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IB DIPLOMA CHEMISTRY · FIRST ASSESSMENT 2025

Reactivity 2.3 Dynamic Equilibrium and Le Chatelier's Principle

Booklet 5 · Understandings 2.3.1 – 2.3.4

How far? What dynamic equilibrium is, how the equilibrium law turns an equation into an equilibrium constant, what the size of K tells you, and how concentration, pressure, temperature and catalysts affect an equilibrium and its yield

Complete revision notes, 16 worked examples, model answers & 36 practice questions · Standard Level & Higher Level

How the level tags work in this booklet

SL + HL Understandings 2.3.1 to 2.3.4 are common to both levels, so the whole booklet is core material.

HL The HL-only part of Reactivity 2.3 (the reaction quotient, *Q*, and calculating *K* or equilibrium concentrations from initial amounts, 2.3.5 onwards) is covered in a separate HL booklet. ★ marks harder examples and questions.

Inside this booklet

1. What the syllabus actually asks of you
2. 2.3.1 — Dynamic equilibrium
3. 2.3.2 — The equilibrium law
4. 2.3.3 — The size of *K*
5. 2.3.4 — Le Chatelier's principle
6. 2.3.4 — Equilibria in industry
7. Key points to memorise
8. Check yourself
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1 What the syllabus actually asks of you

Reactivity 2 asks three questions about a reaction: how much (2.1), how fast (2.2) and how far (2.3). Many reactions do not go to completion: they are reversible, and they settle into a mixture of reactants and products in which nothing seems to change. This booklet covers the SL + HL understandings: what that state of dynamic equilibrium is, how the equilibrium law describes its composition with a single number, *K*, and how chemists use Le Chatelier's principle to shift an equilibrium, for example to make more ammonia for fertilizers. Expect short questions on *K* expressions and Le Chatelier in Paper 1A, and longer explanations, often set in an industrial process, in Paper 2.

Understanding	What it says	What you must be able to do	Level
2.3.1 Dynamic equilibrium	A state of dynamic equilibrium is reached in a closed system when the rates of forward and backward reactions are equal.	Describe the characteristics of a physical and a chemical system at equilibrium.	SL+HL
2.3.2 Equilibrium law	The equilibrium law describes how the equilibrium constant, *K*, can be determined from the stoichiometry of a reaction.	Deduce the equilibrium constant expression from an equation for a **homogeneous** reaction.	SL+HL
2.3.3 Size of K	The magnitude of the equilibrium constant indicates the extent of a reaction at equilibrium and is temperature dependent.	Determine the relationships between *K* values for reactions that are the reverse of each other at the same temperature. **Include the extent of reaction for $K \ll 1$, $K < 1$, $K \approx 1$, $K > 1$ and $K \gg 1$.**	SL+HL
2.3.4 Le Chatelier	Le Chatelier's principle enables the prediction of the qualitative effects of changes in concentration, temperature and pressure to a system at equilibrium.	Apply Le Chatelier's principle to predict and explain responses to changes of systems at equilibrium. **Include the effects on the value of *K* and on the equilibrium composition.** Le Chatelier's principle can be applied to heterogeneous equilibria such as X(g) ⇌ X(aq).	SL+HL

Linking questions and connections for 2.3.1 – 2.3.4

- **Reactivity 3.1:** how does the value of *K* for the dissociation of an acid convey information about the strength of the acid? → section 4.1
- **Reactivity 2.2:** why do catalysts have no effect on the value of *K* or on the equilibrium composition? → section 5.5
- **Reactivity 2.2:** rates explain how equilibrium is reached, and the equilibrium constant *K* (upper case) must not be confused with the rate constant *k* (lower case). → section 2.2
- **Reactivity 2.1:** a reversible reaction can never give a 100 % yield, and atom economy is a separate measure → section 6.1
- **Reactivity 1.4:** the Gibbs energy change and *K* both describe the position of equilibrium (developed at HL).

What the data booklet does and does not give you

It gives you: the gas constant and general data, but nothing specific to these understandings.

It does not give you: the form of the equilibrium constant expression; the meaning of the size of K; the relationship between K for a reaction and its reverse; or Le Chatelier's principle and its effects. All of these must be learned. You are not expected to learn the conditions used in particular industrial processes, but you must be able to apply Le Chatelier's principle and rate arguments to them.

2 Reactivity 2.3.1 — Dynamic equilibrium SL + HL

2.1 A physical equilibrium

Imagine running down an escalator that is moving up at exactly your speed. Photographs taken every few seconds would show you standing still, although you and the escalator are both moving. A system at equilibrium is like this: two opposite processes go on at the same rate, so no overall change is seen.

Put a little liquid bromine in a sealed jar. Bromine is volatile, so some molecules escape from the liquid as vapour (evaporation). Because the jar is sealed, the vapour cannot escape and its concentration rises. Vapour molecules collide with the liquid surface and rejoin it (condensation). The rate of evaporation stays constant, because the surface area of the liquid does not change, but the rate of condensation rises as the vapour concentration increases. Eventually the two rates are equal: $Br_2(l) \rightleftharpoons Br_2(g)$ has reached equilibrium, and the amounts of liquid and vapour, and so the depth of the orange-brown colour, stay constant. In an open jar the vapour would escape, and the liquid would eventually all evaporate.

2.2 A chemical equilibrium

Hydrogen iodide decomposes into hydrogen and iodine, which is a purple gas: $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$. At first the forward reaction is fast, because [HI] is high, and the backward reaction does not happen at all, because there is no H_2 or I_2. As HI is used up the forward rate falls, and as H_2 and I_2 build up the backward rate rises. When the two rates become equal, the concentrations stop changing and the purple colour stays constant (Figure 1). The reaction has not stopped: both reactions continue, so the equilibrium is **dynamic**.

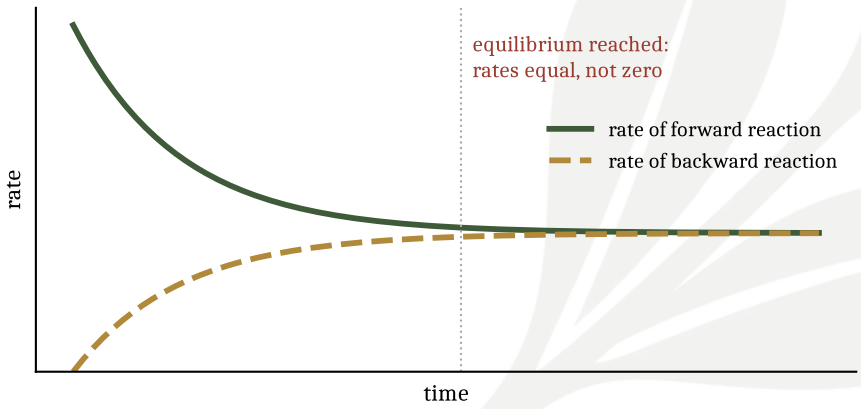


Figure 1 — As a reversible reaction approaches equilibrium, the forward rate falls and the backward rate rises until they are equal.

