MEGA LECTURE

IB DP CHEMISTRY

Reactivity 1: What Drives Chemical Reactions?

Reactivity 1.4 Entropy and Spontaneity

Revision Notes · Higher Level

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Original notes prepared for the IB Diploma Programme Chemistry course (first assessment 2025)

What the syllabus requires

Reactivity 1.4 asks a single, deep question: why does one reaction happen on its own while another, though it releases energy, refuses to go? The answer combines the enthalpy change you met in R1.2 with a new quantity, **entropy**, through the Gibbs energy equation. Almost all of this material is examined at Higher Level.

Understanding	You should be able to...
Entropy, S	Describe entropy as a measure of the dispersal of energy and matter, and predict the sign of ΔS for a physical or chemical change.
Absolute entropies (HL)	Use standard entropy values to calculate ΔS° for a reaction as $\Sigma\, S^\circ$(products) − $\Sigma\, S^\circ$(reactants).
Gibbs energy (HL)	Apply $\Delta G = \Delta H - T\Delta S$ to decide whether a reaction is spontaneous.
Temperature dependence (HL)	Determine how spontaneity depends on temperature for each combination of signs of ΔH and ΔS, and find the crossover temperature.
Gibbs energy and K (HL)	Relate ΔG° to the equilibrium constant through $\Delta G^\circ = -RT \ln K$.

> **Exam note:** The term 'spontaneous' and the whole Gibbs-energy treatment (sections 3 onward) are HL only. SL students still need the idea of entropy and predicting the sign of ΔS. Every HL section below is flagged.

1. Entropy: the dispersal of energy and matter

Entropy, symbol S, measures how spread out the energy and matter of a system are among the ways they can be arranged. A system with many accessible arrangements (microstates) has high entropy; one with few has low entropy. Nature tends towards states of higher total entropy simply because they are overwhelmingly more probable. The units of entropy are J K^{-1} mol^{-1}.

The physical picture

Think of energy quanta being shared among particles. The more particles there are, the more freely they move, and the more volume they occupy, the more ways there are to distribute that energy — so the higher the entropy. This is why the state of matter matters so much:

- **Solid**: particles locked in a lattice, few arrangements → lowest entropy.
- **Liquid**: particles mobile but still close together → intermediate entropy.
- **Gas**: particles far apart and fast-moving → much the highest entropy.

So for a given substance S(gas) > S(liquid) > S(solid), and the jump in entropy on boiling is far larger than the jump on melting, because the gaseous state opens up an enormous number of new arrangements.

Predicting the sign of ΔS

You are not expected to guess a numerical value, but you must judge whether entropy rises ($\Delta S > 0$) or falls ($\Delta S < 0$). Work through this checklist, in order of importance — the number of moles of gas almost always decides the answer:

Look for...	Effect on ΔS	Why
An increase in the moles of gas	ΔS positive	Gas dominates entropy; more gas particles means far more ways to disperse energy.
A decrease in the moles of gas	ΔS negative	Gas is consumed, removing disorder.
Change of state s → l → g	ΔS positive	Particles gain freedom of movement.
A solid dissolving in water	usually ΔS positive	Ordered lattice breaks up and ions spread through the solution.
More moles of product than reactant (same states)	ΔS positive	More particles over which to share the energy.

Worked example 1 – predicting the sign of ΔS

Predict, with a reason, the sign of ΔS for each change.

(a) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

3 mol of gas become 2 mol of liquid: gas moles fall sharply, so ΔS is **negative**.

(b) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

A gas is produced from a solid: gas moles rise from 0 to 1, so ΔS is **positive**.

(c) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

4 mol of gas become 2 mol of gas: gas moles fall, so ΔS is **negative**.

(d) $NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$

1 mol solid becomes 2 mol gas: a large increase in disorder, so ΔS is **positive**.

