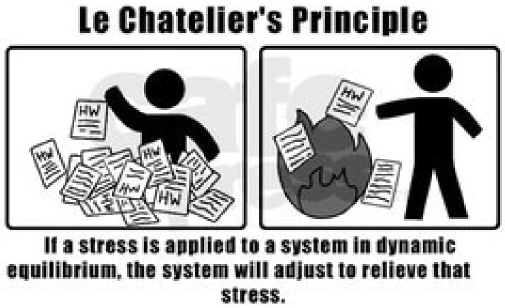
UNIT 3 & 4 CHEM

Name: ____________________

TOPIC 1: EQUILIBRIUM



Syllabus dot-points

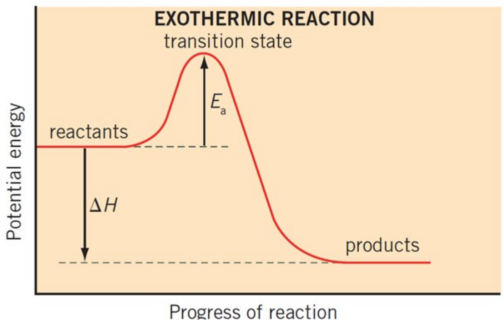
Science Understanding:

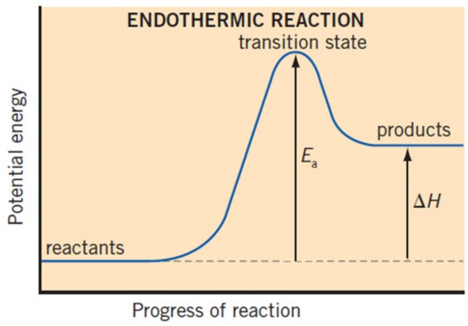
- ☐ collision theory can be used to explain and predict the effects of concentration, temperature, pressure, the presence of catalysts and surface area of reactants on the rates of chemical reactions
- ☐ chemical systems include physical changes and chemical reactions and may be open (which allow matter and energy to be exchanged with the surroundings) or closed (which allow energy, but not matter, to be exchanged with the surroundings)
- ☐ observable changes in chemical reactions and physical changes can be described and explained at an atomic and molecular level
- ☐ over time, in a closed system, reversible physical and chemical changes may reach a state of dynamic equilibrium, with the relative concentrations of products and reactants defining the position of equilibrium
- ☐ the characteristics of a system in dynamic equilibrium can be described and explained in terms of reaction rates and macroscopic properties
- ☐ the reversibility of chemical reactions can be explained in terms of the activation energies of the forward and reverse reactions
- ☐ the effects of changes in temperature, concentration of species in solution, partial pressures of gases, total volume and the addition of a catalyst on equilibrium systems can be predicted using Le Châtelier's Principle
- ☐ the effects of changes in concentration of solutions and partial pressures of gases on chemical systems initially at equilibrium can be predicted and explained by applying collision theory to the forward and reverse reactions
- ☐ the effect of changes of temperature on chemical systems initially at equilibrium can be predicted by considering the enthalpy changes for the forward and reverse reactions; this can be represented on energy profile diagrams and explained by the changes in the rates of the forward and reverse reactions
- ☐ equilibrium law expressions can be written for homogeneous and heterogeneous systems; the equilibrium constant (K), at any given temperature, indicates the relationship between product and reactant concentrations at equilibrium
- ☐ the relative amounts of reactants and products (equilibrium position) can be predicted qualitatively using equilibrium constants (K_c)
- ☐ reagents and reaction conditions are chosen to optimise yield and rate for chemical synthesis processes, including in the production of ammonia (Haber process), sulfuric acid (Contact process)

REACTION RATES

Collision theory: In order for particles to react, they need to collide with correct orientation and sufficient energy to overcome the activation energy.

Energy profile diagrams:

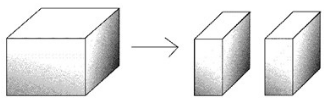




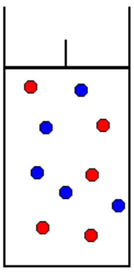
FACTORS AFFECTING REACTION RATES

Concentration Affects number of collisions

Surface area Affects number of collisions

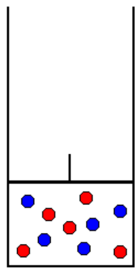


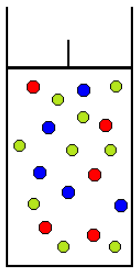
Pressure of gas Depends on how change in pressure was achieved



← Control / Comparison

(Red gas reacts with blue gas)

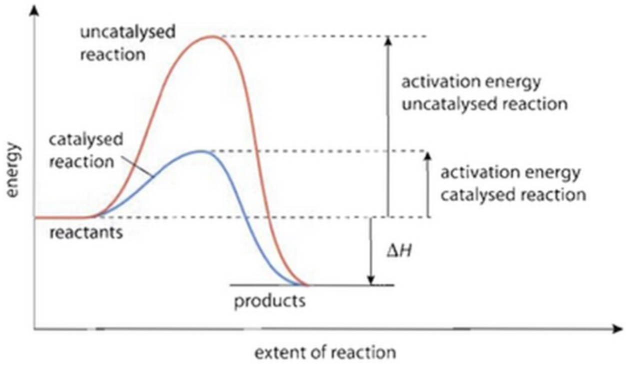


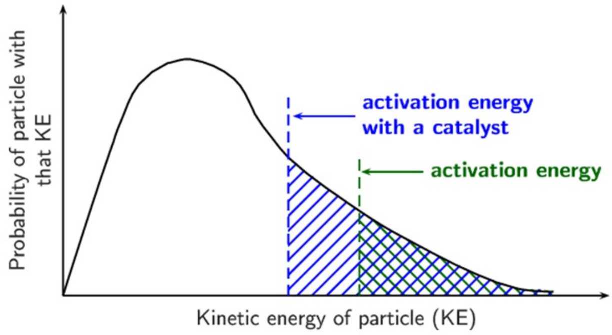


Method for changing pressure	Decrease volume	Add inert gas (green)
Effect on **total** pressure	Increase	Increase
Effect on **partial pressure of reactants**	Increase	**No change**
Effect on **collisions** between **reactants**	Increase	**No change**
Effect on reaction rate	Increase	**No effect**

This is an important distinction and will be relevant later when discussing equilibrium.

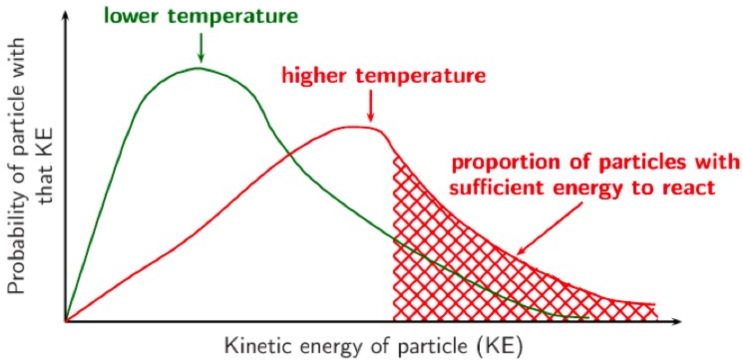
Catalysts Provide an alternate reaction pathway which lowers the activation energy for the reaction. This means a greater proportion of particles have sufficient energy to overcome the activation energy.





Temperature (1) Increases average kinetic energy of particles. More particles have sufficient energy to overcome E_a.

(2) Particles move faster, therefore more collisions



Exam techniques:

- In written answers:
  - Identify the factors affecting reaction rate
  - Incorporate collision theory as part of your answer. Explicitly use the word "collisions".
  - Consider sketching graphs as part of your answer, particularly in extended-answer type questions

- In energy profile diagrams:
  - Common in questions where effect of catalyst needs to be shown
  - Recognise if the reaction is exothermic (-ΔH) or endothermic (+ΔH) and draw correct graph
  - Label the axes correctly. The Y-axis is **<u>Enthalpy</u>** and the units are **<u>kJ mol^{-1}</u>**. Common to see errors here.
  - Label ΔH and Ea

Question 31 **(6 marks)**

Most modern cars are powered by an engine with a 4-stroke combustion cycle. The purpose of each stroke is described below.

1. Intake stroke - the fuel is injected in as a fine mist, where it mixes with air
2. Compression stroke - the fuel/air mixture is compressed into a small volume
3. Combustion stroke - a spark plug ignites the fuel/air mixture, which explodes
4. Exhaust stroke - exhaust fumes leave through the valve

Explain, in terms of the collision theory, how each of the conditions described in **stroke 1, 2 and 3** affect the rate of reaction between the fuel and the air.

Question 28 **(7 marks)**

Consider the following reaction:

$$CO_2(g) + NO(g) \rightarrow CO(g) + NO_2(g) \qquad \Delta H = +\ 226\ kJ\ mol^{-1},\ E_a = 360\ kJ$$

(a) On the axes below draw a potential energy diagram for this reaction. Label the activation energy (E_a) and enthalpy change (ΔH) for the reaction. Include a scale on the vertical axis.

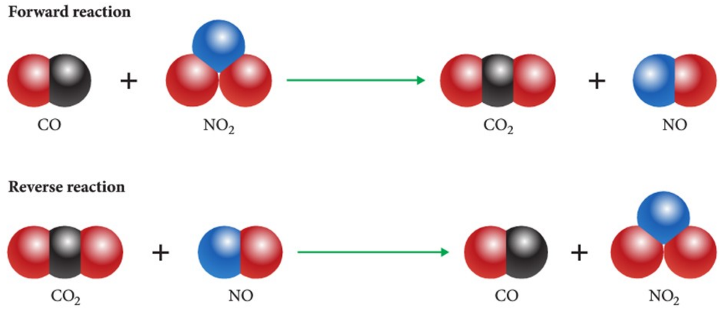
On the same axes, use a dashed line to show a possible catalysed pathway. (5 marks)

REVERSIBLE REACTIONS

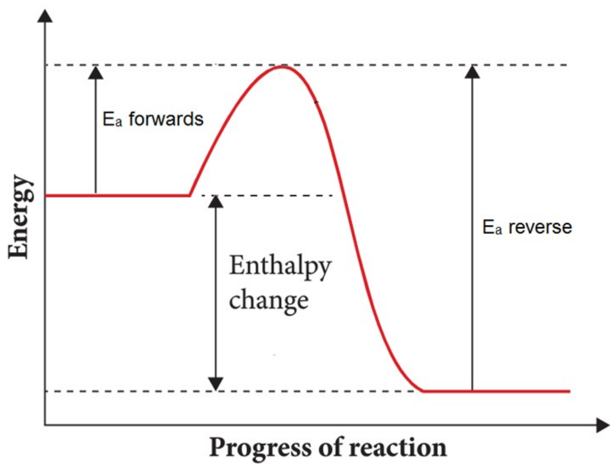
A reversible reaction is a reaction where:

- Reactants form products
- Products form reactants

$$CO + NO_2 \rightleftharpoons CO_2 + NO$$



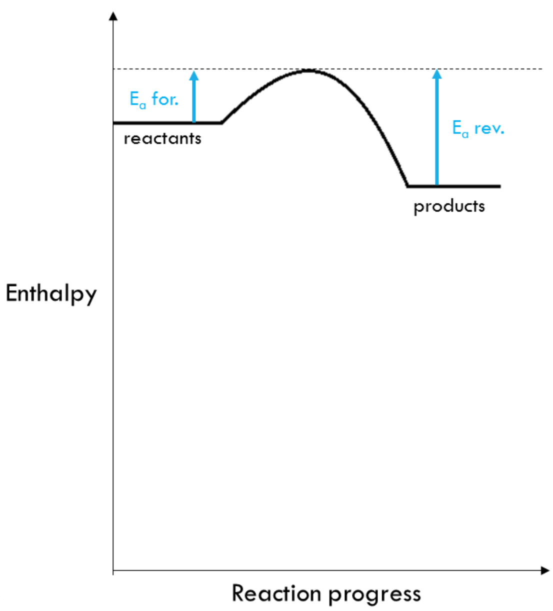
Reversible reactions and energy profile diagrams:

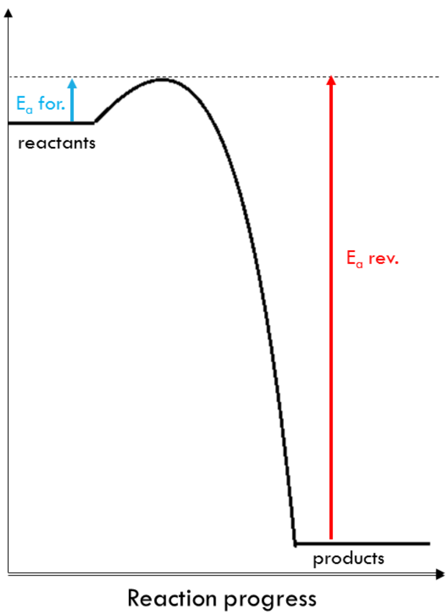


Key features:

- *Forwards reaction is exothermic*
- *Reverse reaction is endothermic*
- *Values of $\Delta H_{forwards}$ and $\Delta H_{reverse}$ will be opposite*
- *Each reaction has a different activation energy*

REVERSIBLE VS IRREVERSIBLE





If the E_a of the reverse reaction is extremely large then the reverse reaction is very unlikely to occur.

