GMS Equations From Irreversible Thermodynamics

ChEn 6603

References

- E. N. Lightfoot, Transport Phenomena and Living Systems, McGraw-Hill, New York 1978.
- R. B. Bird, W. E. Stewart and E. N. Lightfoot, *Transport Phenomena* 2nd ed., Chapter 24 McGraw-Hill, New York 2007.
- D. Jou, J. Casas-Vazquez, Extended Irreversible Thermodynamics, Springer-Verlag, Berlin 1996.
- R. Taylor, R. Krishna Multicomponent Mass Transfer, John Wiley & Sons, 1993.
- R. Haase, Thermodynamics of Irreversible Processes, Addison-Wesley, London, 1969.

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Outline

- Entropy, Entropy transport
- Entropy production: "forces" & "fluxes"
  - Species diffusive fluxes & the Generalized Maxwell-Stefan Equations
  - Heat flux
  - Thermodynamic nonidealities & the "Thermodynamic Factor"
- Example: the ultracentrifuge
- Fick's law (the full version)
- Review

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A Perspective

- Reference velocities
  - Allows us to separate a species flux into convective and diffusive components.
- Governing equations
  - Describe conservation of mass, momentum, energy at the continuum scale.
- GMS equations
  - Provide a general relationship between species diffusion fluxes and diffusion driving force(s).
  - So far, we've assumed:
    - Ideal mixtures (inelastic collisions)
    - "small" pressure gradients
- Goal: obtain a more general form of the GMS equations that represents more physics
  - Body forces acting differently on different species (e.g. electromagnetic fields)
  - Nonideal mixtures
  - Large pressure gradients (centrifugal separations)

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Entropy

Entropy differential: $$T\mathrm{d}s = \mathrm{d}e + p\mathrm{d}v - \sum_{i=1}^{n} \tilde{\mu}_i \mathrm{d}\omega_i$$

$\tilde{\mu}_i = \mu_i / M_i$ Chemical potential per unit mass

e Internal energy

v Specific volume

Total (substantial/material) derivative: $$\frac{\mathrm{D}}{\mathrm{D}t} \equiv \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla$$

$$T\rho \frac{\mathrm{D}s}{\mathrm{D}t} = \rho \frac{\mathrm{D}e}{\mathrm{D}t} + p\rho \frac{\mathrm{D}v}{\mathrm{D}t} - \sum_{i=1}^{n} \tilde{\mu}_i \rho \frac{\mathrm{D}\omega_i}{\mathrm{D}t}$$

$$\rho = 1/v$$

$$T\rho \frac{\mathrm{D}s}{\mathrm{D}t} = \rho \frac{\mathrm{D}e}{\mathrm{D}t} - \frac{p}{\rho}\frac{\mathrm{D}\rho}{\mathrm{D}t} - \sum_{i=1}^{n} \tilde{\mu}_i \rho \frac{\mathrm{D}\omega_i}{\mathrm{D}t}$$

$$\rho \frac{\mathrm{D}e}{\mathrm{D}t} = -\nabla \cdot \mathbf{q} - \tau : \nabla \mathbf{v} - p \nabla \cdot \mathbf{v} + \sum_{i=1}^{n} \mathbf{f}_i \cdot \mathbf{j}_i$$

$$\frac{\mathrm{D}\rho}{\mathrm{D}t} = -\rho \nabla \cdot \mathbf{v}$$

$$\rho \frac{\mathrm{D}\omega_i}{\mathrm{D}t} = -\nabla \cdot \mathbf{j}_i + \sigma_i$$

Entropy Transport

$$
\begin{aligned}
T\rho\frac{\mathrm{D}s}{\mathrm{D}t} &= -\nabla\cdot\mathbf{q} - \tau : \nabla\mathbf{v} - p\nabla\cdot\mathbf{v} + \sum_{i=1}^{n}\mathbf{f}_i\cdot\mathbf{j}_i + \frac{p}{\rho}\rho\nabla\cdot\mathbf{v} - \sum_{i=1}^{n}\tilde{\mu}_i\left(-\nabla\cdot\mathbf{j}_i + \sigma_i\right), \\
&= -\underline{\nabla\cdot\mathbf{q}} - \tau : \nabla\mathbf{v} + \sum_{i=1}^{n}\mathbf{f}_i\cdot\mathbf{j}_i + \underline{\sum_{i=1}^{n}\tilde{\mu}_i\nabla\cdot\mathbf{j}_i} - \sum_{i=1}^{n}\tilde{\mu}_i\sigma_i,
\end{aligned}
$$

chain rule...

$$\nabla(\alpha\beta) = \alpha\nabla\beta + \beta\nabla\alpha$$

$$
\rho\frac{\mathrm{D}s}{\mathrm{D}t} = \underbrace{-\nabla\cdot\left[\frac{1}{T}\left(\mathbf{q} - \sum_{i=1}^{n}\tilde{\mu}_i\mathbf{j}_i\right)\right]}_{\text{Transport of } s} + \underbrace{\mathbf{q}\cdot\nabla\left(\frac{1}{T}\right) - \sum_{i=1}^{n}\mathbf{j}_i\cdot\nabla\left(\frac{\tilde{\mu}_i}{T}\right) - \frac{1}{T}\tau : \nabla\mathbf{v} + \frac{1}{T}\sum_{i=1}^{n}\mathbf{f}_i\cdot\mathbf{j}_i - \frac{1}{T}\sum_{i=1}^{n}\tilde{\mu}_i\sigma_i}_{\text{Production of } s}
$$

