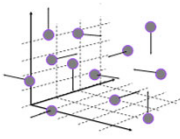



# Now, Cycling Back:

## Diffusion and Mass Transfer

CM3120 Transport/Unit Operations 2

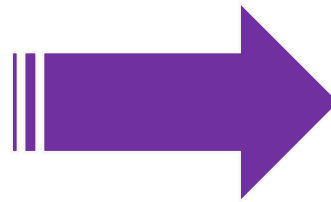
**Diffusion and Mass Transfer**





**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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### Introduction to Diffusion and Mass Transfer in Mixtures

#### Our first introduction to Diffusion:

- Brownian motion
- Slow

Introduction to Diffusion and Mass Transfer in Mixtures

**Diffusion**

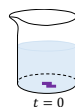
- Is the mixing process caused by random molecular motion (Brownian motion).
- Is part of scientific inquiry (explains how nature works)
- Is slow
- Since it is slow, it acts over short distances

Is the **physics** behind:

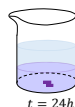
- Transport in living cells
- The efficiency of distillation
- The dispersal of pollutants
- Gas absorption
- Fog formed by rain on snow
- The dyeing of wool

Diffusion progresses at a rate of

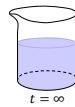
- $\sim 5\text{cm/min}$  (gases)
- $\sim 0.05\text{cm/min}$  (liquids)
- $\sim 10^{-5}\text{cm/min}$  (solids)



$t = 0$



$t = 24\text{h}$



$t = \infty$

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Introduction to Diffusion and Mass Transfer in Mixtures

Our first introduction to Diffusion:

- Proliferation of fluxes and nomenclature

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

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 (left side) = convection (middle term) + diffusion (all directions) (middle term) + source (right side) (mass of species A generated by homogeneous reaction per time)

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  $\underline{v}^*$

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

QUICK START

We skipped to one version of the **Species A mass balance** (and Fick's law) and got some practice.

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

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

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:  $c \left( \frac{\partial x_A}{\partial t} + \underline{v} \cdot \nabla x_A \right) = -\nabla \cdot \underline{J}_A^* + R_A = cD_{AB} \nabla^2 x_A + R_A$
- 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.

Example: Water (at  $25^\circ\text{C}$ , 1.0 atm) slowly and steadily evaporates into nitrogen (at  $25^\circ\text{C}$ , 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. The geometry is as shown in the figure. What is water mole fraction as a function of vertical position? You may assume ideal gas properties. What is the rate of water evaporation?

Example: A water mist forms in an industrial printing operation. Spherical water droplets slowly and steadily evaporate into the air (mostly nitrogen). The evaporation creates a film around the droplets through which the evaporating water diffuses. We can model the diffusion process as shown in the figure. What is the water mole fraction in the film as a function of radial position? You may assume ideal gas properties for air.

Example: Heterogeneous catalysis

An irreversible, instantaneous chemical reaction ( $A \rightarrow B$ ) takes place at a catalytic 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 catalytic surface. Calculate the steady state composition distribution in the film ( $\mu \leq L$ ).

Introduction to Diffusion and Mass Transfer in Mixtures QUICK START

### Recurring Modeling Assumptions in Diffusion

- Near a liquid-gas interface, the region in the gas near the liquid is a film where 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,  $\underline{N}_A = 0$ .
- If  $A$  diffuses through stagnant  $B$ ,  $\underline{N}_B = 0$ .
- If a binary mixture of  $A$  and  $B$  are undergoing steady equimolar counter diffusion,  $\underline{N}_A = -\underline{N}_B$ .
- 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  $-0.5\underline{N}_A = \underline{N}_B$ .
- Because diffusion is slow, we can make a quasi-steady-state assumption
- Homogeneous reactions appear in the mass balance; heterogeneous reactions appear in the boundary conditions
- 
- 

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Introduction to Diffusion and Mass Transfer in Mixtures

### Questions we skipped:

**Where does Fick's law come from?**

**Why so many definitions of flux?**

**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 convection and diffusion)  
 $\underline{B}_A$  – combined mass flux (includes 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  
 $\underline{B}_A$  – 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