∴ irreversible reaction

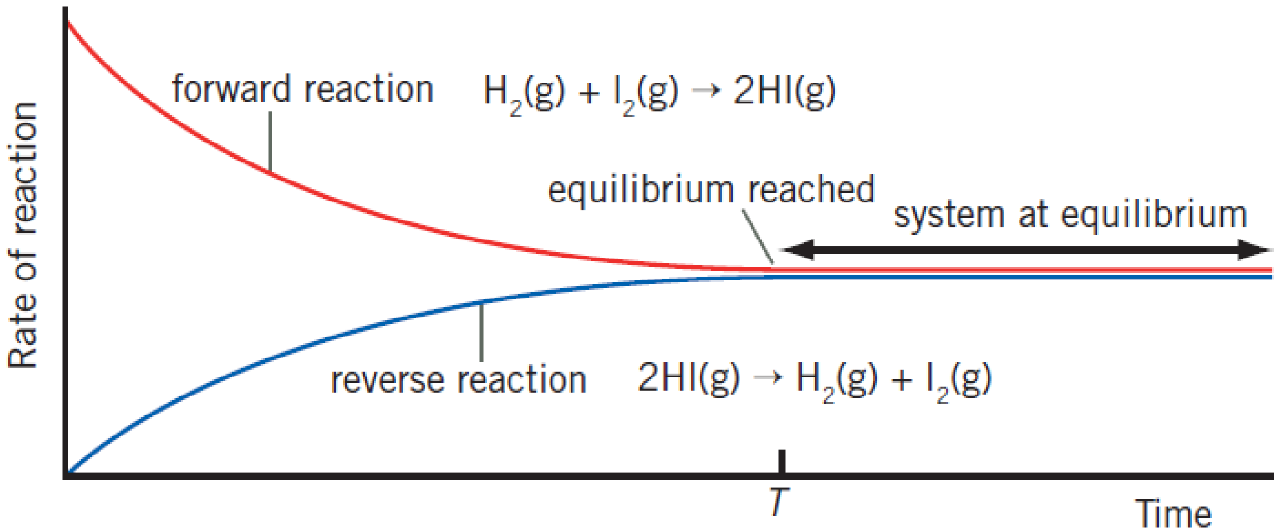
CHARACTERISTICS OF DYNAMIC EQUILIBRIUM

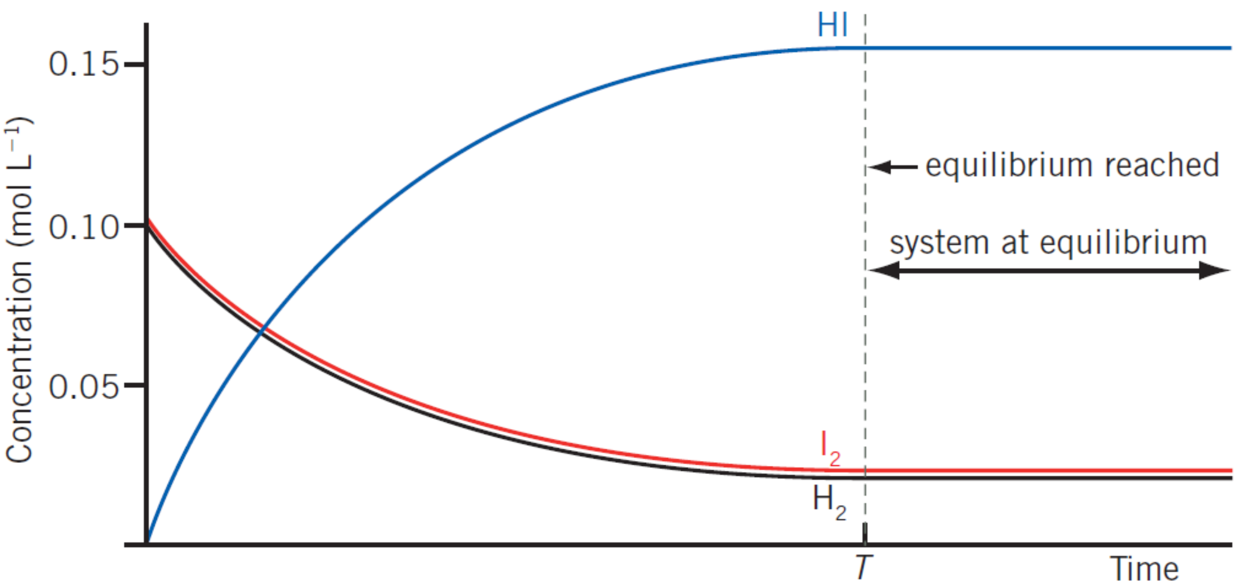
When a system is in **dynamic equilibrium**:

- The rates of forwards and reverse reactions are equal
- The concentrations of reactants and products are constant*
- The macroscopic properties are constant
  - Colour of mixture
  - Mass of solid
  - Pressure of gas

* Constant means unchanging. It doesn't mean equal (to each other). Be very careful with language here.

GRAPHING DYNAMIC EQUILIBRIUM





Explain, using collision theory, what is happening in the system on the left from time=0 to time=T.

Explain the shape of the graph after time=T.

Measure (in cm) the height that the following concentration lines decreased or increased from time=0 to time=T.

- Decrease in [I_2] = ______________ cm

Note: square brackets is shorthand for concentration. [I_2] means "concentration of I_2"

- Decrease in [H_2] = ______________ cm
- Increase in [HI] = ______________ cm

Why do [I_2] and [H_2] decrease at the same rate as each other?

What is significant about the increase in [HI] relative to the decrease in [I_2] and [H_2]? How can this be explained?

HI(g) and H_2(g) are both colourless, and I_2(g) is purple. What would be observed in this mixture throughout the different stages of the experiment? Justify your answer.

Sample Questions

2008 TEE Exam (Question 22):

Consider the following system, which is at equilibrium:

$$C_2H_4(g) + HC\ell(g) \rightleftharpoons CH_3CH_2C\ell(g) \qquad \Delta H = -70 \text{ kJ mol}^{-1}$$

Which one of the following statements about the system is true?

a) The rate of the forward reaction and the rate of the reverse reaction are zero?
b) The concentrations of the reactants will remain constant over time
c) The concentration of C_2H_4 will equal the concentration of $CH_3CH_2C\ell$
d) The sum of the concentrations of C_2H_4 and $HC\ell$ will equal the concentration of $CH_3CH_2C\ell$

2011 WACE Exam (Question 12):

Which of the following properties are characteristic of a gaseous system in dynamic chemical equilibrium?

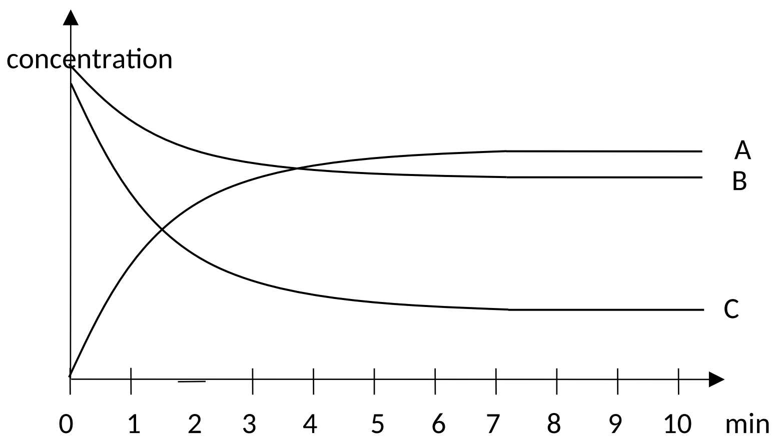
i. The concentrations of reactants are equal to the concentration of products
ii. The concentrations of reactants and products are constant
iii. The rate of the forward reaction is equal to the rate of the reverse reaction
iv. The pressure of the system is constant

a) (i), (ii) and (iii)
b) (i), (ii) and (iv)
c) (ii), (iii) and (iv)
d) (iii) only

Misc. question:

The graph below shows the change in concentration for gases present over a period of time for the reaction that occurs when sulfur dioxide is burnt in oxygen in a closed system.

Reaction: $2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3$; $\Delta H = -99 \text{ kJ mol}^{-1}$



a) Identify which substances are represented by the lines… A: ________ B: ________ C: _________

b) At what point was equilibrium reached? ________________________________

Justify your answer. ____

____

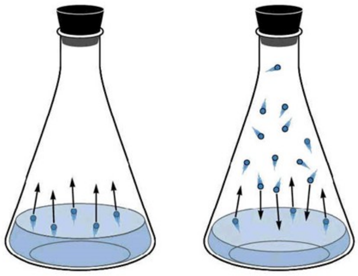
PHYSICAL EQUILIBRIUM

Physical change: A change where no new substances are formed
Chemical change: A change that produces new substances

Vapour Pressure

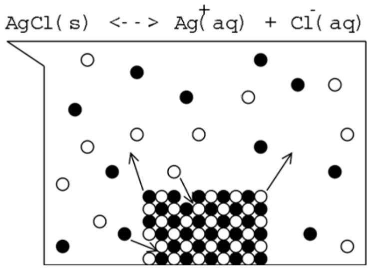
Explain how the diagram shows equilibrium.

Write an equation for this reaction.



Saturated solutions

The diagram to the right shows a saturated solution of silver chloride. Would it be right to say that a solutes stops dissolving in saturated solutions? Explain.



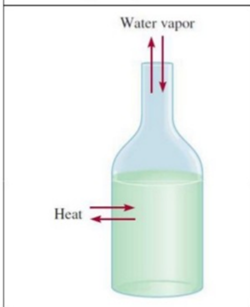
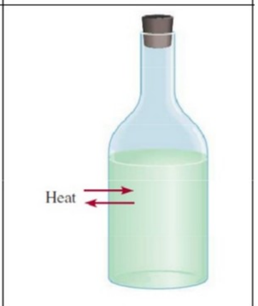
DO ALL SYSTEMS FORM EQUILIBRIUM?

For a system to form dynamic equilibrium there need to be two conditions:

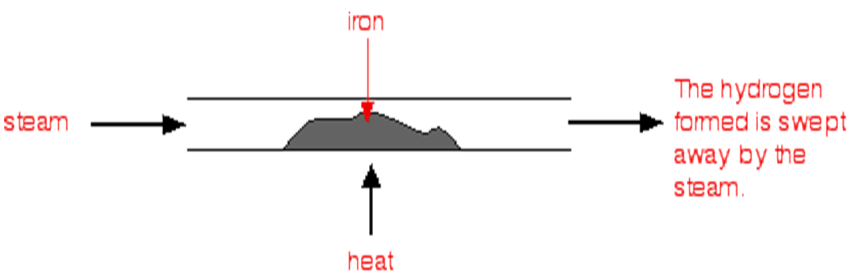
- **1)** The reaction is *reversible*
- **2)** The system is *closed*

Open system:
A chemical system in which substances are able to enter or leave

Closed system:
A chemical system in which no substances are able to enter or leave

Open system	Closed system
	
An ***open system*** *can exchange mass and energy, usually in the form of heat with its surroundings*	***closed system,*** *which allows the transfer of energy (heat) but not mass.*

Example: $3\ Fe(s) + 4\ H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4\ H_2(g)$



By passing steam over the iron you can form Fe_3O_4. The hydrogen is swept away by the steam. Although the reaction is theoretically reversible, the H_2 is removed before it can react with the Fe_3O_4. This is an **<u>open system</u>** and it will ***<u>not</u>*** reach equilibrium.

CHANGES TO CONCENTRATION

In this experiment we will investigation how **concentration** affects the equilibrium between potassium chromate (K_2CrO_4) and potassium dichromate ($K_2Cr_2O_7$).

