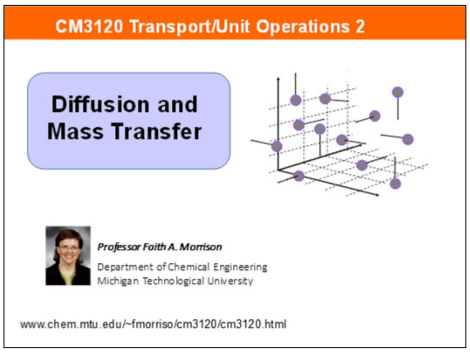
Now, Cycling Back:

Diffusion and Mass Transfer



Introduction to Diffusion and Mass Transfer in Mixtures

Our first introduction to Diffusion:

- Brownian motion
- Slow

Introduction to Diffusion and Mass Transfer in Mixtures

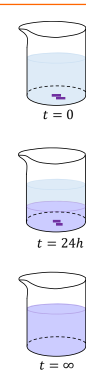
Diffusion

- 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

Diffusion progresses at a rate of
- $\sim 5 cm/min$ (gases)
- $\sim 0.05 cm/min$ (liquids)
- $\sim 10^{-5} cm/min$ (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



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

$$\underbrace{\rho\left(\frac{\partial \omega_A}{\partial t}\right.}_{\text{rate of change}} + \overbrace{\underline{v}\cdot\nabla\omega_A}^{\text{convection}}\left.\vphantom{\frac{\partial \omega_A}{\partial t}}\right) = \underbrace{\rho D_{AB}\nabla^2\omega_A}_{\substack{\text{diffusion}\\ \text{(all directions)}}} + \overbrace{r_A}^{\text{source}}$$

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

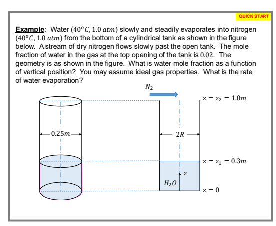
In terms of molar flux and molar concentrations $c\left(\frac{\partial x_A}{\partial t} + \underline{v}^*\cdot\nabla x_A\right) = -\nabla\cdot\underline{J}_A^* + (\ldots = cD_{AB}\nabla^2 x_A \ldots$

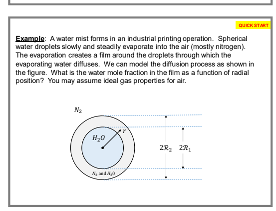
In terms of combined molar flux and molar concentrations $\frac{\partial c_A}{\partial t} = -\nabla\cdot\underline{N}_A + R_A$

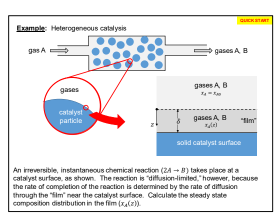
Microscopic species mass balance in terms of combined molar flux $\underline{N}_A$

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.







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 coverts 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

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Flux of what? And due to what mechanism?

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

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

6

Transport Laws, up to now:

Part I: Momentum Transfer

Momentum transfer:

viscosity

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

Newton's law of viscosity

Part II: Heat Transfer

Heat transfer:

thermal conductivity

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

Fourier's law of conduction

Part I: Momentum Transfer

Momentum transfer:

viscosity

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Newton's law of viscosity

Part II: Heat Transfer

Heat transfer:

thermal conductivity

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

Fourier's law of conduction

Now:

Part III: Mass Transfer

Mass transfer:

diffusivity

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

Fick's law of diffusion

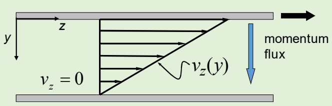
The Physics of the Transport Laws

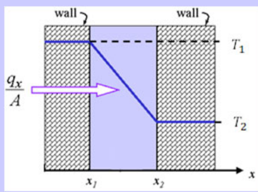
Part I: Momentum Transfer

Momentum transfer:

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

Newton's law of viscosity





Part II: Heat Transfer

Heat transfer:

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

Fourier's law of conduction

Part III: Mass Transfer

Mass transfer:

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

Fick's law of diffusion

Where does this equation come from?