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

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

**Transport Laws, up to now:**

**Part I: Momentum Transfer**  
 Momentum transfer:

$$\tau_{21} = (-\tilde{\tau}_{21}) = -\underbrace{\mu}_{\text{viscosity}} \underbrace{\left(\frac{dv_1}{dx_2}\right)}_{\text{velocity gradient}}$$

momentum flux

Newton's law of viscosity

**Part II: Heat Transfer**  
 Heat transfer:

$$\frac{q_x}{A} = -\underbrace{k}_{\text{thermal conductivity}} \underbrace{\frac{dT}{dx}}_{\text{temperature gradient}}$$

heat flux

Fourier's law of conduction

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**Part I: Momentum Transfer**  
 Momentum transfer:

$$\tau_{21} = (-\tilde{\tau}_{21}) = -\underbrace{\mu}_{\text{viscosity}} \underbrace{\left(\frac{dv_1}{dx_2}\right)}_{\text{velocity gradient}}$$

momentum flux

Newton's law of viscosity

**Part II: Heat Transfer**  
 Heat transfer:

$$\frac{q_x}{A} = -\underbrace{k}_{\text{thermal conductivity}} \underbrace{\frac{dT}{dx}}_{\text{temperature gradient}}$$

heat flux

Fourier's law of conduction

**Now:**

**Part III: Mass Transfer**  
 Mass transfer:

$$\underline{j}_A = -\underbrace{\rho D_{AB}}_{\text{diffusivity}} \underbrace{\frac{\partial \omega_A}{\partial x}}_{\text{species mass fraction gradient}}$$

Mass flux of species A

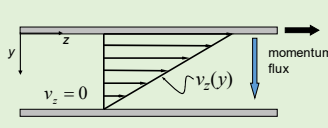
Fick's law of diffusion

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### The Physics of the Transport Laws

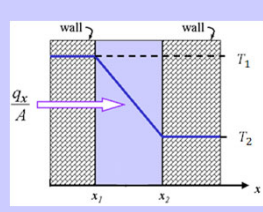
**Part I: Momentum Transfer**  
 Momentum transfer:  

$$\tau_{21} = (-\tilde{\tau}_{21}) = -\mu \left( \frac{dv_1}{dx_2} \right)$$
 momentum flux      velocity gradient      viscosity      **Newton's law of viscosity**



**Part II: Heat Transfer**  
 Heat transfer:  

$$\frac{q_x}{A} = -k \frac{dT}{dx}$$
 heat flux      temperature gradient      thermal conductivity      **Fourier's law of conduction**



**Part III: Mass Transfer**  
 Mass transfer:  

$$\underline{j}_A = -\rho D_{AB} \frac{\partial \omega_A}{\partial x}$$
 Mass flux of species A      species mass fraction gradient      diffusivity      **Fick's law of diffusion**

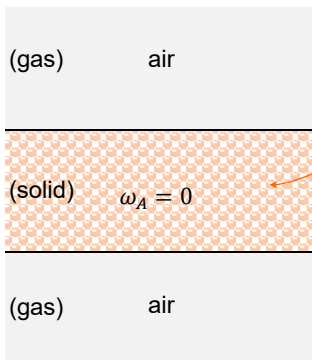
← Where does this equation come from?

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### Simple One-dimensional Species Mass Diffusion

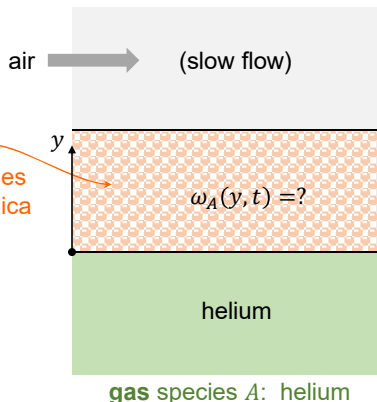
#### What is the diffusion transport law?

Initially:



$\omega_A = 0$

**Suddenly** ( $t = 0$ ):



$\omega_A(y, t) = ?$

**gas species A: helium**

solid species B: fused silica

BSL2, p514

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Simple One-dimensional Species Mass Diffusion

What does  $\omega_A(y, t)$  look like?

( $t \geq 0$ ):

solid species *B*: fused silica

gas species *A*: helium

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Simple One-dimensional Species Mass Diffusion

What does  $\omega_A(y, t)$  look like?

