Thermal & Electrochemical combustion- Enthalpy & Gibbs Free Energy Changes

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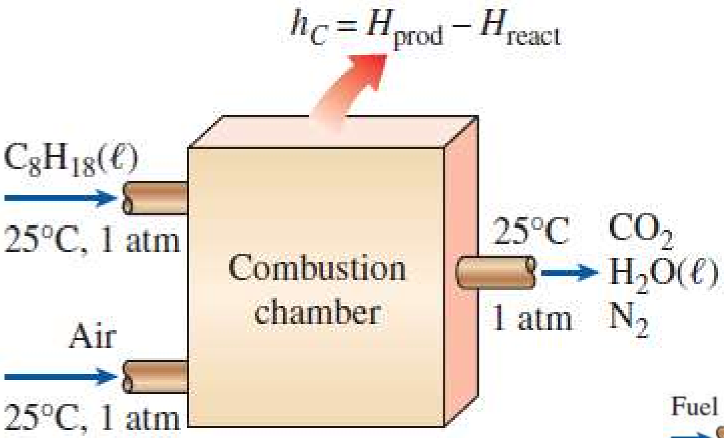
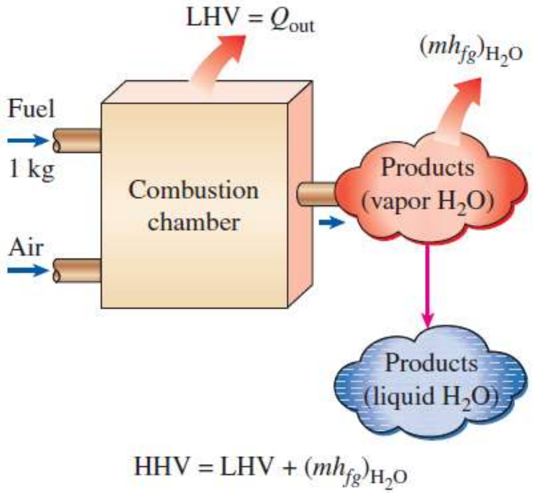
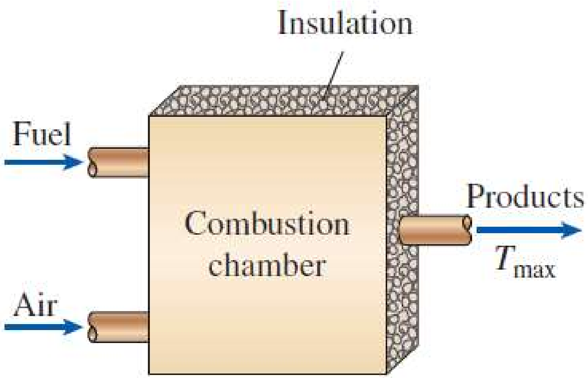
Previously: Energy Challenge & Enthalpy Changes of thermal combustion-

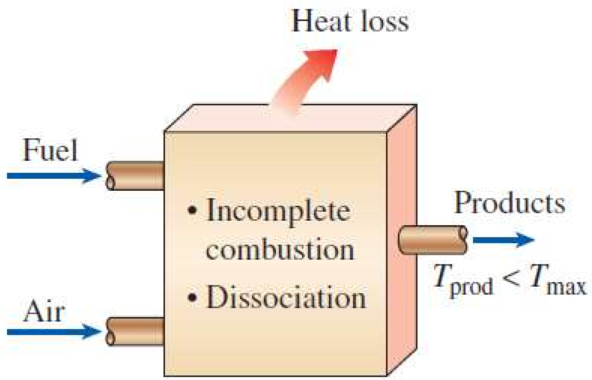
$$\bar{h}(T,p) = \bar{h}_f^\circ + [\bar{h}(T,p) - \bar{h}(T_{ref}, p_{ref})] = \bar{h}_f^\circ + \Delta\bar{h}$$

