Section 4
Equilibrium

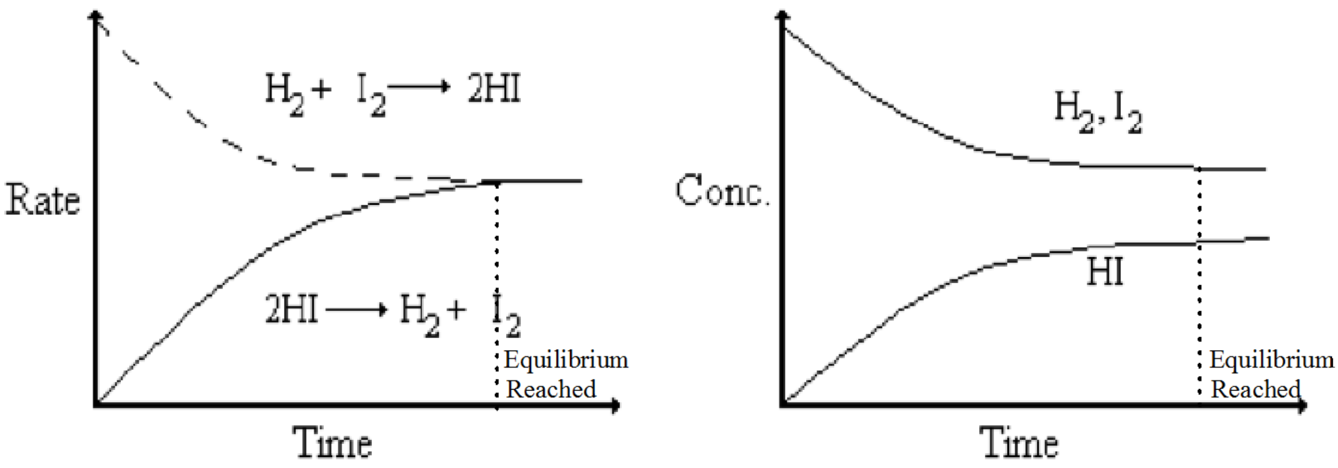
- Dynamic features of a chemical equilibrium
- Factors affecting equilibrium (change in volume, temperature, pressure and concentration as well as addition of inert gases).
- Reaction quotient expressions and the significance of the magnitude of K_c
- K_c calculations
- Industrial applications – the Haber process and the Contact process

Equilibrium

Not all chemical reactions continue until all of the available reactants have been used up. If a mixture of $H_2(g)$ and $I_2(g)$ is placed in a sealed container of fixed volume, some $HI(g)$ molecules are formed by the reaction:

forward reaction	$H_2(g) + I_2(g) \rightarrow 2HI(g)$
reverse reaction	$2HI(g) \rightarrow H_2(g) + I_2(g)$

At the start the reaction is very fast because the concentrations of the two reactants is high. As the reaction proceeds and their concentration decreases, so does the rate of reaction. The chance of two HI molecules decomposing is very small at the start, because their concentration is so small, but as this increases, so does the rate of the reverse reaction.



Eventually, the rates of the forward and reverse reactions become equal and no other net change will occur to the concentrations of all the species present.

This situation can be attained from either direction beginning with only the particles appearing on one side of the reaction.

So that no particles can be allowed to enter or leave, the system needs to be closed.

The characteristics of a system in equilibrium are:

- The system is closed.
- There is no observable change in colour, pressure, temperature and the ratio of reactants to products.
- Both reactants and products are present together, their concentrations remain constant
- Both forward and reverse reactions are occurring, their rates are equal.

Questions 1

Changing the Position of Equilibrium

Once a system has come to equilibrium it stops changing. Only if it is disturbed in some way does a system that has reached equilibrium change. The pattern in the way the equilibrium systems respond to change was first put forward by a French scientist called Le Chatelier.

"***An equilibrium system responds to change in such a way as to lessen the effect of that change***"

Factor	Response of equilibrium systems to change	
Concentration	Increase reactants	Towards products
	Increase products	Towards reactants
Pressure	Increase pressure	Towards the smaller amount of gaseous molecules
	Decrease pressure	Towards the larger number of gaseous molecules
Temperature	Increase temperature	Towards endothermic, ΔH +ve
	Decrease temperature	Towards exothermic, ΔH -ve

A catalyst has no effect on the position of equilibrium. It provides an alternative pathway of a lower activation energy for both forward and reverse reactions which means that equilibrium is reached more quickly but the concentrations of all species present at equilibrium is unchanged.

