REDUCED MECHANISMS

A. Philosophy

- What do you want to match?
- Over what range of ϕ, T, & P?
- What are the criteria for evaluating goodness of fit?

B. Types of mechanisms

1. Global
   - postulate simple mechanism (usually non-elementary)
   - fit data

<u>Example</u>: Hydrocarbon fuels (Westbrook & Dryer)

$$\frac{d[\text{fuel}]}{dt} = A e^{-E/RT} [\text{fuel}]^a [O_2]^b$$

- sensitivity of flame speeds to fuel concentration $\Rightarrow a \cong 0.25$
- pressure dependence of flame speed $\Rightarrow a+b \cong 1.75$
- lean flammability limit could also be used to get a, but relatively insensitive

$\Rightarrow$ good first approximation, but doesn't agree with all data

$\Rightarrow$ 1-step <u>and</u> 2-step global models

$\text{Fuel} + O_2 \rightarrow CO + H_2O$ (1st step)

$CO + \frac{1}{2}O_2 \rightleftarrows CO_2$ (2nd step)

$\Rightarrow$ 2-step agrees better with $T_{adiabatic}$ and postflame CO

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TABLE 6. Single-Step Reaction Rate Parameters, Giving Best Agreement between Experimental Flammability Limits (ϕ_L' and ϕ_R') and Computed Flammability Limits (ϕ_L and ϕ_R)[a]

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Fuel	A	E_a	a	b	ϕ_L'	ϕ_R'	ϕ_L	ϕ_R
CH_4	1.3×10^8	48.4	−0.3	1.3	0.5	0.5	1.6	1.6
CH_4	8.3×10^5	30.0	−0.3	1.3	0.5	0.5	1.6	1.6
C_2H_6	1.1×10^{12}	30.0	0.1	1.65	0.5	0.5	2.7	3.1
C_3H_8	8.6×10^{11}	30.0	0.1	1.65	0.5	0.5	2.8	3.2
C_4H_{10}	7.4×10^{11}	30.0	0.15	1.6	0.5	0.5	3.3	3.4
C_5H_{12}	6.4×10^{11}	30.0	0.25	1.5	0.5	0.5	3.6	3.7
C_6H_{14}	5.7×10^{11}	30.0	0.25	1.5	0.5	0.5	4.0	4.1
C_7H_{16}	5.1×10^{11}	30.0	0.25	1.5	0.5	0.5	4.5	4.5
C_8H_{18}	4.6×10^{11}	30.0	0.25	1.5	0.5	0.5	4.3	4.5
C_8H_{18}	7.2×10^{12}	40.0	0.25	1.5	0.5	0.5	4.3	4.5
C_9H_{20}	4.2×10^{11}	30.0	0.25	1.5	0.5	0.5	4.3	4.5
$C_{10}H_{22}$	3.8×10^{11}	30.0	0.25	1.5	0.5	0.5	4.2	4.5
CH_3OH	3.2×10^{12}	30.0	0.25	1.5	0.5	0.5	4.1	4.0
C_2H_5OH	1.5×10^{12}	30.0	0.15	1.6	0.5	0.5	3.4	3.6
C_6H_6	2.0×10^{11}	30.0	−0.1	1.85	0.5	0.5	3.4	3.6
C_7H_8	1.6×10^{11}	30.0	−0.1	1.85	0.5	0.5	3.2	3.5

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[a] Units are cm-sec-mol-kcal-K.

tion also have this difficulty,[145] and there are several possible solutions to the

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TABLE 7. Parameters for Two-Step Reaction Mechanism, Giving Best Agreement between Experimental and Computed Flammability Limits[a]

Fuel	A	E_a	a	b
CH_4	2.8×10^9	48.4	−0.3	1.3
CH_4	1.5×10^7	30.0	−0.3	1.3
C_2H_6	1.3×10^{12}	30.0	0.1	1.65
C_3H_8	1.0×10^{12}	30.0	0.1	1.65
C_4H_{10}	8.8×10^{11}	30.0	0.15	1.6
C_5H_{12}	7.8×10^{11}	30.0	0.25	1.5
C_6H_{14}	7.0×10^{11}	30.0	0.25	1.5
C_7H_{16}	6.3×10^{11}	30.0	0.25	1.5
C_8H_{18}	5.7×10^{11}	30.0	0.25	1.5
C_8H_{18}	9.6×10^{12}	40.0	0.25	1.5
C_9H_{20}	5.2×10^{11}	30.0	0.25	1.5
$C_{10}H_{22}$	4.7×10^{11}	30.0	0.25	1.5
CH_3OH	3.7×10^{12}	30.0	0.25	1.5
C_2H_5OH	1.8×10^{12}	30.0	0.15	1.6
C_6H_6	2.4×10^{11}	30.0	−0.1	1.85
C_7H_8	1.9×10^{11}	30.0	−0.1	1.85

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[a] Same units as in Table 6.