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$$\rho\frac{\mathrm{D}s}{\mathrm{D}t} = \underbrace{-\nabla\cdot\left[\frac{1}{T}\left(\mathbf{q}-\sum_{i=1}^{n}\tilde{\mu}_i\mathbf{j}_i\right)\right]}_{\text{Transport of } s} + \underbrace{\mathbf{q}\cdot\nabla\left(\frac{1}{T}\right)-\sum_{i=1}^{n}\mathbf{j}_i\cdot\nabla\left(\frac{\tilde{\mu}_i}{T}\right)-\frac{1}{T}\tau:\nabla\mathbf{v}+\frac{1}{T}\sum_{i=1}^{n}\mathbf{f}_i\cdot\mathbf{j}_i-\frac{1}{T}\sum_{i=1}^{n}\tilde{\mu}_i\sigma_i}_{\text{Production of } s}$$

Now let's write this in the form: $\rho\frac{\mathrm{D}s}{\mathrm{D}t} = -\nabla\cdot\mathbf{j}_s + \sigma_s$

$$\mathbf{j}_s = \frac{1}{T}\left(\mathbf{q}-\sum_{i=1}^{n}\tilde{\mu}_i\mathbf{j}_i\right)$$ diffusive transport of entropy

$$\begin{aligned}\sigma_s &= \mathbf{q}\cdot\nabla\left(\frac{1}{T}\right)-\sum_{i=1}^{n}\mathbf{j}_i\cdot\nabla\left(\frac{\tilde{\mu}_i}{T}\right)-\frac{1}{T}\boldsymbol{\tau}:\nabla\mathbf{v}+\frac{1}{T}\sum_{i=1}^{n}\mathbf{f}_i\cdot\mathbf{j}_i-\frac{1}{T}\sum_{i=1}^{n}\tilde{\mu}_i\sigma_i,\\ &= -\frac{\mathbf{q}}{T}\cdot\nabla\ln T-\sum_{i=1}^{n}\mathbf{j}_i\cdot\left[\nabla\left(\frac{\tilde{\mu}_i}{T}\right)-\frac{1}{T}\mathbf{f}_i\right]-\frac{1}{T}\boldsymbol{\tau}:\nabla\mathbf{v}-\frac{1}{T}\sum_{i=1}^{n}\tilde{\mu}_i\sigma_i\end{aligned}$$

production of entropy

$$\begin{aligned}\nabla\left(\frac{\tilde{\mu}_i}{T}\right) &= \frac{\partial\tilde{\mu}_i}{\partial T}\nabla\left(\frac{T}{T}\right)+\frac{1}{T}\frac{\partial\tilde{\mu}_i}{\partial p}\nabla p+\frac{1}{T}\nabla_{T,p}\tilde{\mu}_i,\\ &= \frac{1}{T}\left(\frac{1}{M_i}\frac{\partial\mu_i}{\partial p}\nabla p+\nabla_{T,p}\tilde{\mu}_i\right),\\ &= \frac{1}{T}\left(\frac{\bar{V}_i}{M_i}\nabla p+\nabla_{T,p}\tilde{\mu}_i\right)\end{aligned}$$

Note that we haven't "completed" the chain rule here. We will apply it to species later...

$$T\sigma_s = -\mathbf{q}\cdot\nabla\ln T-\boxed{\sum_{i=1}^{n}\mathbf{j}_i\cdot\underbrace{\left[\nabla_{T,p}\tilde{\mu}_i+\frac{\bar{V}_i}{M_i}\nabla p-\mathbf{f}_i\right]}_{\boldsymbol{\Lambda}_i}}-\boldsymbol{\tau}:\nabla\mathbf{v}-\sum_{i=1}^{n}\tilde{\mu}_i\sigma_i$$

Look at this term
(entropy production due to species diffusion)

Part of the Entropy Source Term…

$$\sum_{i=1}^{n} \mathbf{j}_i \cdot \underbrace{\left[\nabla_{T,p}\tilde{\mu}_i + \frac{\bar{V}_i}{M_i}\nabla p - \mathbf{f}_i\right]}_{\mathbf{\Lambda}_i} = \sum_{i=1}^{n} \mathbf{j}_i \cdot \left(\mathbf{\Lambda}_i - \boxed{\frac{1}{\rho}\nabla p + \sum_{k=1}^{n}\omega_k \mathbf{f}_k}\right)$$

Why can we add this "arbitrary" term?
What does this term represent?

$$\begin{aligned}
\sum_{i=1}^{n} \mathbf{j}_i \cdot \mathbf{\Lambda}_i &= \sum_{i=1}^{n}\left(\rho\omega_i(\mathbf{u}_i - \mathbf{v}) \cdot \left[\nabla_{T,p}\tilde{\mu}_i + \left(\frac{\bar{V}_i}{M_i} - \frac{1}{\rho}\right)\nabla p - \mathbf{f}_i + \sum_{k=1}^{n}\omega_k \mathbf{f}_k\right]\right), \\
&= \sum_{i=1}^{n}\left((\mathbf{u}_i - \mathbf{v}) \cdot \left[\underbrace{c_i \nabla_{T,p}\mu_i + (\phi_i - \omega_i)\nabla p - \rho\omega_i\left(\mathbf{f}_i - \sum_{k=1}^{n}\omega_k \mathbf{f}_k\right)}_{cRT\mathbf{d}_i}\right]\right), \\
&= cRT\sum_{i=1}^{n}\mathbf{d}_i \cdot (\mathbf{u}_i - \mathbf{v}), \\
&= cRT\sum_{i=1}^{n}\frac{1}{\rho\omega_i}\mathbf{d}_i \cdot \mathbf{j}_i
\end{aligned}$$

$$\mathbf{j}_i = \rho\omega_i\left(\mathbf{u}_i - \mathbf{v}\right)$$

$$\frac{\omega_i}{M_i} = \frac{x_i}{M}$$

$$\phi_i = c_i\bar{V}_i$$

$$\tilde{\mu}_i = \frac{\mu_i}{M_i}$$

$\bar{V}_i$ Partial molar volume.