The **value** of Kc is only affected by a change in temperature.

Questions 2

The equilibrium constant(K_c)

Any system at equilibrium has a specific ratio of reactants to products. This ratio can be written as a mathematical formula, called the equilibrium expression and it is constant for any given temperature, usually 25ºC.

For the general equation: $aA + bB \rightleftharpoons cC + dD$

The expression is:

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

The symbol [A] means "the concentration of A in mol L^{-1}". The letters a, b, c, and d represent the numbers in front of each substance in the balanced equation and show the number of times that concentration should be multiplied by itself.

K_c is called the **equilibrium constant**. It is a number that is constant for that temperature.

So for the equation:

$$2H_2S(g) + CH_4(g) \rightleftharpoons 4H_2(g) + CS_2(g) \qquad K_c = \frac{[H_2]^4[CS_2]}{[H_2S]^2[CH_4]}$$

Note:
The concentration of all solids is related to their densities. It is therefore a constant and becomes incorporated into the K_c value. Therefore we leave all solids out of equilibrium expressions.

In addition, water is left out of equilibrium constants if the reaction is taking place in an aqueous environment in other words in solution in water. In that case, water is so much in excess that its concentration is hardly changed by the reaction and it is incorporated into the K_c value.

The equilibrium constant for a reaction tells the chemist whether the reaction favours the reactants or the products. If K_c is large, then the reaction favours the products. A small K_c (less than 0.1) indicates only a small proportion of product will be formed. The expression also shows how changing the concentration of one reagent may be more effective than changing the concentration of one of the other reagents.

Equilibrium Constant Calculations

Example

A mixture of 5.0 mol of H_2 and 10.0 mol of I_2 is placed in a 5 L container at 450 °C and allowed to reach equilibrium. At equilibrium, the [HI] is 1.87 mol L^{-1}. Calculate K_c for the reaction.

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

1. Use the equation to establish mole ratios.
   1 mol H_2 + 1 mol I_2 → 2 mol HI
2. Make sure all initial concentration are expressed in mol L^{-1}.
   Volume = 5L, $[H_2]$ = 1 mol L^{-1}; $[I_2]$ = 2 mol L^{-1}
3. Write out the initial concentration
   Initial concentrations: $[H_2]$ = 1.0 mol L^{-1}; $[I_2]$ = 2 mol L^{-1}; [HI] = 0
4. Find the amounts of each reactant used.
   H_2 used = [HI] × mole ratio H_2 / HI
   = 1.87 × 0.5
   = 0.935 mol L^{-1}
   I_2 used = 1.87 × 0.5
   = 0.935 mol L^{-1}
5. Find the amount of each reactant present at equilibrium.
   H_2 present = initial concentration – amount used
   = 1 – 0.935
   = 0.065 mol L^{-1}
   I_2 present = 2 – 0.935
   = 1.065 mol L^{-1}
6. Write out the final concentration at equilibrium and substitute the values in the equilibrium
   expression to find K_c.
   $[H_2]$ = 0.065 mol L^{-1}; $[I_2]$ = 1.065 mol L^{-1}; [HI] = 1.87
   $K_c = [HI]^2 / [I_2][H_2]$
   $= 1.87^2 / 0.065 \times 1.065$
   = 50.51

Questions 3

Industrial Equilibrium

We will study this using two industrial processes as examples.

The Haber Process

A German chemist, Fritz Haber (1868 – 1934) worked out the suitable conditions for ammonia production in 1908 and the first plant started production in 1913.

The overall reaction in the Haber process is the conversion of nitrogen gas and hydrogen gas into ammonia gas as shown below:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92 \text{ kJ mol}^{-1}$$

In New Zealand ammonia is produced in Taranaki at the Petrochem Ammonia/urea plant. Methane from natural gas is the source of hydrogen. Methane and steam pass over a nickel catalyst at 805 °C to make synthesis gas:

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H = +206 \text{ kJ mol}^{-1}$$

Mixed with air, and stripped of water and oxides of carbon, the nitrogen / hydrogen mixture then enters the ammonia plant.