The resulting mechanism with the constants of Table 7 predicted flame speeds in close agreement with those predicted by the single-step models in Table 6

Types of Mechanisms

2. Full mechanisms

- put in every possible elementary-step reaction

Example: GRI2.11 mechanism ⇒ ~350 steps for

CH_4 + air → N_2, CO, CO_2, NO_x

- Some rates measured (when radical species measured)
- Some rates from Quantum Mechanics
- Rates "tweaked" within "experimental error"

⇒ Don't mess with these!

3. Skeletal mechanisms

- Simply cross out reactions that seem unimportant

⇒ 25-50 steps instead of 350

⇒ additional "tweaking" may be necessary

- still uses elementary step reactions

4. Reduced mechanisms

- start with full mechanism
- use steady-state approximation on minor radical species
- Also use equilibrium and long chain approximations
- get reduced form of mechanism that includes the algebraic manipulations above.

Example:

$$\frac{d[\text{rad}]}{dt} = 0 = \underbrace{\omega_1 - \omega_3 - \omega_5}_{\text{functions of [rad]}}$$

Do algebra to get

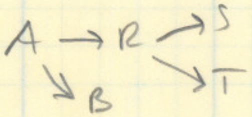
$$[\text{rad}] \cong f(\text{algebra})$$

substitute back in to rate expression for major species

$$\frac{d[\text{maj}]}{dt} = k_1[\text{rad}][\text{other}] = k_1 f(\text{algebra})[\text{other}]$$

C. Use Sensitivity Analysis

A. Determine most important reactions



B. Determine rate constants for set of most important reactions by empirical fitting procedures.

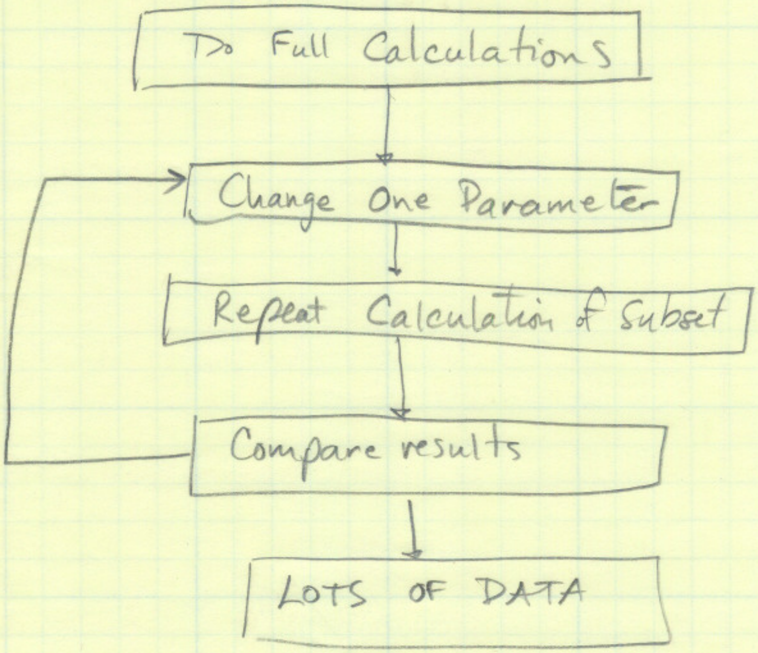
- use data to compare ⇒ get coefficients

<u>OR</u>

- use predictions from full mechanism to compare (Wei Chen)

Lecture 12
Sensitivity Analysis / Reduced Mechanisms

A. Brute Force Method



B. Simpler method (but effective)

<u>Wanted</u>: sensitivity to individual reaction rates, not individual coefficients, at constant T, P, and Y_i.

