

Entropy, Gibbs energy and spontaneity

AP Chemistry · Lesson

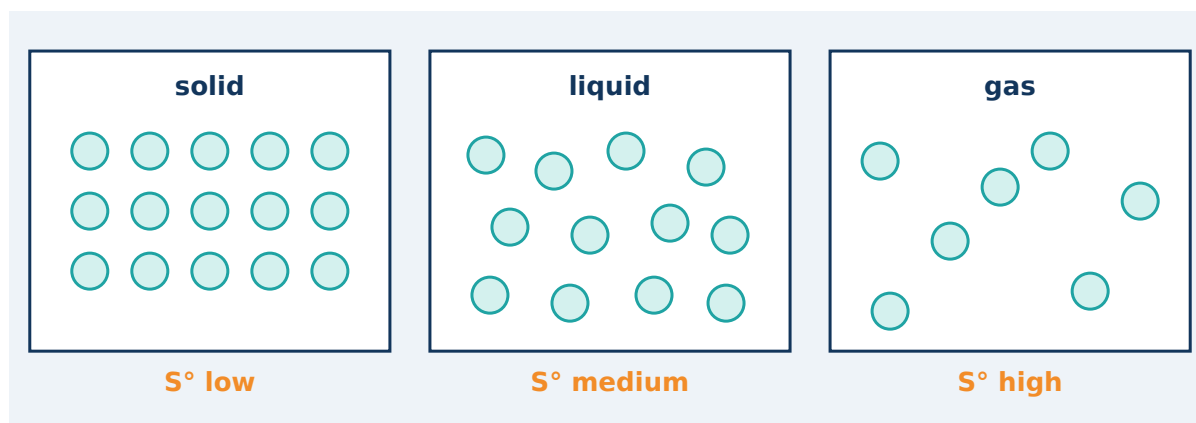
Quick answer: Entropy S measures the dispersal of energy and matter, and the Gibbs free energy change $\Delta G = \Delta H - T\Delta S$ predicts spontaneity: a reaction is spontaneous when ΔG is negative. The standard free energy change is linked to the equilibrium constant by $\Delta G^\circ = -RT \ln K$.

Level: AP Chemistry · **Curriculum:** AP Chem Unit 9

What is entropy?

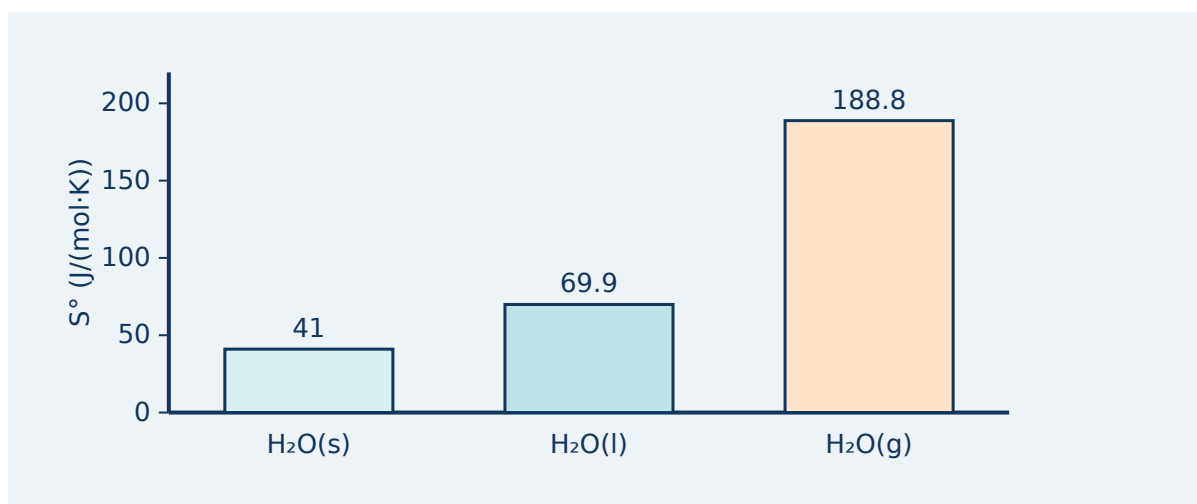
Definition

Entropy (S) measures how many ways the energy and particles of a system can be arranged, the number of microstates W : $S = k \ln W$. Put simply, it measures dispersal. Its unit is $J/(mol \cdot K)$. The **second law** says the total entropy of the universe increases in a spontaneous process.



