

Reversible Reactions

Dynamic Equilibrium

Macroconcept: Systems



A reversible reaction can be considered as a *system* in which changes are taking place. The system is composed of reactants and products that interact with each other following a specific set of *rules*. These rules (set out in Le Chatelier's Principle) allow us to *predict* how the system will respond to changes in concentration, pressure, temperature and the addition of a catalyst. This has important applications in industrial chemistry and the chemistry of biological systems.

Guiding questions:

- What is dynamic equilibrium?
- Why are some reactions reversible while others are not?
- Why can dynamic equilibrium only be reached in a closed system?
- What is happening at the macroscopic (observable) level at equilibrium?
- What is happening at the microscopic (molecular) level at equilibrium?
- How (and why) can changes in variables such as temperature and pressure affect a system that has reached dynamic equilibrium?
- How might the world be different if all reactions were reversible, or if no reactions were reversible?
- How is Le Chatelier's Principle applied to improve the efficiency of reactions carried out on an industrial scale?



- 1. State that some chemical reactions are reversible (*e.g.* manufacture of ammonia).
- 2. Describe the idea that some chemical reactions can be reversed by changing the reaction conditions.
- **3.** Explain, in terms of rates of the forward and reverse reactions, what is meant by a reversible reaction and dynamic equilibrium.
- 4. Use Le Chatelier's principle to deduce qualitatively (from appropriate information) the effects of changes in temperature, concentration, pressure or presence of a catalyst on a system at equilibrium and explain the effects of the changes in terms of rate of reaction.
- Explain the conditions used in the Haber process, as an example of the importance of an understanding of chemical equilibrium in the chemical industry and the application of Le Chatelier's principle.



 Reversible reaction: A reversible reaction is a chemical reaction in which the conversion of reactants to products and the conversion of products to reactants occur simultaneously under suitable conditions.

• For example, ethanoic acid is a *weak acid* because its ionisation in water is *reversible*:

ethanoic acid \Rightarrow ethanoate ion + hydrogen ion

 $CH_3COOH(aq) \rightleftharpoons CH_3COO^{-}(aq) + H^{+}(aq)$

• Ethanoic acid is a weak acid because it is never fully ionised in aqueous solution. This is because some of the ethanoate ions and some of the hydrogen ions always recombine to form molecules of ethanoic acid.

 Instead of using a single-headed arrow (→) showing the reaction only proceeds in one direction, the notation for a reversible reaction is ⇒.

- The *forward* reaction is the reaction that goes from *left-to-right*.
- The *reverse* reaction is the reaction that goes from *right-to-left*.







• Dynamic equilibrium: Dynamic equilibrium occurs in reversible reactions when the *rate* of the forward reaction has become equal to the *rate* of the backward reaction. As a result, there is *no change* in the amount / concentration of the reactants and products.

 Dynamic equilibrium can only be reached in a *closed system* because, in such a system, there is no loss or gain of chemicals to or from the surroundings. This allows the forward and reverse reactions to occur at the same rate, maintaining a constant concentration of reactants and products. In an open system, chemicals could escape or enter, disrupting the balance needed for dynamic equilibrium to be established.

Open System Dynamic equilibrium cannot be established because the iodine vapour escapes from the system.



Closed

System

Dynamic

equilibrium can

be established

because the

iodine vapour

remains in the

system.



Analogy for a reversible reaction.

 Imagine that you stand at the bottom of escalator and start to move upwards.

 For a chemical reaction, this is the same as the reactants colliding to form the products:

 $A + B \rightarrow C + D$



Analogy for a reversible reaction.

 Now imagine that you turn around and start to *run* back *down* the escalator while it is still *slowly* moving *upwards*.

• This is the same as the products colliding to form the reactants again:

 $A + B \leftarrow C + D$



- Analogy for a reversible reaction.
- Now imagine walking back down the escalator at the same rate that the escalator is moving upwards.
- You are now at *equilibrium* on the escalator. It appears that you are standing still, although the escalator is still moving, and you are still walking.



Analogy for a reversible reaction.

