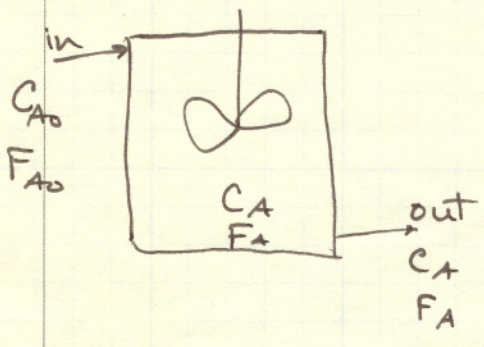
- PSR { - seniors
  - graduate students
- Premixed { - seniors
  - graduate students

(- Discuss projects)

A. Perfectly-Stirred Reactor (for undergrads)



- steady-state
- one reaction
- ideal reactor (easy to analyze)
- composition in reactor is uniform
- composition in reactor is what comes out

Balance on moles:

in = out + disappearance + ~~accumulation~~ 0

F_{A0} = inlet molar flow rate (moles A/time)

r_A = volumetric molar reaction rate (production = +) (moles A/volume/time)

X_A = fractional conversion of A (0 initially, 1 at completion)

C_A = molar concentration of A

V = reactor volume

$$X_A = \frac{F_{A0} - F_A}{F_{A0}} = \frac{C_{A0} - C_A}{C_{A0}}$$ (when V doesn't change or moles don't change)

Balance: $F_{A0} = F_A + (-r_A)V$

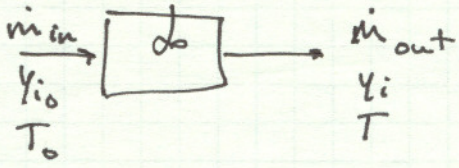
but $F_{A0} - F_A = X_A F_{A0}$

so $X_A F_{A0} = (-r_A)V$, or $\boxed{\frac{V}{F_{A0}} = \frac{X_A}{-r_A}}$

undergrads live and die by this!

Mass Balance

$\dot{m}_{in} = \dot{m}_{out}$



Y_i = mass fraction

Species Mass Balance

in = out + disappearance + accumulation (0)

$$\dot{m} Y_{k_{in}} = \dot{m} Y_{k_{out}} + (-r_k V) MW_k$$

MW_k = molecular wt. of species k

units	$\frac{g_k}{s}$	$\frac{g_k}{s}$	$\frac{mole_k}{cm^3\ s}$	cm^3	$\frac{g_k}{mole_k}$

final form:

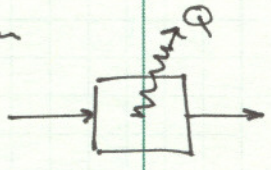
$$\dot{m}\left(Y_{k_{out}} - Y_{k_{in}}\right) + r_k V MW_k = 0$$

($\dot{m}$: known; $Y_{k_{in}}$: known; $r_k V$: known; MW_k: known)

Energy Balance

in = out + disappearance + accumulation (0)

$$\dot{m}\left(\Sigma Y_k h_k\right)_{in} = \dot{m}\left(\Sigma Y_k h_k\right)_{out} + Q$$



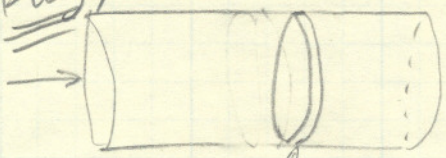
Q = heat lost from system

$$\dot{m}\left(\Sigma\left[\left(Y_k h_k\right)_{out} - \left(Y_k h_k\right)_{in}\right]\right) + Q = 0$$

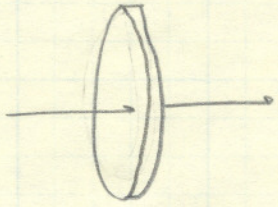
Note: Many systems use a specified T rather than calculating T. When T is calculated, convergence and/or stability problems often occur.