More freedom of movement means more microstates and higher entropy.

Entropy rises when a solid melts or dissolves, when a liquid evaporates, when the number of gas particles increases, and when temperature rises. It falls in the reverse changes. Standard molar entropies S° are tabulated at 298 K, and even a perfect crystal has $S = 0$ only at 0 K.



Standard molar entropy of water in three states.

Formula

$\Delta S^\circ_{\text{rxn}} = \sum nS^\circ(\text{products}) - \sum nS^\circ(\text{reactants})$, where n is the stoichiometric coefficient and S° is in J/(mol·K). The result has the unit J/(mol·K) for the reaction as written.

Worked example 1

Find ΔS° for $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ using $S^\circ = 191.6, 130.7$ and 192.5 J/(mol·K). $\Delta S^\circ = 2(192.5) - [191.6 + 3(130.7)] = 385.0 - 583.7 = \mathbf{-198.7 \text{ J/(mol·K)}}$. Four gas molecules become two, so a negative value was expected.

What does Gibbs free energy tell you?

Spontaneity depends on both the enthalpy change of the reaction and the entropy change. Gibbs combined them in one quantity. A negative ΔG means the process is thermodynamically favourable. It does not say how fast it is, because a spontaneous reaction can be very slow.

Formula

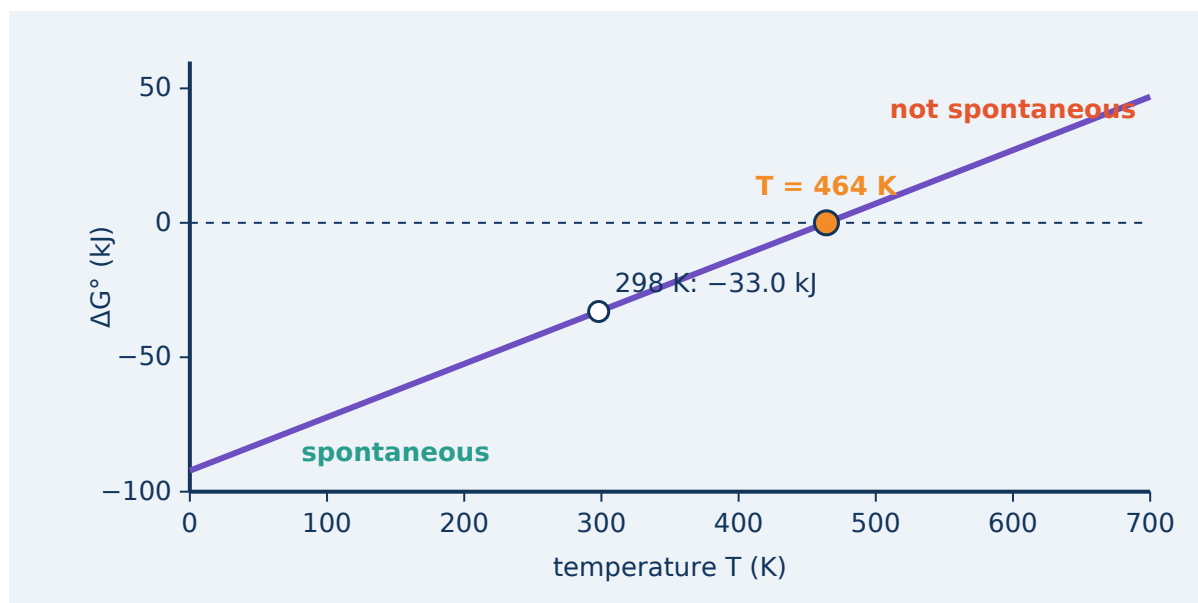
$\Delta G = \Delta H - T\Delta S$, with ΔH in kJ/mol, T in kelvin and ΔS in kJ/(mol·K) (divide J by 1000). A negative ΔG means spontaneous, $\Delta G = 0$ means equilibrium, and a positive ΔG means non-spontaneous in the forward direction.