Definitions to learn

A **reversible reaction** can go in both directions. The left-to-right reaction is the **forward** reaction; the right-to-left reaction is the **backward** (reverse) reaction. The symbol ⇌ shows a reaction at equilibrium.

Dynamic equilibrium is reached in a **closed system** when the rates of the forward and backward reactions are equal, so the concentrations of reactants and products stay constant.

A **closed system** is one in which no matter is exchanged with the surroundings (energy can still be transferred).

2.3 The characteristics of equilibrium

Characteristic	Explanation
1 Equilibrium is dynamic.	The forward and backward reactions are both still happening, at the same rate.
2 It is reached only in a closed system.	Products must stay in contact with the reactants so that the backward reaction can occur.
3 Concentrations of reactants and products stay constant.	Each substance is made and used up at the same rate. Constant does **not** mean equal.
4 Macroscopic properties do not change.	Observable properties, such as colour, density and pressure, depend on the concentrations, so they stay constant.
5 It can be reached from either direction.	Under the same conditions, the same equilibrium mixture forms whether you start with reactants, products or a mixture (Figure 2).

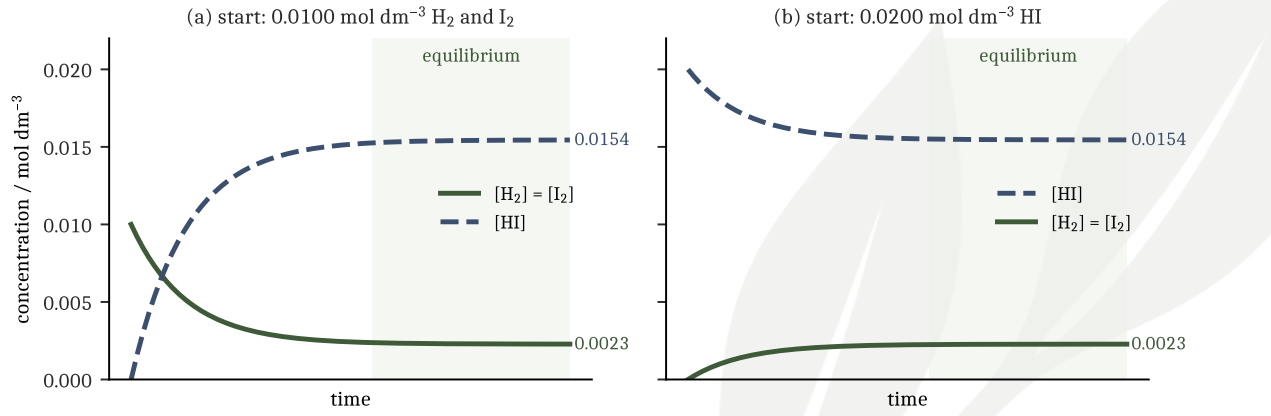


Figure 2 — $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 440 °C. Starting from (a) 0.0100 mol dm^{-3} of H_2 and I_2 or (b) the equivalent 0.0200 mol dm^{-3} of HI, the same equilibrium mixture forms. The concentrations become constant, but they are not equal.

The proportions of reactants and products in the equilibrium mixture are called the **position of equilibrium**. If the mixture is mostly products, the equilibrium "lies to the right"; if it is mostly reactants, it "lies to the left". Strictly, every reaction is an equilibrium, but when the mixture is almost entirely products (as in combustion) we write → and call it irreversible. Changes at the particle level can be followed by isotopic labelling: if some HI made with radioactive iodine is added to an equilibrium mixture, the label soon appears in the I_2 as well, which shows that the reactions have not stopped.

Model answer: "Explain how a state of equilibrium is reached when liquid bromine is placed in a sealed flask, and why the colour of the vapour then stays constant." (3 marks)

Bromine evaporates at a constant rate, and the vapour cannot escape from the sealed (closed) flask, so its concentration increases [1]. The rate of condensation increases as the vapour concentration rises, until it equals the rate of evaporation [1]. Both processes continue at equal rates (dynamic equilibrium), so the concentration of the vapour, and therefore the colour, stays constant [1].

Examiner traps with dynamic equilibrium

- Saying that the reaction has stopped at equilibrium. Both reactions continue at the same rate.
- Saying that the concentrations of reactants and products are **equal**. They are constant, but usually very different.
- Saying that the rates are zero. They are equal, and not zero.
- Forgetting that equilibrium needs a **closed system**.
- Writing → instead of ⇌ for an equilibrium, for example for a weak acid.

3 Reactivity 2.3.2 — The equilibrium law SL + HL

3.1 Finding a pattern in equilibrium mixtures

If the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is started with different amounts of H_2, I_2 and HI at the same temperature, each experiment reaches a different equilibrium mixture. At first sight the concentrations show no pattern. But if the concentration of each substance is raised to the power of its coefficient in the equation, products are put on the top and reactants on the bottom, the result is the same every time (worked example 4). This is the equilibrium law.

Definition to learn: the equilibrium law

For a homogeneous reaction at equilibrium, $aA + bB \rightleftharpoons cC + dD$

$$K = [C]^c[D]^d / [A]^a[B]^b$$

The **equilibrium constant**, K, has a fixed value for a given reaction at a given temperature. The square brackets mean the **equilibrium** concentrations in mol dm^{-3}. Only a change in temperature changes the value of K.

Method — writing an equilibrium constant expression

1. Start from the balanced equation, with state symbols. Check that it is **homogeneous**: all species in the same phase (all gases, or all in the same solution).
2. Put the products on the top (numerator) and the reactants on the bottom (denominator).
3. Raise each concentration to the power of its coefficient; a power of 1 is not written.
4. Multiply terms together; never add them.
5. Give K without units: the IB does not require units for K.

Worked example 1 — writing K expressions

Equation	Equilibrium constant expression
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	$K = [NH_3]^2 / [N_2][H_2]^3$
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	$K = [SO_3]^2 / [SO_2]^2[O_2]$
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$	$K = [NO_2]^2 / [N_2O_4]$
$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$	$K = [CO][H_2]^3 / [CH_4][H_2O]$
$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$	$K = [[Cu(NH_3)_4]^{2+}] / [Cu^{2+}][NH_3]^4$
$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$	$K = [CH_3COO^-][H^+] / [CH_3COOH]$

Worked example 2 — from an expression back to the equation

Q. Write the equation for each reaction: (a) $K = [NO_2]^2 / [NO]^2[O_2]$; (b) $K = [CO][H_2]^3 / [CH_4][H_2O]$; (c) $K = [H_2][I_2] / [HI]^2$.