• A chemical reaction reaches equilibrium when the rate of the forward reaction equals the rate of the backward reaction. It appears that the reaction has stopped, although chemical changes are still taking place:

 $A + B \rightleftharpoons C + D$



Analogy for a reversible reaction.

• You could reach your *equilibrium position* near the top or bottom of the escalator, not only around the middle.

• Likewise, at equilibrium, the concentrations of reactants and products remain constant *but are not necessarily equal*.

 $A + B \rightleftharpoons C + D$

i.e. $[A] + [B] \neq [C] + [D]$





Henry Louis Le Chatelier, 1850 - 1936

 Henry Louis Le Chatelier, a French Chemist, proposed a Principle in 1884 that predicts the effect of a *disturbance* on a system at equilibrium.

 Le Chatelier's Principle: If a system at equilibrium is subjected to a change in conditions which disturbs the equilibrium, the system responds to counteract the effect of the change.

Conditions to Consider:

→ Concentration (amount of substance)

→ Temperature

→ **Pressure** (only for gaseous systems)

→ Addition of a Catalyst



Reversible Reactions – Dynamic Equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -196 \text{ kJ mol}^{-1}$







How Does a Change in *Concentration* Affect the Equilibrium Position of the System?

 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -196 \text{ kJ mol}^{-1}$

Change	Direction of Equilibrium Shift Based on Le Chatelier's Principle	Explanation in Terms of Rate of Reaction	
Add Sulfur Dioxide, SO ₂	Shifts to the to the amount / moles of SO ₂ .	Concentration of SO ₂ so the rate of the forward reaction	
Remove Sulfur Trioxide, SO ₃	Shifts to the to the amount / moles of SO ₃ .	Concentration of SO ₃ , so the rate of the backward reaction	

How Does a Change in *Concentration* Affect the Equilibrium Position of the System?

 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -196 \text{ kJ mol}^{-1}$

Change	Direction of Equilibrium Shift Based on Le Chatelier's Principle	Explanation in Terms of Rate of Reaction
Add Sulfur Dioxide, SO ₂	Shifts to the <mark>right</mark> to decrease the amount / moles of SO ₂ .	Concentration of SO ₂ increases so the rate of the forward reaction increases.
Remove Sulfur Trioxide, SO ₃	Shifts to the <mark>right</mark> to <mark>increase</mark> the amount / moles of SO ₃ .	Concentration of SO ₃ decreases, so the rate of the backward reaction decreases.

How Does a Change in *Concentration* Affect the Equilibrium Position of the System?



Generalisation for Concentration

• Decreasing the concentration of a chemical favours the reaction that produces more moles of that chemical.

• Increasing the concentration of a chemical favours the reaction that produces fewer moles of that chemical.

How Does a Change in *Temperature* Affect the Equilibrium Position of the System?

 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -196 \text{ kJ mol}^{-1}$

Change	Direction of Equilibrium Shift Based on Le Chatelier's Principle	Explanation in Terms of Rate of Reaction	
Decrease Temperature	Shifts to the to the to thermal energy since the forward reaction is	Rate of the reaction increases more than the rate of the reaction.	
*Increase Temperature	Shifts to the to the to the thermal energy since the backward reaction is	Rate of the reaction increases more than the rate of the reaction.	

How Does a Change in *Temperature* Affect the Equilibrium Position of the System?

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	$\Delta H = -196 \text{ kJ mol}^{-1}$
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Change	Direction of Equilibrium Shift Based on Le Chatelier's Principle	Explanation in Terms of Rate of Reaction
Decrease Temperature	Shifts to the <mark>right</mark> to <mark>release</mark> thermal energy since the forward reaction is <mark>exothermic</mark> .	Rate of the <mark>forward</mark> reaction increases more than the rate of the <mark>backward</mark> reaction.
*Increase Temperature	Shifts to the <mark>left</mark> to <mark>absorb</mark> thermal energy since the backward reaction is <mark>endothermic</mark> .	Rate of the <mark>backward</mark> reaction increases more than the rate of the <mark>forward</mark> reaction.

*Note: Increasing the temperature increases the rates of both the forward and backward reactions, but the rate of the endothermic reaction increases more that the rate of the exothermic reaction.

