CHEM 9.5.2 EQUILIBRIUM REACTIONS

Many industrial processes involve manipulation of equilibrium reactions

2.1 Explain **the effect of changing the following factors** on identified equilibrium reactions: **pressure, volume, concentration and temperature**

- Le Chatelier's principle states that when an equilibrium is disturbed, it will move to **minimise** the disturbance
- For an equilibrium, $\mathbf{A + B \rightleftharpoons C + D}$:
- Change in **pressure** (increase)
  - If A is a gas, then increased pressure will shift **equilibrium to the right** to reduce pressure
  - Speeds up rate of reaction as molecules are closer together
- Change in **volume** is similar to pressure (increase)
  - If C is a gas, then increased pressure will shift **equilibrium to the left** to reduce pressure
  - Speeds up rate of reaction as molecules are closer together
- Change in **concentration** (increase)
  - When A is increased **equilibrium shifts to the right** to reduce A+B concentration
- Change in **temperature** (increase)
  - If reaction is exothermic ($\mathrm{C + D + heat}$), then equilibrium will shift **to the left** to reduce heat
  - Speeds up rate of reaction as molecules move faster and there is more chance for them to react

2.2 Interpret the equilibrium **constant expression** (no units required) from the chemical equation of equilibrium reactions

- The equilibrium constant **K** can be measured at specific point of equilibrium
- For example, with the balanced equilibrium $\mathbf{aA + bB \rightleftharpoons lL + mM}$

$$\mathbf{K = \frac{[L]^l[M]^m}{[A]^a[B]^b}}$$

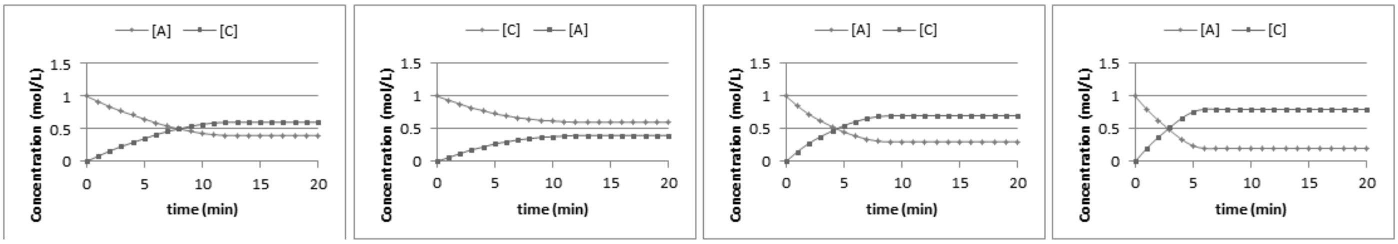
  - Where [] is equilibrium concentrations, only when in equilibrium, otherwise Q, a **reaction variable**
- PORK – **products over reactants**

2.3 Identify that **temperature** is the only factor that **changes the value of the equilibrium constant** (K) for a given equation

- Position of equilibrium, concentration and Q (reaction quotient) may change, but **K does not change**
- Only factor that changes is **temperature** – Le Chatelier's principle
- For **exothermic** reactions ($\mathrm{A + B \rightleftharpoons C + D + heat}$):
  - **Increase in temperature** causes more **reactants** – higher denominator, **K decreases**
  - **Decrease in temperature** causes more **products** – higher numerator, **K increases**
- For **endothermic** reactions ($\mathrm{A + B + heat \rightleftharpoons C + D}$):
  - **Increase in temperature** causes more **products** – higher numerator, **K increases**
  - **Decrease in temperature** causes more **reactants** – higher denominator, **K decreases**

2.P1 Identify data, plan and perform a first-hand investigation to **model an equilibrium reaction**

- **Excel** was used to model **one chemical reaction** ($A + B + \text{heat} \rightleftharpoons C + D$) and the impact of temperature
  - **Task 1**: Only A and B added initially at 20°C
  - **Task 2**: Only C and D added initially at 20°C
  - **Task 3**: A and B at 30°C
  - **Task 4**: A and B at 35°C



- Both 1 and 2 ended with: [A] = 0.4 and [B] = 0.6 K = 0.44
- 3 ended with: [A] = 0.3 and [B] = 0.7 K = 0.18
- 4 ended with: [A] = 0.2 and [B] = 0.8 K = 0.06
  - Therefore as **temperature increases,** the K **value decreases (endothermic)**

2.P2 Choose equipment and perform a first-hand investigation to **gather information** and **qualitatively analyse** an equilibrium reaction