$$\dot{r}_i = A_i T^{\beta_i} e^{-E_i/RT} \qquad (1)$$

What we would like, then, is the change in the solution with respect to small changes in the reaction rate for individual elementary reactions, or

$$\frac{\Delta F}{\Delta \dot{r}_i} \qquad (2)$$

To accomplish this, an additional term is added to the reaction rate equation (1), which is initially unity and then varied slightly:

$$\dot{r}_i = \gamma_i A_i T^{\beta_i} e^{-E_i/RT} = \gamma_i \dot{r}_i^{\circ}$$

$$\Delta \dot{r}_i = (\gamma_i + \delta)\dot{r}_i^{\circ} - \gamma_i \dot{r}_i^{\circ} = \delta \dot{r}_i^{\circ}$$

or

$$d\dot{r}_i = \dot{r}_i^{\circ} \delta$$

The normalized sensitivity is

reaction rates (individual)

$$\frac{\alpha}{Y}\frac{\partial Y}{\partial \alpha}\bigg|_{T,P,Y_i} \quad \text{(in general terms)}, \quad \text{OR}$$

$$\frac{\dot{r}_i}{Y_j}\frac{\partial Y_j}{\partial \dot{r}_i}\bigg|_{T,P,Y_i} \quad) \qquad \text{OR}$$

$$\frac{\gamma \dot{r}_i^{\,o}}{Y_j}\frac{\partial Y_j}{\partial(\gamma \dot{r}_i^{\,o})}\bigg|_{T,P,Y_i} = \frac{\gamma}{Y_j}\frac{\partial Y_j}{\partial \gamma}\bigg|_{T,P,Y_i}$$

This serves as a way to perturb the system by slightly changing one reaction rate and seeing how this small perturbation affects the solution.

*This explanation is a change from what is in the manuals. The reason for the change is that sometimes the reaction rate coefficients become strange functions of pressure, etc., and the γ factor still allows you to perturb the entire reaction rate, while the A_i might not always do so!

* Based on conversations with Bob Kee, then at Sandia Nat. Labs in Livermore, CA, Sept.-Oct. 1994.

How is this done in the code?

$$F(\phi) = 0 \quad \text{(all conservation equations)}$$

$$\frac{dF}{d\alpha} = \underset{\substack{\uparrow \\ \text{Jacobian} \\ \text{matrix}}}{\frac{\partial F}{\partial \phi}} \; \underset{\substack{\uparrow \\ \text{sensitivity} \\ \text{matrix} \\ \text{we want}}}{\frac{\partial \phi}{\partial \alpha}} + \underset{\substack{\uparrow \\ \text{need to compute this}}}{\frac{\partial F}{\partial \alpha}} = 0$$

from $\frac{\Delta F}{\Delta \alpha} = \frac{\Delta F}{\dot{r}_i^0 \delta}$ for small δ

EXAMPLE

Remember,

$$\frac{\partial F}{\partial \phi} = \begin{bmatrix} \frac{\partial f_1}{\partial \phi_1} & \frac{\partial f_1}{\partial \phi_2} & \cdots \\ \frac{\partial f_2}{\partial \phi_1} & \frac{\partial f_2}{\partial \phi_2} & \cdots \\ \frac{\partial f_3}{\partial \phi_1} & \frac{\partial f_3}{\partial \phi_2} & \cdots \\ \vdots & & \end{bmatrix}$$

Pick reaction j

$$\left[\frac{\partial F}{\partial \phi}\right]\left[\frac{\partial \phi}{\partial \alpha_j}\right] + \left(\frac{\partial F}{\partial \alpha_j}\right) = 0$$

$$\begin{bmatrix} \\ N \times N \text{ matrix} \\ \\ \end{bmatrix} \underbrace{\begin{bmatrix} \frac{\partial \phi_1}{\partial \alpha_j} \\ \frac{\partial \phi_2}{\partial \alpha_j} \\ \frac{\partial \phi_3}{\partial \alpha_j} \\ \vdots \end{bmatrix}}_{\text{wanted}} = - \begin{bmatrix} \frac{\partial f_1}{\partial \alpha_j} \\ \frac{\partial f_2}{\partial \alpha_j} \\ \frac{\partial f_3}{\partial \alpha_j} \\ \vdots \end{bmatrix} \qquad (3)$$

where N is # of species.