2. Absolute entropies and $\Delta S°$ (HL)

Unlike enthalpy, entropy has a natural zero: the third law of thermodynamics states that a perfect crystal at absolute zero (0 K) has $S = 0$. Because of this we can assign every substance an **absolute standard entropy**, S°, measured at 298 K and 100 kPa. These are always positive (even for elements) and are tabulated in the data booklet in J K^{-1} mol^{-1}.

Some representative values (J K^{-1} mol^{-1}):

Substance	S°	Substance	S°
$H_2(g)$	130.6	$H_2O(l)$	69.9
$O_2(g)$	205.0	$H_2O(g)$	188.7
$N_2(g)$	191.6	$CO_2(g)$	213.7
$NH_3(g)$	192.5	$CaCO_3(s)$	92.9
$SO_2(g)$	248.2	$CaO(s)$	39.7

Substance	S°	Substance	S°
$SO_3(g)$	256.8	C(graphite)	5.7

Notice the trend: gases (large values) far exceed liquids and solids; the hard, highly ordered graphite lattice sits right at the bottom at only 5.7 J K^{-1} mol^{-1}.

Calculating the standard entropy change

For any reaction the standard entropy change is the total entropy of the products minus that of the reactants, each multiplied by its stoichiometric coefficient:

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

where Σ means 'the sum over each species, weighted by its coefficient'. The answer comes out in J K^{-1} mol^{-1} — keep this unit firmly in mind, because it will clash with the kJ of enthalpy in the next section.

Worked example 2 — calculating ΔS°

Calculate ΔS° for the thermal decomposition of calcium carbonate:

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

$\Delta S^\circ = [S^\circ(CaO) + S^\circ(CO_2)] - S^\circ(CaCO_3)$

$= (39.7 + 213.7) - 92.9 =$ **+160.5 J K^{-1} mol^{-1}**

The positive sign is exactly what we predicted in section 1: a gas is generated from a solid, so the system becomes more disordered.

Worked example 3 — a reaction that loses entropy

Calculate ΔS° for the Haber process, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$.

$\Delta S^\circ = 2 \times S^\circ(NH_3) - [S^\circ(N_2) + 3 \times S^\circ(H_2)]$

$= (2 \times 192.5) - (191.6 + 3 \times 130.6)$

$= 385.0 - 583.4 =$ **−198.4 J K^{-1} mol^{-1}**

Negative, as expected: 4 mol of gas collapse into 2 mol of gas.

Worked example 4 — entropy of vaporisation

Calculate ΔS° when one mole of water evaporates: $H_2O(l) \rightarrow H_2O(g)$.

$\Delta S^\circ = S^\circ(H_2O, g) - S^\circ(H_2O, l) = 188.7 - 69.9 =$ **+118.8 J K^{-1} mol^{-1}**

A large positive value: going from the liquid to the gas hugely increases the freedom of the molecules. Every simple s→l→g change follows the same pattern.