These two species exist in equilibrium with each other:

$$\mathbf{2\ CrO_4^{2-} + 2\ H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O}$$

yellow orange

Method:

1. Place about 1 mL of 0.1 mol L^{-1} K_2CrO_4 into each of two test tubes and note the colour of the solution. Use one of the test tubes for comparison of colours.
2. Place about 1 mL of 0.1 mol L^{-1} $K_2Cr_2O_7$ into each of two test tubes and note the colour of the solution. Use one of the test tubes for comparison of colours.

Reactions of potassium chromate:

3. To one of the test tubes of $KCrO_4$ add 0.2 mol L^{-1} HCℓ dropwise until a colour change is noted
4. To the same solution now add 0.2 mol L^{-1} NaOH dropwise until another colour change is noted.

Reactions of potassium dichromate:

5. To one of the test tubes of $K_2Cr_2O_7$ add 0.2 mol L^{-1} NaOH dropwise until a colour change is observed.
6. To the same solution now add 0.2 mol L^{-1} HCℓ dropwise until another colour change is noted.

Results:

Initial solution	**Change**	**Observation**	**Inference**
Potassium chromate (K_2CrO_4)	Add HCℓ		
	then add NaOH		
Potassium dichromate ($K_2Cr_2O_7$)	Add NaOH		
	then add HCℓ		

Question:

What evidence is there that the system is in dynamic equilibrium prior to adding HCℓ or NaOH?

What evidence is there that adding HCℓ or NaOH temporarily disrupts equilibrium?

LE CHÂTELIER'S PRINCIPLE

Le Châtelier's principle is a useful tool for **predicting** the effects of changes to systems at equilibrium.

It states:

"If a system at equilibrium is subject to a change in conditions, then the system will behave in such a way as to partially counteract the change."

Le Châtelier's principle **predicts how** a system will react, but does not **explain why** the system reacts in such a way. To explain in written answers you will need to use collision theory.

APPLYING L.C.P. TO CONCENTRATION

$$2\ CrO_4^{2-} + 2\ H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

Imposed change: Adding HCℓ increased the $[H^+]$ *$[H^+]$ = concentration of H^+*

↓

Effect: The system shifted to the ______________ to ______________ the $[H^+]$

LEFT/RIGHT INCREASE/DECREASE

This caused the [____________] to increase, ∴ solution became more _______________

ORANGE/YELLOW

$$2\ CrO_4^{2-} + 2\ H^+ \rightleftharpoons Cr_2O_7^{2-}\ +\ H_2O$$

Imposed change: Adding NaOH decreased the $[H^+]$

Effect: The system shifted to the ______________ to ______________ the $[H^+]$

LEFT/RIGHT INCREASE/DECREASE

This caused the [____________] to increase, ∴ solution became more _______________

ORANGE/YELLOW

APPLYING L.C.P. TO CONCENTRATION

Important notes about changes in concentration:

- Changes in concentration relate to aqueous and gaseous species
- Adding a liquid does not change its concentration and will not affect equilibrium*
- Adding an insoluble solid does not change its concentration and will not affect equilibrium

* If you add H_2O to a system with dissolved ions, you won't change the concentration of the water itself, but you *will* change the concentration of substances dissolved in the water. We will look at this advanced example later.

Complete the following tables for the changes shown. For each change show:

- the direction of shift (*left, right* or *no change)*
- a comparison of the concentration of species at the new equilibrium compared to the old equilibrium *(increased, decrease* or *no change)*

Equation: $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$

pale yellow — clear — reddish-brown

Change	Direction of shift	Concentration of species at new equilibrium			Observations
		Fe^{3+}	SCN^{-}	$FeSCN^{2+}$	
Add some additional $Fe^{3+}(aq)$					

Equation: $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$

pale yellow — clear — reddish-brown

Change	Direction of shift	Concentration of species at new equilibrium			Observations
		Fe^{3+}	SCN^{-}	$FeSCN^{2+}$	
Add some additional $SCN^{-}(aq)$					

Equation: $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$

pale yellow — clear — reddish-brown

Change	Direction of shift	Concentration of species at new equilibrium			Observations
		Fe^{3+}	SCN^{-}	$FeSCN^{2+}$	
Add some F^{-} reacts with Fe^{3+} to form FeF_6^{3-}					

Equation: $3\,Cu(s) + 2\,NO_3^{-}(aq) + 8\,H^{+}(aq) \rightleftharpoons 3\,Cu^{2+}(aq) + 2\,NO(g) + 4\,H_2O(\ell)$

Change	Direction of shift	Concentration of species at new equilibrium			
		$[NO_3^{-}]$	$[H^{+}]$	$[Cu^{2+}]$	[NO]
Add some concentrated HCℓ					

Equation: $3\,Cu(s) + 2\,NO_3^{-}(aq) + 8\,H^{+}(aq) \rightleftharpoons 3\,Cu^{2+}(aq) + 2\,NO(g) + 4\,H_2O(\ell)$

Change	Direction of shift	Concentration of species at new equilibrium			
		$[NO_3^-]$	$[H^+]$	$[Cu^{2+}]$	$[NO]$
Dissolve some $CuSO_4(s)$					

Equation: $3\ Cu(s) + 2\ NO_3^-(aq) + 8\ H^+(aq) \rightleftharpoons 3\ Cu^{2+}(aq) + 2\ NO(g) + 4\ H_2O(\ell)$

Change	Direction of shift	Concentration of species at new equilibrium			
		$[NO_3^-]$	$[H^+]$	$[Cu^{2+}]$	$[NO]$
Add 5 drops of concentrated KOH					

Equation: $3\ Cu(s) + 2\ NO_3^-(aq) + 8\ H^+(aq) \rightleftharpoons 3\ Cu^{2+}(aq) + 2\ NO(g) + 4\ H_2O(\ell)$

Change	Direction of shift	Concentration of species at new equilibrium			
		$[NO_3^-]$	$[H^+]$	$[Cu^{2+}]$	$[NO]$
Add more copper metal to the container					

Equation: $3\ Cu(s) + 2\ NO_3^-(aq) + 8\ H^+(aq) \rightleftharpoons 3\ Cu^{2+}(aq) + 2\ NO(g) + 4\ H_2O(\ell)$

Change	Direction of shift	Concentration of species at new equilibrium			
		$[NO_3^-]$	$[H^+]$	$[Cu^{2+}]$	$[NO]$
Open the container to let out the NO(g) and then close it again					

CHANGES TO CONCENTRATION

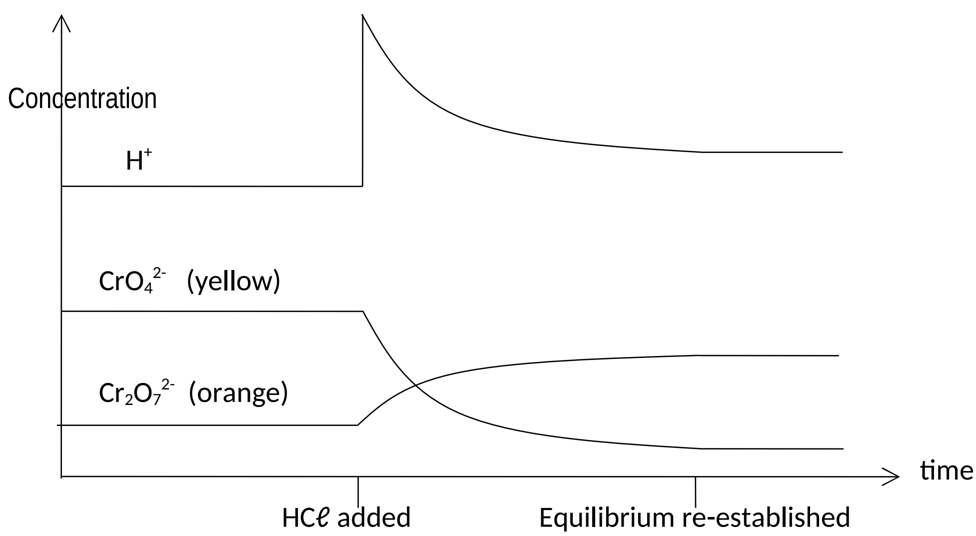
Use collision theory to **explain** the change that occurs when HCℓ is added to chromate/dichromate.

$$2\ CrO_4^{2-} + 2\ H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

yellow orange

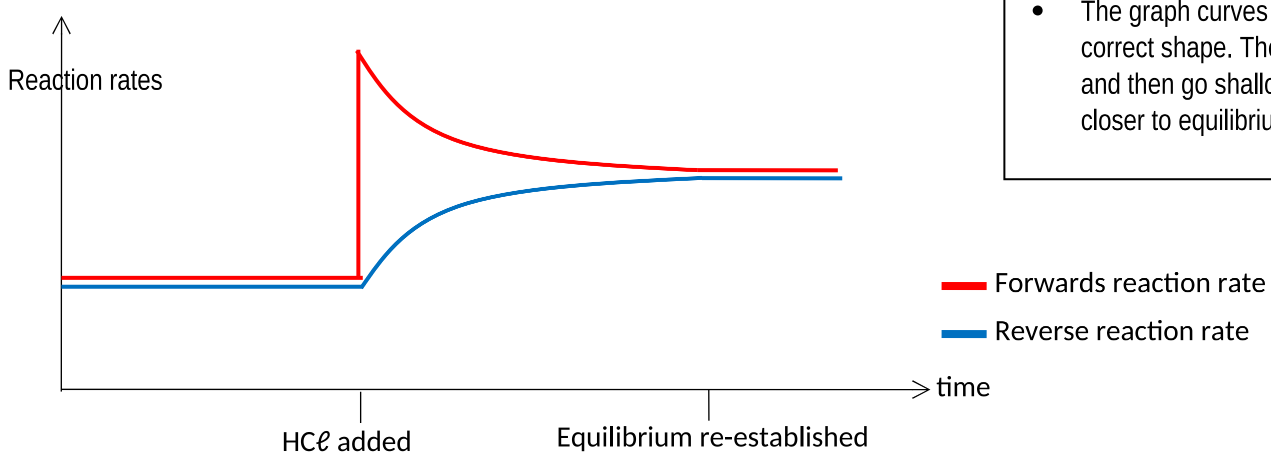
- Adding HCℓ increases the $[H^+]$. This increases the rate of **forwards reaction** due to more collisions between H^+ and CrO_4^{2-}.
- The system is no longer at equilibrium because **forwards rate** > **reverse rate**.
- Over time, this leads to [reactants] decreasing and [products] increasing, causing **forwards rate** to decrease and **reverse rate** to increase until equilibrium is re-established
- The colour change from yellow to orange is due to increasing $[Cr_2O_7^{2-}]$ as equilibrium is re-established

These changes can be represented using concentration-time and rate-time graphs.



Pay attention to the following:

- There is an <u>initial change</u> (sudden spike in $[H^+]$) followed by a <u>change over time</u> as equilibrium is re-established
- The concentration of H^+ only <u>partially</u> decreases as equilibrium is restored. It doesn't reach its original value.
- The graph shows the correct **mole ratio**. The H^+ and CrO_4^{2-} lines decrease twice as much as $Cr_2O_7^{2-}$ increases.
- The graph curves need to be to correct shape. They start of steep and then go shallower as it gets closer to equilibrium.



Addition of NaOH to potassium dichromate solution. $2\ CrO_4^{2-} + 2\ H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$

Explain the colour change observed when NaOH was added to the potassium dichromate solution. Include a diagram of concentration and reaction rates as part of your answer.