Premixed (for undergrads)

A. Plug, 1-reaction



examine this slice



dV

in = out + disappearance + accumulation

mole balance, one reaction

in = F_A (F_A = molar flow rate of A, moles/time)

out = $F_A + dF_A$

disappearance = $-r_A dV$

$$F_A = F_A + dF_A - r_A dV$$

$$F_A = F_{A0}(1 - X_A)$$

$$dF_A = -F_{A0} dX_A$$

$$0 = -F_{A0} dX_A - r_A dV$$

$$F_{A0} dX_A = -r_A dV$$

or

$$\int_0^V \frac{dV}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{-r_A}$$

or

$$\boxed{\frac{V}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{-r_A}}$$

Assumptions:

- no diffusion in axial direction!
- no radial variation in any property

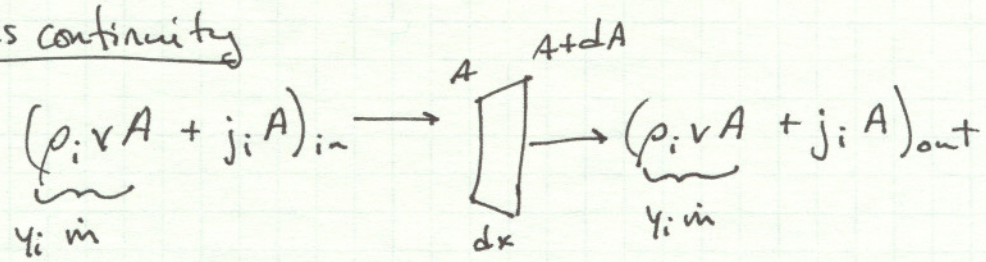
Premixed, multiple reactions

- steady state
- multi-component diffusion
- no radial variation
- no radiation
- no wall heat loss

mass balance

$$\dot{m} = \rho V A \qquad (V: \text{velocity})$$

species continuity



$$\text{rate of disappearance} = -R_i A dx \, MW_i$$

$$\rho_i = Y_i \rho$$

$$\Rightarrow \frac{(\dot{m} Y_i + j_i A)_{out} - (\dot{m} Y_i + j_i A)_{in}}{dx} - R_i A MW_i = 0$$

$$\dot{m} \frac{\partial Y_i}{\partial x} + \frac{\partial}{\partial x}(j_i A) - R_i A MW_i = 0$$

$$A j_i = \rho A V_i Y_i$$

(V_i: diffusion velocity)

Alternatively, from BSL $\quad \frac{D}{Dt}\rho_i = -\rho_i \vec{\nabla}\cdot\vec{v} - \vec{\nabla}\cdot\vec{j}_i + R_i MW_i$

at steady state,

$$v \frac{\partial \rho_i}{\partial x} + \rho_i \frac{\partial v}{\partial x} + \frac{\partial j_i}{\partial x} - R_i MW_i = 0$$

$$\frac{\partial \rho_i v}{\partial x} + \frac{\partial j_i}{\partial x} - R_i MW_i = 0$$

$$\frac{\partial \rho_i v A}{\partial x} + \frac{\partial A j_i}{\partial x} - R_i MW_i A = 0$$

$$\dot{m} \frac{\partial Y_i}{\partial x} + \frac{\partial A j_i}{\partial x} - R_i MW_i A = 0$$

Premixed, Energy Balance

New edition - Table 11.4-1, p. 340, Eqn. 11.2-5 (J)

Where do we start? BSL, P. 562, Eqn. F (Table 18.3-1)

$$\rho \hat{C}_p \frac{DT}{Dt} = -\nabla \cdot q - \tau : \nabla v + \sum j_i g_i + \left(\frac{\partial \ln V}{\partial T}\right)_{p,x_i} \frac{Dp}{Dt}$$

(per mass; viscous forces; body force; $\to 0$ (ideal gas); per mole)

$$+ \sum \bar{H}_i \left((\nabla \cdot J_i) - R_i \right)$$

$$\rho \hat{C}_p \left(\frac{\partial T}{\partial t} + v \frac{\partial T}{\partial x} \right) = -\nabla \cdot q + \sum \bar{H}_i \left((\nabla \cdot J_i) - R_i \right)$$

($\partial T/\partial t \to 0$)

$$q = q^{(c)} + q^{(d)}$$

$$q^{(c)} = -k \nabla T$$

$$q^{(d)} = \sum \frac{\bar{H}_i}{M_i} j_i = \sum \bar{H}_i J_i \left(= \sum \hat{H}_i j_i \right)$$

$$\rho v \hat{C}_p \frac{\partial T}{\partial x} = -\frac{\partial}{\partial x}\left(-k \frac{\partial T}{\partial x}\right) - \frac{\partial}{\partial x} \sum \bar{H}_i J_i + \sum \bar{H}_i \nabla J_i - \sum \bar{H}_i R_i$$