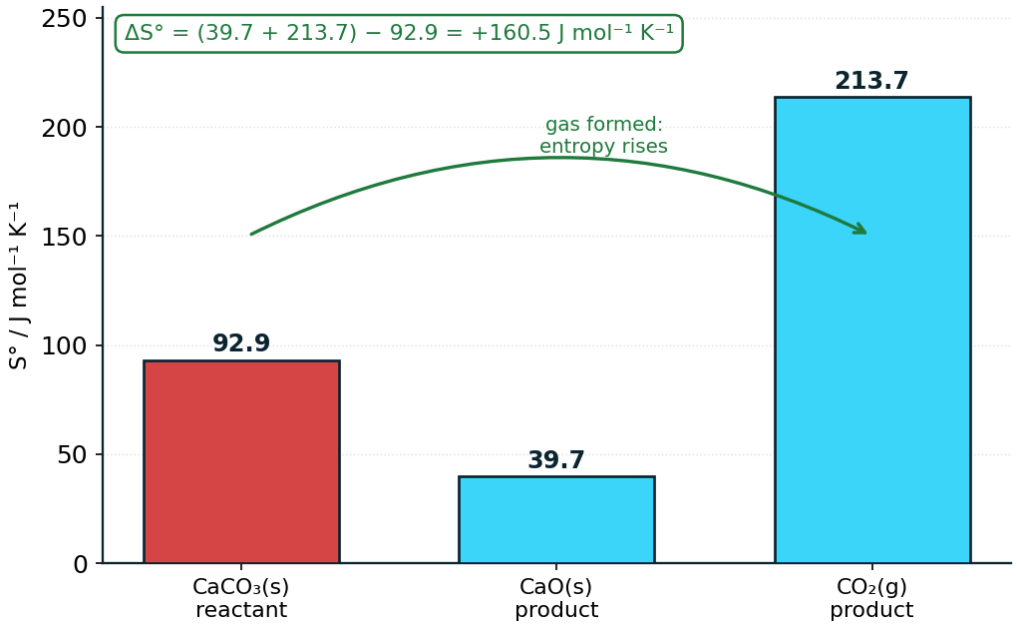

Figure. Standard molar entropies for $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$. A gas is produced, so $\Delta S^\circ = \Sigma\, S^\circ(\text{products}) - \Sigma\, S^\circ(\text{reactants}) = +160.5\ \text{J K}^{-1}\ \text{mol}^{-1}$ (positive).

3. Spontaneity and Gibbs energy (HL)

A **spontaneous** reaction is one that, once started, proceeds without any continuous outside help — it is thermodynamically 'downhill'. Whether a reaction is spontaneous depends on *both* the enthalpy change and the entropy change, combined into a single quantity, the **Gibbs energy change**:

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

where T is the absolute temperature in kelvin. Under standard conditions this is written $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. The sign of ΔG is the single test for spontaneity:

Sign of ΔG	Meaning	Reaction...
$\Delta G < 0$ (negative)	products lower in Gibbs energy	is spontaneous (feasible) in the forward direction
$\Delta G = 0$	no net driving force	is at equilibrium
$\Delta G > 0$ (positive)	products higher in Gibbs energy	is non-spontaneous forward; the reverse is spontaneous

> **Critical unit warning:** ΔH is quoted in **kJ** mol^{-1} but ΔS in **J** K^{-1} mol^{-1}. Before subtracting, convert ΔS to kJ by dividing by 1000 (or convert ΔH to J). Forgetting this is the single most common mistake in this whole topic.

Two opposing tendencies

Read the equation as a competition. The ΔH term rewards reactions that release energy (exothermic, $\Delta H < 0$). The $-T\Delta S$ term rewards reactions that increase disorder ($\Delta S > 0$), and its influence grows with temperature. Sometimes they pull the same way; sometimes they conflict, and then temperature decides the winner — the subject of the next section.

Worked example 5 — deciding spontaneity

The dissolving of ammonium nitrate, $NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$, has $\Delta H° = +25.7$ kJ mol^{-1} and $\Delta S° = +108.7$ J K^{-1} mol^{-1}. Is it spontaneous at 298 K?

$\Delta G° = \Delta H° - T\Delta S° = 25.7 - 298(0.1087)$

$= 25.7 - 32.4 = \mathbf{-6.7\ kJ\ mol^{-1}}$

$\Delta G°$ is negative, so dissolving is spontaneous even though it is endothermic — the cold pack still works. The favourable entropy of mixing outweighs the unfavourable enthalpy.

4. The four cases and the crossover temperature (HL)

Because $\Delta G = \Delta H - T\Delta S$, the way spontaneity depends on temperature is fixed entirely by the *signs* of ΔH and ΔS. There are four possible combinations.

