Properties of organic compounds

This chapter covers AS 91391 (Chemistry 3.5)

Essential exam notes

Isomers

Isomers (molecules that cannot be superimposed on each other by rotation about single bonds) can be classified in different categories.

Structural (constitutional) isomers – same molecular formula but different structures as a result of different chain length due to branching, or shifting of the position of a functional group, or changing the nature of the functional group. They have different physical properties (e.g. melting point and boiling point); chemical properties may differ, depending on the nature of the functional group.

Stereoisomers – atoms linked in the same order but different 3-dimensional arrangement. They may be:

- **geometric isomers** – molecules with different orientation of functional groups due to the presence of a double bond or a ring in a cyclic compound; they differ in physical properties

cis-but-2-ene   *trans*-but-2-ene
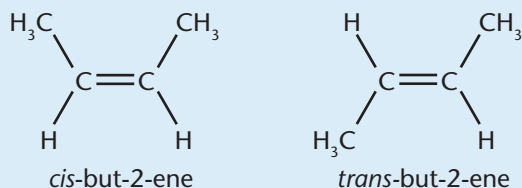
- **optical isomers** or **enantiomers** – molecules that are non-superimposable mirror images are chiral molecules; they contain a stereogenic (chiral) carbon atom that has four different groups attached
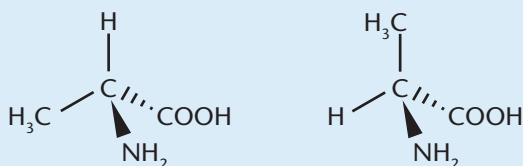
Enantiomers have identical physical properties except that they **rotate** the plane of polarised light in opposite directions. They have identical chemical properties except in their reactions with other optical isomers.

Functional groups and their reactions

Alkanes

The general formula for acyclic alkanes (without rings) is C_nH_{2n+2}. The general formula for a cyclic alkane with one ring is C_nH_{2n}. They are non-polar and insoluble in water.

Alkanes are used as fuels and undergo **combustion**. In **excess** air (oxygen), products are CO_2 and H_2O. When air supply is limited, products are H_2O and C or CO.

Alkanes *slowly* decolourise orange Br_2 solution in the presence of UV light. The reaction is a **substitution** and the products of a monosubstitution reaction are a monobromoalkane and hydrogen bromide (an acidic gas which turns moist blue litmus paper pink).

$$CH_3CH_2CH_2CH_2CH_3 \; + \; Br_2 \; \xrightarrow{\; UV \;} \; CH_3CH_2CH_2CH_2CH_2Br \; + \; HBr$$
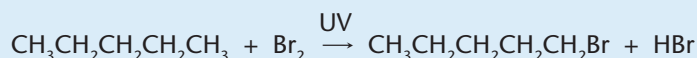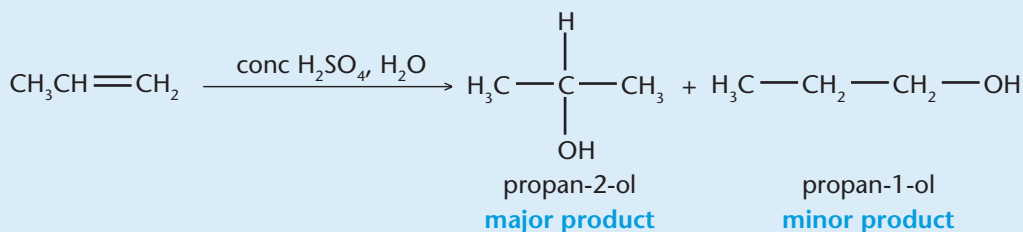
Alkenes

Alkenes are unsaturated hydrocarbons with at least one double bond (a functional group). They are non-polar, and hence insoluble in water. They can be used as fuels and undergo **combustion** as for alkanes, although they often burn with a sooty flame.

