CM3120: Module 3

Diffusion and Mass Transfer I

I. Introduction to diffusion/mass transfer
II. Classic diffusion and mass transfer—Quick Start a): 1D Evaporation
III. Classic diffusion and mass transfer—Quick Start b): 1D Radial droplet
IV. Cycle back: Fick's mass transport law
V. Microscopic species A mass balance
VI. Classic diffusion and mass transfer—c): 1D Mass transfer with chemical reaction

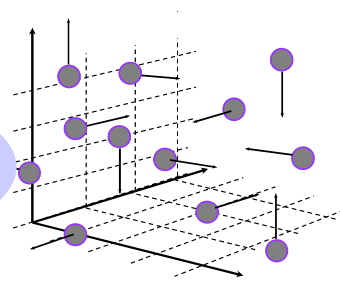
 1

CM3120: Module 3

Module 3 Lecture VI

Classic Diffusion & Mass Transfer

(Heterogeneous Reaction)



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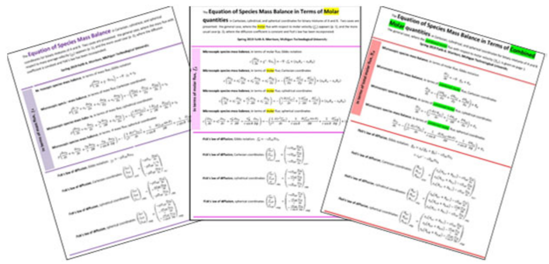
www.chem.mtu.edu/~fmorriso/cm3120/cm3120.html

 2

Let’s put this to use



Various forms of the Microscopic Species A Mass Balance

Microscopic species A mass balance—~~Six~~ Five forms

In terms of mass flux and mass concentrations	$\rho\left(\frac{\partial \omega_A}{\partial t} + \underline{v}\cdot\nabla\omega_A\right) = -\nabla\cdot\underline{j}_A + r_A$ $= \rho D_{AB}\nabla^2\omega_A + r_A$
In terms of molar flux and molar concentrations	$c\left(\frac{\partial x_A}{\partial t} + \underline{v}^*\cdot\nabla x_A\right) = -\nabla\cdot\underline{J}_A^* + (x_B R_A - x_A R_B)$ $= cD_{AB}\nabla^2 x_A + (x_B R_A - x_A R_B)$
In terms of combined molar flux and molar concentrations	$\frac{\partial c_A}{\partial t} = -\nabla\cdot\underline{N}_A + R_A$

 3

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In terms of combined molar flux and molar concentrations	$\frac{\partial c_A}{\partial t} = -\nabla\cdot\underline{N}_A + R_A$

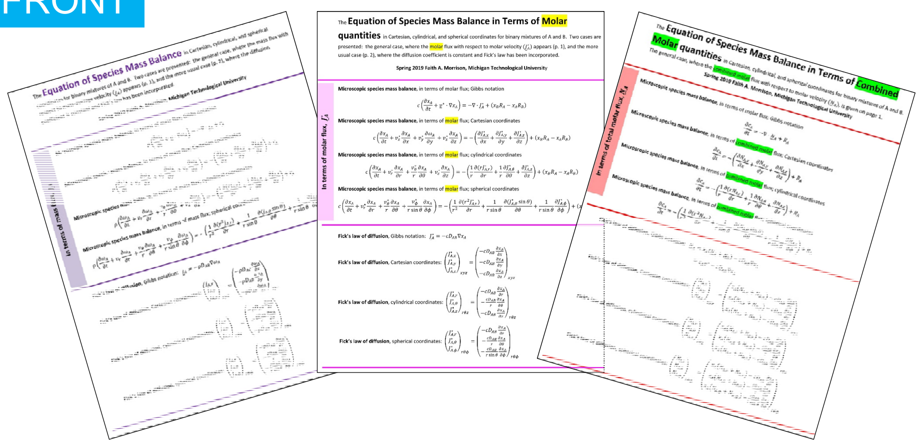
(The combined molar flux version cannot easily have Fick’s law substituted in.)

4

Various forms of Fick's Law (and the species mass balances that employ them)

Mass flux	Molar flux	Combined molar flux
$\underline{j}_A = -\rho D_{AB} \nabla \omega_A$	$\underline{J}_A^* = -c D_{AB} \nabla x_A$	$\underline{N}_A = x_A(\underline{N}_A + \underline{N}_B) - c D_{AB} \nabla x_A$

