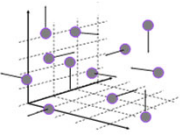



# NEXT: Diffusion and Mass Transfer

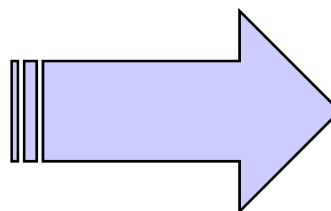
CM3120 Transport/Unit Operations 2

**Diffusion and Mass Transfer**



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Department of Chemical Engineering  
Michigan Technological University

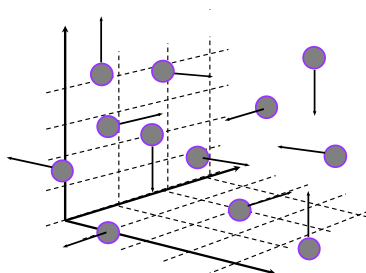
[www.chem.mtu.edu/~fmorriso/cm3120/cm3120.html](http://www.chem.mtu.edu/~fmorriso/cm3120/cm3120.html)



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## CM3120 Transport/Unit Operations 2

### Diffusion and Mass Transfer



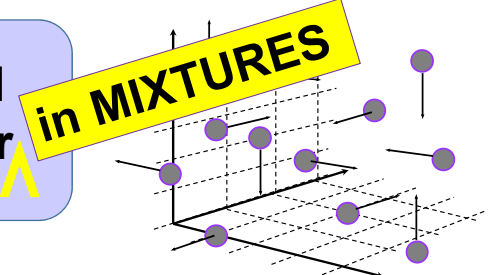
**Professor Faith A. Morrison**  
Department of Chemical Engineering  
Michigan Technological University


[www.chem.mtu.edu/~fmorriso/cm3120/cm3120.html](http://www.chem.mtu.edu/~fmorriso/cm3120/cm3120.html)

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**CM3120 Transport/Unit Operations 2**

## Diffusion and Mass Transfer





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[www.chem.mtu.edu/~fmorriso/cm3120/cm3120.html](http://www.chem.mtu.edu/~fmorriso/cm3120/cm3120.html)

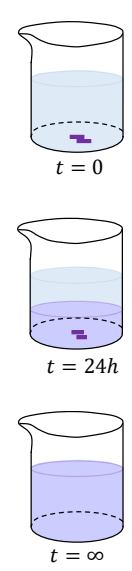
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Introduction to Diffusion and Mass Transfer in Mixtures

## Diffusion

- Is the mixing process caused by random molecular motion.
- Is part of scientific inquiry (explains how nature works)

**Diffusion/  
mass transfer  
concerns the  
physics of  
mixtures.**



## Mass Transfer

- Encompasses all mass-transfer mechanisms and any issues of mixed physics
- Controls the cost of processes like chemical purification and environmental control
- Is *practical* (is basic to the engineering of chemical processes)

*References:*  
E. L. Cussler, *Diffusion: Mass Transfer in Fluid Systems*, 3<sup>rd</sup> edition, Cambridge University Press, 2016.  
R. B. Bird, W. E. Stewart, E. N. Lightfoot, *Transport Phenomena*, 2<sup>nd</sup> edition, 2002.  
J. R. Welty, G. L. Rorrer, and D. G. Foster, *Fundamentals of Momentum, Heat and Mass Transfer*, 6<sup>th</sup> edition, 2015.

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Introduction to Diffusion and Mass Transfer in Mixtures

## Diffusion

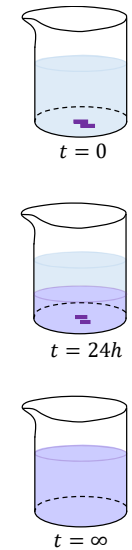
- Is the mixing process caused by random molecular motion (Brownian motion).
- Is part of scientific inquiry (explains how nature works)
- Is **slow**
- Since it is slow, it acts over short distances

Diffusion progresses at a rate of

- $\sim 5\text{cm/min}$  (gases)
- $\sim 0.05\text{cm/min}$  (liquids)
- $\sim 10^{-5}\text{cm/min}$  (solids)

Is the **physics** behind:


- Transport in living cells
- The efficiency of distillation
- The dispersal of pollutants
- Gas absorption
- Fog formed by rain on snow
- The dyeing of wool



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Introduction to Diffusion and Mass Transfer in Mixtures

**Example:** A friend walks into the far end of the room plates of a delicious-smelling warm lunch including French fries. How did the smell of lunch reach your nostrils?



