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 an constant temperature + constant pressure

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

$$H \equiv U + pV \longleftarrow \text{total energy to create the system and put it in an environment}$$

$$dH = đQ + dW_{other}$$

New quantity analogous to enthalpy

Helmholtz Free Energy $\to$ 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

So to get the work <u>we</u> 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 <u>minus</u> the heat we get to subtract from surroundings

Together these are thermodynamic potentials.

$$dF = dU - TdS$$

$$dF = \mathchar'26\mkern-12mu dQ + \mathchar'26\mkern-12mu dW - TdS$$

for a reversible process: (no new entropy created)

$$\mathchar'26\mkern-12mu dQ_{rev} = TdS$$

then, $dF = T\cancel{dS} + \mathchar'26\mkern-12mu dW - T\cancel{dS}$

$$dF = \mathchar'26\mkern-12mu dW \longrightarrow \text{work done on the system}$$

otherwise,

$$dF \leq \mathchar'26\mkern-12mu dW$$

Now for the changes in Gibbs

$$dG = dU - TdS + pdV$$

$$dG = đQ + đW - TdS + pdV$$

for reversible processes,

$$đQ = TdS$$

$$đW = \underbrace{-pdV}_{\substack{\text{compression} \\ \text{work}}} + đW_{other}$$

$\hookrightarrow$ electrical work, etc

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

$$dG = + đW_{other}$$

for other than reversible processes

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

ΔG is very useful so how do you measure it?
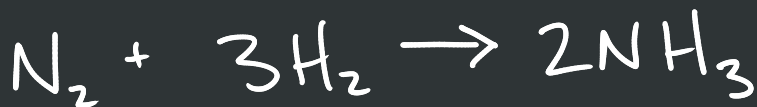
First measure ΔH → heat absorbed/released for a reaction at constant pressure + no other work is done.

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

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

$T = 298K$

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

$\Delta H = 0 kJ/mol$

$S = 191.6 \, J/K \, mol$

$\Delta H = 0 kJ/mol$

$S = 130.68 \, J/K \, mol$

$\Delta H = -46.11 \, kJ/mol$

$S = 192.45 \, J/K \, mol$

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

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

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

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

$+59.23 kJ$

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

Electrolysis, Fuel Cells, Batteries.

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$

electrical work has to be done

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

to run forward we have to put in this much energy

$\rightarrow$ some of this energy will push the environment away

$$pV_1 = n_1RT$$
$$pV_2 = n_2RT$$
$\longrightarrow$
$$p\Delta V = \Delta n \cdot R \cdot T = 1.5 \text{ mol} \cdot (8.31 \text{ J}/_{Kmol})(300K)$$
$$?$$
$$= 3739 \text{ J}$$
$$= 3.7 \text{ kJ} \approx 4 \text{ kJ} \leftarrow$$

So $\underline{282\,kJ}$ will remain in the system in the form of potential energy in chemical bonds

↪ Do we need to do all of this work or can we get some <u>heat</u> from surroundings?

What is the change in entropy for the system?

$$S_{H_2O} = 70\,J/K \qquad S_{H_2} = 131\,J/K \qquad S_{O_2} = 205\,J/K$$

$$\underbrace{\phantom{S_{H_2} = 131\,J/K \qquad S_{O_2} = 205\,J/K}}_{products}$$

$$S_p = 131\,J/K + \frac{1}{2}\cdot205\,J/K = 233.5\,J/K$$

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

entropy increase

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

$$Q = T \Delta S = 300 K \cdot 163.5 \, J/K$$

$$= 49 \, kJ$$

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

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

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

In reverse, we can extract 237 kJ of electrical work!
→ 49 kJ waste heat goes to the environment
→ $\Delta U = 282 kJ \rightsquigarrow$ comes from chemical reaction
→ $P \Delta V = 4 kJ \rightsquigarrow$ comes from collapse of gas → liquid

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

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

237 kJ

$\underbrace{\hspace{3cm}}$

this is great!