Introduce $\dot{M} = \rho v A$, ; remember that A goes inside the 2nd derivative term

$$\underbrace{\rho v A}_{\dot{M}} \frac{\partial T}{\partial x} = +\frac{1}{\hat{C}_p} \frac{\partial}{\partial x}\left(A k \frac{\partial T}{\partial x} \right) + \frac{A}{\hat{C}_p} \sum \left(-\frac{\partial}{\partial x}(\bar{H}_i J_i) + \bar{H}_i \nabla J_i - \bar{H}_i R_i \right)$$

(minus sign)

$$\frac{\partial (\bar{H}_i J_i)}{\partial x} = \bar{H}_i \frac{\partial J_i}{\partial x} + J_i \frac{\partial \bar{H}_i}{\partial x}$$

$$-\frac{\partial (\bar{H}_i J_i)}{\partial x} + \bar{H}_i \frac{\partial J_i}{\partial x} = -J_i \frac{\partial \bar{H}_i}{\partial x}$$

$$\dot{M} \frac{\partial T}{\partial x} = \frac{1}{\hat{C}_p} \frac{\partial}{\partial x}\left(A k \frac{\partial T}{\partial x} \right) + \frac{A}{\hat{C}_p} \sum \left[-J_i \frac{\partial \bar{H}_i}{\partial x} - \bar{H}_i R_i \right]$$

- Now change $J_i \frac{\partial \bar{H}_i}{\partial x}$

$$\frac{\partial \bar{H}_i}{\partial x} = \bar{C}_{pi} \frac{\partial T}{\partial x}$$

$$J_i \bar{C}_{pi} \frac{\partial T}{\partial x} = j_i \hat{C}_{pi} \frac{\partial T}{\partial x} = \rho V_i Y_i \hat{C}_{pi} \frac{\partial T}{\partial x}$$

- Also change $\bar{H}_i R_i$

$$\bar{H}_i R_i = \hat{H}_i MW_i R_i$$

$$\dot{M} \frac{\partial T}{\partial x} - \frac{1}{\hat{C}_p} \frac{\partial}{\partial x}\left(kA \frac{\partial T}{\partial x}\right) + \frac{A}{\hat{C}_p} \sum \rho Y_i V_i \hat{C}_{pi} \frac{\partial T}{\partial x} + \frac{A}{\hat{C}_p} \sum \hat{H}_i R_i MW_i$$

units: $\frac{g-k}{s-cm}$ $\frac{g-k}{cal-cm} \frac{cal}{cm^2 \cdot s \cdot K} \frac{cm^2 K}{cm}$ $\frac{cm^3 g-k}{cal} \frac{g}{cm^3} \frac{cm}{s} \frac{cal}{g-k} \frac{k}{cm}$ $\frac{cm^2 g-k}{cal} \frac{cal}{g} \frac{grade}{cm^3 s} \frac{g}{grade}$

$\frac{g-k}{s-cm}$ $\frac{g-k}{s-cm}$ $\frac{g-k}{cm-s}$

Diffusion Velocities

Too much for one lecture

$$V_i = \mathcal{V}_i + \mathcal{W}_i + V_c$$

$\mathcal{V}_i$ = ordinary diffusion velocity (Curtiss-Hirschfelder, 1949)

$$= D_i \frac{1}{X_i} \frac{dX_i}{dx}, \quad X_i = \text{mole fraction}$$

$$D_i = \frac{1 - Y_i}{\sum_{i \neq j} X_j / \mathcal{D}_{ij}}$$

$\mathcal{W}_i$ = thermal diffusion (low molecular wt species, such as H, H_2 and He)

$$\mathcal{W}_i = \frac{D_i k_{T_i}}{X_i} \frac{1}{T} \frac{dT}{dx}$$

k_{T_i} = thermal diffusion ratio

Lecture 9

- Diffusion velocities
- Final hints on PSR, Premixed
- Numerical Techniques

Note on Diffusion Velocities

from mass point of view,

$$j_i = -\rho D_{im}^{mass} \nabla Y_i \qquad \text{where } Y_i = \text{mass fraction}$$

Also,

$$j_i = \rho_i V_i^{mass} = Y_i \rho V_i^{mass}$$

or

$$V_i^{mass} = \frac{j_i}{Y_i \rho} = -\frac{\rho D_{im}^{mass} \nabla Y_i}{Y_i \rho} = -D_{im}^{mass} \frac{\nabla Y_i}{Y_i}$$

How do you get D_{im}^{m}?

