**Chemical Thermodynamics**

Energy - capacity to do work
Work - Force x distance
Internal energy $E$ of the system $\Delta E = E_2 - E_1$

expansion work $w = P\Delta V$

**First Law of Thermodynamics:**
Total amount of energy in Universe is constant

$\Delta E_{\text{system}} + \Delta E_{\text{sur.}} = 0$

**Enthalpy Change** = amount of heat, $q$, when only work done is expansion against constant pressure, $\Delta H = q$

$\Delta E = q + w = \Delta H + w$

If $P\Delta V = 0 \quad \Delta E = \Delta H$

$\Delta H^\circ = \sum \Delta H^\circ (\text{products}) - \sum \Delta H^\circ (\text{reactants})$

$\Delta H$ positive for endothermic reactions
$\Delta H$ negative for exothermic reactions

**Hess's Law**
Hess pointed out that the heat absorbed (or evolved) in a given chemical reaction is the same whether the process takes one step or in several steps.
The **Direction of Reactions**.

The spontaneity of a reaction is an indication of the direction of a reaction.

A spontaneous process is one that proceeds on its own without any external influence.

For reversible reactions:
If $Q < K$, the reaction proceeds in the forward direction.
If $Q > K$, the reaction proceeds in the reverse reaction.

The melting of ice at temperatures above $0\,^\circ\text{C}$ is spontaneous.
The reverse process is not spontaneous.

Expansion of a gas into an evacuated space is spontaneous.
The gas molecules collecting in one flask is not spontaneous.

$$\left(\frac{1}{2}\right)^n$$

Probability:
$$\left(\frac{1}{2}\right)^2 = \frac{1}{4}$$
$$\left(\frac{1}{2}\right)^3 = \frac{1}{8}$$
$$\left(\frac{1}{2}\right)^{100} = 8 \times 10^{-31}$$

$$\left(\frac{1}{2}\right)^N \quad N = 6.02 \times 10^{23}$$
Entropy

Processes in which the disorder of the system increases tend to occur spontaneously.

Dissolution of salts, such as NH\textsubscript{4}NO\textsubscript{3} and KCl, in water is an endothermic process, yet occurs spontaneously. (Increase in the disorder of system).

The disorder is expressed by the thermodynamic quantity \textbf{entropy, } S.

\textbf{Entropy change} \equiv \text{amount of disorder in system, } \Delta S

\[ \Delta S = \frac{q}{T} \quad \Delta S = \frac{\Delta H}{T} \quad \Delta S > 0 \text{ more disorder} \]

\[ \Delta S = \frac{\Delta H_{\text{vap}}}{T_b} \]

Boiling Point:

The tendency in universe is towards disorder (The Big Bang).

Examples: Predict the sign of \( \Delta S \) in the system for:

a. \( I_2(\text{s}) \rightarrow I_2(\text{g}) \)

b. \( H_2O(\text{g}) \rightarrow H_2O(\text{l}) \)

c. \( \text{PbS(s) + 2 HNO}_3(\text{aq}) \rightarrow H_2S(\text{g}) + \text{Pb(NO}_3)_2(\text{aq}) \).\)
For spontaneous processes, \( \Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr} > 0 \)

\( \Delta S_{system} = S_{final} - S_{initial} \)

\( \Delta S^{\circ}_{system} = \sum \Delta S^{\circ} (products) - \sum \Delta S^{\circ} (reactants) \)

**Boltzman S = klnW**

**W-number of states**

Energy Diagram

\[ \Delta S_{system} = \sum \Delta S^{\circ} (products) - \sum \Delta S^{\circ} (reactants) \]

\( S_2 > S_1 \) because excited state is more available

Energy States
- Electronic transitions

Energy

Thermodynamics 4
• Molecular Vibrations

\[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{H}
\end{array}
\quad \begin{array}{c}
\text{H} \\
\text{O} \\
\text{H}
\end{array}
\quad \begin{array}{c}
\text{H} \\
\text{O} \\
\text{H}
\end{array}
\]

• Rotational Motion

\[
\begin{array}{c}
\text{O} \\
\text{H} \\
\text{H}
\end{array}
\]

• Translational Motion

\[\Delta S_{\text{gas}} \gg \Delta S_{\text{liquid}} > \Delta S_{\text{solid}}\]

