Reversible Reactions and Equilibrium
Irreversible reactions

- Most Chemical reactions are considered irreversible in that products are not readily changed back into reactants.

- When magnesium reacts with acid it is not easy to unreact it and get back the magnesium.

- When wood burns it is pretty difficult to un-burn it back into wood again!
Although most chemical reactions are difficult to reverse it is possible to find reactions ranging from irreversible to the fully reversible.

Indeed many of the biochemical reactions that take place in living things are reversible.

There are also some very important industrial reactions, like the Haber Process, that are reversible.
Heating ammonium chloride

Ammonium salts are made by reacting ammonia with an acid but some of these salts will decompose back into reactants when heated.

Heat makes the solid disappear as it changes into gases. Solid reappears as it changes back again in the cool part of the tube.

\[
\text{ammonium chloride} \rightleftharpoons \text{Ammonia} + \text{hydrogen chloride}
\]

\[
\text{NH}_4\text{Cl}(s) \rightleftharpoons \text{NH}_3(g) + \text{HCl}(g)
\]
Simple reversible reactions

Heating copper sulphate

• The change from blue hydrated copper sulphate to white anhydrous copper sulphate is one of the most commonly known reversible reactions.

\[ \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 + 5\text{H}_2\text{O} \]
A reversible reaction is where products can, under appropriate conditions, turn back into reactants.

- There will be a range of conditions over which both the forward and backward reaction will take place and this can lead to a state of balance with both reactants and products present in unchanging amounts.
- This is called a **dynamic equilibrium**.

\[
\begin{align*}
A + B & \rightleftharpoons \text{these combine} \\
\text{these decompose} & \quad A + B
\end{align*}
\]
Equilibrium – because of the unchanging amounts

Dynamic – because reaction is still occurring

It is rather like the situation where a man is walking the wrong way along a moving pavement or escalator. Neither have stopped but the man could remain in the same place for ever!

The symbol ⇌ is used to mean dynamic equilibrium.

The man stays in the same place!
In reversible reactions equilibrium means balance but this balance does not have to be at the half-way point.

We may have mostly reactants with just a little product or vice versa.

There are 2 factors that we can change that influence the position of an equilibrium:
- Temperature
- Concentration (or pressure in gas reactions)

Finding the conditions that gives the most product is really important in industrial chemical reactions.
All reactions are exothermic (give out heat) in one direction and endothermic (take in heat) in the other. E.g. nitrogen dioxide ($\text{NO}_2$) joins to form dinitrogen tetroxide ($\text{N}_2\text{O}_4$) exothermically.

$\text{2NO}_2 \iff \text{N}_2\text{O}_4$

- Heating will give more $\text{NO}_2$ in the equilibrium mixture
- Cooling would give more $\text{N}_2\text{O}_4$ in the equilibrium mixture.

The rule is:

The hotter a reaction is, the more likely it is to go in the endothermic direction.
The reaction of nitrogen and hydrogen to form ammonia (NH$_3$) is exothermic.

How will temperature affect the composition of the equilibrium mixture?

- Gets cold going backward (endothermic)
- Gets hot going forward (exothermic)

Which direction is endothermic? **backward**

Which direction do reactions move when heated? **backward**

Will heating give more or less NH$_3$ in the equilibrium mixture? **less**
This applies to gas reactions. Here the rule depends upon the number of gas molecules on each side of the equation.

Get more gas molecules in backward direction

\[2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)\]

Get less gas molecules in forward direction

The higher the pressure the more the reaction moves in the direction with less gas molecules.

- Increasing the pressure will give more \(\text{N}_2\text{O}_4\)
- Decreasing pressure gives more \(\text{NO}_2\) at equilibrium.
Look at the reaction of nitrogen and hydrogen to form ammonia.

Get more gas molecules in backward direction

\[ 3\text{H}_2(g) + \text{N}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]

Get less gas molecules in forward direction

Which direction produces less gas molecules. \( \text{forward} \)

Which direction do reactions move when compressed? \( \text{The side that has less gas molecules} \)

Will high pressure give more or less NH3 in the equilibrium mixture? \( \text{more} \)
Concentration

• This applies to reactions in solution.

Increasing the concentration of a substance tips the equilibrium in the direction that uses up (decreases) the concentration of the substance added.

• Eg. Bismuth chloride reacts with water to give a white precipitate of bismuth oxychloride.

\[
\text{BiCl}_3(\text{aq}) + \text{H}_2\text{O (l)} \quad \Leftrightarrow \quad \text{BiOCl(s)} + 2\text{HCl(aq)}
\]

Adding water will produce more BiOCl solid (to use up the H\textsubscript{2}O).

