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IB DIPLOMA CHEMISTRY · FIRST ASSESSMENT 2025

Reactivity 1.4 Entropy and Spontaneity

Booklet 5 · Higher Level · Understandings 1.4.1 – 1.4.4

Entropy and the second law, entropy changes of the system and the surroundings, Gibbs energy, the temperature at which a reaction becomes spontaneous, and the link between $\Delta G^{\ominus}$ and the equilibrium constant

Complete revision notes, 13 worked examples, model answers & 32 practice questions · Higher Level

How the level tags work in this booklet

HL Reactivity 1.4 is entirely **additional higher level** material. Standard level students do not need this booklet.

★ marks harder, multi-step questions. The booklet uses ΔH_f calculations from **Booklet 3** throughout, and its final section leads directly into Reactivity 2.3 (equilibrium).

Inside this booklet

1. What the syllabus actually asks of you
2. 1.4.1 — Entropy and the second law
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1 What the syllabus actually asks of you

Reactivity 1.1 left a puzzle unsolved. Most spontaneous reactions are exothermic, yet some strongly endothermic changes, such as ammonium nitrate dissolving in water, also happen by themselves. Enthalpy alone cannot decide the direction of change. This topic supplies the missing quantity, **entropy**, and combines it with enthalpy in a single function, the **Gibbs energy**, whose sign tells you whether a reaction is spontaneous at a given temperature and whose value tells you where the equilibrium lies. The topic is highly quantitative: expect calculations of ΔS, ΔG, a crossover temperature and K in every HL Paper 1 and Paper 2.

Understanding	What it says	What you must be able to do	Level
1.4.1 Entropy	Entropy, S, is a measure of the dispersal or distribution of matter and/or energy in a system. The more ways the energy can be distributed, the higher the entropy. Under the same conditions, the entropy of a gas is greater than that of a liquid, which in turn is greater than that of a solid.	Predict whether a physical or chemical change will result in an increase or decrease in entropy of a system. Calculate standard entropy changes, $\Delta S^{\ominus}$, from standard entropy values, $S^{\ominus}$. Standard entropy values are given in the data booklet.	HL
1.4.2 Gibbs energy	Change in Gibbs energy, ΔG, relates the energy that can be obtained from a chemical reaction to the change in enthalpy, ΔH, change in entropy, ΔS, and absolute temperature, T.	Apply the equation $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ to calculate unknown values of these terms. Note the units: ΔH in kJ mol^{-1}; ΔS in J K^{-1} mol^{-1}; ΔG in kJ mol^{-1}.	HL
1.4.3 Spontaneity	At constant pressure, a change is spontaneous if the change in Gibbs energy, ΔG, is negative.	Interpret the sign of ΔG calculated from thermodynamic data. Determine the temperature at which a reaction becomes spontaneous.	HL
1.4.4 Equilibrium	As a reaction approaches equilibrium, ΔG becomes less negative and finally reaches zero.	Perform calculations using the equation $\Delta G = \Delta G^{\ominus} + RT \ln Q$ and its application to a system at equilibrium, $\Delta G^{\ominus} = -RT \ln K$. The equations are given in the data booklet.	HL

Linking questions and connections for 1.4.1 – 1.4.4

- **Structure 1.1:** why is the entropy of a perfect crystal at 0 K predicted to be zero? → section 2.3
- **Reactivity 1.1 and 1.2:** ΔH and ΔH_f calculations are the first half of every ΔG calculation (Booklets 1 and 3).
- **Reactivity 1.3:** $-\Delta G$ is the maximum useful work, which is why fuel cells can beat heat engines. → section 5.3
- **Reactivity 2.2:** a negative ΔG says nothing about rate; some spontaneous reactions need heating to overcome E_a. → section 6.4
- **Reactivity 2.3:** what is the likely composition of an equilibrium mixture when $\Delta G^{\ominus}$ is positive? → section 7
- **Reactivity 3.2:** how can electrochemical data be used to predict spontaneity? ($\Delta G^{\ominus} = -nFE^{\ominus}$, later in the course.)

What the data booklet gives you — and what it does not

The data booklet gives $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$, $\Delta G = \Delta G^\ominus + RT \ln Q$, $\Delta G^\ominus = -RT \ln K$, the gas constant $R = 8.31\ J\ K^{-1}\ mol^{-1}$, and tables of $S^\ominus$, $\Delta H_f^\ominus$ and $\Delta G_f^\ominus$ values. It does not give $\Delta S = \Sigma S(\text{products}) - \Sigma S(\text{reactants})$, $\Delta S_{\text{surroundings}} = -\Delta H/T$, the expression $T = \Delta H/\Delta S$, or the warning about mixing J and kJ. The values used in this booklet are typical literature values; always use those given in a question.

Data used in this booklet (298 K)

Substance	$S^\ominus$ / J K^{-1} mol^{-1}	$\Delta H_f^\ominus$ / kJ mol^{-1}	Substance	$S^\ominus$ / J K^{-1} mol^{-1}	$\Delta H_f^\ominus$ / kJ mol^{-1}
$H_2(g)$	131	0	$CO(g)$	198	−111
$O_2(g)$	205	0	$CO_2(g)$	214	−394
$N_2(g)$	192	0	$CH_4(g)$	186	−75
C(graphite)	5.7	0	$NH_3(g)$	193	−46
$H_2O(l)$	70.0	−286	$C_2H_5OH(l)$	161	−278
$H_2O(g)$	189	−242	$C_2H_5OH(g)$	283	−235
$MgCO_3(s)$	65.7	−1096	$CaCO_3(s)$	92.9	−1207
MgO(s)	26.9	−602	CaO(s)	39.7	−635

2 Reactivity 1.4.1 — Entropy and the second law HL

2.1 Spontaneous change and dispersal

A hot cup of coffee cools; it never heats itself up by drawing heat from the cooler room. A bottle of fizzy drink left open goes flat; the carbon dioxide never returns. Perfume spreads through a room. Each of these is a **spontaneous change**: one that happens naturally, without work being done on the system. The reverse changes are possible, but only at the expense of work: a refrigerator can cool food, and electrolysis can split sodium chloride into sodium and chlorine.

Definitions to learn

A **spontaneous change** is one that occurs without the need for work to be done on the system (beyond supplying any activation energy needed to start it).

Entropy, S, is a measure of the dispersal or distribution of matter and/or energy in a system. The more ways the particles and their energy can be arranged, the higher the entropy.

The second law of thermodynamics: in a spontaneous change, the total entropy of the universe (system + surroundings) increases.

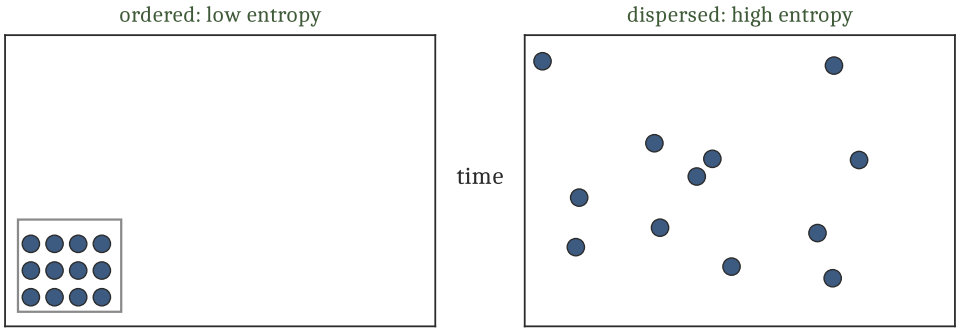


Figure 1 — Gas particles released in a corner spread throughout the container. The dispersed arrangement can be achieved in vastly more ways, so it has higher entropy and is overwhelmingly more probable.

