

## Diffusion and Mass Transfer

CM3120 Transport/Unit Operations 2

Diffusion and Mass Transfer

in MIXTURES

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

It turns out that there are many interesting and applicable problems we can address readily with **this** form of the species mass balance.

**Microscopic species A mass balance—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	$c \left( \frac{\partial x_A}{\partial t} + \underline{v}^* \cdot \nabla x_A \right) = -\nabla \cdot \underline{J}_A + R_A$
	$= c D_{AB} \nabla^2 x_A$
In terms of <b>combined molar flux</b> and molar concentrations	$\frac{\partial c_A}{\partial t} = -\nabla \cdot \underline{N}_A + R_A$

We'll do a "Quick Start" and get into some examples and return to the "why" of it all a bit later.

QUICK START

(to problem solving)

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QUICK START

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### Diffusion and Mass Transfer QUICK START

Using the **microscopic species mass balance** in terms of combined molar flux and molar concentrations

$$\frac{\partial c_A}{\partial t} = -\nabla \cdot \underline{N}_A + R_A$$

**QUICK START**

$$c_A [=] \frac{\text{moles } A}{\text{volume mix}} = x_A c = \text{the concentration of } A \text{ in the mixture}$$

$$\underline{N}_A [=] \frac{\text{moles } A}{\text{area} \cdot \text{time}} = \text{combined molar flux of } A \text{ (both diffusion and convection) relative to stationary coordinates}$$

$$R_A [=] \frac{\text{moles } A}{\text{volume mix} \cdot \text{time}} = \text{rate of production of } A \text{ by reaction per unit volume mixture}$$

$$c [=] \frac{\text{moles mix}}{\text{volume mix}} = \text{molar density of the mixture (for ideal gases } c = \frac{n}{V} = \frac{P}{RT})$$

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### Diffusion and Mass Transfer QUICK START

Using **Fick's law of diffusion** in terms of the same combined molar flux:

$$\underline{N}_A = x_A (\underline{N}_A + \underline{N}_B) - c D_{AB} \nabla x_A$$

**QUICK START**

$$\underline{N}_A [=] \frac{\text{moles } A}{\text{area} \cdot \text{time}} = \text{combined molar flux of } A \text{ (both diffusion and convection) relative to stationary coordinates}$$

$$x_A [=] \frac{\text{moles } A}{\text{moles mix}} = \text{mole fraction of } A$$

$$D_{AB} [=] \frac{\text{cm}^2}{\text{s}} = \text{diffusion coefficient (diffusivity) of } A \text{ in } B$$

$$c [=] \frac{\text{moles mix}}{\text{volume mix}} = \text{molar density of the mixture (for ideal gases } c = \frac{n}{V} = \frac{P}{RT})$$

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## Diffusion and Mass Transfer QUICK START

Using **handy worksheets** to learn the common modeling assumptions

**QUICK START**

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**The Equation of Species Mass Balance in Terms of Combined Molar quantities** in Cartesian, cylindrical, and spherical coordinates for binary mixtures of A and B. The general case, where the **combined molar flux** with respect to molar velocity ( $\underline{N}_A$ ), is given on page 1. Spring 2019 Faith A. Morrison, Michigan Technological University

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

$$\frac{\partial c_A}{\partial t} = -\nabla \cdot \underline{N}_A + R_A$$

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

$$\frac{\partial c_A}{\partial t} = -\left(\frac{\partial N_{Ax}}{\partial x} + \frac{\partial N_{Ay}}{\partial y} + \frac{\partial N_{Az}}{\partial z}\right) + R_A$$

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

$$\frac{\partial c_A}{\partial t} = -\left(\frac{1}{r} \frac{\partial(rN_{A,r})}{\partial r} + \frac{\partial N_{A,\theta}}{\partial \theta} + \frac{\partial N_{A,z}}{\partial z}\right) + R_A$$

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

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


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**Fick's law of diffusion, Gibbs notation:**  $\underline{N}_A = c_A \underline{v}_A + \underline{D}_{A1} \nabla c_A = c_A \underline{v}^* - c_A \underline{D}_{A1} \nabla c_A$

**Fick's law of diffusion, Cartesian coordinates:**  $\begin{pmatrix} N_{Ax} \\ N_{Ay} \\ N_{Az} \end{pmatrix} = \begin{pmatrix} c_A(v_{Ax} + N_{Ax}) - c_A D_{A1} \frac{\partial c_A}{\partial x} \\ c_A(v_{Ay} + N_{Ay}) - c_A D_{A1} \frac{\partial c_A}{\partial y} \\ c_A(v_{Az} + N_{Az}) - c_A D_{A1} \frac{\partial c_A}{\partial z} \end{pmatrix}$