Adding acid (HCl) will result in less BiOCl solid to use up the HCl.
Chlorine gas reacts with iodine chloride (a brown liquid) converting it to iodine trichloride (a yellow solid).

\[
\text{ICl}(l) + \text{Cl}_2(g) \rightleftharpoons \text{ICl}_3(s)
\]

Brown pale green yellow

What effect will adding more chlorine have upon the colour of the mixture in the U-tube?

Produce more ICl₃ and so more yellow solid.

If the U-tube is turned on its side heavy chlorine gas pours out of the tube.

Which way will this tip the equilibrium?

Produce less ICl and so more brown liquid.
1. Is the forward reaction exothermic or endothermic? **exothermic**

2. Will heating the mixture give an equilibrium mixture with more or less ammonia? **less**

3. Are there more gas molecules of reactant or product? **reactant**

4. Will raising the pressure give an equilibrium mixture with more or less ammonia? **more**

\[ 3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \quad \Delta H = -92\text{kJ/mol} \]
The Haber Compromise

1. What does the graph show about the effect of temperature on the Haber process?

2. Suggest why a temperature of 400°C is chosen when a lower temperature gives an equilibrium mixture with greater % conversion to ammonia.

\[ 3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \quad \Delta H = -92\text{kJ/mol} \]

Hint: reaction rates?

Reduces % conversion
The Haber Compromise

1. What does the graph show about the effect of pressure on the Haber process? **Increases % conversion**

2. Suggest why a pressure of 200 atm is chosen when a higher pressure gives an equilibrium mixture with greater % conversion to ammonia. **Hint: costs?**

![Graph showing the relationship between pressure and % conversion for the Haber process at a temperature of 400°C. The reaction is: 3H₂(g) + N₂(g) ⇌ 2NH₃(g) ΔH=-92kJ/mol.](image)
1. The aim of the chemical industry is not to make chemicals. It is to make money!

2. If we use low temperatures it takes ages to reach equilibrium. It’s better to get a 40% yield in 2 minutes than an 80% yield in 2 hours!

3. If we use *very* high pressures the cost of the equipment used increases drastically and there are also safety issues. Better 90% conversion at 200 atm than 95% conversion at 600 atm.

4. Unchanged reactants can always be recycled.

\[ 3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \quad \Delta H=-92\text{kJ/mol} \]
Haber Process - manufacture of ammonia

\[ 3H_2 + N_2 \rightleftharpoons 2NH_3 \]

-compress (200 atmospheres) and heat (400°C)
-
-Reactio Vessel containing iron catalyst
-
-separation by cooling and condensing the ammonia
-
-ammonia
-

unreacted nitrogen and hydrogen recycled
The Haber Process - manufacture of ammonia

Click on the blue buttons to explore the animation step by step.
The Haber Process - manufacture of ammonia
Click on the play sequence button to explore the animation as a whole.
Which of these is true about a dynamic equilibrium?

A. All the product molecules are used up.
B. All the reactants molecules are used up.
C. The reaction has stopped both in the forward and backward directions.
D. The composition of the reaction mixture remains the same.
Which of these is a reversible process?

A. Reacting acid with alkali.
B. Heating hydrated (blue) copper sulphate.
C. Burning coal.
D. Dissolving magnesium in acid.
Which of these is true about the effect of pressure on the reaction below?

\[2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)\]

A. Increased pressure gives more \(\text{N}_2\text{O}_4\).
B. Increased pressure does not affect the equilibrium.
C. Increased pressure makes \(\text{N}_2\text{O}_4\) decompose.
D. Increased pressure slows down the reaction.
Which of these is true about the effect of increased temperature on the reaction?

\[ \text{2NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \quad \Delta H=-58\text{kJ/mol} \]

A. gives more N\textsubscript{2}O\textsubscript{4}.
B. does not affect the equilibrium.
C. slows down the reactions.
D. Achieves equilibrium more quickly.
Which of these is **NOT** true about the Haber Process?

$$3H_2(g) + N_2(g) \leftrightharpoons 2NH_3(g) \quad \Delta H=-92\text{kJ/mol}$$

A. An iron catalyst is used.

B. Heat is used to increase the ammonia present in the equilibrium mixture.

C. High pressure is used to increase the ammonia present in the equilibrium mixture.

D. Unreacted starting materials are recycled.