The second law is statistical. Nothing forbids the gas particles in Figure 1 from gathering back in the corner; it is just so unlikely, given the enormous number of particles, that it is never observed. A purple crystal of potassium manganate(VII) placed in water slowly spreads its colour through the whole dish for the same reason: the aqueous ions are far more dispersed than the solid. Ordered states can arise locally, as in a growing plant, a living cell or a building, but only at the expense of a greater increase in entropy elsewhere in the universe.

2.2 What affects the entropy of a substance

Factor	Effect on S	Example
Physical state	S(gas) ≫ S(liquid) > S(solid). Gas particles move freely through the whole volume; solid particles only vibrate about fixed positions.	H_2O: ice 48, liquid 70.0, steam 189 J K^{-1} mol^{-1}
Temperature	S increases with T: the particles have more energy and more ways to distribute it.	every $S^{\ominus}$ value is positive above 0 K
Amount	S doubles when the amount doubles (S is quoted per mole).	2 mol O_2: 2 × 205 = 410 J K^{-1}
Complexity	larger, more complex particles have more ways to vibrate and rotate, so higher S.	CH_4 186 < C_2H_6 230; graphite 5.7 (rigid lattice)
Mixing / dissolving	mixing different particles, or a solid dissolving into aqueous ions, usually increases S.	$KMnO_4(s) \rightarrow K^+(aq) + MnO_4^-(aq)$

2.3 Absolute entropy and the third law

Unlike enthalpy, entropy has an absolute zero point. A **perfectly ordered crystal at 0 K** has only one possible arrangement of its particles and no thermal energy to distribute, so its entropy is zero (the third law of thermodynamics). Every real substance at any higher temperature therefore has a **positive** standard entropy, $S^{\ominus}$, measured at 100 kPa and usually 298 K. This is why tabulated $S^{\ominus}$ values are never zero, even for elements, unlike $\Delta H_f^{\ominus}$.

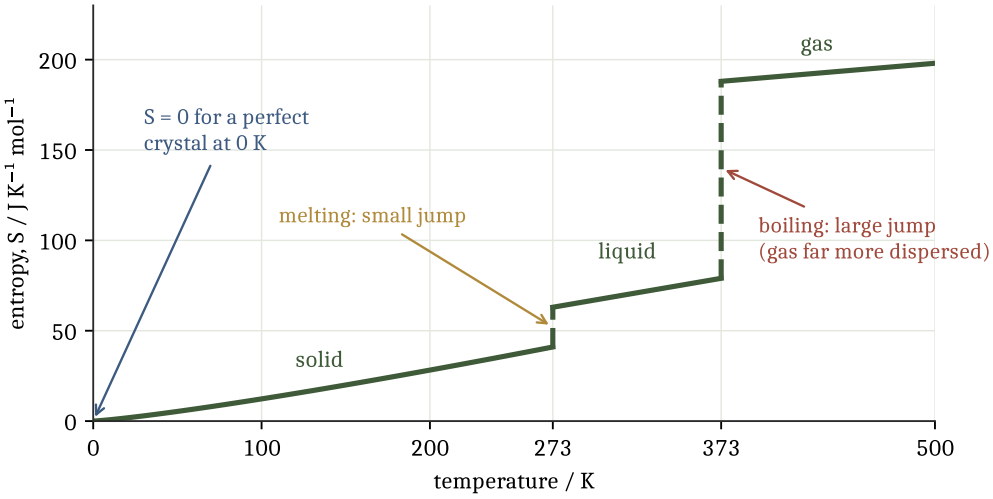


Figure 2 — Entropy of water from 0 K. S rises gradually within each state, with a jump at each change of state. The jump on boiling is far larger than on melting, because the gas is so much more dispersed than the liquid.

Examiner traps in entropy definitions

- Writing "entropy is disorder" alone. Use the syllabus wording: **dispersal or distribution of matter and/or energy**.
- Giving an element an $S^{\ominus}$ value of zero, as for ΔH_f. Only a perfect crystal at 0 K has S = 0.
- Stating the second law as "entropy always increases". It is the **total** entropy of the **universe** that increases; the entropy of a system can fall.

3 Reactivity 1.4.1 — Predicting and calculating ΔS HL

3.1 Predicting the sign of ΔS

Method — look at the gases first

1. Count the **moles of gas** on each side. More gas in the products → ΔS positive; fewer → ΔS negative. This is usually the decisive factor.
2. If the moles of gas are equal, look at changes of state (s → l → aq → g increase S) and the total number of particles.
3. If nothing changes much, say ΔS ≈ 0 (it cannot be predicted reliably).

Worked example 1 — predicting the sign of ΔS

Change	Reasoning	ΔS
$H_2O(s) \rightarrow H_2O(l)$	solid becomes liquid: more freedom of movement	+
$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$	0 mol gas → 1 mol gas	+
$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$	3 mol gas → 2 mol gas	−
$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$	two mobile aqueous ions become one ordered solid	−
$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$	ordered lattice disperses into aqueous ions	+
$H_2(g) + I_2(g) \rightarrow 2HI(g)$	2 mol gas → 2 mol gas; no change of state	≈ 0

3.2 Calculating $\Delta S^\ominus$

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

multiply each $S^\ominus$ by its coefficient · elements are **not** zero · units J K^{-1} mol^{-1}

The method is the same as for ΔH from ΔH_f (Booklet 3), with two differences: elements have non-zero entropies, and the units are J, not kJ. Always predict the sign first, then check your answer against it.

Worked example 2 — the Haber process

Q. Calculate $\Delta S^\ominus$ for $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$.

Prediction: 4 mol gas → 2 mol gas, so ΔS should be negative.

$\Delta S^\ominus = 2(193) - [192 + 3(131)] = 386 - 585 =$ **-199 J K^{-1} mol^{-1}** ✓ negative, as predicted

Worked example 3 — combustion of ethanol

Q. Calculate $\Delta S^\ominus$ for $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$.

Prediction: 3 mol gas → 2 mol gas, so ΔS negative.

$\Delta S^\ominus = [2(214) + 3(70.0)] - [161 + 3(205)] = 638 - 776 =$ **-138 J K^{-1} mol^{-1}**

The O_2 term (3 × 205) is large: forgetting it because oxygen is an element is the commonest error in these calculations.

Model answer: "Predict and explain the sign of the entropy change for the thermal decomposition of calcium carbonate." (2 marks)

ΔS is positive **[1]**. One mole of solid produces one mole of solid and one mole of gas; gas particles are far more dispersed, so there are more ways of distributing the matter and energy **[1]**.

Examiner traps in ΔS calculations

- Setting $S^{\ominus}$ of elements (O_2, H_2, N_2, C) to zero.
- Forgetting to multiply by the coefficients.
- Explaining a sign by "more moles": the key is **moles of gas**.
- Giving ΔS in kJ: keep it in J K^{-1} mol^{-1} as the syllabus states, and convert only when you put it into ΔG = ΔH − TΔS.

4 Reactivity 1.4.2 — Entropy of the surroundings HL

4.1 Why ΔS of the system is not enough

The combustion of ethanol has a negative ΔS for the system (worked example 3), yet it is obviously spontaneous. Freezing water has a negative ΔS, yet water freezes below 0 °C. The missing piece is the surroundings. When a reaction is **exothermic**, the heat released disperses into the surroundings, increasing their entropy. When it is **endothermic**, heat is taken from the surroundings and their entropy falls.

$$\Delta S_{surroundings} = -\Delta H_{system} / T$$

ΔH in J mol^{-1} (multiply kJ by 1000) · T in kelvin

- The **minus sign**: an exothermic reaction (ΔH negative) increases the entropy of the surroundings.
- The **T in the denominator**: the same amount of heat makes a much bigger difference to cold surroundings than to hot ones, just as a sneeze is much more disruptive in a quiet library than in a busy street.

