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 at 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

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

New quantity analogous to enthalpy

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

$$F \equiv U - TS$$

↳ all work done on the system by us and/or surroundings

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

↳ 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 these are thermodynamic potentials.

$$dF = dU - TdS$$

$$dF = \text{đ}Q + \text{đ}W - TdS$$

for a reversible process: (no new entropy created)

$$\text{đ}Q_{rev} = TdS$$

then, $dF = TdS + \text{đ}W - TdS$

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

otherwise,

$$dF \leq \text{đ}W$$

Now for the changes in Gibbs

$$dG = dU - TdS + pdV$$

$$dG = đQ + đW - TdS + pdV$$

for reversible processes,

$$đQ = TdS$$

$$đW = \underbrace{-pdV}_{\text{compression work}} + đW_{other}$$ ← electrical work, etc

$$dG = \cancel{TdS} - \cancel{pdV} + đW_{other} \cancel{-TdS} + \cancel{pdV}$$

$$dG = đW_{other}$$

for other than reversible processes

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

ΔG is very useful so how do you measure it?

First measure ΔH → heat absorbed/released for a reaction at constant pressure + no other work is done.

Then what? Calculated ΔS from initial + final states using heat capacity data

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

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

Ex: Problem 5.2

$$N_2 + 3H_2 \rightarrow 2NH_3$$

$T = 298\,K$

$p = 1\ bar = 10^5\ Pa \simeq 1\ atm = 1.01 \cdot 10^5\ Pa$

N_2: $\Delta H = 0\ kJ/mol$, $S = 191.6\ J/K\,mol$

$3H_2$: $\Delta H = 0\ kJ/mol$, $S = 130.68\ J/K\,mol$

$2NH_3$: $\Delta H = -46.11\ kJ/mol$, $S = 192.45\ J/K\,mol$

$$\Delta H = -46.11\ kJ/mol \cdot 2\,mol = -92.22\ kJ$$

$$\Delta S = 2\,mol \cdot 192.45\ J/K\,mol - 3 \cdot 130.68 - 1 \cdot 191.6\ J/K = -198.75\ J/K$$

$$\Delta G = \Delta H - T\Delta S = -92.22\,kJ - 298\,K\left(-198.75\ J/K\right)$$

Joules

$$\Delta G = \boxed{-32.99\ kJ}$$

$+59.23\,kJ$

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

Electrolysis, Fuel Cells, Batteries