TD of thermal combustion-Enthalpy Changes

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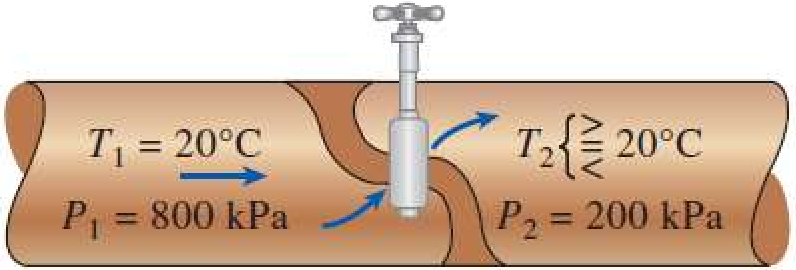
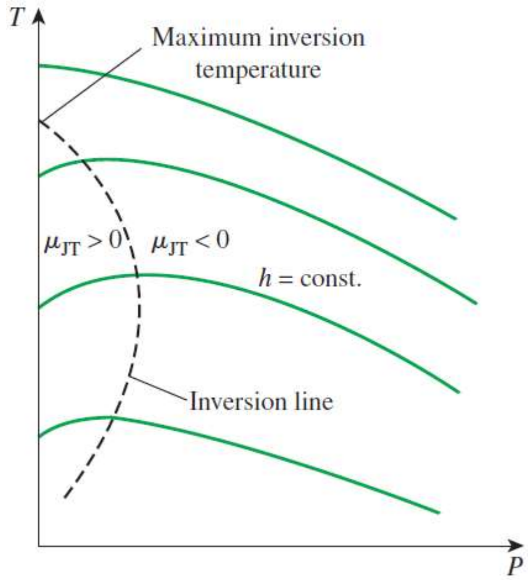
Previously: J-T Coef. & TD relationships in real gases

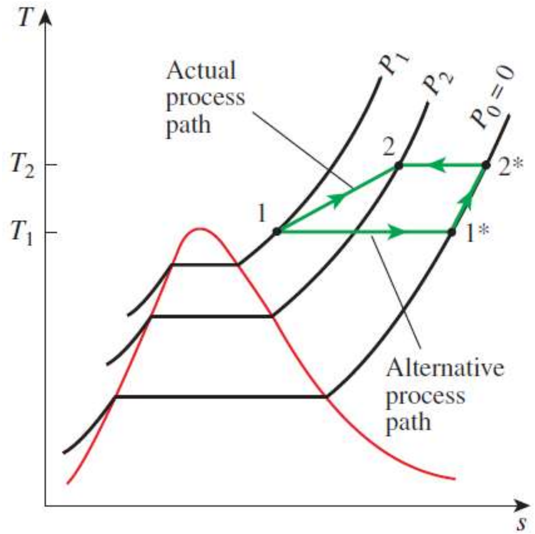


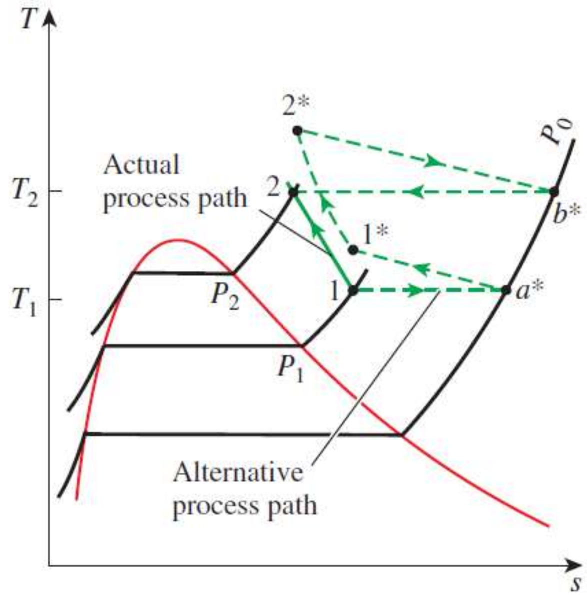
$$\mu = \left(\frac{\partial T}{\partial P}\right)_h$$

$$\mu_{JT} \begin{cases} < 0 & \text{temperature increases} \\ = 0 & \text{temperature remains constant} \\ > 0 & \text{temperature decreases} \end{cases}$$