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} > 0 \text{ for a spontaneous change}$$

Worked example 4 — total entropy change for burning methane

Q. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$, $\Delta H^{\ominus} = -891$ kJ mol^{-1}. Show that the reaction is spontaneous at 298 K.

$\Delta S_{system} = [214 + 2(70.0)] - [186 + 2(205)] = 354 - 596 = -242$ J K^{-1} mol^{-1}

$\Delta S_{surroundings} = -(-891\,000)/298 = +2990$ J K^{-1} mol^{-1}

$\Delta S_{total} = -242 + 2990 =$ **+2748 J K^{-1} mol^{-1}** → positive, so spontaneous

The decrease in entropy of the system is overwhelmed by the huge increase in entropy of the surroundings. This is why exothermic reactions are so much more common than endothermic ones.

Worked example 5 — how an endothermic change can be spontaneous

Q. For $NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$, $\Delta H^{\ominus} = +25.7$ kJ mol^{-1} and $\Delta S^{\ominus} = +108.7$ J K^{-1} mol^{-1}. Explain why ammonium nitrate dissolves spontaneously at 298 K.

$\Delta S_{surroundings} = -25\,700/298 = -86.2$ J K^{-1} mol^{-1}

$\Delta S_{total} = +108.7 + (-86.2) =$ **+22.5 J K^{-1} mol^{-1}** → spontaneous

The surroundings lose entropy as heat flows into the system (the beaker feels cold), but the dispersal of the ordered lattice into aqueous ions increases the entropy of the system by more. The same idea explains the strongly endothermic reaction of solid barium hydroxide with ammonium thiocyanate: three moles of solid become ten moles of liquid water, three moles of aqueous compounds and some ammonia.

5 Reactivity 1.4.2 — Gibbs energy HL

5.1 From total entropy to ΔG

Calculating the entropy of the surroundings every time is clumsy. Start from the second law and substitute for $\Delta S_{surroundings}$:

$$\Delta S_{total} = \Delta S_{system} - \Delta H_{system}/T > 0$$

multiply by −T (T is positive, so the inequality reverses): $-T\Delta S_{total} = \Delta H_{system} - T\Delta S_{system} < 0$

The combination ΔH − TΔS of the **system** is called the change in **Gibbs energy**, ΔG, after Josiah Willard Gibbs (1839–1903). Because $\Delta G = -T\Delta S_{total}$, a negative ΔG is simply a re-statement of the second law: it means the total entropy of the universe increases.

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

ΔG and ΔH in kJ mol^{-1} · ΔS in J K^{-1} mol^{-1}, so divide by 1000 · T in K · **ΔG negative ⇒ spontaneous**

5.2 Two ways to calculate ΔG⊖

Method	Formula	Use it when
from $\Delta G_f^\ominus$	$\Delta G^\ominus = \Sigma\Delta G_f^\ominus(\text{products}) - \Sigma\Delta G_f^\ominus(\text{reactants})$	ΔG_f data are given; only valid at **298 K**. $\Delta G_f^\ominus$ of an element in its standard state is zero, just as for ΔH_f.
from ΔH and ΔS	$\Delta G = \Delta H^\ominus - T\Delta S^\ominus$	at **any temperature**, assuming ΔH and ΔS do not change significantly with temperature

Worked example 6 — ΔG⊖ from Gibbs energies of formation

Q. Calculate ΔG⊖ for $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$. $\Delta G_f^\ominus$ / kJ mol^{-1}: $CH_4(g)$ −50.5, $CO_2(g)$ −394.4, $H_2O(l)$ −237.1.

$\Delta G^\ominus = [-394.4 + 2(-237.1)] - [-50.5 + 2(0)] = -868.6 + 50.5 =$ **−818.1 kJ mol^{-1}**

Check with ΔG = ΔH − TΔS, using worked example 4: −891 − 298(−0.242) = −891 + 72.1 = −818.9 kJ mol^{-1}. The two methods agree to within rounding.

Worked example 7 — ΔG from ΔH and ΔS, and the crossover temperature

Q. Magnesium carbonate decomposes: $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$. Use the data table on page 3 to calculate (a) ΔH⊖, (b) ΔS⊖, (c) ΔG⊖ at 298 K, and (d) the minimum temperature for spontaneous decomposition.

(a) $\Delta H^\ominus = (-602 - 394) - (-1096) =$ **+100 kJ mol^{-1}**

(b) $\Delta S^\ominus = (26.9 + 214) - 65.7 =$ **+175.2 J K^{-1} mol^{-1}** = +0.1752 kJ K^{-1} mol^{-1}

(c) $\Delta G^\ominus = 100 - 298 \times 0.1752 = 100 - 52.2 =$ **+47.8 kJ mol^{-1}** → not spontaneous at 298 K

(d) At the crossover, $\Delta G = 0$: $T = \Delta H/\Delta S = 100 / 0.1752 =$ **571 K** (298 °C); spontaneous above this

The answer is an estimate: it assumes ΔH and ΔS stay constant as the temperature rises, and it gives the temperature at which CO_2 would be released at a standard pressure of 100 kPa.

The units trap — the most common error in this topic

ΔH is in **kJ** mol^{-1} but ΔS is in **J** K^{-1} mol^{-1}. Before using $\Delta G = \Delta H - T\Delta S$, **divide ΔS by 1000** (or multiply ΔH by 1000). Using +175.2 instead of +0.1752 in worked example 7 gives $\Delta G = 100 - 52\,210 = -52\,110$ kJ mol^{-1}: absurdly large and with the wrong sign. Temperatures must be in **kelvin**.

5.3 ΔG as the energy available to do useful work

ΔH measures the *quantity* of heat released; ΔG measures its *quality*. When a reaction has a negative ΔS_{system}, some of the energy released must be transferred to the surroundings as heat to make the total entropy increase. Only the remainder, −ΔG, is free to do useful work (hence the older name, Gibbs *free* energy).

Worked example 8 — the maximum work from a hydrogen fuel cell

Q. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$, $\Delta H^\ominus = -286$ kJ mol^{-1}. Calculate the maximum electrical energy a fuel cell could deliver per mole of hydrogen at 298 K, and the maximum efficiency.

$\Delta S^\ominus = 70.0 - [131 + \frac{1}{2}(205)] = -163.5$ J K^{-1} mol^{-1}

heat that must go to the surroundings = $-T\Delta S = 298 \times 0.1635 = 48.7$ kJ

$\Delta G^\ominus = -286 + 48.7 =$ **−237.3 kJ mol^{-1}** → up to 237 kJ of electrical energy

maximum efficiency = 237.3/286 × 100 = **83 %**

A heat engine burning the same hydrogen is limited much further by the temperatures it works between. This is why fuel cells (Reactivity 1.3) can be so efficient. In Reactivity 3.2 you will see that ΔG is directly linked to the cell potential.

6 Reactivity 1.4.3 — ΔG and spontaneity HL

6.1 The four combinations of ΔH and ΔS

Because $\Delta G = \Delta H - T\Delta S$, temperature acts like a "tap" that controls how important the entropy term is. At low T, $\Delta G \approx \Delta H$; at high T, the $-T\Delta S$ term dominates.

