



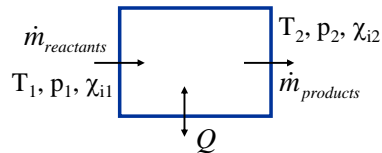
Chemical TD: Motivation

- **Previous TD Analysis**
 - considered systems where composition of fluid was “frozen” – fixed chemical composition
- **Chemically Reacting Flow**
 - but there are numerous situations in propulsion systems where chemical reactions can occur
 - burning (jet engine combustors, augmentors, rocket combustion chambers, piston engines)
 - supersonic compression (supersonic inlets)
 - supersonic expansion (rocket nozzles)
 - other (fuel cells, monopropellant decomposition)



Basic Problem

- Usually **Given**:
 - reactant state (composition, $\dot{m}_{reactants}$, temp., pressure)
 - constraints (heat transfer, residence time, ...)
- Want to **Find**: product state (χ_{i2} , T_2 , p_2)
- **Approach**: (Equilibrium) TD analysis: conservation eqns., state eqns. (and enough time to reach equil.)
- **Issues**: how to deal with
 1. “chemical energy”
 2. specifying equilibrium composition





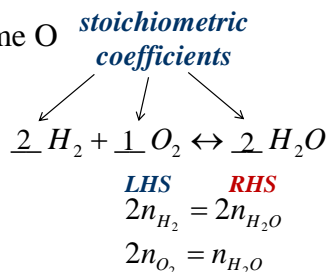
Approach Outline

1. Apply mass conservation
 - atom balances or balancing stoichiometric reactions
2. Apply energy conservation
 - defining chemical “energy” or enthalpy of formation
3. Apply entropy conservation (2nd Law)
 - maximize entropy to find equilibrium



Atom Balances/Stoichiometric Reactions

- If composition can change, we will see the amount of some species decrease and others increase
- Are there any constraints on this process?
 - YES – can’t change the identify of the nuclei (in absence of nuclear reactions)
 - for example, N can not become O
- Two ways to express this
 - “balancing” stoichiometric reaction
 - atom balances





Chemical Energy

- In nonreacting TD
 - we combined all different types of energy into stagnation enthalpy,

$$h_o = h + u^2/2$$
 - but of course, the value of h depends on our choice of reference state; does $h(0K)=0$ or $h(298K)=0$?
- Our goal – for chemically reacting system want to find way to add chemical energy

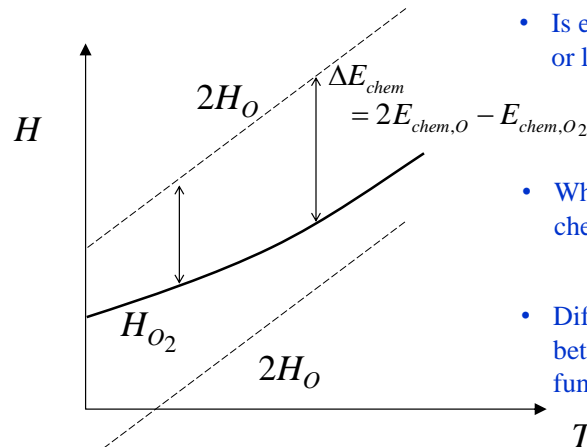
$$h_o = h + u^2/2 + e_{chem}$$

- but to do so, we need to define a reference “state” where chemical energy is zero



Chemical Energy Example

- Consider the energies of O_2 and O $O_2 \leftrightarrow 2O$



- Is energy of O more or less than for O_2 ?

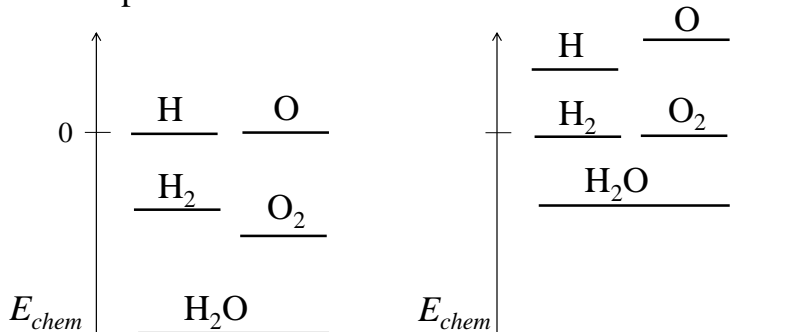
- Which has zero chemical energy?

- Difference in energy between species is function of temp.