(a) **$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$** (b) **$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$** (c) **$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$**

Species on the top are products; the powers become the coefficients.

3.2 Calculating K from equilibrium concentrations

Worked example 3 — K from equilibrium concentrations

Q. At a certain temperature, an equilibrium mixture for $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ contains 0.0400 mol dm^{-3} N_2O_4 and 0.0120 mol dm^{-3} NO_2. Calculate K.

$K = [NO_2]^2 / [N_2O_4] = (0.0120)^2 / 0.0400 = 1.44 \times 10^{-4} / 0.0400 =$ **3.60×10^{-3}**

Worked example 4 — K from amounts in moles

Q. A 2.00 dm^3 flask at equilibrium contains 0.140 mol PCl_5, 0.0600 mol PCl_3 and 0.0600 mol Cl_2: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. Calculate K.

concentrations: $[PCl_5] = 0.140 / 2.00 = 0.0700$; $[PCl_3] = [Cl_2] = 0.0600 / 2.00 = 0.0300$ mol dm^{-3}

$K = [PCl_3][Cl_2] / [PCl_5] = (0.0300 \times 0.0300) / 0.0700 =$ **0.0129**

Always convert amounts to concentrations first. Substituting moles directly gives the wrong answer whenever the numbers of particles on the two sides differ.

Worked example 5 — showing that K is constant

Q. Three equilibrium mixtures for $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 440 °C have the concentrations below (mol dm^{-3}). Show that they obey the equilibrium law.

Mixture	$[H_2]$	$[I_2]$	$[HI]$	$[HI]^2 / [H_2][I_2]$
1	0.0100	0.0100	0.0678	46.0
2	0.0300	0.00600	0.0910	46.0
3	0.00450	0.0150	0.0557	46.0

The concentrations are very different, yet K = 46.0 each time, within experimental error: the equilibrium law holds. A ratio such as $[HI]/[H_2][I_2]$, which ignores the coefficient, would not be constant.

Worked example 6 — an unknown equilibrium concentration ★

Q. For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at a certain temperature, K = 0.105. An equilibrium mixture contains 0.200 mol dm^{-3} N_2 and 0.300 mol dm^{-3} H_2. Calculate $[NH_3]$.

$[NH_3]^2 = K \times [N_2][H_2]^3 = 0.105 \times 0.200 \times (0.300)^3 = 5.67 \times 10^{-4}$

$[NH_3] = \sqrt{(5.67 \times 10^{-4})} =$ **0.0238 mol dm^{-3}**

Examiner traps with K expressions

- Putting reactants on top. Products always go in the numerator.
- Multiplying by the coefficient instead of raising to its power: $[NH_3]^2$, not $2[NH_3]$.
- Adding terms instead of multiplying them.
- Substituting initial concentrations, or amounts in moles, instead of **equilibrium concentrations**.
- Writing an expression for a heterogeneous reaction (solids with gases); the syllabus covers only homogeneous reactions.
- Confusing the equilibrium constant K with the rate constant k. K comes from the stoichiometry; k and the rate equation come only from experiment.

4 Reactivity 2.3.3 — The size of K

SL + HL

4.1 What K tells you

Because products are on the top of the expression, a large K means that the equilibrium mixture contains mostly products, and a small K means mostly reactants.

Value of K	$K \ll 1$	$K < 1$	$K \approx 1$	$K > 1$	$K \gg 1$
extent of reaction	reaction hardly proceeds	lies towards the reactants	significant amounts of both	lies towards the products	almost complete

For example, at 550 K: $H_2 + I_2 \rightleftharpoons 2HI$ has $K \approx 2$; $H_2 + Br_2 \rightleftharpoons 2HBr$, $K \approx 10^{10}$; and $H_2 + Cl_2 \rightleftharpoons 2HCl$, $K \approx 10^{18}$. The H–Cl bond is the strongest of the three, so the reaction with chlorine goes furthest. For a weak acid, $HA \rightleftharpoons H^+ + A^-$, a smaller K means less dissociation and a weaker acid (Reactivity 3.1).

***K* says nothing about rate.** A reaction with a huge K can be immeasurably slow, as a mixture of hydrogen and oxygen at room temperature shows. K tells you how far the reaction will go; kinetics tells you how fast it gets there.

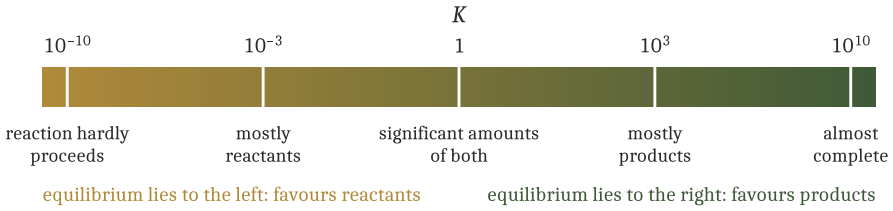


Figure 3 — The value of K shows how far a reaction goes. The boundaries are a rule of thumb, not exact limits.

Worked example 7 — interpreting K values

Q. At 298 K: (a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, $K = 4.5 \times 10^{-31}$; (b) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$, $K = 6.0 \times 10^{13}$; (c) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$, $K \approx 1$ at about 1100 K. Describe each equilibrium mixture.

(a) $K \ll 1$: **almost entirely N_2 and O_2**; the reaction hardly proceeds, which is why air does not turn into NO

(b) $K \gg 1$: **almost entirely NO_2**; the reaction goes almost to completion

(c) $K \approx 1$: **significant amounts of all four gases**

4.2 The reverse reaction, and multiples of an equation

For the reverse reaction, products and reactants swap places, so the expression is turned upside down:

$$K(\text{reverse}) = 1 \,/\, K(\text{forward}) \quad \text{or} \quad K' = K^{-1}$$

It also follows that doubling every coefficient squares K, and halving every coefficient gives $\sqrt{K}$. The syllabus requires the reverse relationship; the multiples are a useful extension. K must always be quoted with the equation it refers to.

Worked example 8 — K for related equations

Q. At a given temperature, $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ has $K = 280$. Find K for (a) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$; (b) $4SO_2(g) + 2O_2(g) \rightleftharpoons 4SO_3(g)$; (c) $SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$; (d) $SO_3(g) \rightleftharpoons SO_2(g) + \tfrac{1}{2}O_2(g)$.

