

# Aerospace Propulsion

Lecture 4  
Combustion: Part II

# Combustion: Part II

- Rich Combustion
- Chemical Equilibrium
- Chemical Reactions
- Rate Coefficients
- Equilibrium Constants

# Rich Combustion

- Recall from last lecture:
  - Lean combustion ( $\phi < 1$ )
    - More air than needed to oxidize all fuel molecules
    - $\text{Fuel} + \text{Air} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{N}_2 + \text{O}_2$
  - Stoichiometric combustion ( $\phi = 1$ )
    - Exactly the right amount of air to oxidize all fuel molecules
    - $\text{Fuel} + \text{Air} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{N}_2$
  - Rich combustion ( $\phi > 1$ )
    - Not enough air to oxidize all fuel molecules
    - Can't just assume fuel remains unchanged like  $\text{O}_2$ , so what does it form?
    - $\text{Fuel} + \text{Air} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{N}_2 + ?$

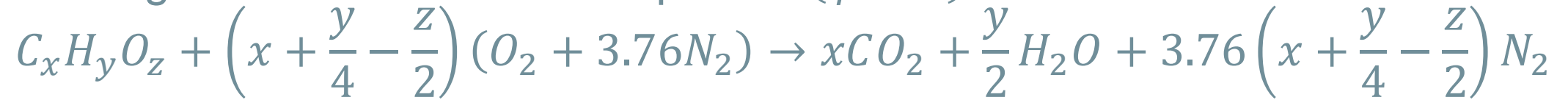
Based on the methods we've been using, how many products can the rich system have without being over/under-determined?

# Rich Combustion (Approach #1)

Can you derive this stoichiometric reaction at  $\phi = 1$ ?

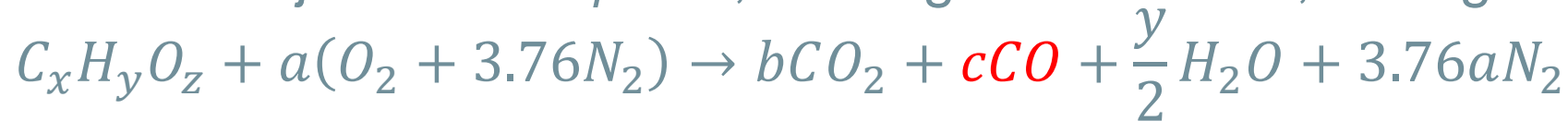
- Step 1:

- The general stoichiometric equation ( $\phi = 1$ ) can be written as:



- Then we can say,  $\left(\frac{F}{A}\right)_{stoich} = 1 / \left(x + \frac{y}{4} - \frac{z}{2}\right)$

- Assume that just above  $\phi = 1$ , we begin to form  $CO$ , then generally:



- $CO$  requires less  $O$  than  $CO_2$  so with higher  $\phi$ , get less  $CO_2$  and more  $CO$

- Range where above products are valid:  $1 \leq \phi \leq \frac{\left(x + \frac{y}{4} - \frac{z}{2}\right)}{\left(\frac{x}{2} + \frac{y}{4} - \frac{z}{2}\right)}$

$$\phi_{max} = \frac{(F/A)_A}{(F/A)_{st}} = \frac{\left(x + \frac{y}{4} - \frac{z}{2}\right)}{\left(\frac{x}{2} + \frac{y}{4} - \frac{z}{2}\right)}$$

Extreme Scenario  $\rightarrow$  no more  $CO_2$

Assume  $b \rightarrow 0$

C:  $X = C$

$$O: z + 2a = C + \frac{y}{2} \Rightarrow a = \frac{x}{2} + \frac{y}{4} - \frac{z}{2}$$

$$\left(\frac{F}{A}\right)_A = \frac{1}{\left(\frac{x}{2} + \frac{y}{4} - \frac{z}{2}\right)}$$

# Rich Combustion (Approach #1)

- Step 2:

- Next, assume we start forming  $H_2$ , then generally:



- $H_2$  requires less  $O$  than  $H_2O$  so with higher  $\phi$ , get less  $H_2O$  and more  $H_2$

- Range where above products are valid:  $\frac{(x + \frac{y}{4} - \frac{z}{2})}{(\frac{x}{2} + \frac{y}{4} - \frac{z}{2})} \leq \phi \leq \frac{(x + \frac{y}{4} - \frac{z}{2})}{(\frac{x}{2} - \frac{z}{2})}$

- Step 3:

- Even less oxygen available, start forming solid carbon instead of  $CO$ ...

