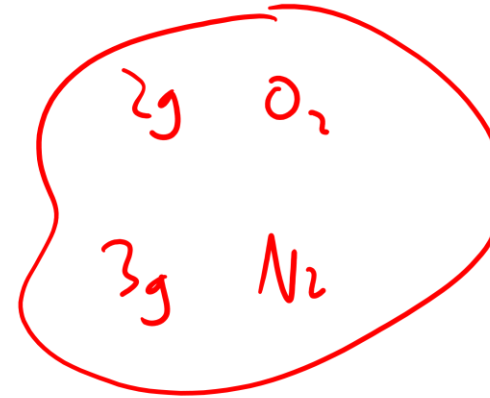# Aerospace Propulsion

Lecture 3

Combustion: Part I

Combustion: Part I

- Ideal Gas Mixtures

- Stoichiometry

- Thermochemistry

- Adiabatic Flame Temperature

Ideal Gas Mixtures

[handwritten annotation: a shape containing "2g O₂" and "3g N₂"]

[handwritten annotations:]
$i = O_2, N_2$

$M = M_{O2} + M_{N2}$
$2g + 3g$
$5g$

- Total Mass and Moles
  - Total Mass: $M = \sum M_i$ (where M_i is the mass of species i)
  - Total Moles: $N = \sum N_i$ (where N_i is the moles of species i)

- Density and Concentration
  - Density: $\rho = \dfrac{M}{V}$, $\rho_i = \dfrac{M_i}{V}$
  - Concentration: $C = \dfrac{N}{V}$, $C_i = \dfrac{N_i}{V}$

[handwritten annotations:]
$N = \#\text{moles}$

$1 \text{ mole} = 6.022 \times 10^{23} \text{ molecules}$

Ideal Gas Mixtures

- Mass Fractions and Mole Fractions
  - Mass Fraction: $Y_i = \frac{M_i}{M} = \frac{\rho_i}{\rho}$
    - $\sum Y_i = \frac{\sum M_i}{M} = 1$
  - Mole Fraction: $X_i = \frac{N_i}{N} = \frac{C_i}{C}$
    - $\sum X_i = \frac{\sum N_i}{N} = 1$
  - Mixture Energy, Enthalpy, Entropy
    - $u = \sum Y_i u_i \qquad \bar{u} = \sum X_i \bar{u}_i$
    - $h = \sum Y_i h_i \qquad \bar{h} = \sum X_i \bar{h}_i$
    - $s = \sum Y_i s_i \qquad \bar{s} = \sum X_i \bar{s}_i$

Ideal Gas Mixtures

- Component Molar Mass: $\bar{M}_i$
  - Average mass of one mole of gas i
  - Molecular gas: sum average molar masses of constituent elements
    - $\bar{M}_H = 1.008 \frac{g}{mol}$ $\bar{M}_C = 12.01 \frac{g}{mol}$ $\bar{M}_N = 14.01 \frac{g}{mol}$ $\bar{M}_O = 16.00 \frac{g}{mol}$
    - Example: $\bar{M}_{H_2O} = 18.016 \frac{g}{mol}$

$$\bar{M}_{H_2O} = 2\bar{M}_H + \bar{M}_O$$

Ideal Gas Mixtures

- Mixture Molar Mass: $\overline{M}$
  - Average mass of one mole of gas mixture

  - $\overline{M} = \sum X_i \overline{M}_i$

$$\widehat{M} = \frac{M}{N} = \frac{\sum M_i}{N} = \sum \frac{M_i}{N} = \sum \left(\frac{M_i}{N_i}\right)\left(\frac{N_i}{N}\right) = \sum_i \overline{M}_i X_i$$

  - $\overline{M} = \dfrac{1}{\sum \dfrac{Y_i}{\overline{M}_i}}$

$$\frac{1}{M} = \frac{N}{M} \qquad \cdot \quad \cdot \cdot$$

Ideal Gas Mixtures

- Converting between mass and mole fractions

- $Y_i = X_i \left(\dfrac{\bar{M}_i}{\bar{M}} \right)$

$$Y_i = \frac{M_i}{M} = \left(\frac{M_i}{N_i} \right)\left(\frac{N_i}{N} \right)\left(\frac{N}{n} \right) = \bar{M}_i \, X_i \, \frac{1}{\bar{M}}$$

