Chemical Energy

- If we knew our product composition, we can find T_o from energy conservation
  - the chemical energy of the reactants is converted to thermal energy of the products
- Example hydrogen/oxygen rocket combustor
  - with no (shaft) work (+ steady, adiabatic) energy conservation gives

$$\dot{m}_{H_2} h_{o_{H_2}} + \dot{m}_{O_2} h_{o_{O_2}} = \dot{m}_{prod} h_{o_{prod}}$$

  - should equation change whether reaction occurs or not?
- No, so chemical energy needs to be included in the stagnation enthalpy h_o

$$h_o = \underbrace{e_{\text{internal}} + pv}_{\equiv \text{sensible enthalpy, e.g, for TPG } dh_{sens} = c_p dT} + \frac{u^2}{2} + chemical\ energy$$

Reference State

- Recall, that we can define a reference point for sensible energy
  - e.g., h_{sens}=0 at T=298K
- But does that mean at 298 K, $0 = h_{H_2} = h_H = h_{O_2} = h_O = h_{H_2O}$?
- We need to define a reference point for chemical energy
  - e.g., a chemical state that has zero chemical energy

$$\int dh_{sens} = \int_{T_{ref}}^{T} c_p dT$$

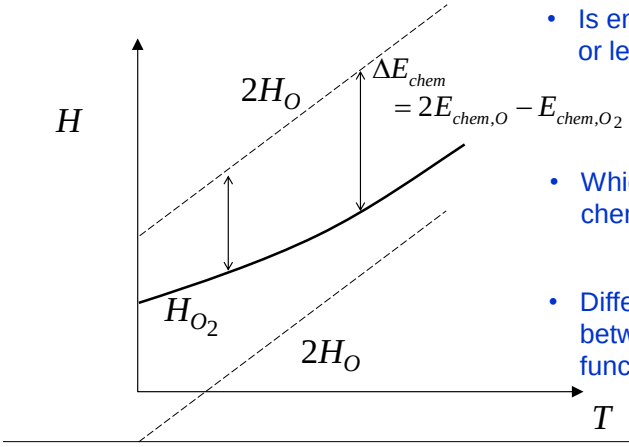
$$\left(h - h_{ref}\right)_{sens} = \int_{T_{ref}}^{T} c_p dT$$

$$h_{sens} = \int_{298K}^{T} c_p dT$$

$$h = h_{sens} + e_{chem}$$

Chemical Energy Reference

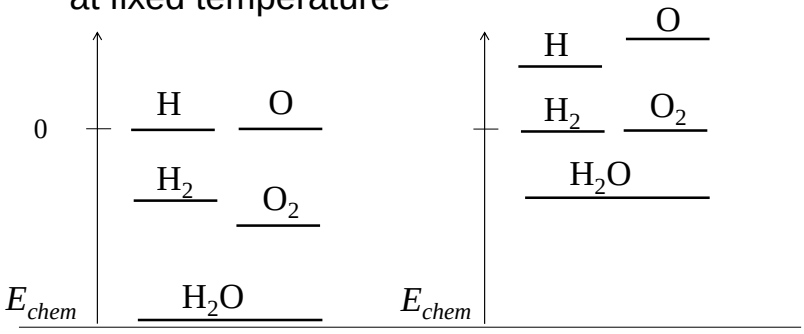
- Consider the energies of O_2 and O $O_2 \leftrightarrow 2O$



- 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 nuclei types?
  - ways to define *zero chemical energy state*
- Example: various H and O containing species at fixed temperature



Heat of "Reaction"

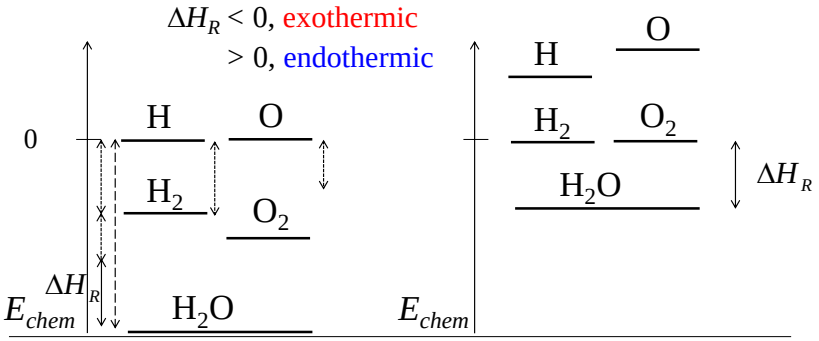
- What is energy difference between 2 chemical states if p,T doesn't change, e.g., $H_2 + 1/2\,O_2 \leftrightarrow H_2O$

Heat of Reaction

$$\Delta H_R = E_{chem,H_2O} - \left(E_{chem,H_2} + 1/2\,E_{chem,O_2}\right) = H_p - H_r$$

$\Delta H_R < 0$, exothermic

> 0, endothermic



Enthalpy (Heat) of Formation

- Two common ways to define zero chemical energy state (i.e, composition) - this state defines the **elements**
  - (neutral) atoms
  - most common form of a single type of nuclei at standard T and p