ΔH	ΔS	$-T\Delta S$	Spontaneous when?	Example
− (exo)	+	always negative	at **all** temperatures (ΔG always < 0)	$C(s) + O_2(g) \rightarrow CO_2(g)$
+ (endo)	−	always positive	at **no** temperature (ΔG always > 0)	$3O_2(g) \rightarrow 2O_3(g)$
− (exo)	−	positive	only at **low** temperature	$N_2 + 3H_2 \rightarrow 2NH_3$
+ (endo)	+	negative	only at **high** temperature	$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

Figure. The four sign combinations of ΔH and ΔS. Where enthalpy and entropy agree the outcome is fixed (always / never); where they conflict, temperature decides via $\Delta G = \Delta H - T\Delta S$.

The first two cases are decided outright, with enthalpy and entropy agreeing. The last two are the interesting ones: enthalpy and entropy disagree, so there is a particular temperature at which the reaction switches between spontaneous and non-spontaneous.

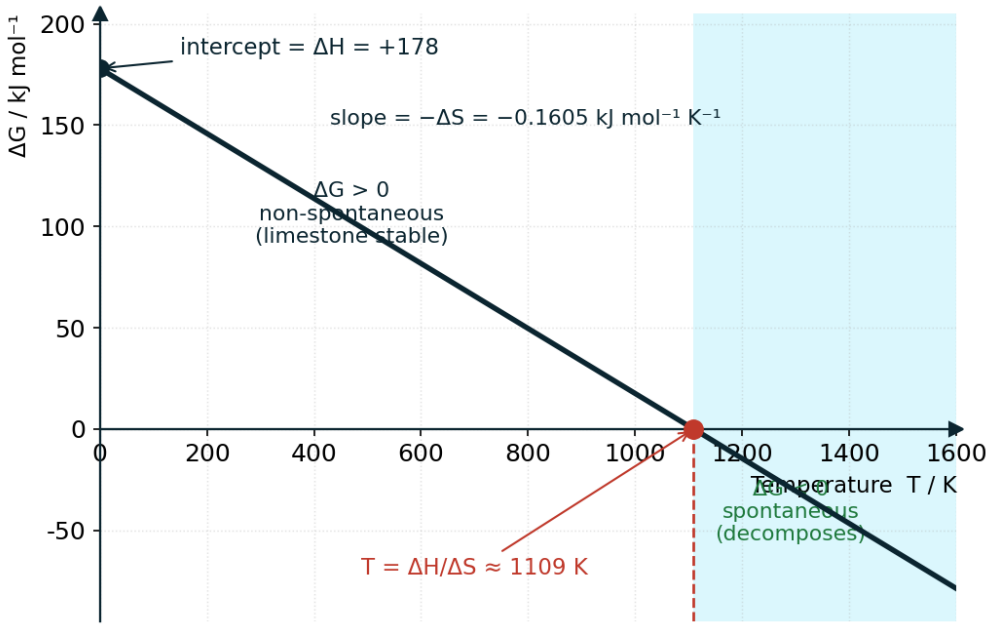

Figure. ΔG = ΔH − TΔS for $CaCO_3$ decomposition: a straight line of slope −ΔS and intercept ΔH. ΔG = 0 at the crossover T = ΔH/ΔS ≈ 1109 K; above it decomposition is spontaneous.

Finding the crossover temperature

At the switchover point $\Delta G = 0$, so setting $\Delta H - T\Delta S = 0$ gives the **crossover temperature**:

$$T = \Delta H / \Delta S$$

Use consistent units (both in J, or both in kJ). For an endothermic reaction with $\Delta S > 0$ (like limestone decomposing), the reaction becomes spontaneous *above* this temperature. For an exothermic reaction with $\Delta S < 0$ (like the Haber process), it is spontaneous only *below* it.

Worked example 6 — crossover temperature for limestone

For $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, $\Delta H° = +178$ kJ mol^{-1} and $\Delta S° = +160.5$ J K^{-1} mol^{-1}. Above what temperature does decomposition become spontaneous?

Set $\Delta G° = 0$: $T = \Delta H° / \Delta S°$

Convert $\Delta S°$ to kJ: 160.5 / 1000 = 0.1605 kJ mol^{-1} K^{-1}.

