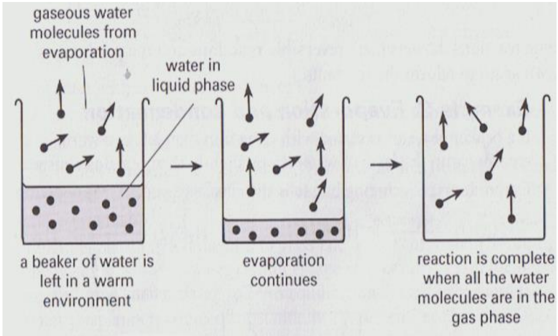
Week 8
EQUILIBRIUM

Learning Outcomes:
- Define dynamic equilibrium using equations of the type: (1)
  A + B $\rightleftharpoons$ C + D
- Describe a closed or an open system (2)
- Explain the system in which an equilibrium can occur (3)
- Define Le Chatelier's principle (1)
- Use Le Chatelier's principle to explain the qualitative effects of changing the:
  a) (1) Temperature (3)
  b) (2) Concentration (3)
  c) (3) Total pressure (reduction in volume results in an increase in pressure) (3)
- Describe the effect of catalysts on equilibrium systems (2)
- Explain how Le Chatelier's principle is applied in the:
  a. Haber process (ammonia production)
  b. Contact Process (sulphur trioxide) as commercial examples of equilibrium reactions (3)
- Account for unfamiliar equilibrium system using Le Chatelier's principles (3)
- Discuss how Le Chatelier's principle is applied in the Haber process (ammonia production) or Contact process (sulphur trioxide) as commercial examples of equilibrium reactions (4)
- Justify unfamiliar equilibrium system using Le Chatelier's principles (4)

INTRODUCTION

- Some physical and chemical reactions continue until one of the reactants has been used up – the reaction is said to have gone to completion.

  Example: Water evaporating
  If a beaker of water is left unsealed in a warm environment, evaporation occurs and the level of water drops until no water is left.



Physical process going to completion

- Some reactions however are reversible and the products may break down again to reform the reactants.

  Example: Evaporation and Condensation
  If a beaker of water is sealed then left in a warm environment, the level of water drops slightly then remains constant.

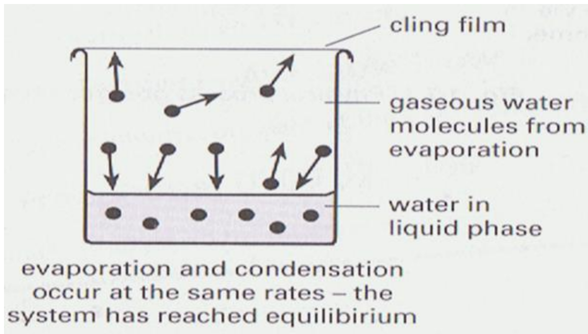


Fig. 10.3: *Physical process in equilibrium*

- Evaporation is occurring but so is the opposing process, condensation.

$$H_2O_{(l)} \xrightarrow{\text{evaporation}} H_2O_{(g)}$$
$$H_2O_{(g)} \xrightarrow{\text{condensation}} H_2O_{(l)}$$

- This can be written as:

$$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$$

- The seal beaker forms a **closed system,** as water molecules cannot escape from the container.
- The reaction mixture contains a mixture of both reactants and products.

<u>Equilibrium</u>
- Chemical equilibrium applies to reactions that can occur in both directions. In a reaction such as:

$$\rightleftharpoons$$

$CH_4(g) + H_2O(g) \qquad CO(g) + 3H_2(g)$

- When reversible reactions reach the point where the rate of forward reaction equals rate of backward reaction, the system is said to have reached **equilibrium.**
- Equilibrium can only be attained if the situation in which the chemical reaction occurs is a closed-system.
- The equilibrium is a dynamic equilibrium. The definition for a **dynamic equilibrium** is when the forward and backward reactions do not stop.
- When equilibrium is reached they proceeds at the same rates so the amounts of reactants and products remain constant.(They are not equal but constant. Also, both reactions are still occurring.)