ΔH	ΔS	ΔG at low T	ΔG at high T	Spontaneous?	Example
−	+	negative	negative	**at all temperatures**	$H_2 + Cl_2 \rightarrow 2HCl$
+	−	positive	positive	**never**	$3O_2 \rightarrow 2O_3$
−	−	negative (≈ ΔH)	positive (≈ −TΔS)	**below** T = ΔH/ΔS	Haber process; freezing
+	+	positive (≈ ΔH)	negative (≈ −TΔS)	**above** T = ΔH/ΔS	$CaCO_3$ decomposition; melting

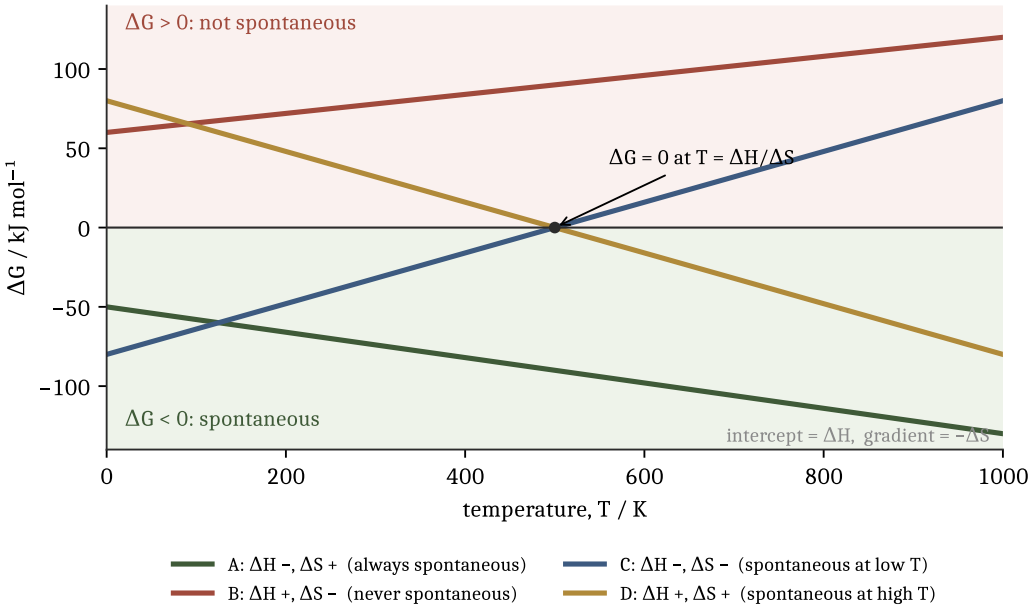


Figure 3 — ΔG against T is a straight line with intercept ΔH and gradient −ΔS. Lines C and D cross zero at T = ΔH/ΔS: the temperature at which the reaction switches direction.

Don't memorise the table — derive it

Ask two questions: **(1)** Is ΔH − TΔS negative when T is small (sign of ΔH)? **(2)** Is it negative when T is large (sign of −ΔS)? If the answers differ, the crossover temperature is T = ΔH/ΔS, with ΔS in kJ K^{-1} mol^{-1}.

6.2 Changes of state

At the normal melting or boiling point, the two phases are in equilibrium and ΔG = 0, so T = ΔH/ΔS. Below the boiling point, ΔG for boiling is positive; above it, negative.

Worked example 9 — predicting a boiling point

Q. Use the data table on page 3 to estimate the boiling point of ethanol, $C_2H_5OH(l) \rightarrow C_2H_5OH(g)$.

ΔH = −235 − (−278) = +43 kJ mol^{-1} (more precisely +42.6) · ΔS = 283 − 161 = +122 J K^{-1} mol^{-1}

T = ΔH/ΔS = 42.6 / 0.122 = **349 K (76 °C)**; the measured value is 78 °C

The small difference arises because ΔH and ΔS were measured at 298 K, not at the boiling point. The same method gives 370 K for water (actual 373 K).

6.3 A reaction that reverses with temperature

Worked example 10 — the Haber process ★

Q. For $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, $\Delta H^\ominus = -92$ kJ mol^{-1} and $\Delta S^\ominus = -199$ J K^{-1} mol^{-1}. (a) Calculate ΔG at 298 K and 700 K. (b) Find the temperature above which ammonia formation is not spontaneous. (c) Comment on the industrial operating temperature of about 700 K.

(a) 298 K: $\Delta G = -92 - 298(-0.199) = -92 + 59.3 =$ **−32.7 kJ mol^{-1}** (spontaneous)

700 K: $\Delta G = -92 + 700(0.199) =$ **+47.3 kJ mol^{-1}** (not spontaneous under standard conditions)

(b) $T = \Delta H/\Delta S = -92 / -0.199 =$ **462 K**

(c) Thermodynamics favours low temperatures, but the rate at 298 K is negligible (high E_a, a very strong N≡N bond). Industry accepts an unfavourable $\Delta G^\ominus$ at 700 K, uses high pressure to push the equilibrium towards ammonia, and recycles the unreacted gases. This compromise between thermodynamics and kinetics is studied in Reactivity 2.3.

6.4 Spontaneous does not mean fast

A negative ΔG means a reaction is **thermodynamically feasible**; it says nothing about how fast it goes. $H_2 + Cl_2 \rightarrow 2HCl$ has $\Delta G^\ominus = -191$ kJ mol^{-1} but does not happen in the dark at room temperature; diamond turning into graphite is spontaneous but immeasurably slow. Such reactions are **kinetically** stable because of a high activation energy (Reactivity 2.2). Some spontaneous reactions therefore need heating or a catalyst to start.

Model answer: "For a reaction, ΔH is positive and ΔS is positive. Explain how the spontaneity of the reaction depends on temperature." (3 marks)

ΔG = ΔH − TΔS **[1]**. At low temperature the TΔS term is small, so ΔG ≈ ΔH, which is positive: not spontaneous **[1]**. At high temperature TΔS becomes larger than ΔH, so ΔG is negative and the reaction is spontaneous above T = ΔH/ΔS **[1]**.

Examiner traps in spontaneity questions

- Using °C in ΔG = ΔH − TΔS. Always kelvin.
- Quoting the crossover temperature without saying whether the reaction is spontaneous **above** or **below** it.
- Saying a reaction with negative ΔG "will happen quickly" or "will happen at room temperature".
- Using ΔG_f data to find ΔG at a temperature other than 298 K.

7 Reactivity 1.4.4 — ΔG and equilibrium HL

7.1 Why reactions stop at equilibrium

So far we have treated reactions as going completely from reactants to products. In reality, a mixture of reactants and products has a higher entropy than either on its own (mixing increases entropy), so the Gibbs energy of the **mixture** is lower than that of pure reactants or pure products. As the reaction proceeds, G falls until it reaches a **minimum**. That minimum is the **equilibrium** position: any further change in either direction would raise G, and so would decrease the total entropy of the universe.

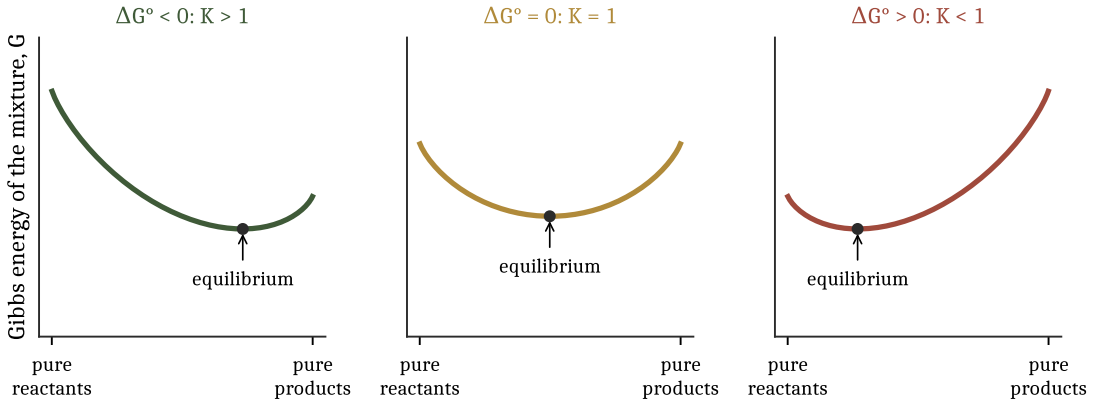


Figure 4 — The Gibbs energy of a reaction mixture against its composition. The equilibrium mixture is at the minimum. When $\Delta G^{\ominus}$ is negative, the products have lower standard Gibbs energy and the minimum lies towards the products (K > 1); when $\Delta G^{\ominus}$ is positive, it lies towards the reactants (K < 1).