$$cRT\mathbf{d}_i = c_i\nabla_{T,p}\mu_i + (\phi_i - \omega_i)\nabla p - \omega_i\rho\left(\mathbf{f}_i - \sum_{k=1}^{n}\omega_k \mathbf{f}_k\right)$$

From physical reasoning (recall $\mathbf{d}_i$ represents force per unit volume driving diffusion) or the Gibbs-Duhem equation,

$$\sum_{i=1}^{n}\mathbf{d}_i = 0$$

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The Entropy Source Term - Summary

$$\rho \frac{\mathrm{D}s}{\mathrm{D}t} = -\nabla \cdot \mathbf{j}_s + \sigma_s$$

$$\mathbf{j}_s = \frac{1}{T}\left(\mathbf{q} - \sum_{i=1}^{n} \tilde{\mu}_i \mathbf{j}_i\right)$$

From the previous slide:

$$\sum_{i=1}^{n} \mathbf{j}_i \cdot \mathbf{\Lambda}_i = cRT \sum_{i=1}^{n} \frac{\mathbf{d}_i \cdot \mathbf{j}_i}{\rho_i}$$

$$cRT\mathbf{d}_i = c_i \nabla_{T,p}\mu_i + (\phi_i - \omega_i)\nabla p - \omega_i \rho \left(\mathbf{f}_i - \sum_{k=1}^{n} \omega_k \mathbf{f}_k\right)$$

$$\begin{aligned} T\sigma_s &= -\mathbf{q}\cdot\nabla \ln T - \sum_{i=1}^{n} \mathbf{j}_i \cdot \underbrace{\left[\nabla_{T,p}\tilde{\mu}_i + \frac{\bar{V}_i}{M_i}\nabla p - \mathbf{f}_i\right]}_{\mathbf{\Lambda}_i} - \tau : \nabla \mathbf{v} - \sum_{i=1}^{n} \tilde{\mu}_i \sigma_i \\ &= -\underbrace{\mathbf{q}\cdot\nabla \ln T}_{1} - \underbrace{\sum_{i=1}^{n} \frac{cRT}{\rho_i}\mathbf{d}_i \cdot \mathbf{j}_i}_{2} - \underbrace{\tau : \nabla \mathbf{v}}_{3} - \underbrace{\sum_{i=1}^{n} \tilde{\mu}_i \sigma_i}_{4} \end{aligned}$$

Interpretation of each term???

$\sigma_s \sim$ Forces $\cdot$ Fluxes

$$T\sigma_s = -\mathbf{q}\cdot\nabla\ln T - \sum_{i=1}^{n}\frac{cRT}{\rho_i}\mathbf{d}_i\cdot\mathbf{j}_i - \tau : \nabla\mathbf{v} - \sum_{i=1}^{n}\tilde{\mu}_i\sigma_i$$

Fundamental principle of irreversible thermodynamics:

$$\sigma_s = \sum_\alpha J_\alpha F_\alpha$$

Flux, J_α	Force, F_α
$\mathbf{q}$	$-\nabla\ln T$
$\mathbf{j}_i$	$-\frac{cRT}{\rho_i}\mathbf{d}_i$
τ	$-\nabla\mathbf{v}$

- <u>Fluxes</u> are functions of:
  - Thermodynamic state variables: T, p, ω_i.
  - <u>Forces</u> of same *tensorial order* (Curie's postulate)
    - What does this mean?
    - More soon…

$$J_\alpha = J_\alpha(F_1, F_2, \ldots, F_\beta; T, p, \omega_i)$$

$$J_\alpha = \sum_\beta \left(\frac{\partial J_\alpha}{\partial F_\beta}\right) F_\beta + \mathcal{O}\left(F_\beta F_\gamma\right)$$

$$\approx \sum_\beta L_{\alpha\beta} F_\beta \qquad L_{\alpha\beta} \equiv \frac{\partial J_\alpha}{\partial F_\beta}$$

$$L_{\alpha\beta} = L_{\beta\alpha}$$

$L_{\alpha\beta}$ - Onsager (phenomenological) coefficients

Species Diffusive Fluxes

Tensorial order of "1" ⇒ any *vector* force may contribute.

Flux: J_α	$\mathbf{q}$	$\mathbf{j}_i$	τ
Force: F_α	$-\nabla \ln T$	$-\frac{cRT}{\rho_i}\mathbf{d}_i$	$-\nabla \mathbf{v}$

Index form:	n-1 dimensional matrix form
From irreversible thermo: $$\mathbf{j}_i = -\sum_{j=1}^{n-1} L_{ij}\frac{cRT}{\rho_j}\mathbf{d}_j - L_i q \nabla \ln T$$	$$(\mathbf{j}) = -\rho\left[\mathcal{L}\right](\mathbf{d}) + \nabla \ln T(\beta_q)$$
Fick's Law: $$\mathbf{j}_i = -\rho\sum_{j=1}^{n-1} D^\circ_{ij}\mathbf{d}_j - D^T_i \nabla \ln T$$ D_{ij} - Fickian diffusivity D^T_i - Thermal Diffusivity	$$(\mathbf{j}) = -\rho\left[D^\circ\right](\mathbf{d}) - \left(D^T\right)\nabla \ln T$$
Generalized Maxwell-Stefan Equations: $$\mathbf{d}_i = -\sum_{j\neq i}^{n}\frac{x_i x_j}{\rho \text{Đ}_{ij}}\left(\frac{\mathbf{j}_i}{\omega_i} - \frac{\mathbf{j}_j}{\omega_j}\right) - \nabla \ln T \sum_{j\neq i}^{n} x_i x_j \alpha^T_{ij}$$ $$\alpha^T_{ij} = \frac{1}{\text{Đ}_{ij}}\left(\frac{D^T_i}{\rho_i} - \frac{D^T_i}{\rho_j}\right)$$	$$\rho(\mathbf{d}) = -[B^{on}](\mathbf{j}) - \nabla \ln T\,[\Upsilon](D^T)$$

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Constitutive Law: Heat Flux

Tensorial order of "1" ⇒ any *vector* force may contribute.