FRONT



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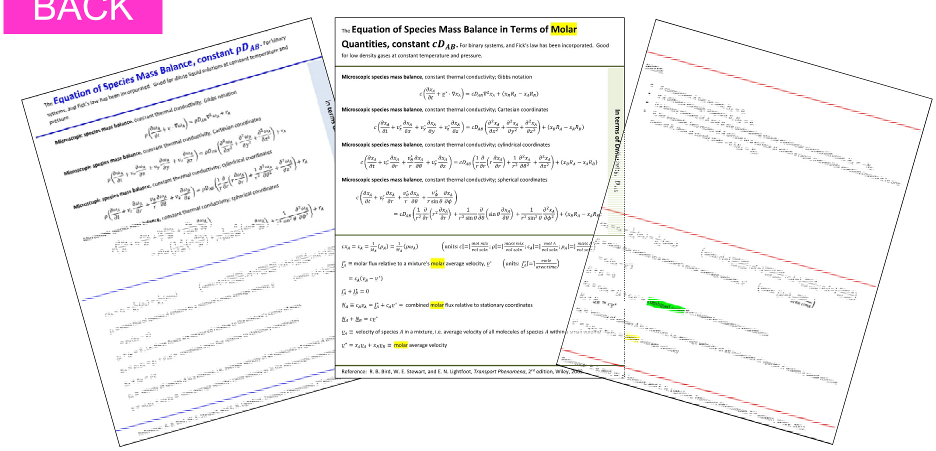
BACK



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SUMMARY: Various quantities in diffusion and mass transfer

How much is present: $cx_A = c_A = \frac{1}{M_A}(\rho_A) = \frac{1}{M_A}(\rho\omega_A)$

$\underline{j}_A \equiv$ **mass** flux of species A relative to a mixture's **mass average velocity**, $\underline{v}$
$= \rho_A(\underline{v}_A - \underline{v})$
$\underline{j}_A + \underline{j}_B = 0$, i.e. these fluxes are measured relative to the mixture's center of mass

$\underline{n}_A \equiv \rho_A \underline{v}_A = \underline{j}_A + \rho_A \underline{v} =$ **combined mass** flux relative to **stationary coordinates**
$\underline{n}_A + \underline{n}_B = \rho \underline{v}$

$\underline{J}_A^* \equiv$ **molar** flux relative to a mixture's **molar average velocity**, $\underline{v}^*$
$= c_A(\underline{v}_A - \underline{v}^*)$
$\underline{J}_A^* + \underline{J}_B^* = 0$

$\underline{N}_A \equiv c_A \underline{v}_A = \underline{J}_A^* + c_A \underline{v}^* =$ **combined molar** flux relative to **stationary coordinates**
$\underline{N}_A + \underline{N}_B = c\underline{v}^*$

$\underline{v}_A \equiv$ velocity of species A in a mixture, i.e. average velocity of all molecules of species A within a small volume
$\underline{v} = \omega_A \underline{v}_A + \omega_B \underline{v}_B \equiv$ *mass* average velocity; same velocity as in the microscopic momentum and energy balances
$\underline{v}^* = x_A \underline{v}_A + x_B \underline{v}_B \equiv$ *molar* average velocity

7

1D Steady Diffusion

Let's put this to use

1D Steady Diffusion Problems

a. 1D simple rectangular mass transfer (evaporating tank, **Ex 1**) QUICK START
b. 1D radial mass transfer (evaporating droplet, **Ex 2**) QUICK START
c. More…

8

Classic 1D Steady Diffusion Summary

a. 1D rectangular mass transfer (evaporating tank, **Ex 1**)

b. 1D radial mass transfer (evaporating droplet, **Ex 2**)

c. Heterogeneous chemical reaction (catalytic converter, **Ex 3**)

Example 3: Heterogeneous catalysis in a reactor

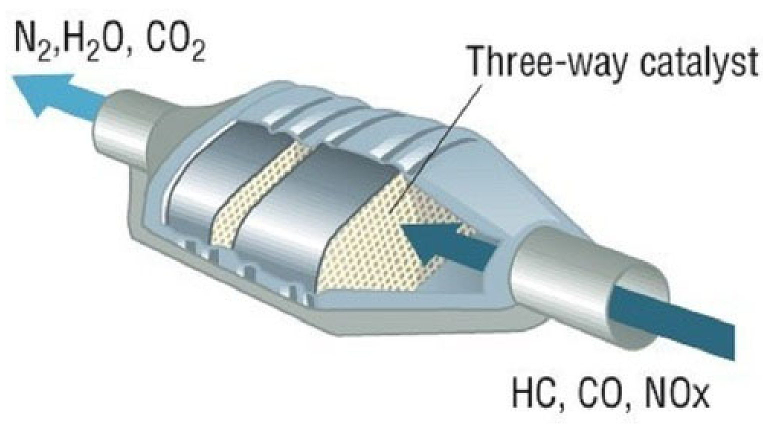

Image source: https://www.indiamart.com/proddetail/three-way-catalytic-converter-16802815188.html

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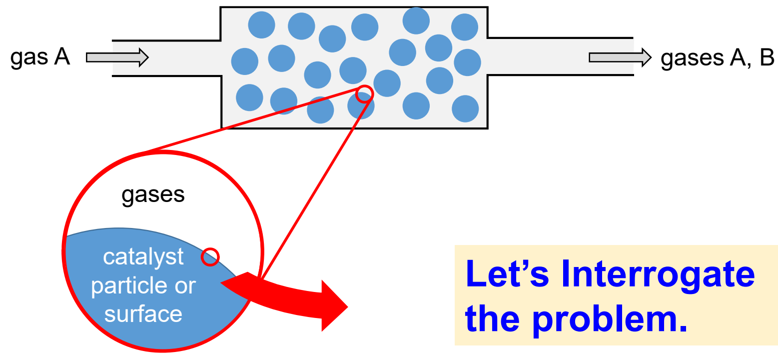
1D Steady Diffusion—Heterogeneous Chemical Reaction

Example 3: Heterogeneous catalysis



Let's Interrogate the problem.