<u>Equilibrium Changes</u>

- Once a reversible reaction has reached equilibrium, it will remain at equilibrium indefinitely unless changes occur which upset the equilibrium.
- These changes, which arise from variations in *temperature, pressure or composition*, result in either:

  (i) an <u>increase in the rate of the forward reaction</u>, changing more reactants into products. The equilibrium position is said to 'move to the right'

  reactants $\longrightarrow$ products
  or

  (ii) an <u>increase in the rate of the reverse reaction,</u>increasing the rate at which products break down to reactants. The equilibrium position is said to 'move to the left'

  reactants $\longleftarrow$ products

- Eventually equilibrium is re-established and the rates of the forward and reverse reactions become equal again.

  reactants $\rightleftharpoons$ products

<u>Le Chatelier's Principle</u>

- Henri Louis Le Chatelier (1850 – 1936) was a French scientist who studied equilibrium systems.
- He established a principle used to **predict** the effect different changes would have on a system at equilibrium.

A statement of Le Chatelier's Principle

"If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change."

Note:

- The principle is used to predict the *direction* of change. It does not predict the *extent* of change.
- There are instances where Le Chatelier's Principle does not predict an equilibrium outcome; it is therefore not a true scientific principle. However it is still used as a very good guideline to predict changes in equilibria.

1) Using Le Chatelier's Principle with a change of concentration

- Suppose you have an equilibrium established between four substances A, B, C and D.

$$A + 2B \rightleftharpoons C + D$$

What would happen if you changed the conditions by increasing the concentration of A?

- According to Le Chatelier, the position of equilibrium will move in such a way as to counteract the change.
- That means that the position of equilibrium will move so that the concentration of A decreases again - by reacting it with **B** and turning it into **C + D.**
- The position of equilibrium moves to the right.

$$A + 2B \rightleftharpoons C + D$$

The position of equilibrium moves to the right if you increase the concentration of A.

- This is a useful way of converting the maximum possible amount of B into C and D.
- You might use it if, for example, B was a relatively expensive material whereas A was cheap and plentiful.

What would happen if you changed the conditions by decreasing the concentration of A?

- According to Le Chatelier, the position of equilibrium will move so that the concentration of **A** increases again.
- That means that more **C** and **D** will react to replace the A that has been removed. The position of equilibrium moves to the left.

$$A + 2B \rightleftharpoons C + D$$

The position of equilibrium moves to the left if you decrease the concentration of A.

- This is essentially what happens if you remove one of the products of the reaction as soon as it is formed.
- If, for example, you removed **C** as soon as it was formed, the position of equilibrium would move to the right to replace it.
- If you kept on removing it, the equilibrium position would keep on moving rightwards - turning this into a one-way reaction.

<u>Example: The Haber Process</u>

– In the Haber process, ammonia is produced according to the reaction:

$$\mathbf{N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3(g)}}$$

– The ammonia is removed by absorbing it in water or by condensing it to form liquid ammonia.
– As ammonia is removed, the remaining reactants react to produce more ammonia.
– For equilibrium reactions in aqueous solutions, the equilibrium position can be shifted by precipitation.

2) Using Le Chatelier's Principle with a change of pressure

- This only applies to reactions involving gases:

$$A_{(g)} + 2B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$$

What would happen if you changed the conditions by increasing the pressure?

- According to Le Chatelier, the position of equilibrium will move in such a way as to counteract the change. That means that the position of equilibrium will move so that the pressure is reduced again.
- Pressure is caused by gas molecules hitting the sides of their container.
- The more molecules you have in the container, the higher the pressure will be. The system can reduce the pressure by reacting in such a way as to produce fewer molecules.
- In this case, there are 3 molecules on the left-hand side of the equation, but only 2 on the right.
- By forming more C and D, the system causes the pressure to reduce.
- *Increasing the pressure* on a gas reaction shifts the position of equilibrium towards the side with *fewer* molecules.

$$A_{(g)} + 2B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$$

The position of equilibrium moves to the right if you increase the pressure on the reaction.