You try.

( $t \geq 0$ ):

solid species *B*: fused silica

Gas species *A*: helium

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Simple One-dimensional Species Mass Diffusion

**What does  $\omega_A(y, t)$  look like?**

**Suddenly ( $t = 0$ ):**

air (slow flow) sink

solid species B: fused silica

helium source

Gas species A: helium

At steady state,  
 $\omega_A(y, t) = -\frac{\omega_{A,0}}{D}y + \omega_{A,0}$

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Simple One-dimensional Species Mass Diffusion

**At steady state,**  
 $\omega_A(y, t) = -\frac{\omega_{A,0}}{D}y + \omega_{A,0}$

flux =  $\rho D_{AB} \left( \frac{0 - \omega_{A,0}}{y_2 - y_1} \right)$

$$\underline{j_{A,y}} = -\rho D_{AB} \frac{d\omega_A}{dy}$$

Fick's law of diffusion

(in terms of mass flux)

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

$\underline{j_{A,y}}$  = mass flux of A through B

**Suddenly ( $t = 0$ ):**

air (slow flow)

helium

Gas species A: helium

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Simple One-dimensional Species Mass Diffusion

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

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

Fick's law of diffusion

(in terms of mass flux)

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

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

**Suddenly (t = 0):**

Gas species A: helium

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**Law of Species Diffusion**

**This is the fundamental version of Fick's Law (3D)**

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

Fick's law

$$\underline{j}_A = \begin{pmatrix} -\rho D_{AB} \frac{\partial \omega_A}{\partial x} \\ -\rho D_{AB} \frac{\partial \omega_A}{\partial y} \\ -\rho D_{AB} \frac{\partial \omega_A}{\partial z} \end{pmatrix}_{xyz}$$

- Mass diffuses flows **down** a concentration gradient
- Flux is proportional to magnitude of concentration gradient

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## Law of Species Diffusion

### QUESTION:

Why so many versions of species A flux?

### Species Fluxes

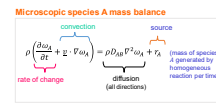
The community has found use for **four** (actually more) different fluxes. The differences in the various fluxes are related to several questions:

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

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 $\dot{M}_A$  – combined mass flux (includes convection and diffusion)  
 $\dot{J}_A$  – mass flux (diffusion only)  
 $\dot{J}_A^*$  – molar flux (diffusion only)

#### Written relative to what velocity?

$N_A$  – relative to stationary coordinates  
 $\dot{M}_A$  – relative to stationary coordinates  
 $\dot{J}_A$  – relative to the mass average velocity  $\underline{v}$   
 $\dot{J}_A^*$  – relative to the molar average velocity  $\underline{v}^*$



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

### Answer:

“Breaking into” the continuum view to analyze the motion of individual species in a mixture complicates the situation. There are several options, and none is perfect.

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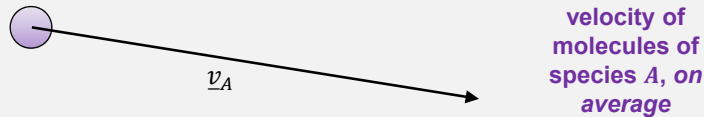
## “Flux” of Species A in a Mixture with Species B

### Describing Binary Diffusion

A mixture of two species: *What goes where and why*

- There are many molecules of species A in some region of interest
- In the region of interest,  $\underline{v}_A$  is the **average velocity** (speed and direction) of the A molecules:

$$\underline{v}_A = \frac{1}{m} \sum_{i=1}^m \underline{v}_{A,i} \quad (\text{a regular average})$$



- The motion of A **molecules** is a combination (potentially) of
  - **bulk motion**—this is the motion caused by driving pressure gradients, by moving boundaries, by all the causes studied for homogeneous materials when we studied momentum conservation
  - **Diffusion**—this motion is caused primarily by concentration gradients.
  - **These two motions need not be collinear**

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"Flux" of Species *A* in a Mixture with Species *B*

- The motion of *A* **molecules** is a combination (potentially) of
  - **bulk motion** of the mixture—this is the motion caused by driving pressure gradients, by moving boundaries, by all the causes studied for **homogeneous** materials when we studied momentum conservation
  - **diffusion**—this motion is caused by **concentration** gradients.
  - **These two motions need not be collinear**

$\underline{v}_A$   
velocity of molecules of species *A*, on average

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"Flux" of Species *A* in a Mixture with Species *B*

- The motion of *A* **molecules** is a combination (potentially) of
  - **bulk motion** of the mixture—this is the motion caused by driving pressure gradients, by moving boundaries, by all the causes studied for **homogeneous** materials when we studied momentum conservation
  - **diffusion**—this motion is caused by **concentration** gradients.
  - **These two motions need not be collinear**

How do we write expressions for these?