Alternatively,

$$J_i^* = -c D_{im}^{mole} \nabla X_i \qquad \text{where } X_i = \text{mole fraction}$$

$$= c_i V_i^{mole} = X_i c V_i^{mole}$$

$$V_i^{mole} = \frac{J_i^*}{X_i c} = -\frac{c D_{im}^{mole} \nabla X_i}{X_i c} = -D_{im}^{mole} \frac{\nabla X_i}{X_i}$$

note:

$$\frac{\nabla X_i}{X_i} \neq \frac{\nabla Y_i}{Y_i}$$

$$D_{im}^{mole} \neq D_{im}^{mass}$$

$$V_i^{mole} \neq V_i^{mass}$$

Diffusion Velocities in Chemkin

$$V_i = \mathcal{V}_i + \mathcal{W}_i + V_c$$

$\mathcal{V}_i$ = ordinary diffusion velocity (Curtiss-Hirschfelder, 1949)

$$= -D_{im} \frac{1}{X_i} \frac{dX_i}{dx}$$, X_i = mole fraction

$$D_{im} = \frac{1 - Y_i}{\sum_{i \neq j} X_j / D_{ij}}$$ Y_i = mass fraction

See eqn. 18.4-25

$\mathcal{W}_i$ = thermal diffusion (low (only) molecular weight species, such as H, H_2, & He)

$$\mathcal{W}_i = \frac{D_{im} k_{T_i}}{X_i} \frac{1}{T} \frac{dT}{dx}$$

k_{T_i} = thermal diffusion ratio

V_c = correction velocity

a. insures that $\sum Y_i = 1$

b. $\sum Y_i V_i = 0$

– correction velocity is not needed if a full multicomponent model is used (Dixon-Lewis, 1968)
(i.e., don't use D_{im} but do it correctly!)

Additional Notes

(I can't find this eqn in the new edition)

Eqn. 18.4-22 in BS:L says: p. 571

$$\frac{1}{\mathcal{D}_{im}} = \frac{\sum_{j=1}^{n} \frac{1}{c\mathcal{D}_{ij}} (x_j N_i - x_i N_j)}{N_i - x_i \sum_{j=1}^{n} N_j}$$

let $i=1$

numerator term with $i=j$ cancel, as do "c" terms.

$$\frac{1}{\mathcal{D}_{1m}} = \frac{\sum_{j=2}^{n} \frac{1}{\mathcal{D}_{1j}} (x_j N_1 - x_1 N_j)}{N_1 - x_1 \sum_{j=2}^{n} N_j - x_1 N_1}$$

$N_j = C_j \nu_j$, and for $j \neq 1$, all $\nu_j = \nu_0$

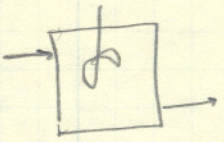
$$\frac{1}{\mathcal{D}_{1m}} = \frac{\sum_{j=2}^{n} \frac{1}{\mathcal{D}_{1j}} (x_j N_1) - \sum_{j=2}^{n} \frac{x_1 C_j \nu_0}{\mathcal{D}_{1j}}}{N_1(1-x_1) - x_1 \sum_{j=2}^{n} C_j \nu_0}$$

$$= \frac{N_1 \sum_{j=2}^{n} \frac{x_j}{\mathcal{D}_{1j}} - x_1 C \nu_0 \sum_{j=2}^{n} \frac{x_j}{\mathcal{D}_{1j}}}{N_1(1-x_1) - x_1 C \nu_0 \sum_{j=2}^{n} x_j}$$

but $\sum_{j=2}^{n} x_j = 1 - x_1$

$$\frac{1}{\mathcal{D}_{1m}} = \frac{(N_1 - x_1 C \nu_0) \sum_{j=2}^{n} \frac{x_j}{\mathcal{D}_{1j}}}{(N_1 - x_1 C \nu_0)(1-x_1)} = \frac{\sum_{j=2}^{n} \frac{x_j}{\mathcal{D}_{1j}}}{1-x_1}$$

Additional thoughts on PSR



What can you change?