- This is not how it happens, but is a decent approximation

Extreme case: no more  $H_2O$   
 $b \rightarrow 0$  |  $H: y = 2c$  |  $C = y/2$  |  $(\frac{F}{A})_A = \frac{1}{\frac{x}{2} - \frac{z}{2}}$  |  $\phi_{max} = \frac{(x + y/4 - z/2)}{(\frac{x}{2} - \frac{z}{2})}$   
 $O: z + 2a = x$  |  $a = \frac{x}{2} - \frac{z}{2}$

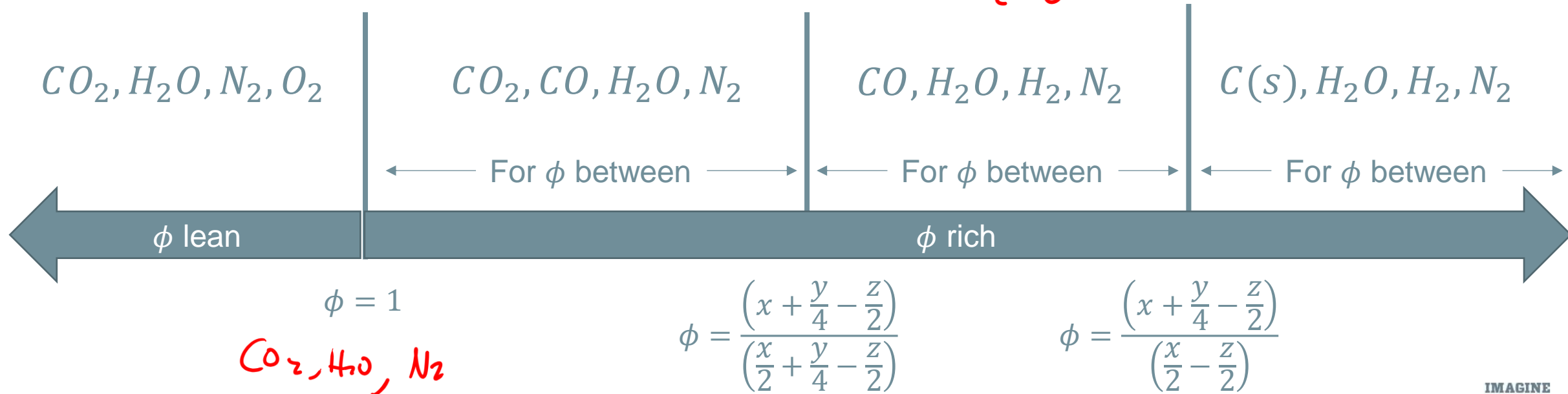
# Rich Combustion (Approach #1)

- Summary

- For fuel  $C_xH_yO_z$  reacting with air

E.g.  
 $CH_4$   
 $x=1$   
 $y=4$   
 $z=0$

Products to consider:

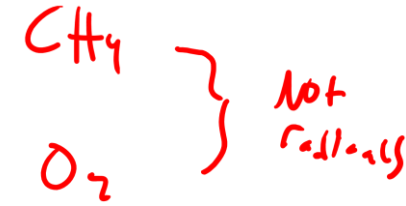


# Chemical Reactions

- Global Reactions
  - $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
  - Global reactions do not actually occur
  - Chemistry proceeds through a series of “elementary reactions”
    - Elementary reactions describe physical collisions between actual molecules
    - Elementary reactions can go forward or backwards
  - For example, Methane combustion relies on these reactions:



# Chemical Reactions



- Radicals and Chain Reactions
  - Combustion chemistry driven by production of radicals (molecules with unpaired valence electrons)
    - Examples:  $\text{OH}$ ,  $\text{H}$ ,  $\text{O}$ ,  $\text{CH}_3$
    - Radicals generally present in very small concentrations
    - However, they are extremely reactive
  - Explosive mixtures (i.e., ignition) require radical production to be faster than consumption
    - Chain Branching



