The Gibbs Energy (G) and the Helmholtz Energy (A)

- Previously, we determined all the properties of Entropy and obtained A and G from Entropy (and P,V and T).
- Now use A and G for reactions and transformations.
- Energy type terms: U, H, TS, PV. All are extensive. (T and P by themselves are intensive). What combinations of these terms give meaningful expressions and why?

\[ U \quad A \]
\[ PV \downarrow \quad \downarrow PV \]
\[ H \quad G \xrightarrow{-TS} \]

Four distinct energies are U,H,A,G.
Helmholtz Energies

Spontaneity condition:

$$\Delta S + \Delta S_{surroundings} > 0 \quad w = -P_{\text{external}} dV + w_{\text{nonexpansion}}$$

$$w_{\text{rev}} \leq w \implies q_{\text{rev}} = T dS \geq q$$

$$dU = T dS + w_{\text{rev}} \leq T dS + w$$

$$dU - T dS \leq w$$

Isothermal:

$$dT = 0 \quad T dS = d(TS) \quad dA \leq w$$

$$dU - T dS = d(U - TS) = dA$$

$$\boxed{dA \leq w}$$

For an isothermal process, dA is the maximum work one can get from the process.

If you don’t want work, w=0, then dA<0 determines whether the process will occur at all (if kept isothermal).
Spontaneity Criteria

For processes occurring at constant T and P (and this implies a chemical reaction or other complicated multi-component process): The criterion for the maximum non-PdV (i.e. electrical) work one can have is \( dG \)

\[
\text{for } dT = dP = 0, \quad dG \leq w_{\text{nonexpansion}}
\]

At constant T and P

Proof:

\[
dA \leq w = -PdV + w_{\text{nonexpansion}}
\]

\[
d(A + PV) = dG \leq w_{\text{nonexpansion}}
\]

For a process at constant T and P

\[
G = H - TS
\]

\[
dG = dH - TdS
\]

\[
\Delta G = \Delta H - T\Delta S
\]
Example Problem

Calculate the maximum non-expansion work that can be produced by the fuel cell oxidation reaction \( \text{CH}_4 (g) + 2\text{O}_2 (g) \rightarrow \text{CO}_2 (g) + 2\text{H}_2\text{O} (l) \). \[\text{At constant T and P}\] \( \Delta H_{\text{comb}}^\circ (\text{CH}_4, g) = -890 kJ \)

\[
\Delta G_{\text{comb,rxn}}^\circ = \Delta H_{\text{comb}}^\circ (\text{CH}_4, g) - T\left(S^\circ (\text{CO}_2, g) + 2S^\circ (\text{H}_2\text{O}, l) - S^\circ (\text{CH}_4, g) - 2S^\circ (\text{O}_2, g)\right)
\]
\[= -890 kJ \]
\[\quad - 298.15 \cdot 10^{-3} \cdot (213.74 + 2x \cdot 69.61 - 186.26 - 3x \cdot 205.138) kJ \]

\( \Delta G_{\text{comb,rxn}}^\circ = -818 kJ \) One mole of methane is worth 2 to 3 cups of yogurt in energy.

Compare the available work done by a reversible heat engine and that done by an electrochemical fuel cell for methane combustion. For \( T_{\text{hot}} = 600 K \) and \( T_{\text{cold}} = 300 K \), \( \varepsilon = 0.50 \). set \( q_{\text{hot}} = \Delta H \) and \( w = \varepsilon q_{\text{hot}} \). The maximum work available from the heat engine is 59% of that available in the electrochemical fuel cell.
Direction of Spontaneous Change for a constant T,P Process

\[ \Delta G = \Delta H - T\Delta S \]  

Spontaneous when \[ dG \leq 0 \]

There are two contributions to \( \Delta G \) that determine if an isothermal, isobaric chemical transformation is spontaneous: the energetic contribution, \( \Delta H \), and the entropic contribution, \( T\Delta S \).

• The entropic contribution to \( \Delta G \) is larger at higher temperatures.

• A chemical transformation is always spontaneous if \( \Delta H < 0 \) (an exothermic reaction) and \( \Delta S > 0 \).

• A chemical transformation is never spontaneous if \( \Delta H > 0 \) (an endothermic reaction) and \( \Delta S < 0 \).