Flux: J_α	$\mathbf{q}$	$\mathbf{j}_i$	τ
Force: F_α	$-\nabla \ln T$	$-\frac{cRT}{\rho_i}\mathbf{d}_i$	$-\nabla \mathbf{v}$

$$\mathbf{q} = \boxed{-L_{qq}\nabla \ln T} - \boxed{\sum_{i=1}^{n} L_{qi}\frac{cRT}{\rho_i}\mathbf{d}_i}$$

Choose $L_{qq}=\lambda T$ to obtain "Fourier's Law"

"Dufuor" effect - mass driving force can cause heat flux! Usually neglected.

$$\mathbf{q} = \underbrace{-\lambda\nabla T}_{\text{Fourier}} + \underbrace{\sum_{i=1}^{n} h_i\mathbf{j}_i}_{\text{Species}} + \underbrace{\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{cRTD^T x_i x_j}{\rho_i Đ_{ij}}\left(\frac{\mathbf{j}_i}{\rho_i} - \frac{\mathbf{j}_j}{\rho_j}\right)}_{\text{Dufour}}$$

here we have substituted the RHS of the GMS equations for $\mathbf{d}_i$.

Note: the Dufour effect is usually neglected.

The "Species" term is typically included here, even though it does not come from irreversible thermodynamics. Occasionally radiative terms are also included here...

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Observations on the GMS Equations

$$\mathbf{d}_i = \sum_{j=1}^{n} \frac{x_i \mathbf{J}_j - x_j \mathbf{J}_i}{c Đ_{ij}} - \nabla \ln T \sum_{j=1}^{n} x_i x_j \alpha_{ij}^T$$

$$cRT\mathbf{d}_i = c_i \nabla_{T,p} \mu_i + (\phi_i - \omega_i) \nabla p - \omega_i \rho \left(\mathbf{f}_i - \sum_{k=1}^{n} \omega_k \mathbf{f}_k \right)$$

- What have we gained?
  - Thermal diffusion (Soret/Dufuor) & its origins.
    - Typically neglected.
  - "Full" diffusion driving force
    - Chemical potential gradient (rather than mole fraction). More later.
    - Pressure driving force.
      - When will $\phi_i \neq \omega_i$? More later.
    - Body force term.
      - Does gravity enter here?
- Onsager coefficients themselves not too important from a "practical" point of view.
- Still don't know how to get the binary diffusivities.

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The Thermodynamic Factor, Γ

$$\mathbf{d}_i = \frac{x_i}{RT}\nabla_{T,p}\mu_i + \frac{1}{c_t RT}(\phi_i - \omega_i)\nabla p - \frac{\rho_i}{c_t RT}\left(\mathbf{f}_i - \sum_{k=1}^{n}\omega_k \mathbf{f}_k\right)$$

$$\begin{aligned}
\mu_i &= \mu_i(T,p,x_j) \\
\nabla_{T,p}\mu_i &= \sum_{j=1}^{n-1}\left.\frac{\partial \mu_i}{\partial x_j}\right|_{T,p,\Sigma}\nabla x_j
\end{aligned}$$

$$\mu_i(T,p) = \mu_i^\circ + RT\ln\gamma_i x_i$$

$$\begin{aligned}
\frac{x_i}{RT}\nabla_{T,p}\mu_i &= \frac{x_i}{RT}\sum_{j=1}^{n-1}\left.\frac{\partial \mu_i}{\partial x_j}\right|_{T,p,\Sigma}\nabla x_j, \\
&= \frac{x_i}{RT}\sum_{j=1}^{n-1} RT\left.\frac{\partial \ln\gamma_i x_i}{\partial x_j}\right|_{T,p,\Sigma}\nabla x_j, \\
&= x_i\sum_{j=1}^{n-1}\left(\frac{\partial \ln x_i}{\partial x_j} + \left.\frac{\partial \ln\gamma_i}{\partial x_j}\right|_{T,P,\Sigma}\right)\nabla x_j, \\
&= \sum_{j=1}^{n-1}\left(\delta_{ij} + x_i\left.\frac{\partial \ln\gamma_i}{\partial x_j}\right|_{T,p,\Sigma}\right)\nabla x_j, \\
&= \sum_{j=1}^{n-1}\Gamma_{ij}\nabla x_j
\end{aligned}$$

γ - Activity coefficient
Many models available
(see T&K Appendix D)