Diffusion progresses at a rate of

- $\sim 5\text{cm/min}$  (gases)
- $\sim 0.05\text{cm/min}$  (liquids)
- $\sim 10^{-5}\text{cm/min}$  (solids)

# You try.

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## Introduction to Diffusion and Mass Transfer in Mixtures

**Mass Transfer**

- Encompasses all mass-transfer mechanisms: random motion, convection, thermodynamics-driven (specific interaction).
  - Controls the cost of processes like chemical purification and environmental control
  - Is practical (is basic to the engineering of chemical processes)
  - Is also slow
- 
- There is an analogy to heat transfer (but care must be taken not to over emphasize)
  - Dilute mass transfer is emphasized
  - Is the **modeling** behind (for example):
    - ✓ Differential distillation (common) versus staged distillation (less common)
    - ✓ Adsorption
    - ✓ Important applications of mass transfer in biology and medicine
    - ✓ Much more

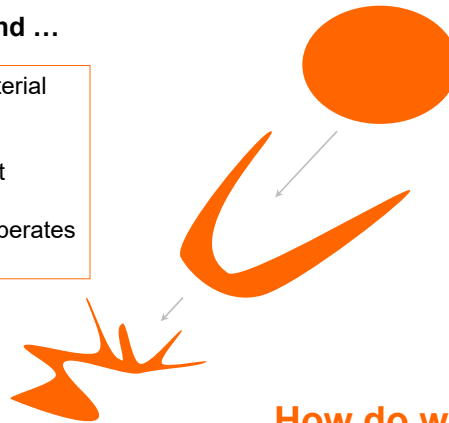
p. xix

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## Introduction to Diffusion and Mass Transfer in Mixtures

**Mass Transfer****Convection and Diffusion and ...**

- Agitation or stirring moves material over long distances
- Exposing new fluid elements
- Diffusion mixes newly adjacent material
- Because diffusion is **slow**, it operates only over short distances



**How do we  
model diffusion?**

Reference:  
E. L. Cussler, *Diffusion: Mass Transfer in Fluid  
Systems*, 3<sup>rd</sup> edition, Cambridge University Press, 2016.

p. 1

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Diffusion/Mass Transfer Recap and Planning

### Summary *(in advance)*

## Diffusion and Mass Transfer

**Mixtures**

**Diffusion:**

- Brownian motion (random molecular motion),
- Fick's law of diffusion,  $D_{AB}$
- slow,
- operates over short distances

**Mass Transfer:**

- Includes all mechanisms (e.g. diffusion, convection, thermodynamics-driven),
- Linear-driving-force model,
- slow,
- also acts over short distances but convection extends it a bit

$t = 0$

$t = 24h$

$t = \infty$

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Diffusion/Mass Transfer Recap and Planning

### Recap:

## Diffusion/Mass Transfer (so far, and beyond)

**Modeling:**

Microscopic species A mass balance  
(continuum modeling tricky with mixtures; also issues of units, (mass versus moles) and reference coordinates)

- Four fluxes  $\underline{N}_A, \underline{J}_A^*, \underline{n}_A, \underline{j}_A$
- Three summary sheets using  $\underline{N}_A, \underline{J}_A^*, \underline{j}_A$

Fick's law (diffusion)

- Diffusion coefficient  $D_{AB}$
- Four forms using  $\underline{N}_A, \underline{J}_A^*, \underline{n}_A, \underline{j}_A$

Linear-driving-force model (mass transfer; analogous to Newton's law of cooling)—  
mass transfer coefficient  $k_{various\ designations}$

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

Mass flux	Molar flux	Continuum model flux
$\underline{J}_A = -\rho D_{AB} \nabla x_A$	$\underline{J}_A^* = -c D_{AB} \nabla x_A$	$\underline{J}_A = x_A (\underline{E}_A + \underline{D}_A) - c D_{AB} \nabla x_A$

[Notes] [Pages 11-12: 601-611; Morrison 31.2019meworks\_Recap9a.pdf]

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We start here, with diffusion

Diffusion/Mass Transfer Recap and Planning

**Recap:**  
**Diffusion/Mass Transfer (so far, and beyond)**

**Modeling:**

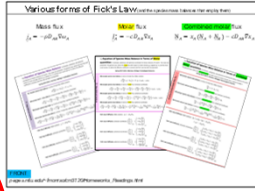
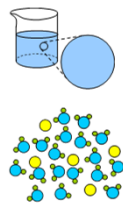
Microscopic species A mass balance  
 (continuum modeling tricky with mixtures; also issues of units, (mass versus moles) and reference coordinates)

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 mass transfer coefficient  $k_{\text{various designations}}$