(a) reverse: $1/280 =$ **3.57×10^{-3}** (b) doubled: $280^2 =$ **7.84×10^{4}**

(c) halved: $\sqrt{280} =$ **16.7** (d) halved and reversed: $1/\sqrt{280} =$ **0.0598**

Model answer: "The equilibrium constant for a reaction is 5.0×10^{12} at 298 K. State and explain what this shows about the equilibrium mixture, and what it does not show." (2 marks)

K is much greater than 1, so the equilibrium lies far to the right: the mixture is almost entirely products and the reaction goes almost to completion [1]. It gives no information about the rate, so it does not show how quickly equilibrium is reached [1].

Examiner traps with the size of K

- Thinking a large K means a fast reaction.
- Forgetting that K changes with temperature: a value of K needs a temperature.
- Reversing an equation but keeping the same K. Take the reciprocal.
- Saying $K = 1$ means equal concentrations of every substance. It means significant amounts of both sides.

5 Reactivity 2.3.4 — Le Chatelier's principle SL + HL

Definition to learn

Le Chatelier's principle: when a system at equilibrium is subjected to a change, it responds in such a way as to minimize the effect of the change.

Put simply, the system does the opposite of what you do to it. Add something and it removes some of it; remove something and it replaces some of it; heat it and it absorbs heat. A new equilibrium forms with a different composition. Le Chatelier's principle predicts the direction of the shift, but not how big it will be.

5.1 Changing a concentration

Adding a reactant increases the rate of the forward reaction only, so the rates are no longer equal. More product forms until the rates are equal again: the equilibrium **shifts to the right**. Removing a product slows the backward reaction and has the same effect. Adding product, or removing reactant, shifts the equilibrium to the left. In every case the concentrations change but ***K* stays the same**, because the temperature has not changed.

Worked example 9 — predicting colour changes

Q. In water, yellow chromate ions and orange dichromate ions are in equilibrium: $2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$. Predict the colour change when (a) acid is added and (b) sodium hydroxide is added.

(a) $[H^+]$ increases; the system removes H^+ by favouring the forward reaction: equilibrium shifts right, **yellow → orange**

(b) OH^- removes H^+ ($H^+ + OH^- \rightarrow H_2O$); the system replaces H^+ by favouring the backward reaction: shifts left, **orange → yellow**

The same reasoning explains the cobalt chloride test for water: $[Co(H_2O)_6]^{2+}$ (pink) + $4Cl^- \rightleftharpoons CoCl_4^{2-}$ (blue) + $6H_2O$. Adding water turns the blue form pink.

5.2 Changing the pressure

For reactions of gases, pressure is proportional to the number of gas molecules in a given volume. Increasing the pressure (for example by reducing the volume of the container) shifts the equilibrium towards the side with **fewer gas molecules**, which reduces the pressure. Decreasing the pressure shifts it towards the side with more gas molecules. If both sides have the same number of gas molecules, pressure has **no effect** on the position of equilibrium. Pressure never changes K. Count only gases: solids and liquids are ignored.

Worked example 10 — the effect of increasing the pressure

Equilibrium	Gas molecules, left : right	Effect of higher pressure
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	4 : 2	shifts **right**: more NH_3
$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$	3 : 1	shifts **right**: more methanol
$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$	2 : 3	shifts **left**: less CO
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	2 : 2	**no shift** (rates increase equally)
$CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$	3 : 5	shifts **left**

5.3 Changing the temperature

Temperature is different: it is the only change that alters K. The sign of ΔH given with an equation refers to the forward reaction; the backward reaction has the same value with the opposite sign. Raising the temperature favours the **endothermic** direction, which absorbs the added heat; lowering it favours the **exothermic** direction.

Forward reaction	Increase in temperature	Decrease in temperature
exothermic ($\Delta H < 0$)	shifts left; ***K* decreases**	shifts right; ***K* increases**
endothermic ($\Delta H > 0$)	shifts right; ***K* increases**	shifts left; ***K* decreases**

For example, $2NO_2(g)$ (brown) $\rightleftharpoons N_2O_4(g)$ (colourless), $\Delta H = -57$ kJ mol^{-1}, has $K = 1300$ at 273 K but only 170 at 298 K: a sealed tube of the gases goes darker when warmed and paler when cooled. In terms of rates, a temperature rise speeds up both reactions, but it speeds up the reaction with the higher activation energy, the endothermic one, by a larger factor.

Worked example 11 — deducing the sign of ΔH from K values

Q. For $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, $K = 4.5 \times 10^{-31}$ at 298 K, 6.7×10^{-10} at 900 K and 1.7×10^{-3} at 2300 K. Deduce whether the forward reaction is exothermic or endothermic, and explain why car engines produce NO.

K increases as the temperature rises, so higher temperature favours the forward reaction: **the forward reaction is endothermic** ($\Delta H = +181$ kJ mol^{-1})

At air temperature K is tiny, so almost no NO forms. In the very hot cylinder of an engine K is much larger and the reaction is fast, so **significant NO forms**, which then forms brown NO_2 in polluted air.

5.4 Interpreting concentration–time graphs

Each kind of change leaves a different signature on a graph of concentration against time. A **concentration** change makes one line jump suddenly, and the others then adjust smoothly. A **temperature** change causes no sudden jump: all lines curve gradually to new values. A **pressure** change by changing the volume makes **all** the gas concentrations jump at once, by the same factor, before they adjust.

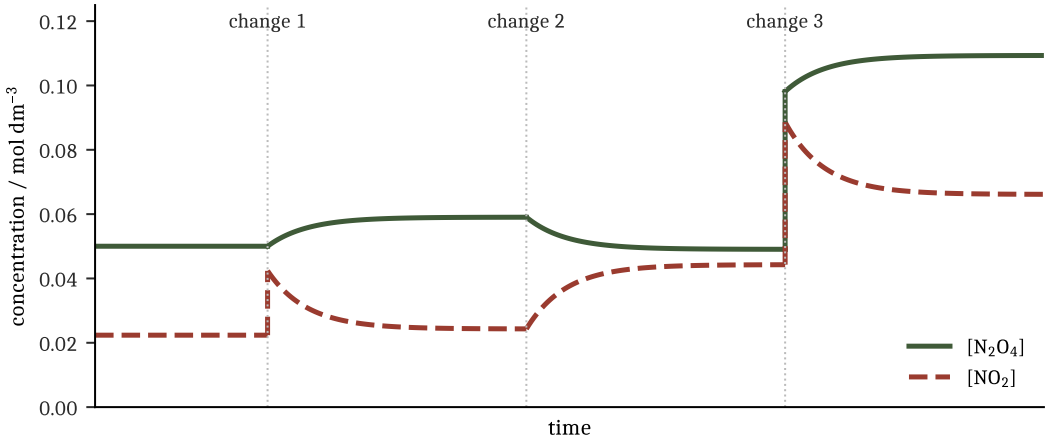


Figure 4 — $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, $\Delta H = +57$ kJ mol^{-1}. Three changes are made to the equilibrium mixture (worked example 12).

