

Entropy, Gibbs energy and reaction feasibility

Chemistry grades 11-12 (A Level · IB · Class 11-12) · Lesson

Quick answer: Entropy measures how many ways particles and energy can be arranged; it rises from solid to liquid to gas. The Gibbs energy change, $\Delta G = \Delta H - T\Delta S$, decides feasibility: a reaction is spontaneous when ΔG is negative. It becomes spontaneous above $T = \Delta H/\Delta S$ when both ΔH and ΔS are positive.

Level: Chemistry grades 11-12 (A Level · IB · Class 11-12) · **Curriculum:** IB R1.4

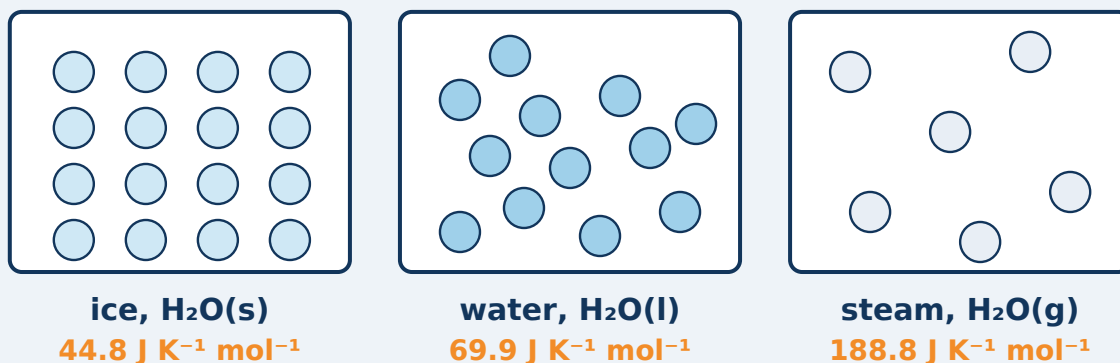
What is entropy?

Entropy, symbol S , measures how widely the energy of a system is spread over its particles. A system with more ways to arrange its particles and share energy has higher entropy. It is often described as disorder, but the real idea is the number of possible arrangements.

Definition

Entropy S is a measure of the number of ways in which particles and their energy can be arranged. Standard molar entropy S° is measured in $\text{J K}^{-1} \text{mol}^{-1}$ at 298 K and 100 kPa. Entropy is never zero for a substance above absolute zero.

Standard molar entropy of water in three states



more freedom of movement and energy storage: entropy rises

Entropy rises sharply from solid to liquid to gas.

These rules help you predict the sign of an entropy change without a calculator.

- Gases have much higher entropy than liquids, and liquids higher than solids.
- More moles of gas on the product side means ΔS is positive.
- Dissolving a solid, or heating any substance, raises entropy.
- Larger and more complex molecules have higher entropy than small ones.

Substance	S° (J K ⁻¹ mol ⁻¹)
H ₂ (g)	130.7
N ₂ (g)	191.6
NH ₃ (g)	192.5
H ₂ O(l)	69.9
CaCO ₃ (s)	92.9
Diamond, C(s)	2.4

How do you calculate the entropy change of a reaction?

Formula

$$\Delta S^\circ = \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants})$$

Each S° is multiplied by its coefficient in the balanced equation. ΔS° is in J K⁻¹ mol⁻¹ of reaction.

Worked example 1

Find ΔS° for $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$.

Products: $2 \times 192.5 = 385.0$. Reactants: $191.6 + 3 \times 130.7 = 583.7$.

$$\Delta S^\circ = 385.0 - 583.7 = -198.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

Four moles of gas become two, so a decrease in entropy is expected.

Why can endothermic changes happen by themselves?

The second law of thermodynamics says that the total entropy of the system plus its surroundings must increase in any spontaneous change. An exothermic reaction releases heat that spreads the surroundings' energy over more particles, raising their entropy.