And develop a model.

An irreversible, instantaneous chemical reaction ($2A \rightarrow B$) takes place at a catalyst surface in a reactor as shown. How might mass transfer affect the observed rate of reaction?

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11

QUICK START

Let's Interrogate the problem.

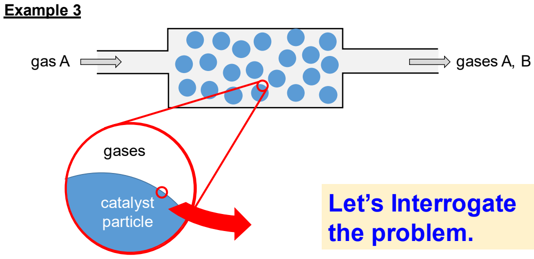
What is the geometry? What does it affect?

How does diffusion affect how fast the chemical transformation takes?

How would diffusion take place (look for sources, sinks)

What is the governing physics?

Example 3



Let's Interrogate the problem.

Example 3: Heterogeneous catalysis
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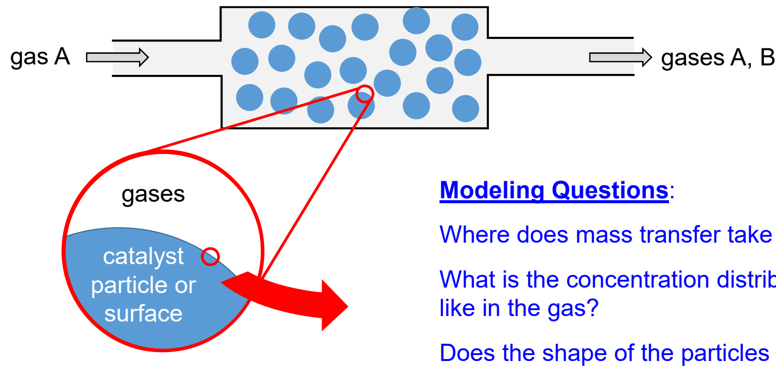
12

1D Steady Diffusion—Heterogeneous Chemical Reaction

Example 3: Heterogeneous catalysis



An irreversible, instantaneous chemical reaction ($2A \rightarrow B$) takes place at a catalyst surface in a reactor as shown. How might mass transfer affect the observed rate of reaction?

Modeling Questions:

Where does mass transfer take place?

What is the concentration distribution like in the gas?

Does the shape of the particles matter?

What is the impact of the overall (bulk) flow?

What should be our first modeling problem?

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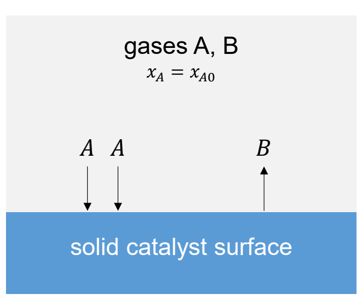
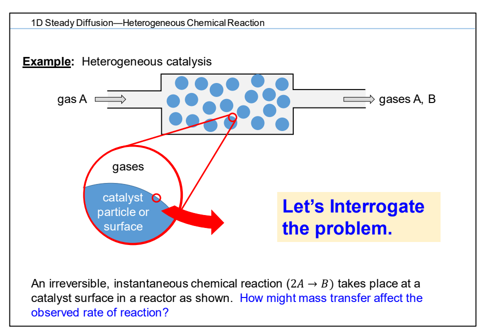
13

1D Steady Diffusion—Heterogeneous Chemical Reaction

Example 3: Heterogeneous catalysis

An irreversible, instantaneous chemical reaction ($2A \rightarrow B$)





More Modeling Questions:

How fast will this happen?

Does it depend on the reaction rate?

What else does it depend on?

What can we learn about the unit's mass transfer character?

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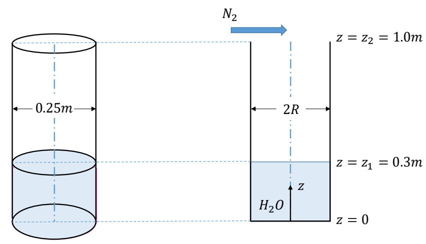
14

Modeling Inspiration:

There may be a stagnant region between the *source* and *sink* that must be traversed.