Diffusion/Mass Transfer Recap and Planning

**Recap:**  
**Diffusion/Mass Transfer (so far, and beyond)**

**Modeling:**

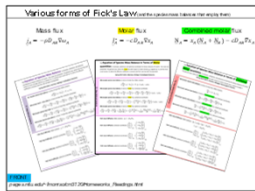
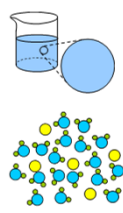
Microscopic species A mass balance  
 (continuum modeling tricky with mixtures; also issues of units, (mass versus moles) and reference coordinates)

- Four fluxes  $\underline{N}_A, \underline{j}_A^*, \underline{u}_A, \underline{j}_A$
- Three summary sheets using  $\underline{N}_A, \underline{j}_A, \underline{j}_A$

Fick's law (diffusion)


- Diffusion coefficient  $D_{AB}$
- Four forms using  $\underline{N}_A, \underline{j}_A^*, \underline{u}_A, \underline{j}_A$

Linear-driving-force model (mass transfer; analogous to Newton's law of cooling)—  
 mass transfer coefficient  $k_{\text{various designations}}$

Later, we turn to the linear-driving-force model (mass transfer coefficient)

Linear Driving Force Model for Mass Transfer


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CM3120  
 Transport II  
 Part II: Diffusion and Mass Transfer

Simple One-dimensional Species Mass Diffusion

This is the fundamental version of Fick's Law (1D)

$\dot{j}_{A,y} = -\rho D_{AB} \frac{d\omega_A}{dy}$

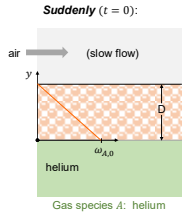
Fick's law of diffusion

(in terms of mass flux)

$D_{AB}$  = Diffusion coefficient of A through B


$\dot{j}_{A,y}$  = mass flux of A through B

Suddenly ( $t = 0$ ):



Diffusion —

Fick's Law of Mass Transfer



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 Michigan Technological University

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Introduction to Diffusion and Mass Transfer in Mixtures

## Transport Analogy (flux proportional to driving gradient)

<b><u>Momentum</u></b>	$-\tilde{\tau}_{yz} = -\mu \frac{\partial v_y}{\partial z}$	Newton's Law
<b><u>Heat</u></b>	$\frac{q_z}{A} = -k \frac{\partial T}{\partial z}$	Fourier's Law
<b><u>Species A Mass</u></b> <span style="font-size: small; color: yellow;">in a mixture with B</span>	$j_{A,z} = -\rho D_{AB} \frac{\partial \omega_A}{\partial z}$	Fick's Law

- ✓ **Momentum** goes down a velocity gradient
- ✓ **Heat** goes down a temperature gradient
- ✓ **Mass of species A** goes down a gradient in concentration of A in a mixture

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

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Introduction to Diffusion and Mass Transfer in Mixtures

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## Transport Analogy (flux proportional to driving gradient)

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<b><u>Species A Mass</u></b> <i>in a mixture with B</i>	$j_{A,z} = -\rho D_{AB} \frac{\partial \omega_A}{\partial z}$	Fick's Law

Mass of species A diffusing in the z-direction, per area per time

✓ Mass of species A goes down a gradient in concentration of A in a mixture

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

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Introduction to Diffusion and Mass Transfer in Mixtures

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<b><u>Species A Mass</u></b> <i>in a mixture with B</i>	$j_{A,z} = -\rho D_{AB} \frac{\partial \omega_A}{\partial z}$	Fick's Law

There is a transport analogy but

- topics important to diffusion but not to fluid flow tend to be omitted or deemphasized when the transport analogy is emphasized (e.g. simultaneous diffusion and chemical reaction)
- Numerous topics unrelated to the transport law are deemphasized (in fluid mechanics non-Newtonian flow and heat transfer & some aspects of macroscopic modeling)

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

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Introduction to Diffusion and Mass Transfer in Mixtures

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## Transport Analogy (flux proportional to driving gradient)

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- topics important to diffusion but not to fluid flow tend to be omitted or deemphasized when the transport analogy is emphasized (e.g. simultaneous diffusion and chemical reaction)
- Numerous topics unrelated to the transport analogy (e.g. fluid mechanics non-Newtonian flow and heat transfer macroscopic modeling)

How do we model diffusion?

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

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Introduction to Diffusion and Mass Transfer in Mixtures

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## Modeling Diffusion/Mass Transfer:

**Mass is Conserved** Both:

- overall mass
- individual species' masses in a mixture

As was true in momentum transfer and heat transfer, solving problems with shell balances on individual control volumes is tricky, and it is easy to make errors.