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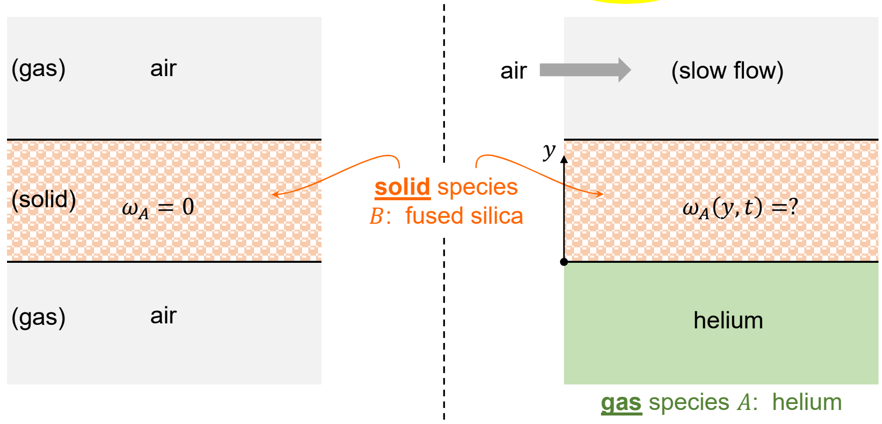
Simple One-dimensional Species Mass Diffusion

What is the diffusion transport law?

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



BSL2, p514

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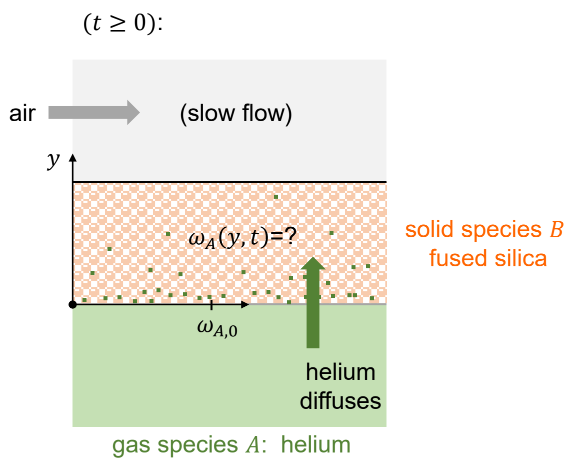
Simple One-dimensional Species Mass Diffusion

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



BSL2, p514

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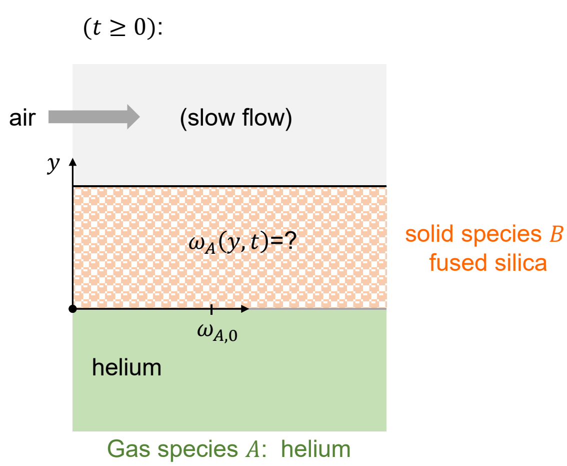
Simple One-dimensional Species Mass Diffusion

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

You try.



