

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

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

ΔG is very useful so how do you measure it?

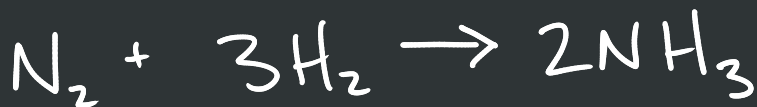
First measure $\Delta H \rightarrow$ heat absorbed/released for a reaction at constant pressure + no other work is done.

Then what? Calculated 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



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

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

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

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

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

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

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

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

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

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

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

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

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

Electrolysis, Fuel Cells, Batteries.



↑ electrical work has to be done

$\Delta H = \underline{\underline{286 \text{ kJ}}}$ \rightsquigarrow heat out when
this reaction runs
in reverse

↑ to run forward we have to put
in this much energy

→ some of this energy will push
the environment away

$$\begin{aligned} pV_1 &= n_1RT \\ pV_2 &= n_2RT \end{aligned} \quad \rightarrow \quad p\Delta V = \Delta n \cdot R \cdot T = 1.5 \text{ mol} \cdot (8.31 \text{ J/Kmol}) (300 \text{ K})$$

?

$$= 3739 \text{ J}$$
$$= 3.7 \text{ kJ} \approx 4 \text{ kJ} \leftarrow$$

So 282 kJ will remain in the syst
in the form of potential energy in chemical bonds
→ Do we need to do all of this work
or can we get some heat from surroundings?

What is the change in entropy for the system?

$$S_{\text{H}_2\text{O}} = 70 \text{ J/K} \quad S_{\text{H}_2} = 131 \text{ J/K} \quad S_{\text{O}_2} = 205 \text{ J/K}$$

products

$$S_p = 131 \text{ J/K} + \frac{1}{2} \cdot 205 \text{ J/K} = 233.5 \text{ J/K}$$

$$\Delta S_{\text{reaction}} = 233.5 \text{ J/K} - 70 \text{ J/K} = 163.5 \text{ J/K}$$

entropy increase

$$\Delta Q \leq T \Delta S$$

$$Q = T \Delta S = 300 \text{ K} \cdot 163.5 \text{ J/K} \\ = 49 \text{ kJ}$$

So of 286 kJ that go in, 49 kJ come from the surroundings

$$286 \text{ kJ} - 49 \text{ kJ} = \underline{\underline{237 \text{ kJ}}} \rightarrow \text{comes from} \\ \underline{\text{electrical work}}$$

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

In reverse, we can extract 237 kJ of electrical work!

→ 49 kJ waste heat goes to the environment

→ $\Delta U = 282 \text{ kJ}$ → comes from chemical reaction

→ $P \Delta V = 4 \text{ kJ}$ → comes from collapse of gas → liquid

$$\text{efficiency} = \frac{\text{get}}{\text{pay for}}$$

$$\frac{\text{fuel cell}}{\frac{237 \text{ kJ}}{286 \text{ kJ}}} = 83\%$$

⏟
this is great!

Carnot → • extreme case in
cycle chapter 4 → 66%

→ • car engine
 $e_{\text{max}} = 50\%$

$e_{\text{actual}} = 20\%$