Instead, we use the general equation, derived for all circumstances:

Equation of Species A Mass Balance

(microscopic species mass balance)

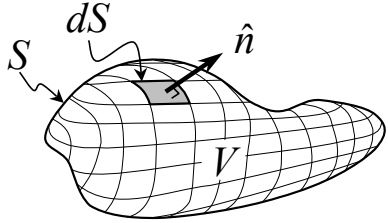
Recall the other microscopic balances, all written in terms of

Continuum Modeling

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**Microscopic Momentum Balance:**

Equation of Motion



Microscopic **momentum** balance written on an arbitrarily shaped control volume,  $V$ , enclosed by a surface,  $S$

Gibbs notation: 
$$\rho \left( \frac{\partial \underline{v}}{\partial t} + \underline{v} \cdot \nabla \underline{v} \right) = -\nabla p + \nabla \cdot \underline{\underline{\tau}} + \rho \underline{g}$$
 **general fluid**

Gibbs notation: 
$$\rho \left( \frac{\partial \underline{v}}{\partial t} + \underline{v} \cdot \nabla \underline{v} \right) = -\nabla p + \mu \nabla^2 \underline{v} + \rho \underline{g}$$
 **Newtonian fluid**

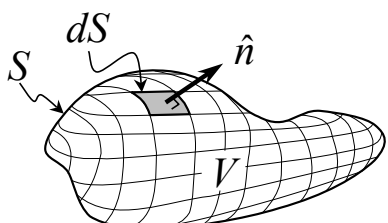
Navier-Stokes Equation; constant viscosity

Microscopic momentum balance is a vector equation.

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**Microscopic Energy Balance:**

Equation of Thermal Energy



Microscopic **energy** balance written on an arbitrarily shaped volume,  $V$ , enclosed by a surface,  $S$

Gibbs notation: 
$$\rho \left( \frac{\partial \hat{E}}{\partial t} + \underline{v} \cdot \nabla \hat{E} \right) = -\nabla \cdot \underline{\underline{q}} + S_e$$
 **general conduction**

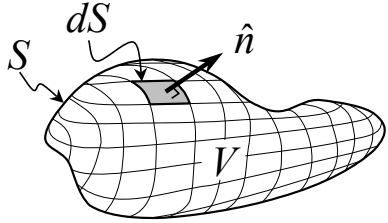
Gibbs notation: 
$$\rho \hat{C}_p \left( \frac{\partial T}{\partial t} + \underline{v} \cdot \nabla T \right) = k \nabla^2 T + S_e$$
 **Fourier conduction**

(incompressible fluid, constant pressure, neglect  $\hat{E}_k, \hat{E}_p$ , viscous dissipation, constant  $k$ )

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### Microscopic Species A Mass Balance:

**Equation of Species Mass Balance**



Gibbs notation: 
$$\rho \left( \frac{\partial \omega_A}{\partial t} + \underline{v} \cdot \nabla \omega_A \right) = -\nabla \cdot \underline{j}_A + r_A$$
 **general mass transfer**

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

(written in terms of mass quantities; constant  $\rho D_{AB}$ )

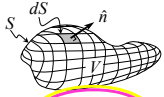
Microscopic **species A mass** balance written on an arbitrarily shaped volume,  $V$ , enclosed by a surface,  $S$

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### Introduction to Diffusion and Mass Transfer in Mixtures

**Recall Microscopic Momentum Balance:**

**Equation of Motion**



Gibbs notation: 
$$\rho \left( \frac{\partial \underline{v}}{\partial t} + \underline{v} \cdot \nabla \underline{v} \right) = -\nabla p + \nabla \cdot \underline{\underline{\tau}} + \rho \underline{g}$$
 **general fluid**

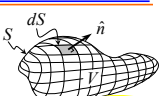
Gibbs notation: 
$$\rho \left( \frac{\partial \underline{v}}{\partial t} + \underline{v} \cdot \nabla \underline{v} \right) = -\nabla p + \mu \nabla^2 \underline{v} + \rho \underline{g}$$
 **Newtonian fluid**

Navier-Stokes Equation

Microscopic momentum balance is a vector equation.