NASA Tables

JANNAF

$He, H_2, O_2, N_2, C\,(s)_{\text{graphite}}, \ldots$

- Can define the chemical energy of any species relative to these **elements**
  - how much chemical energy difference between **ONE mole** of species *i* from the **elements** at some fixed T and standard pressure (°)
  - or **ONE unit of mass**

Enthalpy of Formation

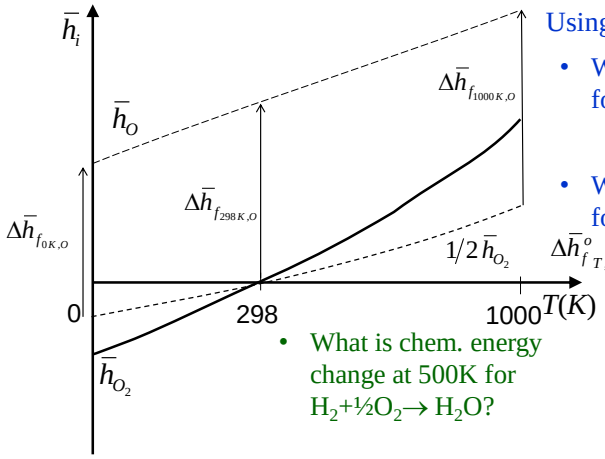
$$\Delta \bar{h}^o_{f\,T,i}$$

$$\Delta h^o_{f\,T,i}$$

Enthalpy of Formation Example

- Consider again O_2 and O

$$1/2\,O_2 \leftrightarrow O$$



Using JANNAF def'n.

- What is enthalpy of formation of O_2?
- What is enthalpy of formation of O?

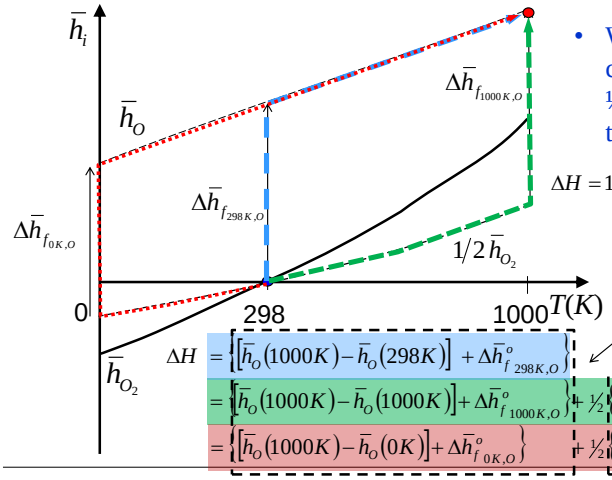
$$\Delta\bar{h}^o_{f\,T,O} = \bar{h}_O(T) - 1/2\,\bar{h}_{O_2}(T)$$

- What is chem. energy change at 500K for $H_2 + ½O_2 \rightarrow H_2O$?

Heat of Formation Example

- Consider again O_2 and O

$$1/2\,O_2 \leftrightarrow O$$



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

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

O enthalpy **O_2 enthalpy**

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

General Expression for Enthalpy

- So from the previous path example, we can write in general for a species *i*

$$\bar{h}_i(T) = \bar{h}_i\Big|_{T_{ref}}^{T} + \Delta\bar{h}^o_{f_{T_{ref}},i} = \int_{T_{ref}}^{T} \bar{c}_{p,i}\,dT + \Delta\bar{h}^o_{f\,T_{ref},i}$$

sensible term; chemical term

for an ideal gas (TPG), ≠ function (pressure)

- or on a per mass basis

$$h_i(T) = \int_{T_{ref}}^{T} c_{p,i}\,dT + \Delta h^o_{f\,T_{ref},i}$$

Example Enthalpies of Formation

Species	$\Delta\bar{h}^o_{f,298.15\,K}$ kJ/mol	Species	$\Delta\bar{h}^o_{f,298.15\,K}$ kJ/mol
Al (s)	0.00	H_2O	-241.83
Al_2O_3(l)	-1620.57	NH_3	-45.90
CO	-110.53	N_2H_4 (l)	50.63
CO_2	-393.52	N_2O_4 (l)	-19.56
CH_4	-74.87	O	249.17
H	218.00	OH	38.99

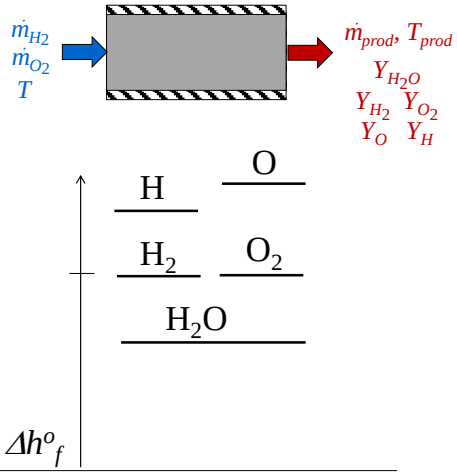
From NIST-JANNAF database 4th edition (1998)
(e.g., kinetics.nist.gov/janaf)

can find newer updates to data

- High formation enthalpy species
  - H, O
- Low formation enthalpy
  - Al_2O_3, CO_2, H_2O
- Why?