Chemical Energy Example

- What happens if we have multiple types of nuclei?
 - ways to define *zero chemical energy state*
- Example: H and O containing species at fixed temperature



Equl Chem TD-7
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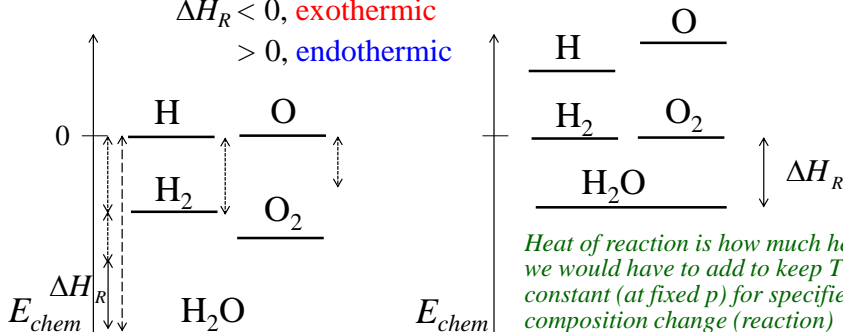


Heat of "Reaction"

- What is the energy difference between the *products* and *reactants* if p,T don't change, e.g., $H_2 + 1/2 O_2 \leftrightarrow H_2O$

Heat of Reaction Q_R or $\Delta H_R = E_{chem,H_2O} - (E_{chem,H_2} + 1/2 E_{chem,O_2}) = H_p - H_r$
result can't depend on what we call zero energy (reference state)

$\Delta H_R < 0$, **exothermic**
 > 0 , **endothermic**



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Heat of Formation

- Heat of reaction if form ONE mole of species i from the ZERO energy species (the *elements*) at fixed temperature T and standard pressure ($^\circ$)

$$\Delta \bar{h}_{f,T,i}^\circ$$

– or on a per mass basis

$$\Delta h_{f,T,i}^\circ$$

- Two common choices for elements
 - the (neutral) atoms
 - the most common form of a single type of nuclei at standard T and p

NASA Tables

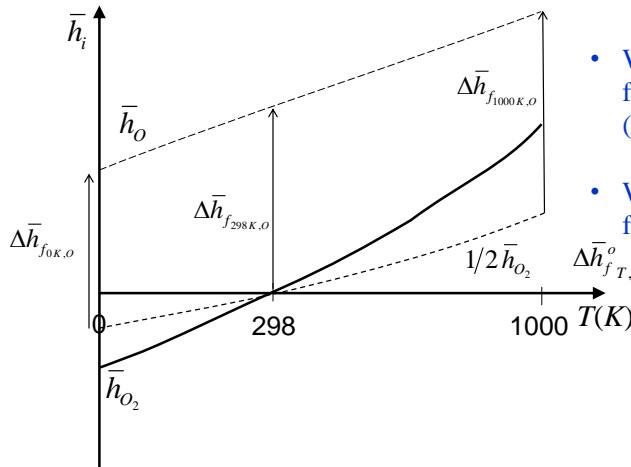
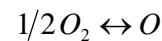
JANNAF

H₂, O₂, N₂,
Ar, C (s) graphite



Heat of Formation Example

- Consider again O₂ and O



- What is enthalpy of formation of O₂ (JANNAF)?

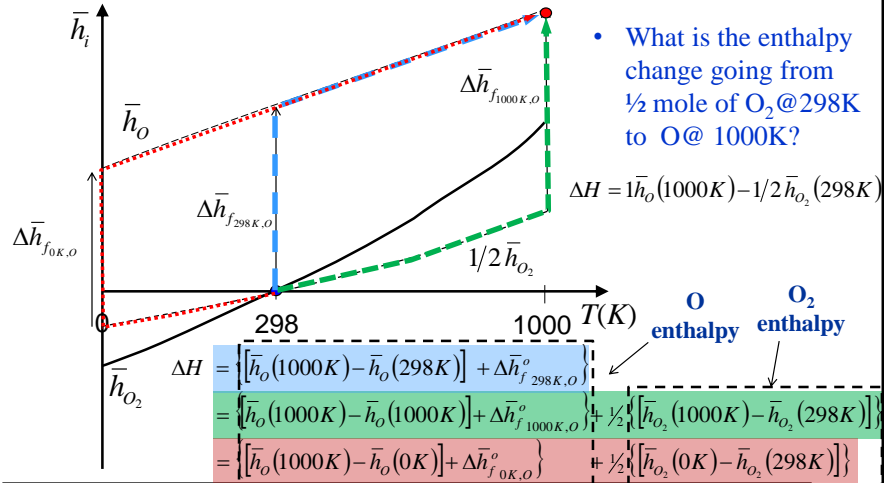
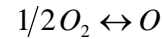
- What is enthalpy of formation of O?

$$\Delta \bar{h}_{f,T,O}^\circ = \bar{h}_O(T) - 1/2 \bar{h}_{O_2}(T)$$



Heat of Formation Example

- Consider again O₂ and O



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General Expression for Enthalpy