How Does a Change in *Temperature* Affect the Equilibrium Position of the System?



Generalisation for Temperature

• **Decreasing** temperature favours the **exothermic** reaction (to release more thermal energy, thereby increasing temperature).

 Increasing temperature favours the endothermic reaction (to absorb excess thermal energy, thereby decreasing temperature).

How Does a Change in *Pressure* Affect the Equilibrium Position of the System?

 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -196 \text{ kJ mol}^{-1}$

Change	Direction of Equilibrium Shift Based on Le Chatelier's Principle		Explanation in Terms of Rate of Reaction	
Decrease Pressure (increase volume of reaction vessel)	Shifts to the to pressure since there are moles of gas on the side of the equation.		Rate of the reaction increas	ses more than reaction.
Increase Pressure (reduce volume of reaction vessel)	Shifts to there are on the eq	o the c to pressure since moles of gas side of the uation.	Rate of the increases more the	reaction e than rate of reaction.

How Does a Change in *Pressure* Affect the Equilibrium Position of the System?

 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -196 \text{ kJ mol}^{-1}$

Change	Direction of Equilibrium Shift Based on Le Chatelier's Principle	Explanation in Terms of Rate of Reaction
Decrease Pressure (increase volume of reaction vessel)	Shifts to the left to increase pressure since there are more moles of gas on the left side of the equation.	Rate of the <mark>backward</mark> reaction increases more than rate of the <mark>forward</mark> reaction.
Increase Pressure (reduce volume of reaction vessel)	Shifts to the right to decrease pressure since there are fewer moles of gas on the right side of the equation.	Rate of the <mark>forward</mark> reaction increases more than rate of the <mark>backward</mark> reaction.

How Does a Change in *Pressure* Affect the Equilibrium Position of the System?



Generalisation for Pressure

• Decreasing pressure favours the reaction that produces more moles of gas, thereby increasing pressure.

• Increasing pressure favours the reaction that produces fewer moles of gas, thereby decreasing pressure.


How Does the Addition of a *Catalyst* Affect the Equilibrium Position of the System?



Generalisation for a Catalyst

• Addition of a catalyst **does not change** the equilibrium position.

• A catalyst lowers the activation energy of both the forward reaction and backward reaction by the same extent.

 Hence, rates of both the forward reaction and backward reaction increase by the same extent.

• Therefore, catalysts only allow reactions to reach equilibrium faster.





 $2CrO_4^{2-}(aq)$ (yellow) + $2H^+(aq) \Rightarrow Cr_2O_7^{2-}(aq)$ (orange) + $H_2O(l)$

Video: 28 Seconds

How Does a Change in *Concentration* Affect the Equilibrium Position of the System?

 $2CrO_4^{2-}(aq) (yellow) + 2H^{+}(aq) \Rightarrow Cr_2O_7^{2-}(aq) (orange) + H_2O(l)$

Change	Direction of Equilibrium Shift Based on Le Chatelier's Principle	Explanation in Terms of Rate of Reaction
Add Dilute Acid, H⁺(aq)	Shifts to the to the concentration of H ⁺ (aq) – solution changes to .	Concentration of H⁺(aq) so the rate of the forward reaction
Add Dilute Alkali, OH⁻(aq)	Shifts to the to to the concentration of H ⁺ (aq) – solution changes to .	$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ Concentration of H ⁺ (aq) , so the rate of the forward reaction

How Does a Change in *Concentration* Affect the Equilibrium Position of the System?

 $2CrO_4^{2-}(aq) (yellow) + 2H^{+}(aq) \Rightarrow Cr_2O_7^{2-}(aq) (orange) + H_2O(l)$

Change	Direction of Equilibrium Shift Based on Le Chatelier's Principle	Explanation in Terms of Rate of Reaction
Add Dilute Acid, H⁺(aq)	Shifts to the <mark>right</mark> to decrease the concentration of H ⁺ (aq) – solution changes yellow to orange.	Concentration of H ⁺ (aq) increases so the rate of the forward reaction increases.
Add Dilute Alkali, OH⁻(aq)	Shifts to the <mark>left</mark> to increase the concentration of H ⁺ (aq) – solution changes <mark>orange</mark> to <mark>yellow</mark> .	$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ Concentration of H ⁺ (aq) decreases, so the rate of the forward reaction decreases.



