Jet and Rocket Propulsion

AE4451

LECTURE 6

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Overview

what we saw last time:

- mixtures of perfect gases
  - calculations: summation over constituents and averaged properties

today:

- chemical equilibrium thermodynamics

Chemical equilibrium thermodynamics

- up to this point, we've considered "frozen" flows:
  - no changes to chemical composition

- chemically-reacting flows are relevant to several propulsion systems
  - e.g. rocket combustion chambers

some helpful assumptions are generally made:

(a) individual gases can be treated as perfect

(b) generally, chemically processes occur between states that are in equilibrium

- chemically-reacting flows are relevant to several propulsion systems
  - e.g. rocket combustion chambers

Chemical transformations

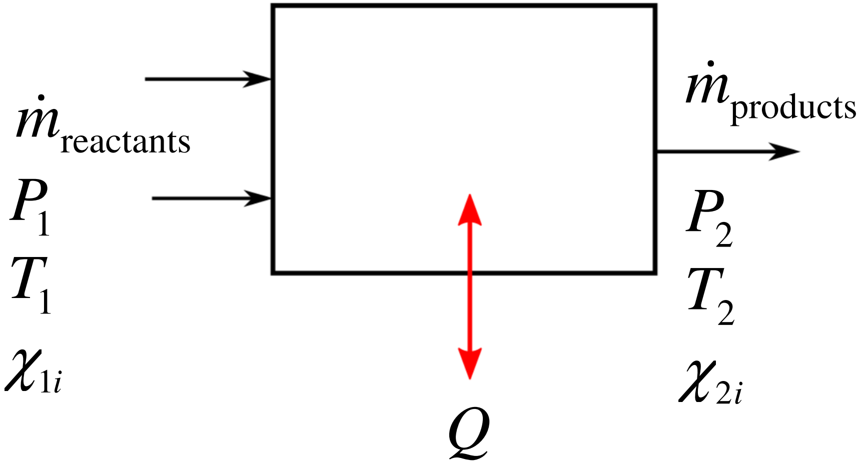
- determining the heat of reaction

let's consider a steady-flow process + no work

$Q = \Delta H$ heat transfer of the fluid through the control volume = change in enthalpy

for one mole of product

$$Q = Q_r = H_{\text{products}} - H_{\text{reactants}}$$



T_f temperature at which Qr is measured

Chemical transformations

- General approach

1. apply mass conservation
   → atom balances or balancing stoichiometric reactions $\alpha A + \beta B + \ldots \rightarrow \gamma C + \delta D + \ldots$
2. apply energy conservation
   → defining chemical “energy” or enthalpy of formation
3. apply entropy conservation (2nd Law)
   → maximize entropy to find equilibrium

Chemical energy

- in nonreacting thermodynamics we combined all different types of energy into **stagnation** or **total enthalpy**,

$$h_0 = h + u^2/2$$

h_t

recall:

$$\underline{\dot{Q}_{in} - \dot{W}_{shaft} + \int_{CV} \rho \vec{f} \cdot \vec{u}\, dV - \int_{CS} p(\vec{u} - \vec{u}_{rel}) \cdot \hat{n}\, dA = \frac{\mathrm{d}}{\mathrm{d}t} \int_{CV} \rho e_o\, dV + \int_{CS} \rho h_o (\vec{u}_{rel} \cdot \hat{n})\, dA}$$

- value of *h* depends on our choice of reference state; does *h*(0 K) = 0 or h(298 K) = 0?