- So from the previous path example, we can write in general

$$\bar{h}_i(T) = \underbrace{(\bar{h}_T - \bar{h}_{T_{ref}})_i}_{\text{sensible } h \text{ change}} + \underbrace{\Delta \bar{h}_{f,T_{ref},i}^\circ}_{\text{chem. energy}} = \int_{T_{ref}}^T \bar{c}_{p,i} dT + \Delta \bar{h}_{f,T_{ref},i}^\circ$$

(II.14a)

- or on a per mass basis

(II.14b)

$$h_i(T) = (h_T - h_{T_{ref}})_i + \Delta h_{f,T_{ref},i}^\circ = \int_{T_{ref}}^T c_{p,i} dT + \Delta h_{f,T_{ref},i}^\circ$$

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Example Enthalpies of Formation

Species	$\Delta h_{f,298.15\text{ K}}^{\circ}$ kJ/mol
CO	-110.53
CO ₂	-393.52
CH ₄	-74.87
H	218.00
H ₂ O	-241.83
O	249.17
OH	38.99

From NIST-JANNAF
database 4th edition
(1998)
(e.g., kinetics.nist.gov/janaf)

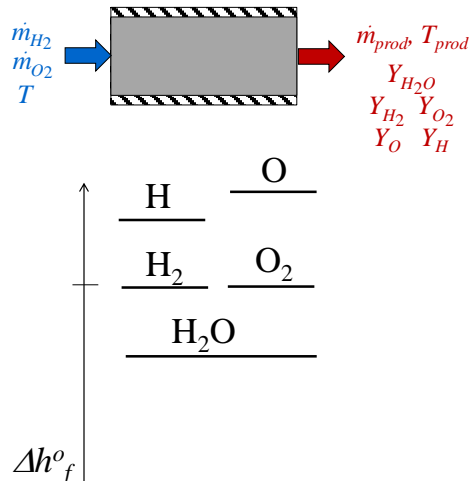
can find newer updates
to data

- High formation enthalpy species
 - H, O
 - High energy*
⇒ hard to make (unstable atoms)
- Low formation enthalpy
 - CO₂, H₂O
 - Low energy (<<0)*
⇒ very stable at "low" T



Composition Influence on Temperature

- So if the products have more H, O, H₂, O₂ vs. H₂O
 - T_{prod} will be lower than **if** we could shift them toward water

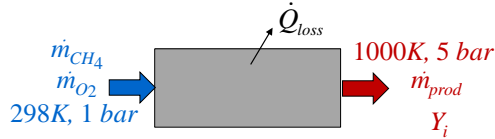




Example: Methane/Oxygen Combustor

• **Given:**

- Gaseous methane and oxygen entering non-adiabatic combustor at 298 K, 1 bar (stagnation conditions)
- Mass flowrate ratio of oxygen is 5× that for methane
- Heat loss results in 1000 K product temperature



• **Find:**

- Heat loss rate per unit mass flow rate, \dot{Q}_{loss}/\dot{m}

• **Assume:**

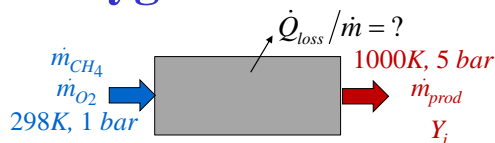
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Example: Methane/Oxygen Combustor

• **Solution**

- mass
 $\dot{m}_{in} = \dot{m}_{exit} \equiv \dot{m}$
- energy cons. (PICO)



- need to know composition of reactants and products

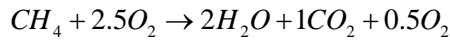
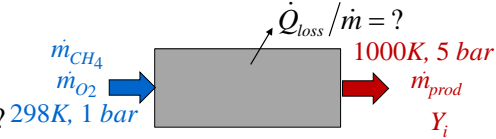
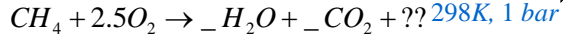
- reactants $\frac{\dot{m}_{O_2}}{\dot{m}_{CH_4}} = \frac{5}{1} \Rightarrow \frac{n_{O_2}}{n_{CH_4}} = \frac{2.5}{1}$



Example: Methane/Oxygen Combustor

• Solution

– products?

