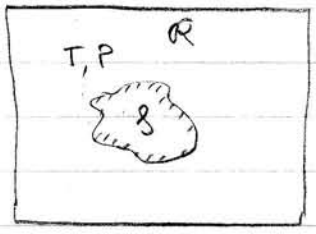
Lecture 19 - Gibbs free energy

In lecture and homework, we introduced Gibbs free energy which is useful when system S is held at constant p, T by reservoir R



$$G \equiv \underbrace{U + PV}_{H} - TS$$

enthalpy

In homework, showed that G of S is minimized at equilibrium. Total system $R+S$ is isolated so:

$$dS_{R+S} = \underbrace{dS_R} + dS_S = 0 \qquad \text{at equilibrium}$$

$$\frac{dU_R}{T} + \frac{P}{T} dV_R \qquad \text{from thermo. identity}$$

$$P_R = P_S = P \quad \text{and} \quad T_R = T_S = T$$

U_{R+S} and V_{R+S} are fixed so $dU_R = -dU_S$ $\quad dV_R = -dV_S$

$$\therefore \quad dS_{R+S} = 0 = -\frac{dU_S}{T} - \frac{P}{T} dV_S + dS_S$$

$$= -\frac{1}{T} d\left(U_S + PV_S - TS_S\right)$$

$$= -\frac{dG_S}{T}$$

So $dG_S = 0$ at equilibrium and it is a minimum (- sign)

To recap different ensembles:

Constant U, V (microcanonical): $\Delta S \geq 0$ (= at equilibrium)
Constant T, V (canonical): $\Delta F \leq 0$ "
Constant T, p: $\Delta G \leq 0$ "

Also last time we showed that:

$U = U(S,V)$ $\quad dU = TdS - pdV + \mu dN$
$F = F(T,V)$ $\quad dF = -SdT - pdV + \mu dN$
$G = G(T,p)$ $\quad dG = -SdT - Vdp + \mu dN$

If particles exchange we add $+\mu dN$

We also related these quantities to work:

$W \geq \Delta F$ (= when process is reversible, i.e. at equilibrium throughout)

$W' \geq \Delta G$ $\quad W' = W + p\Delta V$ "effective work" = all work except $-p\Delta V$ automatically done by atmosphere R

W' is the work we can extract from a system going from $G_1 \to G_2 < G_1$

Extensive vs. intensive:

U, F, G, H, S, V, N are extensive. If S doubles in size these quantities double

$p, T, \mu, n = \frac{N}{V}$ are intensive, independent of S size

$\left(\frac{1}{T} = \frac{\partial S}{\partial U} \right)$ so $S \to 2S$, $U \to 2U$ leaves T constant)

Gibbs free energy and chemical potential

Ex: ideal monatomic gas $\quad \mathcal{Z} = \frac{(n_Q V)^N}{N!}$

$$F = -k_B T \ln \mathcal{Z} = -k_B T \ln \frac{(n_Q V)^N}{N!}$$

$$= -k_B T \left(N \ln (n_Q V) - N \ln N + N \right) \qquad \text{using Stirling's approx.}$$

$$= N k_B T \left[\ln \left(\frac{n}{n_Q} \right) - 1 \right] \qquad \text{which is extensive}$$

Recall that $\mu_{ideal} = k_B T \ln \left(\frac{n}{n_Q} \right)$

$$\therefore \quad F = N(\mu - k_B T)$$

$$G = U - TS + PV = F + PV$$

$$= N(\mu - k_B T) + PV \qquad \text{since } PV = N k_B T$$

$$\therefore \quad G = N\mu \qquad \text{also extensive}$$

(Notice even though G, μ have units of energy G is extensive μ is intensive. Can't have quantities like $G + \mu$)

This equation $G = N\mu$ turns out to be true generally:

$G = G(T, P, N)$ is extensive $\therefore$ if we double the system size:

$$G(T, P, N) \rightarrow 2G(T, P, N \rightarrow 2N)$$

Since T, P are intensive, it must be that $G \propto N$

$$\therefore \quad \boxed{G(T, P, N) = N \psi(P, T)}$$

But, $dG = -SdT + Vdp + \underbrace{\mu dN}$

$\left(\frac{\partial G}{\partial N}\right)_{T,p}$

and $\left(\frac{\partial G}{\partial N}\right)_{T,p} = \varphi(p,T)$ $\quad\therefore\quad$ $\varphi(p,T) = \mu$

$$\boxed{G(T,p,N) = N\mu(T,p)}$$

(Note: this argument works only because G depends on only one extensive quantity N. For $F(T,V,N)$ both V, N are extensive $\therefore$ $F \neq N\varphi(T,V)$)

For a system with more than one species, generalize this:

$$G(T,p,N_1 \cdots N_n) = \sum_{i=1}^{n} \mu_i N_i = U - TS + pV$$

$$dG = -SdT - Vdp + \sum_{i=1}^{n} \underbrace{\mu_i dN_i}$$

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_{j\neq i}}$$

These relations will be very useful for understanding <u>chemical reactions</u>, which are at constant T, p

<u>Chemical equilibrium</u> is reached when $G = \sum \mu_i N_i$ is minimized

Ex: consider the reaction:

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

called "nitrogen fixation". Puts nitrogen in a form that can be used by plants to synthesize amino acids, etc.

Write this as an equation:

$$-1 \cdot N_2 - 3 \cdot H_2 + 2 \cdot NH_3 = 0$$

or generally:

$$\nu_1 A_1 + \nu_2 A_2 + \cdots \nu_n A_n = 0 \qquad A_i = i\text{th species}$$

Equilibrium reached when $G(T, p, N_1 \cdots N_n)$ is minimized

$$G = \sum_i \mu_i N_i = \sum_i G_i$$

At constant T, p:

$$dG = 0 = \underbrace{\left(\frac{\partial G_1}{\partial N_1}\right)_{T,p,N_{i\neq 1}}}_{\mu_1} dN_1 + \underbrace{\left(\frac{\partial G_2}{\partial N_2}\right)_{T,p,N_{i\neq 2}}}_{\mu_2} dN_2 \cdots \underbrace{\left(\frac{\partial G_n}{\partial N_n}\right)_{T,p,N_{i\neq n}}}_{\mu_n} dN_n$$

dN_i are the changes in # of molecules of each species

For nitrogen fixation reaction:

$$dN_{N_2} = -1 \cdot d\hat{N} \qquad dN_{H_2} = -3 \cdot d\hat{N} \qquad dN_{NH_3} = +2 \cdot d\hat{N}$$

$d\hat{N}$ = # of reaction cycles

$\therefore$ In general $dN_i = \nu_i d\hat{N}$ and equilibrium condition is:

$$\boxed{\mu_1 \nu_1 + \mu_2 \nu_2 + \cdots \mu_n \nu_n = \sum_{i=1}^{\hat{}} \mu_i \nu_i = 0}$$

For our reaction: $-\mu_{N_2} - 3\mu_{H_2} + 2\mu_{NH_3} = 0$

Treat N_2, H_2, NH_3 as ideal gases

$\mu_i = k_B T \ln\left(\frac{n_i}{n_q}\right)$ Useful to write in terms of partial pressure

$p_i = \frac{N_i k_B T}{V_i} = n_i k_B T$

$\mu_i = k_B T \ln\left(\frac{p_i}{n_q k_B T}\right)$ Usually write μ_i relative to some standard condition p_0 (typically 1 atm)

$\mu_i(T, p_i) = \mu_i^\circ + k_B T \ln\left(p_i/p_0\right)$ $\qquad \mu_i^\circ \equiv \mu_i(T, p_0)$

$\therefore \; -\mu_{N_2}^\circ - k_B T \ln\left(\frac{p_{N_2}}{p_0}\right) - 3\mu_{H_2}^\circ - 3k_B T \ln\left(\frac{p_{H_2}}{p_0}\right)$

$+ 2\mu_{NH_3}^\circ + 2 k_B T \ln\left(\frac{p_{NH_3}}{p_0}\right) = 0$

$k_B T \ln\left(\frac{p_{N_2} p_{H_2}^3}{p_{NH_3}^2 p_0^2}\right) = \underbrace{2\mu_{NH_3}^\circ - \mu_{N_2}^\circ - 3\mu_{H_2}^\circ}_{\Delta G^\circ = \Delta G(T, p_0)}$

$$\boxed{\frac{p_{NH_3}^2 p_0^2}{p_{N_2} p_{H_2}^3} = e^{-\Delta G^\circ / k_B T} \equiv K(T)}$$