BSL2, p514

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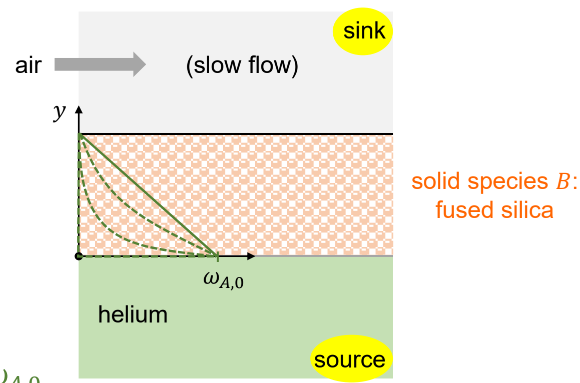
Simple One-dimensional Species Mass Diffusion

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

Suddenly $(t=0)$:



Gas species A: helium

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

BSL2, p514

Simple One-dimensional Species Mass Diffusion

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

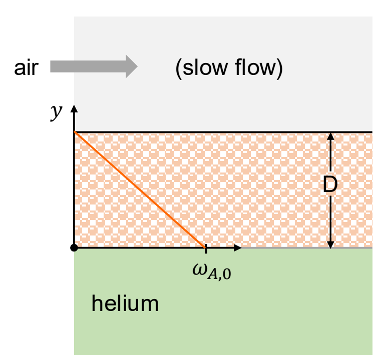
$$\text{flux} = \rho D_{AB}\left(\frac{0-\omega_{A,0}}{y_2 - y_1}\right)$$

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

Fick's law of diffusion

(in terms of mass flux)

Suddenly $(t=0)$:



Gas species A: helium

D_{AB} = Diffusion coefficient of A through B

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

BSL2, p514

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

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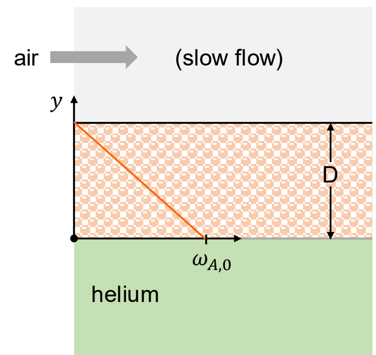

Gas species A: helium

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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

Law of Species Diffusion

QUESTION:

Why so many versions of species A flux?

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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.

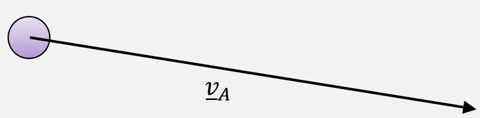
"Flux" of Species A in a Mixture with Species B

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:

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



velocity of molecules of species A, *on 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**

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

- The motion of A **molecules** is a combination (potentially) of
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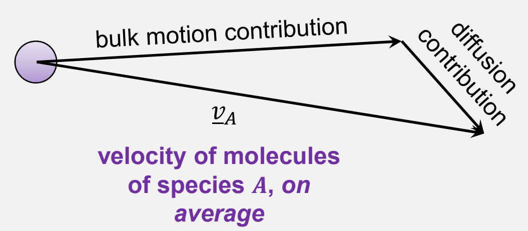

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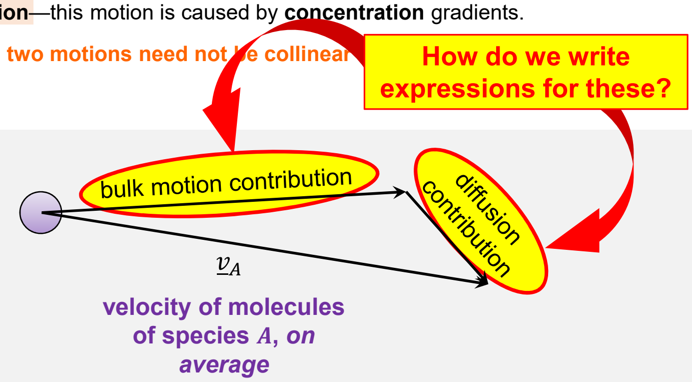