- $X_i = Y_i \left(\dfrac{\bar{M}}{\bar{M}_i} \right)$

Ideal Gas Mixtures

- Partial Pressure
  - Pressure of component i of the mixture if it were isolated at same T, V
  - $p_i = X_i p$ ← pressure

Partial Pressure of i

mole fraction of i

For Component

$$p_i V = N_i RT$$

$$p_i = \frac{N_i RT}{V}$$
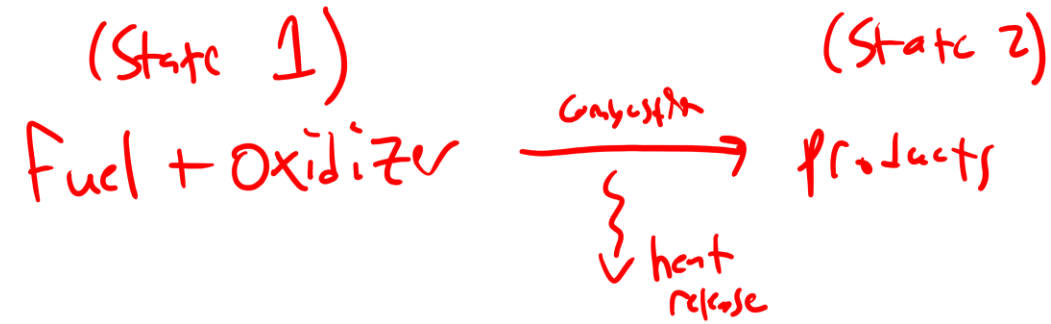
Recall

$$X_i = \frac{N_i}{N}$$

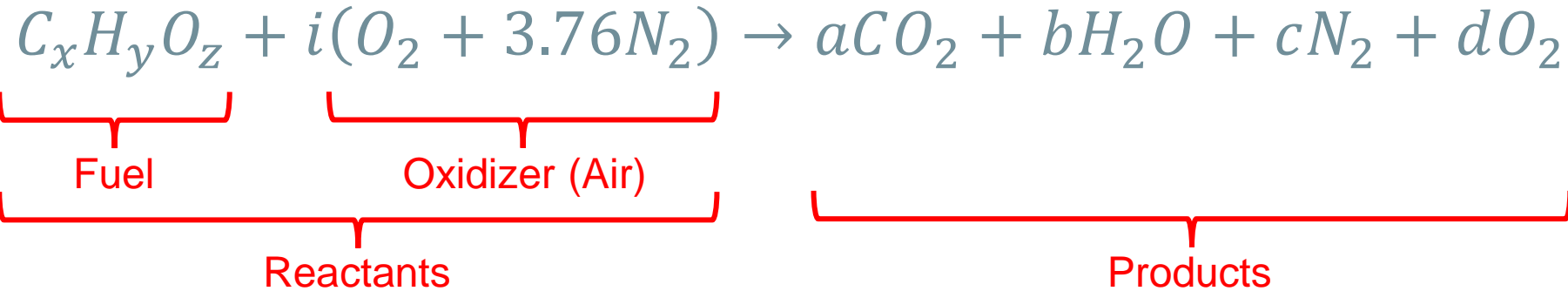$$N_i = N X_i$$

Combine

$$p_i = X_i \boxed{\frac{NRT}{V}}\; \text{``p''} \quad \Rightarrow \quad p_i = X_i p$$

Stoichiometry

(State 1)

