Temperature-dependence of G

As before, we can use Tables to calculate $\Delta G = \sum G_f^\circ(\text{products}) - \sum G_f^\circ(\text{reactant}$

But what if we need to calculate ΔG at a <u>non-standard</u> temperature?

From last lecture:

$$dG = VdP - SdT + dw^*_{rev}$$

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

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

then $dG = VdP - SdT$ — all <u>state</u> variables, so it's <u>general</u>.

if P = const $dG = -SdT$

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

$$\int_{T_1}^{T_2} dG = -\int_{T_1}^{T_2} S\,dT$$

$$\bar{G}(T_2) - \bar{G}(T_1) = -\int_{T_1}^{T_2} \bar{S}\,dT$$

← switch to per <u>molar</u>.

Remember that for

$$n_A A + n_B B \longrightarrow n_C C + n_D D$$

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

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

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

$$\boxed{\frac{d\Delta G}{dT} = -\Delta S}$$

$$\int_{\Delta G_{T_1}}^{\Delta G_{T_2}} d\Delta G = -\int_{T_1}^{T_2} \Delta S \, dT$$

if ΔS is reasonably indep of T

then

$$\boxed{\Delta G(T_2) - \Delta G(T_1) = -\Delta S \, (T_2 - T_1)}$$

<u>We won't derive, BUT also</u>

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

<u>if</u> ΔH indep of T $\rightarrow$ $$\approx \Delta H \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

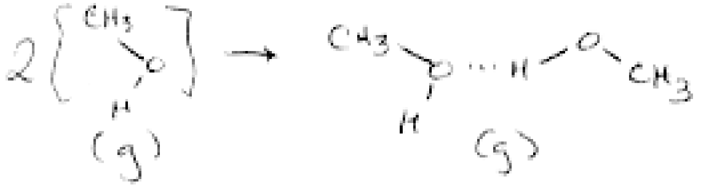
Skip Pressure dependence of G and Helmholtz (ΔA) pp 95 - 97

Noncovalent Reactions – Foundations of Biochemistry!

		ΔH°
$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$	Ionic	-785 kJ mol^{-1}
$Na^+(aq) + Cl^-(aq) \rightarrow NaCl(s) + (H_2O)$	Ionic + Dipole	-4 kJ mol^{-1}
$Ar(g) \rightarrow Ar(s)$	London	-8 kJ mol^{-1}

nteractions between vnt and te must strong!

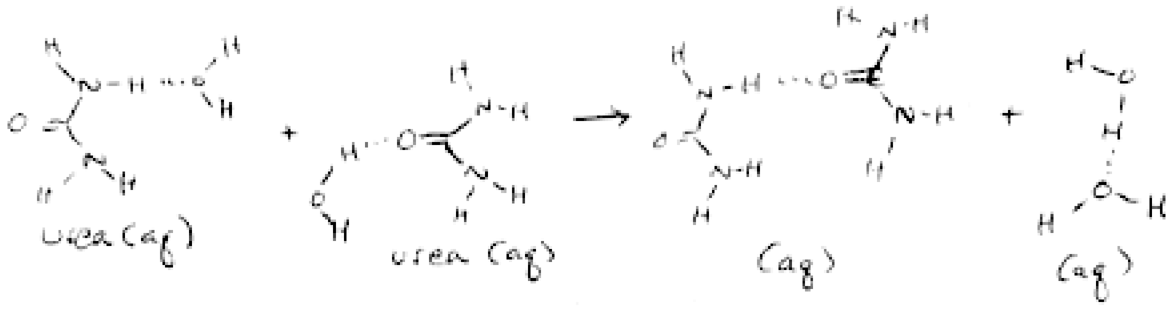
Q: BUT we know that Ar is ~100% gas at RT Why? A: S



H-bond $-\underline{20}$ kJ mol^{-1}

others in organic solvent -15 kJ mol^{-1}

Draw First w/out waters

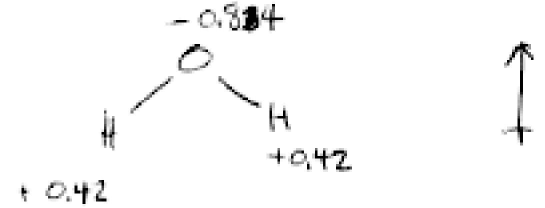


$$\Delta H^\circ = -5 \text{ kJ mol}^{-1}$$

"What's a H-bond worth energetically?"

Benzene (l) + $H_2O(l)$ → benzene (aq) $\Delta H = 0$

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



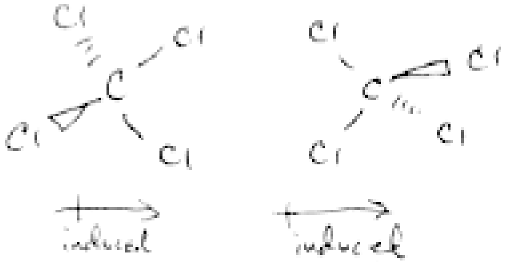
Ion-dipole Interactions

Ion - Induced Dipole Interactions

NO NET DIPOLE UNTIL ⊕ approaches

on-specific ttractive

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^{-1}
for covalent bonds.