 $2NO_2(g)$ (brown) \Rightarrow $N_2O_4(g)$ (colourless)

 $\Delta H = -58.0 \text{ kJ mol}^{-1}$

Video: 64 Seconds





 $2NO_2(g)$ (brown) $\Rightarrow N_2O_4(g)$ (colourless) $\Delta H = -58.0 \text{ kJ mol}^{-1}$



How Does a Change in *Temperature* Affect the Equilibrium Position of the System?

Change	Direction of Equilibrium Shift Based on Le Chatelier's Principle	Explanation in Terms of Rate of Reaction
Decrease Temperature	Shifts to the to to the thermal energy since the forward reaction is . System changes from to .	Rate of the reaction increases more than the rate of the reaction.
*Increase Temperature	Shifts to the to the to thermal energy since the backward reaction is System changes form to to .	Rate of the reaction increases more than the rate of the reaction.

How Does a Change in *Temperature* Affect the Equilibrium Position of the System?

 $2NO_2(g)$ (brown) \Rightarrow $N_2O_4(g)$ (colourless) $\Delta H = -58.0$ kJ mol⁻¹

Change	Direction of Equilibrium Shift Based on Le Chatelier's Principle	Explanation in Terms of Rate of Reaction
Decrease Temperature	Shifts to the right to release thermal energy since the forward reaction is exothermic . System changes from brown to colourless .	Rate of the <mark>forward</mark> reaction increases more than the rate of the <mark>backward</mark> reaction.
*Increase Temperature	Shifts to the left to absorb thermal energy since the backward reaction is endothermic . System changes form colourless to brown .	Rate of the <mark>backward</mark> reaction increases more than the rate of the <mark>forward</mark> reaction.

*Note: Increasing the temperature increases the rates of both the forward and backward reactions, but the rate of the endothermic reaction increases more that the rate of the exothermic reaction.



How Does a Change in *Pressure* Affect the Equilibrium Position of the System?

Change	Direction of Equilibrium Shift Based on Le Chatelier's Principle	Explanation in Terms of Rate of Reaction
Decrease Pressure (increase volume of reaction vessel)	Shifts to the to pressure since there are moles of gas on the side of the equation. System changes to to .	Rate of the reaction increases more than rate of the reaction.
Increase Pressure (reduce volume of reaction vessel)	Shifts to the to pressure since there are moles of gas on the side of the equation. System changes to .	Rate of the reaction increases more than rate of the the reaction.

How Does a Change in *Pressure* Affect the Equilibrium Position of the System?

Change	Direction of Equilibrium Shift Based on Le Chatelier's Principle	Explanation in Terms of Rate of Reaction
Decrease Pressure (increase volume of reaction vessel)	Shifts to the left to increase pressure since there are more moles of gas on the left side of the equation. System changes colourless to brown .	Rate of the <mark>backward</mark> reaction increases more than rate of the <mark>forward</mark> reaction.
Increase Pressure (reduce volume of reaction vessel)	Shifts to the right to decrease pressure since there are fewer moles of gas on the right side of the equation. System changes brown to colourless .	Rate of the <mark>forward</mark> reaction increases more than rate of the <mark>backward</mark> reaction.

How Does a Change in *Concentration* Affect the Equilibrium Position of the System?

 $2NO_2(g)$ (brown) \Rightarrow $N_2O_4(g)$ (colourless) $\Delta H = -58.0$ kJ mol⁻¹



 What is observed when the amount / moles of N₂O₄(g) is increased or decreased?

How Does a Change in *Concentration* Affect the Equilibrium Position of the System?