Fuel + Oxidizer $\xrightarrow{\text{Combustion}}$ Products

$\{$ heat release

- **Complete Combustion**
  - All fuel is fully converted to <u>major</u> products (e.g., CO_2 and H_2O)
  - In general, complete combustion of fuel (containing C, H and, O) and air:
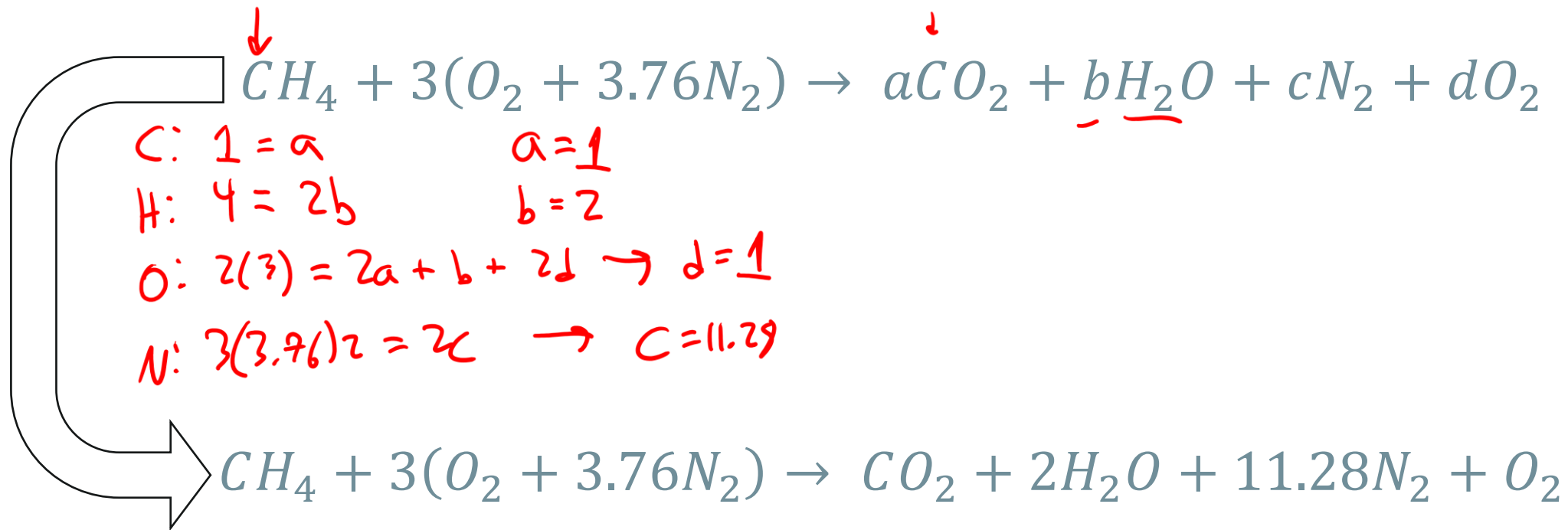
$$C_xH_yO_z + i(O_2 + 3.76N_2) \rightarrow aCO_2 + bH_2O + cN_2 + dO_2$$

e.g.
CH4
H2
C2H4

Fuel | Oxidizer (Air)

Reactants

Products

  - x, y, z specify the specific fuel being burned
  - i specifies the molar ratio between fuel and air
  - a, b, c, d are solved for through element conservation

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Stoichiometry

- Example reaction: 1 mole of methane with 3 "moles of air"

$$CH_4 + 3(O_2 + 3.76N_2) \rightarrow aCO_2 + bH_2O + cN_2 + dO_2$$

C: $1 = a$ $a = \underline{1}$

H: $4 = 2b$ $b = 2$

O: $2(3) = 2a + b + 2d \rightarrow d = \underline{1}$

N: $3(3.76)2 = 2c \rightarrow c = 11.28$

$$CH_4 + 3(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 11.28N_2 + O_2$$

Stoichiometry

$$\boxed{X_i = \frac{N_i}{N}}$$

$$X_{R,CH_4} = \frac{N_{R,CH_4}}{N_R}$$

$$Y_{R,CH_4} = \frac{M_{R,CH_4}}{M_R}$$

- **Stoichiometric Combustion**
  - Subcase of complete combustion
  - Exactly enough oxidizer to react with all fuel

$$X_{R,CH_4} = \frac{1}{1+2+7.52}$$
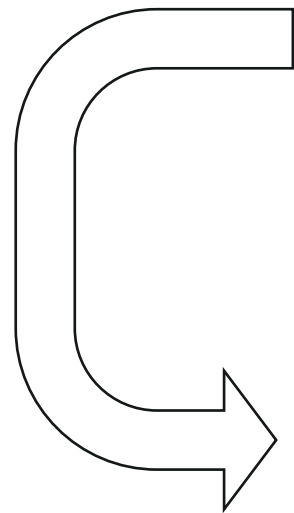
$$X_{R,CH_4} = 0.0947$$

$$Y_{R,CH_4} = \frac{(N_{R,CH_4})(\bar{M}_{CH_4})}{(N_{R,CH_4})(\bar{M}_{CH_4}) + (N_{R,O_2})(\bar{M}_{O_2}) + (N_{R,N_2})(\bar{M}_{N_2})}$$