QUICK START

Example: Water ($40^o C, 1.0\, atm$) slowly and steadily evaporates into nitrogen ($40^o C, 1.0\, atm$) from the bottom of a cylindrical tank as shown in the figure below. A stream of dry nitrogen flows slowly past the open tank. The mole fraction of water in the gas at the top opening of the tank is 0.02. **What is the rate of water evaporation?**



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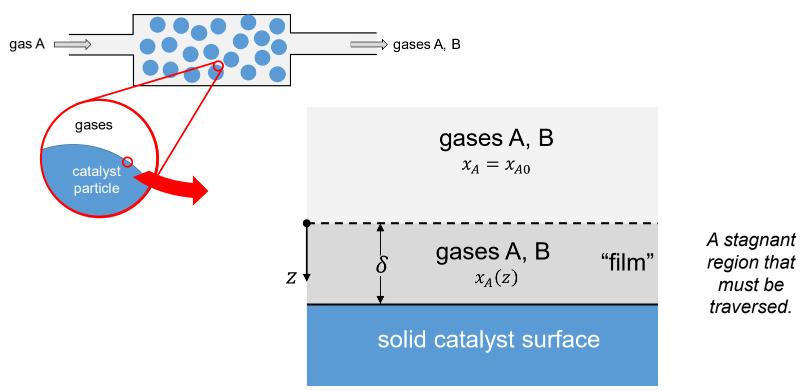
15

Example 3: Heterogeneous catalysis (revisit)

Use a "*film model*"



An irreversible, instantaneous chemical reaction ($2A \rightarrow B$) takes place at a catalyst surface, as shown. The reaction is "diffusion-limited," however, because the rate of completion of the reaction is determined by the rate of diffusion through the "film" near the catalyst surface. Calculate the steady state composition distribution in the film ($x_A(z)$).

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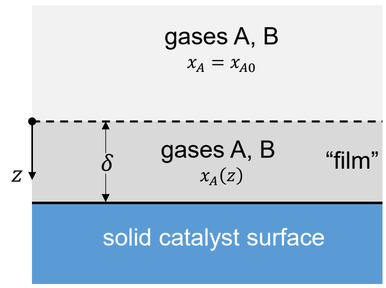
16

Film model of mass transfer (more complex)

QUICK START

Example 3: Heterogeneous catalysis
An irreversible, instantaneous chemical reaction ($2A \rightarrow B$) takes place at a catalyst surface, as shown. The reaction is "diffusion-limited," however, because the rate of completion of the reaction is determined by the rate of diffusion through a "film" near the catalyst surface. Calculate the steady state composition distribution in the film $x_A(z)$ and the flux of product B away from the surface.

(sketch, choose a coordinate system …)



- Deploy the "film model"
- It has become *a way of thinking about* diffusion in some circumstances

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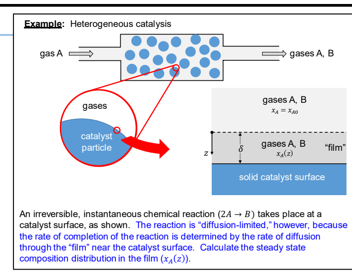
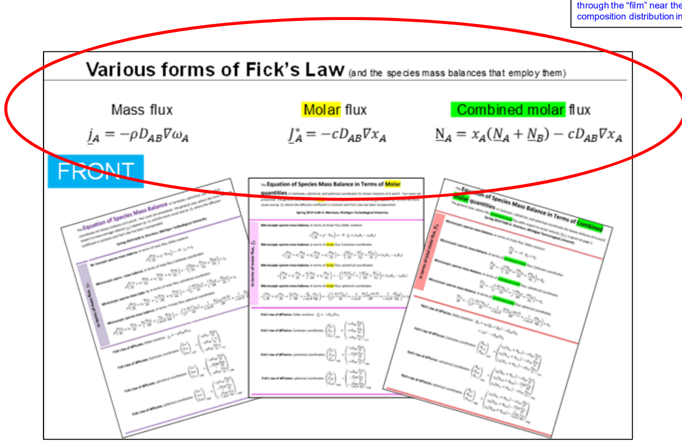
1D Steady Diffusion—Heterogeneous Chemical Reaction



Which microscopic species A mass balance is best for solving the model?



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1D Steady Diffusion—Heterogeneous Chemical Reaction

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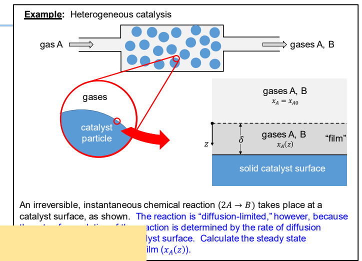