**Fick's law of diffusion, cylindrical coordinates:**  $\begin{pmatrix} N_{A,r} \\ N_{A,\theta} \\ N_{A,z} \end{pmatrix} = \begin{pmatrix} c_A(v_{A,r} + N_{A,r}) - c_A D_{A1} \frac{\partial c_A}{\partial r} \\ c_A(v_{A,\theta} + N_{A,\theta}) - \frac{c_A D_{A1}}{r} \frac{\partial c_A}{\partial \theta} \\ c_A(v_{A,z} + N_{A,z}) - c_A D_{A1} \frac{\partial c_A}{\partial z} \end{pmatrix}$

**Fick's law of diffusion, spherical coordinates:**  $\begin{pmatrix} N_{A,r} \\ N_{A,\theta} \\ N_{A,\phi} \end{pmatrix} = \begin{pmatrix} c_A(v_{A,r} + N_{A,r}) - c_A D_{A1} \frac{\partial c_A}{\partial r} \\ c_A(v_{A,\theta} + N_{A,\theta}) - \frac{c_A D_{A1}}{r \sin \theta} \frac{\partial c_A}{\partial \theta} \\ c_A(v_{A,\phi} + N_{A,\phi}) - \frac{c_A D_{A1}}{r \sin \theta} \frac{\partial c_A}{\partial \phi} \end{pmatrix}$

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**NOTES:**

- If component A has no sink,  $R_A = 0$ .
- If A diffuses through stagnant B,  $N_B = 0$ .
- If a binary mixture of A and B are undergoing steady equimolar counterdiffusion,  $N_A = -N_B$ .
- If, for example, two moles of A diffuse to a surface at which a rapid, irreversible reaction converts it to one mole of B, then at steady state  $-0.5N_A = N_B$ .

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$c_A = c_A \frac{V_A}{V} = \frac{1}{V} (n_{A,V})$  (units:  $[\text{mol}] / [\text{m}^3]$ )

$\underline{J}_A$  = molar flux relative to a mixture's molar average velocity

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

$\underline{J}_A + \underline{J}_B = 0$

$\underline{N}_A = c_A \underline{v}_A + \underline{J}_A = c_A \underline{v}^*$  = flux relative to stationary coordinates

$N_A + N_B = c \underline{v}^*$

$\underline{v}_A$  = velocity of species A in a mixture, i.e. average velocity of all molecules of species A within a small volume

$\underline{v}^* = x_A \underline{v}_A + x_B \underline{v}_B$  = **total** average velocity

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Reference: R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, 2<sup>nd</sup> edn, Wiley, 2002.

[https://pages.mtu.edu/~fmorriso/cm3120/species\\_mass\\_bal\\_3\\_combinedmolarflux.pdf](https://pages.mtu.edu/~fmorriso/cm3120/species_mass_bal_3_combinedmolarflux.pdf)

## Microscopic Species Mass Balance

**QUICK START**

**The Equation of Species Mass Balance in Terms of Combined Molar quantities** in Cartesian, cylindrical, and spherical coordinates for binary mixtures of A and B. The general case, where the **combined molar flux** with respect to molar velocity ( $\underline{N}_A$ ), is given on page 1. Spring 2019 Faith A. Morrison, Michigan Technological University

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

$$\frac{\partial c_A}{\partial t} = -\nabla \cdot \underline{N}_A + R_A$$

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

$$\frac{\partial c_A}{\partial t} = -\left(\frac{\partial N_{Ax}}{\partial x} + \frac{\partial N_{Ay}}{\partial y} + \frac{\partial N_{Az}}{\partial z}\right) + R_A$$

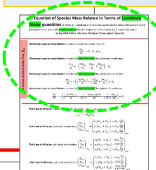
**Microscopic species mass balance, in terms of combined molar flux; cylindrical coordinates**

$$\frac{\partial c_A}{\partial t} = -\left(\frac{1}{r} \frac{\partial(rN_{A,r})}{\partial r} + \frac{\partial N_{A,\theta}}{\partial \theta} + \frac{\partial N_{A,z}}{\partial z}\right) + R_A$$

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

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

Note: this handout is on the web



[pages.mtu.edu/~fmorriso/cm3120/Homeworks\\_Readings.html](https://pages.mtu.edu/~fmorriso/cm3120/Homeworks_Readings.html)

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Fick's Law of Diffusion in terms of Combined Molar Flux  $\underline{N}_A$

QUICK START

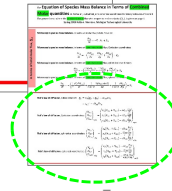
Fick's law of diffusion, Gibbs notation:  $\underline{N}_A = x_A(\underline{N}_A + \underline{N}_B) - cD_{AB}\nabla x_A$   
 $= c_A \underline{v}^* - cD_{AB}\nabla x_A$