Key ideas

- At **equilibrium**: G is at a **minimum**, the total entropy of the universe is at a **maximum**, and **$\Delta G = 0$**.
- $\Delta G^{\ominus}$ (standard conditions, all concentrations 1 mol dm^{-3}) is a fixed value at a given temperature; ΔG depends on the actual composition of the mixture.
- As a reaction approaches equilibrium, ΔG becomes **less negative** and finally reaches **zero**.

7.2 The reaction quotient, Q

The composition of a mixture is described by the **reaction quotient**, Q, which has the same form as the equilibrium constant expression but uses the concentrations at any moment (Reactivity 2.3). For aA + bB ⇌ cC + dD:

$$Q = [C]^c[D]^d / [A]^a[B]^b \qquad \text{at equilibrium, } Q = K$$

$$\Delta G = \Delta G^{\ominus} + RT \ln Q$$

R = 8.31 J K^{-1} mol^{-1} · $\Delta G^{\ominus}$ must be in J mol^{-1} · ln is the natural logarithm

Comparison	Sign of ΔG	What happens
Q < K	negative	forward reaction is spontaneous: more products form
Q = K	zero	at equilibrium: no net change
Q > K	positive	reverse reaction is spontaneous: more reactants form

7.3 $\Delta G^{\ominus}$ and the equilibrium constant

At equilibrium ΔG = 0 and Q = K. Substituting into $\Delta G = \Delta G^{\ominus} + RT \ln Q$:

$$\Delta G^{\ominus} = -RT \ln K \quad \text{or} \quad K = e^{-\Delta G^{\ominus}/RT}$$

$\Delta G^{\ominus}$ in J mol^{-1} · T in K

$\Delta G^{\ominus}$	K	Equilibrium mixture (at 298 K)
more negative than about −30 kJ mol^{-1}	$K \gg 1$	reaction essentially goes to completion
negative	$K > 1$	mainly products
zero	$K = 1$	appreciable amounts of both
positive	$K < 1$	mainly reactants
more positive than about +30 kJ mol^{-1}	$K \ll 1$	essentially no reaction

Because K depends exponentially on $\Delta G^{\ominus}$, a change of only 5.7 kJ mol^{-1} changes K by a factor of 10 at 298 K. At ±30 kJ mol^{-1}, $K \approx 2 \times 10^{5}$ or 5×10^{-6}.

Worked example 11 — K from $\Delta G^{\ominus}$

Q. Calculate K for the Haber process at 298 K, using $\Delta G^{\ominus} = -32.7$ kJ mol^{-1} from worked example 10.

$\ln K = -\Delta G^{\ominus}/RT = 32\,700 / (8.31 \times 298) = 13.20$

$K = e^{13.20} =$ **5.4×10^{5}** → equilibrium lies far to the right at 298 K

Worked example 12 — $\Delta G^{\ominus}$ from K

Q. For $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, K = 54 at 700 K. Calculate $\Delta G^{\ominus}$ at this temperature.

$\Delta G^{\ominus} = -RT \ln K = -8.31 \times 700 \times \ln 54 = -8.31 \times 700 \times 3.99 = -23\,200$ J mol^{-1} = **−23.2 kJ mol^{-1}**

Worked example 13 — predicting the direction of change with Q ★

Q. For $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ at 298 K, $\Delta G^{\ominus} = +4.70$ kJ mol^{-1}. (a) Calculate K. (b) A mixture has Q = 0.010. Calculate ΔG and deduce the direction of change.

(a) $\ln K = -4700 / (8.31 \times 298) = -1.898 \rightarrow K = \mathbf{0.150}$ ($K < 1$, as expected for positive $\Delta G^{\ominus}$)

(b) $\Delta G = 4700 + 8.31 \times 298 \times \ln 0.010 = 4700 + 2476 \times (-4.605) = 4700 - 11\,400 = \mathbf{-6.70\ kJ\ mol^{-1}}$

ΔG is negative ($Q < K$), so the forward reaction is spontaneous: N_2O_4 dissociates until $Q = 0.150$.

A positive $\Delta G^{\ominus}$ does not mean "no reaction": starting from pure N_2O_4 ($Q = 0$), some NO_2 always forms.

Model answer: "Explain why a reaction with a positive value of $\Delta G^{\ominus}$ still produces some products." (2 marks)

When only reactants are present $Q = 0$, so the $RT \ln Q$ term is very large and negative and $\Delta G = \Delta G^{\ominus} + RT \ln Q$ is negative: the forward reaction is spontaneous **[1]**. Reaction continues until $\Delta G = 0$ at equilibrium, where $K < 1$, so the mixture contains mainly reactants but some products (mixing lowers the Gibbs energy) **[1]**.

Examiner traps in ΔG and equilibrium

- Using $\Delta G^{\ominus}$ in kJ with R in J: convert $\Delta G^{\ominus}$ to J mol^{-1} first.
- Using $\log_{10}$ instead of ln, or forgetting the minus sign in $\Delta G^{\ominus} = -RT \ln K$.
- Confusing ΔG (depends on composition, zero at equilibrium) with $\Delta G^{\ominus}$ (a constant that fixes K).
- Saying "$\Delta G^{\ominus} = 0$ at equilibrium". It is ΔG that is zero; $\Delta G^{\ominus} = 0$ only when $K = 1$.

8 Key points to memorise

Everything below is either wording that examiners look for or knowledge you must carry into the exam yourself.

A Definitions and laws

- **Entropy:** a measure of the dispersal or distribution of matter and/or energy in a system. S(g) ≫ S(l) > S(s).
- **Second law:** in a spontaneous change, the total entropy of the universe increases. **Third law:** a perfect crystal at 0 K has zero entropy.
- **Spontaneous change:** occurs without work being done on the system; at constant pressure, $\Delta G < 0$.
- At **equilibrium**: $\Delta G = 0$, G is at a minimum and the total entropy is at a maximum.

B Equations (with units)

- $\Delta S^\ominus = \Sigma S^\ominus(\text{products}) - \Sigma S^\ominus(\text{reactants})$ — J K^{-1} mol^{-1}; elements are not zero.
- $\Delta S_{surr} = -\Delta H/T$ (ΔH in J) · $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} > 0$ for spontaneous change.
- $\Delta G = \Delta H - T\Delta S$ (divide ΔS by 1000; T in K) · $\Delta G^\ominus = \Sigma \Delta G_f^\ominus(\text{products}) - \Sigma \Delta G_f^\ominus(\text{reactants})$ at 298 K only.
- Crossover temperature: $T = \Delta H/\Delta S$. · $\Delta G = \Delta G^\ominus + RT \ln Q$ · $\Delta G^\ominus = -RT \ln K$ ($\Delta G^\ominus$ in J; R = 8.31).