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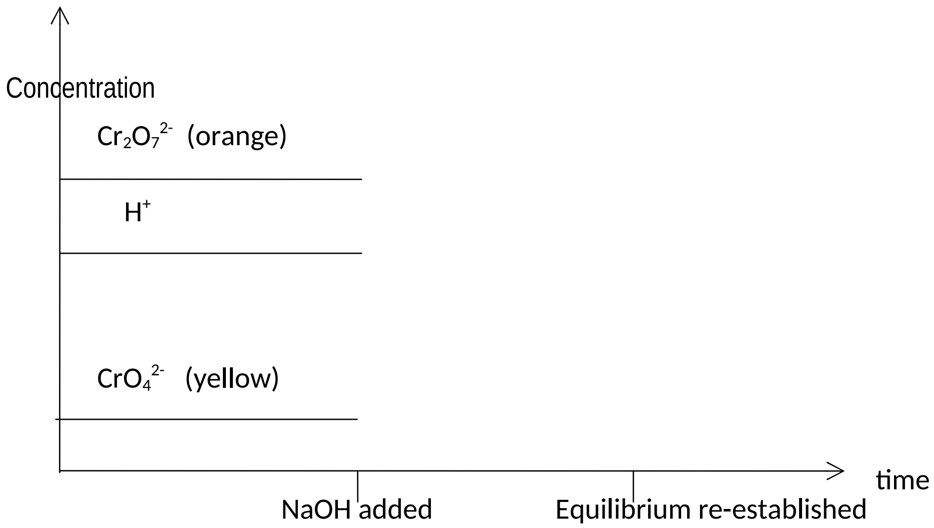
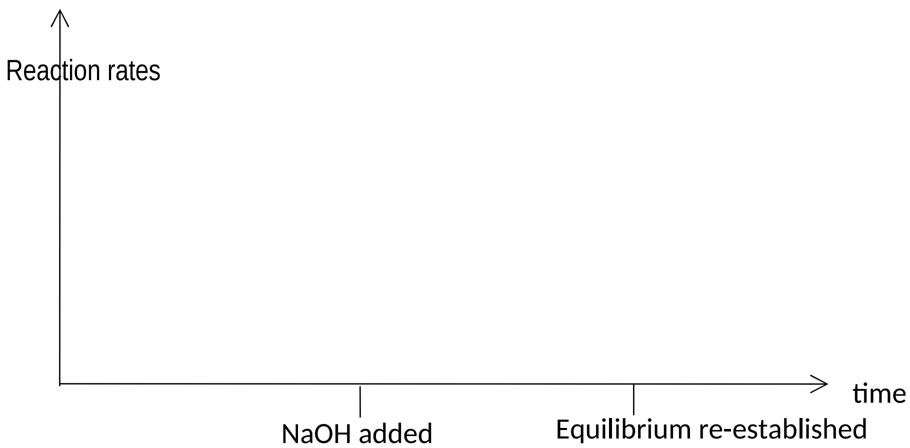


Order for drawing the graphs:

1. What is the **initial** change in concentration?
2. What is the **initial** (immediate) effect of this change on forward **and/or** reverse reaction rate?
3. What will happen to the forward and reverse reaction rates as equilibrium is re-established?
4. What will happen to the concentrations of the reactants and products as equilibrium is re-established? *(Hint: Look at which reaction rate is faster in the graph underneath…)*
5. Double check mole ratios and curve shapes.



Forwards reaction rate
Reverse reaction rate

Changes to Concentration:

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

(colourless) **(red)**

A solution of Fe^{3+}/SCN^{-}/$FeSCN^{2+}$ is initially at equilibrium. The solution is a pale red colour.
Explain what would happen if a soluble salt containing **$FeSCN^{2+}$ ions** was added to the water.

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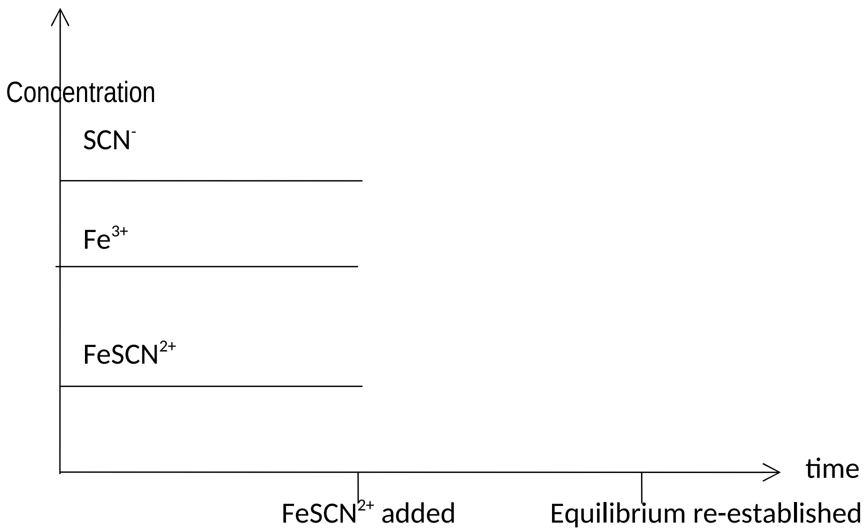

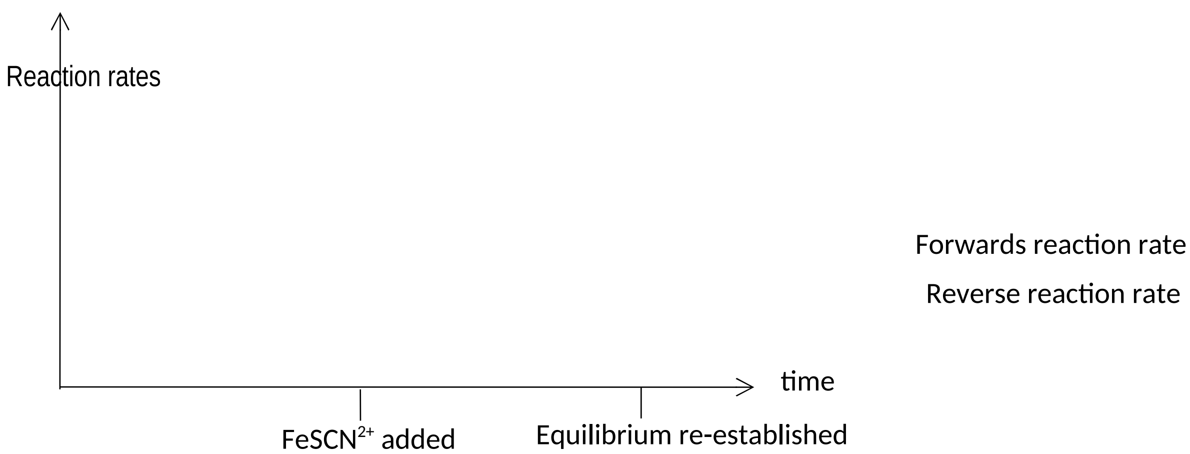

Changes to Concentration:

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

(colourless) **(red)**

A solution of $Fe^{3+}/SCN^{-}/FeSCN^{2+}$ is initially at equilibrium. The solution is a pale red colour.
Explain what would happen if drops of concentrated **potassium hydroxide** were added to the water.

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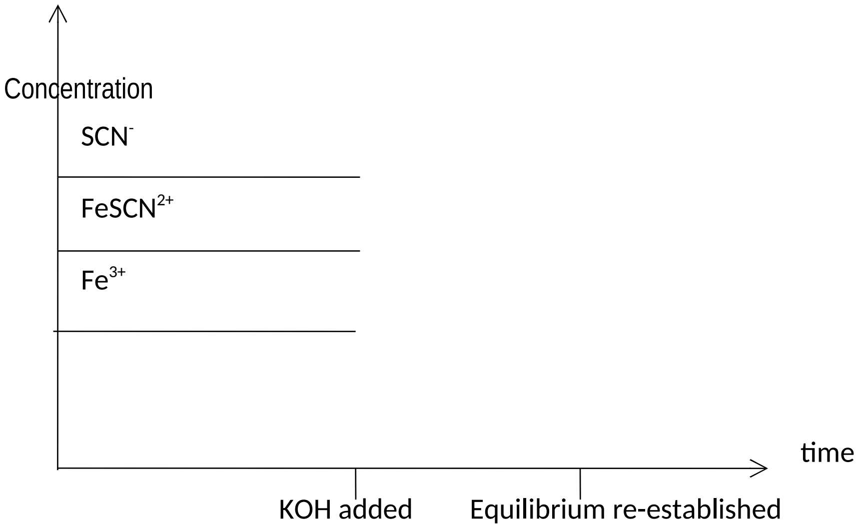
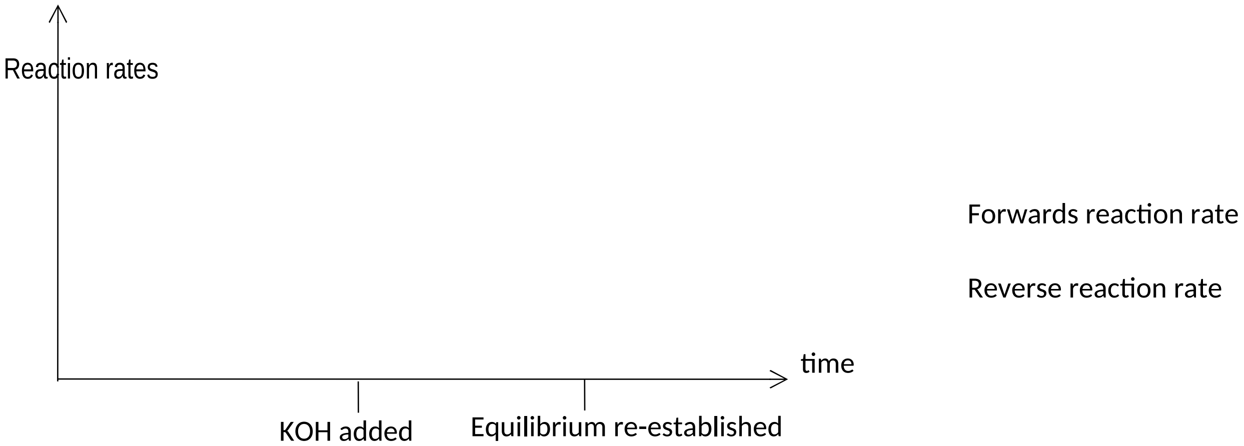




DILUTING SOLUTIONS

If water is added to a system with multiple (aq) substances, it will decrease the concentration of <u>**all**</u> aqueous species.

Le Châtelier's principle predicts the reaction will favour whichever side produces more moles of (aq) as this will <u>increase</u> the overall concentration of ions.

If both sides of the equation have equal moles of (aq), then the reaction will not shift. These reactions remain at equilibrium when diluted.

Example: $$\underbrace{PbI_2(s)}_{\text{0 moles (aq)}} \rightleftharpoons \underbrace{Pb^{2+}(aq) + 2\,I^-(aq)}_{\text{3 moles (aq)}}$$

Prediction of shift: Diluting a saturated solution of lead(II) iodide causes the reaction to shift right, as the R.H.S. has more moles of aqueous substances (3 mol vs 0 mol).

Observation: More of the yellow solid dissolves

Predict how the following systems would be affected by addition of water:

Reaction	Moles of aqueous substances		Direction of shift when diluted
	L.H.S.	R.H.S.	
$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$			
$[Cu(H_2O)_6]^{2+}(aq) + 4\,C\ell^-(aq) \rightleftharpoons [CuC\ell_4]^{2-}(aq) + 6\,H_2O(\ell)$			
$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$			
$H_2O(\ell) \rightleftharpoons H_2O(g)$			
$CO_2(g) + NaOH(aq) \rightleftharpoons NaHCO_3(aq)$			
$Cu(s) + 2\,Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2\,Ag(s)$			
$2\,FeC\ell_3(aq) + SnC\ell_2(aq) \rightleftharpoons 2\,FeC\ell_2(aq) + SnC\ell_4(aq)$			

CHANGES TO PARTIAL PRESSURE

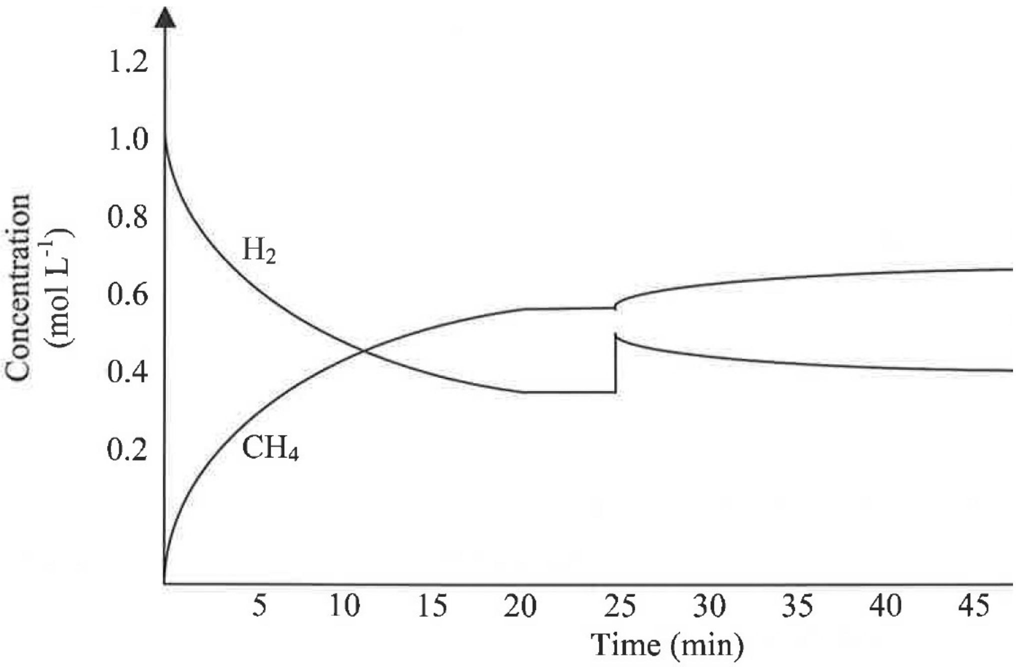
'Partial pressure' refers to the pressure of an individual gas within a mixture.
It is changed by adding or removing the gas from the mixture.

