

Entropy Change for a Phase Transition

water (l) \rightarrow water (g)

$$\Delta S_{tr} = \frac{\Delta H_{tr}}{T_{tr}}$$

"tr" \Rightarrow equilibrium temperature
(and pressure)

So for $P=1\text{atm}$ $T=100^\circ\text{C}$,
gaseous water and liquid water are
at equilibrium (boiling point)

Only valid at equilibrium because it's only
reversible at equilibrium.

Evaporation from your arm at 35°C

Not at equilibrium. Evaporation is
spontaneous. Won't go back equally.

$$\Delta S_{\text{water } l \rightarrow g} \neq \frac{\Delta H_{35^\circ\text{C}}}{T=35^\circ\text{C}}$$

Start from 0 K \rightarrow 298K liquid $T_m = 273\text{K}$

$$\bar{S}_0_{25^\circ\text{C } 1\text{atm}} = \bar{S}_0_{T=0\text{K}} + \int_0^{T_m} \bar{C}_p(s) \frac{dT}{T} + \frac{\Delta H_{\text{melt}}^0}{T_{\text{melt}}} + \int_{T_m}^{298} \bar{C}_p(l) \frac{dT}{T}$$

$0 + (\text{>0}) + (\text{>0}) + (\text{>0})$
0 \rightarrow T_m Melt

From first principles \uparrow

Gibbs Free Energy

We usually consider constant T and P, ^{not} isolated

Define

$$G = H - TS \quad \leftarrow \text{extensive, state variable}$$

"Spontaneity" of a process \leftarrow will/can it go?

$$dG = dH - Tds - SdT$$

$$= dE + PdV + VdP - Tds - SdT$$

$$= dq_{rev} + dw_{rev} + PdV + VdP - Tds - SdT$$

$$= Tds + dw_{rev} + PdV + VdP - Tds - SdT$$

$$= dw_{rev} + PdV + VdP - SdT$$

Note: $dw_{rev} = -PdV + dw_{rev}^*$ \leftarrow All non-PdV work

$$= -PdV + dw_{rev}^* + PdV + VdP - SdT$$

\Rightarrow Now, at constant P and T

$$dG = dw_{rev}^* \quad \leftarrow \text{non-expansion (useful) work}$$

ie. left-over after necessary
(by $PV=nRT$) work

We saw, but didn't prove, that w_{rev} is the maximum amount of work that can be done (irrev leads to less work).

$$w_{irrev} < w_{rev}$$

So $-\Delta G$ is the maximum amount of non-PdV work (e.g. electrical) that the system can do on the surroundings.

reverse of usual definition,
so negative sign.

Only if ΔG is negative for a reaction, can the reaction be used to do nonexpansion work on the surroundings.

Intuition says that only spontaneous things can do work (weight falling, water flowing downhill)

$\Delta G < 0$ spontaneous - can do work

$\Delta G = 0$ equilibrium - no work

$\Delta G > 0$ unspontaneous - goes other way

Table Lookups - Same old, Same old

If we know \bar{H}° and \bar{S}° for all reactants and products, then we can calculate ΔH° , ΔS° , and ΔG°

Temperature-dependence of ΔG

IF ΔH and ΔS independent of T

THEN $\Delta G = \Delta H - T\Delta S - \Delta T^\circ$

look up values for ΔH , ΔS at 25°C

the $\Delta G_{37^\circ\text{C}} \approx \Delta H_{25-37^\circ\text{C}} - T\Delta S_{25^\circ\text{C}}$

$$\Delta G_{37^\circ} - \Delta G_{25^\circ} = \Delta H_{37^\circ} - \Delta H_{25^\circ} - T_{37^\circ} \Delta S_{37^\circ} + T_{25^\circ} \Delta S_{25^\circ}$$

$$\text{IF } \Delta H_{37^\circ} \approx \Delta H_{25^\circ} \quad \Delta S_{37^\circ} \approx \Delta S_{25^\circ}$$

$$\text{the } \Delta G_{37^\circ} = \Delta G_{25^\circ} - \underbrace{(310\text{K} - 298\text{K}) \Delta S_{25^\circ}}$$

ΔS describes how ΔG depends on temperature.

$\Delta S < 0 \rightarrow \Delta G$ increases with increasing T

310
298
12
298
273
25

From before: $dG = VdP - SdT + dw_{rev}^*$

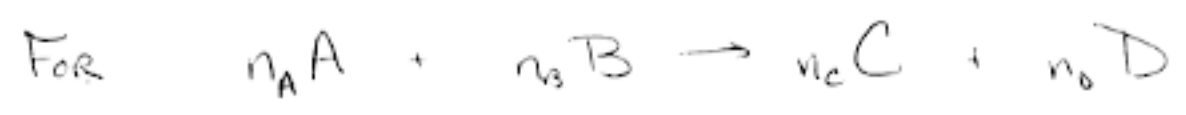
For a reversible path w/ only ~~work~~^{PV} work, ($dw_{rev}^* = 0$)

$dG = VdP - SdT$

But all are state variables,
so true also for irrev paths

At constant P, $dG = -SdT$ (related to last derivation)

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



$\Delta G_{rxn} = \underbrace{n_C \bar{G}_C + n_D \bar{G}_D}_{\text{products}} - \underbrace{n_A \bar{G}_A + n_B \bar{G}_B}_{\text{reactants}}$

$\frac{d\Delta G}{dT} = n_C \frac{d\bar{G}_C}{dT} + n_D \frac{d\bar{G}_D}{dT} - n_A \frac{d\bar{G}_A}{dT} - n_B \frac{d\bar{G}_B}{dT}$

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

$\frac{d\Delta G_{rxn}}{dT} = -\Delta S_{rxn}$

$\int_{T_1}^{T_2} d\Delta G_{rxn} = -\int_{T_1}^{T_2} \Delta S_{rxn} dT$

$\Delta G^{T_2} - \Delta G^{T_1} = -\Delta S_{rxn} (T_2 - T_1)$

(C)

Can derive (p. 93)

Gibbs-Helmholtz Equation

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

IF $\Delta H \approx$ independent of T , then easy answer.

SKIP \Rightarrow P-dependence of ΔG

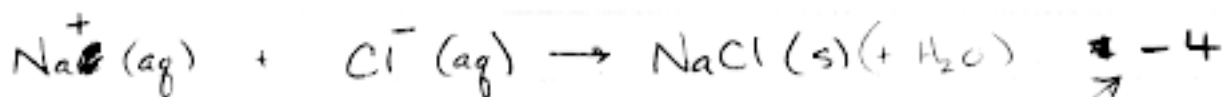
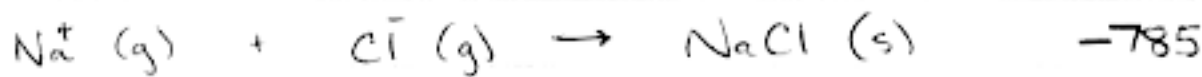
SKIP \Rightarrow Helmholtz free energy ΔA

NONCOVALENT REACTIONS

e.g. ligand binding, dimerization, protein folding

NONCOVALENT REACTIONS

Bond energies
 ΔH° kcal/mol



very small
(≈ 1 kcal/mol)