Free Energy

● Second Law of Thermodynamics:

$$\Delta_{\mathrm{tot}} S = \Delta_{\mathrm{sys}} S + \Delta_{\mathrm{surr}} S \geq 0 \tag{1}$$

for all spontaneous processes. The $=$ sign holds if the process is reversible.

● Entropy change of the surroundings. The surroundings is (usually) taken to be a heat bath of temperature T_s. The heat going into the environment is $-$ the enthalpy change of the system:

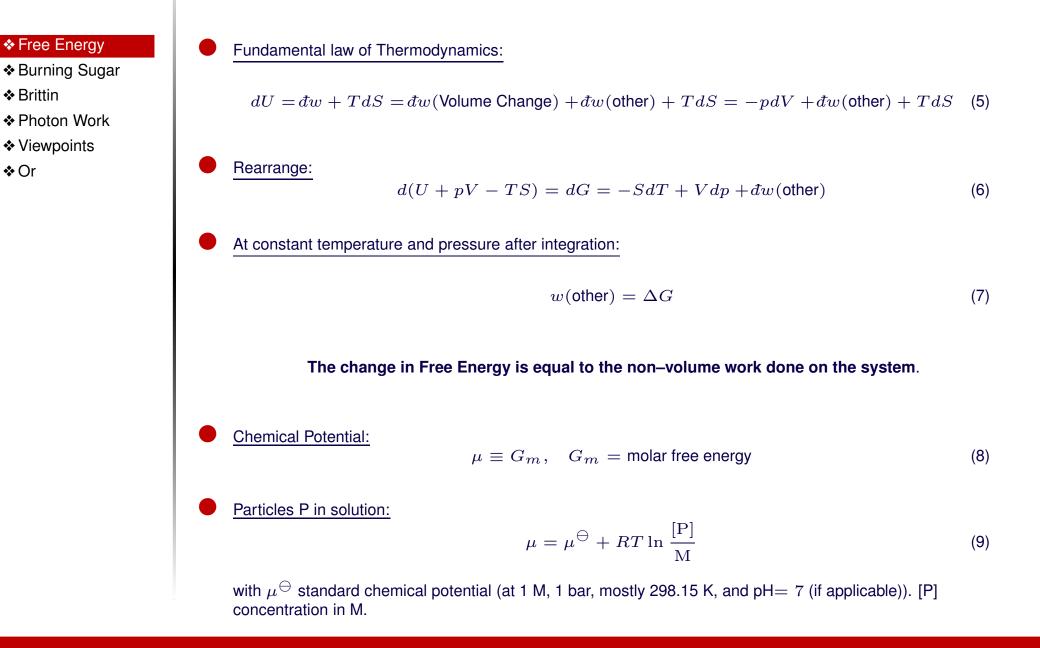$$\Delta_{\mathrm{surr}} S = \frac{q}{T_s} = -\frac{\Delta_{\mathrm{sys}} H}{T_s} \tag{2}$$

✦ Little sidebar: for systems other than gases the difference between enthalpy and internal energy is negligible.

● Putting Eq. (2) into Eq. (1) gives after some minor rearranging:

$$\Delta_{\mathrm{sys}} S + \Delta_{\mathrm{surr}} S = -\frac{1}{T_s} \left[\Delta_{\mathrm{sys}} H - T_s \Delta_{\mathrm{sys}} S \right] \tag{3}$$

● Free Energy:

$$\Delta_{rmsys} G \equiv \Delta G = \Delta_{\mathrm{sys}} H - T_s \Delta_{\mathrm{sys}} \equiv \Delta H - T \Delta S \leq 0 \tag{4}$$

For a spontaneous process the free energy change (G) of the **system** must be negative. For reversible processess it is zero.

Free Energy and work

● Fundamental law of Thermodynamics:

$$dU = đw + TdS = đw(\text{Volume Change}) + đw(\text{other}) + TdS = -pdV + đw(\text{other}) + TdS \quad (5)$$

● Rearrange:

$$d(U + pV - TS) = dG = -SdT + V\,dp + đw(\text{other}) \quad (6)$$

● At constant temperature and pressure after integration:

$$w(\text{other}) = \Delta G \quad (7)$$

The change in Free Energy is equal to the non–volume work done on the system.

● Chemical Potential:

$$\mu \equiv G_m, \quad G_m = \text{molar free energy} \quad (8)$$

● Particles P in solution:

$$\mu = \mu^{\ominus} + RT \ln \frac{[\text{P}]}{\text{M}} \quad (9)$$

with $\mu^{\ominus}$ standard chemical potential (at 1 M, 1 bar, mostly 298.15 K, and pH= 7 (if applicable)). [P] concentration in M.

Burning Sugar

● Overall photosynthesis reaction:

$$6H_2O + 6CO_2 \longrightarrow C_6H_{12}O_6 + 6O_2 \tag{10}$$

This is the reverse of the combustion reaction.

● Combustion of Sugar:

$$\Delta_c H^{\ominus} = -2801\,\mathrm{kJ/mol}$$
$$\Delta_c S^{\ominus} = 265\,\mathrm{J\,mol^{-1}K^{-1}}$$
$$\Delta_c G^{\ominus} = -2880\,\mathrm{kJ/mol} \tag{11}$$

● Photosynthesis:

$$\Delta_{\mathrm{ph}} H^{\ominus} = 2801\,\mathrm{kJ/mol}$$
$$\Delta_{\mathrm{ph}} S^{\ominus} = -265\,\mathrm{J\,mol^{-1}K^{-1}}$$
$$\Delta_{\mathrm{ph}} G^{\ominus} = 2880\,\mathrm{kJ/mol} \tag{12}$$

Brittin's Paper

● Brittin uses photons of 4×10^{14} s^{-1}. That is the equivalent of 13333 cm^{-1} or 750 nm.