A change to the partial pressure of a gas is effectively the same as a change in concentration. It can be explained in terms of collision theory using very similar terminology.

Example:
The reaction between carbon and hydrogen gas to form methane can be presented by the following equation.

$$C(s) + 2\,H_2(g) \rightleftharpoons CH_4(g) + 75\text{ kJ}$$

The concentrations of hydrogen and methane were plotted over time and the following graph produced.



Q: At what time did the reaction (first) reach equilibrium? Justify your answer.

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Q: What could have caused the change at occurred after 25 minutes?

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Q: Explain the change in shape from t=25 to t=45.

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Changes to Partial Pressure: $I_2(g) + H_2(g) \rightleftharpoons 2\ HI(g)$

(purple) **(colourless)**

Use **collision theory** to **explain** the changes that occur when additional $I_2(g)$ is added to the container.

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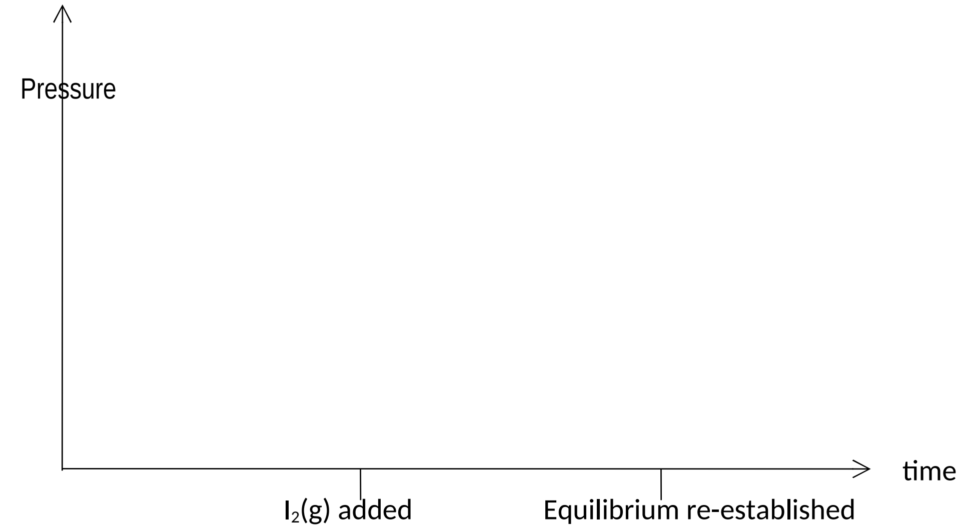

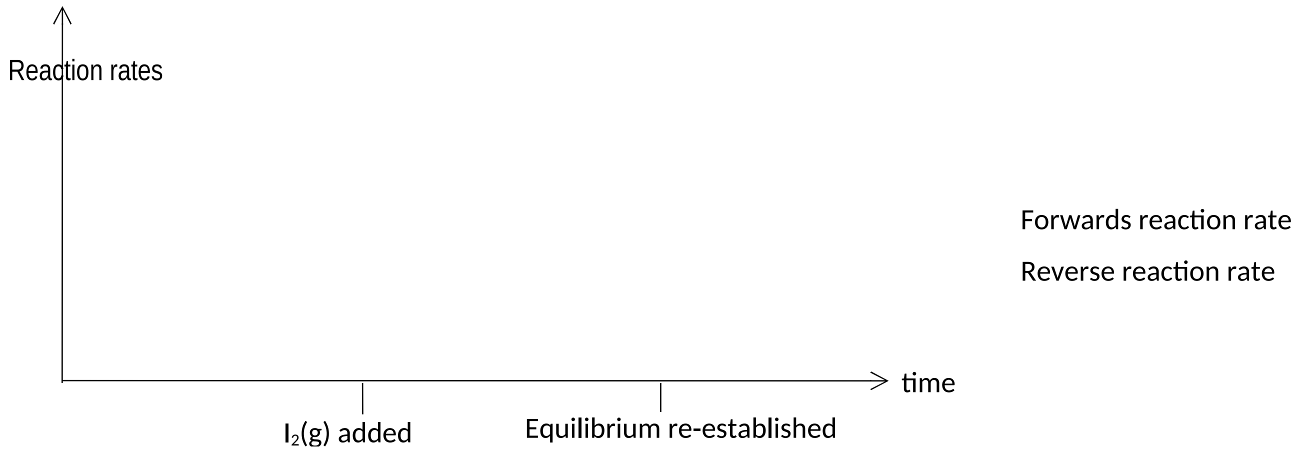

Describe observations for the system over this time period.

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CHANGES TO PRESSURE – SIZE OF CONTAINER

Changing the size of a container will change the partial pressures of **all** gaseous substances.

If you **reduce the size** of the container you will **increase overall pressure**.

Le Châtelier's principle predicts the system will oppose this change by favouring the side of the reaction with the **least moles of gas.**

If you **increase the size** of the container you will **decrease overall pressure**.

Le Châtelier's principle predicts the system will oppose this change by favouring the side of the reaction with the **most moles of gas**.

Example #1: $$\underbrace{3\ H_2(g) + N_2(g)}_{\text{4 moles of gas}} \rightleftharpoons \underbrace{2\ NH_3(g)}_{\text{2 moles of gas}}$$

Change: Decrease the volume of the container, causing overall pressure to increase

Effect: According to Le Châtelier's principle, the system will shift in a way to reduce overall pressure. Reaction would shift right as the R.H.S. has less moles of gas (2 mol vs. 4 mol).

Example #2: $$\underbrace{N_2(g) + O_2(g)}_{\text{2 moles of gas}} \rightleftharpoons \underbrace{2\ NO(g)}_{\text{2 moles of gas}}$$

Change: Increase the volume of the container, causing overall pressure to decrease

Effect: Both sides have equal moles of gas so they would not be affected by a change in overall pressure.

Complete the table:

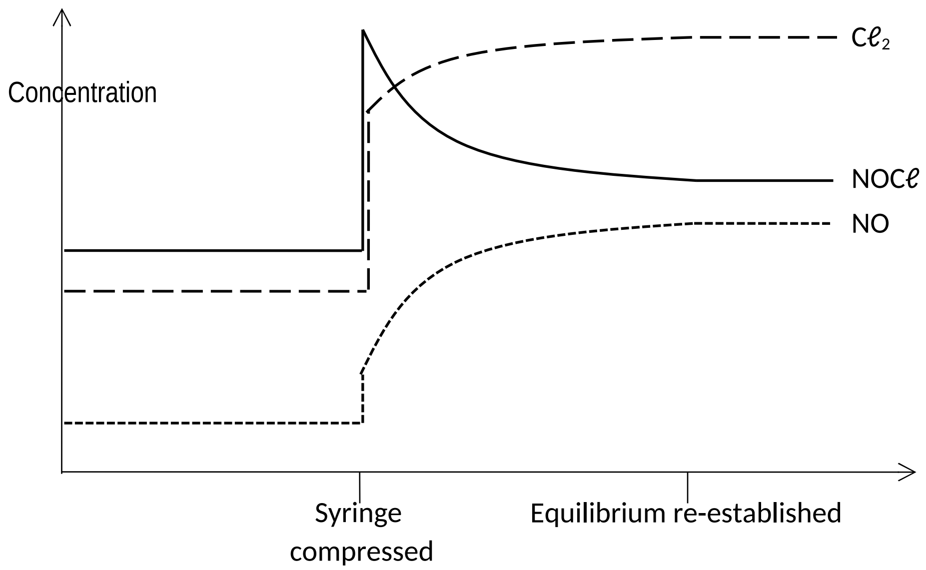
Reaction	**Imposed change**	**Shift in equilibrium**
$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$	Decrease volume	
$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$	Increase volume	
$2\ C_2H_4(g) + 2\ H_2O(g) \rightleftharpoons 2\ C_2H_6(g) + O_2(g)$	Increase volume	
$Ti(s) + 2\ C\ell_2(g) \rightleftharpoons TiC\ell_4(g)$	Decrease volume	

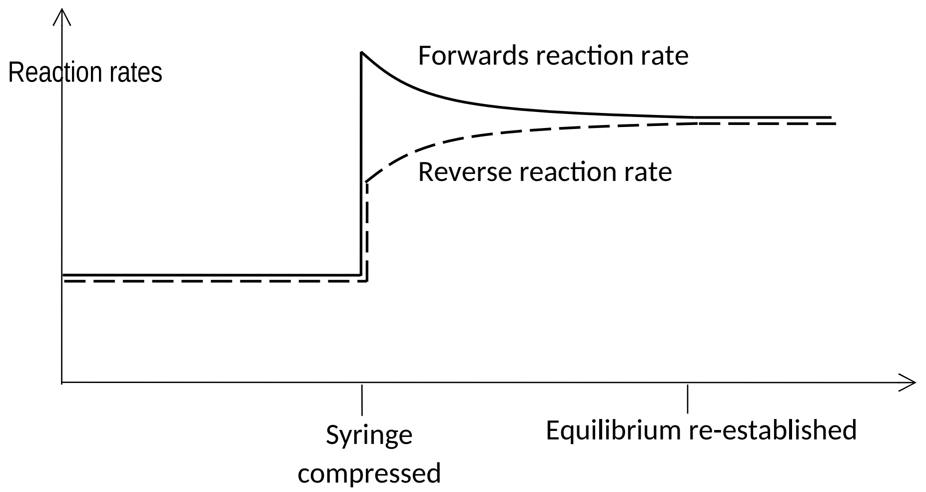
CHANGES TO PRESSURE – SIZE OF CONTAINER

Use Le Châtelier's Principle to predict the changes the occur when a syringe containing the following gases is compressed:

$$2\ NOC\ell(g) \rightleftharpoons 2\ NO(g) + C\ell_2(g)$$

- When the volume of the syringe is compressed it increases the partial pressure (concentration) of **all** gaseous species. This increases the rate of **both** reactions due to more collisions between gaseous particles.
- Le Châtelier's Principle predicts that the system will shift to the left to favour the side of the equation with the least moles of gas (i.e. reverse rate is faster than forwards rate).
- Over time the [reactants] increases and [products] decreases, causing the **forwards rate** to increase and **reverse rate** to decrease until equilibrium is re-established





Pay attention to the following:

- Unlike the concentration graphs, a change in volume causes an **instant change** in the concentration of **all** gases. Think carefully about whether the change will increase or decrease **concentration**.
  "Increase in volume" = "Decrease in concentration"
- The **initial** changes in conc. is **not** related to the mole ratio. In this example, all concentrations were **doubled** for the initial change (i.e.volume **halved**)
- If the forward and reverse reactions both involve gases then they will **both** be affected by a change in volume. i.e. **both** increase or **both** decrease instantly. Think about the direction of shift to figure out which increases or decreases more than the other. In this case LCP predicts reaction will shift right, so forward rate must increase more than reverse rate.