Change	Direction of Equilibrium Shift Based on Le Chatelier's Principle	Explanation in Terms of Rate of Reaction
Increase the Amount of $N_2O_4(g)$	Shifts to the to the amount of $N_2O_4(g)$ since there are moles of $N_2O_4(g)$ on the side of the equation. System changes to to .	Rate of the section reaction because the amount of $N_2O_4(g)$ on the right-hand-side has .
Decrease the Amount of $N_2O_4(g)$	Shifts to the to the amount of $N_2O_4(g)$ since there are moles of $N_2O_4(g)$ on the side of the equation. System changes to to .	Rate of the section reaction because the amount of $N_2O_4(g)$ on the right-hand-side has .

How Does a Change in *Concentration* Affect the Equilibrium Position of the System?

Change	Direction of Equilibrium Shift Based on Le Chatelier's Principle	Explanation in Terms of Rate of Reaction
Increase the Amount of N ₂ O ₄ (g)	Shifts to the left to decrease the amount of $N_2O_4(g)$ since there are fewer moles of $N_2O_4(g)$ on the left side of the equation. System changes colourless to brown .	Rate of the <mark>backward</mark> reaction increases because the amount of N ₂ O ₄ (g) on the right-hand-side has increased.
Decrease the Amount of N ₂ O ₄ (g)	Shifts to the right to increase the amount of $N_2O_4(g)$ since there are more moles of $N_2O_4(g)$ on the right side of the equation. System changes brown to colourless .	Rate of the <mark>backward</mark> reaction decreases because the amount of N ₂ O ₄ (g) on the right-hand-side has decreased.



General Guideline to Answering Questions

a) State whether the equilibrium position shifts towards the left-hand-side or the right-hand-side.

b) With reference to Le Chatelier's Principle, explain *why* the equilibrium position shifts in response to the change.

c) State whether the forward or backward reaction is favoured.

d) State any consequences due to the change in equilibrium position, *e.g.* change in colour.

Reversible Reactions – Dynamic Equilibrium $C_2H_4(g) + H_2O(g) \Rightarrow C_2H_5OH(l)$ ΔH is positive 1. Add $C_2H_4(g)$ Reversible Reactions – Dynamic Equilibrium $C_2H_4(g) + H_2O(g) \Rightarrow C_2H_5OH(l)$ ΔH is positive 1. Add $C_2H_4(g)$

a) As the amount / moles of C_2H_4 increases, the equilibrium position will shift to the right.

b) By Le Chatelier's Principle, the equilibrium position will shift to the right to reduce the amount / moles of C_2H_4 .

c) This favours the forward reaction (left-to-right).

d) Which increases the yield of ethanol (C_2H_5OH).

Reversible Reactions – Dynamic Equilibrium $C_2H_4(g) + H_2O(g) \Rightarrow C_2H_5OH(l)$ ΔH is positive **2.** Remove C_2H_5OH **Reversible Reactions – Dynamic Equilibrium** $C_2H_4(g) + H_2O(g) \Rightarrow C_2H_5OH(l)$ ΔH is positive **2.** Remove C_2H_5OH

a) As the amount / moles of C_2H_5OH decreases, the equilibrium position will shift to the right.

b) By Le Chatelier's Principle, the equilibrium position will shift to the right to increase the amount / moles of C_2H_5OH .

c) This favours the forward reaction (left-to-right).

d) Which increases the yield of ethanol (C_2H_5OH).

 $C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(l) \quad \Delta H \text{ is positive}$

3. Increase Temperature

Reversible Reactions – Dynamic Equilibrium $C_2H_4(g) + H_2O(g) \Rightarrow C_2H_5OH(l)$ **AH is positive 3.** Increase Temperature

a) As the temperature increases, the equilibrium position will shift to the right.

b) By Le Chatelier's Principle, as the temperature increases, the equilibrium position will shift in the direction that absorbs thermal energy (endothermic direction) and lowers the temperature.

c) This favours the forward reaction (left-to-right).

d) Which increases the yield of ethanol (C_2H_5OH).

 $C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(l) \quad \Delta H \text{ is positive}$

4. Increase Pressure

Reversible Reactions – Dynamic Equilibrium $C_2H_4(g) + H_2O(g) \Rightarrow C_2H_5OH(l)$ ΔH is positive **4.** Increase Pressure

a) As the pressure increases, the equilibrium position will shift to the right.

b) By Le Chatelier's Principle, the equilibrium position will shift to the right to reduce the pressure because the right-hand-side contains fewer moles of gas (lower pressure) compared to the left-hand-side (higher pressure).

c) This favours the forward reaction (left-to-right).

d) Which increases the yield of ethanol (C_2H_5OH).



