Chapter 19: Chemical Thermodynamics

**Thermodynamics** - the study of energy in chemical reactions. Three Laws.

**First Law** - The total energy of the universe is fixed.

\[ \Delta E = q + w \]

\[ \Delta H \text{ (for constant Pressure)} \]
Is $\Delta H$ alone an accurate indicator if a process will occur? **NOOOOOOOO!**

**Spontaneous** a process
that occurs without intervention. It has a certain order (sequence). Spontaneous in one direction non spontaneous in the reverse.
(a) Evacuated

(b) Spontaneous

Not spontaneous

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**Second Law** - The total entropy of the universe is increasing

**Entropy, \( S^\circ, S \),** - a measure of the disorder (randomness) of the system. State function.\[ \Delta S = S_{\text{final}} - S_{\text{initial}} \]

\[ \Delta S = \frac{q_{(rev)}}{T} \]

Entropy explains certain observations regarding spontaneity
Third Law - the entropy of a perfect crystalline solid is zero at absolute zero, 0K.

The third Law allows the absolute entropies of substances to be evaluated.
$S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$

In general $S$ increases for:
- liquids/solutions from
solids
-gases from solids/liquids
- # gas molecules increase
temp. subs increases

Calculate $\Delta S_{Rx}^\circ$ of the following reactions using Appendix C

$\Delta S_{Rx}^\circ = \sum S_{\text{prod.}}^\circ - \sum S_{\text{react.}}^\circ$

$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$

$2\text{KClO}_3(\text{s}) \rightarrow 2\text{KCl}(\text{s}) + 3\text{O}_2(\text{g})$

Which wins in predicting
spon.? $\Delta H_{\text{sys}}$ or $\Delta S_{\text{sys}}$? neither

A Rx is SPON if:
$\Delta S_{\text{universe}} > 0$

$\Delta S_{\text{universe}} = \Delta S_{\text{surroundings}} + \Delta S_{\text{system}}$

$\Delta S_{\text{universe}} = -\Delta H_{\text{system}}/T + \Delta S_{\text{system}}$

$-T\Delta S_{\text{universe}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$

by defin.  $-T\Delta S_{\text{universe}} = \Delta G$

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

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
**Gibbs Free Energy, ΔG** - the thermodynamic state function defining ΔG as, ΔH_{sys} - TΔS_{sys}. The sign of ΔG indicates Rx. spontaneity. *(Free???)*

ΔG < 0  Rx. Spon.
ΔG >0   Rx. Non-Spon.
ΔG=0   Rx. @ Equil.
Effect of sign of $\Delta H$ and $\Delta S$ on spontaniety of a reaction. (Table 19.4)

<table>
<thead>
<tr>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
<th>$-T\Delta S$</th>
<th>$\Delta G = \Delta H - T\Delta S$</th>
<th>Reaction Characteristics</th>
<th>Example</th>
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<tbody>
<tr>
<td>$-$</td>
<td>$+$</td>
<td>$-$</td>
<td>$-$</td>
<td>Spontaneous at all temperatures</td>
<td>$2 \text{O}_2(g) \rightarrow 3 \text{O}_3(g)$</td>
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<tr>
<td>$+$</td>
<td>$-$</td>
<td>$+$</td>
<td>$+$</td>
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<td>$3 \text{O}_2(g) \rightarrow 2 \text{O}_3(g)$</td>
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<tr>
<td>$-$</td>
<td>$-$</td>
<td>$+$</td>
<td>$+$ or $-$</td>
<td>Spontaneous at low $T$; nonspontaneous at high $T$</td>
<td>$\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s)$</td>
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<td>$\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$</td>
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<tr>
<td>$\Delta H$</td>
<td>$\Delta S$</td>
<td><strong>result</strong></td>
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<td>&lt;0</td>
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<td>spon. at all T</td>
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<td>&gt;0</td>
<td>&lt;0</td>
<td>non-spon. at all T</td>
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<td>spon. at low T</td>
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<td>T&lt;\Delta H/\Delta S</td>
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Calculation of $\Delta G_{Rx}$ can be done by 1) the above approach or 2) from $\Delta G_f^\circ$ data analogous to $\Delta H$ and $\Delta S$ calc. (Appendix C)
\[ \Delta G_{Rx}^0 = \Sigma \Delta G^\circ_{f,\text{prod}} - \Sigma \Delta G^\circ_{f,\text{react}} \]

Calculate \( \Delta G^\circ \) for the following reaction using the \( \Delta G_f^\circ \) data of App. C.

\[ 2\text{KClO}_3(s) \rightarrow 2\text{KCl}(s) + 3\text{O}_2(g) \]

**The standard molar free energy of formation, \( \Delta G_f^\circ \) and enthalpy of formation, \( \Delta H_f^\circ \) values of elements (stable form) are defined as ZERO!!!**
Calculate $\Delta G^\circ$ for the foll. Rx using the Gibbs Eq and from $\Delta G_f^\circ$ data of App. C. $\Delta H^\circ = -92.38$ kJ $\Delta S^\circ = -198.3$J/K $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Calculate the temperature at which the production of ammonia becomes spontaneous.

At equilibrium $\Delta G_{Rx}=0$ ($\Delta G_{Rx}^\circ \neq 0$)

$\Delta G = 0 = \Delta H - T\Delta S$
\[ T = \Delta H / \Delta S \]

\[ T = -92.38 \text{kJ/}.1983 \text{kJ/K} \]

\[ T = 465.9 \text{ K} \]

SPON below, non SPON above 466 K

Under non-standard conditions

\[ \Delta G = \Delta G^0 + RT \ln Q \]

Calculate \( \Delta G \) when P of \( N_2 \),
H₂, and NH₃ are 1.00, 3.00, and 1.00 ATM respectively. (non STD. conditions) This result is consistent with LeChat. Prin.

Relationship between ΔG and the equilibrium constant, K.

@equilibrium, Q=K, ΔG=0

ΔG° = -RTlnK = -2.30RTlogK

ΔG° < 0   K>1 Spon.
ΔG° >0    K<1 Non-Spon.
Calculate the equilibrium constant for the following Rx at 298K.

\[ \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \]

Energy is released on the
way to equilibrium not at equilibrium

How do you get unfavored reactions to occur?
- temperature (in some cases)
- couple to another favored reaction (many bio Rxs)

\[
\begin{align*}
\Delta G^0 (kJ) \\
\text{Cu}_2\text{S} & \rightarrow 2\text{Cu} + \text{S} \quad 86.2 \text{kJ} \\
\text{S} + \text{O}_2 & \rightarrow \text{SO}_2 \quad -300.4 \\
\text{Cu}_2\text{S} + \text{O}_2 & \rightarrow 2\text{Cu} + \text{SO}_2
\end{align*}
\]
Review of methods of calculating $\Delta H_{Rx}^\circ$, $\Delta G_{Rx}^\circ$, and $\Delta S_{Rx}^\circ$.

1) From data of App C

$$\Delta H_{Rx}^\circ = \Sigma \Delta H^\circ_{f, \text{prod.}} - \Sigma \Delta H^\circ_{f, \text{react}}$$

$$\Delta G_{Rx}^\circ = \Sigma \Delta G^\circ_{f, \text{prod.}} - \Sigma \Delta G^\circ_{f, \text{react.}}$$
Remember that $\Delta G_f^\circ$ and $\Delta H_f^\circ$ values of elements are ZERO
$\Delta S_{Rx}^\circ = \sum S_{\text{prod.}}^\circ - \sum S_{\text{react.}}^\circ$
S terms ARE NOT ZERO except at 0K.

2) From Gibbs equation

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