9/17/01 (1 0)(5)

Entropy Change for a Phase Transition

water (l) → water (g)

$$\Delta S_{tr} = \frac{\Delta H_{tr}}{T_{tr}}$$ "tr" ⇒ equilibrium temperature (and pressure)

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

Only valid at <u>equilibrium</u> because it's only <u>reversible</u> at equilibrium.

Evaporation from your arm at 35°C

<u>Not</u> at equilibrium. Evaporation is <u>spontaneous</u>. Won't go back equally.

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

273/0

<u>Start from 0 K</u> → 298K liquid $T_m = 273\,K$

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

$$\uparrow \qquad 0 \quad + \quad (>0) \quad + \quad (>0) \quad + \quad (>0)$$

From first principles

0→Tm Melt

Gibbs Free Energy

We usually consider constant T and P, not isolated

Define

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

"Spontaneity" of a process ⇐ 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: $dw_{rev} = -PdV + dw^*_{rev}$ ← All non-PdV work

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

⇒ Now, at constant P and T

$dG = dw^*_{rev}$ ← non-expansion (useful) work
i.e. 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 $\bar{H}^\circ$ and $\bar{S}^\circ$ for all reactants and products, then we can calculate ΔH°, ΔS°, and ΔG°

Temperature-dependence of ΔG

IFF ΔH and ΔS independent of T

THEN $\Delta G = \Delta H - T\Delta S - S\Delta T^{7\,0}$

look up values for ΔH, ΔS at 25°C

the $\Delta G_{37^\circ C}$? $\Delta H_{25-37^\circ C}$ ~ T

$$\Delta G_{37^\circ} - \Delta G_{25^\circ} = \Delta H_{37^\circ} - \Delta H_{25^\circ} - T_{37^\circ}\Delta S^\circ_{37} + T_{25^\circ}\Delta S_{2}$$

273
37
310

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

~~37~~
25
273
298

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

ΔS describes how ΔG depends on temperature

$\Delta S < 0 \Rightarrow \Delta G$ <u>increases</u> with increasing T

From before: $dG = VdP - SdT + dw^{*}_{REV}$

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

$$\underbrace{dG = VdP - SdT}_{\text{But all are state variables, so true also for irrev paths}}$$

At constant P, $dG = -S\,dT$ (related to last derivation

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

For $n_A A + n_B B \rightarrow n_C C + n_D D$

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

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

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

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

$$\int_{T_1\,[illegible]}^{T_2\,[illegible]} d\Delta G_{RXN} = -\int_{T_1}^{T_2} \Delta S_{RXN}\, dT$$

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

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 ΔH ≈ independent of T, then easy answer.

SKIP ⇒ P-dependence of ΔG
SKIP ⇒ Helmholtz free energy ΔA

NONCOVALENT REACTIONS

e.g. ligand binding, dimerization, protein foldin

Bond energies

NONCOVALENT REACTIONS

		ΔH° kJ/mol
Huge!!	$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$	-785
	$Na^+(aq) + Cl^-(aq) \rightarrow NaCl(s)(+H_2O)$	-4

very small
($\approx$ 1 kcal/mol)