• More complex (floppier) molecules have larger entropies

\[
\begin{array}{c}
\text{CH}_4 < \text{C}_2\text{H}_6 < \text{C}_3\text{H}_8 \\
186.3 \quad 229.6 \quad 269.9 \quad (\text{J/mol} \cdot \text{K})
\end{array}
\]

\[
\begin{array}{c}
\text{Ar} < \text{CO}_2 < \text{C}_3\text{H}_8 \\
154.7 \quad 213.7 \quad 269.9 \quad (\text{J/mol} \cdot \text{K})
\end{array}
\]

• Ionic Solids: entropies are larger as attractive forces become smaller

\[
\begin{array}{c}
\text{CaO} < \text{LiF} < \text{CsI}
\end{array}
\]
• Increases when solids dissolve in liquids

• Increases when gas escapes solution

• If a reaction produces more molecules, entropy increases

\[
\text{CaCO}_3 (s) \rightarrow \text{CaO} (s) + \text{CO}_2 (g) \quad \text{Entropy Increases}
\]

\[
\text{Ag}^+ (aq) + \text{Br}^- (aq) \rightarrow \text{AgBr} (s) \quad \text{Entropy Decreases}
\]

\[\Delta S_{rxn} = \sum nS_f^{\circ} (\text{prod.}) - \sum mS_f^{\circ} (\text{react.})\]

\[N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)\]

\[\Delta S_{rxn}^{\circ} = \left\{ \left[2S^{\circ}(NH_3)\right] - \left[S^{\circ}(N_2) + 3S^{\circ}(H_2)\right]\right\} \]
Two Tendencies for Spontaneity

1. Lose heat $\Delta H < 0$ "exothermic"

2. Disorder $T\Delta S$

- as $T$ rises, $T\Delta S$ rises: more disorder
- want to give "free energy" a negative sign when spontaneous

Free Energy Change $\equiv$ amount of energy to do chemical work

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

Sum of two tendencies
- heat to evolve
- randomness

Spontaneous reaction $\Delta G < 0$

balance between $\Delta H \& \Delta S$

Standard Free Energy Changes

Standard conditions: 1 atm for gases, pure solids, pure liquids, solutions at 1M

$$\Delta G_{\text{reaction}}^\circ = \sum \Delta G_f^\circ (\text{products}) - \sum \Delta G_f^\circ (\text{reactants})$$

State Functions: H, S, and G are state functions, whose changed values ($\Delta H$, $\Delta S$, $\Delta G$) are determined only by the initial and final values.
\[ \Delta G_{\text{rxn}}^\circ = \sum \Delta G_f^\circ (\text{prod.}) - \sum \Delta G_f^\circ (\text{react.}) \]

\[ \Delta G_{\text{sys}}^\circ = \Delta H_{\text{sys}}^\circ - T \Delta S_{\text{sys}}^\circ \]

A \quad ⇄ \quad B

For \ A \rightarrow B

if \ \Delta G < 0 \quad \text{spontaneous for } A \rightarrow B

if \ \Delta G > 0 \quad \text{not spontaneous (but } B \rightarrow A \text{ is)}

if \ \Delta G = 0 \quad \text{equilibrium}

To estimate the temperature at which \( \Delta G^\circ \) changes from positive to negative, set \( \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = 0. \)

\[ T = \frac{\Delta H^\circ}{\Delta S^\circ} \]
Le Chatelier

Concentration change $A \xrightleftharpoons{} B$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$Q$ - the reaction quotient, an expression having the same form as the equilibrium (concentrations are not necessarily at equilibrium).

At equilibrium, $Q = K$, $\Delta G = 0$

$$0 = \Delta G^\circ + RT \ln K$$

$$\Delta G^\circ = -RT \ln K$$

then disturb equilibrium by adding $A$

so $Q < K = \frac{[B]}{[A]}$ but

$$\Delta G = (-RT \ln K) + RT \ln Q$$

if $Q < K$ $\Delta G < 0$

spontaneous shift to right.
Example: Calculate $\Delta G^\circ$ for the following reaction:

$$\text{C}_2\text{H}_4(\text{g}) + \text{HBr}(\text{g}) \rightarrow \text{C}_2\text{H}_2\text{Br}(\text{g})$$

Given the following:

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta G^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_2\text{H}_4(\text{g})$</td>
<td>68.4</td>
</tr>
<tr>
<td>$\text{HBr}(\text{g})$</td>
<td>-53.4</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_2\text{Br}(\text{g})$</td>
<td>-61.9</td>
</tr>
</tbody>
</table>

Calculate $\Delta G$ for the reaction if $P(\text{C}_2\text{H}_4) = 1.57 \text{ atm}$, $P(\text{HBr}) = 2.01 \text{ atm}$, and $P(\text{C}_2\text{H}_2\text{Br}) = 0.83$.

