Key points For this lecture

• The combined first and second law

• The entropy of a chemical reaction

• Two other forms of Energy, that fold in Entropy

• Entropy is the key to the Thermodynamic Equation of State

• Third Law of thermodynamics; entropy from zero up
How does entropy drive processes?

1) Charge neutralization in a solvent

\[ CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq) \quad \Delta S^o = 148 \text{ J mole}^{-1} \text{ K}^{-1} \]

\[ HC_2O_4^-(aq) + OH^-(aq) \rightarrow C_2O_4^{2-}(aq) + H_2O(l) \quad \Delta S^o = -23 \text{ J mole}^{-1} \text{ K}^{-1} \]

In the first case, the charge is neutralized, while in the second case, there is charge transfer but no neutralization.

Binding of Netropsin by polydA-polydT

\[ \Delta S^o = 141 \text{ J mole}^{-1} \text{ K}^{-1} \]
2) Hydrophobic entropy

\[ C_3H_8(l) \rightarrow C_3H_8(aq) \quad \Delta S_{298K}^o = -80 \text{ J mole}^{-1} \text{K}^{-1} \]

Suppose that each first-shell water molecule could form water-water H-bonds in half of its possible orientations around the solute. Assume that propane is surrounded by 15 first shell water molecules. Calculate the molar change in entropy in microscopic terms and compare it to the number given above.

Ans: \( \Delta S = -86 \text{ J mole}^{-1} \text{K}^{-1} \)
3) Entropy of straight vs. wobbly chains

Proteins prefer a folded state as opposed to being in linear chains. Why?

Why is it that when you pull a rubber band, it pulls back?

Say we have a polymer made of three monomer beads. Fix the first monomer to a wall. The degree of freedom is the position of the other end at distance, $l = 1, 2, \text{ or } 3$. For which length do we have the maximum number of configurations? Which length maximizes entropy?

Ans: $l = 2$
We have learnt that we can calculate $\Delta S$ for an isolated system and determine whether a process is spontaneous or not.

It would be useful to define criteria for spontaneous changes for useful lab conditions such as constant $T$ and $P$ and constant $T$ and $V$.

Let’s start by seeing how entropy contributes to internal energy and enthalpy.
Internal energy: The combined First and Second Laws

\[ dU = dq + dw \quad \rightarrow \quad \text{First Law} \]

\[ dS = \frac{dq_{rev}}{T} \quad \quad dS \geq \frac{dq}{T} \geq 0 \]

Let’s consider only reversible and PV work,

\[ dq = TdS \quad \text{and} \quad dw = -PdV \]

\[ dU = TdS - PdV \]

Recalling the rules of state functions:

\[ T = \left( \frac{\partial U}{\partial S} \right)_V \quad \text{and} \quad P = -\left( \frac{\partial U}{\partial V} \right)_S \]

If \( z(x,y) \) is a state function:

\[ dz = \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x dy \]
II) Enthalpy

\[ dH = dU + PdV + VdP \]

For reversible processes and PV work:
Recalling the rules of state functions:

\[ dH = TdS + VdP \]

\[ T = \left( \frac{\partial H}{\partial S} \right)_P \quad \text{and} \quad V = \left( \frac{\partial H}{\partial P} \right)_S \]
III) Helmholtz Free Energy

\[ A = U - TS \]

\[ dA = dU - TdS - SdT \]

For reversible processes and PV work:

\[ dA = TdS - PdV - TdS - SdT \]

\[ dA = - PdV - SdT \]

Recalling the rules of state functions:

\[ P = - \left( \frac{\partial A}{\partial V} \right)_T \quad \text{and} \quad S = - \left( \frac{\partial A}{\partial T} \right)_V \]

Criteria for spontaneity:

\[ (dA)_{V,T} \leq 0 \]
Helmholtz Free Energy

Why A is useful to tell us about spontaneous processes

\[ dU = TdS + w_{rev} \quad A = U - TS \quad \text{or} \quad dA = d(U - TS) \]

For a process where T is held fixed

\[ dU = TdS + w_{rev} = d(TS) + w_{rev} \]
\[ d(U - TS) = w_{rev} \leq w \]
\[ dA = w_{rev} \leq w \quad \text{for} \quad \Delta T = 0 \]

For any process run at constant temperature the change in Helmholtz Energy is equal to the reversible work. If a process will spontaneously happen then it will produce work so \( w < 0 \) (and this can be done irreversibly)

Criteria for spontaneity: \( (dA)_{V,T} \leq 0 \)
III) Gibbs Free Energy

\[ G = H - TS = U + PV - TS \]

\[ dG = dH - TdS - SdT \]

For reversible processes and PV work:

\[ dG = TdS + VdP - TdS - SdT \]

\[ dG = VdP - SdT \]

Recalling the rules of state functions:

\[ V = \left( \frac{\partial G}{\partial P} \right)_T \quad \text{and} \quad S = -\left( \frac{\partial G}{\partial T} \right)_P \]

Criteria for spontaneity:

\[ (dG)_{P,T} = w_{r \text{ reversible}}^{\text{non-PdV}} \leq w_{\text{non-Pdv}}^{\text{non-PdV}} < 0 \]
Defining criteria for spontaneous reversible processes assuming PV work

<table>
<thead>
<tr>
<th>Energy</th>
<th>Equation</th>
<th>Criterion for spontaneous process</th>
<th>Equilibrium of a process</th>
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</thead>
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Key points of the this lecture

• How entropy drives processes

• Defining criteria for spontaneous process at constant T and V and constant T and P

  • Helmholtz Free Energy, $A = U - TS$

  • Gibbs Free Energy, $G = U + PV - TS = H - TS$