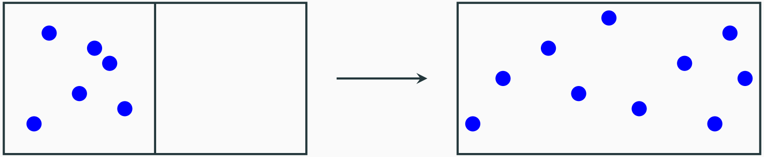
Lecture 16: Entropy

Factors that affect entropy, Standard Molar Entropy, Residual Entropy, Laws of Thermo

Motivation

Currently we don't have a way to describe if a reaction is going to occur or not



Before

After

Entropy

Entropy is a state function, a measure of disorder. Things trend to higher entropy

Differential Form:

$$dS = \frac{dq_{rev}}{T}$$

Low entropy → High entropy

High order → High disorder

Low probability → High probability

Second and Third Laws of Thermodynamics

Second Law

The entropy of the universe is always increasing:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

Entropy of an isolated system increases during spontaneous irreversible processes

$$dS \geq \frac{dq}{T}$$

Where $=$ sign applies for reversible case

Third Law

As T approaches $0\,\mathrm{K}$, entropy of a perfect crystal approaches $0\,\frac{\mathrm{J}}{\mathrm{K}}$

$$\begin{aligned} S &= k_B \ln W \\ &= k_B \ln 1 = 0 \end{aligned}$$

Microstates and Entropy

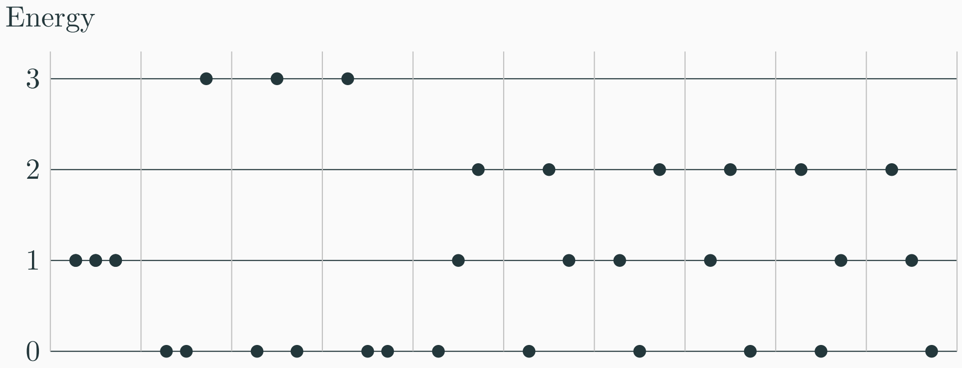
Boltzmann's Entropy Formula

$$S = k_B \ln W$$

W: number of accessible microstates within a macrostate

Microstates vs Macrostate

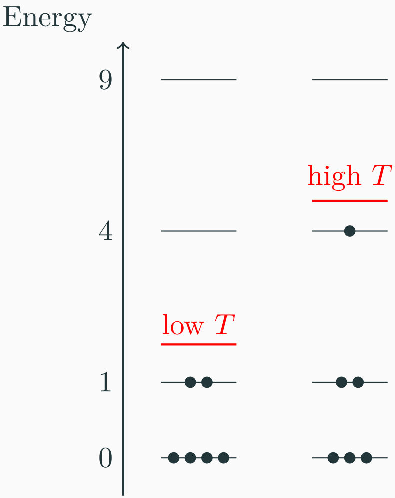
Consider a system of 3 distinguishable particles, $E_{tot} = 3$



10 microstates (absolute arrangements), 3 macrostates (configurations of particles)