Formulae

$$\Delta S(\text{surroundings}) = -\Delta H / T$$

$$\Delta S(\text{total}) = \Delta S(\text{system}) + \Delta S(\text{surroundings})$$

ΔH in J/mol, T in kelvin, so ΔS is in J K⁻¹ mol⁻¹.

What is Gibbs free energy and how does it predict feasibility?

Multiplying $\Delta S(\text{total})$ by $-T$ gives a quantity that depends only on the system: the Gibbs free energy change.

Gibbs equation

$$\Delta G = \Delta H - T\Delta S$$

ΔG = Gibbs energy change (kJ/mol), ΔH = enthalpy change (kJ/mol), T = temperature (K),

ΔS = entropy change of the system (J K⁻¹ mol⁻¹). A reaction is spontaneous when $\Delta G < 0$

and at equilibrium when $\Delta G = 0$.

Signs of ΔH and ΔS decide when a reaction is spontaneous		
	ΔS positive	ΔS negative
ΔH negative	spontaneous at all temperatures	spontaneous at low T only
ΔH positive	spontaneous at high T only	never spontaneous

Four sign combinations of ΔH and ΔS .

Worked example 2

An instant cold pack contains ammonium nitrate, which dissolves with $\Delta H = +25.7 \text{ kJ/mol}$ and $\Delta S = +108.7 \text{ J K}^{-1} \text{ mol}^{-1}$. Is dissolving spontaneous at 298 K?

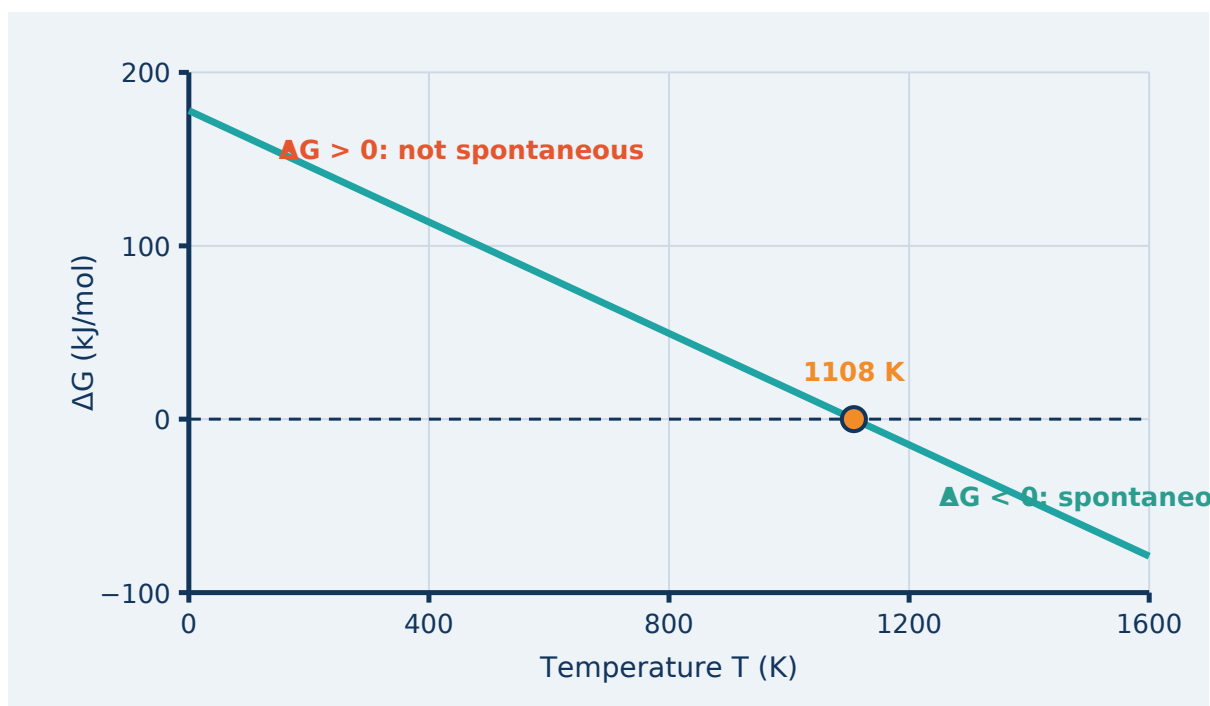
$\Delta S = 0.1087 \text{ kJ K}^{-1} \text{ mol}^{-1}$.