**Microscopic Species A Mass Balance:**

**Equation of Species Mass Balance**

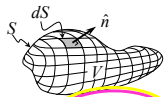


Gibbs notation: 
$$\rho \left( \frac{\partial \omega_A}{\partial t} + \underline{v} \cdot \nabla \omega_A \right) = -\nabla \cdot \underline{j}_A + r_A$$
 **general mass transfer**

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

(written in terms of mass quantities; constant  $\rho D_{AB}$ )

**Equation of Thermal Energy**



Gibbs notation: 
$$\rho \left( \frac{\partial \underline{E}}{\partial t} + \underline{v} \cdot \nabla \underline{E} \right) = -\nabla \cdot \underline{q} + S_e$$
 **general conduction**

Gibbs notation: 
$$\rho \hat{c}_p \left( \frac{\partial T}{\partial t} + \underline{v} \cdot \nabla T \right) = k \nabla^2 T + S_e$$
 **Fourier conduction**

(incompressible fluid, constant pressure, neglect  $\underline{E}_v, \underline{E}_p$ , viscous dissipation)

**Microscopic Balances:**

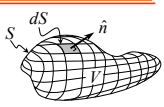
- All three have a convective term on the left-hand side (due to use of control volume as the system and mass or per mass basis)
- All three have two forms, one including the flux and one with the transport law embedded

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### Introduction to Diffusion and Mass Transfer in Mixtures

**Recall Microscopic Momentum Balance:**

**Equation of Motion**



Microscopic **momentum** balance written on an arbitrarily shaped control volume, V, enclosed by a surface, S

Gibbs notation:  $\rho \left( \frac{\partial \underline{v}}{\partial t} + \underline{v} \cdot \nabla \underline{v} \right) = -\nabla p + \nabla \cdot \underline{\underline{\tau}} + \rho \underline{g}$  **general fluid**

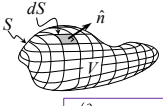
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Navier-Stokes Equation

Microscopic momentum balance is a vector equation.

**Microscopic Species A Mass Balance:**

**Equation of Species Mass Balance**



Microscopic **species A mass** balance written on an arbitrarily shaped volume, V, enclosed by a surface, S

Gibbs notation:  $\rho \left( \frac{\partial \omega_A}{\partial t} + \underline{v} \cdot \nabla \omega_A \right) = -\nabla \cdot \underline{j}_A + r_A$  **general mass transfer**

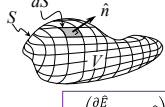
Gibbs notation:  $\rho \left( \frac{\partial \omega_A}{\partial t} + \underline{v} \cdot \nabla \omega_A \right) = \rho D_{AB} \nabla^2 \omega_A + r_A$  **Fickian diffusion**

(written in terms of mass quantities; constant  $\rho D_{AB}$ )

**Microscopic Balances:**

- All three have a convective term on the left-hand side (due to use of control volume as the system and mass or per mass basis)
- All three have two forms, one including the flux and one with the transport law embedded

**Equation of Thermal Energy**



Microscopic **energy** balance written on an arbitrarily shaped volume, V, enclosed by a surface, S

Gibbs notation:  $\rho \left( \frac{\partial \underline{E}}{\partial t} + \underline{v} \cdot \nabla \underline{E} \right) = -\nabla \cdot \underline{q} + S_e$  **general conduction**

Gibbs notation:  $\rho c_p \left( \frac{\partial T}{\partial t} + \underline{v} \cdot \nabla T \right) = k \nabla^2 T + S_e$  **Fourier conduction**

(incompressible fluid, constant pressure, neglect  $E_e, E_p$ , viscous dissipation)

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### Introduction to Diffusion and Mass Transfer in Mixtures

## Microscopic species A mass balance

*in a mixture*

*Appears due to use of stationary coordinates (control volume)*

convection

rate of change

source

diffusion

(all directions)

Appears due to diffusive transport through a surface (control surface)

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

(mass of species A generated by homogeneous reaction per time)

velocity must satisfy equation of motion, equation of continuity

The types of terms that appear are very much like similar mechanisms that we have seen in the other transport fields.

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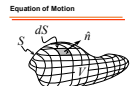
### Introduction to Diffusion and Mass Transfer in Mixtures

An underlying feature of these balances is the assumption that matter forms a **continuum**.

**momentum**

**Recall Microscopic Momentum Balance:**

**Equation of Motion**



Gibbs notation:  $\rho \left( \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \nabla \cdot \boldsymbol{\tau} + \rho \mathbf{g}$  **general fluid**

Gibbs notation:  $\rho \left( \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \mu \nabla^2 \mathbf{u} + \rho \mathbf{g}$  **Newtonian fluid**

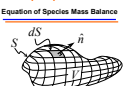
Navier-Stokes Equation

Microscopic momentum balance as a vector equation.