$$Y_{R,CH_4} = 0.0417$$

$$CH_4 + i(O_2 + 3.76N_2) \rightarrow aCO_2 + bH_2O + cN_2$$

$$C: 1 = a \qquad a = 1$$
$$H: 4 = 2b \qquad b = 2$$
$$O: 2i = 2a+b \qquad c = 7.52$$
$$N: 2(3.76)i = 2c \qquad i = 2$$

$$X_{P,H_2O} = \frac{2}{1+2+7.52}$$

$$X_{P,H_2O} = 0.19$$

$$CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 7.52N_2$$

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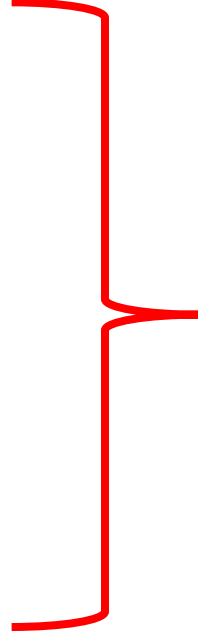
Stoichiometry

- Stoichiometric combustion
  - Exactly enough air to react with all fuel
  - The stoichiometric condition is the dividing line between "lean" and "rich" combustion

Complete combustion (in the ideal case)

- Lean combustion (or fuel-lean combustion)
  - Excess oxidizer (products include oxygen)

- Rich combustion (or fuel-rich combustion)
  - Excess fuel (incomplete combustion)

Incomplete combustion

Stoichiometry

- **Incomplete Combustion**
  - Not all fuel is fully converted to major products

- Rich combustion products are more than CO_2 and H_2O (+ O_2/N_2)
  - Primarily includes CO and H_2, but also many other species
  - More information next lecture

- In practice, is combustion ever actually complete?

  No, entropy plays a role

Stoichiometry

- Fuel-to-Air Ratio
  - Mass ratio of fuel to air: $\dfrac{M_f}{M_a}$
  - Example for stoichiometric methane-air: 0.058

- Equivalence Ratio ϕ
  - Measure of fuel-to-air ratio relative to stoichiometric mixture
  - $\phi = \dfrac{\left(\dfrac{M_f}{M_a}\right)_{actual}}{\left(\dfrac{M_f}{M_a}\right)_{stoich}}$

$\phi < 1$, lean
$\phi = 1$, stoichiometric
$\phi > 1$, rich

General Reaction Equation

1. Start with the stoichiometric equation and compute i_{st}:
$$C_xH_yO_z + i_{st}(O_2 + 3.76N_2) \rightarrow aCO_2 + bH_2O + cN_2$$

2. If problem is stoichiometric, compute a, b, c and you are done.

3. Otherwise, write a reaction with expected products and your equivalence ratio. For example, for lean combustion:
$$\phi C_xH_yO_z + i_{st}(O_2 + 3.76N_2) \rightarrow aCO_2 + bH_2O + cN_2 + dO_2$$

4. Use i_{st} computed above and given ϕ. Compute a, b, c, d.

5. For rich combustion, LHS is the same as in 3. but products on RHS will differ (next lecture).

Thermochemistry

- Enthalpy (and Internal Energy)
  - For pure substances, we previously needed to define a reference temperature to define enthalpy

$$h = \int_{T_{ref}}^{T} c_p \, dT' + h(T_{ref})$$

  - Since we only ever care about *relative* enthalpies, we can conveniently set the enthalpy at reference temperature to zero for **pure substances**

  - For a gas mixture with composition changes, reference enthalpy matters
    - Not all species have the same reference enthalpy

Thermochemistry

- Enthalpy (and Internal Energy)
  - Therefore, also define a reference relative to some **reference species**
    - Reference temperature usually chosen as 298K
    - References species usually chosen as $H_2, N_2, O_2, C(s)$
    - Not every table uses the same references!!!

  - For any other non-reference species, enthalpy at reference temperature is relative to these four reference molecules.
    - Enthalpy of formation of species i: h_{fi}

$$h_i(T) = \int_{T_{ref}}^{T} c_{p,i}\, dT' + h_{fi}(T_{ref}) = \left[h_i(T) - h_i(T_{ref}) \right] + h_{fi}(T_{ref})$$

only for 1 component

Sensible Enthalpy   Enthalpy of Formation   Sensible Enthalpy $= \Delta h_{s,i}$ Enthalpy of Formation

Thermochemistry

Water (H_2O) $H_2O_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1} mol^{-1}				kJ·mol^{-1}		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	-9.904	-238.921	-238.921	INFINITE
100	33.299	152.388	218.534	-6.615	-240.083	-236.584	123.579
200	33.349	175.485	191.896	-3.282	-240.900	-232.766	60.792
298.15	33.590	188.834	188.834	0.	-241.826	-228.582	40.047

Note: We will always work with gaseous water!

