Outline
- Review free energy
- Thermo Chemistry Pt. II
- Chemical Potential
- Real gases
  - Activity, fugacity

Free Energy
\[ \Delta H = U - TS \]
\[ \Delta G = H - TS \]

Energy free to do work other than expansion work
\[ \Delta H \neq W_{\text{total}} \]
\[ \Delta G \neq W_{\text{other}} \]

Spontaneity

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<td>( \Delta S &gt; 0 )</td>
<td>Isolated system</td>
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<td>Helmholtz</td>
<td>( \Delta G &lt; 0 )</td>
<td>Const. ( T, V )</td>
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<tr>
<td>Gibbs</td>
<td>( \Delta G &lt; 0 )</td>
<td>Const. ( T, P )</td>
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Free Energy of reaction
\[ \Delta G_r = \sum n_i \Delta G_i - \sum n_j \Delta G_j \]

Since \( dG(T, P) = -dS + V dp \)

Then \( \left( \frac{\partial G}{\partial T} \right)_P = -S \) and \( \left( \frac{\partial G}{\partial P} \right)_T = V \)

Moreover, \( \left( \frac{\partial \Delta G}{\partial T} \right)_P = -\Delta S \) and \( \left( \frac{\partial \Delta G}{\partial P} \right)_T = \Delta V \)
Suppose we have a state function $X$ and we know what $\Delta X$ is at condition 1, $C_1$. If we want to know what $\Delta X$ is at another condition, then we have to do the following:

$$\Delta X(C_1) \rightarrow \Delta X(C_2) = ?$$

$$\Delta X(C_2) = \Delta X(C_1) + \int_{C_1}^{C_2} \left( \frac{\partial \Delta X}{\partial C} \right) dC$$

**Example:** $\Delta G(T_1) \rightarrow \Delta G(T_2) = ? \quad @ \text{Const.} \ P$

$$\Delta G(T_2) = \Delta G(T_1) + \int_{T_1}^{T_2} \left( \frac{\partial \Delta G}{\partial T} \right)_p dT$$

$$dG = -SdT + VdP \ \Rightarrow \ \left( \frac{\partial \Delta G}{\partial T} \right)_p = -S \ \Rightarrow \ \left( \frac{\partial \Delta G}{\partial T} \right)_p = -\Delta S$$

$$\therefore \ \Delta G(T_2) = \Delta G(T_1) + \int_{T_1}^{T_2} -\Delta S \ dT$$

Back to free energy...

Since $\Delta G = \Delta H - T\Delta S$ we can define the reaction free energy with the following:

$$\Delta G_{rxn} = \sum_i U_i \Delta H_{f_i}^0 - T \sum_i S_i \Delta S_i$$
Note $\Delta G^\circ$ refers to a reaction in standard state (i.e. 298K, 1 bar).

What happens when we are not at equilibrium?

Consider the reaction $v_A A + v_B B \rightarrow v_C C + v_D D$

\[ \Delta G_r = \Delta G_r^\circ + RT \ln Q \]

$Q$: reaction coefficient

\[ Q_{\text{conc}} = \left( \frac{[A]}{[M]} \right)^{v_A} \left( \frac{[B]}{[M]} \right)^{v_B} \]

\[ Q_{\text{pressure}} = \left( \frac{P_A}{P}, \text{bar} \right)^{v_A} \left( \frac{P_B}{P}, \text{bar} \right)^{v_B} \]

When we are at equilibrium, then $\Delta G_r = 0$ (but $\Delta G^\circ \neq 0$)

\[ \Delta G_r = -RT \ln Q = -RT \ln K_{eq} \quad K_{eq} = \text{Equilibrium constant} \]

Changing the temperature will favor one reaction over the other, resulting in a shift of the $K_{eq}$ value.