$\underline{v}_A$   
velocity of molecules of species *A*, on average

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"Flux" of Species A in a Mixture with Species B

**Is this  $\underline{v}$ ?**

**We've already defined  $\underline{v}$  when we studied transport in homogeneous materials using the continuum model.**

**momentum**

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

**energy**

Microscopic Energy Balance:

**Equation of Thermal Energy**

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

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

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

(incompressible fluid, constant pressure, neglect  $E_v$ , viscous dissipation)

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"Flux" of Species A in a Mixture with Species B

**Is this  $\underline{v}$ ?**

**In transport (of momentum and energy) in homogeneous phases:**

local mass flow

$$\rho d\dot{V} = \rho (\hat{n} \cdot \underline{v}) dS$$

**What does this mean when applied to a mixture of A and B?**

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"Flux" of Species A in a Mixture with Species B

---

When we apply the other transport laws to **mixtures** of A and B, **they work**, if  $\underline{v}$  is the **mass** average velocity of the **molecular** velocities  $\underline{v}_A$  and  $\underline{v}_B$

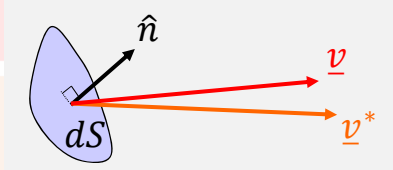
**local mass flow** mass average velocity of individual molecules *(continuum is divided into mass "particles")*

$$\rho d\dot{V} = \rho(\hat{n} \cdot \underline{v}) dS$$

If, however, the **molar** average velocity  $\underline{v}^*$  of the molecules in a mixture is calculated, a local molar flow is readily obtained:

**local molar flow** molar average velocity of individual molecules *(continuum is divided into molar "particles")*

$$c d\dot{V} = c(\hat{n} \cdot \underline{v}^*) dS$$



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"Flux" of Species A in a Mixture with Species B

---

When we apply the other transport laws to **mixtures** of A and B, **they work**, if  $\underline{v}$  is the **mass** average velocity of the **molecular** velocities  $\underline{v}_A$  and  $\underline{v}_B$

**local mass flow** mass average velocity of individual molecules  $\underline{v} = \omega_A \underline{v}_A + \omega_B \underline{v}_B$

$$\rho d\dot{V} = \rho(\hat{n} \cdot \underline{v}) dS$$

If, however, the **molar** average velocity  $\underline{v}^*$  of the molecules in a mixture is calculated, a local molar flow is readily obtained:

**local molar flow** molar average velocity of individual molecules  $\underline{v}^* = x_A \underline{v}_A + x_B \underline{v}_B$

This is what I mean when I say we are "breaking into" the continuum picture.

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**Law of Species Diffusion**

**QUESTION:**  
Why so many versions of species A flux?

**Answer:**  
"Breaking into" the continuum view to analyze the motion of individual species in a mixture complicates the situation. There are several options, and none is perfect.

This is what I mean when I say we are "breaking into" the continuum picture.

We are concerning ourselves with **sub-characteristics** of the continuum.

"Flux" of Species A in a Mixture with Species B

When we apply the other transport laws to mixtures of A and B, they work if  $\bar{v}$  is the mass average velocity of the molecular velocities  $\bar{v}_A$  and  $\bar{v}_B$ .