Note that there are NR (where NR > N) reactions, and therefore NR α_j parameters that we could select (repeat (3) NR times)

C. Different Approaches to Sensitivity Analysis

1. Local sensitivity coefficients
   - $\frac{\partial \phi}{\partial r_i}$ (as in Chemkin)
   - Green's function method
   - Taylor series expansion methods

   } may include higher order terms
2. Global sensitivity coefficients
   - potentially large variation in coefficients
   - interactions between variations in several parameters at once
   - Monte Carlo, stochastic, Pattern methods

Whole idea:

① See which reactions are critical

② see how well you need to specify certain rate coefficients

Example: Miller-Bowman Kinetics

from Bartok & Sarofim's book, p. 242

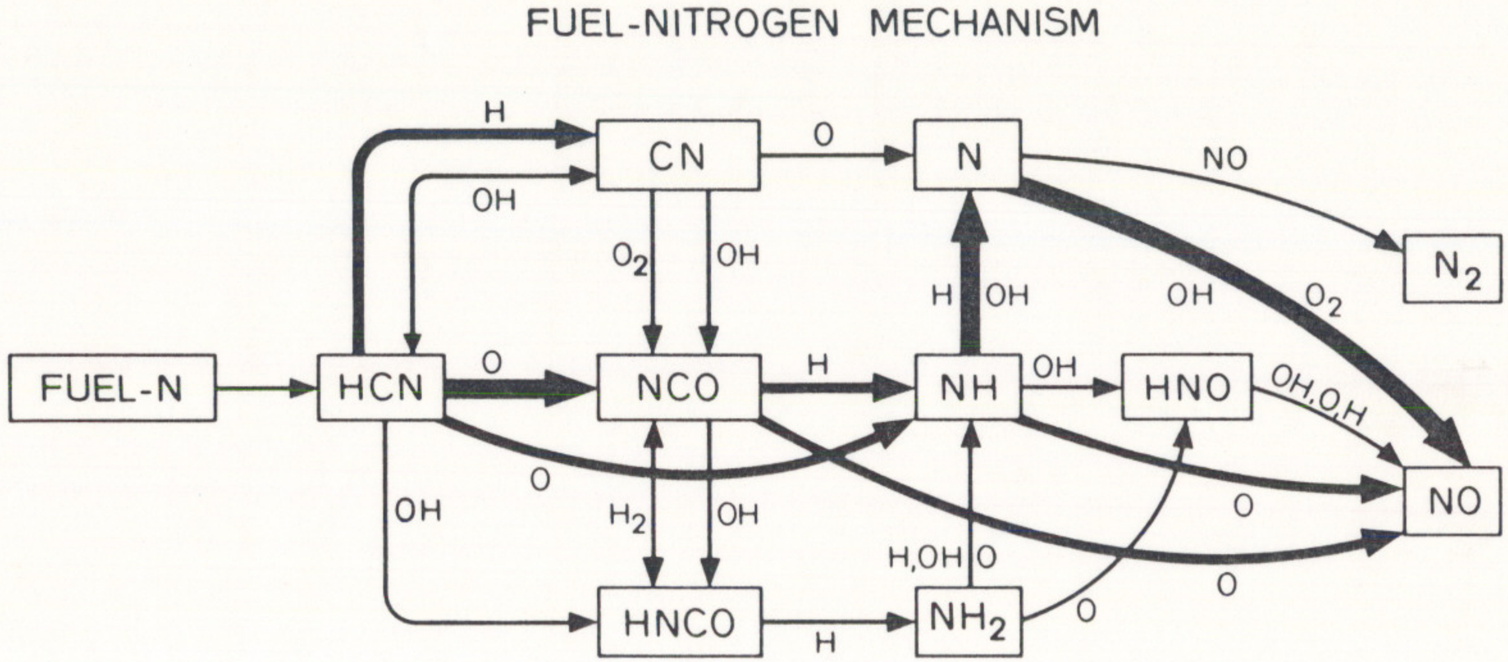


FIGURE 12. Schematic diagram of the principal reaction paths in the fuel nitrogen conversion process in flames.

fossil fuels are not well established. This uncertainty, coupled with the lack of data for reaction paths and rate coefficients for pyrolysis and oxidation of complex nitrogenous species, requires the introduction of simplifications in the model and restricts detailed reaction sets to those relevant to pyrolysis