Worked example 12 — identifying the changes ★

Q. Identify changes 1, 2 and 3 in Figure 4, and state the effect of each on *K*.

change 1: only [NO_2] jumps up, then falls as [N_2O_4] rises: **NO_2 was added**; the equilibrium shifts left; *K* unchanged

change 2: no jump; [NO_2] rises gradually and [N_2O_4] falls: the forward, endothermic reaction is favoured, so **the temperature was increased**; *K* increases

change 3: both concentrations double at once, then [NO_2] falls and [N_2O_4] rises: **the volume was halved** (pressure increased), shifting the equilibrium to the side with fewer gas molecules; *K* unchanged

5.5 Adding a catalyst

A catalyst provides an alternative pathway with a lower activation energy. The forward and backward reactions pass through the same transition state, so the activation energies of **both** are lowered by the same amount (Figure 5) and both rates increase by the same factor. A catalyst therefore has **no effect on the position of equilibrium, the equilibrium yield, or *K***. It only makes the system reach equilibrium sooner. Catalysts are not written in the equation or in the *K* expression.

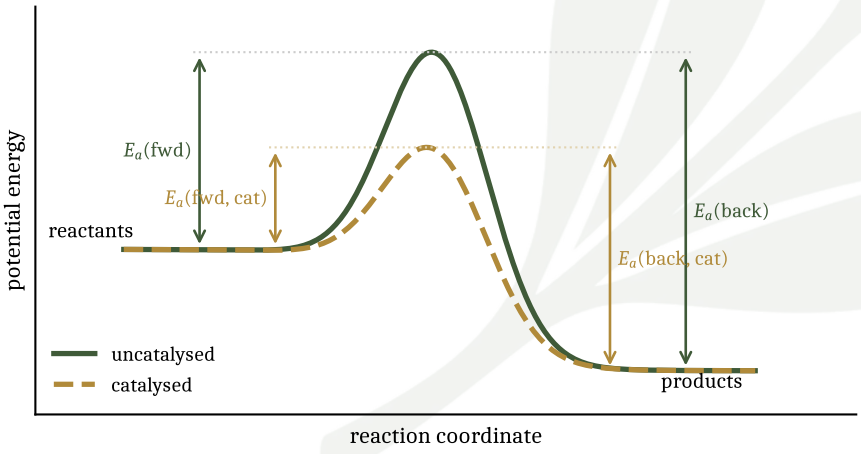


Figure 5 — A catalyst lowers the activation energies of the forward and backward reactions by the same amount.

5.6 Heterogeneous equilibria: a gas dissolving in water

Le Chatelier's principle also applies to equilibria between phases. A fizzy drink contains $CO_2(g) \rightleftharpoons CO_2(aq)$. The drink is bottled under a high pressure of CO_2, which shifts the equilibrium to the right, so a lot of CO_2 dissolves. When the cap is removed, the CO_2 above the liquid escapes; the equilibrium shifts left and bubbles form. If the bottle is resealed, a new equilibrium is reached; left open, CO_2 keeps escaping and the drink goes flat. Gases are also less soluble in warm water, because dissolving a gas is usually exothermic: warm drinks lose their fizz faster, and warm rivers hold less dissolved oxygen.

Worked example 13 — one equilibrium, every change

Q. For $CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$, $\Delta H > 0$, predict the effect of each change on the position of equilibrium and on K.

Change	Position of equilibrium	K
add $H_2(g)$	shifts left	no change
add $CH_4(g)$	shifts right	no change
decrease the volume (3 : 5 gas molecules)	shifts left	no change
remove $CS_2(g)$	shifts right	no change
increase the temperature (endothermic)	shifts right	increases
add a catalyst	no shift; equilibrium reached sooner	no change

Model answer: "Explain why adding a catalyst to the equilibrium $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ does not change the equilibrium yield of ammonia." (2 marks)

The catalyst lowers the activation energy of the forward and backward reactions by the same amount, so both rates increase by the same factor [1]. The rates remain equal, so the position of equilibrium and K are unchanged; equilibrium is only reached more quickly [1].

Examiner traps with Le Chatelier's principle

- Saying K changes when a concentration or pressure changes. Only temperature changes K.
- Saying the system "removes all" of an added substance. It only minimizes the change.
- Counting solids, liquids or aqueous species when deciding the effect of pressure. Count gas molecules only.
- Getting the temperature effect backwards: use the sign of ΔH for the **forward** reaction.
- Saying a catalyst increases the yield. It increases the rate at which equilibrium is reached.
- Writing "the equilibrium shifts to reduce the pressure" without saying it shifts to the side with fewer gas molecules.

6 Reactivity 2.3.4 — Equilibria in industry SL + HL

6.1 Yield versus rate: the compromise

Industrial chemists want a high yield *and* a fast rate at a reasonable cost. Le Chatelier's principle and kinetics sometimes point the same way, and sometimes in opposite directions. For an exothermic reaction, a low temperature gives a better equilibrium yield, but the rate is too slow; a **compromise temperature** is used, with a catalyst to keep the rate up. High pressure favours the side with fewer gas molecules and increases the rate, but it is expensive and dangerous, so a compromise pressure is used too. Unreacted gases are usually **recycled**, so the overall conversion is high even when the yield per pass is low. You do not need to memorize the conditions for any process, but you must be able to explain them.

Worked example 14 — the Haber process

Q. Ammonia is made by $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H = -93$ kJ mol^{-1}, using an iron catalyst at about 450 °C and a high pressure. Explain the choice of conditions.

pressure: 4 gas molecules → 2, so high pressure shifts the equilibrium right (more NH_3) and also increases the rate; very high pressures are too costly and dangerous, so a compromise is used

temperature: the forward reaction is exothermic, so a low temperature gives a higher equilibrium yield (larger K), but the rate would be too slow: a **moderate compromise temperature** of about 450 °C is used

catalyst: iron does not change the yield, but makes equilibrium reached quickly at this moderate temperature

concentration: NH_3 is removed by cooling it to a liquid, which pulls the equilibrium right; unreacted N_2 and H_2 are recycled

Only about 10–20 % of the gases are converted on each pass through the reactor, but recycling raises the overall conversion to about 95 %.

