar flux

$\underset{\sim}{n}_A = \omega_A''(\underset{\sim}{n}_A + \underset{\sim}{n}_B) - \rho\,\mathcal{D}_{AB}\,\underset{\sim}{\nabla}\omega_A$

$\omega_A'' = \rho_A \underset{\sim}{v} = \rho_A \frac{(n_A + n_B)}{\rho} = c\,\omega_A(M_A + M_B)$

$= \rho_A(\omega_A \underset{\sim}{v}_A + \omega_B \underset{\sim}{v}_B) - \rho\,\mathcal{D}_{AB}\,\underset{\sim}{\nabla}\omega_A$

and $\underset{\sim}{N}_A = x_A(\underset{\sim}{N}_A + \underset{\sim}{N}_B) - c\,\mathcal{D}_{AB}\,\underset{\sim}{\nabla} x_A$

$= C_A(x_A \underset{\sim}{v}_A + x_B \underset{\sim}{v}_B) - c\,\mathcal{D}_{AB}\,\underset{\sim}{\nabla} x_A$

Do prob. 16.K

What is magnitude of $\mathcal{D}_{AB}$?

Gas-Gas ⇒ mean free path, velocities are large

∴ $\mathcal{D}_{AB}$ in range $10^{-5} - 5\times10^{-5}$ m^2/sec

$\Rightarrow (0.1 - 0.5\ cm^2/sec)$

From kinetic theory, $\mathcal{D}_{AB} \approx \frac{1}{3} \bar{u} \lambda$ → mean free path
rms velocity

$\bar{u} \sim T^{1/2}$, $\lambda \sim \frac{T}{P}$

$\therefore \mathcal{D}_{AB} \sim T^{3/2} P^{-1}$

and is almost composition indep. (i.e., not $f^n(x_A, x_B)$)

Read through ch 16: provides variety theoretical & empirical corr. for det. $\mathcal{D}_{AB}$

Liquid-Liquid: mean free path much smaller
$\therefore \mathcal{D}_{AB}$ lower:

$$\mathcal{D}_{AB} \sim O\left(10^{-9} \frac{m^2}{sec} = 10^{-5} \frac{cm^2}{sec}\right) \quad (\text{in } H_2O)$$

will, in general, depend strongly on x_A, x_B & increase w/ temp as velocity increases.

For liquids, can approach diffusivity different way; from hydrodynamics, obtain

Nernst-Einstein eq'n: $\mathcal{D}_{AB} = kT \frac{u_A}{F_A}$

where $\frac{u_A}{F_A}$ = mobility ⇒ velocity attained by particle (A) moving through medium (B) under action of unit force. If (A) were a rigid sphere (solution of small particles or large molecules of radius R_A, have Stokes law:

$$\frac{u_A}{F_A} = \frac{1}{6\pi\mu_B R_A}$$

Obtained for $Re \ll 1$, inertial effects unimp. for small sizes.

$$\therefore \quad \mathcal{D}_{AB} = \frac{KT}{6\pi\mu_B R_A} \quad \text{— Stokes–Einstein eq'n}$$

Accurate for dilute susp. small part ($< 1\mu m$) & lge macro-molecules where $R_A \equiv$ radius gyration.

For smaller R_A, must consider poss. slip at surface (breakdown of continuity). If slip exists, may solve for mobility:

$$F_A = 6\pi\mu_B u_A R_A \left(\frac{2\mu_B + R_A \beta_{AB}}{3\mu_B + R_A \beta_{AB}} \right)$$

↳ coeff. sliding friction

β_{AB} lge $\equiv$ no slip

$\beta_{AB} = 0 \equiv$ sol'n for a bubble

To use for liquids, must est. R_A => for cubic lattice,

$$2R_A \approx \left(\tilde{V}_A / \tilde{N} \right)^{1/3}$$

and, for self-diffusion, $\frac{\mathcal{D}_{AA}\mu_A}{KT} = \frac{1}{2\pi}\left(\frac{\tilde{N}}{\tilde{V}_A}\right)^{1/3}$ ↙ assumes slip, i.e. bubble

is good to about ±12% from exp't.

Diff. in solids also occurs, but much slower.