C Explanations you will be asked for

- Predict ΔS from moles of gas first, then changes of state and number of particles.
- Endothermic reactions are spontaneous only if ΔS_{sys} is large and positive and T is high enough.
- ΔH −, ΔS + always spontaneous; ΔH +, ΔS − never; ΔH −, ΔS − below $\Delta H/\Delta S$; ΔH +, ΔS + above $\Delta H/\Delta S$.
- $-\Delta G$ is the maximum useful work available. Negative ΔG says nothing about rate (kinetic stability, E_a).
- $\Delta G^\ominus$ negative → K > 1, mainly products; positive → K < 1, mainly reactants; zero → K = 1.

9 Check yourself

Use the data table on page 3 unless a question gives other values. R = 8.31 J K^{-1} mol^{-1}. Marks are shown in brackets; allow about 1.2 minutes per mark. Full answers are in section 10.

Part A — Multiple choice HL

1. Which process has a value of ΔS closest to zero?

A $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
B $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$
C $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
D $H_2O(l) \rightarrow H_2O(g)$

2. Which reaction has the largest increase in entropy?

A $C(s) + O_2(g) \rightarrow CO_2(g)$
B $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$
C $NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$
D $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

3. Which change does **not** increase the entropy of a system?

A dissolving potassium nitrate in water
B heating a sample of nitrogen
C condensing steam
D mixing two different gases

4. What is $\Delta S^\ominus$, in J K^{-1} mol^{-1}, for $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$?

A −189 **B** −173 **C** +16 **D** +173

5. Which statement explains why a perfect crystal at 0 K has zero entropy?

A Its particles have no mass.
B Its particles can be arranged in only one way and have no thermal energy to distribute.
C It is an element in its standard state.
D Its enthalpy of formation is zero.

6. A reaction has $\Delta H = -100$ kJ mol^{-1}. What is $\Delta S_{surroundings}$ at 400 K?

A +250 J K^{-1} mol^{-1} **B** −250 J K^{-1} mol^{-1} **C** +0.25 J K^{-1} mol^{-1} **D** −40 000 J K^{-1} mol^{-1}

7. A reaction has $\Delta H^\ominus = +10.0$ kJ mol^{-1} and $\Delta S^\ominus = +10.0$ J K^{-1} mol^{-1}. What is $\Delta G^\ominus$ at 298 K, in kJ mol^{-1}?

A +9.97 **B** +7.02 **C** −290 **D** −2970

8. Which combination gives a reaction that is spontaneous at low temperatures but not at high temperatures?

A $\Delta H -$, $\Delta S -$ **B** $\Delta H -$, $\Delta S +$ **C** $\Delta H +$, $\Delta S +$ **D** $\Delta H +$, $\Delta S -$

9. Ammonium chloride dissolves spontaneously in water although the process is endothermic. What is the best explanation?

A Endothermic processes are always spontaneous in water.
B The increase in entropy of the system outweighs the decrease in entropy of the surroundings.
C The entropy of the surroundings increases.
D The activation energy is zero.

10. A reaction has $\Delta H = +50$ kJ mol^{-1} and $\Delta S = +125$ J K^{-1} mol^{-1}. Above which temperature is it spontaneous?

A 0.40 K **B** 2.5 K **C** 400 K **D** 6250 K

11. A graph of ΔG against T for a reaction is a straight line with a positive intercept on the ΔG axis and a negative gradient. What are the signs of ΔH and ΔS?

A ΔH +, ΔS + **B** ΔH +, ΔS − **C** ΔH −, ΔS + **D** ΔH −, ΔS −

12. Which has a standard Gibbs energy of formation of zero?

A $H_2O(l)$ **B** $O_2(g)$ **C** $O_3(g)$ **D** C(diamond)

13. Which statements are correct for a reaction mixture at equilibrium?

I. The Gibbs energy of the mixture is at a minimum. II. $Q = K$. III. $\Delta G^\ominus = 0$.

A I and II only **B** I and III only **C** II and III only **D** I, II and III

14. A reaction has $\Delta G^\ominus = +5.70$ kJ mol^{-1} at 298 K. What is the value of K?

A 0.100 **B** 0.998 **C** 1.002 **D** 10.0

15. For a reaction mixture, Q is greater than K. Which statement is correct?

A ΔG is negative and more products form.
B ΔG is positive and more reactants form.
C ΔG is zero and the mixture is at equilibrium.
D $\Delta G^\ominus$ must be positive.

16. Which conclusion about a reaction with $\Delta G^\ominus = -120$ kJ mol^{-1} at 298 K is correct?

A The reaction is fast at 298 K.
B The equilibrium mixture contains mainly reactants.
C K is very much greater than 1, but the reaction may be very slow.
D The reaction is endothermic.

Part B — Structured questions HL

17. Predict the sign of ΔS for each change, or state that it is approximately zero, and explain your answer: [6]

(a) $NaCl(s) \rightarrow NaCl(aq)$ (b) $2O_3(g) \rightarrow 3O_2(g)$ (c) $Br_2(l) \rightarrow Br_2(g)$

(d) $CuCO_3(s) \rightarrow CuO(s) + CO_2(g)$ (e) $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$ (f) $N_2(g) + O_2(g) \rightarrow 2NO(g)$

18. (a) Sketch a graph to show how the entropy of ammonia changes as it is heated from 0 K to 300 K. Ammonia melts at 195 K and boils at 240 K. [3]

(b) Explain why the step at the boiling point is much larger than the step at the melting point. [1]

19. Calculate $\Delta S^\ominus$ for each reaction. Additional data / J K^{-1} mol^{-1}: $C_3H_8(g)$ 270, Fe(s) 27.3, $Fe_2O_3(s)$ 87.4, $NaHCO_3(s)$ 102, $Na_2CO_3(s)$ 135. [4]

(a) $H_2O(g) \rightarrow H_2O(l)$ (b) $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

(c) $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ (d) $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$

20. Sodium hydrogencarbonate is the active ingredient of baking powder: $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$. $\Delta H_f^\ominus$ / kJ mol^{-1}: $NaHCO_3(s)$ −951, $Na_2CO_3(s)$ −1131.

(a) Calculate $\Delta H^\ominus$. [2]

(b) Using $\Delta S^\ominus$ from question 19(d), calculate $\Delta G^\ominus$ at 298 K and state whether the reaction is spontaneous. [2]

(c) Calculate the minimum temperature, in °C, for spontaneous decomposition and comment on its use in baking. [2]

21. $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$: $\Delta H^\ominus = -185$ kJ mol^{-1}, $\Delta S^\ominus = +20.1$ J K^{-1} mol^{-1}.

(a) Calculate $\Delta G^\ominus$ at 298 K. [1]

(b) Deduce whether there is any temperature at which the reaction is not spontaneous. [1]

(c) A mixture of hydrogen and chlorine can be stored in the dark without reacting. Explain why. [2]

22. Iron reacts with oxygen: $2Fe(s) + 1½O_2(g) \rightarrow Fe_2O_3(s)$, $\Delta H^\ominus = -824$ kJ mol^{-1}.

(a) Calculate $\Delta S^\ominus$ using the data in question 19 and the table on page 3. [1]

(b) Calculate $\Delta G^\ominus$ at 298 K. [1]

(c) Calculate the temperature above which the reaction is no longer spontaneous and comment on its value. [2]

23. For $Mg(s) + ½O_2(g) \rightarrow MgO(s)$, $\Delta H^\ominus = -602$ kJ mol^{-1} and $\Delta G^\ominus = -569$ kJ mol^{-1} at 298 K.