Worked example 15 — the Contact process

Q. In making sulfuric acid, $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $\Delta H = -198$ kJ mol^{-1}, is carried out at about 450 °C, slightly above atmospheric pressure, over a vanadium(V) oxide catalyst, with excess air. Explain these conditions.

temperature: exothermic, so a lower temperature favours SO_3, but the rate would be too slow; about 450 °C is a compromise

pressure: 3 gas molecules → 2, so high pressure would favour SO_3; but K is already large and conversion is about 99 %, so the extra cost of high pressure is not worth it

excess air (O_2): increases $[O_2]$, shifting the equilibrium right and making the more valuable SO_2 the limiting reactant

catalyst: V_2O_5 increases the rate; it does not change the yield

Worked example 16 — designing conditions for a new process ★

Q. Methanol is made by $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$, $\Delta H = -90$ kJ mol^{-1}. Suggest suitable conditions, and explain why the yield per pass and the atom economy are different measures.

high pressure (3 → 1 gas molecules), moderate compromise temperature (exothermic, but the rate must be acceptable), a catalyst, and recycling of unreacted gases

atom economy = 32.05 / (28.01 + 4.04) × 100 = **100 %**: an addition reaction with one product

but the equilibrium yield per pass is well below 100 %, because the reaction is reversible: atom economy assumes complete conversion, yield measures what is actually obtained (Reactivity 2.1)

Model answer: "Explain why the Haber process is operated at about 450 °C, although a lower temperature would give a higher equilibrium yield." (3 marks)

The forward reaction is exothermic, so a lower temperature shifts the equilibrium to the right and increases the yield (and K) [1]. But at a lower temperature fewer particles have energy ≥ E_a, so the rate is too slow to be economical [1]. A compromise temperature gives a reasonable yield at an acceptable rate, and the iron catalyst further increases the rate [1].

7 Key points to memorise

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

A Definitions

- **Dynamic equilibrium:** reached in a closed system when the rates of the forward and backward reactions are equal; concentrations stay constant.
- **Closed system:** no exchange of matter with the surroundings.
- **Position of equilibrium:** the proportions of reactants and products in the equilibrium mixture.
- **Equilibrium law:** $K = [\text{products}]^{\text{coefficients}} / [\text{reactants}]^{\text{coefficients}}$, using equilibrium concentrations; constant at a given temperature.
- **Le Chatelier's principle:** a system at equilibrium responds to a change so as to minimize the effect of the change.

B Equations and rules

- For $aA + bB \rightleftharpoons cC + dD$: $K = [C]^c[D]^d / [A]^a[B]^b$ (homogeneous reactions; no units required).
- K(reverse) = 1 / K(forward); doubled coefficients → K^2; halved → $\sqrt{K}$.
- $K \ll 1$ hardly proceeds; $K < 1$ mostly reactants; $K \approx 1$ both; $K > 1$ mostly products; $K \gg 1$ almost complete.
- Only temperature changes K: increases with T for endothermic, decreases with T for exothermic forward reactions.

C Explanations you will be asked for

- At equilibrium the reactions have not stopped; concentrations are constant but not equal.
- Concentration: adding reactant or removing product shifts right; K unchanged.
- Pressure: increase shifts towards fewer gas molecules; no effect if equal numbers; K unchanged.
- Temperature: increase favours the endothermic direction; K changes.
- Catalyst: lowers E_a of both directions equally; no change in position, yield or K; equilibrium reached faster.
- K gives the extent of reaction, not the rate. Industry uses compromise conditions, catalysts and recycling.

8 Check yourself

Use A_r values from the data booklet where needed. Marks are shown in brackets; allow about 1.2 minutes per mark. Full answers are in section 9.

Part A — Multiple choice SL + HL

1. Which statements are correct for a reaction at equilibrium? I. The forward and backward reactions both continue. II. The rates of the forward and backward reactions are equal. III. The concentrations of reactants and products are equal.

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

2. Which statement about a mixture of ice and water at equilibrium at 0 °C is **not** correct?

A The rates of melting and freezing are equal.
B The amounts of ice and water are equal.
C There is no observable change.
D Water molecules are still changing state.

3. What is the equilibrium constant expression for $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$?

A $[NO]^4[H_2O]^6 / [NH_3]^4[O_2]^5$ **B** $[NH_3]^4[O_2]^5 / [NO]^4[H_2O]^6$
C $4[NO] \times 6[H_2O] / 4[NH_3] \times 5[O_2]$ **D** $([NO] + [H_2O]) / ([NH_3] + [O_2])$

4. Which equation has the expression $K = [CO][H_2]^3 / [CH_4][H_2O]$?

A $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$
B $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$
C $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$
D $CH_4(g) + 3H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

5. At equilibrium, $[N_2O_4] = 1.62$ and $[NO_2] = 1.80$ mol dm^{-3} for $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. What is K?

A 0.500 **B** 1.11 **C** 2.00 **D** 2.22

6. K for $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ is 0.040 at a certain temperature. What is K for $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at the same temperature?

A 0.040 **B** 0.20 **C** 5.0 **D** 25

7. Which value of K shows the equilibrium mixture with the highest proportion of products?

A 1×10^{-10} **B** 1×10^{-1} **C** 1 **D** 1×10^{10}

8. Which change alters the value of K for a reaction?

A adding a catalyst
B increasing the pressure
C changing the temperature
D adding more reactant

9. Which changes shift $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$ to the right? I. adding a catalyst II. decreasing $[O_2]$ III. increasing the volume of the container

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

10. For $Br_2(g) + Cl_2(g) \rightleftharpoons 2BrCl(g)$, $\Delta H = +14$ kJ mol^{-1}, what happens when the temperature is increased?

A shifts to reactants; K decreases
B shifts to reactants; K increases
C shifts to products; K decreases
D shifts to products; K increases

11. Which equilibrium is **not** affected by a change in pressure?

A $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
B $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$
C $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
D $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

12. What is the effect of adding a catalyst to $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ at equilibrium?

A The forward rate increases and the backward rate decreases.
B The rates of the forward and backward reactions both increase.
C The value of ΔH increases.
D The yield of SO_3 increases.

13. For $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $\Delta H = -198$ kJ mol^{-1}, which conditions give the greatest **equilibrium** amount of SO_3?

A low temperature, low pressure
B low temperature, high pressure
C high temperature, high pressure
D high temperature, low pressure

14. What effect does the iron catalyst have in the Haber process?

A rate increases; amount of NH_3 increases
B rate increases; amount of NH_3 decreases
C rate increases; amount of NH_3 unchanged
D rate unchanged; amount of NH_3 increases

15. When a bottle of fizzy drink is opened, bubbles form. Which explains this for $CO_2(g) \rightleftharpoons CO_2(aq)$?

A The pressure of CO_2 above the liquid falls, so the equilibrium shifts left.
B The value of K decreases.
C The temperature of the drink rises.
D The equilibrium shifts right.