What would happen if you changed the conditions by decreasing the pressure?

- The equilibrium will move in such a way that the pressure increases again.
- It can do that by producing more molecules. In this case, the position of equilibrium will move towards the left-hand side of the reaction.

$$A_{(g)} + 2B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$$

The position of equilibrium moves to the left if you decrease the pressure on the reaction.

What happens if there are the same number of molecules on both sides of the equilibrium reaction?

- In this case, increasing the pressure has no effect whatsoever on the position of the equilibrium. Because you have the same numbers of molecules on both sides, the equilibrium can't move in any way that will reduce the pressure again.

3) Using Le Chatelier's Principle with a change of temperature

- For this, you need to know whether heat is given out or absorbed during the reaction. Assume that our forward reaction is exothermic (heat is evolved):

$$A + 2B \rightleftharpoons C + D \quad \Delta H = -250 \text{ kJ mol}^{-1}$$

- This shows that 250 kJ is evolved (hence the negative sign) when 1 mole of A reacts completely with 2 moles of B.
- For reversible reactions, the value is always given as if the reaction was one-way in the forward direction.
- The back reaction (the conversion of C and D into A and B) would be **endothermic** by exactly the same amount.

250 kJ is **evolved** when A and B react completely to give C and D.

$$A + 2B \rightleftharpoons C + D \quad \Delta H = -250 \text{ kJ mol}^{-1}$$

250 kJ is **absorbed** when C and D react completely to give A and B.

What would happen if you changed the conditions by increasing the temperature?

- According to Le Chatelier, the position of equilibrium will move in such a way as to counteract the change. That means that the position of equilibrium will move so that the temperature is reduced again.
- Suppose the system is in equilibrium at 300°C, and you increase the temperature to 500°C. How can the reaction counteract the change you have made? How can it cool itself down again?
- To cool down, it needs to absorb the extra heat that you have just put in. In the case we are looking at, the *back reaction* absorbs heat.
- The position of equilibrium therefore moves to the left. The new equilibrium mixture contains more A and B, and less C and D.

$$A + 2B \rightleftharpoons C + D \quad \Delta H = -250 \text{ kJ mol}^{-1}$$

The position of equilibrium moves to the left if you increase the temperature.

- If you were aiming to make as much C and D as possible, increasing the temperature on a reversible reaction where the forward reaction is exothermic isn't a good idea!

What would happen if you changed the conditions by decreasing the temperature?

- The equilibrium will move in such a way that the temperature increases again.
- Suppose the system is in equilibrium at 500°C and you reduce the temperature to 400°C. The reaction will tend to heat itself up again to return to the original temperature.
- It can do that by favouring the exothermic reaction.
- The position of equilibrium will move to the right. More A and B are converted into C and D at the lower temperature.

$$A + 2B \rightleftharpoons C + D \quad \Delta H = -250$$

The position of equilibrium moves to the right if you decrease the temperature.

Summary

- Increasing the temperature of a system in dynamic equilibrium favours the endothermic reaction. The system counteracts the change you have made by absorbing the extra heat.
- Decreasing the temperature of a system in dynamic equilibrium favours the exothermic reaction. The system counteracts the change you have made by producing more heat.

4) Le Chatelier's Principle and catalysts

- Catalysts have sneaked onto this page under false pretences, because *adding a catalyst makes absolutely no difference to the position of equilibrium,* and Le Chatelier's Principle doesn't apply to them.
- This is because a catalyst speeds up the forward and back reaction to the same extent. Because adding a catalyst doesn't affect the relative rates of the two reactions, it can't affect the position of equilibrium. So why use a catalyst?
- For a dynamic equilibrium to be set up, the rates of the forward reaction and the back reaction have to become equal. This doesn't happen instantly.
- For a very slow reaction, it could take years!
- A catalyst speeds up the rate at which a reaction reaches dynamic equilibrium.