In theory running the reaction at a very high pressure and room temperature should maximise the yield of ammonia produced. The pressure chosen is a matter of economics. While high pressure increases the yield of ammonia, vessels capable of withstanding these pressures and energy to run the compressors to achieve them are costly. The operating temperature is also a matter of balancing opposing factors At the low temperatures that favour a higher yield of ammonia, the time taken to reach equilibrium even when catalysed is too long to be economic. Raising the temperature to achieve an acceptable reaction rate decreases the yield, but this cannot be helped. Most modern Haber plants operate at about 400 °C and 320 atmospheres with an Fe_2O_3 catalyst. This produces a 15% yield, which is removed by cooling into a liquid and then the unreacted gases are recylcled to pass over the catalyst again.

A small amount of the ammonia produced is sold for use as a refrigerant. Most is converted into urea ($CO(NH_2)_2$), which is used as a nitrogen-rich fertiliser and in the production of urea-formaldehyde resins.

Compressed carbon dioxide (removed from the synthesis gas during ammonia production) and liquid ammonia are combined at 237 atmospheres and 200 °C.
The overall reaction is

$$2NH_3(l) + CO_2(g) \rightarrow CO(NH_2)_2(l) + H_2O(g) \qquad \Delta H > 0$$

About 70% conversion to urea is reached in about 30 minutes.

The Contact Process

Sulfuric acid is an important industrial chemical. Its main use in New Zealand is in making fertilisers.

To make sulfuric acid, sulfur is burnt in air to make sulfur dioxide:

$$S(s) + O_2(g) \rightarrow SO_2(g) \qquad \Delta H = -296 \text{ kJ mol}^{-1}$$

The sulfur dioxide is burnt in more oxygen to make sulfur trioxide:

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

and the sulfur trioxide reacted with water to make sulfuric acid:

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

The hard part is the conversion of sulfur dioxide to sulfur trioxide. At room temperature the reaction is very slow and reversible.

To produce the maximum yield the reaction should be done
* at high pressure
* at low temperature
* with an excess of reactants
* with products removed.

To increase the reaction rate the reaction should be done
* at high pressure
* at high temperature
* with a catalyst.

Actually, although the reaction is an equilibrium reaction, the yield of SO_3 is just about 100% until the temperature rises above 350° C. The main problem is the slow rate of reaction. By using a catalyst of vanadium pentoxide (V_2O_5) the reaction rate is sufficient so that a high-pressure plant (which is expensive) need not be used. The reaction is exothermic, so the temperature rises as the reaction proceeds. With the rise in temperature comes the decomposition of SO_3. To limit this, the gases are passed over the catalyst bed several times, and cooled back to 420 °C between passes. Using this system, conversions of 98% or better can be achieved.

In the final step if sulfur trioxide is mixed directly with water it forms a mist which is difficult to handle. Instead, the gas is bubbled into concentrated (98%) sulfuric acid (which still contains a small amount of water). This acid is then diluted to the required strength.

Questions 4

Questions 1

Which of the following processes are examples of dynamic equilibrium?

a. The liquid and vaporous mercury in a sealed thermometer at a given temperature.

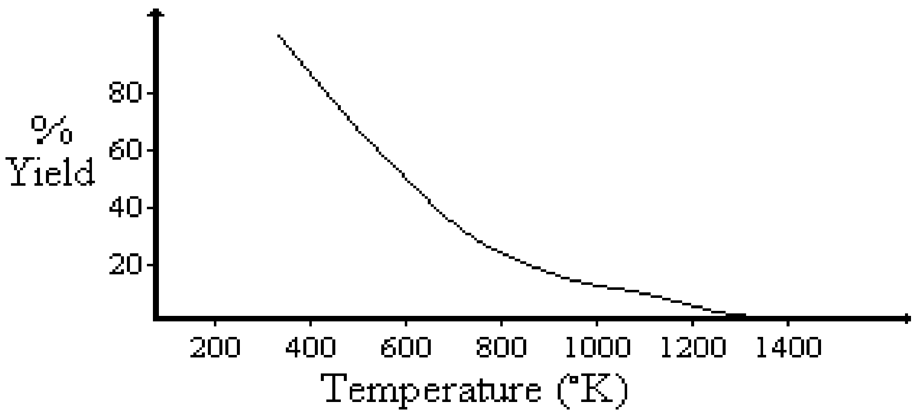
b. Water running into a lake at the same rate at which it is leaving.

c. A saturated solution of $PbCl_2$ with some white precipitate in a beaker, at a given temperature.

Questions 2

1. Temperature effects and yields are investigated for the reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H < 0$$



The results are shown on the graph.

a Explain why these results are consistent with those predicted by Le Chatelier.

b What is the advantage in higher temperatures to the industrial engineer?

c What is the disadvantage?