**species mass**

**Microscopic Species A Mass Balance:**

**Equation of Species A Mass Balance**



Gibbs notation:  $\rho \left( \frac{\partial \omega_A}{\partial t} + \mathbf{u} \cdot \nabla \omega_A \right) = -\nabla \cdot \mathbf{j}_A + \mathcal{R}_A$  **general mass transfer**

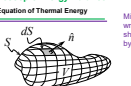
Gibbs notation:  $\rho \left( \frac{\partial \omega_A}{\partial t} + \mathbf{u} \cdot \nabla \omega_A \right) = \rho D_{AB} \nabla^2 \omega_A + \mathcal{R}_A$  **Fickian diffusion**

(written in terms of mass quantities, constant  $\rho D_{AB}$ )

**energy**

**Microscopic Energy Balance:**

**Equation of Thermal Energy**



Gibbs notation:  $\rho \left( \frac{\partial E}{\partial t} + \mathbf{u} \cdot \nabla E \right) = -\nabla \cdot \mathbf{q} + S_v$  **general conduction**

Gibbs notation:  $\rho c_p \left( \frac{\partial T}{\partial t} + \mathbf{u} \cdot \nabla T \right) = k \nabla^2 T + S_v$  **Fourier conduction**

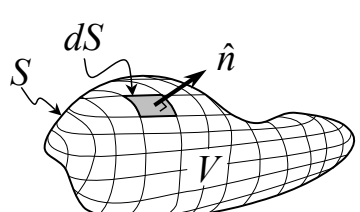
(incompressible fluid, constant pressure, neglect  $\dot{E}_v, \dot{E}_p$ , viscous dissipation)

To model diffusion and mass transfer within this familiar structure, we must adapt our notion of the **continuum**.

to accommodate aspects that are important in a mixture

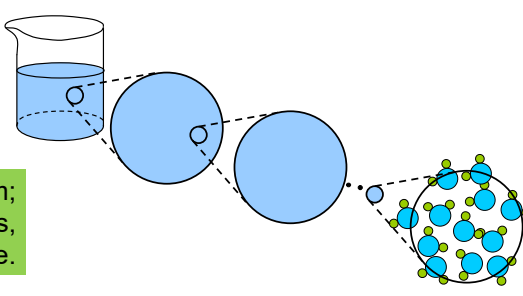
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### Continuum Modeling



*Microscopic* balances are written on an arbitrarily shaped microscopic volume,  $V$ , enclosed by a surface,  $S$

- A **continuum** is infinitely divisible
- Material properties ( $\mu, k, \rho$ ) are shared by all volume elements

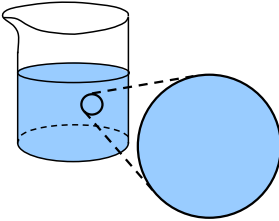


**BUT:** Real matter is *not* a continuum; at small enough length scales, molecules are discrete.


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**Continuum Modeling**

- A **continuum** is infinitely divisible
- Material properties ( $\mu, k, \rho$ ) are shared by all volume elements

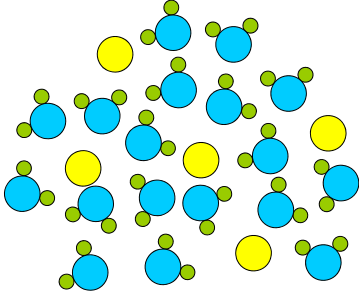


- In a **binary mixture**, different pieces of matter have different material identities and different material properties

**Species A:**   $x_A$ , mole fraction A

**Species B:**   $x_B$ , mole fraction B

$C, \frac{(\text{moles mixture})}{(\text{volume mixture})}$



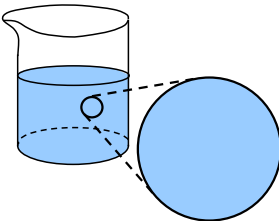
**MOLAR basis**

Moles are easier when reactions occur...


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**Continuum Modeling**

- A **continuum** is infinitely divisible
- Material properties ( $\mu, k, \rho$ ) are shared by all volume elements

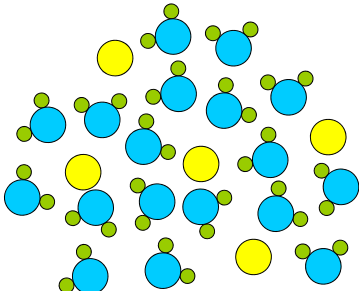


- In a **binary mixture**, different pieces of matter have different material identities and different material properties

**Species A:**   $\omega_A$ , mass fraction A

**Species B:**   $\omega_B$ , mass fraction B

$\rho, \frac{(\text{mass mixture})}{(\text{volume mixture})}$



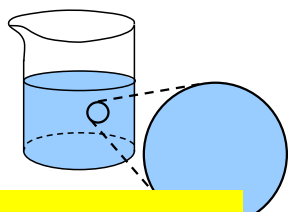
**MASS basis**

Only mass is conserved...