$\tau = \frac{\rho V}{\dot{m}}$ ← volume

— specify 2 of 3 $\tau, V, \dot{m}$

(ρ is from T ; Y_i)

— specify Y_{i_0}'s

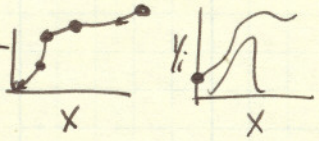
— specify pressure (P_0)

— specify T_0

Additional thoughts on Premixed

A. Simplest Case

- specify temperature field



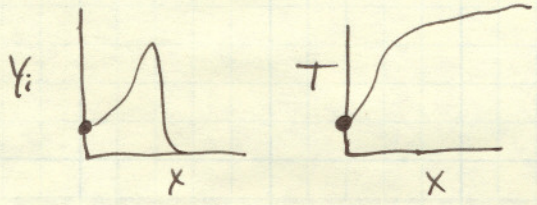
$\dot{m}$ specified

(no need to solve energy eqn.)

- calculate species profiles from species continuity eqn.

B. Hard case

- Solve <u>both</u> energy eqn. ; species cont. from initial conditions



$\dot{m}$ specified

C. Harder case

- solve both energy eqn ; species continuity iteratively to get flame speed ($\dot{m}$ calculated, not specified!)

i.e., change $\dot{m}$ so that you find flame speed!

Numerical Methods

A. PSR

- Cast into form $F(\phi) = 0$

  ϕ is vector $= (T, Y_1, Y_2, \ldots, Y_k)$

- Newton's method

  a. one variable → Taylor's expansion

$$f_1 = f_0 + (x_1 - x_0) f_0' + \underbrace{\frac{(x_1 - x_0)^2}{2!} f_0'' + \frac{(x_1 - x_0)^3}{3!} y_0''' + \ldots}_{\text{neglect}}$$

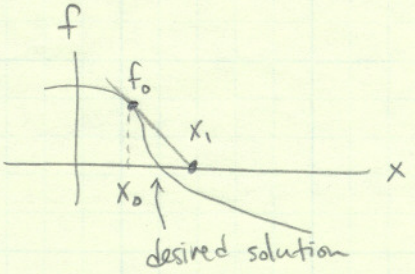
  f_1: $f(x_1)$; f_0: $f(x_0)$

  ⇒ find x_1 so that $f_1(x)$ goes to zero

$$0 = f_0 + (x_1 - x_0) f_0'$$

$$x_1 = x_0 - \frac{y_0}{f_0'}$$

  ↑ new guess for x_0



  b. two variables $\left.\begin{aligned} f_1(x,y) &= 0 \\ f_2(x,y) &= 0 \end{aligned}\right\}$ 2 eqns., 2 unknowns

  Taylor expansion

$$f_1(x_1, y_1) = f_1(x_0, y_0) + (x_1 - x_0) \left.\frac{\partial f_1}{\partial x}\right|_{x_0, y_0} + (y_1 - y_0) \left.\frac{\partial f_1}{\partial y}\right|_{x_0, y_0}$$

$$+ \frac{(x_1 - x_0)^2}{2!} \left.\frac{\partial^2 f_1}{\partial x^2}\right|_{x_0, y_0} + \frac{(y_1 - y_0)^2}{2!} \left.\frac{\partial^2 f_1}{\partial x^2}\right|_{x_0, y_0} + \ldots$$

$$f_2(x_1, y_1) = f_2(x_0, y_0) + (x_1 - x_0) \left.\frac{\partial f_2}{\partial x}\right|_{x_0, y_0} + (y_1 - y_0) \left.\frac{\partial f_2}{\partial y}\right|_{x_0, y_0} + \ldots$$

  presuming $f_1(x_1, y_1) = 0$ and $f_2(x_1, y_1) = 0$, find x_1, y_1

$$\delta_{x_1} = x_1 - x_0$$

$$\delta_{y_1} = y_1 - y_0$$

$$\delta_{x_1} \left.\frac{\partial f_1}{\partial x}\right|_{x_0,y_0} + \delta_{y_1} \left.\frac{\partial f_1}{\partial y}\right|_{x_0,y_0} = -f_1(x_0,y_0)$$

$$\delta_{x_1} \left.\frac{\partial f_2}{\partial x}\right|_{x_0,y_0} + \delta_{y_1} \left.\frac{\partial f_2}{\partial y}\right|_{x_0,y_0} = -f_2(x_0,y_0)$$