• Enthalpy of Formation (h_{fi})

   • For this class, our source will be the JANAF tables (janaf.nist.gov)
   • Enthalpy of formation is the energy to make/break chemical bonds
   • Corresponds to energy required to form molecules from reference molecules at T_{ref}
   • **Always evaluate this quantity at T_{ref}!!!**

   • Example: Look up enthalpy of formation of H_2O

$$h_{f, H_2O}(T_{ref}) = -241.826 \frac{kJ}{mol}$$

Thermochemistry

Water (H_2O) $H_2O_1(g)$

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298.15	33.590	188.834	188.834	0.	-241.826	-228.582	40.047

- Entropy
  - Evaluate component entropy with partial pressure

$$s_i(T) = s_i(T_{ref}, p_{ref}) + \int_{T_{ref}}^{T} c_{p,i}\frac{dT'}{T'} - R_i \ln\frac{p_i}{p_{ref}}$$

one component → ↗ 0   ← *Partial Pressure*

  - No need for reference composition for entropy
    - Entropy for all species is zero at entropy reference T and p ($T = 0$ K and $P = 1$ atm)
    - $s_i(T_{ref}, p_{ref}) = 0$
  - Notation most useful for table lookup:

Always true

$$s_i(T) = \int_{0K}^{T} c_{p,i}\frac{dT'}{T'} - R_i \ln\frac{p_i}{p_{ref}} = s_i^0(T) - R_i \ln\frac{p_i}{p_{ref}}$$

Adiabatic Flame Temperature

- The adiabatic flame temperature is the theoretical maximum temperature for complete, adiabatic combustion at constant volume or pressure
  - Would we ever actually reach this temperature?

  No, entropy

- Recall the first law for an adiabatic system
  - Generally: $du = -pdv$ and $dh = vdp$
  - Constant volume: $du = 0$
  - Constant pressure: $dh = 0$

> What burns hotter, a flame at constant pressure or constant volume?

Adiabatic Flame Temperature

Slide 11
for Y
Calculations

- Computing the adiabatic flame temperature (isobaric example)
  - $CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 7.52N_2$ (methane-air, $\phi = 1$)
  - Reactants are at T_0, while products have been heated to T_{ad}