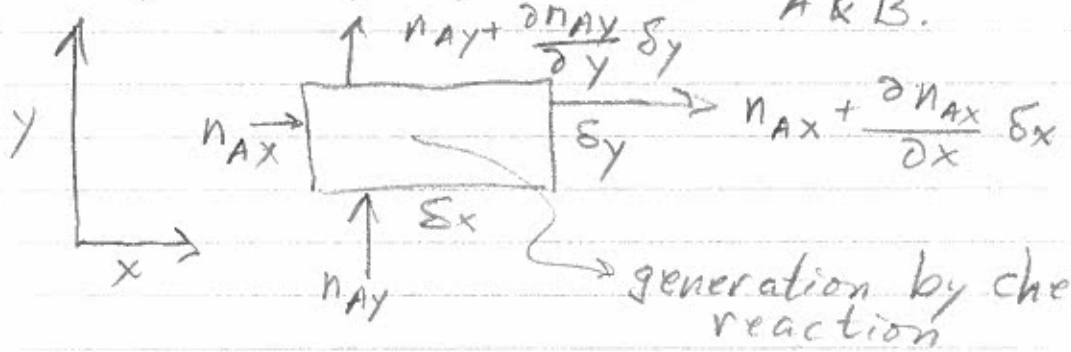
Gas-Solid $\sim O(10^{-9}\ cm^2/sec)$

Solid-Solid $\sim O(10^{-20}\ cm^2/sec)$

→ lge variation between materials

Equations of Change, Multi-component systems

Start w/ Binary system / Conservation for A & B.



$$\therefore \frac{\partial \rho_A}{\partial t} = -\underset{\sim}{\nabla} \cdot \underset{\sim}{n}_A + r_A \quad \leftarrow \text{production of A } \left(\frac{\text{mass}}{\text{vol}\cdot\text{sec}}\right)$$

Similarly, $\frac{\partial \rho_B}{\partial t} = -\underset{\sim}{\nabla} \cdot \underset{\sim}{n}_B + r_B$

Now if we only have reaction $A \rightarrow 2B$, then $r_A + r_B = 0$ and

$$\frac{\partial (\rho_A + \rho_B)}{\partial t} = -\underset{\sim}{\nabla} \cdot (\underbrace{\underset{\sim}{n}_A + \underset{\sim}{n}_B}_{\rho \underset{\sim}{V}}) + \underbrace{(r_A \neq r_B)}_{0}$$

ρ

$$\therefore \frac{\partial \rho}{\partial t} = -\underset{\sim}{\nabla} \cdot (\rho \underset{\sim}{V}) \text{ as before}$$

Sim., in molar units:

$$\frac{\partial C_A}{\partial t} + \underset{\sim}{\nabla} \cdot \underset{\sim}{N}_A = R_A ,$$

$$\frac{\partial C_B}{\partial t} + \underset{\sim}{\nabla} \cdot \underset{\sim}{N}_B = R_B$$

$$\frac{\partial C}{\partial t} + \underset{\sim}{\nabla} \cdot (C \underset{\sim}{V}^*) = (R_A + R_B)$$

↳ not nec. zero

More convenient forms obtained by using eqns for $\underset{\sim}{r}_A$ & $\underset{\sim}{N}_A$ in terms of $\underset{\sim}{\nabla} x_A$, $\underset{\sim}{\nabla} \omega_A$:

$$\therefore \frac{\partial \rho_A}{\partial t} + \underset{\sim}{\nabla} \cdot (\rho_A \underset{\sim}{V}) = \underset{\sim}{\nabla} \cdot (\rho \mathcal{D}_{AB} \underset{\sim}{\nabla} \omega_A) + r_A ,$$

$$\frac{\partial C_A}{\partial t} + \underset{\sim}{\nabla} \cdot (C_A \underset{\sim}{V}^*) = \underset{\sim}{\nabla} \cdot (c \mathcal{D}_{AB} \underset{\sim}{\nabla} x_A) + R_A$$

if ρ and $\mathcal{D}_{AB}$ = cst, ($\underset{\sim}{\nabla} \cdot \underset{\sim}{V} = 0$) these give

$$\underbrace{\frac{\partial \rho_A}{\partial t}}_{\text{acc.}} + \underbrace{\underset{\sim}{V} \cdot \underset{\sim}{\nabla} \rho_A}_{\text{conv.}} = \underbrace{\mathcal{D}_{AB} \nabla^2 \rho_A}_{\text{diff.}} + \underbrace{r_A}_{\text{source/sink}}$$

sim. $$\frac{\partial C_A}{\partial t} + \underset{\sim}{V} \cdot \underset{\sim}{\nabla} C_A = \mathcal{D}_{AB} \nabla^2 C_A + R_A$$

End lec. 32

$$\frac{D C_A}{D t}$$

Test next ~~Monday~~ Friday 4/10 ~~4/14~~, mat'l thru ~~Wed~~ Monday

Now look at some simple problems: (BS&L ch 17 (gases, so molar basis):