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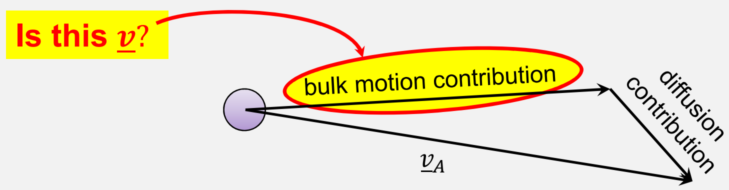
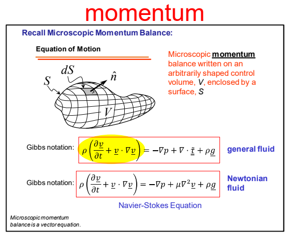
"Flux" of Species A in a Mixture with Species B

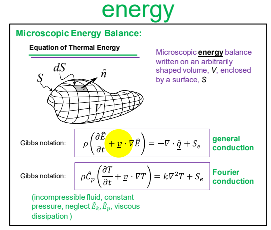


We've already defined $\underline{v}$ when we studied transport in homogeneous materials using the continuum model.

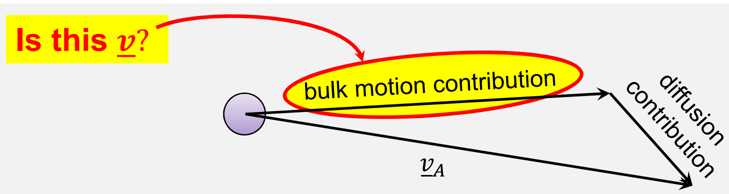
momentum



energy

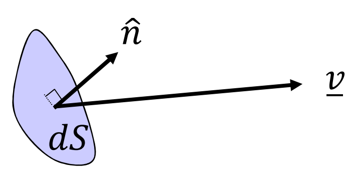


"Flux" of Species A in a Mixture with Species B



In transport (*of momentum and energy*) in <u>homogeneous</u> phases:

$$\underbrace{\rho\, d\dot{V}}_{\text{local mass flow}} = \rho(\,\hat{n}\cdot\underline{v})\,dS$$



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

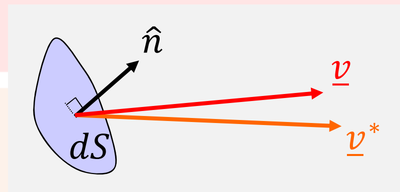
“Flux” of Species A in a Mixture with Species B

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 $\underline{v}_B$

$$\underbrace{\rho\, d\dot{V}}_{\text{local mass flow}} = \rho(\hat{n}\cdot\underline{v})\, dS$$

mass average velocity of individual molecules

(continuum is divided into mass “particles”)



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

$$\underbrace{c\, d\dot{V}}_{\text{local molar flow}} = c(\hat{n}\cdot\underline{v}^*)\, dS$$

molar average velocity of individual molecules

(continuum is divided into molar “particles”)

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

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mass average velocity of individual molecules

$$\underline{v} = \omega_A \underline{v}_A + \omega_B \underline{v}_B$$

This is what I mean when I say we are **“breaking into”** the continuum picture.

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molar average velocity of individual molecules

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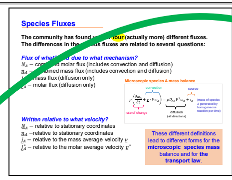
Law of Species Diffusion



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.

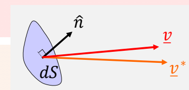
"Flux" of Species A in a Mixture with Species B

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

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

$$\underline{v} = \omega_A \underline{v}_A + \omega_B \underline{v}_B$$



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

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

molar average velocity of individual molecules

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

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

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
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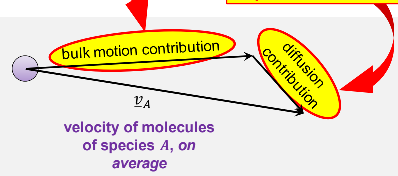
  - These two motions need not be collinear

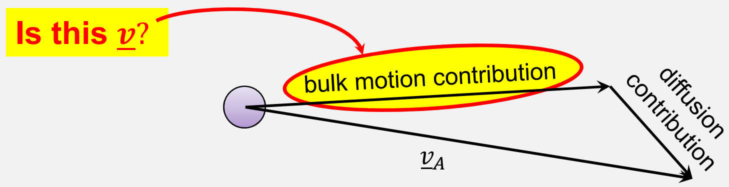
How do we write expressions for these?