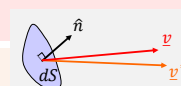
**local mass flow**  $\rho dV = \rho(\hat{n} \cdot \bar{v}) dS$

*mass average velocity of individual molecules*  
 $\bar{v} = \omega_A \bar{v}_A + \omega_B \bar{v}_B$

if, however, the molar average velocity  $\bar{v}^*$  of the molecules in a mixture is calculated, a local molar flow is readily obtained:

**local molar flow**  $c dV = c(\hat{n} \cdot \bar{v}^*) dS$

*molar average velocity of individual molecules*  
 $\bar{v}^* = x_A \bar{v}_A + x_B \bar{v}_B$



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**So, what's the answer?**

**How do we write expressions for the two contributions to the average motion of molecules when diffusion is present?**

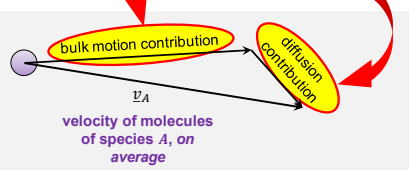
**Two contributions:**

- **Bulk motion**
- **Diffusion**

"Flux" of Species A in a Mixture with Species B

- The motion of A molecules is a combination (potentially) of
  - **bulk motion** of the mixture—this is the motion caused by driving pressure gradients, by moving boundaries, by all the causes studied for homogeneous materials when we studied momentum conservation
  - **diffusion**—this motion is caused by concentration gradients.
- These two motions need not be collinear

**How do we write expressions for these?**



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"Flux" of Species *A* in a Mixture with Species *B* First Approach

**How do we write expressions for the two contributions to the average motion of molecules when diffusion is present?**

**Is this  $\underline{v}$ ?**

**Answer:**  
**It can be.**

If the diffusion contribution is calculated as the mass flux relative to  $(\underline{v}_A - \underline{v})$ , then the model works.

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"Flux" of Species *A* in a Mixture with Species *B* First Approach

**Choose: Bulk contribution expressed as  $\underline{v}$**

**Now, what is this?**

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"Flux" of Species A in a Mixture with Species B

**First Approach**

**Choose: Bulk contribution expressed as  $\underline{v}$**

bulk motion contribution  $\underline{v}$

diffusion contribution  $(\underline{v}_A - \underline{v})$

$\underline{v}_A$

**Start with mass flux:**

**Mass flux of A**  $\equiv \frac{\text{mass A diffusing}}{\text{area} \cdot \text{time}}$

$$= (\underline{v}_A - \underline{v}) \rho \omega_A \quad \equiv \underline{j}_A = -\rho D_{AB} \nabla \omega_A$$

**Fick's law**

volumetric flow rate per area in the direction of diffusion

$$= \left( \frac{\cancel{\text{volume}}}{\text{area} \cdot \text{time}} \right) \left( \frac{\text{mass A}}{\cancel{\text{volume}}} \right)$$

Recall in a pipe:  $\frac{\dot{V}}{\text{area}} = \langle v \rangle$

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"Flux" of Species A in a Mixture with Species B

**Second Approach**

**How do we write expressions for the two contributions to the average motion of molecules when diffusion is present?**

bulk motion contribution

diffusion contribution

$\underline{v}_A$

**What if I want to use a molar flux?**

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Second Approach

**“Flux” of Species A in a Mixture with Species B**

**How do we write expressions for the two contributions to the average motion of molecules when diffusion is present?**

**Answer:**  
**This is possible too.**

**What if I want to use a molar flux?**

To express diffusion in moles the bulk motion contribution, however, cannot be given by the mass average velocity; instead we must use the **molar average velocity  $\underline{v}^*$** .

**bulk molar contribution  $\neq \underline{v}$**

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Second Approach

**“Flux” of Species A in a Mixture with Species B**

**Choose: Bulk contribution expressed as  $\underline{v}^*$**

**Start with molar flux:**

**Molar flux of A**  $\equiv \frac{\text{moles A diffusing}}{\text{area} \cdot \text{time}}$

$= \underbrace{(\underline{v}_A - \underline{v}^*)}_{\text{volumetric flow rate per area in the direction of diffusion}} c x_A \equiv J_A^* = ?$

Recall in a pipe:  $\frac{\dot{V}}{\text{area}} = \langle v \rangle$

$= \left( \frac{\cancel{\text{volume}}}{\text{area} \cdot \text{time}} \right) \left( \frac{\text{moles A}}{\cancel{\text{volume}}} \right)$

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"Flux" of Species A in a Mixture with Species B Second Approach

Choose: Bulk contribution expressed as  $\underline{v}^*$

A vector diagram starting from a purple circle. One arrow points right and slightly up, labeled "bulk motion contribution" and  $\underline{v}^*$ . A second arrow points right and slightly down, labeled "diffusion contribution" and  $(\underline{v}_A - \underline{v}^*)$ . A third arrow, the sum of the first two, points right and slightly down, labeled  $\underline{v}_A$ .