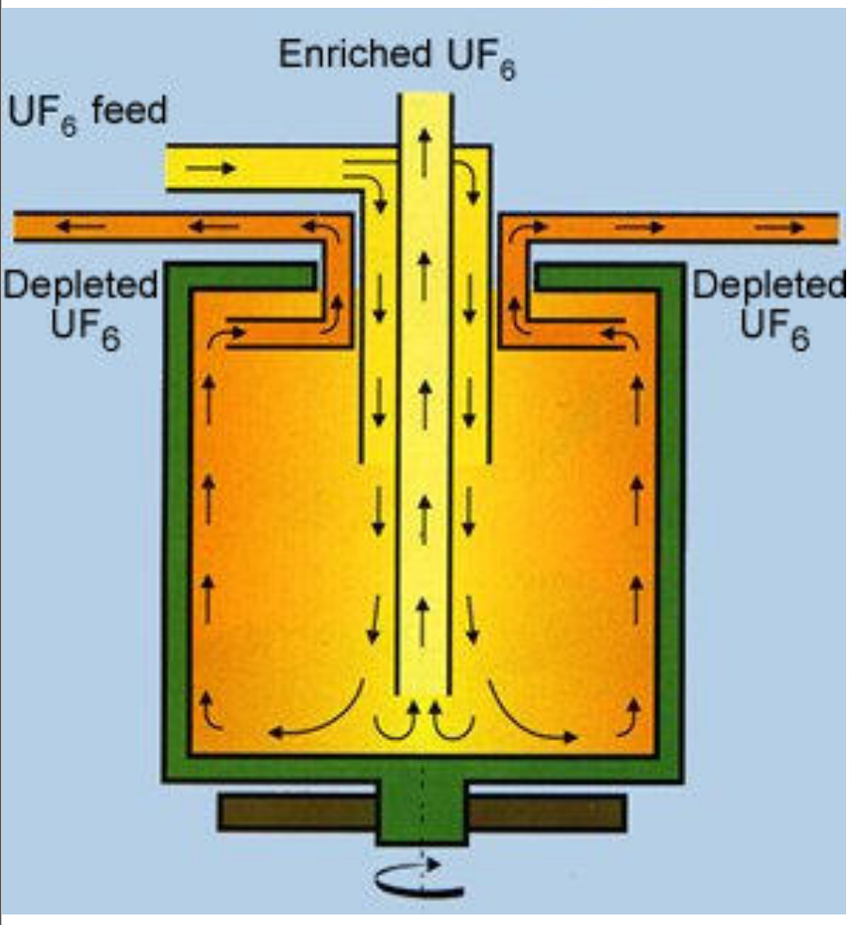
$$\Gamma_{ij} \equiv \delta_{ij} + x_i\left.\frac{\partial \ln\gamma_i}{\partial x_j}\right|_{T,p,\Sigma}$$

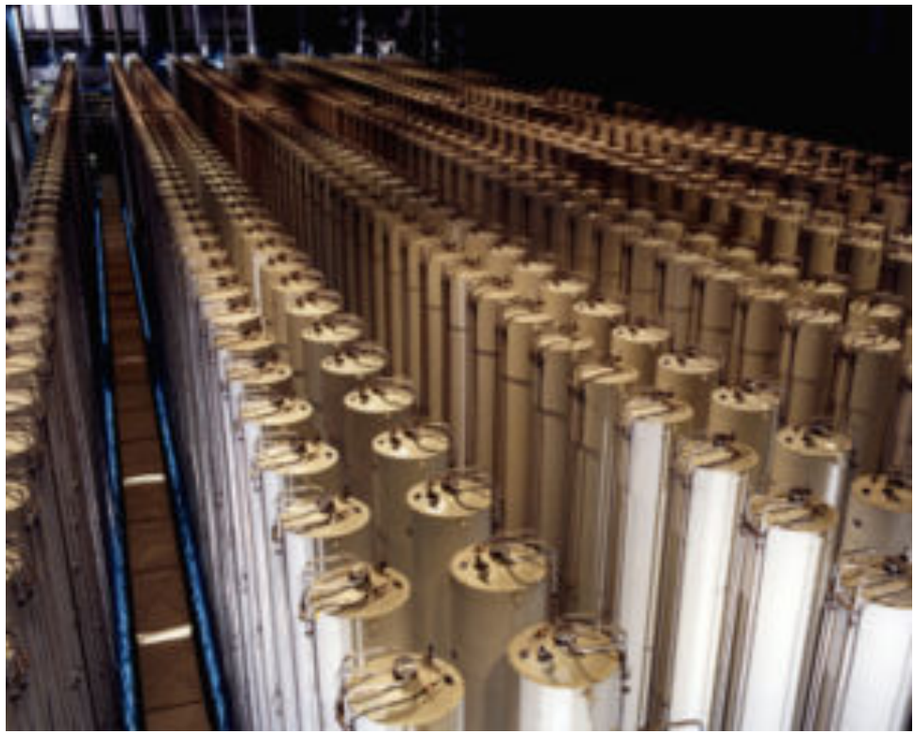
$$\mathbf{d}_i = \sum_{j=1}^{n-1}\Gamma_{ij}\nabla x_j + \frac{1}{c_t RT}(\phi_i - \omega_i)\nabla p - \frac{\rho_i}{c_t RT}\left(\mathbf{f}_i - \sum_{k=1}^{n}\omega_k \mathbf{f}_k\right)$$

Note: for ideal gas, $p = c_t RT$

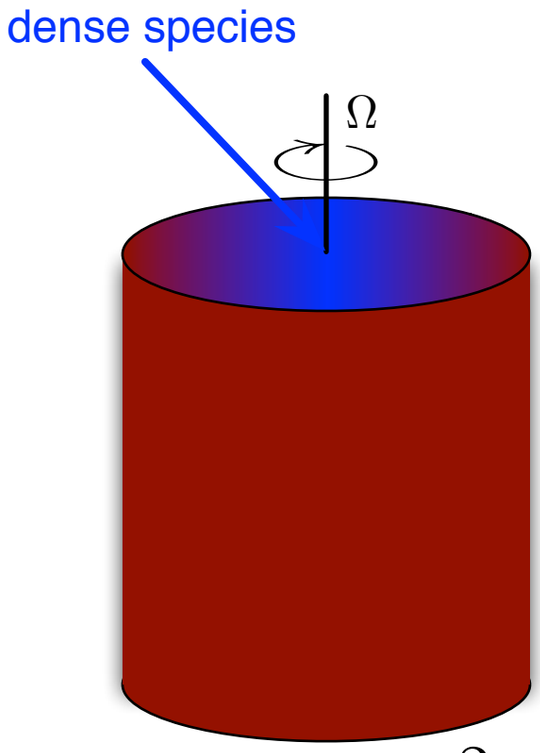
Example: The Ultracentrifuge

Used for separating mixtures based on components' molecular weight.