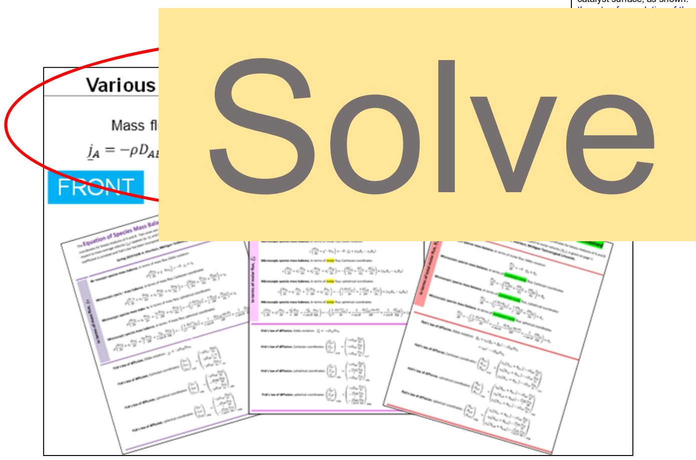

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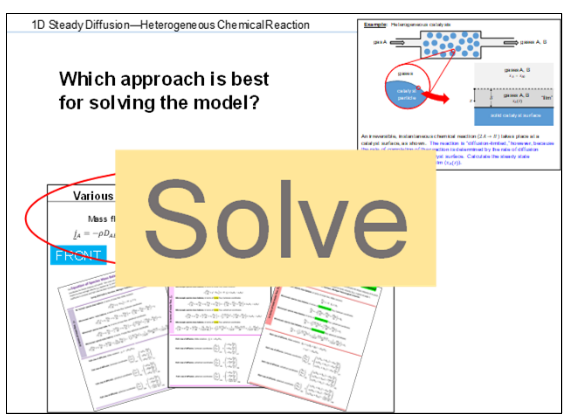
19

See hand notes for the start (Example 3)
Solution assigned in HW3.10



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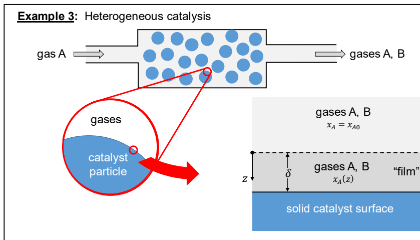
20

Film model of mass transfer (more complex)

Example 3: Heterogeneous catalysis



An irreversible, instantaneous chemical reaction ($2A \rightarrow B$) takes place at a catalyst surface, as shown. The reaction is "diffusion-limited," however, because the rate of completion of the reaction is determined by the rate of diffusion through the "film" near the catalyst surface. Calculate the steady state composition distribution in the film ($x_A(z)$) and the flux of product B away from the surface.

Assumptions:
- Fast, irreversible reaction at surface
- Diffusion through film at surface limits rate of reaction
- Steady state
- Constant T, P

Solution:

$$x_A(z)$$

$$\left(1-\frac{1}{2}x_A\right)=\left(1-\frac{1}{2}x_{A0}\right)^{(1-z/\delta)}$$

Open: How would we "answer the question" in this problem?

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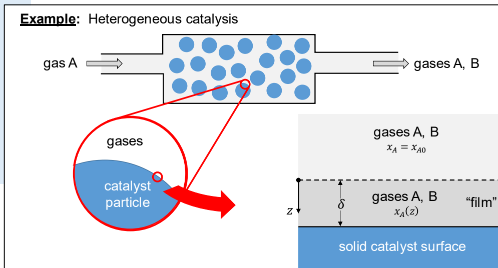
21

1D Steady Diffusion—Heterogeneous Chemical Reaction

Problem Summary: Heterogeneous Chemical Reaction

- One-dimensional (1D)
- Steady
- Use molar flux (due to reaction)
- Use combined molar flux $\underline{N}_A$; we can draw modeling simplifications about $\underline{N}_B$ due to *fast reaction*)
- Needed stoichiometry
- Boundary conditions: concentrations known (fast reaction ⇒ A disappears at surface.

Example: Heterogeneous catalysis



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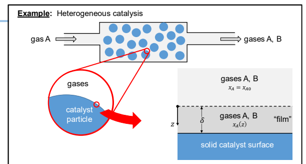
22

1D Steady Diffusion—Heterogeneous Chemical Reaction

Example: Heterogeneous catalysis



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Could we have used $\underline{J}_A^*$ instead?

Various forms of Fick's Law (and the species mass balances th

Mass flux	Molar flux	Combined molar flux
$\underline{j}_A = -\rho D_{AB} \nabla \omega_A$	$\underline{J}_A^* = -c D_{AB} \nabla x_A$	$\underline{N}_A = x_A(\underline{N}_A + \underline{N}_B) - c D_{AB} \nabla x_A$

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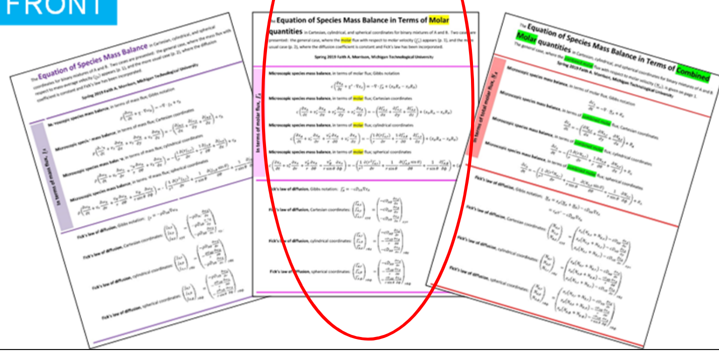

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 23

1D Steady Diffusion—Heterogeneous Chemical Reaction

The **Equation of Species Mass Balance in Terms of Molar quantities** in Cartesian, cylindrical, and spherical coordinates for binary mixtures of A and B. Two cases are presented: the general case, where the molar flux with respect to molar velocity ($\underline{J}_A^*$) appears (p. 1), and the more usual case (p. 2), where the diffusion coefficient is constant and Fick's law has been incorporated.