Start with molar flux:

**Molar** flux of A  $\equiv \frac{\text{moles A diffusing}}{\text{area} \cdot \text{time}}$

$= (\underline{v}_A - \underline{v}^*) c x_A \equiv J_A^* = ?$

volumetric flow rate per area  
in the direction of diffusion

$= \left( \frac{\cancel{\text{volume}}}{\text{area} \cdot \text{time}} \right) \left( \frac{\text{moles A}}{\cancel{\text{volume}}} \right)$

**What is Fick's law in terms of this molar flux?**

Recall in a pipe:  $\frac{\dot{V}}{\text{area}} = \langle v \rangle$

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"Flux" of Species A in a Mixture with Species B Second Approach

Choose: Bulk contribution expressed as  $\underline{v}^*$

A vector diagram starting from a purple circle. One arrow points right and slightly up, labeled "bulk motion contribution" and  $\underline{v}^*$ . A second arrow points right and slightly down, labeled "diffusion contribution" and  $(\underline{v}_A - \underline{v}^*)$ . A third arrow, the sum of the first two, points right and slightly down, labeled  $\underline{v}_A$ .

Start with molar flux:

**Molar** flux of A  $\equiv \frac{\text{moles A diffusing}}{\text{area} \cdot \text{time}}$

$= (\underline{v}_A - \underline{v}^*) c x_A \equiv J_A^* = ?$

**What is Fick's law in terms of this molar flux?**

**To answer, we start with the other version of Fick's law and do the math...**

(change units, change reference velocity)

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"Flux" of Species A in a Mixture with Species B Second Approach

Choose: Bulk contribution expressed as  $\underline{v}^*$

A vector diagram starting from a purple circle. One vector points right and is labeled  $\underline{v}^*$  (bulk motion contribution). Another vector points down and right from the tip of the first vector, labeled "diffusion contribution ( $\underline{v}_A - \underline{v}^*$ )". A third vector points down and right from the start, labeled  $\underline{v}_A$ .

Start with molar flux:

**Molar** flux of A  $\equiv \frac{\text{moles A diffusing}}{\text{area} \cdot \text{time}}$

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

volumetric flow rate per area  
in the direction of diffusion

$$= \left( \frac{\cancel{\text{volume}}}{\text{area} \cdot \text{time}} \right) \left( \frac{\text{moles A}}{\cancel{\text{volume}}} \right)$$

Result:

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

Fick's law

Recall:  $\frac{\dot{V}}{\text{area}} = \langle v \rangle$

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Various forms of Fick's Law

**Summary:**

Possible fluxes so far:

$$\underline{J}_A^* = (\underline{v}_A - \underline{v}^*) c x_A = \text{molar flux relative to molar average velocity } \underline{v}^*$$

$$\underline{j}_A = (\underline{v}_A - \underline{v}) \rho \omega_A = \text{mass flux relative to mass average velocity } \underline{v}$$

Combined fluxes are also in use:

$\underline{N}_A$  = combined molar flux relative to **stationary coordinates**

$\underline{n}_A$  = combined mass flux relative to **stationary coordinates**

Mass

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

$$= \rho \omega_A \underline{v}_A - \rho \omega_A \underline{v}$$

$$\underline{n}_A \equiv \underline{j}_A + \rho \omega_A \underline{v} = \rho \omega_A \underline{v}_A$$

Moles

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

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

$$\underline{N}_A \equiv \underline{J}_A^* + c x_A \underline{v}^* = c x_A \underline{v}_A$$

All our previous flux expressions (momentum and energy) have been with respect to stationary coordinates. In diffusion, this points to the combined fluxes.