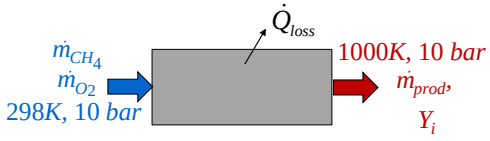
Composition Influence on Temperature

- 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



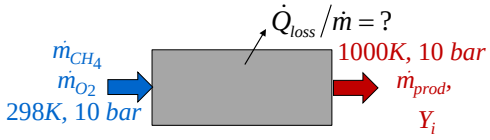
Ex.: Methane/Oxygen Comb. Chamber

- **Given**:
  - Gaseous methane and oxygen entering non-adiabatic combustion chamber at 298 K, 10 bar
  - Mass flowrate ratio of oxygen is 5× that for methane
  - Heat loss results in 1000 K product temperature
- **Find**:
  - Heat loss per unit mass flow, $\dot{Q}_{loss}/\dot{m}$
- **Assume**: steady state, negligible KE



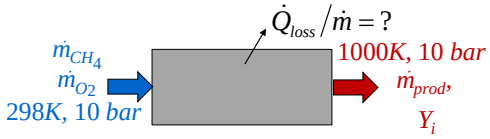
Ex.: Methane/Oxygen Comb. Chamber

- **Solution**



Ex.: Methane/Oxygen Comb. Chamber

- **Solution**



JANNAF Table Extract

M_r = 44.0098 Carbon Dioxide (CO_2) — C_1O_2(g)

$\Delta_f H°(0\ K) = -393.151 \pm 0.05$ kJ·mol^{-1}
$(298.15\ K) = -393.522 \pm 0.05$ kJ·mol^{-1}

- From 4th edition

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

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−9.364	−393.151	−393.151	INFINITE
100	29.208	179.009	243.568	−6.456	−393.208	−393.683	205.639
200	32.359	199.975	217.046	−3.414	−393.404	−394.085	102.924
298.15	37.129	213.795	213.795	0.	−393.522	−394.389	69.095
300	37.221	214.025	213.795	0.069	−393.523	−394.394	68.670
400	41.325	225.314	215.307	4.003	−393.583	−394.675	51.539
500	44.627	234.901	218.290	8.305	−393.666	−394.939	41.259
600	47.321	243.283	221.772	12.907	−393.803	−395.182	34.404
700	49.564	250.750	225.388	17.754	−393.983	−395.398	29.505
800	51.434	257.494	228.986	22.806	−394.188	−395.586	25.829
900	52.999	263.645	232.500	28.030	−394.405	−395.748	22.969
1000	54.308	269.299	235.901	33.397	−394.623	−395.886	20.679
1100	55.409	274.528	239.178	38.884	−394.838	−396.001	18.805
1200	56.342	279.390	242.329	44.473	−395.050	−396.098	17.242
1300	57.137	283.932	245.356	50.148	−395.257	−396.177	15.919
1400	57.802	288.191	248.265	55.896	−395.462	−396.240	14.784
1500	58.379	292.199	251.062	61.705	−395.668	−396.288	13.800
1600	58.886	295.983	253.753	67.569	−395.876	−396.323	12.939
1700	59.317	299.566	256.343	73.480	−396.090	−396.344	12.178
1800	59.701	302.968	258.840	79.431	−396.311	−396.353	11.502
1900	60.049	306.205	261.248	85.419	−396.542	−396.349	10.896
2000	60.350	309.293	263.574	91.439	−396.784	−396.333	10.351

$$\bar{h}_i\Big|_{T_{ref}}^{T} \qquad \Delta\bar{h}_{f\ T_{ref},i}^{o}$$

Specific Heat Polynomials

- Data also available in polynomial forms
- NASA polynomial form for specific heats

$$\frac{c_p}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 = \frac{\bar{c}_p}{\bar{R}}$$

$$\bar{h}_{sensible,i}(T) - \bar{h}_{sensible,i}(T_{ref}) = \int_{T_{ref}}^{T} \bar{c}_{p,i}\, dT$$

- Examples (*valid for 1000-3500* K)

Gas	a_1	a_2	a_3	a_4	a_5
O_2	3.28254	1.4831×10^{-3}	-7.5797×10^{-7}	2.0947×10^{-10}	-2.1672×10^{-14}
H_2	3.33728	-4.9403×10^{-5}	4.9946×10^{-7}	-1.7957×10^{-10}	2.0026×10^{-14}
H_2O	3.03399	2.1769×10^{-3}	-1.6407×10^{-7}	-9.7042×10^{-11}	1.6820×10^{-14}