Temperature - dependence of $\Delta G$

As before, we can use Tables to calculate $\Delta G = \Sigma G^\circ_{\text{(products)}} - \Sigma G^\circ_{\text{(reactants)}}$

But what if we need to calculate $\Delta G$ at a non-standard temperature?

From last lecture:

$$dG = Vdp - SdT + dw^*_\text{rev}$$

(at constant $T$ and $P$, this $\Rightarrow$ $dG = dw^*_\text{rev}$)

Now assume $dw^*_\text{rev} = 0$ (only Vdp work)

then

$$dG = Vdp - SdT$$

if $P = \text{const}$

$$dG = -StdT$$

or

$$\frac{dG}{dT} = -S$$

$$\int_{T_1}^{T_2} dG = -\int_{T_1}^{T_2} SdT$$

$$\overline{G}(T_2) - \overline{G}(T_1) = -\int_{T_1}^{T_2} SdT$$

switch to per mol
Remember that for

\[ n_A A + n_B B \rightarrow n_C C + n_D D \]
\[ \Delta G = n_C \bar{C} + n_D \bar{D} - n_A \bar{A} - n_B \bar{B} \]

\[ \frac{d\Delta G}{dt} = n_C \frac{d\bar{C}}{dT} + n_D \frac{d\bar{D}}{dT} - n_A \frac{d\bar{A}}{dT} - n_B \frac{d\bar{B}}{dT} \]

\[ = -n_C \bar{S}_C - n_D \bar{S}_D + n_A \bar{S}_A + n_B \bar{S}_B \]

\[ \frac{d\Delta G}{dt} = -\Delta S \]

\[ \int_{T_1}^{T_2} \Delta S \, dt = -\int_{T_1}^{T_2} \Delta S \, dt \]

If \( \Delta S \) is reasonably independent of \( T \)

then

\[ \Delta G(T_2) - \Delta G(T_1) = -\Delta S (T_2 - T_1) \]

We won't derive, but also

\[ \frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} = -\int_{T_1}^{T_2} \frac{\Delta H(T)}{T^2} \, dT \]

\[ \text{If } \Delta H \text{ independent of } T \rightarrow \approx \Delta H \left[ \frac{1}{T_2} - \frac{1}{T_1} \right] \]
Pressure dependence of G and Helmholtz ($\Delta A$)

Noncovalent Reactions — Foundations of Biochemistry

$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \quad \text{Ionic} \quad \frac{\Delta H^0}{-785 \text{ kJ mol}^{-1}}$$

$$Na^+(aq) + Cl^-(aq) \rightarrow NaCl(s) \ (H_2O) \quad \text{Ionic} \quad \text{Dipole} \quad -4 \text{ kJ mol}^{-1}$$

$$Ar(g) \rightarrow Ar(s) \quad \text{London} \quad -8 \text{ kJ mol}^{-1}$$

Q: But we know that Ar is ~90% gas at RT. Why? A: $\leq$

$$2\left(\text{CH}_3\right) \rightarrow \text{CH}_3-O-H-O-\text{CH}_3 \quad \text{H-bond} \quad -20 \text{ kJ mol}^{-1}$$

Others in organic solvent: $-15 \text{ kJ mol}^{-1}$

$\Delta H^0 = -5 \text{ kJ mol}^{-1}$

"What's a H-bond worth energetically?"
Benzene (l) + H₂O(l) → benzene (aq) \[ \Delta H = 0 \]

So we know that benzene is not soluble in water, it must be opposed by entropy.

**Ion-dipole Interactions**

**Ion-Induced Dipole Interactions**

Induced Dipole - Induced Dipole (London interactions) = Always attractive

Transient induced dipoles exist. One influences a nearby neighbor.

Van der Waals

Dipole-Dipole interactions for uncharged molecules
H-Bonds

15-20 kJ/mol,
compared to ~400 kJ/mol
for covalent bonds.

But net strength is less because of water.
~5 kJ/mol but varies. (2-1 kcal/mol)

Hydrophobic Interactions "(Bonds?)"

Propane C₃H₈ in water.

C₃H₈ (l) + ∞ H₂O → C₃H₈ (aq)

\[ \Delta H^{\circ}_{298} = -8 \text{ kJ mol}^{-1} \quad \text{favorable} \]

\[ \Delta S^{\circ}_{298} = -80 \text{ J K}^{-1} \text{ mol}^{-1} \quad \text{unfavorable} \]

\[ \Delta G^{\circ}_{298} = +16 \text{ kJ mol}^{-1} \quad \text{unfavorable} \]

Still lots of H-bonds, but fewer ways to do it.
The "bending" here is the water. But not the ΔH of the water. Rather, it's the ΔS of the water that drives phase separation.

Proteins

Amphiphilic
(both)

O = hydrophobic side chains
Δ = hydrophilic

Protein-Folding
Equals
Taking Benzene out of water!