Consider a closed system...



$$\mathbf{f} = \mathbf{f}_i = \Omega^2 r$$

For a closed centrifuge (no flow) with a known initial charge, what is the equilibrium species profile?

Species equations: $$\frac{\partial \rho_i}{\partial t} = -\nabla \cdot \mathbf{n_i} + s_i$$ steady, 1D, no reaction $$\frac{\partial n_i}{\partial r} = 0$$

$$n_i = \rho_i v_r + j_{i,r} = 0 \quad \Rightarrow \quad j_{i,r} = J_{i,r} = 0$$

GMS Equations: $$\mathbf{d}_i = \sum_{j=1}^{n} \frac{x_i \mathbf{J}_j - x_j \mathbf{J}_i}{c Đ_{ij}} = 0$$

The generalized diffusion driving force:

$$\mathbf{d}_i = \sum_{j=1}^{n-1} \Gamma_{ij} \nabla x_j + \frac{1}{c_t RT}(\phi_i - \omega_i)\nabla p - \frac{\omega_i \rho}{c_t RT}\left(\mathbf{f}_i - \sum_{k=1}^{n} \omega_k \mathbf{f}_k\right)$$

$$0 = \sum_{j=1}^{n-1} \Gamma_{ij} \frac{\mathrm{d}x_j}{\mathrm{d}r} + \frac{1}{c_t RT}(\phi_i - \omega_i)\frac{\mathrm{d}p}{\mathrm{d}r} - \frac{\omega_i \rho}{c_t RT}\left(\Omega^2 r - \sum_{k=1}^{n} \omega_k \Omega^2 r\right)$$

$$\sum_{j=1}^{n-1} \Gamma_{ij} \frac{\mathrm{d}x_j}{\mathrm{d}r} = \frac{1}{c_t RT}(\omega_i - \phi_i)\frac{\mathrm{d}p}{\mathrm{d}r}$$

For an ideal gas mixture, $\phi_i = x_i$, and $\Gamma_{ij} = \delta_{ij}$.

$$\frac{\mathrm{d}x_i}{\mathrm{d}r} = \frac{1}{c_t RT}(\omega_i - x_i)\frac{\mathrm{d}p}{\mathrm{d}r}$$

We don't know $\mathrm{d}p/\mathrm{d}r$ or x_{i0} (composition at $r = 0$).

$$\frac{\mathrm{d}x_i}{\mathrm{d}r} = \frac{1}{c_t RT}(\omega_i - x_i)\frac{\mathrm{d}p}{\mathrm{d}r}$$

Species mole balance:

$$\int_0^{r_L} c x_i 2\pi r \,\mathrm{d}r = \int_0^{r_L} c^* x_i^* 2\pi r \,\mathrm{d}r$$

* indicates the initial condition (pure stream).

For species i, $$\int_0^{r_L} \underline{p}\, x_i\, r \,\mathrm{d}r = p^* x_i^* \frac{r_L^2}{2}$$

Must know $p(r)$ and $x_i(r)$ to integrate this.

Species mole balance constrains the species profile solution (dictates the species boundary condition)

Momentum: $$\frac{\partial \rho \mathbf{v}}{\partial t} = -\nabla \cdot (\rho \mathbf{v}\mathbf{v}) - \nabla \cdot \boldsymbol{\tau} - \nabla p + \rho \sum_{i=1}^{n} \omega_i \mathbf{f_i}$$

at steady state (no flow): $$\frac{\mathrm{d}p}{\mathrm{d}r} = \rho \sum_{i=1}^{n} \omega_i f_{r,i} = \rho \Omega^2 r$$

$$\frac{\mathrm{d}p}{\mathrm{d}r} = \rho \Omega^2 r = \frac{pM}{RT}\Omega^2 r$$

We don't know p_0 (pressure at $r = 0$).

The momentum equation gives the pressure profile, but is coupled to the species equations through M.

Total mole balance (at equilibrium):

$$\int_{\mathrm{V}} c\,\mathrm{dV} = \int_{\mathrm{V}} c^*\,\mathrm{dV}$$

* indicates the initial condition (pure stream).

$$\int_0^{r_L} cr\,\mathrm{d}r = c^*\frac{r_L^2}{2} \qquad \mathrm{dV} = L2\pi r\mathrm{d}r \qquad c = \frac{p}{RT}$$

$$\int_0^{r_L} pr\,\mathrm{d}r = p^*\frac{r_L^2}{2}$$

Substitute $p(r)$ and solve this for p_0...

Total mole balance constrains the pressure solution (dictates the pressure boundary condition)

Solve these equations:

$$\frac{\mathrm{d}x_i}{\mathrm{d}r} = \frac{M}{RT}(\omega_i - x_i)\Omega^2 r \qquad \frac{\mathrm{d}p}{\mathrm{d}r} = \rho\Omega^2 r = \frac{pM}{RT}\Omega^2 r$$

With these constraints:

$$\int_0^{r_L} p\,x_i\,r\,\mathrm{d}r = p^* x_i^* \frac{r_L^2}{2} \qquad \int_0^{r_L} pr\,\mathrm{d}r = p^*\frac{r_L^2}{2}$$

Note: M couples all of the equations together and makes them nonlinear.

