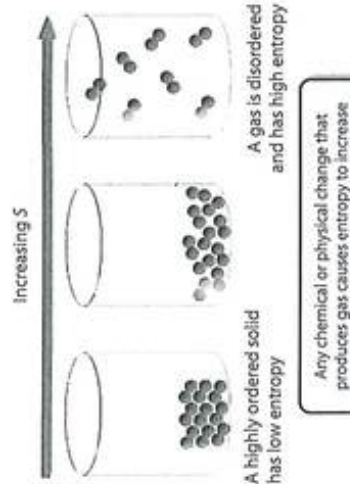
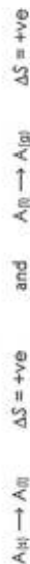


ENTROPY and FREE ENERGY

Entropy a measure of the disorder of a system, has the symbol S and units $\text{J K}^{-1} \text{mol}^{-1}$. Systems with high S have energy spread out. Those with low S are highly ordered with energy unevenly distributed.

If you heat a solid so that it melts then boils, the particles change from being in fixed places (solid) to moving around and being more disordered (liquid). When the liquid boils, the particles move away from each other, becoming even more disordered, filling the container, and spreading energy through it.

The change in entropy during a process is written as ΔS . Melting and boiling involve an increase in entropy, so could be written as:



FREE ENERGY, G

The change in **free energy** (ΔG) that occurs during the reaction can be considered as the total change in energy, including both the change in enthalpy from the loss or gain of heat energy and the change in how energy is spread out, relating to the change in entropy. This is expressed in the **Gibbs equation**: $\Delta G = \Delta H - T\Delta S$

T is the temperature of the reaction – you must use the units K , not $^{\circ}\text{C}$

ΔH alone cannot tell you if a reaction is feasible (likely to happen spontaneously) or not because ΔS also influences feasibility. The change in free energy of a reaction, balancing ΔH with ΔS can predict feasibility. **Reactions where $\Delta G \leq 0$ are feasible.**

Example: Use the data given to calculate whether this reaction is feasible at room temperature (298 K).



First calculate the change in entropy:

$$\Delta S = (2 \times 211) - (192 + 205) = +25 \text{ J K}^{-1} \text{mol}^{-1} = +0.025 \text{ kJ K}^{-1} \text{mol}^{-1}$$

Then use the Gibbs equation to calculate the change in free energy:

$$\Delta G = 180 - (298 \times 0.025) = +173 \text{ kJ mol}^{-1}$$

ΔG is positive – so the reaction is **not** feasible at 298 K (but it may become feasible at another temperature).

Substance	$\text{N}_2(\text{g})$	$\text{O}_2(\text{g})$	$\text{NO}(\text{g})$
$S \text{ (J K}^{-1} \text{mol}^{-1})$	192	205	211

EXAM TIP

Convert the units of S to $\text{kJ K}^{-1} \text{mol}^{-1}$ ($\div 1000$) to match the units of H

WHAT ΔG DOES NOT TELL YOU ABOUT REACTIONS

Although a negative value of ΔG for a reaction means that the reaction *should* happen spontaneously, this may not be what you observe. The reaction of methane with oxygen has a value for ΔG at room temperature of -951 kJ mol^{-1} . The reaction is *feasible*, but if you open a gas tap in the laboratory, methane mixes with oxygen in the air but you do not get a jet of flame shooting out of the gas taps. Why doesn't methane spontaneously combust? Why do you need to make the reaction happen (e.g. by lighting the gas with a match)?

The value of ΔG does not tell us anything about the **activation energy** of a reaction. Collision theory says that for a reaction to occur, particles have to collide with **enough energy** (the **activation energy**). Even if ΔG is negative at a certain temperature, there may be so few particles with enough energy for a successful collision at that temperature that the reaction proceeds so slowly that effectively it isn't happening at all.

The best way to think of what you can predict about a reaction when you know ΔG is this:

- if $\Delta G < 0$ at a certain temperature, the reaction will happen spontaneously at that temperature *once it has begun*
- if $\Delta G > 0$ at a certain temperature, the reaction will not happen spontaneously at that temperature
- ΔG tells you nothing about what is necessary for the reaction to get going

CALCULATING ENTROPY CHANGES

Data books list the entropy of many elements and compounds. You can calculate the entropy change for a reaction using this formula: $\Delta S = \sum S(\text{products}) - \sum S(\text{reactants})$.

Example 1: Calculate the entropy change for:



Using the data in the table on the right:

$$\Delta S = (214 + 2 \times 189) - (186 + 205) = +201 \text{ J K}^{-1} \text{mol}^{-1}$$

Two moles in balanced equation

Example 2: Calculate the entropy change for ice melting: $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l})$

Using the data in the table on the right:

$$\Delta S = 70 - 38 = +32 \text{ J K}^{-1} \text{mol}^{-1}$$

Substance	$\text{CH}_4(\text{g})$	$\text{O}_2(\text{g})$	$\text{CO}_2(\text{g})$	$\text{H}_2\text{O}(\text{g})$
$S \text{ (J K}^{-1} \text{mol}^{-1})$	186	205	214	189

EXAM TIP

When reading tables of data, make sure you read the correct formula and the correct state – (s), (l) or (g)

Substance	$\text{H}_2\text{O}(\text{s})$	$\text{H}_2\text{O}(\text{l})$
$S \text{ (J K}^{-1} \text{mol}^{-1})$	38	70

VARIATION OF ΔG WITH TEMPERATURE

$\Delta G = \Delta H - T\Delta S$ shows that as temperature increases, ΔG will change as $T\Delta S$ changes.

This means that a reaction that is not feasible because ΔG is positive at room temperature may become feasible if the temperature changes.

- if $\Delta S = +ve$ then increasing temperature will decrease ΔG – reactions require **higher** temperatures to become feasible.
- if $\Delta S = -ve$ then increasing temperature will increase ΔG – reactions require **lower** temperatures to become feasible.

You can calculate the minimum temperature at which a reaction becomes feasible by letting $\Delta G = 0$ and substituting the value of ΔH into the Gibbs equation to find T .

e.g. for the reaction of N_2 and O_2 shown on the left: $\Delta G = 180 - (T \times 0.025)$

$$\text{If } \Delta G = 0, \text{ then } 180 - (T \times 0.025) = 0 \quad \text{Rearranging gives: } T = \frac{180}{0.025} = 7200 \text{ K}$$

So, N_2 and O_2 will only react to form NO when the temperature is above 7200 K.



When a gas tap is opened, a flame does not spontaneously appear – it must be ignited even though ΔG for the combustion of methane is negative.