“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?



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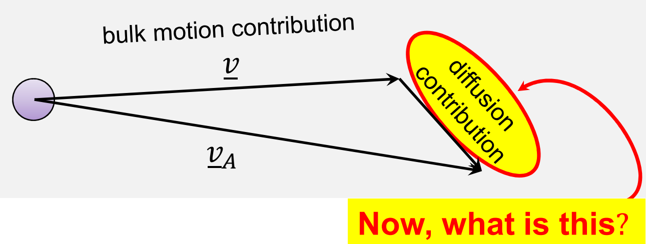
“Flux” of Species A in a Mixture with Species B

First Approach

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



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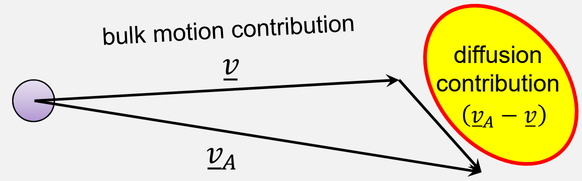
"Flux" of Species A in a Mixture with Species B

First Approach

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



Start with mass flux:

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

$$= \underbrace{(\underline{v}_A - \underline{v})}_{\substack{\text{volumetric flow rate per area}\\ \text{in the direction of diffusion}}} \rho\, \omega_A \quad \boxed{\equiv \underline{j}_A = -\rho D_{AB} \nabla \omega_A}$$

Fick's law

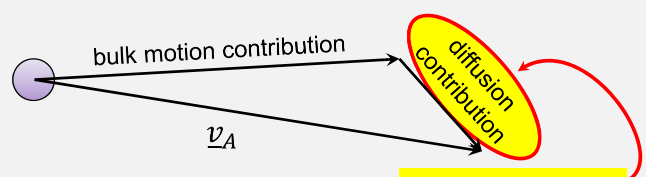
$$= \left(\frac{\cancel{volume}}{area \cdot time}\right)\left(\frac{mass\ A}{\cancel{volume}}\right)$$

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

"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?

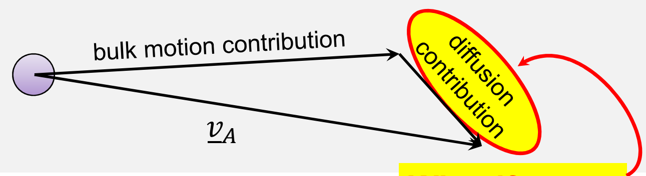


What if I want to use a molar flux?

“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?



What if I want to use a molar flux?

Answer:

This is possible too.

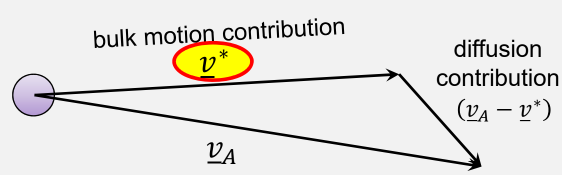
To express diffusion in moles the bulk motion contribution, however, cannot be given by the mass average velocity; instead we must use the **molar average velocity** $\underline{v}^*$.

