

Entropy & Free Energy

Entropy trends, ΔS° , ΔG° , spontaneity, the free-energy/K link, and crossover temperature.

01 Entropy trends

CORE RULE

More freedom $\rightarrow$ more entropy: $S(\text{gas}) > S(\text{liquid}) > S(\text{solid})$.
Melting and vaporizing raise entropy.

02 Predicting the sign of ΔS

CORE RULE

Compare moles of gas on each side: more gas moles = higher entropy.
Dissolving a solid into ions raises entropy; precipitating lowers it.

03 ΔS° from standard entropies

CORE RULE

$\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$, each $S^\circ \times$ its coefficient.
(Standard molar entropies are tabulated and nonzero, even for elements.)

04 ΔG° from formation values

CORE RULE

$\Delta G^\circ = \sum \Delta G^\circ_f(\text{products}) - \sum \Delta G^\circ_f(\text{reactants})$. $\Delta G^\circ_f = 0$ for an element in its standard state.

05 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

CORE RULE

When ΔG°_f isn't available, use $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (T in K). Watch units: ΔH° in kJ, ΔS° in J/K, so divide ΔS° by 1000 first.

06 Spontaneity

CORE RULE

$\Delta G^\circ < 0$ spontaneous; $\Delta G^\circ > 0$ nonspontaneous; $\Delta G^\circ = 0$ at equilibrium.

07 Free energy & K

CORE RULE

$\Delta G^\circ = -RT \ln K$ (T in K, $R = 8.314 \text{ J}/(\text{mol}\cdot\text{K})$). $K > 1 \leftrightarrow \Delta G^\circ < 0$ (product-favored).

08 Non-standard ΔG

CORE RULE

$\Delta G = \Delta G^\circ + RT \ln Q$. $\Delta G < 0 \rightarrow$ proceeds forward; $\Delta G > 0 \rightarrow$ reverse; $\Delta G = 0 \rightarrow$ at equilibrium.

09 Second law

CORE RULE

$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$, with $\Delta S_{\text{surr}} = -\Delta H_{\text{sys}}/T$ (const T , P). Spontaneous $\leftrightarrow \Delta S_{\text{univ}} > 0$.

10 Crossover temperature

CORE RULE

When ΔH° and ΔS° are both positive, the reaction turns spontaneous above $T = \Delta H^\circ/\Delta S^\circ$ (where ΔG° changes sign).

11 Phase transitions

CORE RULE

At a boiling or freezing point the two phases are at equilibrium, so $\Delta G^\circ = 0$ and the transition temperature is $T = \Delta H^\circ/\Delta S^\circ$ for that phase change.