- for a chemically reacting system we want to find a way to add chemical energy

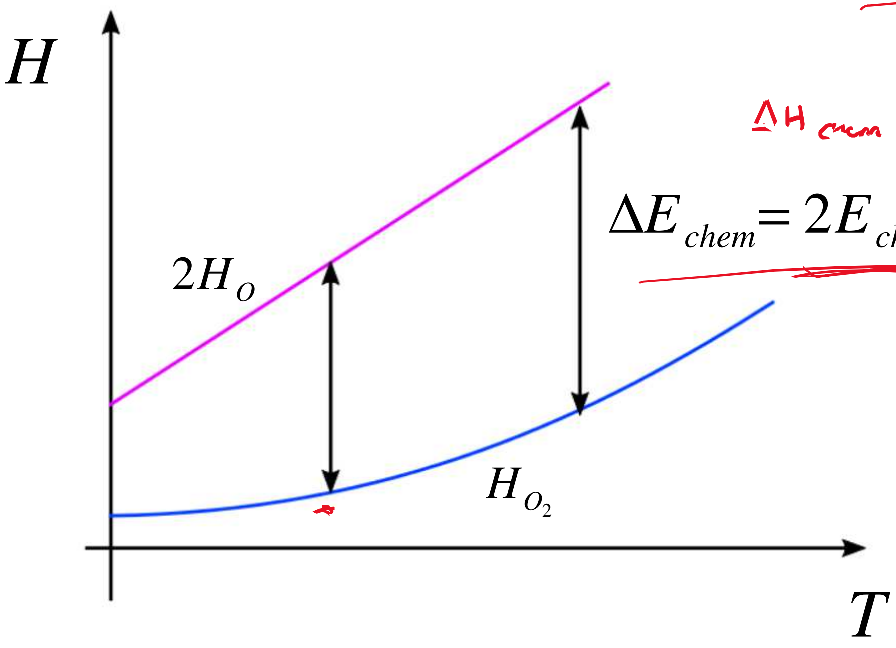
$$h_0 = h + u^2/2 + E_{chem}$$

- first, need to define a reference state where chemical energy is zero

Chemical energy

- enthalpy-temperature diagrams

single species example: $O_2 \leftrightarrow 2O$

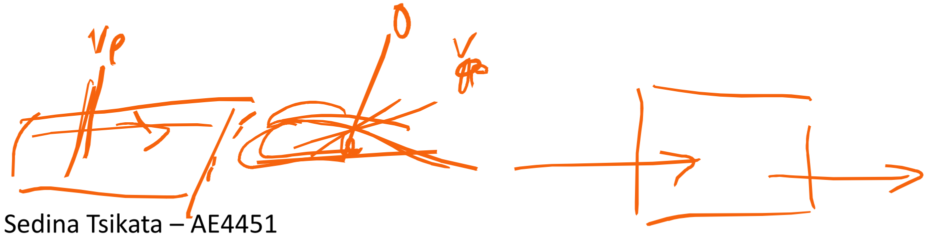


$\Delta H_{chem} = 2H_{chem,O} - H_{chem,O_2}$

$$\Delta E_{chem} = 2E_{chem,O} - E_{chem,O_2}$$

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

- difference in energy between species is function of temperature

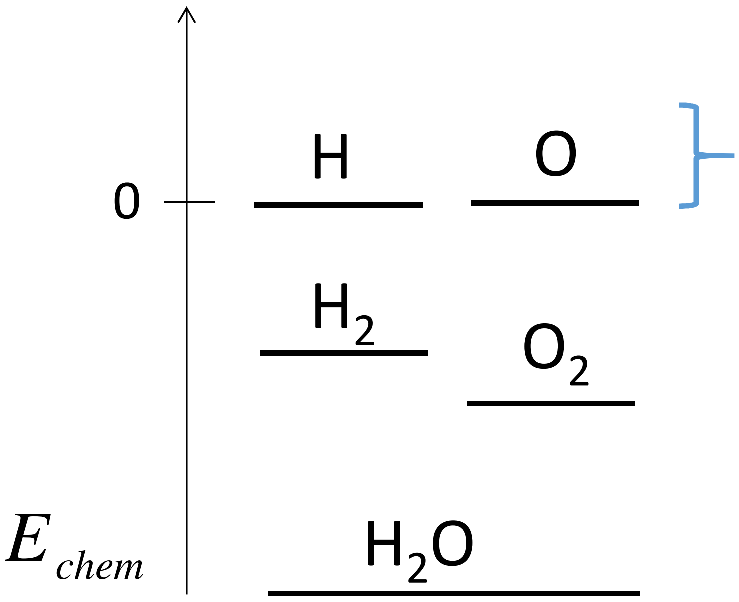


Chemical energy

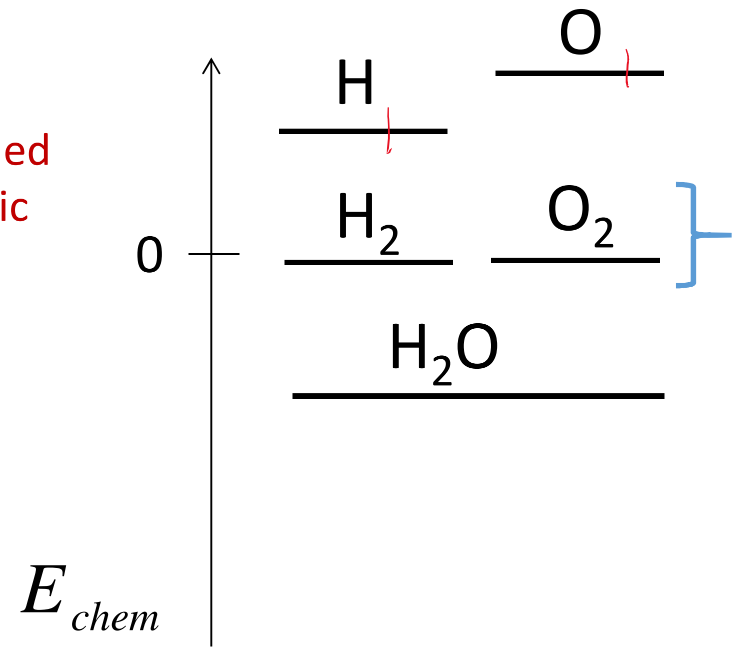
- enthalpy-temperature diagrams

H, O, H_2O, H_2, O_2

multispecies example: how to define the zero energy state



zero E state defined using monoatomic species



using diatomic species

Heat of reaction

Q. What is the energy difference between the *products* and *reactants* if p,T constant? e.g.,

$$H_2 + 1/2\, O_2 \leftrightarrow \underline{H_2O}$$

$$Q_R \text{ or } \underbrace{\Delta H_R}_{\text{heat of reaction}} = \underline{E_{chem,H_2O}} - \left(E_{chem,H_2} + 1/2\, E_{chem,O_2}\right) = \underbrace{H_p}_{\text{products}} - \underbrace{H_r}_{\text{reactants}}$$

must be independent of the zero energy reference state we define

the transformation is characterized as

exothermic (giving off heat) $\underline{\Delta H_R < 0}$

endothermic (requiring heat) $\Delta H_R > 0$

Heat of reaction = how much heat we would have to add to keep T constant (at fixed p) for specified composition change (reaction)

- we will often want to solve for the product state (p, T, χ_i) and determine the heat of a reaction

Heat of formation

Heat of formation:

heat of reaction if we form 1 mole of species *i* from the zero energy species (the *elements*) at fixed temperature *T* and standard pressure (p)

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

formation

temp.