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

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

Second Approach

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



Start with molar flux:

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

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

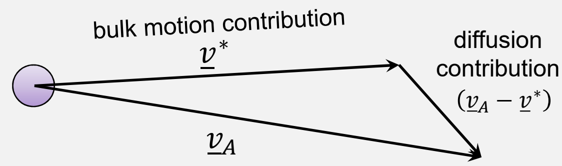
Recall in a pipe: $\frac{\dot{V}}{area} = \langle v \rangle$

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

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

Second Approach

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



Start with molar flux:

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

$= \underbrace{(\underline{v}_A - \underline{v}^*)}_{}\ c\ x_A \quad \equiv \underline{J}_A^* = ?$

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

volumetric flow rate per area
in the direction of diffusion

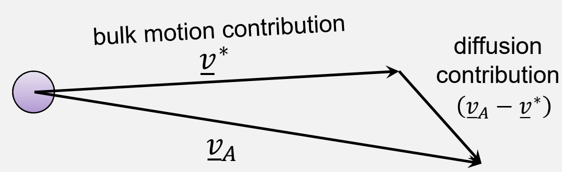
Recall in a pipe: $\frac{\dot{V}}{area} = \langle v \rangle$

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

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

Second Approach

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



Start with molar flux:

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

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

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

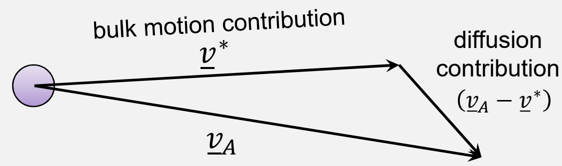
To answer, we start with the other version of Fick's law and do the math…

(change units, change reference velocity)

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

Second Approach

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



Start with molar flux:

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

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

Result:

$$\boxed{\equiv \underline{J}_A^* = cD_{AB}\nabla x_A}$$

Fick's law

volumetric flow rate per area
in the direction of diffusion

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

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

Various forms of Fick's Law

Summary:

Possible fluxes so far:

$\underline{J}_A^* = (\underline{v}_A - \underline{v}^*)\, cx_A$ = **molar** flux relative to molar average velocity $\underline{v}^*$
$\underline{j}_A = (\underline{v}_A - \underline{v})\, \rho\omega_A$ = **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

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

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

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

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

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.

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.

WRF p440

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

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 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

WRF p440

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

WRF p440

What now?

Four Fluxes.
Four Microscopic Species A Balances.

Various forms of Fick's Law

What now?

Four Fluxes.

~~Four~~ Three Microscopic Species A Balances.

(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**)

$$\boxed{\frac{dM_B}{dt} = 0}$$

Law of Mass Conservation:
(on a **control volume**)

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

WRF, p467

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Various forms of the Microscopic Species A Mass Balance

Species A Mass Balance:

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

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

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

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

the *usual* convective term: net mass convected in

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

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Various forms of the Microscopic Species A Mass Balance

Species A Mass Balance:

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

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

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

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

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

the *usual* convective term: net mass convected in

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

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Various forms of the Microscopic Species A Mass Balance

Species A Mass Balance, on a CV:

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

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

...

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

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

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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)

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

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

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

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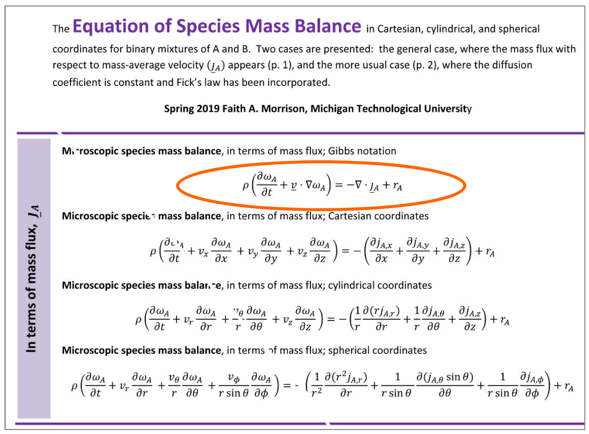
Various forms of the Microscopic Species A Mass Balance

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.