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Various forms of Fick's Law

### When do we use what?

**Four possible fluxes:**

- $J_A^*$  = molar flux relative to molar average velocity  $v^*$
- $j_A$  = mass flux relative to mass average velocity  $v$
- $N_A$  = combined molar flux relative to stationary coordinates
- $n_A$  = combined mass flux relative to stationary coordinates

The fluxes  $J_A^*$  and  $j_A$  are used to describe the mass transfer in diffusion cells used for measuring the diffusion coefficient.

The fluxes relative to coordinates fixed in space  $n_A$  and  $N_A$  are often used to describe engineering operations within process equipment.

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Various forms of Fick's Law

### When do we use what?

**Four possible fluxes:**

- $J_A^*$  = molar flux relative to molar average velocity  $v^*$
- $j_A$  = mass flux relative to mass average velocity  $v$
- $N_A$  = combined molar flux relative to stationary coordinates
- $n_A$  = combined mass flux relative to stationary coordinates

The mass fluxes  $n_A$  and  $j_A$  are used when the Navier-Stokes equations are also required to describe the process.

Since chemical reactions are described in terms of moles of the participating reactants, the molar fluxes  $J_A^*$  and  $N_A$  are used to describe mass-transfer operations in which homogeneous chemical reactions are involved

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## Various forms of Fick's Law

**When do we use what?****Four possible fluxes:**

$\underline{J}_A^*$  = molar flux relative to molar average velocity  $\underline{v}^*$

$\underline{j}_A$  = mass flux relative to mass average velocity  $\underline{v}$

$\underline{N}_A$  = combined molar flux relative to stationary coordinates

$\underline{n}_A$  = combined mass flux relative to stationary coordinates

1. The mass fluxes  $\underline{n}_A$  and  $\underline{j}_A$  are used when the Navier-Stokes equations are also required to describe the process since they use  $\underline{v}$ .
2. Since chemical reactions are described in terms of moles of the participating reactants, the molar fluxes  $\underline{J}_A^*$  and  $\underline{N}_A$  are used to describe mass-transfer operations in which homogeneous chemical reactions are involved.
3. The fluxes relative to coordinates fixed in space  $\underline{n}_A$  and  $\underline{N}_A$  are often used to describe **engineering operations within process equipment**
4. The fluxes  $\underline{J}_A^*$  and  $\underline{j}_A$  are used to describe the mass transfer in diffusion cells used for measuring the diffusion coefficient

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## Various forms of Fick's Law

**What now?****Four Fluxes.****Four Microscopic Species A Balances.**

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Various forms of Fick's Law

**What now?**

**Four Fluxes.**  
~~Four~~ **Microscopic Species A Balances.**  
**Three**

*(We do not often use the combined mass flux version,  $\underline{n}_A$ ).*

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Various forms of the Microscopic Species A Mass Balance

**Quick tour**

**Mass Balance: Body versus Control Volume**

Law Mass Conservation: (on a **body**)  $\frac{dM_B}{dt} = 0$

Law of Mass Conservation: (on a **control volume**)  $\frac{dM_{CV}}{dt} = \iint_{CS} -(\hat{n} \cdot \underline{v})\rho dS$

} the usual convective term:  
net mass convected in

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Various forms of the Microscopic Species A Mass Balance

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### Species A Mass Balance:

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Law of Species Mass Conservation:  
(on a **body**, with homogeneous reaction)

$$\frac{dM_{A,B}}{dt} = r_A$$

Law of Species Mass Conservation:  
(on a **control volume**, with homogeneous reaction)

$$\frac{dM_{A,CV}}{dt} = \underbrace{\iint_{CS} -(\hat{n} \cdot \underline{v})\rho dS}_{\text{the usual convective term: net mass convected in}} + r_A$$

PLUS mass of species A that **diffuses** into control volume

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Various forms of the Microscopic Species A Mass Balance

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### Species A Mass Balance:

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Law of Species Mass Conservation:  
(on a **body**, with homogeneous reaction)

$$\frac{dM_{A,B}}{dt} = r_A$$

Law of Species Mass Conservation:  
(on a **control volume**, with homogeneous reaction)

$$\frac{dM_{A,CV}}{dt} = \underbrace{\iint_{CS} -(\hat{n} \cdot \underline{v})\rho dS}_{\text{the usual convective term: net mass convected in}} + r_A$$

**Diffusion is the study of *species motion in mixtures*.**

PLUS mass of species A that **diffuses** into control volume

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Various forms of the Microscopic Species A Mass Balance

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**Species A Mass Balance, on a CV:**

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Law of Species Mass Conservation: (on a control volume, with homogeneous reaction)

$$\frac{dM_{A,CV}}{dt} = \iint_{CS} -(\hat{n} \cdot \underline{v}) dS + r_A$$

...

