

Entropy and Gibbs Free Energy

What decides whether a reaction is spontaneous, and how do entropy and Gibbs free energy predict it?

●●● Advanced

Thermochemistry & Thermodynamics

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Before you start: it helps to understand [Enthalpy and Calorimetry](#) and [Hess's Law and Enthalpies of Formation](#).

What is it?

Some reactions happen on their own once started (they are **spontaneous**); others need a continuous input of energy. Enthalpy alone cannot decide which: ice melts spontaneously at room temperature even though melting is **endothermic**. A second quantity is needed.

Entropy, S , measures how spread out energy and matter are: the number of ways the particles and their energy can be arranged. Gases have high entropy, liquids less, and solids the least.

The **second law of thermodynamics**: in a spontaneous process, the total entropy of the universe increases.

Chemists combine enthalpy and entropy into the **Gibbs free energy** change:

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

where T is the temperature in **kelvin**.

KEY IDEA

At constant temperature and pressure, a reaction is **spontaneous** when ΔG is **negative**, at equilibrium when $\Delta G = 0$, and non-spontaneous (the reverse is spontaneous) when ΔG is positive. “Spontaneous” says nothing about speed: diamond turning into graphite is spontaneous, but immeasurably slow.

Why does it matter?

- **Predicting reactions.** ΔG tells chemists whether a reaction can go at all, and at what temperature it becomes possible, before they try it.
- **Industry.** Lime (CaO) is made by heating limestone above about 850°C , the temperature at which ΔG for the decomposition becomes negative.

- **Life and batteries.** Cells couple reactions with negative ΔG (such as using ATP) to drive ones with positive ΔG ; a battery's voltage is a direct measure of ΔG ($\Delta G = -nFE$).

How does it work?

1. Predicting the sign of ΔS

Entropy **increases** (ΔS positive) when:

- a solid melts or a liquid boils (solid $\rightarrow$ liquid $\rightarrow$ gas);
- the number of **moles of gas** increases, for example $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$;
- a solid dissolves to form ions in solution (usually);
- the temperature rises.

Entropy **decreases** when gas molecules combine into fewer molecules, for example $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ (4 mol of gas $\rightarrow$ 2 mol).

2. Calculating ΔS°

Unlike enthalpies of formation, **absolute** standard entropies, S° , can be measured for every substance, including elements (they are not zero). Then:

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

S° values are in $\text{J mol}^{-1} \text{K}^{-1}$, so ΔS° comes out in J/K. **Convert it to kJ/K** before combining it with ΔH° in kJ.

3. The four cases

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$	Spontaneous?
–	+	always negative	at all temperatures
+	–	always positive	never (the reverse is)
–	–	negative when T is low	at low temperature
+	+	negative when T is high	at high temperature

In the last two cases, the reaction switches at the temperature where $\Delta G = 0$:

$$T = \frac{\Delta H}{\Delta S}$$

4. ΔG° and the equilibrium constant

The standard free energy change is linked to the equilibrium constant:

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

with $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. A large negative ΔG° means a large K (products favoured); a positive ΔG° means K is less than 1.

∞ THINK OF IT LIKE THIS

Think of a tidy bedroom. Left alone, it gets messier, because there are far more messy arrangements than tidy ones: that is entropy. Tidying it needs energy (an enthalpy cost). Whether the room ends up tidy depends on both: how much energy you put in, and how strongly “messiness” wins. Temperature sets how much weight entropy gets in the balance.

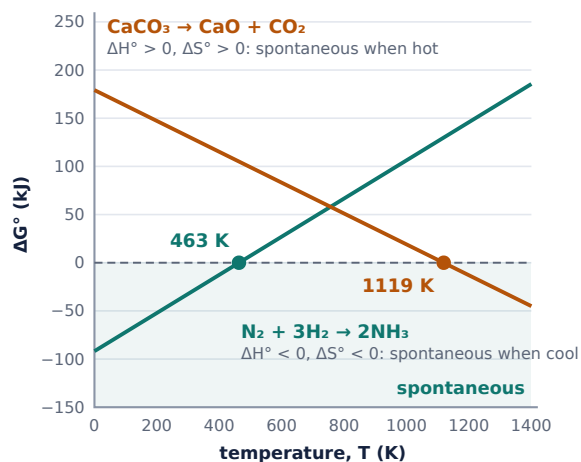
🔍 MORE PRECISELY

ΔG is the maximum useful (non-expansion) work a process can do at constant temperature and pressure. The relation $\Delta G = \Delta H - T\Delta S$ comes from the total entropy change: $\Delta S_{\text{universe}} = \Delta S_{\text{system}} - \Delta H/T$, so $\Delta G = -T\Delta S_{\text{universe}}$, and a negative ΔG is the same as an increase in the entropy of the universe. Using ΔH° and ΔS° at 298 K for other temperatures is an approximation, because both change a little with temperature.

Visualise it

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ changes with T

Below the dashed line (ΔG° negative) the reaction is spontaneous



Crossing point: $T = \Delta H^\circ / \Delta S^\circ$.