T = 178 / 0.1605 = **1109 K** (about 836 °C).

Below 1109 K, $\Delta G° > 0$ and limestone is stable; above it, $\Delta G° < 0$ and it decomposes. This is why a lime kiln must be run red-hot.

Worked example 7 — crossover temperature for the Haber process

For $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, $\Delta H° = -92.2$ kJ mol^{-1} and $\Delta S° = -198.4$ J K^{-1} mol^{-1}. Below what temperature is the forward reaction spontaneous?

$T = \Delta H° / \Delta S° = (-92.2) / (-0.1984) =$ **465 K** (about 192 °C).

Both terms are negative, so this is a 'low-temperature' case: $\Delta G° < 0$ (spontaneous) below 465 K, and $\Delta G° > 0$ (non-spontaneous) above it. Industry still runs the reaction near 450 °C for an acceptable rate, accepting a lower equilibrium yield.

5. Calculating $\Delta G°$ (HL)

There are two standard routes to $\Delta G°$. Choose whichever matches the data you are given.

Route A: from $\Delta H°$ and $\Delta S°$

Substitute directly into $\Delta G° = \Delta H° - T\Delta S°$, remembering to convert $\Delta S°$ into kJ and to use T in kelvin. Unless told otherwise, take $T = 298$ K.

Worked example 8 — $\Delta G°$ from $\Delta H°$ and $\Delta S°$

For the Haber process $\Delta H° = -92.2$ kJ mol^{-1} and $\Delta S° = -198.4$ J K^{-1} mol^{-1}. Find $\Delta G°$ at 298 K and comment.

$\Delta G° = \Delta H° - T\Delta S°$

$= -92.2 - (298 \times (-198.4/1000))$

$= -92.2 - (-59.1) = -92.2 + 59.1 =$ **-33.1 kJ mol^{-1}**

$\Delta G°$ is negative, so ammonia synthesis is spontaneous at 298 K. (It is nonetheless run hot to gain an acceptable *rate* — see section 6.)

Route B: from standard Gibbs energies of formation

Just as with enthalpy, we can tabulate the standard Gibbs energy of formation ΔG_f° of each compound (zero for elements in their standard states). Then, by Hess's law,

$$\Delta G^\circ = \Sigma\, \Delta G_f^\circ(\text{products}) - \Sigma\, \Delta G_f^\circ(\text{reactants})$$

Worked example 9 — $\Delta G°$ from ΔG_f° values

Find $\Delta G°$ for the complete combustion of methane at 298 K:

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

Data (kJ mol^{-1}): $\Delta G_f^\circ[CH_4] = -50.8$; $[CO_2] = -394.4$; $[H_2O(l)] = -237.1$; $O_2 = 0$.

$\Delta G° = [(-394.4) + 2(-237.1)] - [(-50.8) + 0]$

$= -868.6 - (-50.8) = \mathbf{-817.8\ kJ\ mol^{-1}}$

Strongly negative, confirming that methane combustion is highly spontaneous.

6. Gibbs energy, equilibrium and rate (HL)

Spontaneity is about the *position* a reaction settles into, not how fast it gets there. Two further ideas complete the picture.

Linking $\Delta G°$ to the equilibrium constant

The standard Gibbs energy change is quantitatively tied to the equilibrium constant K by

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

where $R = 8.31$ J K^{-1} mol^{-1}. The relationship tells us at a glance which side of an equilibrium is favoured:

$\Delta G°$	ln K	K	Position of equilibrium
negative	positive	$K > 1$	products favoured
zero	0	$K = 1$	neither side favoured
positive	negative	$K < 1$	reactants favoured

Worked example 10 — from $\Delta G°$ to K

For the Haber process $\Delta G° = -33.1$ kJ mol^{-1} at 298 K. Estimate K.

Rearrange: $\ln K = -\Delta G° / (RT)$. Put $\Delta G°$ in joules: -33100 J mol^{-1}.