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Continuum Modeling


- A **continuum** is infinitely divisible
- Material properties ( $\mu, k, \rho$ ) are shared by all volume elements

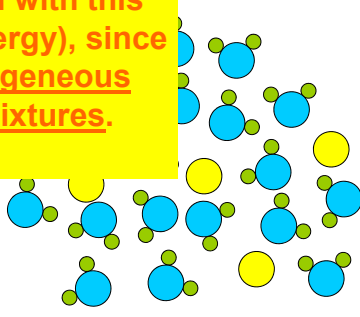


We didn't have to deal with this before (momentum, energy), since we considered homogeneous materials and not mixtures.

In a **binary mixture**, matter have different chemical identities and different material properties

Species A:   $\omega_B$ , mass fraction B

Species B:   $\rho, \frac{(\text{mass mixture})}{(\text{volume mixture})}$





**MASS basis**  
Only mass is conserved...

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Continuum Modeling

### Mass versus Moles

- A complication with the microscopic species mass balance is that we are accustomed to modeling systems as a **continuum**.
- In a continuum, material properties ( $\mu, k, \rho$ ) are shared by all volume elements.
- But now, we're interested in species A and B as separate entities.
- Chemical identity manifests as a distribution of atoms/molecules (or **moles** of either) and also as a distribution of **mass**.
- Molar and mass distributions **are not the same distribution**.

$x_A$ , mole fraction A $x_B$ , mole fraction B $C, \frac{(\text{moles mixture})}{(\text{volume mixture})}$	<p>Species A: </p> <p>Species B: </p>	$\omega_A$ , mass fraction A $\omega_B$ , mass fraction B $\rho, \frac{(\text{mass mixture})}{(\text{volume mixture})}$
<b>MOLAR basis</b>	Moles are easier when reactions occur...	<b>MASS basis</b>

Only mass is conserved...

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Continuum Modeling

### Mass versus Moles

$\omega_A$ , mass fraction A  
 $\omega_B$ , mass fraction B  
 $\rho$ ,  $\frac{(\text{mass mixture})}{(\text{volume mixture})}$

Species A:

Species B:

$x_A$ , mole fraction A  
 $x_B$ , mole fraction B  
 $C$ ,  $\frac{(\text{moles mixture})}{(\text{volume mixture})}$

**Should we express the diffusion of molecules in terms of moles or in terms of mass?**

**Does it matter?**

Answer? It depends.

**MASS!**

Fits well with previous microscopic balances (in a mixture,  $\underline{v}$  is the **mass average velocity**)

**MOLES!**

When reactions take place, reactions are naturally analyzed in terms of **moles**

**This tradeoff has led to an increase of nomenclature.**

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## Species Fluxes

The community has found use for **four** (actually more) different fluxes. The differences in the various fluxes are related to several questions:

**Flux of what? And due to what mechanism?**

- $\underline{N}_A$  – combined molar flux (includes both convection and diffusion)
- $\underline{n}_A$  – combined mass flux (includes both convection and diffusion)
- $\underline{j}_A$  – mass flux (diffusion only)
- $\underline{J}_A^*$  – molar flux (diffusion only)

**Written relative to what velocity?**

- $\underline{N}_A$  – relative to stationary coordinates
- $\underline{n}_A$  – relative to stationary coordinates
- $\underline{j}_A$  – relative to the mass average velocity  $\underline{v}$
- $\underline{J}_A^*$  – relative to the molar average velocity  $\underline{v}^*$

Microscopic species A mass balance

$$\rho \underbrace{\left( \frac{\partial \omega_A}{\partial t} + \underline{v} \cdot \nabla \omega_A \right)}_{\text{rate of change}} = \underbrace{\rho D_{AB} \nabla^2 \omega_A}_{\text{diffusion (all directions)}} + \underbrace{r_A}_{\text{source}} \quad \left( \text{mass of species A generated by homogeneous reaction per time} \right)$$

These different definitions lead to different forms for the microscopic species mass balance and for the transport law.

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### Species Fluxes

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**Flux of what? And due to what mechanism?**

- $\underline{N}_A$  – combined molar flux (includes both convection and diffusion)
- $\underline{m}_A$  – combined mass flux (includes both convection and diffusion)
- $\underline{j}_A$  – mass flux (diffusion only)
- $\underline{J}_A$  – molar flux (diffusion only)

**Written relative to what velocity?**

- $\underline{N}_A$  – relative to stationary coordinates
- $\underline{m}_A$  – relative to stationary coordinates
- $\underline{j}_A$  – relative to the mass average velocity  $\underline{v}$
- $\underline{J}_A$  – relative to the molar average velocity  $\underline{v}^*$

Microscopic species A mass balance

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

rate of change      diffusion (all directions)      source (mass of species A generated by homogeneous reaction per time)

These different definitions lead to different forms for the **microscopic species mass balance** and for the **transport law**.