$$dh = c_p\, dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right] dP$$







$$(h^* - h)_T = -RT^2 \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}$$

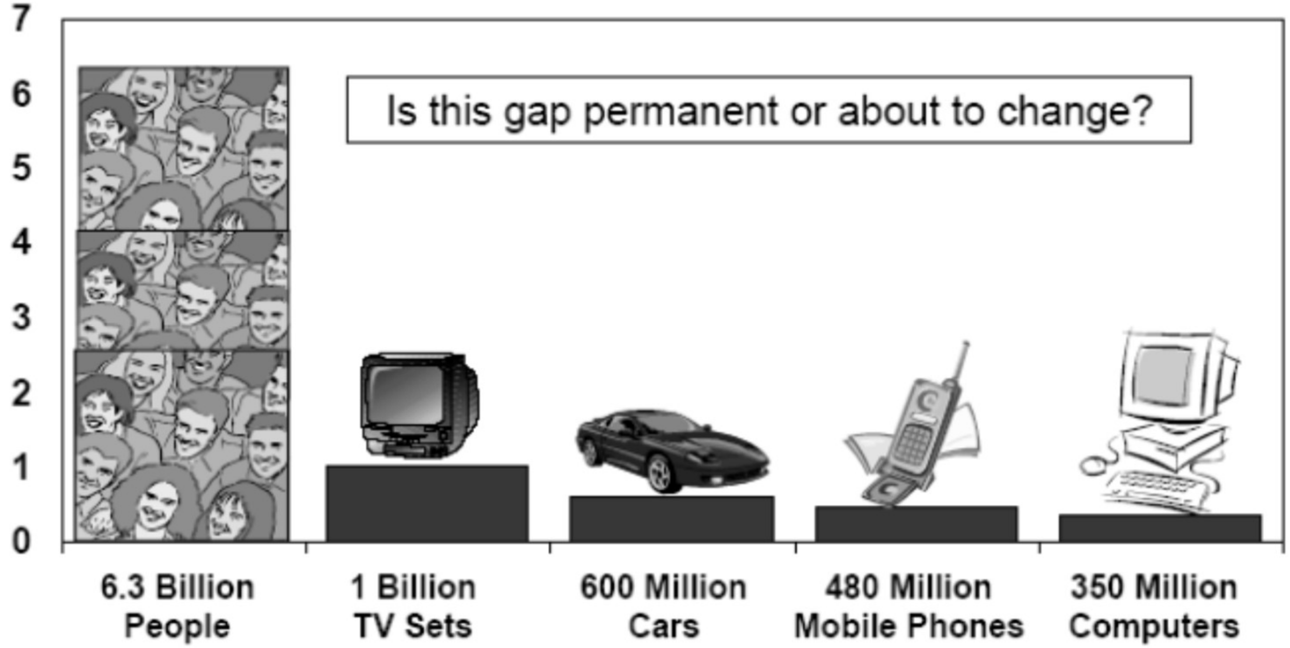
$$s_2 - s_1 = (s_2 - s_b^*) + (s_b^* - s_2^*) + (s_2^* - s_1^*) + (s_1^* - s_a^*) + (s_a^* - s_1)$$

Figs: TD-Cengel & Boles

Smalley's top ten ventures to save the world!
MRS Bulletin Volume 30, June 2005 Pg 412