16. A reaction has $K = 3 \times 10^{20}$ at 298 K. What can be deduced?

A The reaction is very fast.
B The reaction goes almost to completion, but its rate is unknown.
C The reaction is endothermic.
D The reaction hardly proceeds.

Part B — Structured questions SL + HL

17. Some hydrogen iodide is placed in a sealed flask and heated: $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$. The purple colour of iodine appears, deepens, then stays constant.

(a) Explain, in terms of rates, why the colour stops changing. [3]

(b) State two other characteristics of the system once the colour is constant. [2]

(c) Sketch, on one set of axes, how the rates of the forward and backward reactions change with time from the start. [2]

18. Write the equilibrium constant expression for: (a) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$; (b) $N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g)$; (c) $CH_3Cl(aq) + OH^-(aq) \rightleftharpoons CH_3OH(aq) + Cl^-(aq)$; (d) fluorine and chlorine combining to form $ClF_3(g)$; (e) $NO(g)$ decomposing into its elements; (f) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$. [6]

19. Write balanced equations for the reactions with these expressions: (a) $K = [NO_2]^2 / [N_2O_4]$; (b) $K = [SO_2]^2[O_2] / [SO_3]^2$. [2]

20. A 1.50 dm^3 flask at equilibrium contains 0.0450 mol N_2O_4 and 0.0300 mol NO_2 at a certain temperature. Calculate K for $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. [3]

21. Three equilibrium mixtures for $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at the same temperature contain (in mol dm^{-3}): (1) $[H_2] = [I_2] = 0.0050$, $[HI] = 0.0339$; (2) $[H_2] = 0.0100$, $[I_2] = 0.0040$, $[HI] = 0.0429$; (3) $[H_2] = 0.0020$, $[I_2] = 0.0200$, $[HI] = 0.0429$.

(a) Calculate K for each mixture. [2]

(b) Comment on your answers. [1]

22. For $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, $K = 0.0130$ at a certain temperature. An equilibrium mixture contains $[PCl_5] = 0.0500$ and $[Cl_2] = 0.0200$ mol dm^{-3}. Calculate $[PCl_3]$. [2]

23. At 298 K, $K = 170$ for $2NO_2(g) \rightleftharpoons N_2O_4(g)$. Calculate K at 298 K for (a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$; (b) $NO_2(g) \rightleftharpoons \tfrac{1}{2}N_2O_4(g)$; (c) $\tfrac{1}{2}N_2O_4(g) \rightleftharpoons NO_2(g)$. [3]

24. At a given temperature: X, $K = 7.4 \times 10^{26}$; Y, $K = 2.7 \times 10^{-18}$; Z, $K = 0.85$.

(a) Describe the composition of the equilibrium mixture for each reaction. [3]

(b) A student says that reaction X must be the fastest. Comment. [1]

25. Pink $[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons$ blue $CoCl_4^{2-}(aq) + 6H_2O(l)$, $\Delta H > 0$.

(a) Predict and explain the colour change when concentrated hydrochloric acid is added. [2]

(b) Predict and explain the colour change when the solution is cooled in ice. [2]

26. Predict the effect of increasing the pressure on the position of each equilibrium: (a) $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$; (b) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$; (c) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$; (d) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; (e) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. [5]

27. K for a gas-phase reaction is 1.2×10^3 at 300 K, 85 at 400 K and 12 at 500 K.

(a) Deduce whether the forward reaction is exothermic or endothermic. [2]

(b) State how the equilibrium yield of product changes as the temperature rises. [1]

28. $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$, $\Delta H = +206$ kJ mol^{-1}. State the effect of each change on the position of equilibrium and on K.

(a) adding steam; (b) removing H_2; (c) increasing the pressure; (d) increasing the temperature; (e) adding a catalyst; (f) adding CO [6]

29. $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$, $\Delta H = -566$ kJ mol^{-1}. State whether the amount of CO at equilibrium increases, decreases or stays the same when:

(a) the volume is decreased; (b) O_2 is added; (c) the temperature is increased; (d) platinum catalyst is added. [4]

30. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is at equilibrium. At time *t*, extra H_2 is added at constant temperature and volume.

(a) Sketch the concentrations of N_2, H_2 and NH_3 against time, before and after *t*. [3]

(b) State the effect on *K*. [1]

31. The Haber process: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H = -93$ kJ mol^{-1}.

(a) Explain why a high pressure is used, and why it is not even higher. [2]

(b) Explain why a moderate temperature of about 450 °C is used. [3]

(c) State the effect of the iron catalyst on the yield and on the rate. [1]

(d) Predict how *K* changes as the temperature increases, and explain its significance. [2]

(e) Explain why the overall conversion is about 95 % although only 15 % is converted per pass. [1]

32. The Contact process uses $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $\Delta H = -198$ kJ mol^{-1}, at about 1–2 atm.

(a) Explain why excess air is used. [2]

(b) Suggest why a high pressure is not used, although it would favour SO_3. [1]

(c) State the effect of the vanadium(V) oxide catalyst on the equilibrium yield of SO_3. [1]

33. Oxygen dissolves in water: $O_2(g) \rightleftharpoons O_2(aq)$, $\Delta H < 0$.

(a) Explain why warm water discharged from a power station into a river can harm fish. [2]

(b) Explain why a diver breathing compressed air has more dissolved gas in the blood at depth. [1]

34. Sketch an energy profile for an exothermic reversible reaction with and without a catalyst, labelling the activation energies of the forward and backward reactions. Use it to explain why a catalyst does not change the value of *K*. [4]

35. ★ $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, $\Delta H = +181$ kJ mol^{-1}, $K = 4.5 \times 10^{-31}$ at 298 K. Explain why there is almost no NO in clean air, why NO forms in car engines, and why polluted city air often has a brownish haze. [4]

36. ★ A 2.00 dm^3 vessel at equilibrium contains 0.0200 mol SO_2, 0.0100 mol O_2 and 0.180 mol SO_3: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$. Calculate *K*, and comment on the position of equilibrium. [4]

Part A: 16 marks · Part B: 84 marks · Total: 100 marks (about 2 hours)

9 Answers

Part A

1. A. Concentrations are constant, not equal.

2. B.

3. A.

4. B.

5. C. $1.80^2/1.62 = 2.00$.

6. D. $1/0.040 = 25$.

7. D.

8. C.

9. C. A catalyst does not shift the equilibrium; a larger volume favours the side with more gas molecules.

10. D. Endothermic forward reaction.

11. B. Two gas molecules on each side.

12. B.

13. B.

14. C.

15. A.

16. B.

Part B

17. (a) At first the forward rate is high and the backward rate is zero [1]; as HI is used up the forward rate falls, and as H_2 and I_2 build up the backward rate rises [1]; when the rates become equal, $[I_2]$ stays constant, so the colour stops changing (dynamic equilibrium) [1]. (b) Any two: both reactions continue; concentrations of all species are constant (but not equal); the system is closed; the same mixture would form starting from H_2 and I_2 [2]. (c) Forward rate falling from a high value and backward rate rising from zero [1], meeting and becoming equal and constant, not zero [1].