per mass: $\underline{\Delta h^{o}_{f\,T,i}}$

enthalpies of formation of common species from JANAF Thermochemical Tables

e.g. H_2, O_2, N_2, Ar, C (s) graphite

H

O

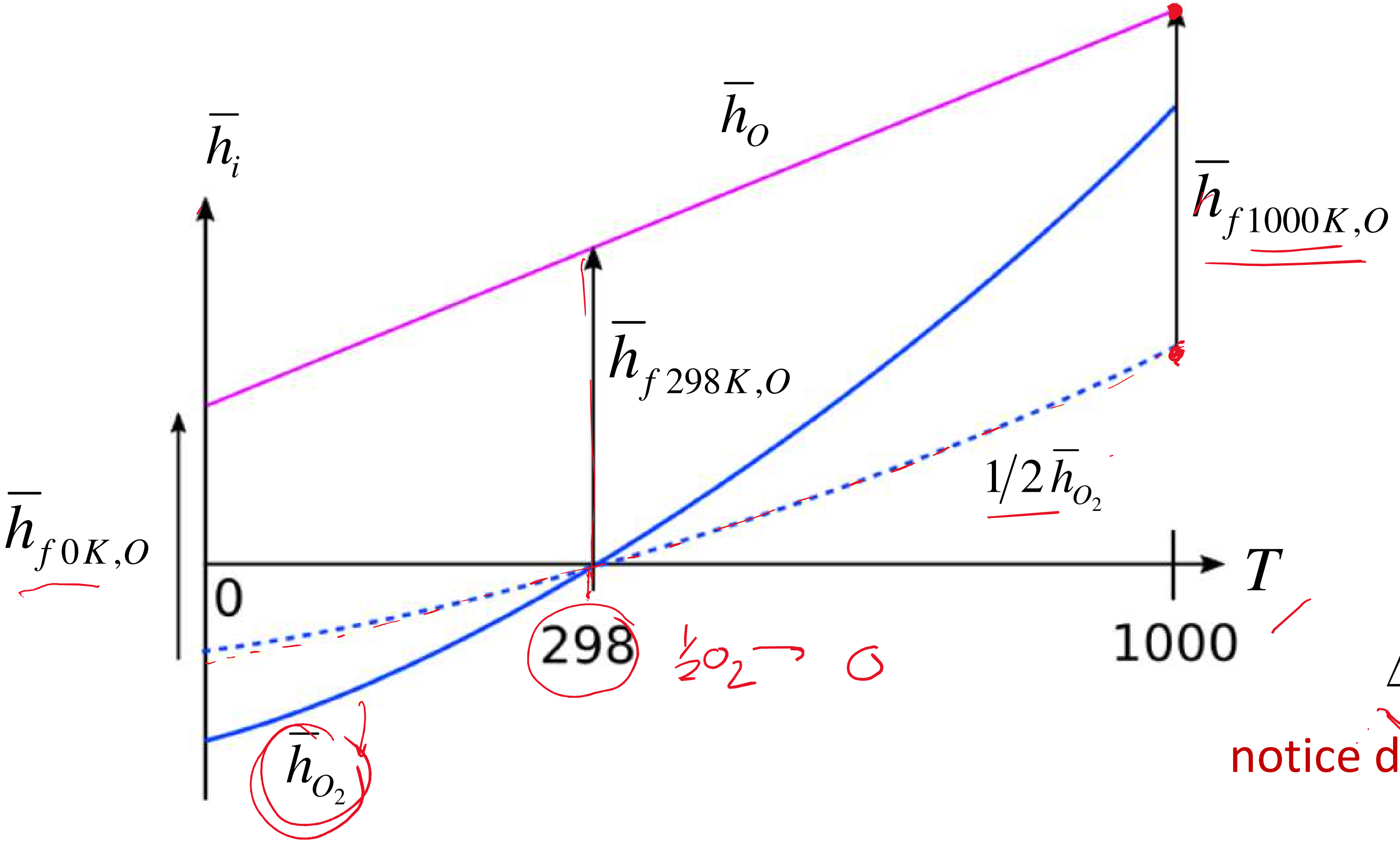
- Two common choices for elements:

the (neutral) atoms

the most common form of a single type of nucleus at standard *T* and *p*

Heat of formation: example

considering again O_2 and O: $1/2\,O_2 \leftrightarrow O$



Q. what is enthalpy of formation of O2?

kinetics.nist.gov/janaf

O

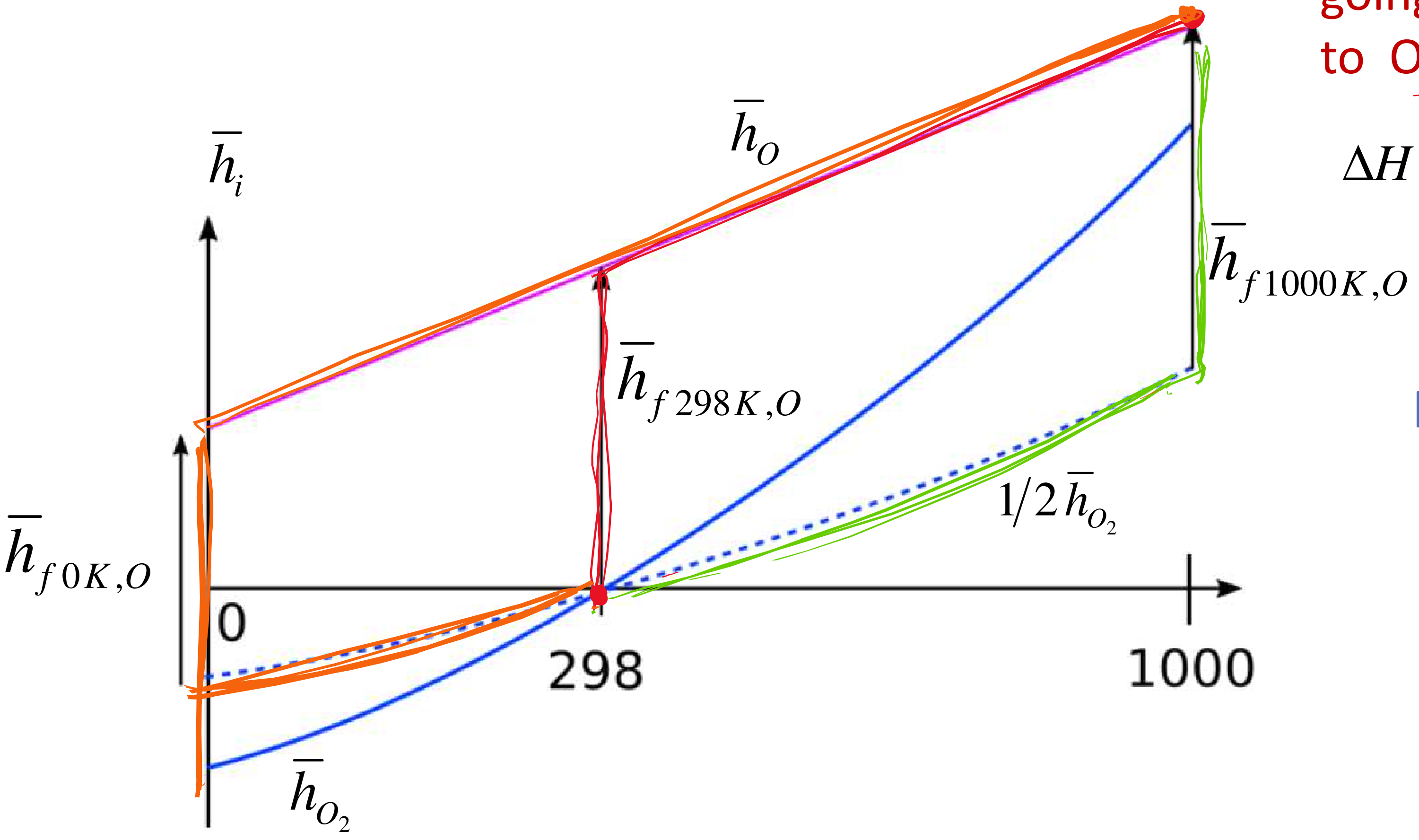
Q. what is enthalpy of formation of O?