Spring 2019 Faith A. Morrison, Michigan Technological University

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

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

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

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

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

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

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

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

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

FRONT

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

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Various forms of the Microscopic Species A Mass Balance

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

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

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

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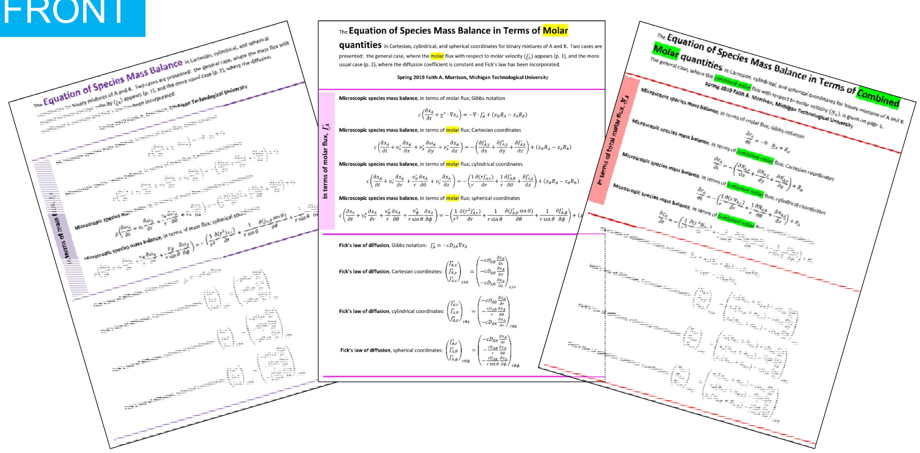
Various forms of Fick's Law (and the species mass balances that employ them)

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

FRONT



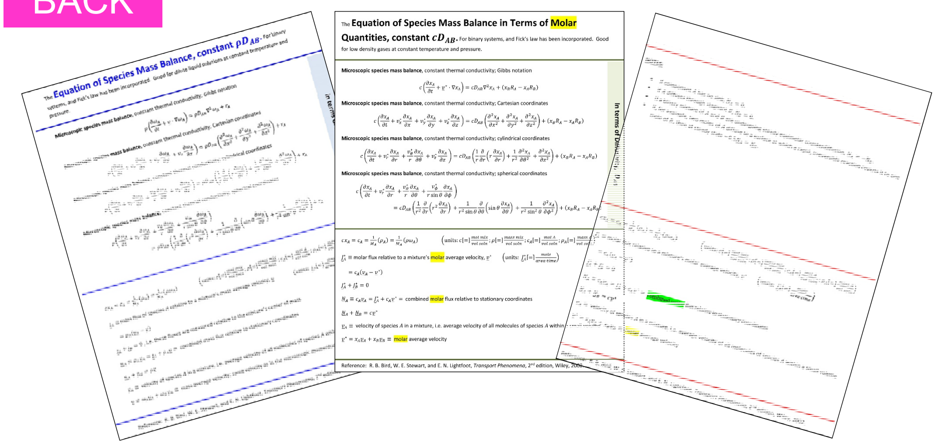
pages.mtu.edu/~fmorriso/cm3120/Homeworks_Readings.html

50

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

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

BACK



pages.mtu.edu/~fmorriso/cm3120/Homeworks_Readings.html

Various quantities in diffusion and mass transfer

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

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

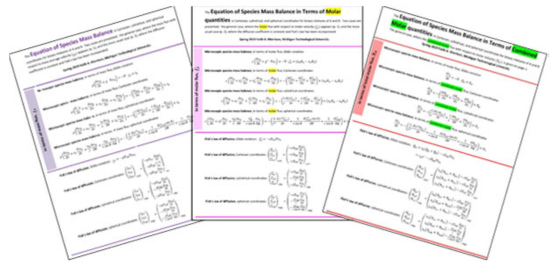
$\underline{n}_A \equiv \rho_A \underline{v}_A = \underline{j}_A + \rho_A \underline{v} =$ **combined mass** flux relative to **stationary coordinates**
$\underline{n}_A + \underline{n}_B = \rho \underline{v}$

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

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

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

Let's put this to use



Various forms of the Microscopic Species A Mass Balance

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

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