Reversible Reactions – Dynamic Equilibrium Industrial Manufacture of Ammonia – Haber Process

Reversible Reactions – Dynamic Equilibrium Industrial Manufacture of Ammonia – Haber Process

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Reversible Reactions – Dynamic Equilibrium Industrial Manufacture of Ammonia – Haber Process nitrogen + hydrogen 🔁 ammonia 1 H. H(Ν (H) $\left(\mathbf{H}\right)$ H(H)Ν Ν +Н H(H)Ν H. H. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \Delta H = -92.4 \text{ kJ mol}^{-1}$ 1 mole 1 mole 1 mole 1 mole 1 mole 1 mole 24 dm³ 24 dm³ 24 dm³ 24 dm³ 24 dm³ 24 dm³

Reversible Reactions – Dynamic Equilibrium Industrial Manufacture of Ammonia – Haber Process nitrogen + hydrogen 🖨 ammonia



 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \Delta H = -92.4 \text{ kJ mol}^{-1}$

• Ammonia is manufactured on an industrial scale by reacting nitrogen gas directly with hydrogen gas under a specialised set of conditions.

Reversible Reactions – Dynamic Equilibrium Industrial Manufacture of Ammonia – Haber Process nitrogen + hydrogen 🖨 ammonia



 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \Delta H = -92.4 \text{ kJ mol}^{-1}$

 The chemical reaction used to manufacture ammonia on an industrial scale is *reversible*. This means that while nitrogen and hydrogen react to form ammonia, ammonia reacts to form nitrogen and hydrogen.

 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \Delta H = -92.4 \text{ kJ mol}^{-1}$

1. Add $N_2(g)$ and $H_2(g)$

 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \Delta H = -92.4 \text{ kJ mol}^{-1}$

1. Add $N_2(g)$ and $H_2(g)$

a) As the amount / moles of $N_2(g)$ and $H_2(g)$ increases, the equilibrium position will shift to the right.

b) By Le Chatelier's Principle, the equilibrium position will shift to the right to reduce the amount / moles of $N_2(g)$ and $H_2(g)$.

c) This favours the forward reaction (left-to-right).

d) Which increases the yield of $NH_3(g)$.

 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \Delta H = -92.4 \text{ kJ mol}^{-1}$

2. Remove NH₃(g)
Reversible Reactions – Dynamic Equilibrium $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \Delta H = -92.4 \text{ kJ mol}^{-1}$ **2.** Remove $NH_3(g)$

a) As the amount / moles of NH₃(g) decreases, the equilibrium position will shift to the right.

b) By Le Chatelier's Principle, the equilibrium position will shift to the right to increase the amount / moles of $NH_3(g)$.

c) This favours the forward reaction (left-to-right).

d) Which increases the yield of $NH_3(g)$.

 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \Delta H = -92.4 \text{ kJ mol}^{-1}$

3. Reduce Temperature

 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \Delta H = -92.4 \text{ kJ mol}^{-1}$

3. Reduce Temperature

a) As the temperature decreases, the equilibrium position will shift to the right.

b) By Le Chatelier's Principle, as the temperature decreases, the equilibrium position will shift in the direction that releases thermal energy (exothermic direction) and increases the temperature.

c) This favours the forward reaction (left-to-right).

d) Which increases the yield of $NH_3(g)$.

 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \Delta H = -92.4 \text{ kJ mol}^{-1}$

4. Increase Pressure

 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \Delta H = -92.4 \text{ kJ mol}^{-1}$

4. Increase Pressure

a) As the pressure increases, the equilibrium position will shift to the right.

b) By Le Chatelier's Principle, the equilibrium position will shift to the right to reduce the pressure because the right-hand-side contains fewer moles of gas (lower pressure) compared to the left-hand-side (higher pressure).

c) This favours the forward reaction (left-to-right).

d) Which increases the yield of $NH_3(g)$.