Eq'ns:

$$\underset{\sim}{N}_A = x_A(\underbrace{\underset{\sim}{N}_A + \underset{\sim}{N}_B}_{\text{total molar flux}}) - c\mathcal{D}_{AB}\underset{\sim}{\nabla}x_A \quad \text{(relative molar flux)}$$

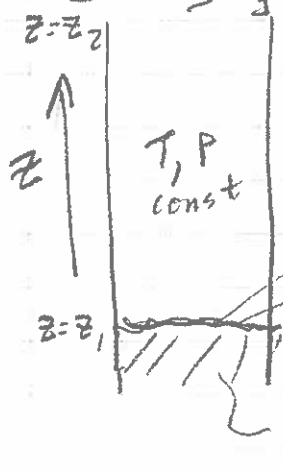
$\underset{\sim}{N}_A$: molar flux of A

$$= c_A(x_A\underset{\sim}{v}_A + x_B\underset{\sim}{v}_B) - c\mathcal{D}_{AB}\underset{\sim}{\nabla}x_A$$

$$= c_A\underset{\sim}{v}^* - c\mathcal{D}_{AB}\underset{\sim}{\nabla}x_A,$$

$$\frac{\partial c_A}{\partial t} + \underset{\sim}{\nabla}\cdot\underset{\sim}{N}_A = R_A$$

Diffusion thru stagnant gas film (stefan tube ⇒ useful for meas. $\mathcal{D}_{AB}$)



level assumed stationary ⇒ pseudo steady state

↳ will change as A evap, but slowly

Further assume ideal gas mixture, none of (B) dissolved in A.

A

$$\frac{\partial c_A}{\partial t} + \frac{\partial N_{Az}}{\partial z} = R_A$$

($\partial c_A/\partial t = 0$; $R_A = 0$)

$$\therefore \frac{\partial N_{Az}}{\partial z} = 0$$

B

$$\frac{\partial c_B}{\partial t} + \frac{\partial N_{Bz}}{\partial z} = R_B$$

($\partial c_B/\partial t = 0$; $R_B = 0$)

$$\therefore \frac{\partial N_{Bz}}{\partial z} = 0$$

Thus $N_{Az} = cst$, $N_{Bz} = cst$

look at (B): $N_{Bz} = C_1$, at $z = z_1$ $N_{Bz} = 0$ (no dissolution of B in A), $\therefore C_1 = 0$

$$N_{Az} = x_A (N_{Az} + \cancel{N_{Bz}}^{0}) - c \mathcal{D}_{AB} \frac{\partial x_A}{\partial z}$$

$$\therefore \quad -c \mathcal{D}_{AB} \frac{\partial x_A}{\partial z} = (1 - x_A) N_{Az}$$

let $N_{Az} = C_2$

$$\therefore \quad -c \mathcal{D}_{AB} \frac{\partial x_A}{\partial z} = C_2 (1 - x_A)$$

Now $c = cst$ as $T, P = cst$

$$\therefore \quad \ln (1 - x_A) = \frac{C_2 z}{c \mathcal{D}_{AB}} + C_3$$

at $z = z_1$, $x_A = x_{A_1}$

$$\therefore \quad \ln \left(\frac{1 - x_A}{1 - x_{A_1}} \right) = \frac{C_2 (z - z_1)}{c \mathcal{D}_{AB}} \quad \therefore \left(\frac{1 - x_A}{1 - x_{A_1}} \right)^{\frac{1}{z - z_1}} = cst$$

and from condition at $z = z_2$:

$$\frac{x_B}{x_{B_1}} = \left(\frac{1 - x_A}{1 - x_{A_1}} \right) = \left(\frac{1 - x_{A_2}}{1 - x_{A_1}} \right)^{\frac{z - z_1}{z_2 - z_1}} = \left(\frac{x_{B_2}}{x_{B_1}} \right)^{\frac{z - z_1}{z_2 - z_1}}$$

which gives x_A a decreasing fn (z)

May obtain:

$$N_{Az}\Big|_{z_1} = -\frac{c\mathcal{D}_{AB}}{1-x_{A_1}}\frac{\partial x_A}{\partial z}\Big|_{z_1} = \frac{c\mathcal{D}_{AB}}{z_2-z_1}\ln\left(\frac{x_{B_2}}{x_{B_1}}\right)$$

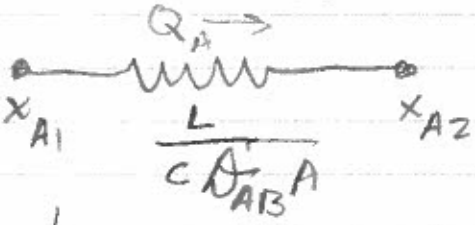
which is related to rate of drop in fluid level