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In terms of molar flux, $\underline{J}_A^*$

Microscopic species mass balance, in terms of molar flux; Gibbs notation

$$c\left(\frac{\partial x_A}{\partial t} + \underline{v}^* \cdot \nabla x_A\right) = -\nabla \cdot \underline{J}_A^* + (x_B R_A - x_A R_B)$$

Microscopic species mass balance, in terms of molar flux; Cartesian coordinates

$$c\left(\frac{\partial x_A}{\partial t} + v_x^*\frac{\partial x_A}{\partial x} + v_y^*\frac{\partial \omega_A}{\partial y} + v_z^*\frac{\partial x_A}{\partial z}\right) = -\left(\frac{\partial J_{A,x}^*}{\partial x} + \frac{\partial J_{A,y}^*}{\partial y} + \frac{\partial J_{A,z}^*}{\partial z}\right) + (x_B R_A - x_A R_B)$$

Microscopic species mass balance, in terms of molar flux; cylindrical coordinates

$$c\left(\frac{\partial x_A}{\partial t} + v_r^*\frac{\partial x_A}{\partial r} + \frac{v_\theta^*}{r}\frac{\partial x_A}{\partial \theta} + v_z^*\frac{\partial x_A}{\partial z}\right) = -\left(\frac{1}{r}\frac{\partial (r J_{A,r}^*)}{\partial r} + \frac{1}{r}\frac{\partial J_{A,\theta}^*}{\partial \theta} + \frac{\partial J_{A,z}^*}{\partial z}\right) + (x_B R_A - x_A R_B)$$

Microscopic species mass balance, in terms of molar flux; spherical coordinates

$$c\left(\frac{\partial x_A}{\partial t} + v_r^*\frac{\partial x_A}{\partial r} + \frac{v_\theta^*}{r}\frac{\partial x_A}{\partial \theta} + \frac{v_\phi^*}{r\sin\theta}\frac{\partial x_A}{\partial \phi}\right) = -\left(\frac{1}{r^2}\frac{\partial (r^2 J_{A,r}^*)}{\partial r} + \frac{1}{r\sin\theta}\frac{\partial (J_{A,\theta}^*\sin\theta)}{\partial \theta} + \frac{1}{r\sin\theta}\frac{\partial J_{A,\phi}^*}{\partial \phi}\right) + (x_B R_A - x_A$$

Fick's law of diffusion, Gibbs notation: $\underline{J}_A^* = -c D_{AB} \nabla x_A$

Fick's law of diffusion, Cartesian coordinates:
$$\begin{pmatrix} J_{A,x}^* \\ J_{A,y}^* \\ J_{A,z}^* \end{pmatrix}_{xyz} = \begin{pmatrix} -c D_{AB}\frac{\partial x_A}{\partial x} \\ -c D_{AB}\frac{\partial x_A}{\partial y} \\ -c D_{AB}\frac{\partial x_A}{\partial z} \end{pmatrix}_{xyz}$$

Fick's law of diffusion, cylindrical coordinates:
$$\begin{pmatrix} J_{A,r}^* \\ J_{A,\theta}^* \\ J_{A,z}^* \end{pmatrix}_{r\theta z} = \begin{pmatrix} -c D_{AB}\frac{\partial x_A}{\partial r} \\ -\frac{c D_{AB}}{r}\frac{\partial x_A}{\partial \theta} \\ -c D_{AB}\frac{\partial x_A}{\partial z} \end{pmatrix}_{r\theta z}$$

Fick's law of diffusion, spherical coordinates:
$$\begin{pmatrix} J_{A,r}^* \\ J_{A,\theta}^* \\ J_{A,\phi}^* \end{pmatrix}_{r\theta\phi} = \begin{pmatrix} -c D_{AB}\frac{\partial x_A}{\partial r} \\ -\frac{c D_{AB}}{r}\frac{\partial x_A}{\partial \theta} \\ -\frac{c D_{AB}}{r\sin\theta}\frac{\partial x_A}{\partial \phi} \end{pmatrix}_{r\theta\phi}$$

$\underline{J}_A^*$: **Molar flux relative to a mixture's molar average velocity $\underline{v}^*$**

Definition:

$$\underline{J}_A^* = c x_A (\underline{v}_A - \underline{v}^*)$$

Fick's law:

$$\underline{J}_A^* = -c D_{AB} \nabla x_A$$

Microscopic species A mass balance:

$$c\left(\frac{\partial x_A}{\partial t} + \underline{v}^* \cdot \nabla x_A\right) = c D_{AB} \nabla^2 x_A + (x_B R_A - x_A R_B)$$

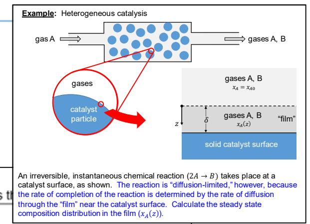
(would not know what to do with this term)

$R_A \equiv$ rate of production of moles of A by homogeneous chemical reaction per volume

 24

1D Steady Diffusion—Heterogeneous Chemical Reaction

Could we have used $\underline{j}_A$ instead?