$\Delta G = 25.7 - 298 \times 0.1087 = 25.7 - 32.4 = -6.7 \text{ kJ/mol}$, so yes. The entropy gain outweighs the energy absorbed, so the pack gets cold.

Worked example 3

Limestone decomposes: $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$, $\Delta H = +178 \text{ kJ/mol}$, $\Delta S = +160.6 \text{ J K}^{-1} \text{ mol}^{-1}$. Find the minimum temperature for spontaneity.

At the changeover $\Delta G = 0$, so $T = \Delta H / \Delta S = 178\,000 \div 160.6 = \mathbf{1108 \text{ K}}$ (835 °C).



$\Delta G = \Delta H - T\Delta S$ for $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$: the reaction becomes spontaneous above 1108 K.

How is ΔG related to the equilibrium constant?

Formula

$$\Delta G^\circ = -RT \ln K$$

$R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$, T in K, K = equilibrium constant. Negative ΔG° gives K greater than 1; positive ΔG° gives K less than 1.

Worked example 4

A reaction has $\Delta G^\circ = -28.6 \text{ kJ/mol}$ at 298 K. Find K .

$$\ln K = 28\,600 \div (8.31 \times 298) = 11.55$$

$$K = e^{11.55} = \mathbf{1.04 \times 10^5}$$

Common mistake

ΔH is normally given in kJ/mol but ΔS in $\text{J K}^{-1} \text{ mol}^{-1}$. If you subtract $T\Delta S$ directly from ΔH , your answer is wrong by a factor of 1000. Convert ΔS to $\text{kJ K}^{-1} \text{ mol}^{-1}$, and always use kelvin, not $^\circ\text{C}$.

Lina's tip

To find the temperature at which a reaction switches from non-spontaneous to spontaneous (or the reverse), set $\Delta G = 0$ and solve $T = \Delta H / \Delta S$. Check the answer lies in the sensible range for the reaction.

Key points to remember

- $\Delta S^\circ = \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants})$, in $\text{J K}^{-1} \text{ mol}^{-1}$.

- Gases have higher entropy than liquids; liquids higher than solids; more gas moles means ΔS positive.
- $\Delta G = \Delta H - T\Delta S$; spontaneous if ΔG is negative, at equilibrium if $\Delta G = 0$.
- Convert ΔS to $\text{kJ K}^{-1} \text{mol}^{-1}$ and T to kelvin before using the Gibbs equation.
- $\Delta G^\circ = -RT \ln K$ links thermodynamics to the equilibrium constant.

Entropy, Gibbs energy and reaction feasibility: frequently asked questions

What does a positive entropy change mean?

It means the system has more ways of arranging its particles and energy after the change, for example when a solid melts, a liquid boils or a reaction produces more gas moles. It does not by itself prove the change is spontaneous.

How do you know if a reaction is spontaneous?

Calculate $\Delta G = \Delta H - T\Delta S$ in consistent units. If ΔG is negative the reaction is thermodynamically feasible at that temperature. A feasible reaction may still be very slow if its activation energy is high.

Why are some endothermic reactions spontaneous?

If the entropy of the system increases enough, the $-T\Delta S$ term makes ΔG negative even when ΔH is positive. Dissolving ammonium nitrate and the decomposition of limestone at high temperature are examples.

What is the link between ΔG and the equilibrium constant?

$\Delta G^\circ = -RT \ln K$. A large negative ΔG° gives a very large K , so products dominate at equilibrium. A large positive ΔG° gives a very small K .

Why must temperature be in kelvin?

The equation $\Delta G = \Delta H - T\Delta S$ uses absolute temperature, since T multiplies ΔS . Using $^\circ\text{C}$ would give zero or negative values at the wrong points and make predictions meaningless.