Calculate $K$ for the reaction.
**Free Energy and Chemical Equilibrium**

The total free energy of a reaction mixture changes as the reaction progresses toward equilibrium.

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

Mostly reactants: \( Q \ll 1 \)

\[ RT \ln Q \ll 0 \]

\[ \Delta G < 0 \quad \text{(NEGATIVE)} \]

The total free energy decreases as the reaction proceeds spontaneously in the forward direction.

Mostly products: \( Q \gg 1 \)

\[ RT \ln Q \gg 0 \]

\[ \Delta G > 0 \quad \text{(POSITIVE)} \]

The total free energy decreases as the reaction proceeds spontaneously in the reverse direction.

Free Energy Curve
\[ \Delta G^\circ = -RT \ln K \]

<table>
<thead>
<tr>
<th>( \Delta G^\circ )</th>
<th>K</th>
<th>Product Formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta G^\circ &lt; 0 )</td>
<td>( K &gt; 1 )</td>
<td>Products favored</td>
</tr>
<tr>
<td>( \Delta G^\circ &gt; 0 )</td>
<td>( K &lt; 1 )</td>
<td>Reactants favored</td>
</tr>
<tr>
<td>( \Delta G^\circ = 0 )</td>
<td>( K = 1 )</td>
<td>At equilibrium when ([A] = [B]) (very rare)</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>( \Delta H )</th>
<th>( \Delta S )</th>
<th>( \Delta G )</th>
<th>Reaction characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>+</td>
<td>Always neg.</td>
<td>reactions is spontaneous at all temperatures</td>
</tr>
<tr>
<td>+</td>
<td>-</td>
<td>always pos.</td>
<td>reaction is non spontaneous at all temperatures: reverse reaction is always spontaneous</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>neg. at low temps: pos at high temps</td>
<td>Reactions is spontaneous at low temperatures but becomes nonsensitive at high temperatures</td>
</tr>
<tr>
<td>+</td>
<td>+</td>
<td>Pos. at low temps: neg at high temps</td>
<td>Reaction is nonsensitive at low temperatures but becomes spontaneous at high temperatures.</td>
</tr>
</tbody>
</table>
\[ \Delta G_{rxn} = \sum \Delta G^\circ_f(\text{prod.}) - \sum \Delta G^\circ_f(\text{react.}) \]

\[ \Delta G^\circ_{sys} = \Delta H^\circ_{sys} - T \Delta S^\circ_{sys} \]

Temperature dependence

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

Concentration dependence

At equilibrium \( \Delta G = 0 \)

\[ 0 = \Delta H^\circ_{sys} - T \Delta S^\circ_{sys} \]

\[ \Delta H^\circ_{sys} = T \Delta S^\circ_{sys} \]

Temperature dependence

\[ 0 = \Delta G^\circ + RT \ln K \]

\[ \Delta G^\circ = -RT \ln K \]

\[ K = e^{-\Delta G^\circ/RT} \]

Concentration dependence
The Laws of Thermodynamics

First Law of Thermodynamics
The total energy of the universe is a constant

\[ \Delta E = q + w \]

\[ \Delta E + \Delta E_{surr} = 0 \]

Second Law of Thermodynamics
The total entropy of the universe is always increasing

\[ \Delta S_{sys} + \Delta S_{surr} = \Delta S_{univ} > 0 \]

Third Law of Thermodynamics
The entropy of a pure, perfectly formed crystalline substance at absolute zero is zero.

\[ S = k \ln W \]

at absolute zero, there is only one possible state available to the crystal, \( W = 1 \),

\[ S = k \ln(1) = 0 \]

Estimate the boiling point of CH$_3$Cl.