

## Chapter 5 - Free Energy

Apply the laws of thermo to non-cyclic processes

↓  
chemical reaction

+ other transformations

↳ most interactions

are not isolated from surroundings

↳ but exchange energy and volume.

↳ most are constant temperature + constant pressure

Enthalpy - internal energy plus work to make room for the system under constant pressure from the environment

$H \equiv U + pV$  ← total energy to create the system and put it in an environment

$$dH = \pm Q + dW_{\text{other}}$$

New quantity analogous to enthalpy

Helmholtz Free Energy  $\rightarrow$  total energy to create the system minus the heat you can extract from the surroundings at constant temperature  $T$

$$F \equiv U - TS$$

$\hookrightarrow$  all work done on the system by us and/or surroundings

$\hookrightarrow$  to get the work we must do (to a system at constant pressure & temp)

$\hookrightarrow$  Gibbs Free Energy

$$G = U - TS + pV$$

$$G = \underline{H - TS}$$

energy to make the system + make room for the system minus the heat we get to subtract from surroundings

Together there are thermodynamic potentials.

$$dF = dU - TdS$$

$$dF = \pm Q + \pm W - TdS$$

for a reversible process: (no new entropy created)

$$\pm Q_{\text{rev}} = TdS$$

$$\text{then, } dF = \cancel{TdS} + \pm W - \cancel{TdS}$$

$$dF = \pm W \rightarrow \text{work done on the system}$$

otherwise,

$$dF \leq \pm W$$

Now for the changes in Gibbs

$$dG = dU - TdS + pdV$$

$$dG = \pm Q + \pm W - TdS + pdV$$

for reversible processes,

$$\pm Q = TdS$$

$$\pm W = \underbrace{-pdV}_{\text{compression work}} + \pm W_{\text{other}}$$

↳ electrical work, etc

$$dG = \cancel{TdS} - \cancel{pdV} + \pm W_{\text{other}} - \cancel{TdS} + \cancel{pdV}$$

$$dG = \pm W_{\text{other}}$$

for other than reversible processes

$$dG \leq \pm W_{\text{other}} \text{ at constant } T, p$$

$\Delta G$  is very useful so how do you measure it?

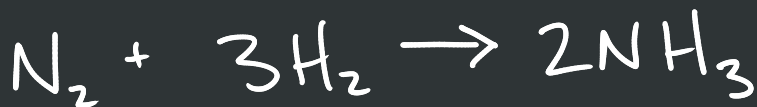
First measure  $\Delta H \rightarrow$  heat absorbed/released for a reaction at constant pressure + no other work is done.

Then what? Calculated  $\Delta S$  from initial + final states using heat capacity data

$$\Delta S = \int_0^T \frac{C_p}{T} dT$$

$$\text{Then, } \Delta G = \Delta H - T\Delta S$$

# Ex: Problem 5.2



$$T = 298\text{K}$$

$$p = 1 \text{ bar} = 10^5 \text{ Pa} \approx 1 \text{ atm} = 1.01 \cdot 10^5 \text{ Pa}$$

$$\Delta H = 0 \text{ kJ/mol}$$

$$S = 191.6 \frac{\text{J}}{\text{K mol}}$$

$$\Delta H = 0 \text{ kJ/mol}$$

$$S = 130.68 \frac{\text{J}}{\text{K mol}}$$

$$\Delta H = -46.11 \text{ kJ/mol}$$

$$S = 192.45 \frac{\text{J}}{\text{K mol}}$$

$$\Delta H = -46.11 \frac{\text{kJ}}{\text{mol}} \cdot 2 \text{ mol} = -92.22 \text{ kJ}$$

$$\Delta S = 2 \text{ mol} \cdot 192.45 \frac{\text{J}}{\text{K mol}} - 3 \cdot 130.68 - 1 \cdot 191.6 \frac{\text{J}}{\text{K}} = -198.75 \frac{\text{J}}{\text{K}}$$

$$\Delta G = \Delta H - T \Delta S = -92.22 \text{ kJ} - 298 \text{ K} \left( -198.75 \frac{\text{J}}{\text{K}} \right) \quad \leftarrow \text{Joules}$$

$$\Delta G = \boxed{-32.99 \text{ kJ}} \quad \underbrace{\quad \quad \quad}_{+59.23 \text{ kJ}}$$

$$\text{Compare to table} \rightarrow \Delta_f G = -16.45 \times 2 \text{ mol} = \boxed{-32.9 \text{ kJ}}$$

# Electrolysis, Fuel Cells, Batteries





