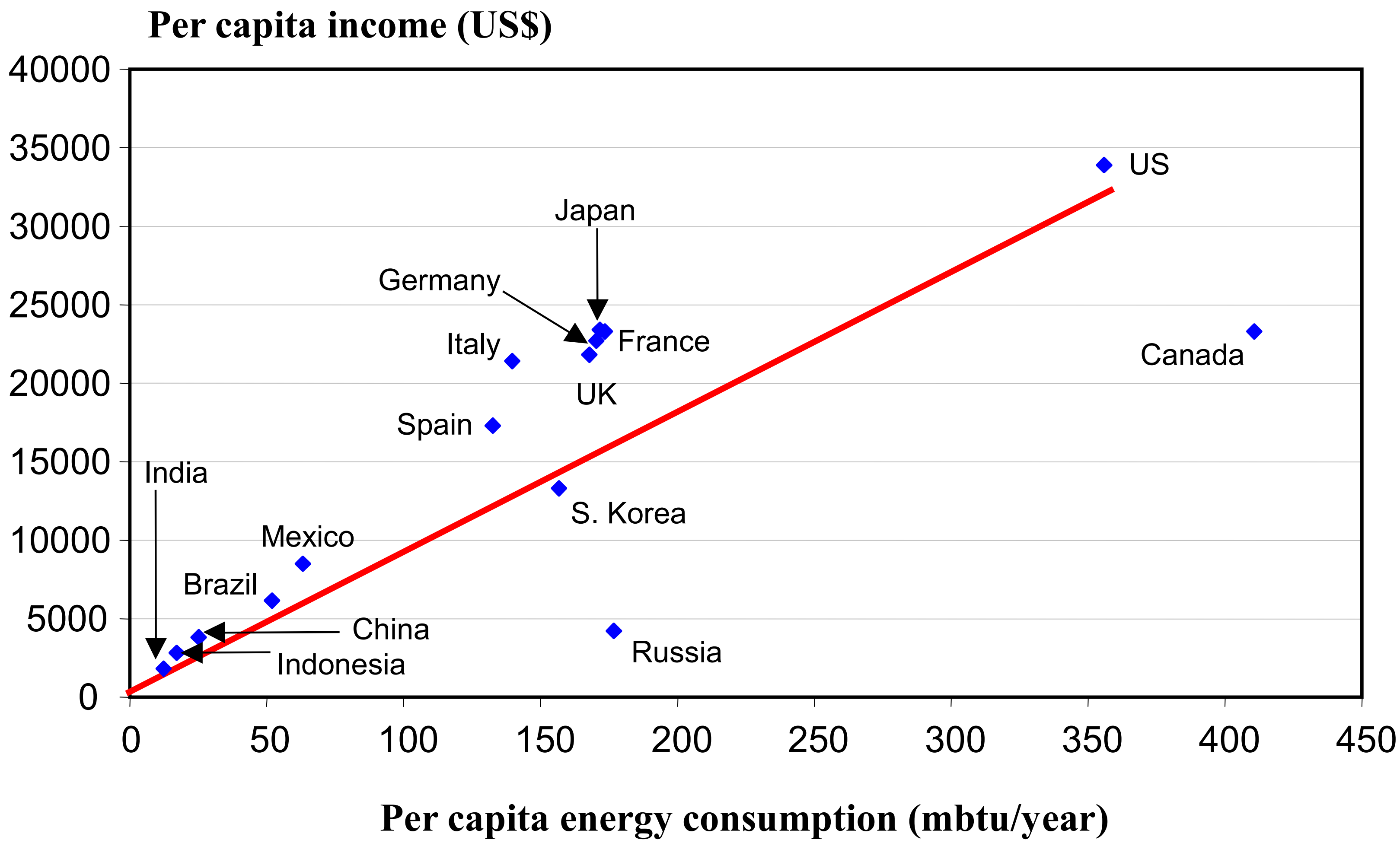
- **10. Population**
- **9. Democracy**
- **8. Education**
- **7. Disease**
- **6. Terrorism and War**
- **5. Poverty**
- **4. Environment**
- **3. Food**
- **2. Water**
- **1. Energy!!!**