Changes to Pressure (volume of container):

Use **Le Châtelier's Principle** to **predict** the changes that occur when a syringe containing the following gases is expanded to take up more volume. Include the expected observations.

$$2\ NO_2(g) \rightleftharpoons N_2O_4(g)$$
(brown) **(colourless)**

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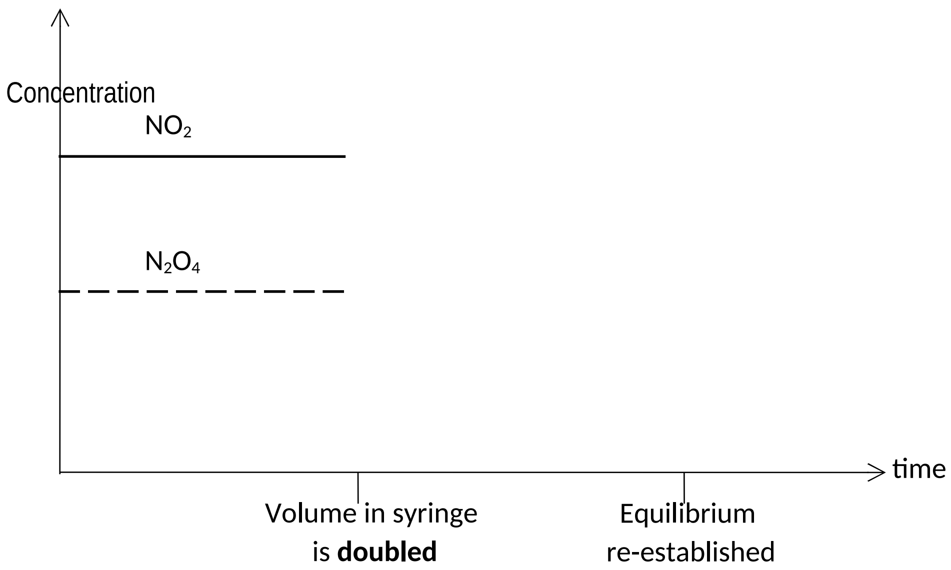
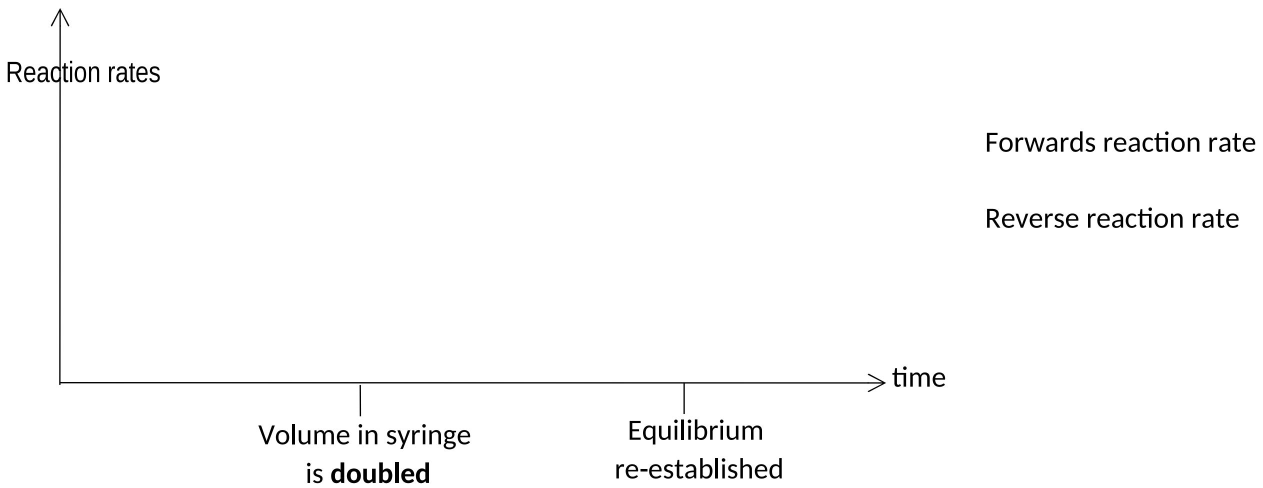


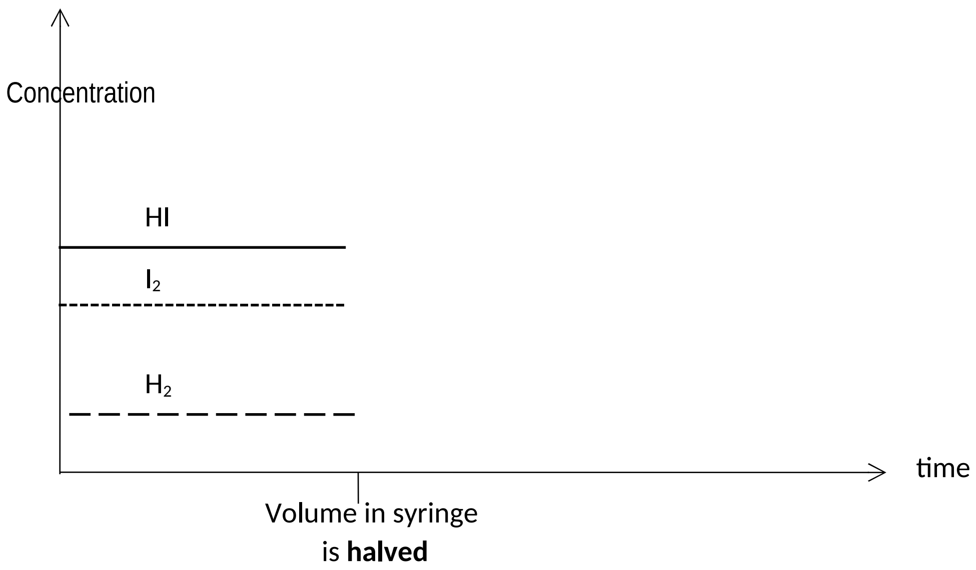


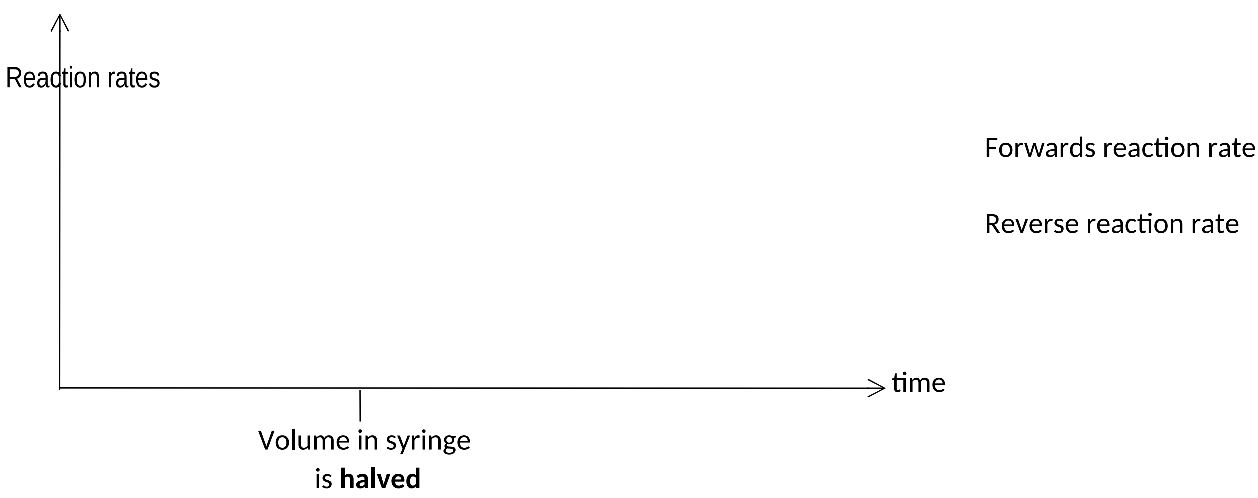
Changes to Pressure (volume of container):

Use **Le Châtelier's Principle** to **predict** the changes that occur when a syringe containing the following gases is compressed. Include the expected observations.

$$I_2(g) + H_2(g) \rightleftharpoons 2\,HI(g)$$

(purple) **(colourless)**





CHANGES TO TEMPERATURES

Changing the temperature will cause the reaction to favour either the endothermic or exothermic reaction.

Imposed change: **Increase** the temperature of a system

Method of counteracting: Favour the **endothermic** reaction *(removes heat)*

Imposed change: **Decrease** the temperature of a system

Method of counteracting: Favour the **exothermic** reaction *(produces heat)*

Reaction	Imposed change	Direction of shift
$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$; $\Delta H = -92$ kJ	Increase the temperature	
$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$; $\Delta H = +52$ kJ	Decrease the temperature	
$Ag^+(aq) + C\ell^-(aq) \rightleftharpoons AgC\ell(s) + 112$ kJ	Decrease the temperature	

Experiment:

$$2\ NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -57 \text{ kJ}$$

brown *colourless*

Predict how temperature will affect the colour of a mixture of NO_2 and N_2O_4. Justify your reasoning using Le Châtelier's principle.

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EXPLAINING EFFECT OF TEMPERATURE

Temperature increases the rate of reaction due to particles having greater kinetic energy, therefore having more energy than the activation energy.

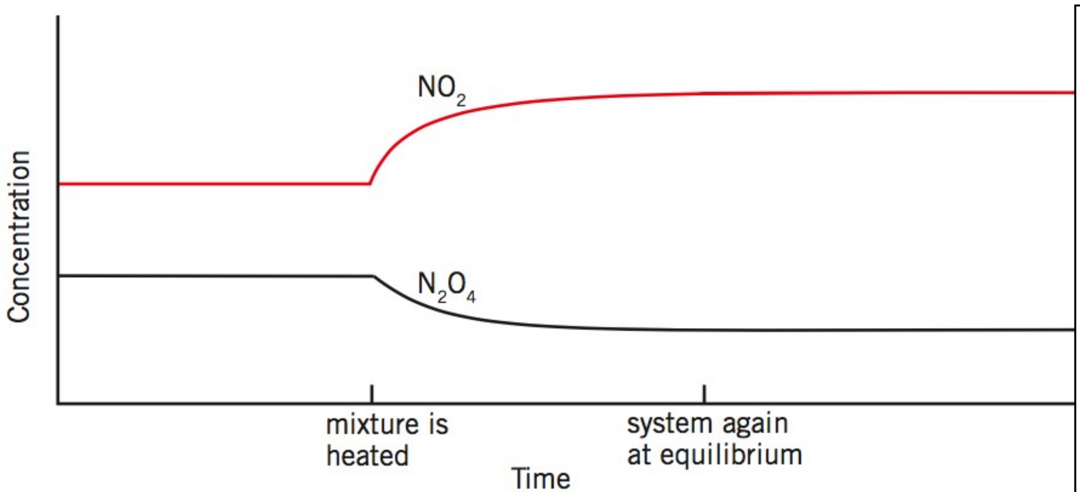
BUT… in a reversible reaction the two reactions have different activation energies.

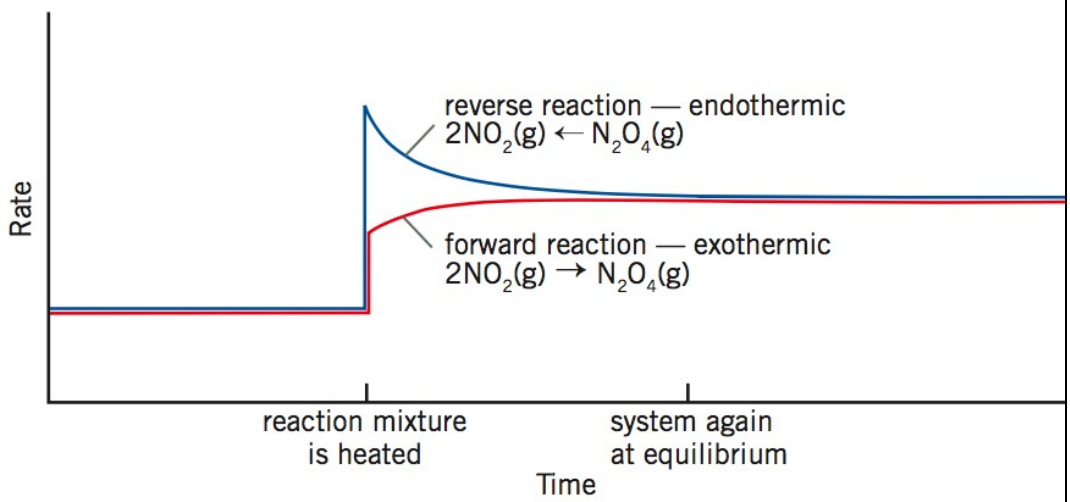
The endothermic reaction has the largest E_a, so it is always affect more by increases or decreases in temperature.