- Different equilibrium equations were used when imposing **different changes of reaction conditions**

CHROMATE-DICHROMATE EQUILIBRIUM

- Effect of changing **pH** using **K_2CrO_4** (yellow) and **K_2CrO_7** (orange)
  - Colour due to anions
  - $2CrO_{4\,(aq)}^{2-} + 2H_{(aq)}^{+} \rightleftharpoons CrO_{7\,(aq)}^{2-} + H_2O_{(l)}$
- Adding **HCl** increases H^+ ions, so **equilibrium shifts right** and turns **orange (CrO_7 ions)**
- Adding **NaOH**, OH^- reacts with H^+ ions to make H_2O, so **equilibrium shifts left** and turns back **yellow**

IRON-THIOCYANATE EQUILIBRIUM

- Effect of changing **concentration** using **KSCN** (white) and **$Fe(NO_3)_3$** (yellow)
  - $FeSCN^{2+}$ is **blood red**, so water added till control is orange red colour
  - $Fe_{(aq)}^{3+} + SCN_{(aq)}^{-} \rightleftharpoons FeSCN_{(aq)}^{2+}$
- Adding **KSCN** increases SCN^- ions, so equilibrium moves **right** and turns **darker red**
- Adding **$Fe(NO_3)_3$** increases Fe^{3+} ions, so equilibrium moves **right** and turns **blood red**
- Adding **NaOH**, Fe^{3+} reacts with OH^- to form $Fe(OH)_3$, equilibrium moves **left** and turns **light yellow**

COBALT CHLORIDE EQUILIBRIUM

- Effect of changing **temperature** using **cobalt chloride solution** (deep red at room temp)
  - Hydrated cobalt (II) $Co(H_2O)_6{}^{2+}{}_{(aq)}$ is **pink-red**, $CoCl_4{}^{2-}$ is **blue**
  - $Co(H_2O)_{6\,(aq)}^{2+} + 4Cl_{(aq)}^{-} \rightleftharpoons CoCl_{4\,(aq)}^{2-} + 6H_2O_{(l)} + \text{heat}$
- Placing in **crushed ice beaker** reduces heat, so equilibrium **moves right** and turns **blue-purple**
- Placing in a **boiling water beaker** increases heat, so equilibrium **moves left** and turns light red

Substance	Safety Issue
K_2CrO_4	• Solid: highly toxic, carcinogenic, avoid skin contact • Solution: wash chemicals in sink
$K_2Cr_2O_7$	• Solid: reacts with active metals • See above
$Fe(NO_3)_3$	• Toxic if ingested
KSCN	• Low amounts in ventilated area, or fume cupboard • Do not add to H_2SO_4 as fumes are toxic
Cobalt Chloride solution	• Slightly toxic, may be carcinogenic

2.P3 Process and present information from secondary sources to **calculate K from equilibrium conditions**

- Equilibrium constant is **only a number** – **solid reactants/products ignored**
- K only measured at equilibrium at constant temperature

Example: Initially, 1L vessel contained 0.25 mol NO and 0.12 mol O_2. After equilibrium, 0.05 mol NO. Calculate equilibrium constant for this reaction: $2NO_{(g)} + O_{2\,(g)} \rightleftharpoons 2NO_{2\,(g)}$

Equation	$2NO_{(g)}$	$O_{2\,(g)}$	$2NO_{2\,(g)}$
Initial	**0.25 mol (given)**	**0.12 mol (given)**	**0 (there are no products yet)**
Change			
Equilibrium	**0.05 mol (given)**		

- Difference between initial and equilibrium is change – in NO, **change =** $\mathbf{0.25 - 0.05 = 0.2}$
  - Therefore **decrease in O_2 is half** that (because of equation, 2 moles NO react with 1 mole O_2)
  - Therefore **increase in NO_2 is the same** (because 2 moles NO react to form 2 moles NO_2)
- Then work out equilibrium:

Equation	$2NO_{(g)}$	$O_{2\,(g)}$	$2NO_{2\,(g)}$
Initial	**0.25 mol**	**0.12 mol**	**0 mol**
Change	-0.2 mol	-0.1 mol	+0.2 mol
Equilibrium	**0.05 mol**	0.02 mol	0.2 mol

- Therefore find K (using PORK): *without units

$$K = \frac{[NO_2]^2}{[NO]^2[O_2]} = \frac{0.2^2}{0.05^2 \times 0.02} = 800$$