Alkenes undergo **addition** reactions. Addition of H_2 with a metal catalyst (e.g. Ni or Pt) produces an alkane; addition of Br_2 produces a dibromoalkane. The common tests for an unsaturated hydrocarbon are:

* *Rapid* decolourisation of an orange solution of bromine, Br_2, in the presence or absence of sunlight.

* Reaction with potassium permanganate – in acid solution, the purple permanganate ion, MnO_4^-, is reduced to colourless manganous ion, Mn^{2+}; in neutral solution, it is reduced to brown manganese dioxide, MnO_2. The organic product is a diol.

Addition of molecules such as HCl and H_2O (using an acid catalyst) to unsymmetric alkenes may result in two possible products. The favoured product is the one in which the H atom is added to the carbon of the double bond that already carries the most H atoms (Markovnikov's rule).
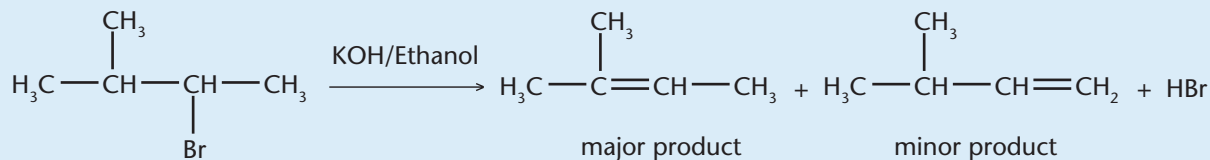
$$CH_3CH = CH_2 \xrightarrow{\text{conc } H_2SO_4,\ H_2O} \underset{\substack{\text{propan-2-ol} \\ \textbf{major product}}}{H_3C - \overset{\displaystyle H}{\underset{\displaystyle OH}{C}} - CH_3} \;+\; \underset{\substack{\text{propan-1-ol} \\ \textbf{minor product}}}{H_3C - CH_2 - CH_2 - OH}$$

Haloalkanes (alkyl halides) RX (where X is F, Cl, Br or I)

Haloalkanes can be classified as **primary RCH_2X**, **secondary R_2CHX** or **tertiary R_3CX**. They are relatively non-polar and insoluble in water.

Haloalkanes undergo reaction by the following.

* **Substitution** – replacing the X with another group such as OH (forming an alcohol using reagent aqueous OH^-) or NH_2 (forming an aminoalkane using NH_3 in an alcoholic solvent).

* **Elimination** – removal of an HX to form an alkene. Elimination is favoured when the solvent used is less polar, e.g. alcoholic (rather than aqueous) KOH. Reaction is more favourable with tertiary haloalkanes than with primary. For haloalkanes that are not symmetric, the favoured product is that in which the H is removed from the C (adjacent to the C–X) carrying the least number of H atoms in the haloalkane.

Chapter 3

$$H_3C-CH-CH-CH_3 \xrightarrow{\text{KOH/Ethanol}} H_3C-\overset{CH_3}{\underset{}{C}}=CH-CH_3 + H_3C-\overset{CH_3}{\underset{}{CH}}-CH=CH_2 + HBr$$

with CH$_3$ and Br substituents shown; major product and minor product labeled.

Amines (alkanamines)

Amines may be **primary, RNH$_2$**; **secondary, R$_2$NH**; or **tertiary, R$_3$N**. Smaller amines, up to C$_5$, are soluble in water, but larger amines are insoluble. Water soluble amines form basic solutions and aqueous solutions of amines turn litmus blue.

$$RNH_2 + H_2O \longrightarrow RNH_3^+ + OH^-$$

Amines undergo an **acid-base** reaction with acids to form ionic salts and this increases the solubility.