# Chemical Reactions

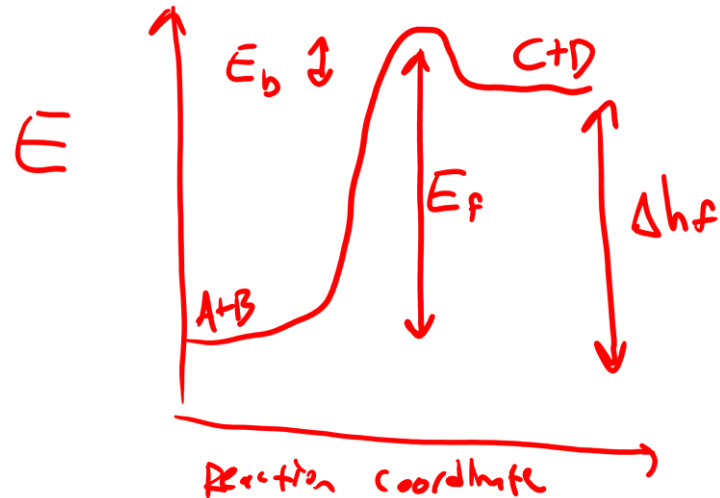
- Chain Branching
  - Series of reactions that ultimately increases total number of **radicals**
  - Combustion chemistry shares a common chain branching mechanism
    - $H + O_2 \leftrightarrow O + OH$
    - $H_2 + O \leftrightarrow OH + H$
    - $H_2 + OH \leftrightarrow H_2O + H$
    - $H_2 + OH \leftrightarrow H_2O + H$
  - Net:  $3H_2 + O_2 \rightarrow 2H_2O + 2H$

# Chemical Reactions

- Chain Initiation
  - Initial formation of radicals from stable species
  - Example:  $CH_4 \leftrightarrow CH_3 + H$
- Chain Termination
  - Consumption of radicals to form stable species
  - Example:  $H + OH + M \leftrightarrow H_2O + M$

# Chemical Reactions

- How quickly do reactions occurs?
  - Consider a general bimolecular reaction:  $A + B \leftrightarrow C + D$



- # reactions per time = (# collisions per time)  $\times$  (probability that collision partners have sufficient energy)

# Chemical Reactions



- How quickly do reactions occurs?
  - Number of collisions per time:  $A(T)C_A C_B$ 
    - Comes from kinetic theory
  - Probability of collision having sufficient energy:  $\exp\left(-\frac{E}{\bar{R}T}\right)$ 
    - Comes from statistical mechanics
  - Reaction Rate (Arrhenius Form),  $[w] = \text{mol}/(\text{m}^3\text{s})$

$$w = A(T) \exp\left(-\frac{E}{\bar{R}T}\right) C_A C_B = \underbrace{A(T) \exp\left(-\frac{E}{\bar{R}T}\right)}_{k(T)} C_A C_B$$

$f(T)$  ↙

$k(T)$ : Reaction Rate Coefficient

# Chemical Reactions

- Reaction Rates

- For a general elementary reaction



- Forward reaction rate:  $w_f = A_f(T) \exp\left(-\frac{E_f}{\bar{R}T}\right) C_A^a C_B^b \dots$