Hydrogen required for the manufacture of ammonia is obtained by *cracking* long-chain hydrocarbons from crude oil, *e.g.* C₂₀H₄₂(s) → C₈H₁₆(*l*) + C₁₂H₂₄(*l*) + H₂(g)

 Nitrogen required for the manufacture of ammonia is obtained from the *fractional distillation* of liquefied air (remember, the Earth's atmosphere is approximately 78% nitrogen).



The conditions used for the industrial manufacture of ammonia were discovered 100 years ago by a German scientist called *Fritz Haber*. His discovery was so important that he was awarded the 1918 Nobel Prize in Chemistry. The conditions that he discovered are still used in factories around the world today.



- Based upon the information provided in the graph, what conditions would you use to manufacture ammonia?
- Think about the *yield* of ammonia and the *rate* at which the ammonia is produced.



- What are the different consequences of using a *high* temperature or a low temperature?
- What are the different consequences of using a high pressure or a low pressure?



 A low temperature favours the production of ammonia, but if the temperature is too low, the rate at which the ammonia is formed is very slow. A temperature of 450 °C is a compromise, giving a reasonably good yield of ammonia at an acceptable rate.



→ → Low temperature favours the forward reaction → → $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

 $\leftarrow\leftarrow\leftarrow$ High temperature favours the backward reaction $\leftarrow\leftarrow\leftarrow$



• A *high pressure* favours the production of ammonia, but using a very high pressure on an industrial scale is both expensive and potentially dangerous. A pressure of *250 atm.* is a compromise that gives a reasonably good yield of ammonia, that is both cost effective and relatively safe.



 $\rightarrow \rightarrow \rightarrow$ High pressure favours the forward reaction $\rightarrow \rightarrow \rightarrow N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

 $\leftarrow\leftarrow\leftarrow$ low pressure favours the backward reaction $\leftarrow\leftarrow\leftarrow$



• Apart from *temperature* and *pressure*, what else might affect the yield of ammonia and / or the rate at which the ammonia is produced?



 To increase the rate at which nitrogen and hydrogen react to form ammonia, an *iron catalyst* is used. Note: a catalyst will only increase the *rate* at which the chemical reaction reaches equilibrium, it will not affect the *yield* of the product that is formed.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$



• According to the balanced chemical equation, 1 mol of nitrogen reacts with 3 mol of hydrogen, so the nitrogen and hydrogen are combined together in a ratio of 1:3.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$



$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$



$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$





$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

• Hydrogen is obtained from cracking hydrocarbons.

- Nitrogen is obtained from the fractional distillation of liquefied air.
 - Catalyst = Iron
 - Temperature = 450 °C
 - Pressure = 250 atm.



 Red blood cells contain a pigment called *Haemoglobin*. Haemoglobin is responsible for transporting oxygen around the bodies of mammals.

 Haemoglobin contains iron. The iron can change its oxidation state as it bonds with oxygen in the lungs and releases oxygen in the muscles. This change in oxidation state is reversible:

 $Fe^{2+} \rightleftharpoons Fe^{3+} + e^{-}$

 In aerobic respiration, oxygen is transported to the cells where it is combined with glucose and metabolised to carbon dioxide which is then transported back to the lungs to be expelled.

 Haemoglobin (symbol Hb) takes up oxygen from the air in which it becomes loosely bound in a complex known as oxyhaemoglobin. The oxygen concentration is reduced by 50% at the ends of the capillaries delivering blood to the tissues. Equilibrium is shifted to the left, releasing the oxygen so it can diffuse into the cells:

> haemoglobin + oxygen \rightleftharpoons oxyhaemoglobin Hb + 4O₂ \rightleftharpoons Hb \cdot 4O₂



In a reaction vessel there were *initially* 1.0 mol of SO₂,
1.0 mol of O₂ and 0.0 mol of SO₃.
If the amount of SO₃ at equilibrium was 0.4 mol, calculate the amount of SO₂ and O₂ at equilibrium.