$$CH_3NH_2 + HCl \longrightarrow CH_3NH_3^+Cl^-$$
methanamine   methyl ammonium chloride
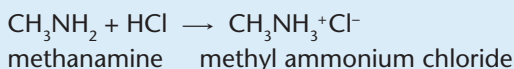
Amines are made by **substitution** reaction between NH$_3$ and haloalkanes, the reaction being carried out using alcohol as a solvent rather than water.
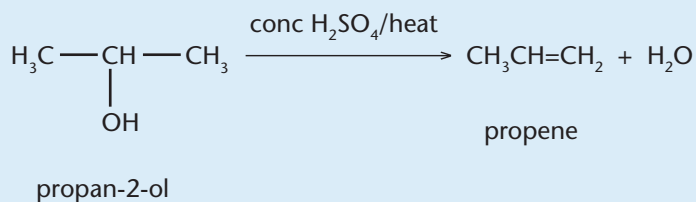
Alcohols (alkanols) – ROH

The alcohol chain is numbered from the end giving the OH the lowest number, regardless of position of any alkyl or halogen substituents. Alcohols are classed as **primary, RCH$_2$OH** (and methanol); **secondary R$_2$CHOH**; and **tertiary R$_3$COH**. Small alcohol molecules are polar and water soluble – presence of OH group means they are able to undergo intermolecular hydrogen bonding. As the length of the non-polar hydrocarbon chain increases, solubility in water decreases. Aqueous solutions are neutral. Alcohols are formed by:

- **substitution** of OH$^-$ for X$^-$ on haloalkanes
- **addition** of H$_2$O to alkenes (e.g. by reaction with conc H$_2$SO$_4$ and water)
- **reduction** of aldehydes and ketones with NaBH$_4$

Reactions of alcohols

Elimination (or dehydration) – forming an alkene and water.

$$H_3C-CH-CH_3 \xrightarrow{\text{conc } H_2SO_4/\text{heat}} CH_3CH=CH_2 + H_2O$$

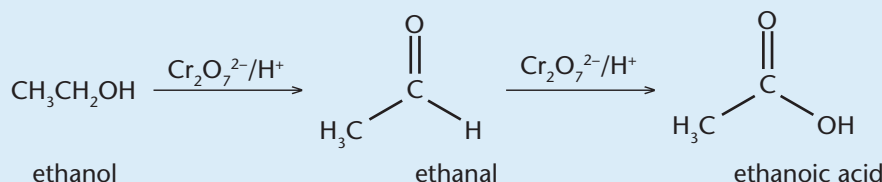with OH substituent shown; propan-2-ol labeled; propene labeled.

Substitution – of the OH$^-$ using conc HCl (with ZnCl$_2$) or SOCl$_2$ to form a chloroalkane.
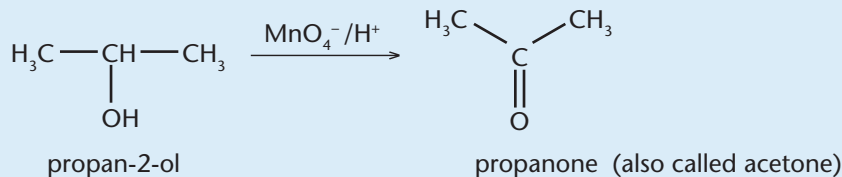
Substitution is faster for tertiary alcohols than for secondary, and slowest for primary alcohols. Rate of substitution of alcohols is increased by heating the reaction mixture under reflux – this way the reaction mixture can be heated for a period of time without material (reactant, product or solvent) evaporating and being lost from the flask.

Oxidation – using acidified KMnO$_4$ or acidified K$_2$Cr$_2$O$_7$.

Primary alcohols, RCH$_2$OH, are oxidised to form aldehydes, RCHO, which are easily oxidised further to form carboxylic acids, RCO$_2$H. If aldehyde is the desired product, the oxidising agent must be added slowly and aldehyde distilled off as it forms (it has a lower boiling point than the alcohol and carboxylic acid, as it cannot undergo intermolecular hydrogen bonding).