People & Things…
Source: Simons & Company



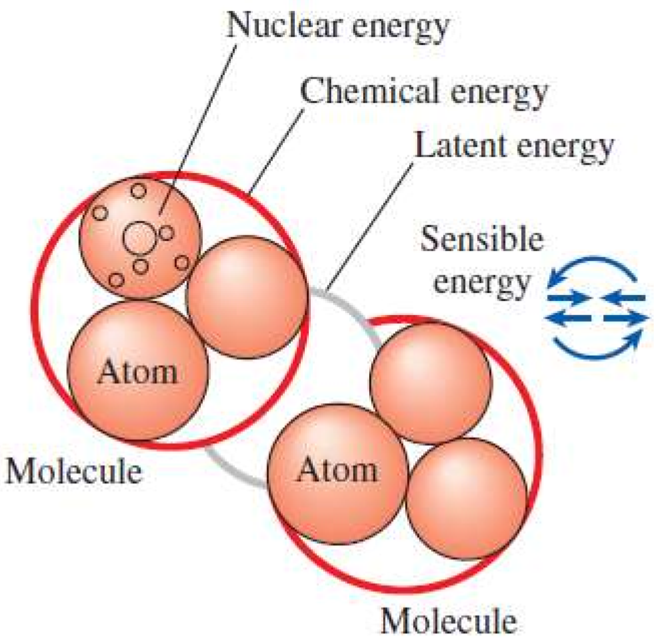
Top 15 World Economies

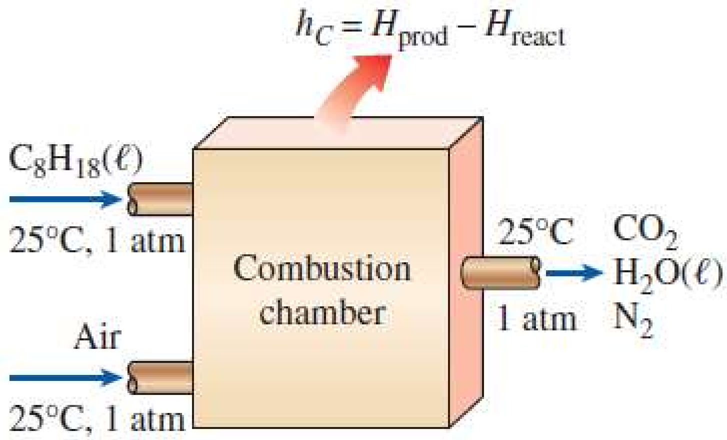
Per Capita Income vs Per Capita Energy Consumption



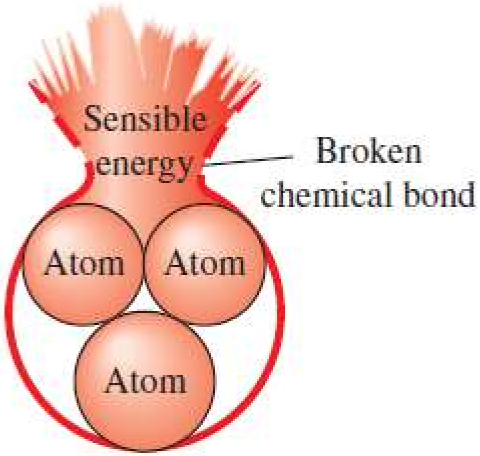
From: Economides on the web…

Enthalpy of formation & combustion





$$C_8H_{18} + a_{th}(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O(\ell) + 3.76a_{th}N_2$$



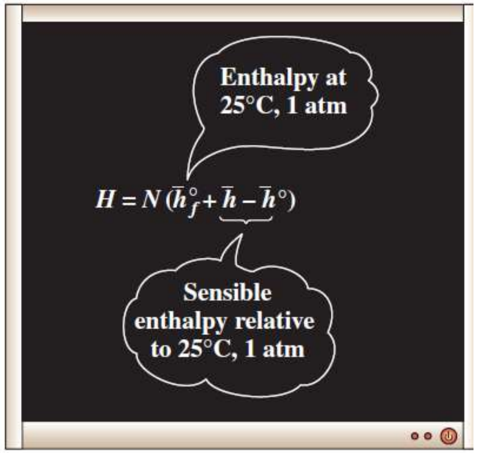
$$\begin{aligned}\bar{h}_C &= H_{prod} - H_{react} \\ &= \sum N_p\bar{h}^\circ_{f,p} - \sum N_r\bar{h}^\circ_{f,r} = (N\bar{h}^\circ_f)_{CO_2} + (N\bar{h}^\circ_f)_{H_2O} - (N\bar{h}^\circ_f)_{C_8H_{18}}\end{aligned}$$

$$\begin{aligned}\bar{h}_C &= (8 \text{ kmol})(-393{,}520 \text{ kJ/kmol}) + (9 \text{ kmol})(-285{,}830 \text{ kJ/kmol}) \\ &\quad -(1 \text{ kmol})(-249{,}950 \text{ kJ/kmol}) \\ &= \mathbf{-5{,}471{,}000\ kJ/kmol\ C_8H_{18} = -47{,}891\ kJ/kg\ C_8H_{18}}\end{aligned}$$

Figs: TD-Cengel & Boles

First law analysis for reacting systems

$$\text{Enthalpy} = \bar{h}_f^\circ + (\bar{h} - \bar{h}^\circ) \qquad \text{(kJ/kmol)}$$



$$\bar{h}(T,p) = \bar{h}_\mathrm{f}^\circ + [\bar{h}(T,p) - \bar{h}(T_\mathrm{ref}, p_\mathrm{ref})] = \boxed{\bar{h}_\mathrm{f}^\circ} + \boxed{\Delta\bar{h}}$$