Explain, using collision theory, why the yield (amount) of N_2O_4 decreases when a tube containing NO_2 and N_2O_4 is heated.

$$2\,NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -57\ kJ$$

- Heating the tube increases both the **forwards** **and** **reverse** reaction rates. This is due to particles having greater E_K, and a greater proportion of particles having $E_K > E_a$. This results in an increased number of collisions, and a greater proportion of those collisions lead to successful reactions.
- Endothermic reactions are more affected by changes in temperature because they have a greater activation energy barrier, therefore the **reverse rate** increases more than the **forwards rate**.
- Reverse rate is favoured, therefore over time $[NO_2]$ increases and $[N_2O_4]$ decreases. This causes reverse rate to increase and forward rate to decrease until equilibrium is re-established (both rates equal)





Pay attention to the following:

- Unlike the other sets of graphs, there is **no change** to the **initial** concentrations*. The reactants and products will be hotter or colder, but not more or less concentrated.
- **Both** reaction rates will be affected by temperature (i.e. both increase or both decrease). The endothermic reaction will change more than the exothermic reaction. This can also be figured out by thinking of the direction of shift using L.C.P.

**Advanced note: If it was a graph of pressure over time then there would be an initial change because pressure of gases is inversely proportional to temperature.*

Changes in temperature:

Predict whether a decrease in temperature will increase or decrease the yield of HI(g). Justify your answer using **Le Châtelier's Principle**. (Yield = Amount)

$$H_2(g) \ + \ I_2(g) \ \rightleftharpoons \ 2\ HI(g) \qquad \Delta H = +52 \text{ kJ mol}^{-1}$$

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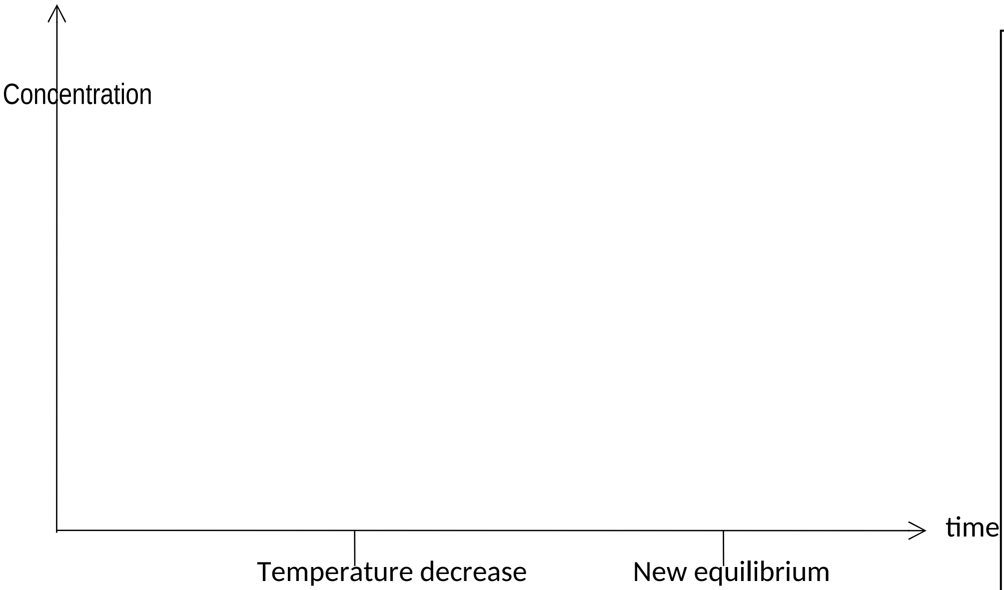
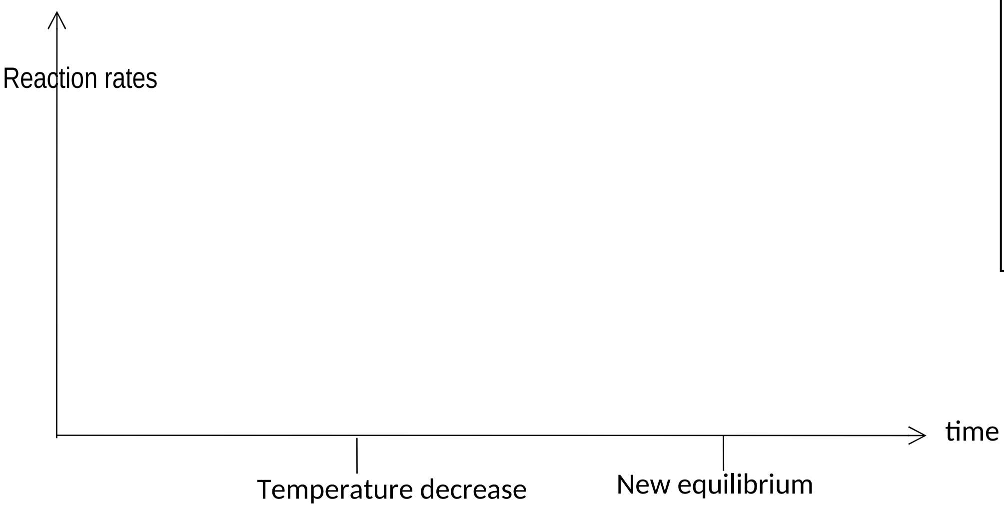


Thought process you should follow:

1. How does a decrease in temperature affect reaction rates?
2. Which reaction (forward or reverse) is affected *more* by changes in temperature?
3. Which reaction is favoured after the temperature changes? What would that mean about the concentration of reactants and products over time?
4. What mole ratio do I need to show while equilibrium is being re-established? How will that affect my curves?



Changes in temperature:

Predict whether an increase in temperature will increase or decrease the yield of $H_2(g)$. Justify your answer using **Le Châtelier's Principle**.

$$C(s) + H_2O(g) + 131\ \text{kJ} \rightleftharpoons CO(g) + H_2(g)$$

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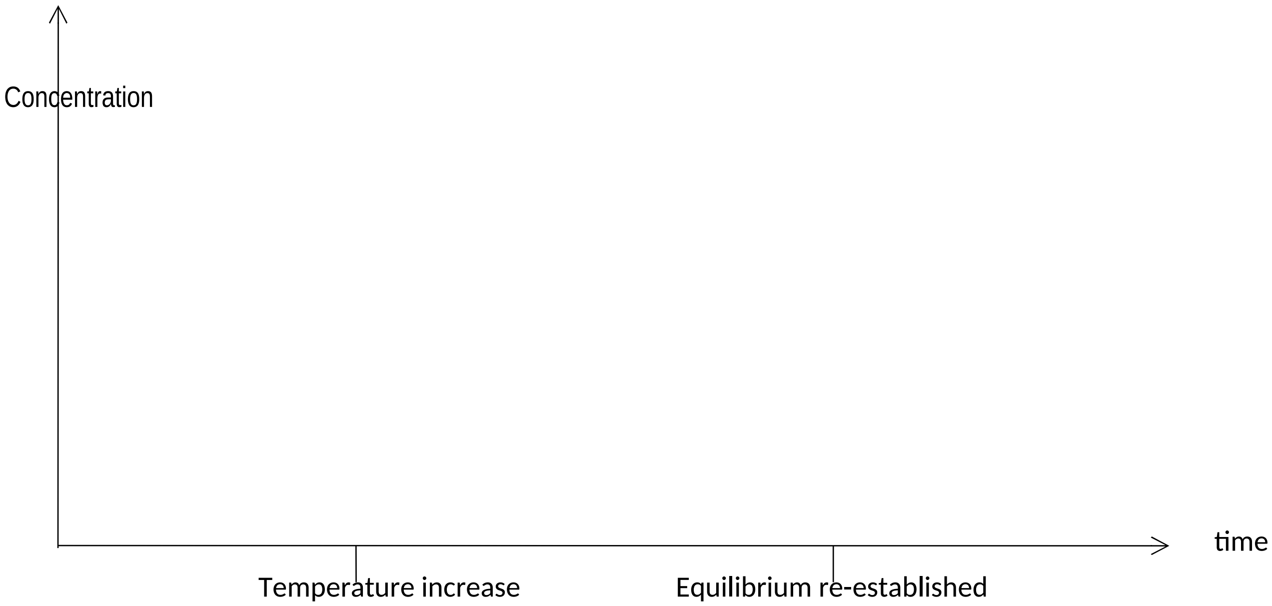
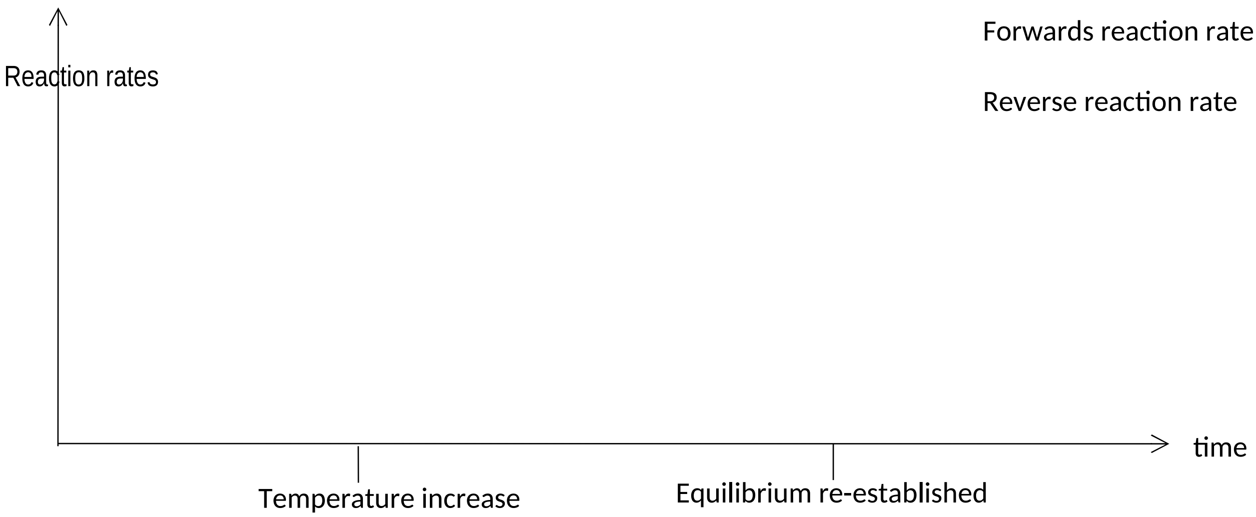


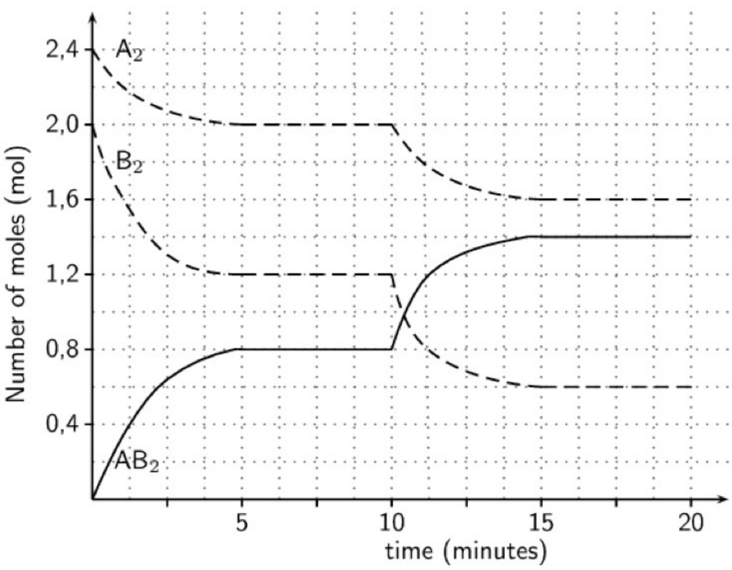


Production of ethanol from ethene:

$CH_2{=}CH_2(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g)$ **ΔH = -45 kJ/mol**

The activation energy for the forwards reaction is 22 kJ/mol.

- Draw a labelled energy profile diagram for this reaction, showing ΔH, Ea and Ea reverse. Use this energy profile diagram to explain the temperature conditions that would be used in an industrial process to achieve the maximum yield (amount) of ethanol.



The reaction pictured left was heated after 10 minutes. The equation is:

$$A_2 + 2\,B_2 \rightleftharpoons 2\,AB_2$$

Is the forwards reaction endothermic or exothermic? Justify your reasoning.

