* BRIEF REVIEW OF ROLE OF $\Delta A$ & $\Delta G$

→ Recall the general statement (of 2nd law)

(I) $\Delta S + \Delta S_{\text{surv}} > 0$,

as indicator of spontaneous change

• Const. - T process $\implies$ $\Delta S_{\text{surv}} = -\frac{q}{T}$

• Const. - V, in addition, $\implies q = \Delta U$

(no non-PV work)

Thus, (I) becomes $\Delta S - \frac{\Delta U}{T} > 0$, or

$-\frac{1}{T}(\Delta U - T\Delta S) > 0$, or

$\Delta(U - TS) < 0$

$\equiv A$

- $-PV$

• Similarly, const. - P $\implies q = \Delta U - \overline{W} = \Delta H$

and $-\frac{1}{T}(\Delta H - T\Delta S') > 0$, or

$\Delta(H - TS') < 0$

$\equiv G$

* M i, S, $\Delta G_{\text{rxn}}$, and chemical equilibrium

• From LECTURE #20's result

$G = \sum_i n_i \mu_i$

for a mixture of pure compounds, it follows that $dG$ for an infinitesimal amount of reaction is given by (with $T$ and $P$ constant)
\[ dG = \sum_i \mu_i \, dn_i \]

**NOTE:** The \( dn_i \)s are linked by the stoichiometric coefficients in the balanced chemical reaction

\[ \nu_A \, A + \nu_B \, B + \ldots \rightleftharpoons \nu_C \, C + \nu_D \, D + \ldots \]

More explicitly, if \( \xi \) is the extent of reaction,

\[ n_i = n_i^{\text{init}} + \nu_i \xi \]

implying

\[ dn_i = \nu_i \, d\xi \]

and, from equation at top of page,

\[ dG = \sum_i \mu_i \nu_i \, d\xi, \]

or

\[ \left( \frac{\partial G}{\partial \xi} \right)_{T,P} = \sum_i \nu_i \mu_i = \ldots \Delta G_{\text{rxn}} \]

- \( \Delta G_{\text{rxn}} = 0 \iff \text{chemical equilibrium} \)
- \( \Delta G_{\text{rxn}} < 0 \Rightarrow \text{rxn proceeds to right} \)
- \( \Delta G_{\text{rxn}} > 0 \Rightarrow \text{rxn proceeds to left} \)

Now just need to substitute

\[ M_i(T,P) = M_i^0(T) + \left( \frac{RT \ln \frac{P_i}{P^0}}{M_i^{\text{pure}}(T,P)} + \frac{RT \ln \frac{P_i}{P^0}}{M_i^{\text{pure}}(T,P)} \right) \]

into \( \sum_i \nu_i M_i = 0 \).
\[
\sum_i \nu_i \left( \mu_i^o(T) + RT \ln \frac{P_i}{P_0} \right) = 0
\]

or
\[
- \sum_i \nu_i \mu_i^o(T) = + \sum_i \nu_i RT \ln \frac{P_i}{P_0}
\]

\[
\Delta G_{rxn}^o = + RT \sum_i \ln \left( \frac{P_i}{P_0} \right)^{\nu_i}
\]

\[
\ln \left[ \left( \frac{P_c}{P_0} \right)^{\nu_c} \left( \frac{P_d}{P_0} \right)^{\nu_d} \right] = - \Delta G_{rxn}^o / RT \equiv K_p
\]

\[
\frac{\left( \frac{P_c}{P_0} \right)^{\nu_c} \left( \frac{P_d}{P_0} \right)^{\nu_d}}{\left( \frac{P_A}{P_0} \right)^{\nu_A} \left( \frac{P_B}{P_0} \right)^{\nu_B}} = K_p
\]

**Note:** \( p_i \) here are \( p_i^{eq} \)

\* Suppose some reagents aren't gaseous

- Then for the liquid or solid components we write

\[ \mu_i(T, p) \approx \mu_i^o(T) \]

because \( G \)'s for liquids & solids are essentially independent of \( p \).

- Substituting into equilibrium condition

\[ \sum_i \nu_i \mu_i = 0 \]

we find that liquid and solid reagents
contribute to $\Delta G^\circ_{\text{rxn}}$ (and hence to the value of $K_p$), but not to quotient of powers of $(P_i/P_o)^s$

**EXAMPLE:**

$$\text{CaCO}_3(s) = \text{CaO}(s) + \text{CO}_2(g)$$

$$\Delta G^\circ_{\text{rxn}} = \Delta G^\circ_f(\text{CO}_2(g)) + \Delta G^\circ_f(\text{CaO}(s)) - \Delta G^\circ_f(\text{CaCO}_3(s))$$

$$K_p = e^{-\Delta G^\circ_{\text{rxn}} / RT}$$

and

$$\frac{P_{\text{CO}_2}}{P^o} = K_p$$