Variation of $K_{eq}$ with $T$

\[ \left( \frac{\partial \ln K}{\partial T} \right)_P = \frac{\Delta H^\circ}{RT^2} \]

\[ \Rightarrow \int_{K_1}^{K_2} \ln K \, dK = \frac{\Delta H^\circ}{R} \int_{T_1}^{T_2} \frac{1}{T^2} \, dT \]

\[ \ln (K_2) - \ln (K_1) = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

\[ \ln \left( \frac{K_2}{K_1} \right) = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]

$k_2$ is the new equilibrium constant when the reaction starts at $T_2$. 
Chemical Potential

Energy that can be transferred due to the change in the number of particles of a given species

\[ M_i = \left( \frac{\partial G}{\partial n_i} \right)_{T, p, n \neq n_i} \]

For an ideal gas, one component (Pure Substance)

\[ M_i = G_i (\text{Partial molar Gibbs}) \Rightarrow \Delta G_r = \Delta M_r \]

For a vessel with more than one species, we must take into account the extent (\( \xi \)) of the reaction.

\[ \xi \]

How does the reaction proceed over time?

\[ \xi = 0 \quad \text{at } t = 0 \]

\[ \xi = \frac{n_{eq} - n_i}{V_i} \quad \text{at equilibrium} \]

Recall for a multicomponent system

\[ dG = -SdT + Vdp + \sum_{i=1}^{n} M_i d\xi_i \]

Where the change in moles \( d\xi_i = V_i d\xi \) then

\[ dG = -SdT + Vdp + \sum_{i=1}^{n} M_i V_i d\xi \]

At constant \( T \) and \( P \)

\[ \frac{\partial G}{\partial \xi} = \sum_{i=1}^{N} M_i V_i d\xi \]

This is in agreement with the one component ideal system.
Recall for the one component system

$$\bar{G}_i = \bar{G}_i^0 + RT \ln \left( \frac{P_i}{P_{1\text{bar}}} \right) \implies \Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^0 + RT \ln (Q_p)$$

Since $dG = \sum_i M_i V_i d\xi$ and $\bar{G}_i = M_i$

Then $M_i = M_i^0 + RT \ln \left( \frac{P_i}{P_{1\text{bar}}} \right) \implies \Delta M_{\text{rxn}} = \Delta M_{\text{rxn}}^0 + RT \ln (Q_p)$

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**Real gases**

Recall that the ideal gas equation fails due to neglect of interactions (attraction and repulsion) and assumption of finite volume.

State functions will deviate from ideal for real gases and this deviation can be described by the compressibility factor

$$z = \frac{V_{\text{actual}}}{V_{\text{ideal}}} = \frac{P V_{\text{actual}}}{RT}$$

- If $z = 1$ gas behaves ideally
- $z > 1$ repulsion forces dominate
- $z < 1$ attractive forces dominate

The compressibility factor is related to the activity and fugacity of the real system.
Fugacity - effective partial pressure of real gas

If \( y_i = y_i^o + RT \ln \left( \frac{P_i}{P^o} \right) \) for ideal

then \( y_i = y_i^o + RT \ln \left( \frac{f_i}{P^o} \right) \) for real

where \( f_i \) is the fugacity

Activity - effective concentration of a species in a mixture

If \( M_i = M_i^o + RT \ln \left( \frac{[I]}{[M]} \right) \) for ideal

then \( M_i = M_i^o + RT \ln \left( \frac{a_i}{a_i^o} \right) \) for real mixture

where \( a_i \) is the activity of component \( i \)

and \( a_i^o = 1 \) unit (bar, molar, etc) (In must have units: input)

Note: \( a_i = \phi_i [I] \) where \( \phi_i \) is the activity coefficient

So for gases \( a_i = f_i = \phi_i P_i \leftarrow \text{Partial pressure} \)

If \( \phi_i = 1 \) (ideal)

Then \( a_i = [I] \)

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<tr>
<th>Solute</th>
<th>gas</th>
<th>Pure liquid or solid</th>
</tr>
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<tbody>
<tr>
<td>( a_i = P_i )</td>
<td>( a_i = 1 )</td>
<td>( a_i = 1 )</td>
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</table>

Relation between activity/fugacity and compressibility factor

\[
\ln \gamma = \ln \frac{f}{p} = - \int_{0}^{p} \frac{2-1}{p} dp
\]

\( \gamma \) is activity coefficient

\( f \) is fugacity

\( 2 \) is compressibility factor