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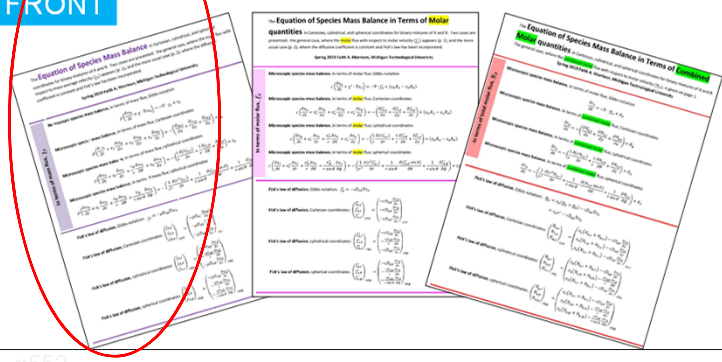

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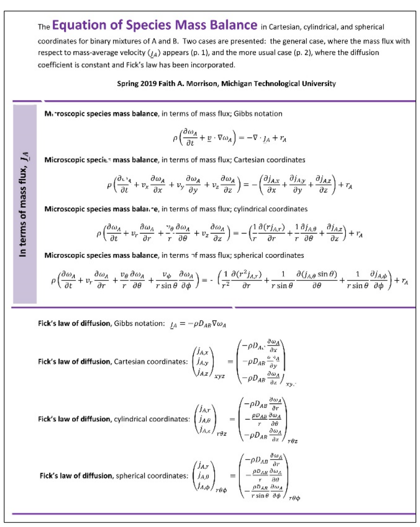
1D Steady Diffusion—Heterogeneous Chemical Reaction



The **Equation of Species Mass Balance** in Cartesian, cylindrical, and spherical coordinates for binary mixtures of A and B. Two cases are presented: the general case, where the mass flux with respect to mass-average velocity ($\underline{j}_A$) appears (p. 1), and the more usual case (p. 2), where the diffusion coefficient is constant and Fick's law has been incorporated.

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In terms of mass flux, $\underline{j}_A$

Microscopic species mass balance, in terms of mass flux; Gibbs notation

$$\rho\left(\frac{\partial \omega_A}{\partial t} + \underline{v} \cdot \nabla \omega_A\right) = -\nabla \cdot \underline{j}_A + r_A$$

Microscopic species mass balance, in terms of mass flux; Cartesian coordinates

$$\rho\left(\frac{\partial \omega_A}{\partial t} + v_x \frac{\partial \omega_A}{\partial x} + v_y \frac{\partial \omega_A}{\partial y} + v_z \frac{\partial \omega_A}{\partial z}\right) = -\left(\frac{\partial j_{A,x}}{\partial x} + \frac{\partial j_{A,y}}{\partial y} + \frac{\partial j_{A,z}}{\partial z}\right) + r_A$$

Microscopic species mass balance, in terms of mass flux; cylindrical coordinates

$$\rho\left(\frac{\partial \omega_A}{\partial t} + v_r \frac{\partial \omega_A}{\partial r} + \frac{v_\theta}{r}\frac{\partial \omega_A}{\partial \theta} + v_z \frac{\partial \omega_A}{\partial z}\right) = -\left(\frac{1}{r}\frac{\partial (r j_{A,r})}{\partial r} + \frac{1}{r}\frac{\partial j_{A,\theta}}{\partial \theta} + \frac{\partial j_{A,z}}{\partial z}\right) + r_A$$

Microscopic species mass balance, in terms of mass flux; spherical coordinates

$$\rho\left(\frac{\partial \omega_A}{\partial t} + v_r \frac{\partial \omega_A}{\partial r} + \frac{v_\theta}{r}\frac{\partial \omega_A}{\partial \theta} + \frac{v_\phi}{r\sin\theta}\frac{\partial \omega_A}{\partial \phi}\right) = -\left(\frac{1}{r^2}\frac{\partial (r^2 j_{A,r})}{\partial r} + \frac{1}{r\sin\theta}\frac{\partial (j_{A,\theta}\sin\theta)}{\partial \theta} + \frac{1}{r\sin\theta}\frac{\partial j_{A,\phi}}{\partial \phi}\right) + r_A$$

Fick's law of diffusion, Gibbs notation: $\underline{j}_A = -\rho D_{AB} \nabla \omega_A$

Fick's law of diffusion, Cartesian coordinates: $\begin{pmatrix} j_{A,x} \\ j_{A,y} \\ j_{A,z} \end{pmatrix}_{xyz} = \begin{pmatrix} -\rho D_{AB}\frac{\partial \omega_A}{\partial x} \\ -\rho D_{AB}\frac{\partial \omega_A}{\partial y} \\ -\rho D_{AB}\frac{\partial \omega_A}{\partial z} \end{pmatrix}_{xyz}$