(a) Calculate $\Delta S^\ominus$. [2]

(b) Explain the sign of $\Delta S^\ominus$. [1]

24. ★ In the Contact process, $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$, $\Delta H^\ominus = -198$ kJ mol^{-1}. $S^\ominus$ / J K^{-1} mol^{-1}: $SO_2(g)$ 248, $SO_3(g)$ 257.

(a) Calculate ΔS_{system}. [1]

(b) Calculate $\Delta S_{surroundings}$ and ΔS_{total} at 298 K and at 1200 K, and deduce whether the reaction is spontaneous at each temperature. [3]

(c) Show that your conclusions agree with the crossover temperature calculated from $T = \Delta H/\Delta S$. [1]

25. ★ For $Br_2(l) \rightarrow Br_2(g)$, $\Delta H^\ominus = +30.9$ kJ mol^{-1}. $S^\ominus$ / J K^{-1} mol^{-1}: $Br_2(l)$ 152, $Br_2(g)$ 245.

(a) Estimate the boiling point of bromine. [2]

(b) Calculate $\Delta G^\ominus$ for vaporization at 298 K. [1]

(c) A bottle of liquid bromine at room temperature always contains brown vapour above the liquid. Explain why this does not contradict your answer to (b). [2]

26. $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$. $\Delta G_f^\ominus$ / kJ mol^{-1}: $NH_3(g)$ −16.4, $NO(g)$ +86.6, $H_2O(g)$ −228.6.

(a) Calculate $\Delta G^\ominus$ at 298 K. [2]

(b) NO has a positive $\Delta G_f^\ominus$. State what this tells you about NO and suggest why NO does not decompose rapidly in air. [2]

27. (a) For the esterification $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$, $K = 4.0$ at 298 K. Calculate $\Delta G^\ominus$. [2]

(b) For $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$, $K_w = 1.0 \times 10^{-14}$ at 298 K. Calculate $\Delta G^\ominus$ and comment. [2]

(c) For $2SO_2 + O_2 \rightleftharpoons 2SO_3$, $\Delta G^\ominus = -142$ kJ mol^{-1} at 298 K. Calculate K and comment. [2]

28. ★ For the Haber process, $\Delta H^\ominus = -92$ kJ mol^{-1} and $\Delta S^\ominus = -199$ J K^{-1} mol^{-1}.

(a) Calculate $\Delta G^\ominus$ and K at 500 K and at 700 K. [4]

(b) Use your answers and worked example 11 to describe how K changes with temperature, and explain why the process is still run at about 700 K. [2]

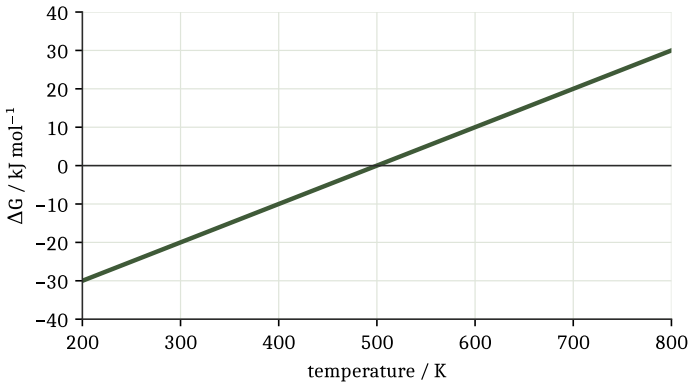
29. For $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ at 298 K, $\Delta G^\ominus = +4.70$ kJ mol^{-1} and $K = 0.150$.

(a) Calculate ΔG for a mixture with $Q = 0.50$ and deduce the direction of change. [2]

(b) Calculate ΔG for a mixture with $Q = 0.10$ and deduce the direction of change. [2]

(c) State the value of ΔG when the mixture reaches equilibrium. [1]

30. The graph shows how ΔG varies with temperature for a reaction.



(a) Use the graph to determine ΔS and ΔH for the reaction. **[3]**

(b) State the temperature range in which the reaction is spontaneous. **[1]**

(c) Suggest one assumption made in drawing the graph as a straight line. **[1]**

31. ★ A hydrogen fuel cell can produce either liquid water or steam. $S^{\ominus}(H_2O, g) = 189\ J\ K^{-1}\ mol^{-1}$; $\Delta H_f^{\ominus}(H_2O, g) = -242\ kJ\ mol^{-1}$.

(a) Calculate $\Delta G^{\ominus}$ at 298 K for $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$. **[2]**

(b) Calculate the maximum efficiency ($\Delta G/\Delta H \times 100$) for forming steam and compare it with the value for liquid water in worked example 8. **[1]**

(c) Explain the difference in terms of the entropy change of the system. **[2]**

32. ★ For $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, use the data table on page 3.

(a) Calculate $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$. **[2]**

(b) Calculate the temperature at which decomposition becomes spontaneous. **[1]**

(c) Calculate ΔG and K at 1500 K, and explain what the value of K means for a lime kiln. **[3]**

Part A: 16 marks · Part B: 78 marks · Total: 94 marks (about 1 hour 55 minutes)

10 Answers

Part A

1. B. 2 mol gas → 2 mol gas. A falls (4 → 2), C and D rise (gas produced).

2. C. 0 mol gas → 2 mol gas. A has no change in gas; B and D decrease.

3. C. Condensing makes a less dispersed liquid.

4. B. 2(214) − [2(198) + 205] = 428 − 601 = −173. C forgets O_2 and the coefficients.

5. B.

6. A. −(−100 000)/400 = +250. C forgets to convert kJ to J.

7. B. 10.0 − 298 × 0.0100 = +7.02. D uses ΔS in J without converting.

8. A. ΔG ≈ ΔH (negative) at low T; −TΔS positive and dominant at high T.

9. B. The surroundings lose entropy (C is wrong); ΔS_{total} is still positive.

10. C. T = 50 / 0.125 = 400 K.

11. A. Intercept = ΔH (positive); gradient = −ΔS (negative), so ΔS is positive.

12. B. An element in its standard state.

13. A. At equilibrium ΔG = 0, not $\Delta G^{\ominus}$; $\Delta G^{\ominus} = 0$ only if K = 1.

14. A. ln K = −5700/(8.31 × 298) = −2.30; K = 0.100.

15. B. RT ln Q > RT ln K = $-\Delta G^{\ominus}$, so ΔG > 0 and the reverse reaction is spontaneous.

16. C. $\Delta G^{\ominus}$ says nothing about rate or the sign of ΔH.

Part B

17. One mark each, sign with reason:
(a) **+**: an ordered lattice disperses into mobile aqueous ions. (b) **+**: 2 mol gas → 3 mol gas. (c) **+**: liquid → gas.
(d) **+**: 0 mol gas → 1 mol gas. (e) **−**: two aqueous ions form one ordered solid. (f) **≈ 0**: 2 mol gas → 2 mol gas; cannot predict reliably (actual +25 J K^{-1} mol^{-1}).

18. (a) Curve starts at S = 0 at 0 K and rises gradually through the solid **[1]**; vertical step at 195 K, then a gradual rise through the liquid **[1]**; a much larger vertical step at 240 K, then a gradual rise through the gas to 300 K **[1]**.
(b) Gas particles are far more dispersed than liquid particles, whereas a liquid is only slightly more disordered than a solid **[1]**.

19. (a) 70.0 − 189 = **−119 [1]**; (b) [2(27.3) + 3(214)] − [87.4 + 3(198)] = 696.6 − 681.4 = **+15.2 [1]**; (c) [3(214) + 4(70.0)] − [270 + 5(205)] = 922 − 1295 = **−373 [1]**; (d) (135 + 214 + 189) − 2(102) = **+334** J K^{-1} mol^{-1} **[1]**.