$W = 1, 3, 6$ for the 3 macrostates

Temperature and Entropy

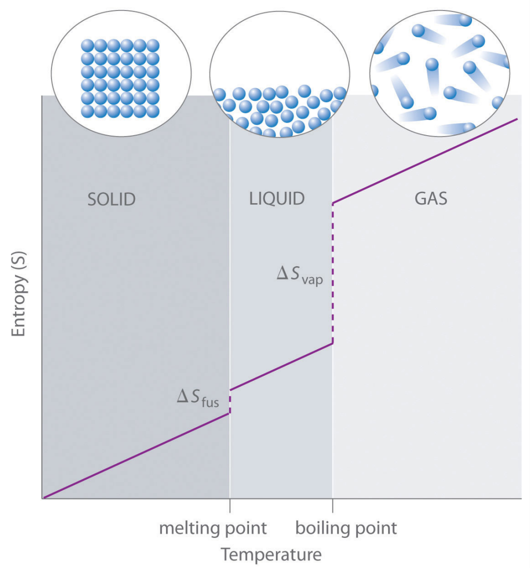


Relationship

$\uparrow T \quad \uparrow S$

Higher thermal energy increases the number of accessible microstates

Phase Change and Entropy



Relationship

Phase changes are associated with large discountinous increases in entropy

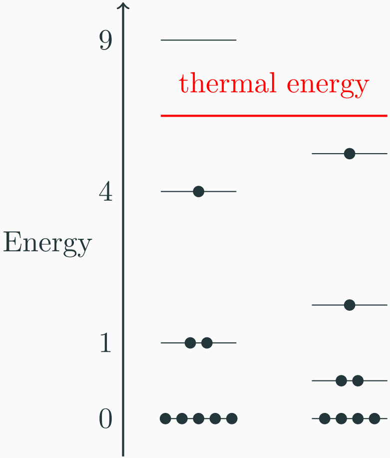
Matter and Entropy

Relationship

$\uparrow n \quad \uparrow S$

Due to more microstates being accessible, same idea as Q

Volume, Molar Mass and Entropy



Relationship

$\uparrow V \quad \uparrow S$ and $\uparrow MW \quad \uparrow S$

Due to more accessible microstates at the same temperature

Recall Particle in a Box model:

$$E_n = \frac{n^2 h^2}{8ma^2}$$

$\uparrow m \quad \downarrow E_n \quad \uparrow$ microstates $\quad \uparrow S$

$\uparrow V \quad \downarrow E_n \quad \uparrow$ microstates $\quad \uparrow S$

Standard Molar Entropy

Standard Molar Entropy S_m°

Absolute entropy of 1 mol at SATP
Units: $\frac{\mathrm{J}}{\mathrm{mol}\cdot\mathrm{K}}$

Ranking entropy order:
gas > liquid > solid
heavier MW > lighter MW
more DOF > less DOF

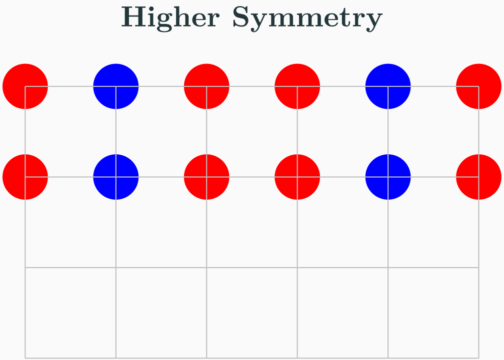
Can be used to find $\Delta S^\circ_{\mathrm{rxn}}$:

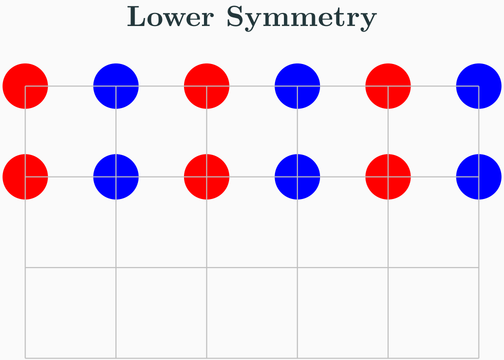
$$\Delta S^\circ_{\mathrm{rxn}} = \sum nS_m^\circ(\text{products}) - \sum nS_m^\circ(\text{reactants})$$

Residual Entropy

Residual Entropy Trends

More symmetry, less residual entropy
Stronger dipoles reduce residual entropy





Example: Predicting Sign of ΔS

Predicting Sign of ΔS

gas > liquid > solid

- $H_2O\,(l) \longrightarrow H_2O\,(g)$
- $Na\,(s) + H_2O\,(l) \longrightarrow Na^+(aq) + \frac{1}{2}\,H_2(g) + OH^-(aq)$
- $H_2(g) + Cl_2(g) \longrightarrow 2\,HCl\,(g)$
- $CH_3CH(OH)CH_3(l) \longrightarrow CH_3CH(OH)CH_3(s)$

Constant Temperature Entropy

Constant Temperature ΔS

$$\Delta S = \frac{q_{rev}}{T}$$

Used for phase change, isothermal

Units: $\frac{\mathrm{J}}{\mathrm{K}}$