18. One mark each: (a) $[NO_2]^2/[NO]^2[O_2]$; (b) $[N_2H_4]/[N_2][H_2]^2$; (c) $[CH_3OH][Cl^-]/[CH_3Cl][OH^-]$; (d) $3F_2 + Cl_2 \rightleftharpoons 2ClF_3$: $[ClF_3]^2/[F_2]^3[Cl_2]$; (e) $2NO \rightleftharpoons N_2 + O_2$: $[N_2][O_2]/[NO]^2$; (f) $[NO]^2[Cl_2]/[NOCl]^2$.

19. (a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ [1]. (b) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ [1].

20. $[N_2O_4] = 0.0450/1.50 = 0.0300$ mol dm^{-3}; $[NO_2] = 0.0300/1.50 = 0.0200$ mol dm^{-3} [1]; $K = (0.0200)^2/0.0300$ [1] = 0.0133 [1].

21. (a) (1) $0.0339^2/(0.0050 \times 0.0050) = 46.0$; (2) $0.0429^2/(0.0100 \times 0.0040) = 46.0$; (3) $0.0429^2/(0.0020 \times 0.0200) = 46.0$ [2]. (b) K is the same for all three, although the concentrations differ: the mixtures obey the equilibrium law at this temperature [1].

22. $[PCl_3] = K[PCl_5]/[Cl_2]$ [1] $= 0.0130 \times 0.0500/0.0200 = 0.0325$ mol dm^{-3} [1].

23. (a) $1/170 = 5.88 \times 10^{-3}$ [1]. (b) $\sqrt{170} = 13.0$ [1]. (c) $1/\sqrt{170} = 0.0767$ [1].

24. (a) X: $K \gg 1$, almost all products, goes almost to completion [1]; Y: $K \ll 1$, almost all reactants, hardly proceeds [1]; Z: $K \approx 1$, significant amounts of both [1]. (b) Incorrect: K gives the extent of reaction, not its rate [1].

25. (a) Turns blue [1]: $[Cl^-]$ increases, so the equilibrium shifts right to remove Cl^- [1]. (b) Turns pink [1]: lowering the temperature favours the exothermic backward reaction, so the equilibrium shifts left [1].

26. (a) Shifts left (2 → 3 gas molecules) [1]. (b) Shifts right (3 → 1) [1]. (c) No shift (2 → 2) [1]. (d) Shifts left (0 → 1 gas molecule) [1]. (e) Shifts left (1 → 2) [1].

27. (a) K decreases as the temperature increases [1], so a higher temperature favours the backward reaction: the forward reaction is exothermic [1]. (b) It decreases [1].

28. One mark each: (a) right, K unchanged; (b) right, unchanged; (c) left (2 → 4 gas molecules), unchanged; (d) right, K increases; (e) no shift, unchanged; (f) left, unchanged.

29. (a) Decreases (shift to fewer gas molecules) [1]. (b) Decreases [1]. (c) Increases (exothermic forward reaction, so shift left) [1]. (d) Stays the same [1].

30. (a) $[H_2]$ jumps up at t, then falls gradually [1]; $[N_2]$ falls gradually from t (no jump) [1]; $[NH_3]$ rises gradually, then all three level off at new constant values [1]. (b) No change [1].

31. (a) 4 gas molecules → 2, so high pressure shifts the equilibrium right (and increases the rate) [1]; higher pressures need expensive, strong equipment and more energy, and are more dangerous [1]. (b) Exothermic, so a low temperature gives a higher equilibrium yield [1]; but the rate would be too slow [1]; 450 °C is a compromise giving a reasonable yield at an acceptable rate [1]. (c) No effect on the yield; increases the rate [1]. (d) K decreases, so the equilibrium yield of NH_3 falls at higher temperature [2]. (e) Ammonia is removed and unreacted N_2 and H_2 are recycled through the reactor [1].

32. (a) A higher $[O_2]$ shifts the equilibrium to the right [1], so more of the SO_2 is converted (O_2 from air is cheap) [1]. (b) The conversion is already very high (about 99 %), so the extra cost of high pressure is not justified [1]. (c) None: it increases the rates of both reactions equally, so equilibrium is reached faster but the yield is unchanged [1].

33. (a) Dissolving is exothermic, so a higher temperature shifts the equilibrium left [1]; less oxygen is dissolved, so fish may not get enough [1]. (b) The higher pressure at depth shifts the gas-solution equilibrium to the right, so more gas dissolves [1].

34. Exothermic profile with products below reactants [1]; lower catalysed curve with the same start and end [1]; E_a(forward) and E_a(backward) labelled for both [1]; both are lowered by the same amount, so both rates increase by the same factor and K (and the position of equilibrium) is unchanged [1].

35. K is extremely small at 298 K, so the equilibrium lies far to the left and the reaction is also very slow [1]; the reaction is endothermic, so at the very high temperatures in an engine K is much larger and NO forms quickly [1]; the NO is released before it can decompose [1]; in air it reacts with oxygen to form brown NO_2 ($2NO + O_2 \rightarrow 2NO_2$) [1].

36. $[SO_2] = 0.0100$, $[O_2] = 0.00500$, $[SO_3] = 0.0900$ mol dm^{-3} [1]; $K = [SO_3]^2/[SO_2]^2[O_2]$ [1] $= 0.0900^2/(0.0100^2 \times 0.00500) = 1.62 \times 10^4$ [1]; $K \gg 1$, so the equilibrium lies far to the right [1].

Where this fits in Reactivity 2

- **Booklets 1–2** — Reactivity 2.1: how much? **Booklets 3–4** — Reactivity 2.2: how fast? **Booklet 5 (this booklet)** — Reactivity 2.3.1–2.3.4 (SL + HL): how far? Dynamic equilibrium, the equilibrium law and Le Chatelier's principle.
- **Next (HL):** Reactivity 2.3.5 onwards: the reaction quotient Q and calculating equilibrium concentrations. **Later:** Reactivity 3.1 applies K to weak acids and bases.

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