Thermochemical Properties of Selected Substances at 298K and 1 atm

Substance	Formula	Molar Mass, M (kg/kmol)	Enthalpy of Formation, $\bar{h}_\mathrm{f}^\circ$ (kJ/kmol)	Gibbs Function of Formation, $\bar{g}_\mathrm{f}^\circ$ (kJ/kmol)	Absolute Entropy, $\bar{s}^\circ$ (kJ/kmol·K)	Heating Values: Higher, HHV (kJ/kg)	Heating Values: Lower, LHV (kJ/kg)
Carbon	C(s)	12.01	0	0	5.74	32,770	32,770
Hydrogen	H_2(g)	2.016	0	0	130.57	141,780	119,950
Nitrogen	N_2(g)	28.01	0	0	191.50	–	–
Oxygen	O_2(g)	32.00	0	0	205.03	–	–
Carbon Monoxide	CO(g)	28.01	–110,530	–137,150	197.54	–	–
Carbon dioxide	CO_2(g)	44.01	–393,520	–394,380	213.69	–	–
Water	H_2O(g)	18.02	–241,820	–228,590	188.72	–	–
Water	H_2O(l)	18.02	–285,830	–237,180	69.95	–	–

Figs: TD-Cengel & Boles; Moran, Shapiro, Boettner & Bailey

First law Balance for reacting systems

$$\dot{E}_{\text{in}} = \dot{E}_{\text{out}}$$

$$\underbrace{\dot{Q}_{\text{in}} + \dot{W}_{\text{in}} + \sum \dot{n}_r(\overline{h}^\circ_f + \overline{h} - \overline{h}^\circ)_r}_{\substack{\text{Rate of net energy transfer in} \\ \text{by heat, work, and mass}}} = \underbrace{\dot{Q}_{\text{out}} + \dot{W}_{\text{out}} + \sum \dot{n}_p(\overline{h}^\circ_f + \overline{h} - \overline{h}^\circ)_p}_{\substack{\text{Rate of net energy transfer out} \\ \text{by heat, work, and mass}}}$$

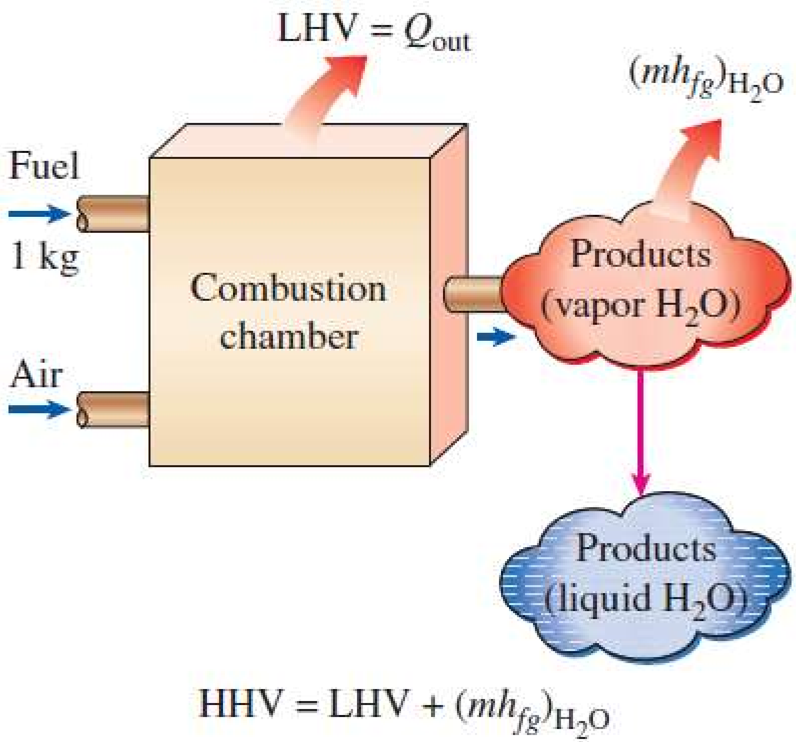
$$\underbrace{Q_{\text{in}} + W_{\text{in}} + \sum N_r(\overline{h}^\circ_f + \overline{h} - \overline{h}^\circ)_r}_{\substack{\text{Energy transfer in per mole of fuel} \\ \text{by heat, work, and mass}}} = \underbrace{Q_{\text{out}} + W_{\text{out}} + \sum N_p(\overline{h}^\circ_f + \overline{h} - \overline{h}^\circ)_p}_{\substack{\text{Energy transfer out per mole of fuel} \\ \text{by heat, work, and mass}}}$$