Fick's law of diffusion, Cartesian coordinates:  $\begin{pmatrix} N_{A,x} \\ N_{A,y} \\ N_{A,z} \end{pmatrix}_{xyz} = \begin{pmatrix} x_A(N_{A,x} + N_{B,x}) - cD_{AB}\frac{\partial x_A}{\partial x} \\ x_A(N_{A,y} + N_{B,y}) - cD_{AB}\frac{\partial x_A}{\partial y} \\ x_A(N_{A,z} + N_{B,z}) - cD_{AB}\frac{\partial x_A}{\partial z} \end{pmatrix}_{xyz}$

Fick's law of diffusion, cylindrical coordinates:  $\begin{pmatrix} N_{A,r} \\ N_{A,\theta} \\ N_{A,z} \end{pmatrix}_{r\theta z} = \begin{pmatrix} x_A(N_{A,r} + N_{B,r}) - cD_{AB}\frac{\partial x_A}{\partial r} \\ x_A(N_{A,\theta} + N_{B,\theta}) - \frac{cD_{AB}}{r}\frac{\partial x_A}{\partial \theta} \\ x_A(N_{A,z} + N_{B,z}) - cD_{AB}\frac{\partial x_A}{\partial z} \end{pmatrix}_{r\theta z}$

Fick's law of diffusion, spherical coordinates:  $\begin{pmatrix} N_{A,r} \\ N_{A,\theta} \\ N_{A,\phi} \end{pmatrix}_{r\theta\phi} = \begin{pmatrix} x_A(N_{A,r} + N_{B,r}) - cD_{AB}\frac{\partial x_A}{\partial r} \\ x_A(N_{A,\theta} + N_{B,\theta}) - \frac{cD_{AB}}{r}\frac{\partial x_A}{\partial \theta} \\ x_A(N_{A,\phi} + N_{B,\phi}) - \frac{cD_{AB}}{r\sin\theta}\frac{\partial x_A}{\partial \phi} \end{pmatrix}_{r\theta\phi}$

Note: this handout is on the web



Handy reminder of definitions and relationships among mixture quantities

QUICK START

$cx_A = c_A = \frac{1}{M_A}(\rho_A) = \frac{1}{M_A}(\rho\omega_A)$  (units:  $c [=] \frac{\text{mol mix}}{\text{vol soltn}}$ ;  $\rho [=] \frac{\text{mass mix}}{\text{vol soltn}}$ ;  $c_A [=] \frac{\text{mol A}}{\text{vol soltn}}$ ;  $\rho_A [=] \frac{\text{mass A}}{\text{vol soltn}}$ )

$J_A^*$   $\equiv$  molar flux relative to a mixture's molar average velocity,  $\underline{v}^*$  (units:  $J_A^* [=] \frac{\text{mole}}{\text{area}\cdot\text{time}}$ )

$= c_A(\underline{v}_A - \underline{v}^*)$

$J_A^* + J_B^* = 0$

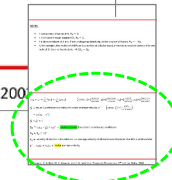
$\underline{N}_A \equiv c_A \underline{v}_A = J_A^* + c_A \underline{v}^* =$  combined molar flux relative to stationary coordinates

$\underline{N}_A + \underline{N}_B = c \underline{v}^*$

$\underline{v}_A \equiv$  velocity of species A in a mixture, i.e. average velocity of all molecules of species A within a sm

$\underline{v}^* = x_A \underline{v}_A + x_B \underline{v}_B \equiv$  molar average velocity

Note: this handout is on the web



Reference: R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, 2<sup>nd</sup> edition, Wiley, 2002

QUICK START

**Example 1:** Water ( $40^\circ\text{C}$ ,  $1.0\text{ atm}$ ) slowly and steadily evaporates into nitrogen ( $40^\circ\text{C}$ ,  $1.0\text{ atm}$ ) 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. The geometry is as shown in the figure. **What is the rate of water evaporation?**