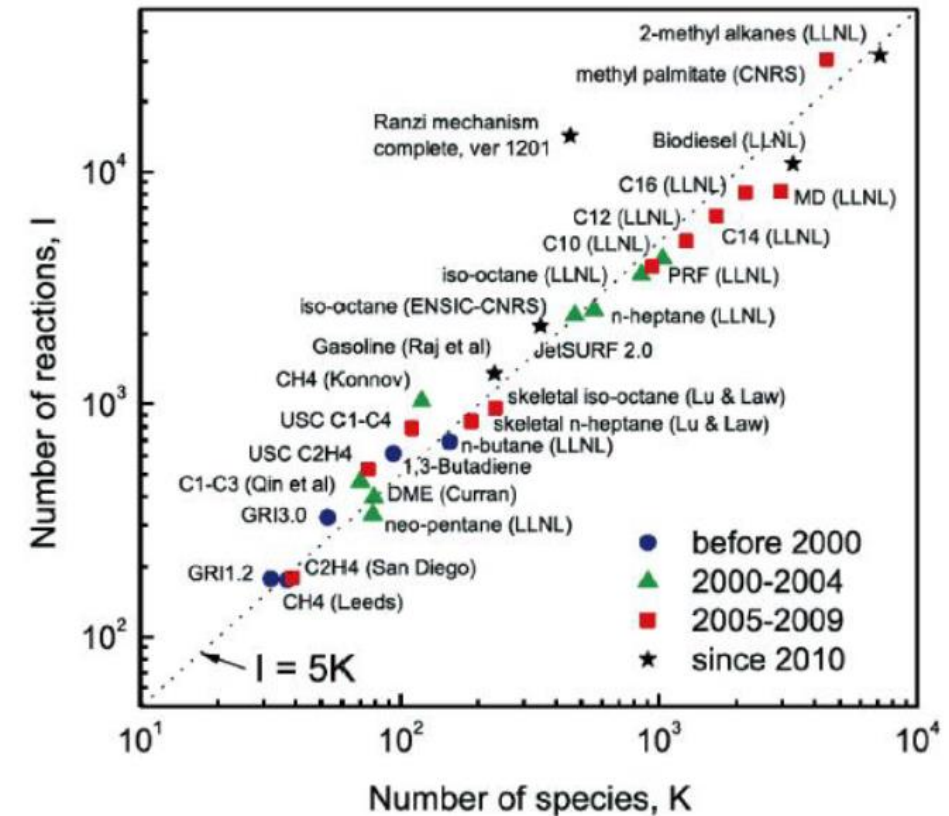
- Backward reaction rate:  $w_b = A_b(T) \exp\left(-\frac{E_b}{\bar{R}T}\right) C_Z^z C_Y^y \dots$