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

→ o car engine
$e_{max} = 50\%$
$e_{actual} = 20\%$

Battery reaction

$$Pb + PbO_2 + 4H^+ + 2SO_4^{-2} \rightarrow 2PbSO_4 + 2H_2O$$

start w/ $\Delta H \rightsquigarrow$ heat in to accomplish the rxn

$$\Delta H = -316 \text{ kJ/mol}$$

↪ energy out from reaction
at constant pressure

what is the Gibbs?

$$\Delta G = -394 \text{ kJ/mol}$$

↪ electrical energy out

more than ΔH!

How? Heat coming in to the system from the
surroundings. How much?

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

$$394 \frac{kJ}{mol} - 316 \frac{kJ}{mol} = 78 \frac{kJ}{mol} = T\Delta S$$

Entropy increases

$$\Delta S = \frac{78,000 \, J/mol}{298 \, K}$$

$$\Delta S = 261.7 \, J/K$$

an entropy increase means the system can absorb heat from the outside.

Energy/charge in this reaction?

voltage

↳ need to know how many e^- move during the reaction:

2e^- are given up at the $(-)$ electrode

2e^- are taken up at the $(+)$ electrode

So since voltage $= \frac{\Delta W_E}{q} = \frac{394\,000 \, J}{2e \cdot 1.6 \cdot 10^{-19} \frac{C}{e} \cdot N_A} = 2.04 \, V$

Thermodynamic identities

$$dU = TdS - pdV + \mu dN$$

↳ how the energy changes
when dS, dV, & dN change

what about H, F, and G?

Enthalpy

$$H = U + pV$$

$$dH = dU + pdV + Vdp$$

$$dH = TdS - \cancel{pdV} + \mu dN + \cancel{pdV} + Vdp$$

$$\rightarrow dH = Td\underline{S} + \mu d\underline{N} + Vd\underline{p}$$

variables have changed from dU.

$\left| \begin{array}{l} dp = 0 \\ dN = 0 \end{array} \right\}$ $dH = TdS \leftarrow$ heat at constant p

Helmholtz Free Energy

$$F = U - TS$$

$$dF = dU - TdS - SdT$$

$$\rightarrow dF = -S\underline{dT} - p\underline{dV} + \mu\underline{dN}$$

Gibbs Free Energy

$$G = U - TS + pV$$

$$\rightarrow dG = -S\underline{dT} + V\underline{dp} + \mu\underline{dN}$$

test Q

$T, p, N \rightarrow$ very natural variables
for experiments in lab.

You can use the thermodynamic identities to derive many useful derivative statements

take $dF = -SdT - pdV + \mu dN$

hold V & N constant

$$dV = 0$$
$$dN = 0$$
$$dF = -SdT$$
so $S = -\left(\dfrac{\partial F}{\partial T}\right)_{V,N}$ ← entropy is the rate of change in F w.r.t T.

and so on, holding the other combinations constant,

$$p = -\left(\dfrac{\partial F}{\partial V}\right)_{T,N} \quad , \quad \mu = \left(\dfrac{\partial F}{\partial N}\right)_{T,V}$$

Similarly for Gibbs!

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} \quad , \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,N} \quad , \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$$

chemical potential $\downarrow$ (pointing to μ)

How does the Gibbs Free Energy change w/ pressure from the reference data?

1 mol of C $\Rightarrow$ $5.3 \cdot 10^{-6} \, m^3$ (graphite)

$\Delta G_c = 0 \, kJ \leftarrow$ most stable form

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N} \quad \Rightarrow \quad V \cdot \partial P = \partial G$$

$$5.3 \cdot 10^{-6} \cdot \partial P = \partial G$$

$\uparrow$ a small increase in pressure

$\nwarrow$ increases the gibbs free energy

Ex: (5.10)

1 mol H_2O at 25°C (298 K)

Gibb's at 30°C (303 K)?

