Entropy and Disorder

- Mixing of ideal gases at constant $T$ and $p$

$$n_A A (g, V_A, T) + n_B A (g, V_B, T) = n (A + B) (g, V, T)$$

To calculate $\Delta S_{mix}$, we need to find a reversible path between the two states.

$$\Delta S_{demix} = -\Delta S_{mix} \quad \text{function of state}$$

For demixing process

$$\Rightarrow \Delta U = 0 \quad \Rightarrow q_{rev} = -w_{rev} = p_A dV_A + p_B dV_B$$

work of compression of each gas

$$\therefore \Delta S_{demix} = \int \frac{dq_{rev}}{T} = \int_V^{V_A} \frac{p_A dV_A}{T} + \int_V^{V_B} \frac{p_B dV_B}{T} = n_A R \ln \frac{V_A}{V} + n_B R \ln \frac{V_B}{V}$$

Put in terms of mole fractions $X_A = \frac{n_A}{n}$, $X_B = \frac{n_B}{n}$

Ideal gas $\Rightarrow X_A = \frac{V_A}{V}$, $X_B = \frac{V_B}{V}$
\[
\Delta S_{\text{mix}} = nR[X_A \ln X_A + X_B \ln X_B]
\]

\[
\Delta S_{\text{mix}} = -nR[X_A \ln X_A + X_B \ln X_B]
\]

Since \( X_A, X_B < 1 \) \( \Rightarrow \Delta S_{\text{mix}} > 0 \) mixing is always spontaneous

The mixed state is more "disordered" or "random" than the demixed state.

\[
S_{\text{mixed}} > S_{\text{demixed}}
\]

This is a general result \( \Rightarrow \)

Entropy is a measure of the disorder of a system

\[
\Delta S = \begin{cases} 
0 & \text{Reversible, no change in disorder} \\
> 0 & \text{Spontaneous, increased randomness} \\
< 0 & \text{Impossible, order cannot "happen" in isolation}
\end{cases}
\]

There is an inexorable drive for the universe to go to a maximally disordered state.

Examples of \( \Delta S \) calculations

In all cases, we must find a reversible path to calculate \( \int \frac{dq_{\text{rev}}}{T} \)

(a) Mixing of ideal gases at constant \( T \) and \( p \)

\[
n_A (g, V_A, T) + n_B (g, V_B, T) = n (A + B) (g, V = V_A + V_B, T)
\]

\[
\Delta S_{\text{mix}} = -nR[X_A \ln X_A + X_B \ln X_B]
\]
(b) Heating (or cooling) at constant $V$

$$A(T_1, V) = A(T_2, V)$$

$$\Delta S = \int_{T_1}^{T_2} \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{C_v dT}{T}$$

if $C_v$ is $T$-independent

$$C_v \ln \frac{T_2}{T_1}$$

[Note $\Delta S > 0$ if $T_2 > T_1$]

(c) Reversible phase change at constant $T$ and $p$

e.g. $H_2O(l, 100^\circ C, 1 \text{ bar}) = H_2O(g, 100^\circ C, 1 \text{ bar})$

$$q_p = \Delta H_{vap}$$

$$\Delta S_{vap}(100^\circ C) = \frac{q_{vap}^p}{T_b} = \frac{\Delta H_{vap}}{T_b}$$

($T_b$ = boiling Temp at 1 bar)

(d) Irreversible phase change at constant $T$ and $p$

e.g. $H_2O(l, -10^\circ C, 1 \text{ bar}) = H_2O(s, -10^\circ C, 1 \text{ bar})$

This is **spontaneous** and irreversible.

∴ We need to find a reversible path between the two states to calculate $\Delta S$.

$$H_2O(l, -10^\circ C, 1 \text{ bar}) \begin{array}{c} \text{irreversible} \\ dq_{rev} = C_p(l)dT \end{array} = H_2O(s, -10^\circ C, 1 \text{ bar})$$

$$H_2O(l, 0^\circ C, 1 \text{ bar}) \begin{array}{c} \text{reversible} \\ dq_{rev} = C_p(s)dT \end{array} = H_2O(s, 0^\circ C, 1 \text{ bar})$$

$$q_p^{rev} = -\Delta H_{fus}$$
\[ \Delta S = \Delta S_{\text{heating}} + \Delta S_{\text{fus}} + \Delta S_{\text{cooling}} \]
\[ = \int_{T_1}^{T_{fas}} \frac{C_p(\ell)}{T} dT + \frac{-\Delta H_{fas}}{T_{fas}} + \int_{T_{fas}}^{T_1} \frac{C_p(s)}{T} dT \]

\[ \therefore \Delta S = \frac{-\Delta H_{fas}}{T} + \int_{T_1}^{T_{fas}} \left[ C_p(\ell) - C_p(s) \right] \frac{dT}{T} \]

\[ \Delta S = \frac{-\Delta H_{fas}}{T} + \left[ C_p(\ell) - C_p(s) \right] \ln \frac{T_{fas}}{T_1} \]

if \( C_p \) values are \( T \)-independent.