Fick's law of diffusion, cylindrical coordinates: $\begin{pmatrix} j_{A,r} \\ j_{A,\theta} \\ j_{A,z} \end{pmatrix}_{r\theta z} = \begin{pmatrix} -\rho D_{AB}\frac{\partial \omega_A}{\partial r} \\ -\frac{\rho D_{AB}}{r}\frac{\partial \omega_A}{\partial \theta} \\ -\rho D_{AB}\frac{\partial \omega_A}{\partial z} \end{pmatrix}_{r\theta z}$

Fick's law of diffusion, spherical coordinates: $\begin{pmatrix} j_{A,r} \\ j_{A,\theta} \\ j_{A,\phi} \end{pmatrix}_{r\theta\phi} = \begin{pmatrix} -\rho D_{AB}\frac{\partial \omega_A}{\partial r} \\ -\frac{\rho D_{AB}}{r}\frac{\partial \omega_A}{\partial \theta} \\ -\frac{\rho D_{AB}}{r\sin\theta}\frac{\partial \omega_A}{\partial \phi} \end{pmatrix}_{r\theta\phi}$

$\underline{j}_A$: Mass flux relative to a mixture's mass average velocity $\underline{v}$

Definition:

$$\underline{j}_A = \rho\omega_A(\underline{v}_A - \underline{v})$$

Fick's law:

$$\underline{j}_A = -\rho D_{AB} \nabla \omega_A$$

Microscopic species A mass balance:

$$\rho\left(\frac{\partial \omega_A}{\partial t} + \underline{v} \cdot \nabla \omega_A\right) = \rho D_{AB} \nabla^2 \omega_A + r_A$$

(would not know what to do with this term)

$r_A \equiv$ rate of production of mass of A by homogeneous chemical reaction per volume

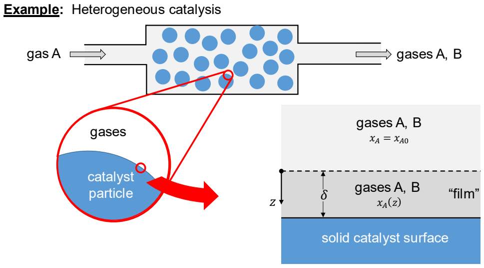
1D Steady Diffusion—Heterogeneous Chemical Reaction

Problem Summary: Heterogeneous Chemical Reaction

- One-dimensional (1D)
- Steady
- Use molar flux (due to reaction)
- Use combined molar flux $\underline{N}_A$; we can draw modeling simplifications about $\underline{N}_B$ due to fast reaction)
- Needed stoichiometry
- Boundary conditions: concentrations known (fast reaction ⇒ A disappears at surface.

Flux choice
Choose:
- **Molar** because there is a reaction
- **Combined molar** because we can work out relationship between N_A and N_B; no imposed convection

Example: Heterogeneous catalysis



An irreversible, instantaneous chemical reaction ($2A \rightarrow B$) takes place at a catalyst surface, as shown. The reaction is "diffusion-limited," however, because the rate of completion of the reaction is determined by the rate of diffusion through the "film" near the catalyst surface. Calculate the steady state composition distribution in the film ($x_A(z)$).

27

1D Steady Diffusion

Classic 1D Steady Diffusion Summary

a. 1D rectangular mass transfer (evaporating tank, **Ex 1**)

b. 1D radial mass transfer (evaporating droplet, **Ex 2**)

c. Heterogeneous chemical reaction (catalytic converter, **Ex 3**)

d. More…

28

Introduction to Diffusion and Mass Transfer in Mixtures QUICK START

Recurring Modeling Assumptions in Diffusion ("Classics")

- Near a liquid-gas interface, the region in the gas near the liquid is a film where slow diffusion takes place
- The vapor near the liquid-gas interface is often saturated (Raoult's law, $x_A = p_A^*/p$)
- If component A has no sink, flux $\underline{N}_A = 0$.
- If A diffuses through stagnant B, $\underline{N}_B = 0$.
- If A is dilute in B, we can neglect the convection term ($N_{Az} = J_{Az}^*$)
- Because diffusion is slow, we can make a quasi-steady-state assumption
-
- And now?
-
-
-
-

29

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Introduction to Diffusion and Mass Transfer in Mixtures QUICK START

Recurring Modeling Assumptions in Diffusion ("Classics")

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- If A is dilute in B, we can neglect the convection term ($N_{Az} = J_{Az}^*$)
- Because diffusion is slow, we can make a quasi-steady-state assumption
- If, for example, two moles of A diffuse to a surface at which a rapid, irreversible reaction coverts it to one mole of B, then at steady state $-0.5\underline{N}_A = \underline{N}_B$.
- Homogeneous reactions appear in the mass balance; heterogeneous reactions appear in the boundary conditions and relate fluxes
- If a binary mixture of A and B are undergoing steady equimolar counter diffusion, $\underline{N}_A = -\underline{N}_B$. (coming)

30

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