$\ln K = -(-33100) / (8.31 \times 298) = 33100 / 2476 = 13.4$

$K = e^{13.4} \approx \mathbf{6 \times 10^5}$.

A large K: at equilibrium the mixture is rich in ammonia, consistent with the negative $\Delta G°$.

Spontaneous does not mean fast

This is the distinction examiners test most often. Gibbs energy is a **thermodynamic** quantity: a negative $\Delta G°$ tells you a reaction *can* happen and how far it will go, but says nothing about the **rate**, which is a **kinetic** question governed by activation energy (R2.2). A reaction can be strongly spontaneous yet immeasurably slow.

> **Classic illustration:** The conversion of diamond to graphite has $\Delta G^\circ \approx -2.9$ kJ mol^{-1} at room temperature, so it is spontaneous — yet diamonds do not visibly change, because the activation energy is enormous and the rate is effectively zero. 'Spontaneous' means feasible, not quick.

7. Bringing it all together

The Contact process step $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ lets us use every tool in this topic on a single reaction. Given $\Delta H^\circ = -197.8$ kJ mol^{-1}.

Worked example 11 — a full thermodynamic analysis

(i) Predict the sign of ΔS°: 3 mol of gas become 2 mol of gas, so gas moles fall and ΔS° should be **negative**.

(ii) Calculate ΔS°: $= 2(256.8) - [2(248.2) + 205.0] = 513.6 - 701.4 = \mathbf{-187.8\ J\ K^{-1}\ mol^{-1}}$. The sign confirms the prediction.

(iii) Calculate ΔG° **at 298 K**: $= -197.8 - 298(-0.1878) = -197.8 + 56.0 = \mathbf{-141.8\ kJ\ mol^{-1}}$ → spontaneous.

(iv) Crossover temperature: $T = \Delta H^\circ/\Delta S^\circ = (-197800)/(-187.8) = \mathbf{1053\ K}$. Being an exo/− case, the reaction is spontaneous *below* 1053 K.

(v) Estimate K **at 298 K**: $\ln K = 141800/(8.31 \times 298) = 57.3$, so $K = e^{57.3} \approx \mathbf{8 \times 10^{24}}$ — essentially complete. In practice the plant runs near 450 °C (723 K), still well below the crossover, sacrificing a little yield to gain a workable rate.

8. Common pitfalls

- **Unit mismatch:** subtracting ΔS in J directly from ΔH in kJ. Always convert ΔS to kJ (divide by 1000) first.
- **Temperature in °C:** the T in $\Delta G = \Delta H - T\Delta S$ must be in kelvin. Add 273 to any Celsius value.
- **Confusing feasibility with speed:** $\Delta G < 0$ means the reaction is possible, not that it is observably occurring.
- **Sign slips:** a double negative in the $-T\Delta S$ term (when ΔS is negative) becomes a plus — track it carefully.
- **Forgetting states:** the sign of ΔS hinges on gas moles, so you must include state symbols before judging it.
- **Treating** ΔH° **and** ΔS° **as temperature-independent** is an approximation the IB accepts, but ΔG° itself varies strongly with T.

9. Quick reference

Idea	Statement
Entropy	S = dispersal of energy and matter; units J K^{-1} mol^{-1}; $S(g) > S(l) > S(s)$
Sign of ΔS	positive if gas moles increase, a solid dissolves, or the particle count rises
Entropy change	$\Delta S^\circ = \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants})$
Gibbs energy	$\Delta G = \Delta H - T\Delta S$ (ΔH in kJ, ΔS in kJ, T in K)
Spontaneity test	$\Delta G < 0$ spontaneous; $= 0$ equilibrium; > 0 non-spontaneous
Crossover T	$T = \Delta H / \Delta S$ (the temperature where $\Delta G = 0$)
Gibbs from formation	$\Delta G^\circ = \Sigma \Delta G_f^\circ(\text{products}) - \Sigma \Delta G_f^\circ(\text{reactants})$
Gibbs and K	$\Delta G^\circ = -RT \ln K$; $\Delta G^\circ < 0 \rightarrow K > 1$

10. Test yourself

Attempt these before checking the fully worked answers below. Assume T = 298 K and use the entropy data of section 2 where needed.