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

Hydrophobic Interactions "(Bonds?)"

water fear

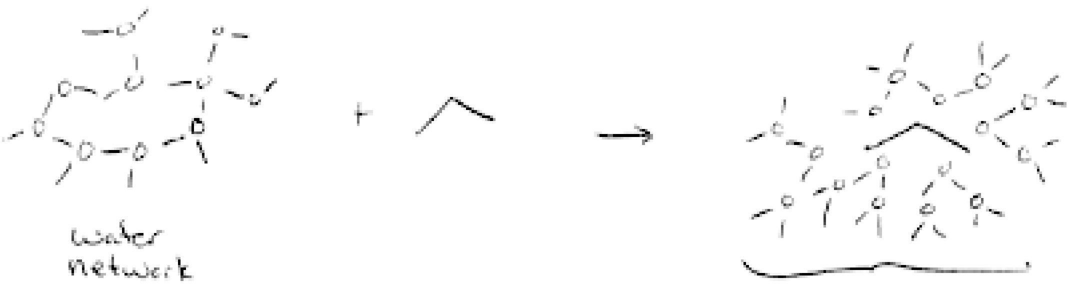
Propane C_3H_8 in water.

$$C_3H_8\ (l) + \infty H_2O \rightarrow C_3H_8\ (aq)$$

$\Delta H^\circ_{298} = -8\ kJ\ mol^{-1}$ favorable

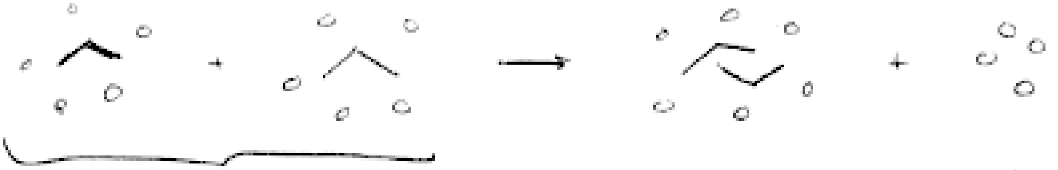
$\Delta S^\circ_{298} = -80\ J\ K^{-1}\ mol^{-1}$ unfavorable

$\Delta G^\circ_{298} = +16\ kJ\ mol^{-1}$ unfavorable NET.



Lots of H-bonds

Still lots of H-bonds, but fewer ways to do it.

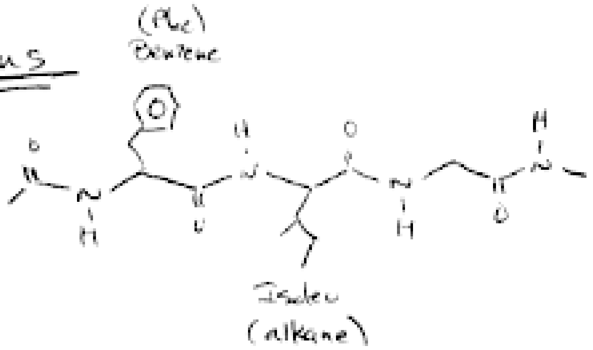


The "bonding" here is the water.

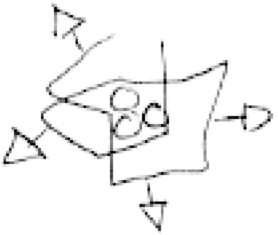
Entropy ⇒ This drives the phase separation of oils (propane is an alkane) in water

But not the ΔH of the water.
Rather, it's the ΔS of the water that drives phase separation.

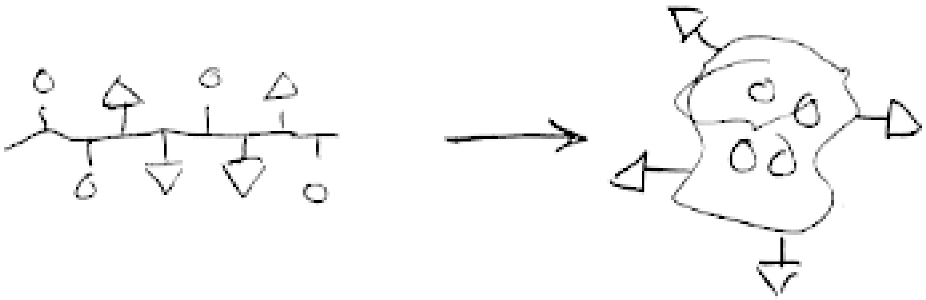
Proteins



Amphiphilic
(Both)



○ ≡ hydrophobic side chains
△ = hydrophilic



Protein-Folding
Equals
Taking Benzene
out of water!