• For all other cases, (when \( \Delta H \) and \( T\Delta S \) have the same sign) the relative magnitudes and signs of \( \Delta H \) and \( T\Delta S \) determine if the chemical transformation is spontaneous.
Phase Transition

$$\Delta G = \Delta H - T \Delta S \quad \frac{\Delta H}{\Delta S} = T_m > 0 \quad \Delta G = \Delta S (T_m - T)$$

- Consider a phase transition from the more stable form to the less stable form (e.g. from solid to liquid, like ice to water at 0°C). DH is positive, because Heat must go into the material to break the bonds. But heat in under constant P (and T) is q-reversible so $DS = DH/Tm$ and is also positive. Notice that $DG=0$ at this point. So $DG=0$ is the transition between spontaneous and not spontaneous.

- Assume that $DS$ and $DH$ are insensitive to $T$ (and you did this calculation for the ice to water transition), then when $T>0$ the $TDS$ term dominates and $DG < 0$ so ice melts above the transition temperature. Conversely it freezes below it because the $DH$ term is larger (and it is positive), so $DG > 0$ when $T< Tm$. 
The Dependence of the Gibbs and Helmholtz Energies on $P$, $V$, and $T$

$$dG = -SdT + VdP \quad \Rightarrow \quad \left( \frac{\partial G}{\partial T} \right)_P = -S \quad \text{and} \quad \left( \frac{\partial G}{\partial P} \right)_T = V$$

For a change in $P$ at constant $T$

$$\Delta G = \int_{G^o}^{G} dG = \int_{P^o}^{P} \left( \frac{\partial G}{\partial P} \right)_T dP = \int_{P^o}^{P} VdP$$

For liquids and solids

$$\Delta G = G(T, P) - G^o(T, P^o) = \int_{P^o}^{P} VdP \approx \bar{V} \left( P - P^o \right) = \bar{V} \Delta P$$
By contrast, the volume of a gaseous system changes appreciably with pressure.

\[ \Delta G = G(T, P) - G^\circ(T) = \int VdP = \int_{P^\circ}^{P} \frac{nRT}{P} dP = nRT \ln \frac{P}{P^\circ} \]

We will use this relation many times.
Chemical Reactions

- Review: How H and S are written for chemical reactions, when T and P are fixed.
- In a Chemical Reaction, the concentration of all species are tied together.

\[ 0 \overset{\sum_{i=1}^{N} \nu_i \Phi_i}{\longleftrightarrow} 0 \overset{2NH_3 \rightarrow 1N_2 + 3H_2}{\longleftrightarrow} \]

\[ n_i = n_i^0 + \nu_i X \]
\[ dn_i = \nu_i dx \]

X, or dX is the extent of advancement (or retardation if X is negative). Get X from any species concentration change specified.
Reaction H and S (at constant T and P)

For a reaction, the change in the number of moles is controlled by the value of $X$, the advancement parameter.

$$dH = \left( \frac{\partial H}{\partial T} \right)_{P,n_1,n_2...} dT + \left( \frac{\partial H}{\partial P} \right)_{T,n_1,n_2...} dP$$

$$+ \left( \frac{\partial H}{\partial n_1} \right)_{T,P,n_2...} dn_1 + \left( \frac{\partial H}{\partial n_2} \right)_{T,P,n_1...} dn_1 + ......$$

Fixed $T$ and $P$: $dH = \sum_{i=1}^{N} d\nu_i \left( \frac{\partial H}{\partial \nu_i} \right)_{T,P,n_j} = dx \sum_{i=1}^{N} \nu_i \left( \frac{\partial H}{\partial \nu_i} \right)_{T,P,n_j}$.

$$dS = dx \sum_{i=1}^{N} \nu_i \left( \frac{\partial S}{\partial \nu_i} \right)_{T,P,n_j} = dx \sum_{i=1}^{N} \nu_i S^o_i (i)$$

$\Delta G_{rxn} = \Delta H_{rxn} - T \Delta S_{rxn}$
The Gibbs Energy of a Reaction Mixture

\[
dG = \left( \frac{\partial G}{\partial T} \right)_{P,n_1,n_2...} \ dT + \left( \frac{\partial G}{\partial P} \right)_{T,n_1,n_2...} \ dP + \left( \frac{\partial G}{\partial n_1} \right)_{T,P,n_2...} \ dn_1 + \left( \frac{\partial G}{\partial n_2} \right)_{T,P,n_1...} \ dn_1 + .......
\]

define the chemical potential, the molar Gibbs energy \( \mu_i \), as

\[
\mu_i \equiv \left( \frac{\partial G}{\partial n_i} \right)_{P,T,n_j \neq n_i}
\]

\[
dG = \left( \frac{\partial G}{\partial T} \right)_{P,n_1,n_2...} \ dT + \left( \frac{\partial G}{\partial P} \right)_{T,n_1,n_2...} \ dP + \sum_i \mu_i dn_i
\]

\[
dG = \sum_i \mu_i dn_i = dx \sum_i \mu_i \nu_i
\]