Option A:

1. Guess x_{i0}, p_0.
2. Numerically solve the ODEs for x_i, p.
3. Are the constraints met? If not, return to step 1.

Option B:

Try to simplify the problem by making approximations.

Note: for tips on solving ODEs numerically in Matlab, see my wiki page.

Example: separation of Air into N_2, O_2.

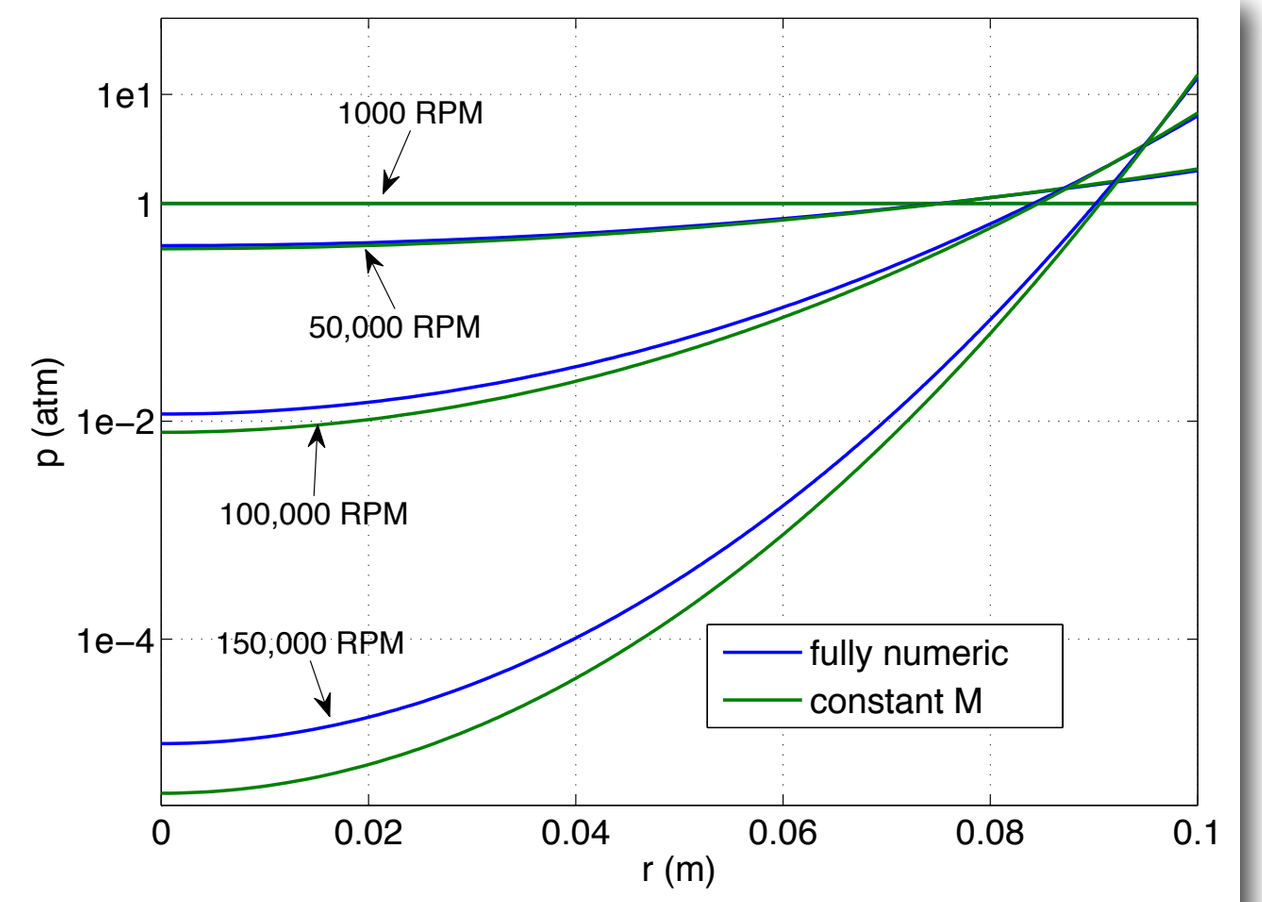
- Centrifuge diameter: 20 cm
- Air initially at STP