2. The equilibrium between nitrogen dioxide and dinitrogen tetroxide is represented by:

$$\underset{\text{(dark brown)}}{2NO_2(g)} \rightleftharpoons \underset{\text{(colourless)}}{N_2O_4(g)} \qquad \Delta H = -46.2 \text{ kJ mol}^{-1}$$

Some of the equilibrium mixture was placed in a 60 mL syringe.

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

b List two observations that would be made when the syringe is placed in iced water to cool it down.

c What colour change occurs when the plunger is secured in one position and the syringe is placed in iced water? Explain why this colour change occurs.

3. For the following equilibrium systems, say whether the forward or back reaction will be favoured by a *decrease* in temperature.

   a. $2O_3(g) \rightleftharpoons 3O_2(g)$ $\Delta H = -285$ kJ

   b. $C(s) + H_2O(g) \rightleftharpoons H_2(g) + CO(g)$ $\Delta H = +130$ kJ

Questions 3

1. Each reaction below is at equilibrium then the indicated change is applied. Comment on the change (if any) to the amount of underlined substance. Comment on any change in the value of K_c.

   a. $2SO_2(g) + \underline{O_2(g)} \rightleftharpoons 2SO_3(g)$ $\Delta H < 0$ (Temperature increased).

   b. $\underline{Cr_2O_7^{2-}(aq)} + OH^-(aq) \rightleftharpoons 2CrO_4^{2-}(aq) + H^+(aq)$ (Add dilute HCl).

   c. $\underline{N_2(g)} + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (Catalyst added).

   d. $\underline{AgCl(s)} \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ (NaCl added).

   e. $2NO_2(g) \rightleftharpoons \underline{N_2O_4(g)}$ $\Delta H < 0$ (Pressure and temperature increased).

2. For the following problems write the expression for K_c and then use the given data to calculate the value of K_c.

   a. $2NO_2(g) \rightleftharpoons N_2O_4(g)$ {$[NO_2] = 0.072$; $[N_2O_4] = 0.014$}

   b. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ {$[N_2] = 0.20$; $[H_2] = 0.20$; $[NH_3] = 0.016$}

   c. $NCl_3(g) + Cl_2(g) \rightleftharpoons NCl_5(g)$ {Equilibrium is established when there is 0.0350 mole of NCl_3, 0.0200 mole of Cl_2 and 0.0110 mole of NCl_5 in a volume of 2.5 litres}

3. In an experiment, 10 mol of hydrogen and 10 mol of iodine vapour were placed in a 10 L sealed vessel under a constant temperature and pressure. At equilibrium, 7 mol of hydrogen was found. Calculate the concentration of each substance present at equilibrium and the equilibrium constant K_c.

$$H_2(g) \quad + \quad I_2(g) \quad \leftrightarrow \quad 2HI(g)$$

4. In an experiment, 10 mol of hydrogen and 10 mol of nitrogen were placed in a 10 L sealed vessel under a constant temperature and pressure. At equilibrium, 7 mol of hydrogen was found. Calculate the concentration of each substance present at equilibrium and the equilibrium constant K_c.

$$3H_2(g) \quad + \quad N_2(g) \quad \leftrightarrow \quad 2NH_3(g)$$

Questions 4

The following table gives data which could be used to decide which are the most suitable conditions for the production of ammonia by the Haber process. It shows the percentage yield at various temperatures and pressures.

Temperature (°C)	Pressure (atm)				
	10	50	100	300	1000
200	51%	74%	82%	90%	98%
300	15%	39%	52%	71%	93%
400	4%	15%	25%	47%	80%
500	1%	6%	11%	26%	57%
600	0.5%	2%	5%	14%	13%

a. Write an equation for the formation of ammonia from hydrogen and nitrogen.

b. Write an expression for the equilibrium constant for the above reaction.

c. Using the data in the table, determine the temperature and pressure which gives the greatest yield of ammonia.

d. What is the percentage of ammonia present in the equilibrium mixture at 500°C and 100 atmospheres?

e. A certain industrial plant operates at a temperature of 450 °C and a pressure of 300 atmospheres. Suggest a reason why these conditions are used rather than those in your answer to c.

Summary of Haber and Contact Processes

Industrial Application	The Haber process	The Contact process
Equilibrium reaction equation		
Catalyst		
How to increase the yield of the product by changing concentration?		
How to increase the yield of the product by changing pressure?		
How to increase the yield of the product by changing temperature?		
Final product		
Uses of the product		