 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

	SO ₂	O ₂	SO ₃
Initial moles / mol	1.0	1.0	0.0
Change			
Amount present at equilibrium / mol			0.4

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	SO ₂	O ₂	SO ₃
Initial moles / mol	1.0	1.0	0.0
Change	-0.4	-0.2	+0.4
Amount present at equilibrium / mol	0.6	0.8	0.4

2. There were initially 4.0 mol of NH_3 in a reaction vessel. If the amounts of N_2 , H_2 and NH_3 *at equilibrium* were 2.0 mol, 4.0 mol and 2.0 mol respectively, calculate the initial amounts of N_2 and H_2 before equilibrium was established.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

	N ₂	H ₂	NH_3
Initial moles / mol			4.0
Change			
Amount present at equilibrium / mol	2.0	4.0	2.0

 There were initially 4.0 mol of NH₃ in a reaction vessel. If the amounts of N₂, H₂ and NH₃ at equilibrium were 2.0 mol, 4.0 mol and 2.0 mol respectively, calculate the initial amounts of N₂ and H₂ before equilibrium was established.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

	N ₂	H ₂	NH ₃
Initial moles / mol	1.0	1.0	4.0
Change	+1.0	+3.0	-2.0
Amount present at equilibrium / mol	2.0	4.0	2.0



Equilibrium Constant, K_c

• The position of equilibrium can be estimated by the equilibrium constant K_c, which is the ratio between the amount of reactant and the amount of product. It is used to determine the chemical behaviour of the system.

• Example: For the reaction, $A + 2B \rightleftharpoons C + 3D$

$$K_{c} = \frac{[C][D]^{3}}{[A][B]^{2}}$$

 Larger values of K_c will indicate that the equilibrium lies more to the right.

Acid Dissociation Constant, K_a

- Equilibrium constants can also be defined for the ionization of weak acids. This is known as the acid dissociation constant, K_a.
 - Example: For the reaction, $HA \rightleftharpoons H^+ + A^-$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

 Larger values of K_a indicate that the acid dissociates to a greater extent and is a stronger acid.

Solubility Product Constant, K_{sp}

 Equilibrium constants can also be defined for substances dissolving in water, known as solubility product constant, K_{sp}.

• Example: For the reaction, $AB(s) \rightleftharpoons A^+(aq) + B^-(aq)$

$$K_{sp} = [A^+][B^-]$$

 \bullet Larger values of K_{sp} indicate that the solid is more soluble due to having higher concentrations of ions.



1. Nitrogen reacts with oxygen in an equilibrium reaction.

 $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \quad \Delta H = +170 \text{ kJ/mol}$

When the reaction is at equilibrium, which statement is correct?

- **A** The concentration of nitrogen present will change with time.
- **B** The forward and backward reactions are taking place at the same rate.
- **C** The forward reaction releases heat energy.
- D There are more molecules on the left hand side of the equation than on the right.
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2. In a closed flask, gases **Q** and **R** reach a dynamic equilibrium.

 $\mathbf{Q}(g) \Rightarrow 2\mathbf{R}(g) \quad \Delta H \text{ is positive}$

Which change will move equilibrium to the right?

- **A** Adding a catalyst.
- **B** Decreasing the temperature.
- **C** Increasing the pressure.
- **D** Increasing the volume of the reaction flask.

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3. Elements **X** and **Y** react together in a reversible reaction to form XY_2 .

$$\mathbf{X} + 2\mathbf{Y} \rightleftharpoons \mathbf{X}\mathbf{Y}_2$$

1.0 mol of **X** is mixed with 1.0 mol of **Y** and the mixture is left to react until an equilibrium position is reached.

Which statement(s) about this reaction is / are correct?

- 1 After the equilibrium position has been reached, the reaction stops.
- 2 At equilibrium there is more than 0.5 mol of X present.
- 3 At equilibrium there is less than 0.5 mol of XY_2 present.
- **A** 1, 2 and 3

C 3 only

- **B** 2 only
- **D** 2 and 3 only

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• 30 more multiple-choice questions on reversible reactions:



http://www.chemist.sg/ammonia_equilibrium/equilibrium_mcq_qu.pdf



THE CHEMISTRY OF THE DIFFERENT COLOURS OF BLOOD



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