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







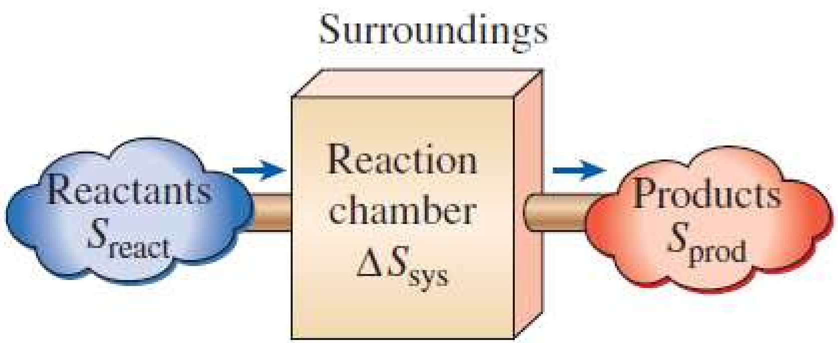


Entropy change for reacting systems

$$\underbrace{S_{\text{in}} - S_{\text{out}}}_{\substack{\text{Net entropy transfer}\\ \text{by heat and mass}}} + \underbrace{S_{\text{gen}}}_{\substack{\text{Entropy}\\ \text{generation}}} = \underbrace{\Delta S_{\text{system}}}_{\substack{\text{Change}\\ \text{in entropy}}} \qquad (\text{kJ/K})$$

$$\sum \frac{Q_k}{T_k} + S_{\text{gen}} = S_{\text{prod}} - S_{\text{react}} \qquad (\text{kJ/K})$$

$$S_{\text{gen,adiabatic}} = S_{\text{prod}} - S_{\text{react}} \geq 0$$



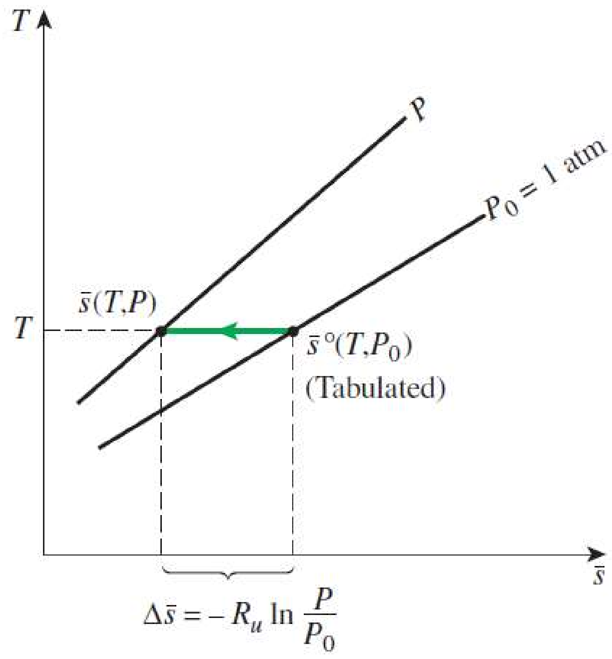
Figs: TD-Cengel & Boles

Approximations to entropy & Absolute Entropy

3rd law: S→ Constant as T→ 0

$$\bar{s}(T,P) = \bar{s}^\circ(T,P_0) - R_u \ln \frac{P}{P_0}$$

$$\bar{s}_i(T,P_i) = \bar{s}^\circ_i(T,P_0) - R_u \ln \frac{y_i P_m}{P_0} \qquad (\text{kJ/kmol}\cdot\text{K})$$



Thermochemical Properties of Selected Substances at 298K and 1 atm

Substance	Formula	Molar Mass, *M* (kg/kmol)	Enthalpy of Formation, $\bar{h}_f^o$ (kJ/kmol)	Gibbs Function of Formation, $\bar{g}_f^o$ (kJ/kmol)	Absolute Entropy, $\bar{s}^o$ (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

2^{nd} law analysis of reacting systems

$$X_{\text{destroyed}} = T_0 S_{\text{gen}} \qquad \text{(kJ)}$$

$$\psi = (h - T_0 s) - (h_0 - T_0 s_0)$$

$$w^{\text{rev}} = \dot{W}^{\text{rev}}/\dot{m} = \sum \left(1 - \frac{T_0}{T_j}\right) q_j + (h_{\text{tot}\,i} - T_0 s_i) - (h_{\text{tot}\,e} - T_0 s_e)$$