- Species Production Rates

- $\frac{dC_A}{dt} = -a(w_f - w_b)$
- $\frac{dC_Z}{dt} = z(w_f - w_b)$

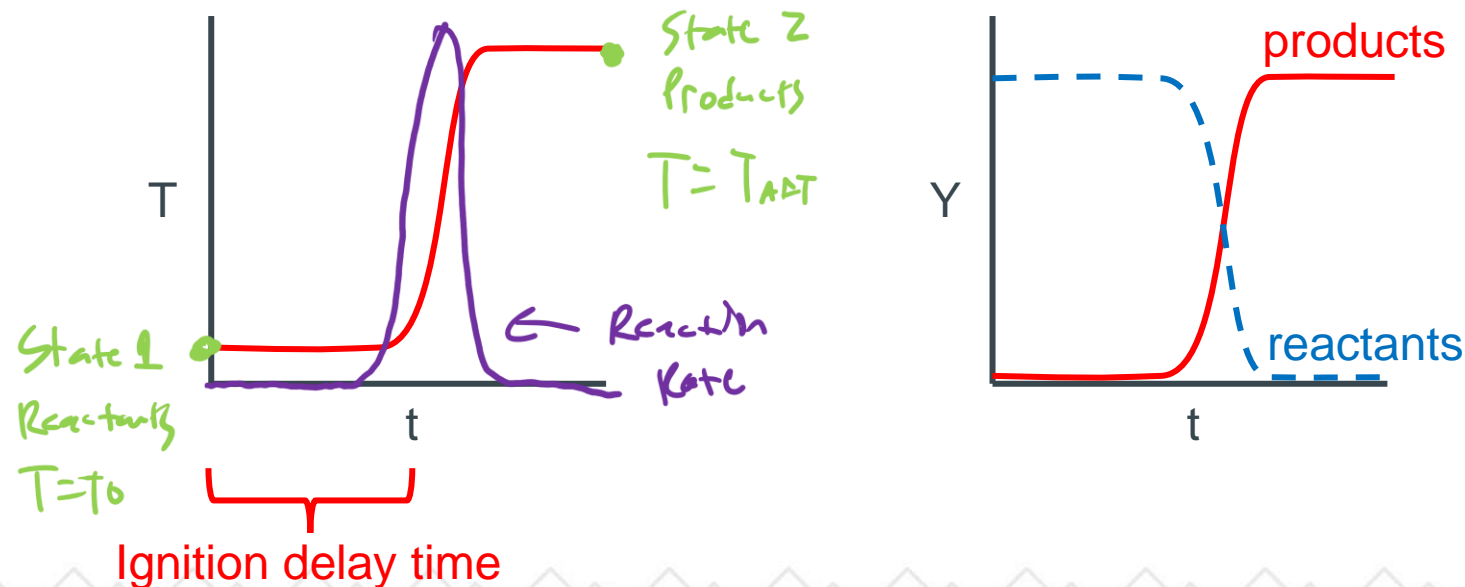
# Chemical Reactions

- Total species production rate is the sum of production rates from many individual elementary reactions
  - Methane combustion is usually described with 10's of species and 100's of reactions
  - Larger hydrocarbons (e.g., transport fuels) require 1000's of species and 100,000's of reactions



# Chemical Reactions

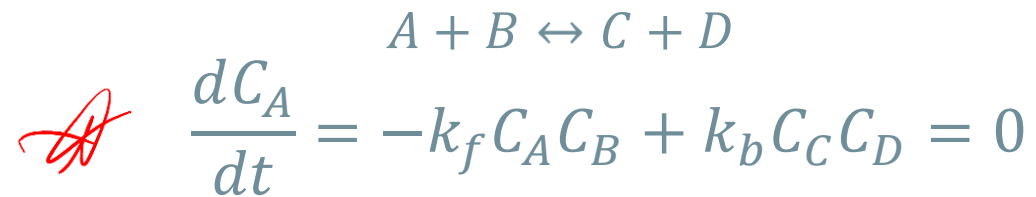
- Ignition delay time
  - Consider an adiabatic box homogeneously filled with reactants
  - Given enough time, reactants will become products
  - Slow at low temperatures, fast at high temperatures



# Equilibrium Constants

- Chemical Equilibrium

- At the molecular scale, molecules are constantly colliding and reacting
- At the macro scale, nothing happens at equilibrium
  - Concentration of each species is not changing



- However, note that it is the **\*sum\*** of forward and backward that is zero, not that either forward or backward is zero



# Equilibrium Constants

- Reaction rates and equilibrium constants



Forward:  $k_f C_A C_B$

Backward:  $k_b C_C C_D$

At equilibrium

$$k_f C_A C_B = k_b C_C C_D$$

$$\frac{k_f}{k_b} = \frac{C_C C_D}{C_A C_B} \equiv K_C$$

equilibrium  
constant  
↓

- For a general elementary reaction:



$$K_C(T) \equiv \frac{C_Z^z C_Y^y \dots}{C_A^a C_B^b \dots} = K_p(T) \left( \frac{p_{ref}}{\bar{R}T} \right)^{z+y+\dots-a-b-\dots} = \frac{k_f}{k_b}$$

Definition

Elementary reaction only

# Rich Combustion (Approach #2)

- How can we include all the products we've considered so far at once without creating an under-determined system?
  - $CO, CO_2, H_2, H_2O$
  - Preferably something valid at all  $\phi$
- Consider chemical equilibrium
  - Adds additional equations to balance our mathematical system
  - For example, water-gas shift reaction:  $CO + H_2O \leftrightarrow CO_2 + H_2$

# Chemical Equilibrium

- In short, chemical equilibrium represents the “steady state” for a chemical system where the ratio of molecules doesn’t change
- For a general reaction:
  - $aA + bB + \dots \leftrightarrow zZ + yY + \dots$  ( $a, b, z, y$ , are moles of molecule  $A, B, Z, Y$ )
  - There exists an **equilibrium constant** which is the ratio of the rate of forward reaction to the rate of backwards reaction at equilibrium.

$$K_p(T) \equiv \frac{\left(\frac{p_Z}{p_{ref}}\right)^z \left(\frac{p_Y}{p_{ref}}\right)^y \dots}{\left(\frac{p_A}{p_{ref}}\right)^a \left(\frac{p_B}{p_{ref}}\right)^b \dots} = \exp\left(-\frac{\Delta \bar{h}}{\bar{R}T}\right) \exp\left(\frac{\Delta \bar{s}^0}{\bar{R}}\right)$$

Additional equation  
relating moles of products

Computed from state

# Rich Combustion (Approach #2)

- Let's look at a rich methane example, what are the products?