$$\Delta \bar h^o_{f\;T,O} = \bar h_O(T) - 1/2\,\bar h_{O_2}(T)$$

notice dependence on temperature

Heat of formation: example

considering again O_2 and O: $1/2\,O_2 \leftrightarrow O$



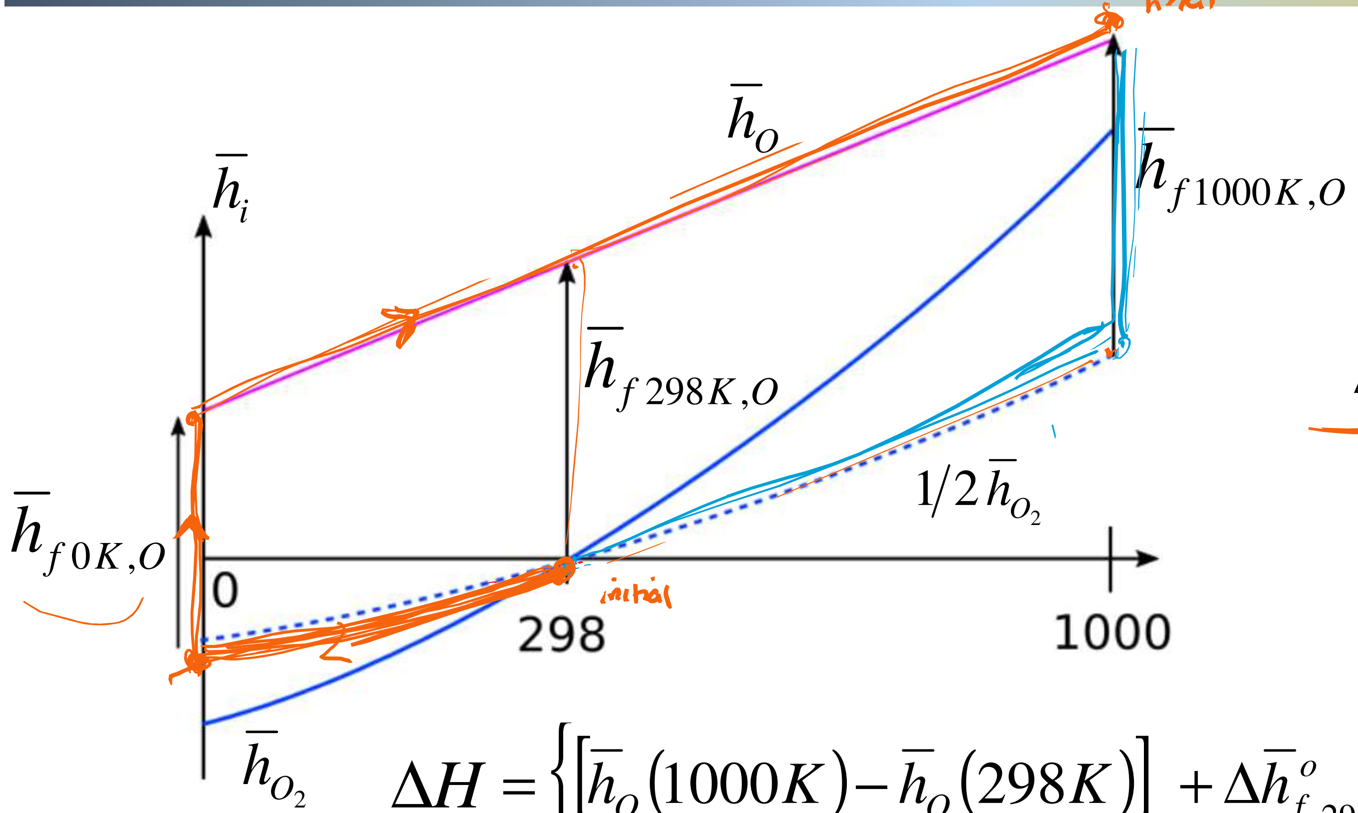
Q. What is the enthalpy change going from ½ mole of O_2@298K to O@ 1000K?

$$\Delta H = 1\bar{h}_O(1000K) - 1/2\,\bar{h}_{O_2}(298K)$$

how many pathways?

Heat of formation: example

$\frac{1}{2}O_2 \rightarrow O$



Q. What is the enthalpy change going from ½ mole of O_2@298K to O@ 1000K?

$$\Delta H = 1\bar{h}_O(1000K) - 1/2\,\bar{h}_{O_2}(298K)$$

* final - initial

$$\Delta H = \left\{\left[\bar{h}_O(1000K) - \bar{h}_O(298K)\right] + \Delta\bar{h}^o_{f\;298K,O}\right\} \checkmark$$

$$= \left\{\left[\cancel{\bar{h}_O(1000K) - \bar{h}_O(1000K)}\right] + \Delta\bar{h}^o_{f\;1000K,O}\right\} + ½\left\{\left[\bar{h}_{O_2}(1000K) - \bar{h}_{O_2}(298K)\right]\right\}$$

$$= \left\{\left[\bar{h}_O(1000K) - \bar{h}_O(0K)\right] + \Delta\bar{h}^o_{f\;0K,O}\right\} + ½\left\{\left[\bar{h}_{O_2}(0K) - \bar{h}_{O_2}(298K)\right]\right\}$$

Heat of formation

So, generally, we can write the enthalpy as

$$\underline{\bar{h}_i(T)} = \underbrace{\left(\bar{h}_T - \bar{h}_{T_{ref}}\right)_i}_{\text{sensible } h \text{ change}} + \underbrace{\Delta\bar{h}^o_{f\,T_{ref},i}}_{\text{chemical energy}} = \underbrace{\int_{T_{ref}}^{T} \bar{c}_{p,i}\,dT}_{} + \Delta\bar{h}^o_{f\,T_{ref},i}$$

or, per unit mass:

$$h_i(T) = \left(h_T - h_{T_{ref}}\right)_i + \underbrace{\Delta h^o_{f\,T_{ref},i}}_{} = \int_{T_{ref}}^{T} c_{p,i}\,dT + \Delta h^o_{f\,T_{ref},i}$$

Examples of enthalpies of formation

Species	**$\Delta h^o_{f,298.15\ K}$ kJ/mol**
CO	-110.53
CO_2	-393.52
CH_4	-74.87
H	218.00
H_2O	-241.83
O	249.17
OH	38.99