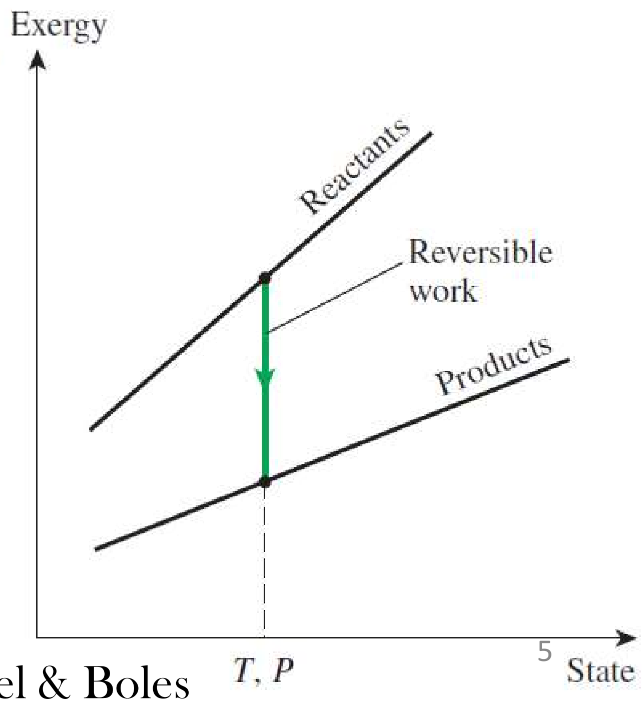
$$W^{\text{rev}} = \sum m_i (h_i - T_0 s_i) - \sum m_e (h_e - T_0 s_e)$$

$$W^{\text{rev}} = \sum_R n_i (\overline{h}_f^0 + \Delta\overline{h} - T_0 \overline{s})_i - \sum_P n_e (\overline{h}_f^0 + \Delta\overline{h} - T_0 \overline{s})_e$$

$$g = h - Ts$$

$$W^{\text{rev}} = \sum_R n_i \overline{g}_i - \sum_P n_e \overline{g}_e = -\Delta G$$

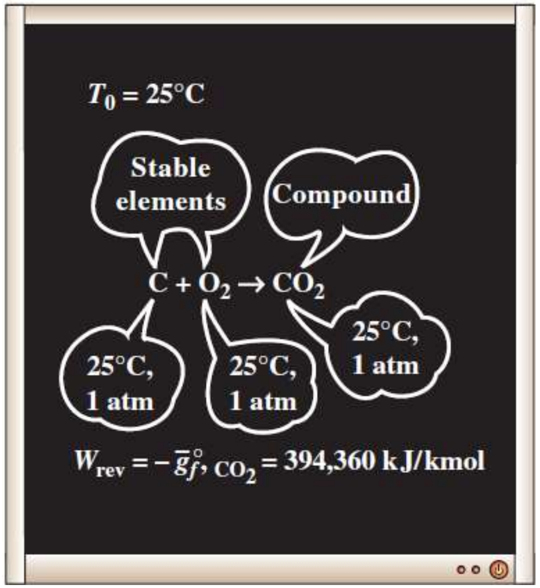
$$\Delta G = \Delta H - T\Delta S$$



Figs: TD-Borgnakke & Sonntag; Cengel & Boles

Reversible work from formation of compounds

$$W_{rev} = \sum N_r \bar{g}^{\circ}_{f,r} - \sum n_p \bar{g}^{\circ}_{f,p} \qquad \text{(kJ)}$$