$$Q - W = \overline{h}^\circ_C + \sum N_p(\overline{h} - \overline{h}^\circ)_p - \sum N_r(\overline{h} - \overline{h}^\circ)_r \qquad \text{(kJ/kmol)}$$

$$Q_{\text{out}} = \underbrace{\sum N_r(\overline{h}^\circ_f + \overline{h} - \overline{h}^\circ)_r}_{\substack{\text{Energy in by mass} \\ \text{per mole of fuel}}} - \underbrace{\sum N_p(\overline{h}^\circ_f + \overline{h} - \overline{h}^\circ)_p}_{\substack{\text{Energy out by mass} \\ \text{per mole of fuel}}}$$

Figs: TD-Cengel & Boles

Higher & Lower Heating Value

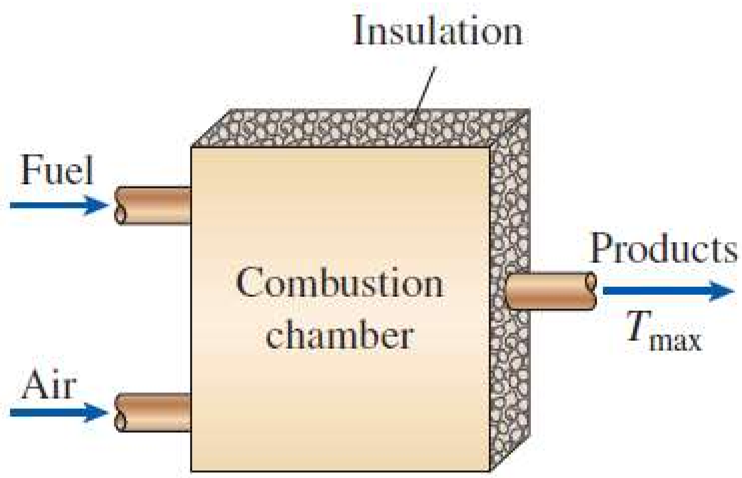


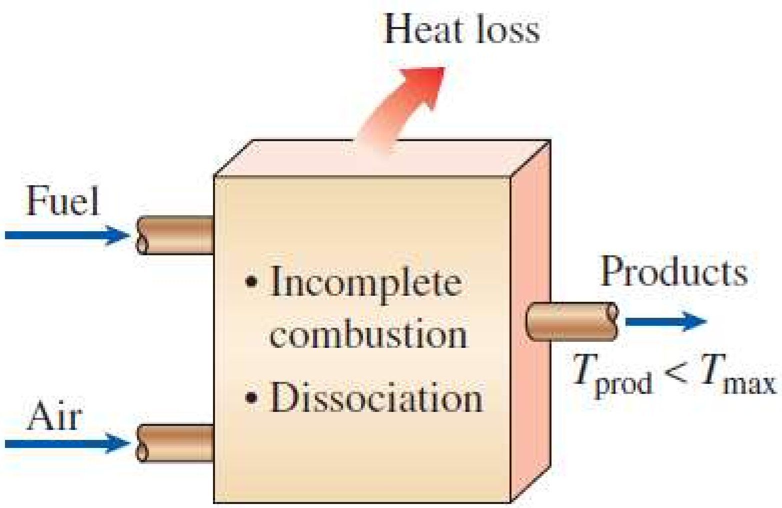
Figs: TD-Cengel & Boles

Adiabatic flame temperature

$H_{prod} = H_{react}$ $\quad$ $Q = 0$ and $W = 0$

$$\sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p = \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r$$





Figs: TD-Cengel & Boles

First law for closed systems

$$E_{\text{in}} - E_{\text{out}} = \Delta E_{\text{system}}$$

$$(Q_{\text{in}} - Q_{\text{out}}) + (W_{\text{in}} - W_{\text{out}}) = U_{\text{prod}} - U_{\text{react}} \qquad \text{(kJ/kmol fuel)}$$