Now in limit $x_A \ll 1$, have analogy w/ energy conduction:

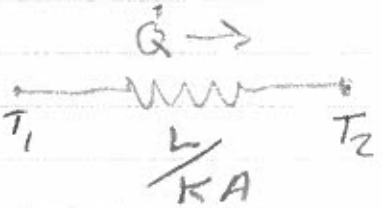
$$N_{Az} = -\frac{c\mathcal{D}_{AB}}{1-x_A}\frac{\partial x_A}{\partial z} \simeq -c\mathcal{D}_{AB}\frac{\partial x_A}{\partial z}$$

$$\therefore \frac{\partial N_{Az}}{\partial z} = 0 \quad \text{or} \quad \frac{\partial^2 x_A}{\partial z^2} = 0$$

$$\Rightarrow N_{Az} = \frac{\dot{Q}_A}{A} = \frac{c\mathcal{D}_{AB}(x_{A_1}-x_{A_2})}{(z_2-z_1)}$$

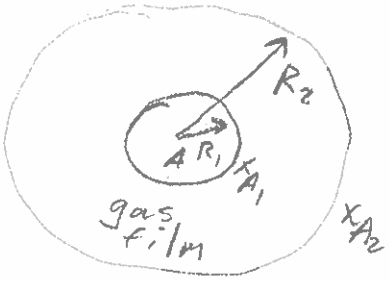


↳ for ht transf.



May solve identical problem in spherical geometry (BS&L 17.6)

Again $\frac{\partial c_A}{\partial t} + \nabla \cdot \underset{\sim}{N}_A = R_A$ (both $\to 0$)



Obtain $\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 N_{Ar}) = 0$

$\therefore r^2 N_{Ar} = cst$

Also $\underset{\sim}{N}_A = x_A(\underset{\sim}{N}_A + \underset{\sim}{N}_B) - c\mathcal{D}_{AB}\nabla x_A$

($\underset{\sim}{N}_B \to 0$ as before)

$\therefore -\frac{c\mathcal{D}_{AB}}{1 - x_A}\left(\frac{\partial x_A}{\partial r}\right) = c_1$

if $\mathcal{D}_{AB}$, c const, may be integ. simply:

$$\frac{x_B}{x_{B_1}} = \left[\frac{x_{B2}}{x_{B_1}}\right]^{\left\{\frac{(1/r_1) - (1/r)}{(1/r_1) - (1/r_2)}\right\}}$$

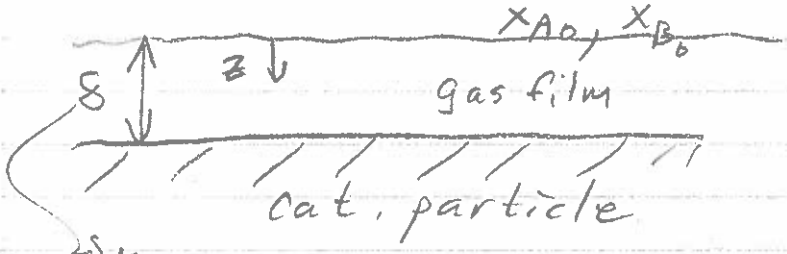
If film is non-isothermal & Temp. profile known a-priori, ← evap. may lower temp

e.g. $\frac{T}{T_1} = \left(\frac{r}{r_1}\right)^n$, $\mathcal{D}_{AB} \propto T^{3/2}$

may integrate eq'n to obtain x_A. If T unknown, solution more difficult: combined energy & mass transp: look at later.

Diff. w/ Instant. & Non-instant heterogeneous Chem RxN

Look at $2A \rightarrow B$ at surface of catalyst



$$\frac{\partial C_A}{\partial t} + \frac{\partial N_{Az}}{\partial z} = R_A$$

$\frac{\partial C_A}{\partial t} = 0$; no rxn in bulk

sim $\frac{\partial N_{Bz}}{\partial z} = 0$, $C_1 = N_{Bz}\big|_\delta$

$\frac{\partial N_{Az}}{\partial z} = 0$, $N_{Az} = C_2$

$C_2 = N_{Az}\big|_\delta$

catalyst surface

at $z = \delta$: $N_{Az}\big|_\delta = -2 N_{Bz}\big|_\delta$ at s.s.

i.e. $C_2 = -2C_1$

$N_{Az} = -2 N_{Bz}$ at all z

$N_{Az} + N_{Bz} = -N_{Bz} = \frac{1}{2} N_{Az}$

$N_{Az} = x_A (N_{Az} + N_{Bz}) - c \mathcal{D}_{AB} \frac{\partial x_A}{\partial z}$