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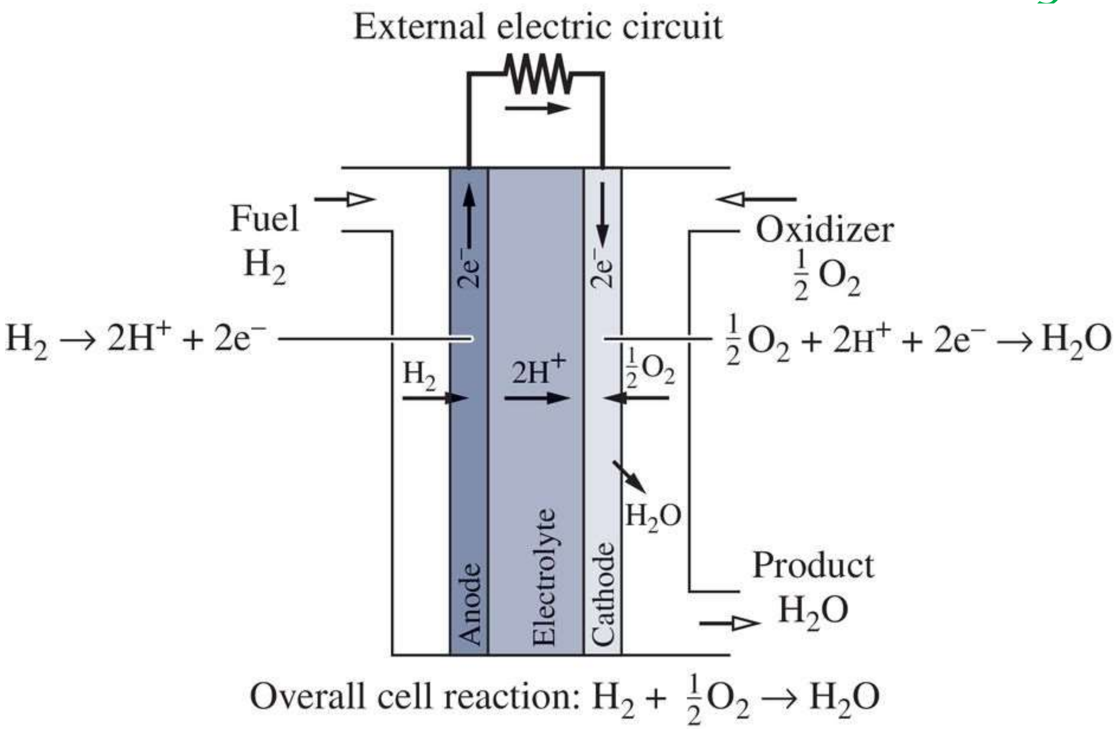
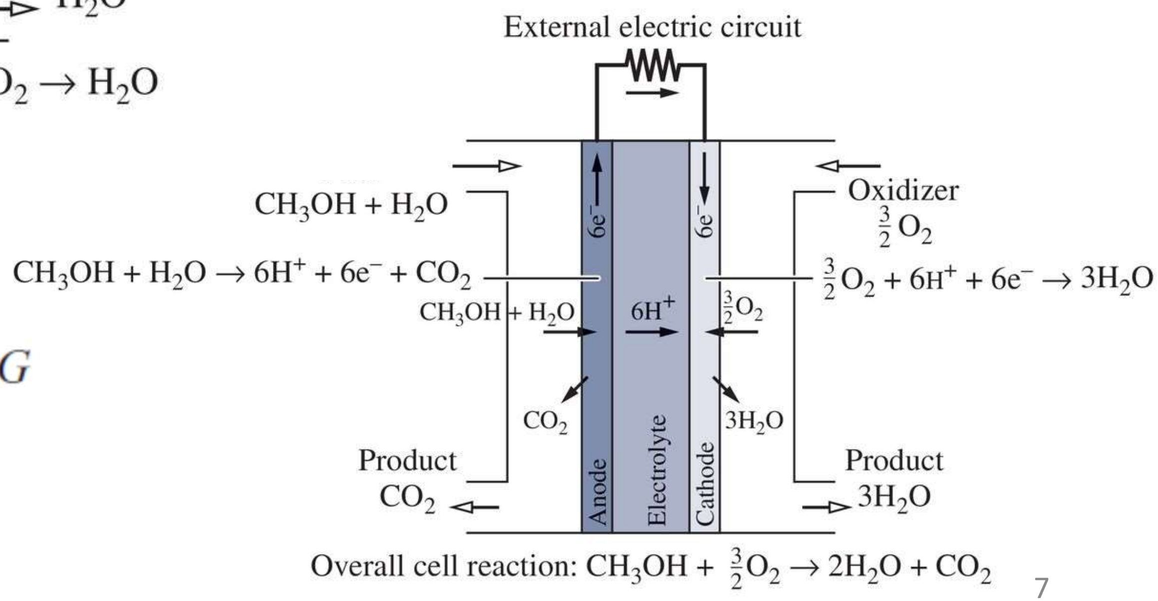
Fuel cells & Batteries: Electrical work unconstrained by Carnot η



(*a*)



$$W = -\left(\sum n_e \bar{g}_e - \sum n_i \bar{g}_i\right) = -\Delta G$$

$\Delta G = -nFE$

(*b*)

Figs: TD-Moran, Shapiro, Boettner & Bailey; Borgnakke & Sonntag

What's next?

- Phase equilibria, Phase rule & Kirchoff equation