Isobaric
$dh = 0$

$h_{reac} = h_{prod}$

Recall
$h = \Sigma_i y_i h_i$
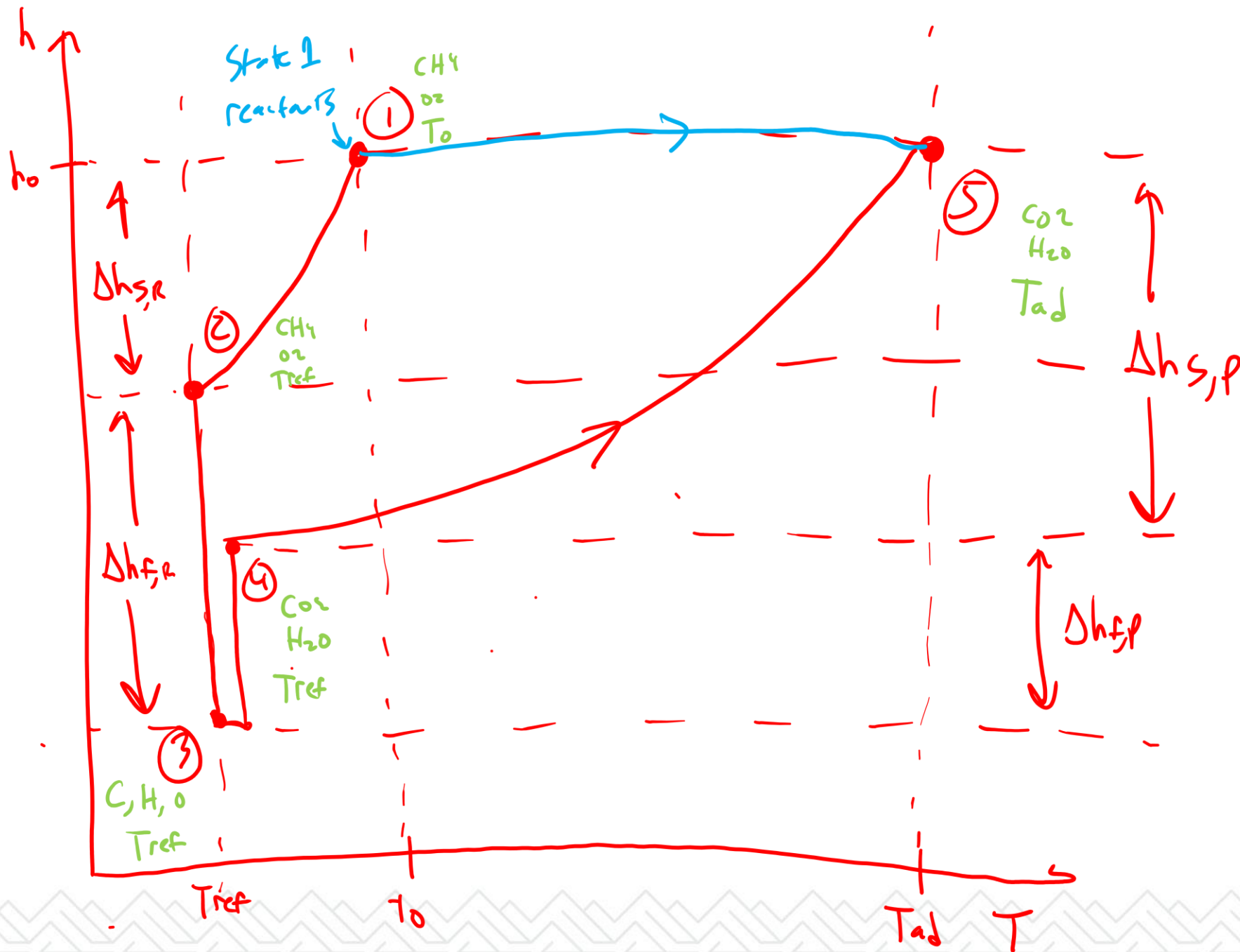
$h_i = \Delta h_{S,i}(T) + h_{F,i}(T_{ref})$

$$Y_{R,CH_4} h_{CH_4}(T_0) + Y_{R,O_2} h_{O_2}(T_0) + Y_{R,N_2} h_{N_2}(T_0) = Y_{P,CO_2} h_{CO_2}(T_{ad}) + Y_{P,H_2O} h_{H_2O}(T_{ad}) + Y_{P,N_2} h_{N_2}(T_{ad})$$

expand all enthalpies

$=$

$$Y_{R,O_2}\left[\Delta h_{S,O_2}(T_0) + h_{F,O_2}(T_{ref})\right]$$

unit conversion!

JANAF
$H - H^0(T_r)$
@ T_0

JANAF
$\Delta_F H^0$
@ T_{ref}

$=$

$$Y_{P,H_2O}\left[\Delta h_{S,H_2O}(T_{ad}) + h_{F,H_2O}(T_{ref})\right]$$

Iterative, $T_{ad} = 2318 K$

$\rightarrow T_{actual} = 2226 K$

with curve fit

IMAGINE
U

$$h = \int_{T_{ref}}^{T} c_p \, dT' + h_f(T_{ref})$$

State 1
reactants

① CH_4, O_2, T_0

⑤ CO_2, H_2O, T_{ad}

$\Delta h_{s,R}$

② CH_4, O_2, T_{ref}

$\Delta h_{s,P}$

$\Delta h_{f,R}$

④ CO_2, H_2O, T_{ref}

$\Delta h_{f,P}$

③ C, H, O, T_{ref}

h_0

T_{ref} T_0 T_{ad} T

Adiabatic Flame Temperature

- Computing the adiabatic flame temperature this way is the most accurate, but is an iterative process
    1. Guess T_{ad}
    2. Look up enthalpies at T_{ad}
    3. Compute enthalpy/energy balance
    4. Repeat 1-3 until equation is successfully balanced

- What if we assume constant specific heats?
    - $\Delta h_{s,i}(T) = c_p \Delta T$ and AFT can be computed directly