Entropy Change For a Phase Transition

water (l) $\rightarrow$ water (g)

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

So for $P=1\text{atm}$, $T=100\degree\text{C}$, 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 $35\degree\text{C}$

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

$$\Delta S_{water} = \Delta H_{35\degree\text{C}} \quad \frac{T=35\degree\text{C}}{T=273\text{K}}$$

Start from $0\text{K}$ $\rightarrow$ $278\text{K}$ liquid $\rightarrow$ $273\text{K}$

$$S^{\circ}_{25\degree\text{C}} = S^{\circ}_{746\text{K}} + S^{\circ}_{Tm} \frac{dT}{T} + \frac{\Delta H_{melt}}{T_{melt}} + \int_{Tm}^{298} C_p (T) \frac{dT}{T}$$

From First Principles
Gibbs Free Energy

We usually consider constant $T$ and $P$, not isolated.

\[ G = H - TS \]  extensive, state variable

"Spontaneity" of a process $\leq \text{will/can it go?}$

\[ dG = dH - TdS - SdT \]

\[ = de + PdV + VdP - TdS - SdT \]

\[ = dq_{rev} + dw_{rev} + PdV + VdP - TdS - SdT \]

\[ = Tds + dw_{rev} + PdV + VdP - TdS - SdT \]

\[ = dw_{rev} + PdV + VdP - SdT \]

\[ \text{Note: } dw_{rev} = -PdV + dw_{rev}^* \]

\[ = -PdV + dw_{rev}^* + PdV + VdP - SdT \]

\[ \Rightarrow \text{Now, at constant } P \text{ and } T \]

\[ dG = dw_{rev}^* \]

\[ \text{non-expansion (useful) work} \]

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 (invar leads to less work).

\[ W_{rev} \leq W_{ext} \]

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 \( \Delta G \) is negative for a reaction, can the reaction be used to do non-expansion 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 $\Delta H^\circ$ and $\Delta S^\circ$ for all reactants and products, then we can calculate $\Delta G^\circ$, $\Delta S^\circ$, and $\Delta G^\circ$.

Temperature—dependence of $\Delta G$

**IFF** \( \Delta H \) and \( \Delta S \) independent of \( T \)

**THEN** \[ \Delta G = \Delta H^\circ - T \Delta S^\circ - S \Delta T \]

look up values for \( \Delta H^\circ, \Delta S^\circ \) at \( 25^\circ C \)

\[ \Delta G^\circ_{273} = \Delta G^\circ_{298} \]

\[ \Delta G^\circ_{273} - \Delta G^\circ_{298} = \Delta H^\circ_{373} - \Delta H^\circ_{298} - T_{373} \Delta S^\circ_{373} + T_{298} \Delta S^\circ_{298} \]

**IF** $\Delta H^\circ_{373} \approx \Delta H^\circ_{298}$, $\Delta S^\circ_{373} \approx \Delta S^\circ_{298}$

**THEN** \[ \Delta G^\circ_{373} = \Delta G^\circ_{298} - (373 K - 298 K) \Delta S^\circ_{298} \]

$\Delta S$ describes how $\Delta G$ depends on temperature.

$\Delta S < 0 \Rightarrow \Delta G$ increases with increasing $T$. 

From before: \( \Delta G = V dP - S dT + dW_{\text{rev}}^* \)

For a reversible path with only \( PV \) work, \( \left( dW_{\text{rev}}^* = 0 \right) \)

\[ \Delta G = V dP - S dT \]

But all are state variables, so true also for irreversible paths.

At constant \( P \), \( \frac{dG}{dT} = -S \)

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For \( n_A + n_B \rightarrow n_C + n_D \)

\[ \Delta G_{\text{rxn}} = n_C \bar{G}_C + n_D \bar{G}_D - n_A \bar{G}_A - n_B \bar{G}_B \]

\[ \frac{d \Delta G_{\text{rxn}}}{dT} = n_C \frac{d \bar{G}_C}{dT} + n_D \frac{d \bar{G}_D}{dT} - n_A \frac{d \bar{G}_A}{dT} - n_B \frac{d \bar{G}_B}{dT} \]

\[ = \Delta S_{\text{rxn}} \]

\[ \Delta G_{\text{rxn}} = \int_{T_1}^{T_2} \Delta S_{\text{rxn}} dT \]

\[ \Delta G_{T_2} - \Delta G_{T_1} = -\Delta S_{\text{rxn}} (T_2 - T_1) \]
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 \( \Delta H \) is independent of \( T \), then easy answers.

Skip \( \Rightarrow \) P-dependence of \( \Delta G \)
Skip \( \Rightarrow \) Helmholtz free energy \( \Delta A \)

Noncovalent Reactions
  \( \text{e.g. ligand binding, dimerization, protein folding.} \)
Noncovalent Reactions

\[ \text{Na}^+ (aq) + \text{Cl}^- (aq) \rightarrow \text{NaCl} (s) \quad \Delta H = -785 \text{ kJ/mol} \]

\[ \text{Na}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{NaCl} (s) + \text{H}_2\text{O} \quad \Delta H = -4 \text{ kcal/mol} \]

Very small

\( \approx 1 \text{ kcal/mol} \)