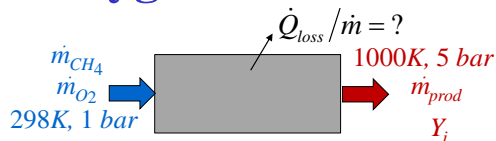


$$\begin{aligned} \chi_{CH_4,r} &= 1/3.5 & \chi_{H_2O,p} &= 2/3.5 \\ \chi_{O_2,r} &= 2/3.5 & \chi_{CO_2,p} &= 1/3.5 \\ & & \chi_{O_2,p} &= 0.5/3.5 \end{aligned}$$



Example: Methane/Oxygen Combustor

• Solution



	$h_{1000K} - h_{298K}$ (kJ/mol)	$\Delta h_{f,298K}$ (kJ/mol)
CH ₄	38.179	-74.87
O ₂	22.703	---
H ₂ O	26.000	-241.83
CO ₂	33.397	-393.52

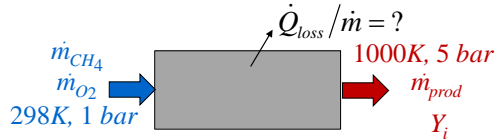
$$\frac{\dot{Q}_{loss}}{\dot{m}} = 7.35 \frac{MJ}{kg} \text{ or } \frac{MW}{kg/s} \quad \text{For just 10 kg/s, would need to have 74 MW of cooling}$$

from janaf.nist.gov, with $T_{ref} = 298K$



Example: Methane/Oxygen Combustor

- Alternate solution



$$\frac{\dot{Q}_{loss}}{\dot{m}} = 7.36 \frac{MJ}{kg} < 1\% \text{ difference}$$

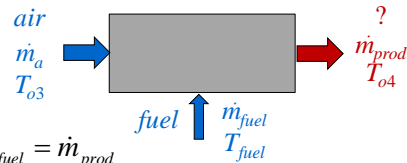
Product	c _p (J/molK)		
	298 K	1000 K	c _{p,avg}
H ₂ O	33.590	41.268	37.43
CO ₂	37.129	54.308	45.72
O ₂	29.376	34.870	32.13

from janaf.nist.gov



Simplified Eqn for Aircraft Combustor

- Want simplified expression we can use for engine cycle modeling
- Consider an adiabatic combustor



– mass conservation $\dot{m}_{air} + \dot{m}_{fuel} = \dot{m}_{prod}$

– energy conserv. $\dot{m}_{air} h_{o3} + \dot{m}_{fuel} h_{fuel} = \dot{m}_{prod} h_{o4}$

– group chem. vs. sensible terms

$$h_i(T) = \Delta h_i|_{T_{ref}}^{T_i} + \Delta h_{f,T_{ref},i}$$

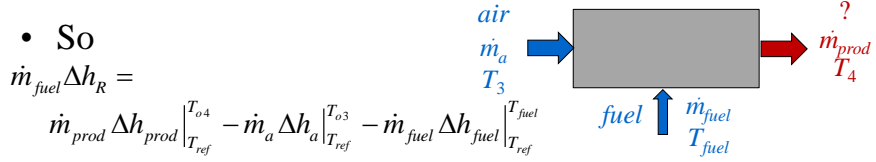
$$\left(\dot{m}_a \Delta h_{f_a}^o + \dot{m}_{fuel} \Delta h_{f_{fuel}}^o - \dot{m}_{prod} \Delta h_{f_{prod}}^o \right)_{T_{ref}} \leftarrow \equiv \dot{m}_{fuel} \Delta h_R$$

Fuel Heating Value
energy release per mass fuel at T_{ref}
~44MJ/kg for jet fuel

$$= \dot{m}_{prod} \Delta h_{prod}|_{T_{ref}}^{T_{o4}} - \dot{m}_a \Delta h_a|_{T_{ref}}^{T_{o3}} - \dot{m}_{fuel} \Delta h_{fuel}|_{T_{ref}}^{T_{fuel}}$$



Simplified Eqn for Aircraft Combustor



• If we assume $h_{sens,i}(T_{ref})=0, T_{fuel} \sim T_{ref}$

$$\dot{m}_{fuel} \Delta h_R = (\dot{m}_a + \dot{m}_{fuel}) h_{o4} - \dot{m}_a h_{o3}$$

Fuel-Air Ratio

$$f \equiv \dot{m}_{fuel} / \dot{m}_a \quad f \Delta h_R = (1 + f) h_{o4} - h_{o3} \quad \text{chem. term } (f \Delta h_R) \text{ looks like heat addition } (Q_R)$$

– assume cp, products and air have same $c_p, T_{ref} \approx 0$

$$\frac{f \Delta h_R}{c_p} = (1 + f) T_{o4} - T_{o3}$$

$$\Rightarrow T_{o4} = \frac{T_{o3} + f \Delta h_R / c_p}{1 + f}$$

$$\text{and } f = \frac{T_{o4} - T_{o3}}{\Delta h_R / c_p - T_{o4}}$$

(II.15a)

(II.15b)