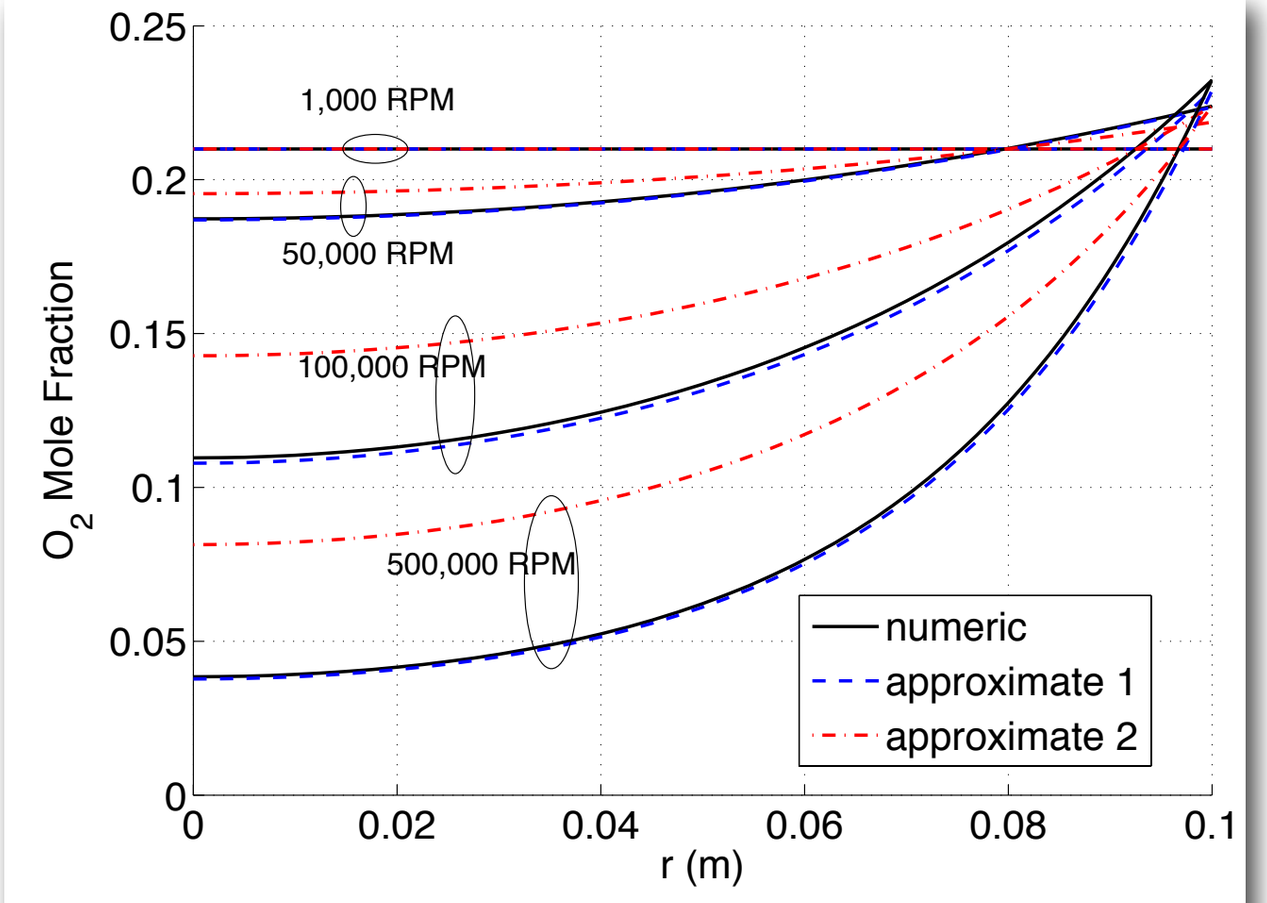
Approximation Level 1

- Approximate M as constant, $(M_{O2}+M_{N2})/2$, for the pressure equation only. This decouples the pressure solution from the species and gives an easy analytic solution for pressure profile.
- Solve species equations numerically, given the analytic pressure profile.

Approximation Level 2

- Approximate M as constant, $(M_{O2}+M_{N2})/2$, for the species and pressure equations.
- Obtain a fully analytic solution for both species and pressure.





Fick's Law (revisited)

$$\mathbf{d}_i = -\sum_{j=1}^{n} \frac{x_i x_j}{\rho Đ_{ij}} \left(\frac{\mathbf{j}_i}{\omega_i} - \frac{\mathbf{j}_j}{\omega_j} \right) - \nabla \ln T \sum_{j=1}^{n} x_i x_j \alpha_{ij}^T$$

$$= -\sum_{j=1}^{n} \frac{x_j \mathbf{J}_i - x_i \mathbf{J}_j}{c Đ_{ij}} - \nabla \ln T \sum_{j=1}^{n} x_i x_j \alpha_{ij}^T$$

$$\mathbf{J} = -c[B]^{-1}(\mathbf{d}) - \nabla \ln T (D^T)$$

This is the same $[B]$ matrix as before (T&K eq. 2.1.21-2.1.22)

$$\mathbf{d}_i = \sum_{j=1}^{n-1} \Gamma_{ij} \nabla x_j + \frac{1}{c_t RT}(\phi_i - \omega_i)\nabla p - \frac{\rho_i}{c_t RT}\left(\mathbf{f}_i - \sum_{k=1}^{n} \omega_k \mathbf{f}_k \right)$$

Ignoring thermal diffusion,

$$(\mathbf{J}) = \underbrace{-c[B]^{-1}[\Gamma](\nabla x)}_{1} - \underbrace{\frac{\nabla p}{RT}[B]^{-1}\left((\phi) - (\omega)\right)}_{2} - \underbrace{\frac{\rho}{RT}[B]^{-1}[\omega]\left((\mathbf{f}) - [\omega](\mathbf{f} + \mathbf{f}_n)\right)}_{3}$$

<u>Notes</u>: $[D]=[B]^{-1}[\Gamma]$

For ideal mixtures: $[\Gamma]=[I]$

In the binary case: $D_{11}=\Gamma_{11}Đ_{12}$

How do we interpret each term?
When is each term important?

Review: Where we are, where we're going…

- Accomplishments
  - Defined "reference velocities" and "diffusion fluxes"
  - Governing equations for multicomponent, reacting flow.
    - mass-averaged velocity…
  - Established a rigorous way to compute the diffusive fluxes from first principles.
    - Can handle diffusion in systems of arbitrary complexity, including:
      - nonideal mixtures, EM fields, large pressure & temperature gradients, multiple species, chemical reaction, *etc.*
  - Simplifications for ideal mixtures, negligible pressure gradients, *etc.*
  - Solutions for "simple" problems.

- Still Missing:
  - Models for binary diffusivities.
    - Given a model, we are good to go!
- Roadmap:
  - Models for binary diffusivities. (T&K Chapter 4) - we won't cover this...
  - Simplified models for multicomponent diffusion
  - Interphase mass transfer (surface discontinuities)
  - Turbulence - models for diffusion in turbulent flow.
  - Combined heat, mass, momentum transfer.

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