20. (a) (−1131 − 394 − 242) − 2(−951) **[1]** = **+135 kJ mol^{-1} [1]**.
(b) $\Delta G^{\ominus}$ = 135 − 298 × 0.334 = **+35.5 kJ mol^{-1} [1]**; positive, so not spontaneous at 298 K (baking powder is stable in the cupboard) **[1]**.
(c) T = 135/0.334 = 404 K = **131 °C [1]**; this is below oven temperatures, so CO_2 is released during baking and makes the mixture rise **[1]**.

21. (a) −185 − 298 × 0.0201 = **−191 kJ mol^{-1} [1]**.
(b) No: ΔH negative and ΔS positive, so ΔG is negative at all temperatures **[1]**.
(c) The reaction has a high activation energy (the H–H and Cl–Cl bonds must be broken) **[1]**, so the rate is negligible; light (UV) supplies the energy to break Cl–Cl bonds and starts the reaction **[1]**.

22. (a) 87.4 − [2(27.3) + 1.5(205)] = **−274.7 J K^{-1} mol^{-1} [1]**.
(b) −824 − 298(−0.2747) = **−742 kJ mol^{-1} [1]**.
(c) T = 824/0.2747 = **3000 K [1]**; far above any normal temperature (and above the melting point of iron, so the data no longer apply), so iron oxidation is spontaneous under all ordinary conditions **[1]**.

23. (a) ΔS = (ΔH − ΔG)/T = (−602 + 569)/298 **[1]** = −0.111 kJ K^{-1} mol^{-1} = **−111 J K^{-1} mol^{-1} [1]**.
(b) Half a mole of gas (O_2) is converted into an ordered solid, so the dispersal of matter decreases **[1]**.

24. (a) 2(257) − [2(248) + 205] = **−187 J K^{-1} mol^{-1} [1]**.
(b) 298 K: ΔS_{surr} = 198 000/298 = +664; ΔS_{total} = +477, spontaneous **[1]**. 1200 K: ΔS_{surr} = 198 000/1200 = +165 **[1]**; ΔS_{total} = −22, not spontaneous **[1]**.
(c) T = 198/0.187 = 1059 K, which lies between 298 K and 1200 K, consistent with the change of sign **[1]**.

25. (a) ΔS = 245 − 152 = +93 J K^{-1} mol^{-1} **[1]**; T = 30.9/0.093 = **332 K (59 °C) [1]**.
(b) 30.9 − 298 × 0.093 = **+3.2 kJ mol^{-1} [1]**.
(c) $\Delta G^{\ominus}$ refers to bromine vapour at the standard pressure of 100 kPa; a positive value means K < 1, i.e. the equilibrium vapour pressure is below 100 kPa **[1]**, but not zero, so some liquid evaporates until the vapour reaches its equilibrium pressure (ΔG = 0 at equilibrium) **[1]**.

26. (a) [4(86.6) + 6(−228.6)] − [4(−16.4) + 0] **[1]** = 346.4 − 1371.6 + 65.6 = **−959.6 kJ mol^{-1} [1]**.
(b) NO is thermodynamically unstable relative to N_2 and O_2 **[1]**; its decomposition has a high activation energy, so it is kinetically stable **[1]**.

27. (a) −8.31 × 298 × ln 4.0 **[1]** = −3430 J mol^{-1} = **−3.43 kJ mol^{-1} [1]**.
(b) −8.31 × 298 × ln(1.0 × 10^{-14}) = **+79.8 kJ mol^{-1} [1]**; large and positive, so water is only very slightly ionized **[1]**.
(c) K = e$^{142\,000/(8.31 \times 298)}$ = **8 × 10^{24} [1]**; the reaction essentially goes to completion at 298 K (but a catalyst is needed because it is very slow) **[1]**.

28. (a) 500 K: $\Delta G^{\ominus}$ = −92 + 500 × 0.199 = **+7.5 kJ mol^{-1} [1]**; K = e$^{-7500/(8.31 \times 500)}$ = **0.16 [1]**. 700 K: $\Delta G^{\ominus}$ = **+47.3 kJ mol^{-1} [1]**; K = e$^{-47\,300/(8.31 \times 700)}$ = **2.9 × 10^{-4} [1]**.
(b) K falls sharply as temperature rises (5.4 × 10^{5} → 0.16 → 2.9 × 10^{-4}), as expected for an exothermic reaction **[1]**; but the rate at low temperatures is far too slow, so a higher temperature, high pressure, an iron catalyst and recycling of unreacted gases are used as a compromise **[1]**.

29. (a) ΔG = 4700 + 8.31 × 298 × ln 0.50 = 4700 − 1716 = **+2.98 kJ mol^{-1} [1]**; positive (Q > K), so the reverse reaction is spontaneous: NO_2 dimerizes **[1]**.
(b) ΔG = 4700 + 8.31 × 298 × ln 0.10 = 4700 − 5702 = **−1.00 kJ mol^{-1} [1]**; negative (Q < K), so more N_2O_4 dissociates **[1]**.
(c) **ΔG = 0 [1]**.

30. (a) gradient = (30 − (−30))/(800 − 200) = +0.100 kJ K^{-1} mol^{-1} = −ΔS, so ΔS = **−100 J K^{-1} mol^{-1} [1]**; at 200 K: −30 = ΔH − 200(−0.100) **[1]**, so ΔH = **−50 kJ mol^{-1} [1]**.
(b) Below **500 K** (where ΔG = 0) **[1]**.
(c) ΔH and ΔS are assumed not to change with temperature (and no change of state occurs in the range) **[1]**.

31. (a) ΔS = 189 − [131 + ½(205)] = −44.5 J K^{-1} mol^{-1} **[1]**; ΔG = −242 − 298(−0.0445) = **−228.7 kJ mol^{-1} [1]**.
(b) 228.7/242 × 100 = **94.5 %**, compared with 83 % when liquid water forms **[1]**.
(c) Forming steam gives a much smaller decrease in the entropy of the system (−44.5 against −163.5 J K^{-1} mol^{-1}) **[1]**, so less of the energy released has to be transferred to the surroundings as heat to satisfy the second law, leaving a larger fraction available as useful work **[1]**.

32. (a) ΔH = (−635 − 394) − (−1207) = **+178 kJ mol^{-1}**; ΔS = (39.7 + 214) − 92.9 = **+160.8 J K^{-1} mol^{-1} [2]**.
(b) T = 178/0.1608 = **1107 K** (834 °C) **[1]**.
(c) ΔG = 178 − 1500 × 0.1608 = **−63.2 kJ mol^{-1} [1]**; K = e$^{63\,200/(8.31 \times 1500)}$ ≈ **160 [1]**; K ≫ 1, so at kiln temperatures the decomposition lies well towards CaO and CO_2 (and removing the CO_2 keeps the reaction going) **[1]**.

Where this fits: Reactivity 1 is complete

- **Booklet 1** — R1.1 measuring enthalpy changes · **Booklets 2 and 3** — R1.2 energy cycles (Booklet 3 HL)
- **Booklet 4** — R1.3 energy from fuels · **Booklet 5** (this booklet) — HL R1.4 entropy and spontaneity
- **Next:** Reactivity 2 — how much, how fast and how far? (amounts of substance, rates, and equilibrium, where $\Delta G^{\ominus} = -RT \ln K$ is used again).

These notes are a free resource, shared for any IB student who finds them useful.

If a particular idea here still isn't clicking, specialist one-to-one support in Physics, Chemistry and Maths from a past A Level examiner is available at iBLaurel — call or message **+44 7404 710097**, or use the contact form at **www.iBLaurel.com**.

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