In matrix form,

$$\left[\begin{array}{cc} \frac{\partial f_1}{\partial x} & \frac{\partial f_1}{\partial y} \\ \frac{\partial f_2}{\partial x} & \frac{\partial f_2}{\partial y} \end{array}\right]_{x_0,y_0} \left[\begin{array}{c} \delta_{x_1} \\ \delta_{y_1} \end{array}\right] = \left[\begin{array}{c} -f_1 \\ -f_2 \end{array}\right]_{x_0,y_0}$$

find $\delta_{x_1}, \delta_{y_1}$

c. multiple variables $f(x_1, x_2, x_3, \ldots) = 0$

initial points are $x_1^{(0)}, x_2^{(0)}, x_3^{(0)}, \ldots$ ← starting guess

find $x_1^{(1)}, x_2^{(1)}, \ldots$

or $\delta_{x_1}^{(1)}, \delta_{x_2}^{(1)}, \ldots$

$$\left[\begin{array}{cccc} \frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} & \frac{\partial f_1}{\partial x_3} & \cdots \\ \frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2} & \cdots & \\ \vdots & & & \\ \frac{\partial f_n}{\partial x_1} & & & \frac{\partial f_n}{\partial x_n} \end{array}\right]_{x_i^{(0)}} \left[\begin{array}{c} \delta_{x_1} \\ \delta_{x_2} \\ \vdots \\ \delta_{x_n} \end{array}\right] = \left[\begin{array}{c} f_1 \\ f_2 \\ f_3 \\ \vdots \\ f_n \end{array}\right]_{x_i^0}$$

solve for solution vector δ_{x_i}

or shorthand notation

$$\underset{\text{Jacobian}}{J^{(0)}} \Delta\phi^{(0)} = F\left(\phi^{(0)}\right)$$

$\phi^{(1)} \leftarrow \phi^0$

PSR tricks for getting solution

A. Damp the correction

$$\Delta\phi^{(n)} = \phi^{(n+1)} - \phi^{(n)} = \lambda^{(n)} \left(J^{(n)} \right)^{-1} F(\phi^{(n)})$$

λ: damping factor < 1 (like under-relaxation)

B. Numerically evaluate Jacobian matrix

$$J_{ij} = \frac{F_i(\phi_j + \delta) - F_i(\phi_j)}{\delta}$$

- δ is small number selected from machine roundoff considerations
- same as saying $\left.\frac{\partial f_1}{\partial x_2}\right|_{x_1^{(0)} x_2^{(0)}} = \frac{f(x_1^{(0)}, x_2^{(0)} + \delta) - f(x_1^{(0)}, x_2^{(0)})}{\delta}$

C. Revert to time-dependent solution when things get really stiff

- leave in the time dependent terms

$$\frac{dT}{dt} = \frac{T_j^{n+1} - T_j^n}{\Delta t}$$

- use backward Euler method

$$\frac{dy}{dx} = f(x, y)$$

$$\frac{y^{(n+1)} - y^{(n)}}{\Delta x} = f\left(x^{(n+1)}, y^{(n+1)}\right)$$

algebraic eqns for $x^{(n+1)}$; y^{n+1}

- use this for a while, then revert back to {Newton / Jacobian} method

Numerical Methods (Premixed)

Ideas

- Finite difference
  - pack more grid points in regions of large gradients
  - central difference some terms,
    "windward" difference other terms (1st order in direction of flow)
  - average diffusion properties at midpoint

- Boundary Conditions

  a. burner $T_1 = T_b$

  $Y_{k,1}$ specified

  n_k (species mass flux) specified

  actually $\epsilon_k = \frac{n_k}{\dot{m}} = Y_k + \frac{\rho_k V_k A}{\dot{m}}$

  (species mass flux fraction)

  b. outlet $\frac{\Delta Y_k}{\Delta x} = 0$.

  $\frac{\Delta T}{\Delta x} = 0$

- Same type of solution

  $F(\phi) = 0$

  $\phi = (T_1, Y_{1,i} \cdots, T_2, Y_{2,i} \cdots, T_J, Y_{J,i} \cdots, \dot{m}_J)$

  last equation $\frac{d\dot{m}}{dx} = 0$

  → use Jacobian / Newton algorithm, damping

  → go transient when needed.

Matrix solver! → LU decomposition
(as far as I can tell)

Good initial guesses help!

What is "stiffness" in equations?

- see handout

Upcoming Schedule

Friday (~~23rd~~) Lab → Workshop, intro to SENKIN
Monday (26th) Sensitivity Analysis
Wednesday (28th) PaSR / kinetic schemes
Friday (30th) Lab
Monday (Oct. 3) Presentations
Wednesday (Oct. 5) Presentations