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

can find newer updates to data

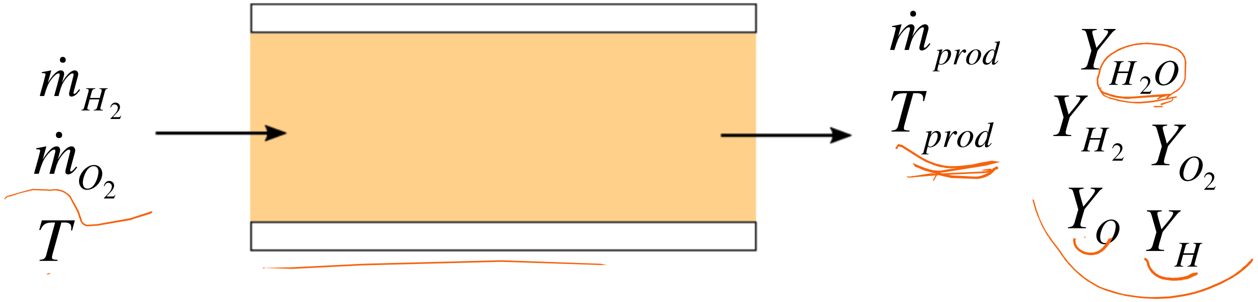
high formation enthalpy species: e.g. H, O

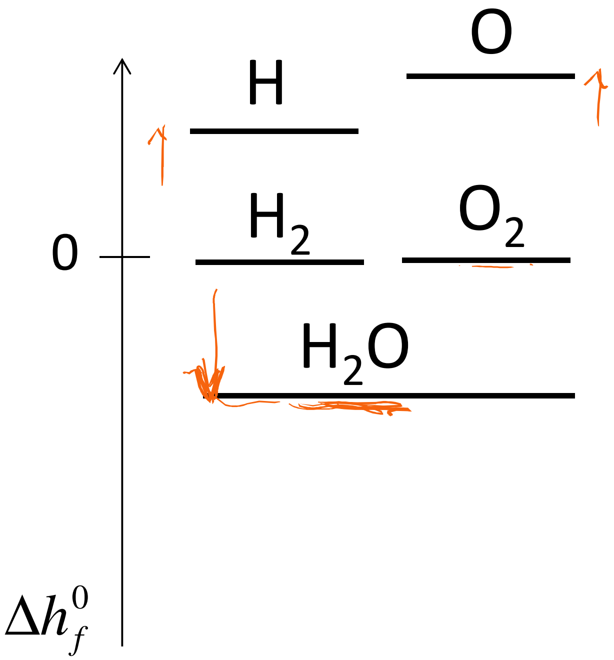
high energy ⇒ hard to make (unstable)

low formation enthalpy species: e.g. CO_2, H_2O

low energy (<<0) ⇒ very stable at low T

Composition influence on temperature



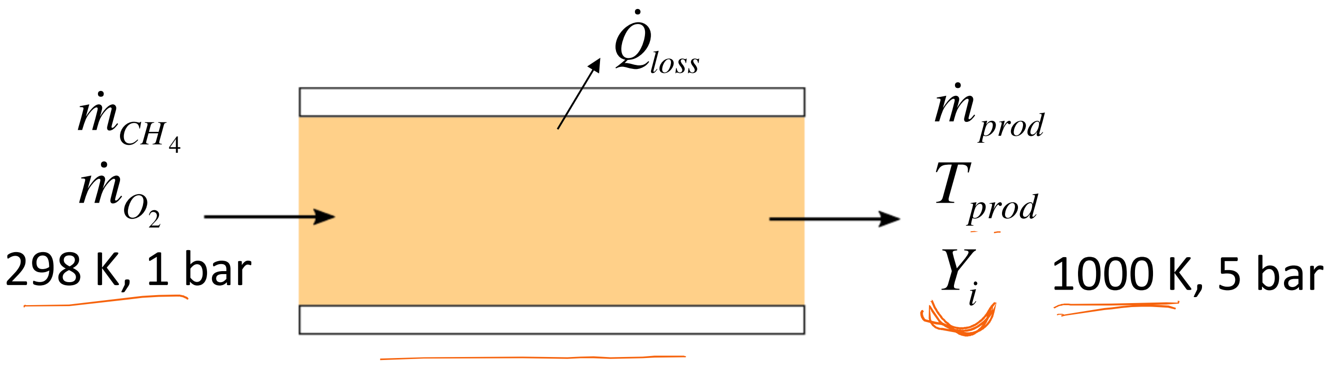


So if the products have more H, O, H_2, O_2 vs. H_2O

T_{prod} will be lower than if we could shift them toward water

Example

Case of a methane-oxygen combustor



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

Q. what is the heat loss rate per unit mass flow rate, $\dot{Q}_{loss}/\dot{m}$?

assume:

$\frac{\phi}{dt} = 0$

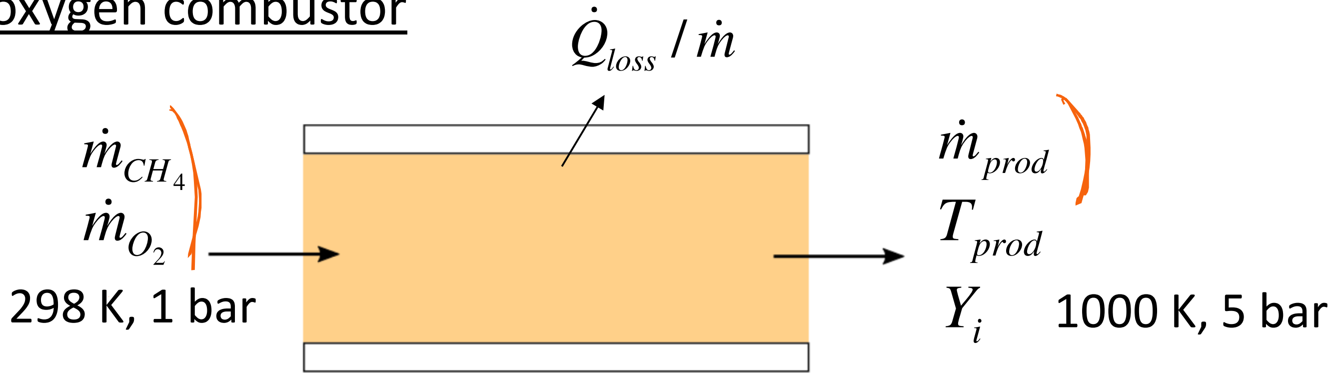
$PV = nRT$

$c_p, c_v \neq 0$

steady state, no “shaft” work, thermally perfect but not calorically perfect gases

Example

Case of a methane-oxygen combustor



1. mass conservation

$$\underbrace{\dot{m}_{in}}_{\text{react}} = \underbrace{\dot{m}_{exit}}_{\text{products}} \equiv \dot{m}$$

$\dot{m}$

$$\boxed{\underline{\dot{Q}_{in}} - \dot{W}_{shaft} + \int_{CV} \rho \vec{f} \cdot \vec{u}\, dV - \int_{CS} p(\vec{u} - \vec{u}_{rel}) \cdot \hat{n}\, dA = \frac{\mathrm{d}}{\mathrm{d}t}\int_{CV} \rho e_o\, dV + \underbrace{\int_{CS} \rho h_o (\vec{u}_{rel} \cdot \hat{n})\, dA}_{\text{ṁ}}}$$

2. energy conservation

$$\underline{\dot{m} h_{o,in}} = \underline{\dot{m} h_{o,exit}} + \underline{\dot{Q}_{loss}}$$

$$\# \quad \dot{Q}_{loss} / \dot{m} = h_{o,in} - h_{o,exit}$$

$$\boxed{\frac{\dot{Q}_{loss}}{\dot{m}} = \underline{h_{o,reactants}} - \underline{h_{o,products}}}$$

assume we know molar properties, so use h = $\bar{h}$ / MW

$$= \frac{1}{MW_r} \sum_{\text{reactants}} \chi_i \left[\underbrace{\left(\bar{h}_{T_{or}} - \bar{h}_{T_{ref}} \right)_i}_{\Delta \text{ enthalpy}} + \underbrace{\Delta \bar{h}^o_{f,T_{ref},i}}_{\text{formation}} \right] - \frac{1}{MW_p} \sum_{\text{products}} \chi_i \left[\left(\bar{h}_{T_{op}} - \bar{h}_{T_{ref}} \right)_i + \underbrace{\Delta \bar{h}^o_{f,T_{ref},i}}_{\text{enthalpy of form.}} \right]$$