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$$

$$S_{H_2O} = 69.91 \text{ J/K}$$

$$\Delta G = -S \cdot \Delta T = -\left(69.91 \text{ J/K}\right) \cdot (5 \text{ K}) = -349.55 \text{ J}$$

$$\underline{\underline{G(303)}} - G(298) = -349.55 \text{ J}$$

$$G(303) = -349.55 \text{ J} + G(298)$$

$$= -0.349 55 \text{ kJ} + (-237.13 \text{ kJ})$$

$$= -237.48 \text{ kJ} \checkmark$$

5.2) Free Energy as a Force toward Equilibrium

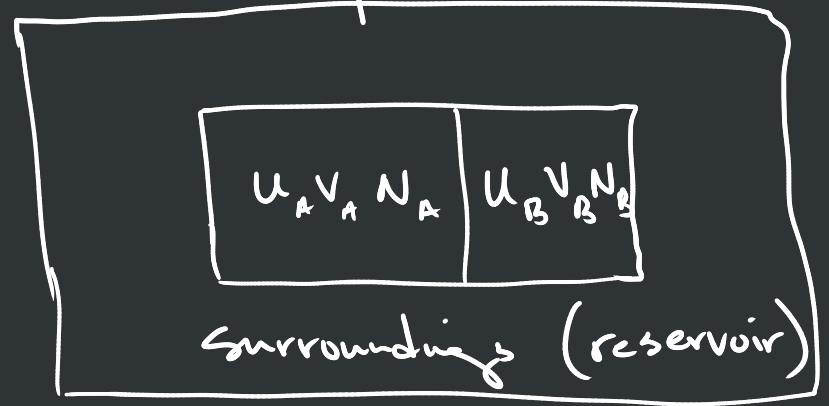$$dS_{total} = dS + \underbrace{dS_R}_{\text{reservoir}}$$

↳ rewrite in terms of system variable

$$dS_R = \frac{1}{T}dU_R + \cancel{\frac{P}{T}dV_R} - \cancel{\frac{\mu}{T}dN_R}$$

$$dS_R = \frac{1}{T}dU_R$$

$$dU_R = -dU \implies dS_R = -\frac{1}{T}dU$$

$$dS_{total} = dS - \frac{1}{T}dU$$

$$= \frac{T}{T}dS - \frac{1}{T}dU$$

(diagram, top right)

$U_A V_A N_A$ | $U_B V_B N_B$

surroundings (reservoir)

$$= -\frac{1}{T}\left(-TdS + dU\right)$$

$$= -\frac{1}{T}\underbrace{\left(dU - TdS\right)}_{\text{Helmholtz!}}$$

$$dF = dU - TdS \underbrace{- SdT}_{\substack{\text{assume} \\ dT = 0}}$$

$$dS_{total} = -\frac{dF}{T}\Big) \Bigg| \begin{array}{l} \text{conditions} \\ dT = 0 \\ dV = 0 \\ dN = 0 \end{array}$$

↑
increase
this

decrease → so the system will minimize
that   its Helmholtz free energy

What about keeping pressure, temperature, and number of particles fixed?

$$dS_{total} = dS + dS_R$$

$$dS_R = \frac{1}{T}dU_R + \frac{P}{T}dV_R - \frac{\mu}{T}dN_R^{\,0}$$

$$dU_R = -dU$$

$$dV_R = -dV$$

$$dS_{total} = dS - \frac{1}{T}dU - \frac{P}{T}dV$$

$$= -\frac{1}{T}\left(\underbrace{dU - TdS + PdV}\right)$$

$$dG \quad \text{if hold } T, P, N \text{ constant}$$

$$dS_{total} = -\frac{dG}{T}$$

System will minimize
Gibbs spontaneously

$$dT = 0$$
$$dP = 0$$
$$dN = 0$$

- At constant energy and volume, S tends to increase
- At constant temperature & volume, F tends to decrease
- At constant temperature & pressure, G tends to decrease