\( \Leftarrow \) When T and P are fixed:

\[
dG_{rxn} = \sum_i \nu_i \mu_i
\]
Why is $\mu_i$ called the chemical potential of species $i$? This can be understood by assuming that the chemical potential for species $i$ has the values $\mu_i^I$ in region $I$, and $\mu_i^{II}$ in region $II$ of a given mixture with $\mu_i^I > \mu_i^{II}$. If $dn_i$ moles of species $i$ are transported from region $I$ to region $II$, at constant $T$ and $p$, the change in $G$ is given by

$$dG = -\mu_i^I dn_i + \mu_i^{II} dn_i = (\mu_i^{II} - \mu_i^I) dn_i < 0$$

Matter flows from a region of high chemical potential to one of low chemical potential.

At equilibrium, the chemical potential of each individual species is the same throughout a mixture.
Ideal gas mixture at constant temperature

After equilibrium has been reached,

\[ \mu^\text{pure}_{H_2} \left( T, P_{H_2} \right) = \mu^\text{mixture}_{H_2} \left( T, P_{H_2} \right) \]

\[ P^\text{pure}_{H_2} = P^\text{mixture}_{H_2} = \chi_{H_2} P_{\text{total}} \]

\[ \mu^\text{mixture}_{H_2} \left( T, P_{H_2} \right) = \mu_{H_2} \left( T, P^o \right) + RT \ln \left( \frac{P_{H_2}}{P^o} \right) \]

The chemical potential of each gas only depends on its own partial pressure.

This comes from the mixing entropy

\[ \mu^o_{H_2} \left( T, P^o \right) + RT \ln \left( \frac{P}{P^o} \right) + RT \ln \left( \chi_{H_2} \right) \]

\[ \mu^o_{H_2} \left( T, P \right) + RT \ln \left( \chi_{H_2} \right) \]
In a mixture of A and B: Compare Gibbs energies due to mixing

- Integrate up the equation for \( dG \) in terms of \( n \) holding the chemical potential fixed:

\[
\mu_i = \mu_i^o(P^o) + RT \ln \frac{P_i}{P_i^o} = \mu_i^o(P) + RT \ln x_i
\]

\[
dG = \sum_i \mu_i dn_i
\]

\[
G = \sum_i \mu_i n_i = \sum_i \mu_i^o n_i + RT \sum_i n_i \ln x_i
\]

\[
G^{\text{pure}} = \sum_i \mu_i^o n_i \quad \text{and} \quad \Delta G^{\text{mix}} = RT \sum_i n_i \ln x_i
\]

Apply to a two component system: \( n = n_A + n_B \)

\[
G^{\text{pure}} = n \left( x_A \mu_A^o + x_B \mu_B^o \right) \quad \text{and} \quad \Delta G^{\text{mix}} = nRT \left( x_A \ln x_A + x_B \ln x_B \right)
\]
In a Chemical Reaction for an Ideal Gas Mixture in Terms of the $\mu_i$, the Gibbs Energy is:

$$0 \Leftrightarrow \sum_i n_i \Phi_i$$

$$dG = \sum_i \mu_i dn_i \quad \text{Use } X: \text{ the extent of reaction}$$

$$n_i = n_i^{initial} + v_i X \quad dn_i = v_i dX$$

$$dG = \left( \sum_i v_i \mu_i \right) dX = \Delta G_{rxn} dX$$

$$\Delta G_{rxn} = \left( \frac{\partial G}{\partial X} \right)_{T,P} = \sum_i v_i \mu_i$$
The direction of spontaneous change is that for which $\Delta G$ is negative. THEREFORE

If $\left(\frac{\partial G}{\partial X}\right)_{T,P} < 0$, the reaction proceeds spontaneously as written.

• If $\left(\frac{\partial G}{\partial X}\right)_{T,P} > 0$, the reaction proceeds spontaneously in the opposite direction, and a negative dX makes the reaction spontaneous in the opposite direction (i.e. make reactants).

• If $\left(\frac{\partial G}{\partial X}\right)_{T,P} = 0$, the reaction system is at equilibrium, and there is no direction of spontaneous change.