- $1 = a + c$

- $2 = b + d$

- $2 = 2a + c + d$

- $\frac{ab}{dc} = \exp\left(-\frac{\Delta\bar{h}}{\bar{R}T}\right) \exp\left(\frac{\Delta\bar{s}^0}{\bar{R}}\right)$

$$\Delta\bar{h}(T) = \bar{h}_{CO_2}(T) + \bar{h}_{H_2}(T) - \bar{h}_{CO}(T) - \bar{h}_{H_2O}(T)$$

$$\Delta\bar{s}^0(T) = \bar{s}^0_{CO_2}(T) + \bar{s}^0_{H_2}(T) - \bar{s}^0_{CO}(T) - \bar{s}^0_{H_2O}(T)$$

- Eq. 4 needs  $T$  of products ( $T_{AFT}$ , must be computed)



$$\left. \begin{array}{l} \text{C: } 1 = a + c \\ \text{H: } 4 = 2b + 2d \\ \text{O: } 2 = 2a + c + d \end{array} \right\} \begin{array}{l} 3 \text{ eq.} \\ 4 \text{ unk.} \end{array}$$

Consider  $\text{H}_2\text{O} \leftrightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$  shift



Assume products @ Equilibrium

$$K_p = \frac{\left(\frac{P_{\text{CO}_2}}{P_{\text{ref}}}\right)^1 \left(\frac{P_{\text{H}_2}}{P_{\text{ref}}}\right)^1}{\left(\frac{P_{\text{CO}}}{P_{\text{ref}}}\right)^1 \left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{ref}}}\right)^1} = \exp\left(-\frac{\Delta \bar{h}}{RT}\right) \exp\left(\frac{\Delta \bar{S}^\circ}{R}\right)$$

$$= \frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}}} = \frac{(X_{\text{CO}_2} P)(X_{\text{H}_2} P)}{(X_{\text{CO}} P)(X_{\text{H}_2\text{O}} P)}$$

$$\frac{X_{\text{CO}_2} X_{\text{H}_2}}{X_{\text{CO}} X_{\text{H}_2\text{O}}} = \left(\frac{a}{a+b+c+d+3.76}\right) \left(\frac{b}{a+b+c+d+3.76}\right) \left(\frac{c}{a+b+c+d+3.76}\right) \left(\frac{d}{a+b+c+d+3.76}\right)$$

$$= \frac{ab}{cd} = \exp\left(\frac{-\Delta \bar{h}}{RT}\right) \exp\left(\frac{\Delta \bar{S}^\circ}{R}\right)$$

Evaluate at the product state

At the product state,

$$T = T_{\text{AFT}}$$

$$\Delta \bar{h}(T) = \Delta \bar{h}(T_{\text{AFT}}) = \bar{h}_{\text{CO}_2} + \bar{h}_{\text{H}_2} - \bar{h}_{\text{CO}} - \bar{h}_{\text{H}_2\text{O}}$$

$$\Delta \bar{S}^\circ(T) = \Delta \bar{S}^\circ(T_{\text{AFT}}) = \bar{S}_{\text{CO}_2}^\circ + \bar{S}_{\text{H}_2}^\circ - \bar{S}_{\text{CO}}^\circ - \bar{S}_{\text{H}_2\text{O}}^\circ$$

$$\frac{ab}{cd} = f(T_{\text{AFT}}) \rightarrow 1 \text{ eqn.}$$

# Rich Combustion (Approach #3)

- In approach #2, we were able to consider an additional product species by adding an additional equilibrium reaction
- In approach #3, we consider every (reasonably) possible chemical species by adding many equilibrium reactions
  - E.g.,  $H_2 + \frac{1}{2} O_2 \leftrightarrow H_2O$      $H_2 + O_2 \leftrightarrow 2OH$      $N_2 + O_2 \leftrightarrow NO$
  - Need  $N_s - 4$  reactions along with  $C, H, O, N$  element balance
  - How do additional species affect the AFT vs. complete combustion?
- This is extraordinarily tedious by hand
- Rely on computational codes to do it for us
  - See pset #2 for more details