These different fluxes are a significant complication.

➔

It will take some time and practice to get used to all this

➔

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

These different definitions lead to **different forms** for the **microscopic species mass balance** and for the **species transport law, Fick's law**.

➔

It will take some time and practice to get used to all this

➔

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Various quantities in diffusion and mass transfer	
How much is present:	$cx_A = c_A = \frac{1}{M_A}(\rho_A) = \frac{1}{M_A}(\rho\omega_A)$
$j_A \equiv$ <b>mass flux</b> of species $A$ relative to a mixture's <b>mass average velocity</b> , $v$	$= \rho_A(v_A - v)$ $j_A + j_B = 0$ , i.e. these fluxes are measured relative to the mixture's center of mass
$n_A \equiv \rho_A v_A = j_A + \rho_A v =$ <b>combined mass flux</b> relative to <b>stationary coordinates</b>	$n_A + n_B = \rho v$
$J_A \equiv$ <b>molar flux</b> relative to a mixture's <b>molar average velocity</b> , $v^*$	$= c_A(v_A - v^*)$ $J_A + J_B = 0$
$N_A \equiv c_A v_A = J_A + c_A v^* =$ <b>combined molar flux</b> relative to <b>stationary coordinates</b>	$N_A + N_B = c v^*$
$v_A \equiv$ velocity of species $A$ in a mixture, i.e. average velocity of all molecules of species $A$ within a small volume	$v = \omega_A v_A + \omega_B v_B \equiv$ mass average velocity; same velocity as in the microscopic momentum and energy balances
$v^* = x_A v_A + x_B v_B \equiv$ molar average velocity	

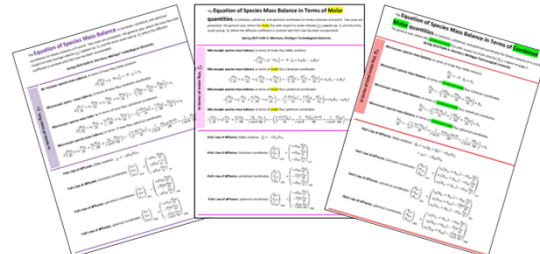
Part of the problem is that we have grown comfortable with the continuum, but now we are peering into the details of the continuum

➔

It will take some time and practice to get used to all this

➔

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Various forms of Fick's Law (and the species mass balances that employ them)		
<p>Mass flux</p> $j_A = -\rho D_{AB} \nabla \omega_A$	<p>Molar flux</p> $J_A = -c D_{AB} \nabla x_A$	<p>Combined molar flux</p> $N_A = x_A(N_A + N_B) - c D_{AB} \nabla x_A$
		
<p><small>FRONT</small> <a href="https://pages.mtu.edu/~fmorriso/cm3120/Homeworks_Readings.html">pages.mtu.edu/~fmorriso/cm3120/Homeworks_Readings.html</a></p>		

We will be introduced to handy worksheets and to the common assumptions and boundary conditions (just like in momentum and energy balances)

➔

It will take some time and practice to get used to all this

➔

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

Let's jump in!

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

Microscopic species mass balance in terms of combined molar flux  $\underline{N}_A$

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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

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

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

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

$c [=] \frac{\text{moles mix}}{\text{volume mix}} =$  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:

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

**QUICK START**

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

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

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

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

## 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 2020 Faith A. Morrison, Michigan Technological University

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

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

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

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

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

$$\frac{\partial N_A}{\partial t} = -\left( \frac{\partial(N_A r)}{\partial r} + \frac{\partial N_{A\theta}}{\partial \theta} + \frac{\partial N_{Az}}{\partial z} \right) + R_A$$

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

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


---

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

**Fick's law of diffusion, Cartesian coordinates:**  $\begin{pmatrix} N_{Ax} \\ N_{Ay} \\ N_{Az} \end{pmatrix} = \begin{pmatrix} x_A(N_{Ax} + N_{Bx}) - cD_{AB} \frac{\partial x_A}{\partial x} \\ x_A(N_{Ay} + N_{By}) - cD_{AB} \frac{\partial x_A}{\partial y} \\ x_A(N_{Az} + N_{Bz}) - cD_{AB} \frac{\partial x_A}{\partial z} \end{pmatrix}$

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

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

**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  $-0.5N_A = N_B$ .

---

$c x_A = c_A = \frac{N_A}{v} = \frac{1}{v} (N_{Ax} + N_{Ay} + N_{Az})$  (units:  $c [=] \frac{\text{mol}}{\text{m}^3}$ )

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

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

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

$\underline{N}_A = c_A \underline{v}_A = \underline{J}_A + c_A \underline{v}^*$  = combined molar 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

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

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

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