When ΔH and ΔS have the same sign, temperature decides: the line crosses $\Delta G^\circ = 0$ at $T = \Delta H^\circ / \Delta S^\circ$.

Worked example

WORKED EXAMPLE: ΔS° , ΔG° and the switching temperature for ammonia synthesis

Question: For $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$, $\Delta H^\circ = -91.8 \text{ kJ}$. Using S° ($\text{J mol}^{-1} \text{ K}^{-1}$): N_2 191.6, H_2 130.7, NH_3 192.8, find ΔS° , ΔG° at 298.15 K, and the temperature above which the reaction is no longer spontaneous.

Step 1 $\Delta S^\circ = 2(192.8) - [191.6 + 3(130.7)] = 385.6 - 583.7 = -198.1 \text{ J/K} = -0.1981 \text{ kJ/K}$ (negative: 4 mol of gas become 2)

Step 2 ΔG° :

$$\begin{aligned}\Delta G^\circ &= -91.8 \text{ kJ} \\ &\quad - (298.15 \text{ K}) \\ &\quad \times (-0.1981 \text{ kJ/K}) \\ &= -91.8 \text{ kJ} + 59.06 \text{ kJ} \\ &= \mathbf{-32.7 \text{ kJ}}\end{aligned}$$

Step 3 Spontaneous at 298 K. Switching temperature: $T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-91.8 \text{ kJ}}{-0.1981 \text{ kJ/K}} = \mathbf{463 \text{ K}}$. Above this, ΔG° is positive.

WORKED EXAMPLE: Why limestone must be heated

Question: For $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$, find ΔH° , ΔS° and ΔG° at 298.15 K, and the minimum temperature for decomposition. (Data in the note above.)

Step 1 $\Delta H^\circ = [-634.9 + (-393.5)] - (-1207.6) = +179.2 \text{ kJ}$

Step 2 $\Delta S^\circ = [38.1 + 213.8] - 91.7 = +160.2 \text{ J/K} = +0.1602 \text{ kJ/K}$

Step 3 $\Delta G^\circ_{298} = 179.2 \text{ kJ} - (298.15 \text{ K})(0.1602 \text{ kJ/K}) = 179.2 \text{ kJ} - 47.76 \text{ kJ} = \mathbf{+131.4 \text{ kJ}}$: not spontaneous at room temperature.

Step 4 $T = \frac{179.2 \text{ kJ}}{0.1602 \text{ kJ/K}} = \mathbf{1119 \text{ K}}$ (about 846 °C). Lime kilns run hotter than this.

 WORKED EXAMPLE: From ΔG° to K

Question: Estimate K at 298.15 K for ammonia synthesis ($\Delta G^\circ = -32.7 \text{ kJ} = -3.27 \times 10^4 \text{ J}$).

Step 1

$$\ln K = -\frac{\Delta G^\circ}{RT} = -\frac{-3.27 \times 10^4 \text{ J/mol}}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})} = 13.2$$

Step 2 $K = e^{13.2} \approx 5 \times 10^5$: products are strongly favoured at 298 K (even though the reaction is too slow without a catalyst).

Common mistake

 COMMON MISTAKE: Mixing J and kJ

ΔS° is usually in J/K but ΔH° in kJ. Convert ΔS° to kJ/K (divide by 1000) before calculating $\Delta H - T\Delta S$, or the entropy term will be 1000 times too large.

 COMMON MISTAKE: Using $^\circ\text{C}$ in $\Delta G = \Delta H - T\Delta S$

T must be in **kelvin**. At 25°C , use 298.15 K; using 25 would make the entropy term about twelve times too small.

 COMMON MISTAKE: Thinking spontaneous means fast

A negative ΔG says a reaction **can** happen, not how fast. Speed is kinetics (activation energy); a mixture of hydrogen and oxygen is spontaneous but does nothing until a spark starts it.

 NOTATION NOTE

- The degree sign ($^\circ$) means standard conditions: 1 bar and, unless stated, 298.15 K.
- Entropy units: $\text{J mol}^{-1} \text{ K}^{-1}$ for S° , J/K for ΔS° of a reaction as written.
- Some books use “feasible” or “thermodynamically favourable” instead of “spontaneous”.

Remember this

REMEMBER THIS

- Entropy: gases high, solids low; ΔS is positive when moles of gas increase.
- $\Delta S^\circ = \sum nS^\circ(\text{products}) - \sum nS^\circ(\text{reactants})$, in J/K; convert to kJ/K.
- $\Delta G = \Delta H - T\Delta S$ (T in K). Negative ΔG : spontaneous. Switching temperature $T = \Delta H / \Delta S$.
- $\Delta G^\circ = -RT \ln K$ and $\Delta G^\circ = -nFE^\circ$.

References

1. Brown, T. L.; LeMay, H. E., Jr.; Bursten, B. E.; Murphy, C. J.; Woodward, P. M.; Stoltzfus, M. W. Chemistry: The Central Science, 15th ed.; Pearson, 2022.

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