Law of Species Mass Conservation: (microscopic control volume, with homogeneous reaction)

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

convection
diffusion

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Various forms of the Microscopic Species A Mass Balance

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**Microscopic Species A Mass Balance, on a CV:**

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Law of Species Mass Conservation: (microscopic control volume, with homogeneous reaction)

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

convection
diffusion

**Diffusion:**  $\underline{j}_A [=] \frac{\text{mass}}{\text{area} \cdot \text{time}}$

$\underline{j}_A \equiv$  mass flux of species A relative to a mixture's mass average velocity  $\underline{v}$

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Various forms of the Microscopic Species A Mass Balance

## Microscopic Species A Mass Balance, on a CV:

Law of Species Mass Conservation: (microscopic control volume, with homogeneous reaction)

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

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**

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

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

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

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

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

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Various forms of the Microscopic Species A Mass Balance

## Microscopic species A mass balance—Six 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

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

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Various forms of the Microscopic Species A Mass Balance

**Microscopic species A mass balance** — ~~Six~~ <sup>Five</sup> 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	$\frac{\partial c_A}{\partial t} = -\nabla \cdot \underline{N}_A + R_A$

(The  $\underline{N}_A$  version, with Fick's law substituted in, provides little advantage.)

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

Mass flux

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

Molar flux

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

Combined molar flux

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

**FRONT**

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

**Mass flux**

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

**Molar flux**

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

**Combined molar flux**

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

BACK

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### Various quantities in diffusion and mass transfer

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

$\underline{j}_A \equiv$  **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**  
 $\underline{n}_A + \underline{n}_B = \rho \underline{v}$

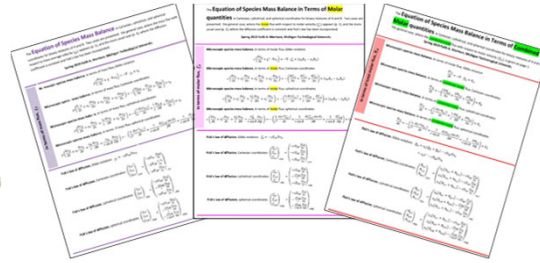
$\underline{J}_A^* \equiv$  **molar flux** relative to a mixture's **molar average velocity**,  $\underline{v}^*$   
 $= c_A(\underline{v}_A - \underline{v}^*)$   
 $\underline{J}_A^* + \underline{J}_B^* = 0$

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

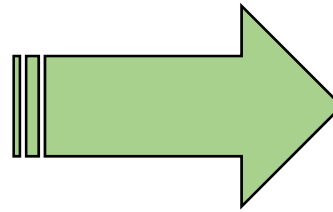
$\underline{v}_A \equiv$  velocity of species  $A$  in a mixture, i.e. average velocity of all molecules of species  $A$  within a small volume  
 $\underline{v} \equiv \omega_A \underline{v}_A + \omega_B \underline{v}_B \equiv$  mass average velocity; same velocity as in the microscopic momentum and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

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Let's put  
this to use



Various forms of the Microscopic Species A Mass Balance	
	<b>Five</b> <del>Six</del> forms
In terms of mass flux and mass concentrations	$\rho \left( \frac{\partial \omega_A}{\partial t} + \mathbf{v} \cdot \nabla \omega_A \right) = -\nabla \cdot \mathbf{j}_A + r_A$ $= \rho D_{AB} \nabla^2 \omega_A + r_A$
In terms of molar flux and molar concentrations	$c \left( \frac{\partial x_A}{\partial t} + \mathbf{v}^* \cdot \nabla x_A \right) = -\nabla \cdot \mathbf{J}_A + (x_B R_A - x_A R_B)$ $= c D_{AB} \nabla^2 x_A + (x_B R_A - x_A R_B)$
In terms of combined molar flux and molar concentrations	$\frac{\partial c_A}{\partial t} = -\nabla \cdot \mathbf{N}_A + R_A$



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