<u>Production of Sulphuric Acid</u>

- Almost 90% of the sulphur extracted world-wide is converted to sulphuric acid, H_2SO_4, using a system called the **contact process**.

The Contact Process

<u>Stage 1:</u>*Sulphur is melted and water removed. The sulphur is then burnt in dry air where it readily oxidises to sulphur dioxide.*

$$S_{(l)} + O_{2(g)} \longrightarrow SO_{2(g)} \quad \Delta H = 300\ kJmol^{-1}$$

The sulphur dioxide is cooled to 400ºC.

<u>Stage 2</u>:*Sulphur dioxide is converted to sulphur trioxide, SO_3, by adding excess dry air.*

$$2SO_{2(g)} + O_2 \rightleftharpoons 2SO_{3(g)} \quad \Delta H = -100kJmol^{-1}$$

- The reaction is extremely slow at normal temperatures and pressures. Since the forward reaction is:
  - (i) **Exothermic,** it is therefore most efficient at low temperatures.
  - (ii) Accompanied by a **decrease in pressure** (3 moles of gas on the left, 2 on the right) it is therefore most efficient at high pressure.
- In practice, a reasonable reaction rate is achieved by using temperatures between 400 – 500ºC and a pressure of 200kPa.
- A catalyst, **vanadium pentoxide, V_2O_5,** is also used, otherwise conversion of SO_3 is virtually nonexistent.

<u>Stage 3:</u> *The sulphur trioxide must now react with water to form sulphuric acid.*

$$SO_{3(g)} + H_2O_{(l)} \longrightarrow H_2SO_{4(l)}$$

- In practice, sulphur trioxide in contact with water produces a troublesome fog of sulphur trioxide and sulphuric acid droplets.
- Consequently, sulphur trioxide is passed through a counter-current of concentrated sulphuric acid in a n absorption tower where the sulphur trioxide and sulphuric acid react to form *fuming sulphuric acid,* $H_2S_2O_7$

The $H_2S_2O_7$ is diluted with water to produce 98% sulphuric acid:

$$H_2S_2O_{7(l)} + H_2O_{(l)} \qquad 2H_2SO_{4(l)}$$

All stages in the manufacture of sulphuric acid release a great deal of heat, which is used for generating steam to drive generators; the electricity produced makes the whole plant energy self-sufficient.

<u>Exercise 11: Equilibrium Changes</u>

1. For the reaction:

   $$\mathbf{PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}}$$

   Predict the effect on the equilibrium of:

   a) Decreasing the pressure.
   b) Adding chlorine gas
   c) Adding a catalyst

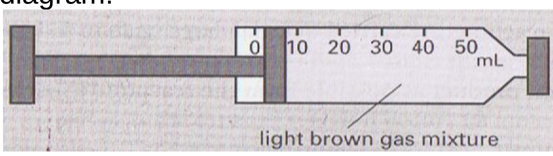
2. Predict the effect of increasing the temperature on each of the following equilibria:

   a) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\Delta H = -92$ kJ
   b) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ $\Delta H = +176$ kJ
   c) $CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$ $\Delta H = +91$ kJ

3. The equilibrium between nitrogen dioxide and dinitrogen tetroxides is represented by:

   $$\underset{\text{dark brown}}{2NO_{2(g)}} \rightleftharpoons \underset{\text{colourless}}{N_2O_{4\,(g)}} \Delta H = -54 \text{ kJmol}^{-1}$$

   Some of the equilibrium mixture is put into a syringe as shown in the diagram:

   a) What would be the effect on the number of molecules of nitrogen dioxide if the plunger was pushed into the 30mL mark on the syringe while the temperature was kept constant?

   b) What colour change would occur if the plunger is held in position but the syringe is placed in ice water? Explain why this colour change occurs.

4. Explain how the concentration of hydrogen gas in the equilibrium system following will be affected by the changes described. Give reasons for your answers.

   $$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \quad \Delta_rH = 131 \text{ kJ/mol}$$

   a) The temperature is increased
   b) The pressure is decreased
   c) CO(g) is removed from the system
   d) C(s) is added to the system