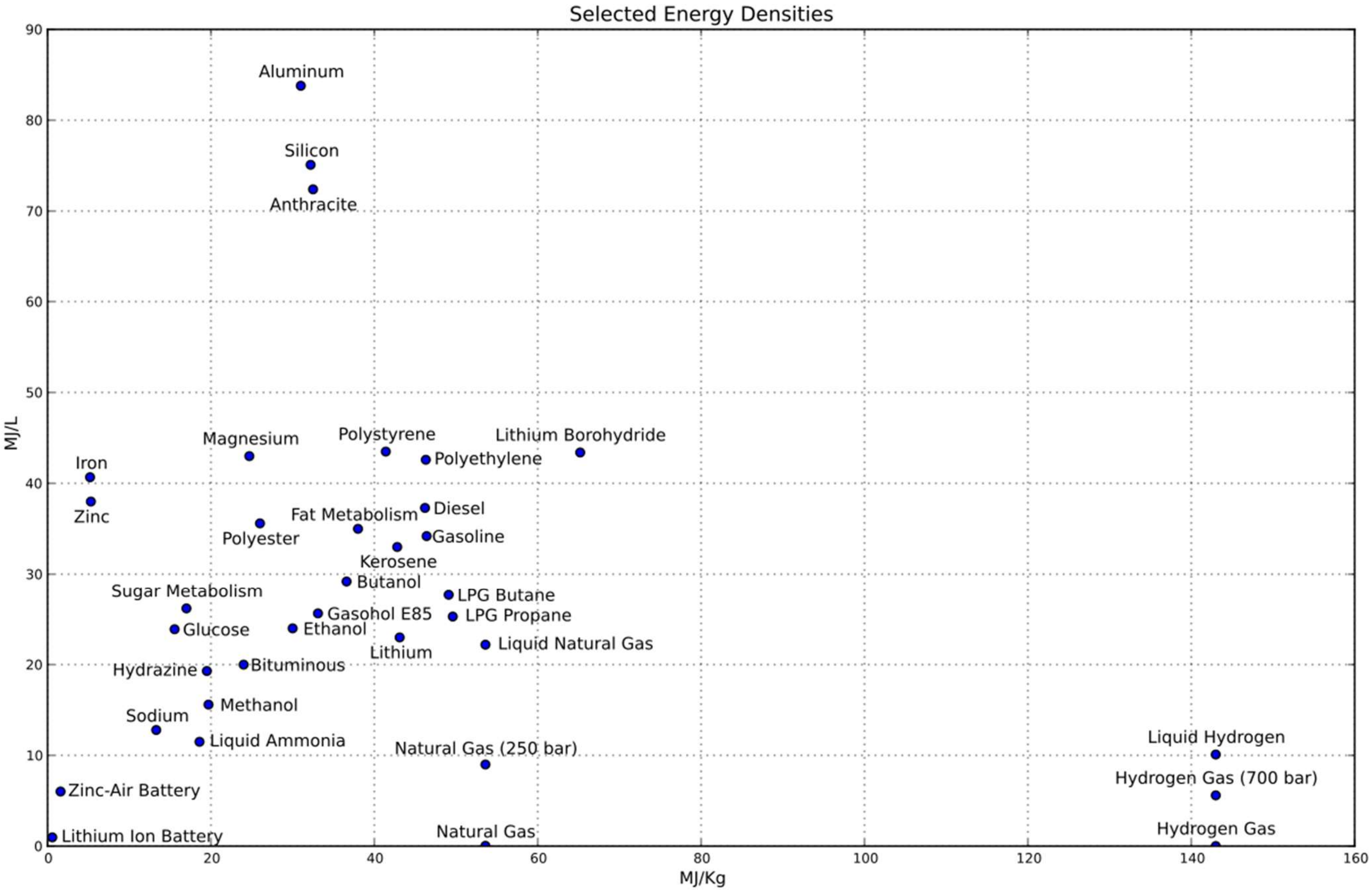
$$\bar{u} = \bar{h} - P\bar{v}$$

$$\bar{u}_f^\circ + \bar{u} - \bar{u}^\circ = \bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v}$$

$$Q - W = \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v})_p - \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v})_r$$

Figs: TD-Cengel & Boles

Energy Density



https://en.wikipedia.org/wiki/Energy_density

What's next?

- Entropy & free energy changes in chemically reacting systems