Law of mass action

$K(T)$ = "equilibrium constant"

ΔG° and K are constants, depend on particular reaction

Equation says that if we increase total pressure $p = p_{H_2} + p_{N_2} + p_{NH_3}$ much more NH_3 is produced (double p_{H_2}, p_{N_2}, p_{NH_3} must quadruple)

For this reaction $\Delta G^\circ = -32.9\ kJ/mol$

$\therefore \; K(T) = \exp\left(\frac{+32.9 \times 10^3}{\underbrace{6\times10^{23} \cdot 1.38\times10^{-23}}_{N_A \cdot k_B = R = 8.315} \cdot 298}\right) = 5.9 \times 10^5$

$\Delta G^\circ < 0$ $K(T) > 1$ means reaction proceeds to the right

G decreases upon production of NH_3 so the reaction tends to the right $N_2 + 3H_2 \rightarrow 2NH_3$ spontaneously

This formalism works beyond ideal gases. Works well for solutions: $\mu_i = \mu_i^\circ + k_B T \ln\left(\frac{n_i}{n_0}\right)$

n_i = concentration of solute i, usually measured in molars = $\frac{\text{mol}}{\text{L}}$

n_0 = standard reference concentration, typically 1 mol/L

Ex: $H_2O \rightarrow H^+ + OH^-$

so $-\mu_{H_2O} + \mu_{H^+} + \mu_{OH^-} = 0$ $\mu_{H_2O} \cong \mu^\circ_{H_2O}$

$\therefore -k_B T \ln\left(\frac{[H^+][OH^-]}{n_0^2}\right) = \mu^\circ_{H^+} + \mu^\circ_{OH^-} - \mu^\circ_{H_2O}$ $[H^+] \approx n_{H^+}$ etc.

$[H^+][OH^-] = n_0^2 \, e^{-\Delta G^\circ / k_B T} = n_0^2 K(T)$

$= 1\left(\frac{\text{mol}}{\text{L}}\right)^2 \, 1\times10^{-14}$

when all H^+, OH^- come from H_2O then

$[H^+] = [OH^-] = 1\times10^{-7}$ mol/L

Define pH as $pH \equiv -\log_{10}[H^+]$ for pure water $pH = 7$

When other substances are dissolved in water, they can add H^+ or OH^-

If $pH < 7$ solution is acidic ($[H^+]$ is high)

$pH > 7$ solution is basic ($[OH^-]$ is high)

Electrolysis

Breaking water into H_2, O_2 $\quad H_2O \longrightarrow H_2 + \frac{1}{2} O_2$

$\Delta G^\circ = 237\ kJ/mol$ under standard conditions ($p = 1\ atm$)

Let's look at what contributes to ΔG°

$$\Delta G^\circ = \underbrace{\Delta U}_{\text{involves changes in chemical bonds}} + \underbrace{p\Delta V}_{\text{involves change in volume during reaction}} - \underbrace{T\Delta S}_{\text{heat from environment that we get for free}}$$

For this reaction:

$\Delta U = 282\ kJ/mol$
$p\Delta V = 4\ kJ/mol$ ↳ amount that pushes atmosphere away when gases H_2, O_2 are produced

$\Delta H = \Delta U + p\Delta V = 286\ kJ/mol$

$T\Delta S = 49\ kJ/mol$ Entropy increased in products

Gives $\Delta G^\circ = 237\ kJ/mol > 0$ which does not happen spontaneously. Must provide energy for reaction to occur, in form of W' = work other than $p\Delta V$

Electrical work $W' = \Delta G^\circ = q\Delta V$ is minimum work required to run reaction $H_2O \rightarrow H_2 + \frac{1}{2} O_2$

Reaction involves net transfer of $2e^-$ so for 1 mole:

$$\Delta V_{min} = \frac{\Delta G^\circ}{2e N_A} = \frac{237\ kJ}{2 \cdot 1.6 \times 10^{-19} \cdot 6 \times 10^{23}} = 1.229\ V$$