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$	Spontaneous?
negative	positive	always negative	at all temperatures
positive	negative	always positive	at no temperature
negative	negative	negative at low T	only at low temperature
positive	positive	negative at high T	only at high temperature

Worked example 2

For the ammonia reaction $\Delta H^\circ = -92.2$ kJ. At 298 K: $\Delta G^\circ = -92.2 - (298)(-0.1987) = -92.2 + 59.2 = \mathbf{-33.0 \text{ kJ}}$, so it is spontaneous. $\Delta G^\circ = 0$ when $T = \Delta H^\circ/\Delta S^\circ = -92.2 /$

$-0.1987 = 464 \text{ K}$. Above this temperature the forward reaction is no longer favourable.



$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ gives a straight line; its slope is $-\Delta S^\circ$ and it crosses zero at $\Delta H^\circ/\Delta S^\circ$.

How are ΔG° and the equilibrium constant related?

The standard free energy change fixes the position of equilibrium. A very negative ΔG° gives a large K , and a positive ΔG° gives K below 1. When the mixture is not at standard conditions, use the reaction quotient Q to find the actual ΔG .

Formulas

$\Delta G^\circ = -RT \ln K$ and $\Delta G = \Delta G^\circ + RT \ln Q$, with $R = 8.314 \text{ J/(mol}\cdot\text{K)}$, T in kelvin and ΔG in joules. At equilibrium $\Delta G = 0$ and $Q = K$.

Worked example 3

Find K at 298 K for $\Delta G^\circ = -33.0 \text{ kJ}$. $\ln K = -\Delta G^\circ/RT = 33\,000 / (8.314 \times 298) = 13.32$, so $K = e^{13.32} = 6.1 \times 10^5$. The equilibrium lies far to the right.

Common mistake

Students mix units: ΔH in kJ with ΔS in $\text{J/(mol}\cdot\text{K)}$. Convert one of them before using $\Delta G = \Delta H - T\Delta S$. Another slip is thinking that a negative ΔG means a fast reaction, or that a positive ΔH means a reaction can never happen.

Lina's tip

Write the signs of ΔH and ΔS first and use the four-case table to predict the answer before calculating. If your calculated ΔG contradicts the table, check your units.

Key points to remember

- $\Delta S^{\circ}_{\text{rxn}} = \sum nS^{\circ}(\text{products}) - \sum nS^{\circ}(\text{reactants})$, in J/(mol·K).
- $\Delta G = \Delta H - T\Delta S$; spontaneous if ΔG is negative; convert ΔS to kJ/(mol·K).
- Crossover temperature: $T = \Delta H/\Delta S$ when ΔH and ΔS have the same sign.
- $\Delta G^{\circ} = -RT \ln K$, with $R = 8.314 \text{ J/(mol·K)}$; $\Delta G = \Delta G^{\circ} + RT \ln Q$.
- Entropy rises for melting, evaporating, dissolving and for more gas particles.

Entropy, Gibbs energy and spontaneity: frequently asked questions

What makes a reaction spontaneous?

A reaction is spontaneous when ΔG is negative, meaning the total entropy of the universe increases. Spontaneous does not mean fast.

How do you find the temperature at which a reaction changes from spontaneous to non-spontaneous?

Set $\Delta G = 0$ and solve $\Delta H - T\Delta S = 0$, so $T = \Delta H/\Delta S$. This only has a meaning when ΔH and ΔS have the same sign.

Why does a gas have higher entropy than a liquid?

Gas particles move freely throughout a larger volume, so they can be arranged in many more ways. More arrangements means more microstates and higher entropy.

How are ΔG° and K linked?

$\Delta G^{\circ} = -RT \ln K$. A negative ΔG° gives K greater than 1, a positive ΔG° gives K less than 1, and $\Delta G^{\circ} = 0$ gives $K = 1$.

Why can an endothermic process be spontaneous?

If the entropy of the system rises enough, the $-T\Delta S$ term outweighs a positive ΔH , so ΔG is negative. A cold pack dissolving ammonium nitrate is a familiar case.