1. Predict the sign of ΔS for: (a) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$; (b) $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$; (c) $H_2O(l) \rightarrow H_2O(s)$.

2. Calculate ΔS° for $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ and comment on its sign.

3. A reaction has ΔH° = +178 kJ mol^{-1} and ΔS° = +160.5 J K^{-1} mol^{-1}. Find ΔG° at (a) 298 K and (b) 1500 K, and state whether each is spontaneous.

4. For an exothermic reaction with $\Delta H^\circ = -92.2$ kJ mol^{-1} and $\Delta S^\circ = -198.4$ J K^{-1} mol^{-1}, find the temperature above which it becomes non-spontaneous.

5. Using $\Delta G_f^\circ[N_2O_4(g)]$ = +97.9 and $[NO_2(g)]$ = +51.3 kJ mol^{-1}, find ΔG° for $N_2O_4(g) \rightarrow 2NO_2(g)$. Is it spontaneous at 298 K?

6. For the reaction in Q5, calculate K at 298 K using $\Delta G^\circ = -RT \ln K$.

7. Explain why the decomposition of limestone is not carried out at room temperature even though it produces useful quicklime.

8. A student claims that because diamond → graphite has a negative ΔG°, a diamond ring will turn grey within a year. Comment on the chemistry of this claim.

Worked answers

1. (a) **Negative** — gas moles fall from 3 to 2. (b) **Positive** — an ordered ionic lattice disperses into mobile hydrated ions. (c) **Negative** — a liquid becomes a more ordered solid.

2. $\Delta S^\circ = 2(69.9) - [2(130.6) + 205.0] = 139.8 - 466.2 =$ **-326.4 J K^{-1} mol^{-1}**. Strongly negative, because 3 mol of gas condense into 2 mol of liquid.

3. Convert $\Delta S^\circ = 0.1605$ kJ mol^{-1} K^{-1}. (a) $\Delta G^\circ = 178 - 298(0.1605) = 178 - 47.8 =$ **+130.2 kJ mol^{-1}**, non-spontaneous. (b) $\Delta G^\circ = 178 - 1500(0.1605) = 178 - 240.8 =$ **-62.8 kJ mol^{-1}**, spontaneous. The reaction turns spontaneous only at high temperature.

4. At the crossover $\Delta G^\circ = 0$, so $T = \Delta H^\circ / \Delta S^\circ = (-92.2) / (-0.1984) =$ **465 K** (192 °C). Since both terms are negative the reaction is spontaneous *below* 465 K and non-spontaneous above it.

5. $\Delta G^\circ = 2(+51.3) - (+97.9) = 102.6 - 97.9 =$ **+4.7 kJ mol^{-1}**. Positive, so the forward reaction is **not** spontaneous under standard conditions at 298 K (though it lies close to equilibrium).

6. $\ln K = -\Delta G^\circ/(RT) = -4700 / (8.31 \times 298) = -4700 / 2476 = -1.90$. So $K = e^{-1.90} =$ **0.15**. As $\Delta G^\circ > 0$, $K < 1$ and reactants (N_2O_4) are favoured, consistent with Q5.

7. Decomposition is endothermic with $\Delta S^\circ > 0$, so ΔG° is positive (non-spontaneous) at room temperature and only becomes negative above about 1100 K (worked example 6). The kiln must be heated strongly to drive the reaction.

8. The claim confuses thermodynamics with kinetics. A negative ΔG° means the change is *feasible*, not that it is *fast*. The activation energy for rearranging the diamond lattice is enormous, so the rate at room temperature is effectively zero and the ring is safe. 'Spontaneous' does not mean observable within any human timescale.