FACTORS THAT DO <u>NOT</u> AFFECT EQUILIBRIUM

In the past pages we have considered how temperature, concentration and pressure affect equilibrium. It is worthwhile also realising that some changes don't have <u>any</u> impact on systems at equilibrium. These include:

<u>Amount of an (insoluble) solid</u>

Solids do not change their concentration.

$$AgC\ell(s) \rightleftharpoons Ag^{+}(aq) + C\ell^{-}(aq)$$

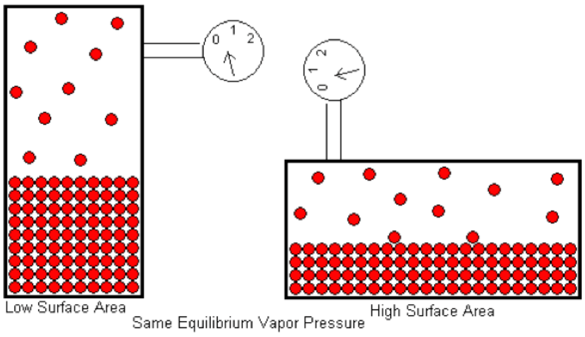
Adding additional $AgC\ell(s)$ to a saturated solution of $AgC\ell$ will not change the concentration of $Ag^{+}(aq)$ or $C\ell^{-}(aq)$. Addition of a solid does not affect equilibrium.

<u>Amount of liquid</u>

Adding a liquid does not change its concentration

Vapour pressure equilibrium: $Br_2(\ell) \rightleftharpoons Br_2(g)$

Increasing surface area will increase rate of evaporation and condensation equally.



***Exception:** Addition of water to a mixture containing (aq) substances will affect the concentration of the (aq) substances, therefore <u>will</u> affect equilibrium.

<u>Inert gases</u>

Equilibrium is affected when the forwards and reaction rates are not equal.

Adding an inert (unreactive) gas increases total pressure, but does not affect collisions between reacting particles and has no effect on forwards and reverse reaction rates. Therefore it will have no effect on equilibrium either.

<u>Adding a catalyst</u>

Adding a catalyst increases both rates **<u>equally</u>**.

Both rates are still equal, $\therefore$ the reaction is still at equilibrium.

EQUILIBRIUM CONSTANTS

Systems at equilibrium will have a certain ratio of reactants to products at a given temperature. This ratio is called the **equilibrium constant (K)**.

Temp. (°C)	Initial concentrations (mol L^{-1})			Final concentrations in the equilibrium mixture (mol L^{-1})			Equilibrium constant $\frac{[HI]^2}{[H_2][I_2]}$
	H_2	I_2	HI	H_2	I_2	HI	
490	1.0	1.0	0	0.228	0.228	1.544	45.9
490	0	0	1.0	0.114	0.114	0.772	45.9
490	1.0	2.0	3.0	0.316	1.316	4.368	45.9

Same temp.   Different starting concentrations   Different final concentrations   **Same ratio**

Equilibrium constants are written as a ratio of [**products**] / [**reactants**].

Solids and liquids are not included in the equilibrium constant because their concentrations do not change during the reaction.

For the reaction: $aA + bB \rightleftharpoons cC + dD$

coefficients   Chemical symbols

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Example: $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

Information given by K:

- K tells you the relative amounts of products and reactants at equilibrium
  - If K is very **large**, reaction heavily favours the **products**
  - If K is very **small**, reaction heavily favours the **reactants**
- K does not tell you anything about the rate of the reaction

Effect of temperature:

- Temperature is the only thing that affects the value of K
  - If increasing the temperature favours **more products,** then increasing temp. will **increase K**
  - If increasing the temperature favours **more reactants,** then increasing temp. will **decrease K**

Past WACE and TEE questions about equilibrium constants: (2000-2014)

Equation	$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$
Equilibrium constant expression	

Equation	$2\ CrO_4^{2-}(aq) + 2\ H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(\ell)$
Equilibrium constant expression	

Equation	$Ca(HCO_3)_2(s) \rightleftharpoons CaO(s) + 2\ CO_2(g) + H_2O(g)$
Equilibrium constant expression	

Equation	$Co(H_2O)_6^{2+}(aq) + 4\ C\ell^-(aq) \rightleftharpoons CoC\ell_4^{2-}(aq) + 6\ H_2O(\ell)$
Equilibrium constant expression	

Equation	$2\ H_2O(\ell) + 4\ Au(s) + O_2(g) + 8\ CN^-(aq) \rightleftharpoons 4\ Au(CN)_2^-(aq) + 4\ OH^-(aq)$
Equilibrium constant expression	

Equation	$PbC\ell_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ C\ell^-(aq)$
Equilibrium constant expression	

Equation	$Fe(H_2O)_5NCS^{2+}(aq) + H_2O(\ell) \rightleftharpoons Fe(H_2O)_6^{3+}(aq) + NCS^-(aq)$
Equilibrium constant expression	

Equation	$2\ NOC\ell(g) \rightleftharpoons 2\ NO(g) + C\ell_2(g)$
Equilibrium constant expression	

Equation	$2\ HI(g) \rightleftharpoons H_2(g) + I_2(g)$
Equilibrium constant expression	

Equation	$4\ NH_3(g) + 3\ O_2(g) \rightleftharpoons 2\ N_2(g) + 6\ H_2O(g)$
Equilibrium constant expression	

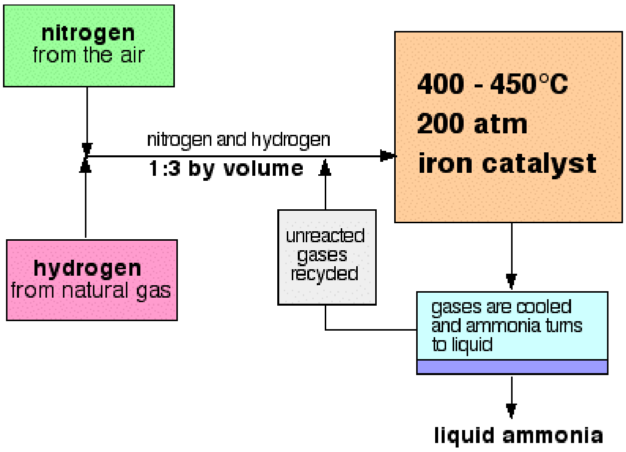
Equation	$C\ell_2(g) + H_2O(\ell) \rightleftharpoons HOC\ell(aq) + H^+(aq) + C\ell^-(aq)$
Equilibrium constant expression	

Equilibrium process	Vaporisation of water
Equation	
Equilibrium constant expression	

Equilibrium process	Dissolution of ammonium chloride
Equation	
Equilibrium constant expression	

Industrial Applications of Equilibrium

HABER PROCESS



$N_2(g)$ + $3\ H_2(g)$ ⇌ $2\ NH_3(g)$ $\Delta H = -92$ kJ

Conditions used:

- Moderate temp (400-450 °C)
- High pressure (200 atm)
- Iron-based catalyst

➢ **Temperature**

High temperatures would increase the **rate** of ammonia production due to particles having greater kinetic energy. More particles would have energy > E_a, so a greater proportion of collisions would be successful.

Low temperatures would increase the **equilibrium yield** of ammonia. According to Le Châtelier's principle, decreasing the temperature would favour the exothermic reaction, which in this case is the forwards reaction.

The Haber process uses moderate temperatures of 400-450 °C. This is used as a compromise between reaction rate and yield. Higher temperatures would have too low of a yield, whereas lower temperatures would have too low of a reaction rate.

➢ **Pressure**

High pressures would increase the **rate** of production due to more collisions between gas particles.

High pressures would also increase the **equilibrium yield** of ammonia. According to Le Châtelier's principle, high pressures favour the side of the reaction with the least moles of gas, which in this case is the right hand side (4 moles → 2 moles).

The chosen pressure of 200 atmospheres is high to maximise rate and yield. Higher pressures are possible and would further increase the yield and reaction rate, but higher pressures are too expensive to maintain and pose additional safety risks and this makes it economically unviable.

➢ **Catalyst**

An iron-base catalyst is used. Catalysts increase the rate of reaction by providing an alternate reaction pathway with a lower activation energy. This means that more particles at a given temperature can react because they have energy greater than the catalysed activation energy.

Catalysts do not affect equilibrium yield because the increase forward and reverse rates equally. This means that catalysts can increase rate without negatively affecting yield, giving them an economic benefit.

➢ **Removing the ammonia and recycling the reactants**

In the final stage of the process the ammonia is liquefied and removed. The unreacted N_2 and H_2 are re-added to the reaction mixture to keep reacting.

Removing the ammonia prevents the reverse reaction from happening, stopping the NH_3 from reacting again to make N_2 and H_2.

When the unreacted gases are added back into the reaction mixture they increase the concentration of reactants and cause the reaction to shift to the right, allowing more NH_3 to be produced.

CONTACT PROCESS

The Contact Process is used for the manufacture of sulfuric acid. It involves multiple steps.

$S(s)$ → $SO_2(g)$ → $SO_3(g)$ → $H_2S_2O_7(\ell)$ → $H_2SO_4(\ell)$

Step 1: Sulfur is combusted in the presence of oxygen. $S(s) + O_2(g) \rightarrow SO_2(g)$

Step 2: Sulfur dioxide is oxidised to form sulfur trioxide. This is a reversible, exothermic reaction.

$$SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g) \quad \Delta H = -196\ kJ$$

Conditions used in Step 2:

- Moderate temp (400-500 °C)
- Low pressure (1 atmosphere)
- Vanadium(V) oxide (V_2O_5) catalyst

➢ **Temperature**:

[The explanation for why a moderate temperature is used in the Contact Process is virtually identical to the explanation for temperature in the Haber Process, previous page. Both reactions are exothermic, so yield is decreased at higher temperatures. A moderate temperature is needed to obtain a satisfactory balance between yield and rate]

➢ **Pressure:**

High pressures would increase the **rate** of production due to more collisions between gas particles.

High pressures would also increase the **equilibrium yield** of sulfur trioxide. According to Le Châtelier's principle, high pressures favour the side of the reaction with the least moles of gas, which in this case is the right hand side (2 moles → 1 mole).

Despite this, the actual pressure used is quite low. This is because the reaction actually has quite a high yield and rate at atmospheric pressures. High pressures are expensive to maintain and add safety risks, so there is no economic benefit in increasing the pressure above 1 atmosphere.

➢ **Catalyst:**

[Once again, this explanation would be identical to the one given for the Haber process, only it would mention the V_2O_5 catalyst instead of the iron-based catalyst]

Step 3 & 4: The $SO_3(g)$ cannot be directly reacted with water to form $H_2SO_4(\ell)$ because the reaction is uncontrollable and forms a fog of sulfuric acid.

Instead, the SO_3 is reacted with concentrated H_2SO_4 to form an intermediate, $H_2S_2O_7(\ell)$ (oleum). The oleum can then be safely reacted with water to produce concentrated sulfuric acid.

Step 3: $SO_3(g) + H_2SO_4(\ell) \rightarrow H_2S_2O_7(\ell)$

Step 4: $H_2S_2O_7(\ell) + H_2O(\ell) \rightarrow 2\ H_2SO_4(\ell)$

<u>Past exam question (TEE 2008):</u>

Nickel ores are predominantly sulphides and oxides. The Mond process is an industrial process used to extract nickel from nickel oxide ores. It involves three steps, with each step conducted at moderate pressures.

Step 1: Nickel oxide is reacted with hydrogen at 200 °C to produce impure nickel metal and water. The impurities present include iron and cobalt. This step goes to completion.

Step 2: The impure nickel is converted into gaseous nickel carbonyl, $Ni(CO)_4$, using an excess of carbon monoxide at 50-80 °C. The reaction is exothermic.

Step 3: The nickel carbonyl is separated from the residue and passed over platinum heated to 220-250 °C. The nickel carbonyl decomposes, giving pure nickel and carbon monoxide. The carbon monoxide is recovered for purifying further batches of nickel.

Explain the conditions used to maximise yield in the Mond process in terms of reaction rates and equilibrium.

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HOMEWORK

Source	Topics	Set/ Chapter	Questions to complete
Essential Chemistry	Reaction rates & collision theory	EC Set 1	… 3 4 5 … 9 10 11
	Characteristics of systems in equilibrium	EC Set 2	1 2 3 4 5
	Changes to concentration	EC Set 2	6 … 9 10 11
	Changes to pressure and temperature	EC Set 2	12 13 14 15 16
	Equilibrium constants	EC Set 2	7 8
	Industrial processes	EC Set **21 (page 172)**	14 15 16 17
Past Exam Questions	Collision theory, reaction rates, energy profile diagrams	Section 1	[MC] Pg: 2 3 4 5
			[SA] Pg: 6 7 8
	Systems in equilibrium, Le Châtelier's Principle, Equilibrium Expressions	Section 2	[MC] Pg: 9 10 11 12 13 14 15 16 17 18 19 20
			[SA] Pg: 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38
	Industrial and environmental applications of rates and equilibrium	Section 3	[SA] Pg: 39 40 41 42 43 44 45 46 47 48 49 50 51 52