● 1 mole of such photons have an energy of 160 kJ. If we move that energy from the hot sun (6000 K) to the cold earth (300 K), we can gain an amount of entropy of

$$\Delta S \approx \frac{160\,\text{J}}{300\,\text{K}} = 533\,\text{J/K} \tag{13}$$

● In contrast to what Brittin claims I would say the formation of glucose requires at least 18 quanta (no idea where het gets 3, the entropy is also wrong). in which case the entropy production would be 9400 J/mol K.

● Note: 38 molecules of ATP are produced by burning one glucose molecule, and about three protons are needed over the membrane to get one ATP.

How much of the photon energy can I use to do work?

Source of the photon a heat bath of temperature T_h, sink for the energy a heat bath of temperature T_c.

● Entropy loss by source:

$$\Delta_h S = -\frac{h\nu}{T_h} \tag{14}$$

● Entropy gain by sink:
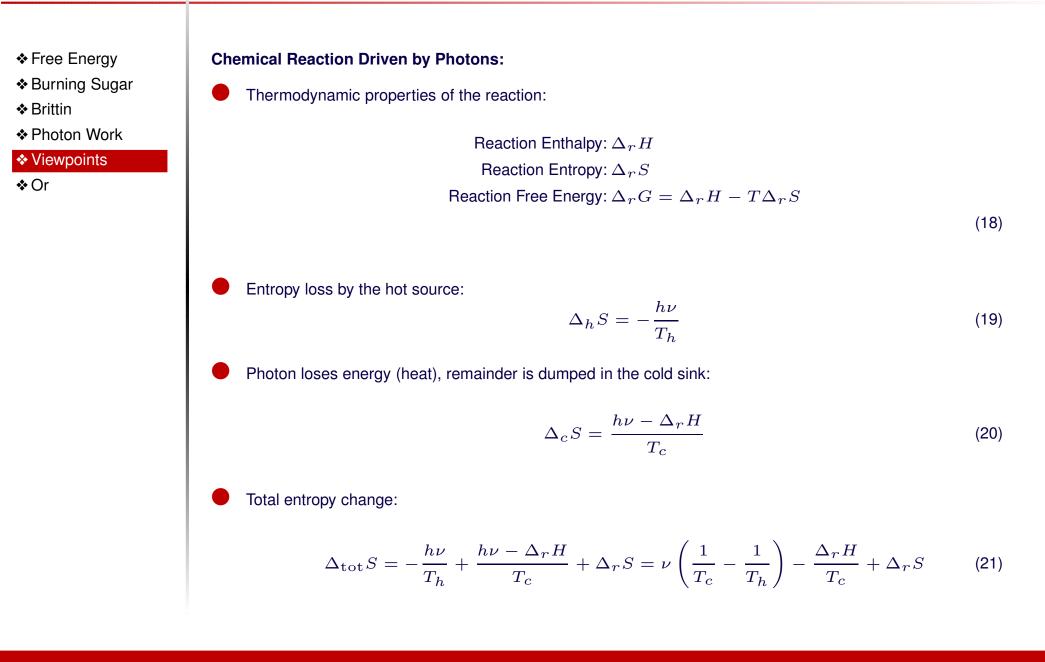
$$\Delta_c S = \frac{h\nu}{T_c} \tag{15}$$

● Total entropy change:

$$\Delta_{\text{tot}} S = -\frac{h\nu}{T_h} + \frac{h\nu}{T_c} \tag{16}$$

● Suppose I want to use part of the photon energy $xh\nu$ for useful work, for which x is the entropy balance still positive?

$$-\frac{h\nu}{T_h} + (1-x)\frac{h\nu}{T_c} \geq 0 \quad \text{or} \quad x \leq 1 - \frac{T_c}{T_h} \tag{17}$$

Two Points of View

Chemical Reaction Driven by Photons:

● Thermodynamic properties of the reaction:

$$\text{Reaction Enthalpy: } \Delta_r H$$
$$\text{Reaction Entropy: } \Delta_r S$$
$$\text{Reaction Free Energy: } \Delta_r G = \Delta_r H - T\Delta_r S$$

$$(18)$$

● Entropy loss by the hot source:

$$\Delta_h S = -\frac{h\nu}{T_h} \tag{19}$$

● Photon loses energy (heat), remainder is dumped in the cold sink:

$$\Delta_c S = \frac{h\nu - \Delta_r H}{T_c} \tag{20}$$

● Total entropy change:

$$\Delta_{\text{tot}} S = -\frac{h\nu}{T_h} + \frac{h\nu - \Delta_r H}{T_c} + \Delta_r S = \nu\left(\frac{1}{T_c} - \frac{1}{T_h}\right) - \frac{\Delta_r H}{T_c} + \Delta_r S \tag{21}$$

Or

● Photon loses amount of work, rest is dumped in the cold reservoir

$$\Delta_c S = \frac{h\nu - w}{T_c} = \frac{h\nu - \Delta_r G}{T_c} \tag{22}$$

● Total entropy change:

$$\Delta_{\text{tot}} S = -\frac{h\nu}{T_h} + \frac{h\nu - \Delta_r G}{T_c} = h\nu \left(\frac{1}{T_c} - \frac{1}{T_h} \right) - \frac{\Delta_r H}{T_c} + \Delta_r S \tag{23}$$

The amount $xh\nu$ of slide 5 should indeed be considered the maximum amount of work.

Maximal efficiency is Carnot efficiency:

$$\eta = \frac{xh\nu}{h\nu} = 1 - \frac{T_c}{T_h} \tag{24}$$