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QUICK START

**Interrogating the problem:**

*Why does the water evaporate?*

*What limits the rate of evaporation?*

*What could be done to accelerate the evaporation?*

*What could be done to slow down the evaporation?*

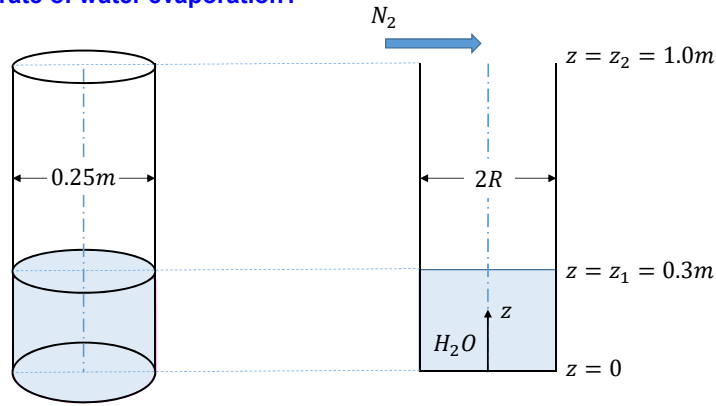
**Example:** Water ( $40^\circ\text{C}$ ,  $1.0\text{ atm}$ ) slowly and steadily evaporates into nitrogen ( $40^\circ\text{C}$ ,  $1.0\text{ atm}$ ) from the bottom of a cylindrical tank as shown in the figure below. A stream of dry nitrogen flows slowly past the open tank. The mole fraction of water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

*What is the driving physics?*

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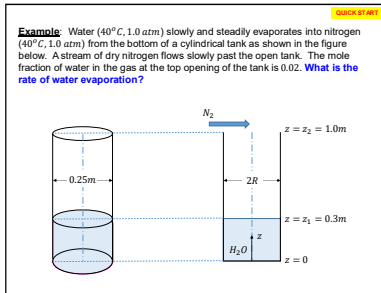
**QUICK START**

**Example 1:** Water ( $40^\circ\text{C}$ ,  $1.0\text{ atm}$ ) slowly and steadily evaporates into nitrogen ( $40^\circ\text{C}$ ,  $1.0\text{ atm}$ ) 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. The geometry is as shown in the figure. What is water mole fraction as a function of vertical position in the tank? You may assume ideal gas properties. **What is the rate of water evaporation?**



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**Solve.**

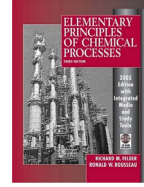
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## Raoult's Law

Reference: **Felder and Rousseau**, 3<sup>rd</sup> Edition, Section 6.3, Gas-Liquid Systems, One Condensable Component



“A law that describes the behavior of gas-liquid systems over a wide range of conditions provides the desired relationship [between  $T, P$ , and  $y_A$ ]. If a gas at temperature  $T$  and pressure  $P$  contains a saturated vapor whose mole fraction is  $y_A$  (mole vapor/mol total gas), and if this vapor is the only species that would condense if the temperature were slightly lowered, then the partial pressure of the vapor in the gas equals the pure-component vapor pressure  $p_A^*(T)$  at the system temperature, [which we look up from tables or data correlations].”

**Raoult's Law**  
(single condensable component)

$$p_A = y_A P = p_A^*(T)$$

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Revisiting and using important concepts/physics

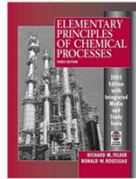
CM3120 Lecture 1

Where are we now?



Michigan Tech

CM2110

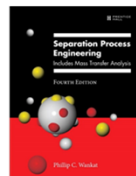


**Summary**

CM2110

1. Steady mass balances
2. Steady energy balances (how to calc. energy)
3. ~~MEB-Mechanical Energy Balance (no friction)~~
4. Phase equilibria (Raoult's Law)

CM2120



CM2120/CM3215

1. MEB-Mechanical Energy Balance (with friction)
2. Pumps
3. Heat Exchangers
4. Introduction to Unit Operations
5. Staged Unit Operations (distillation, absorption)

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## Where do we get the vapor pressure, $p_A^*(T)$ ?

### Raoult's Law

Reference: *Felder and Rousseau, 3<sup>rd</sup> Edition, Section 6.3, Gas-Liquid Systems, One Condensable Component*

"A law that describes the behavior of gas-liquid systems over a wide range of conditions provides the desired relationship [between  $T$ ,  $P$ , and  $y_A$ ]. If a gas at temperature  $T$  and pressure  $P$  contains a saturated vapor whose mole fraction is  $y_A$  (mole vapor/mol total gas), and if this vapor is the only species that would condense if the temperature were slightly lowered, then the partial pressure of the vapor in the gas equals the pure-component vapor pressure  $p_A^*(T)$  at the system temperature, [which we look up from tables or data correlations]."

Raoult's Law  
(single  
condensable  
component)

$$p_A = y_A P = p_A^*(T)$$

1. Tables (water, FR Table B.3)
2. Clausius-Clapeyron equation (constant  $\Delta\hat{H}_v$ , FR Table B.1)

$$\ln(p^*) = -\frac{\Delta\hat{H}_v}{RT} + B$$

3. Antoine equation (FR Table B.4)

$$\log_{10}(p^*) = A - \frac{B}{T + C}$$

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