Chapter 3

$$CH_3CH_2OH \xrightarrow{Cr_2O_7^{2-}/H^+} \underset{\text{ethanal}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-H} \xrightarrow{Cr_2O_7^{2-}/H^+} \underset{\text{ethanoic acid}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-OH}$$

ethanol   ethanal   ethanoic acid

Secondary alcohols, R_2CHOH, are oxidised to ketones, R_2CO.

$$H_3C-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3 \xrightarrow{MnO_4^-/H^+} \overset{H_3C}{\underset{\displaystyle O}{}}\overset{}{C}\overset{CH_3}{}$$

propan-2-ol   propanone (also called acetone)

When using acidified dichromate in either redox reaction, the $Cr_2O_7^{2-}$ is reduced to Cr^{3+}, and the colour changes from orange to green. When using acidified permanganate in these reactions, the purple MnO_4^- ion is reduced to the colourless Mn^{2+} ion.

Tertiary alcohols – *do not react* with oxidising agents – oxidation reactions thus can be used to distinguish tertiary alcohols from primary and secondary alcohols.

Aldehydes (alkanals – RCHO) and ketones (alkanones – RCOR′)

Aldehydes are *oxidised* to carboxylic acids by reaction with $Cr_2O_7^{2-}/H^+$ or MnO_4^-/H^+, as well as mild oxidising agents such as Ag^+ and Cu^{2+}, that are too weak to oxidise alcohols.

Tollens' test – reaction with a complex ion $Ag(NH_3)_2^+$, which on heating gives a silver mirror on the inner surface of the test tube (or a fine black ppt of silver). Reduction half-equation is:

$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$
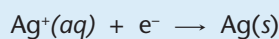
Benedict's test – the blue complex of Cu^{2+} (in Benedict's solution) is reduced to a brick-red precipitate of Cu_2O.

Fehling's test – an alkaline solution containing a deep blue complex ion of Cu^{2+} (copper(II) tartrate complex ion) is reduced to brick-red Cu_2O.

Acidified dichromate and acidified permanganate – orange $Cr_2O_7^{2-}/H^+$ is reduced to green Cr^{3+}, and purple MnO_4^-/H^+ to colourless Mn^{2+}.

Ketones are not oxidised and can readily be distinguished by observing this lack of reaction with an oxidant.

Aldehydes are *reduced* by sodium borohydride, $NaBH_4$, to form primary alcohols; ketones are *reduced* by $NaBH_4$ to form secondary alcohols.

Carboxylic acids (alkanoic acids) – RCOOH

Acids taste sour. Organic acids are weak acids and turn litmus pink.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$
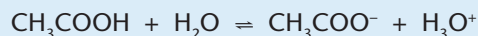
They form metal salts that are basic, e.g. sodium ethanoate. They dissolve in H_2O to produce a solution of Na^+ and CH_3COO^- ions.

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$
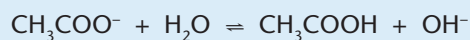
Conversion to a soluble ionic salt by dissolving in basic solution rather than H_2O increases solubility of less soluble acids and can be used as a means of separating them from other non-polar organic solutions.

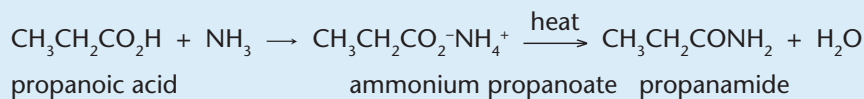**Carboxylic acids can react by substitution of the OH⁻**

Using SOCl₂ (or PCl_3 or PCl_5 but not conc HCl) – carboxylic acids undergo a substitution reaction to form acid chlorides, RCOCl.

ethanoic acid   ethanoyl chloride
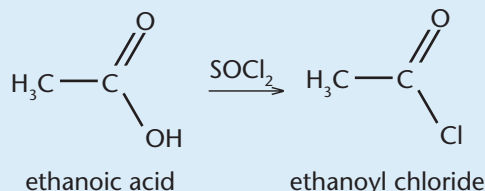
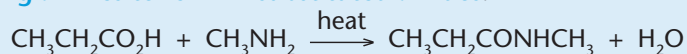**Using alcohols (and an acid catalyst such as conc H_2SO_4)**, carboxylic acids undergo a substitution reaction to form esters, RCO_2R'.

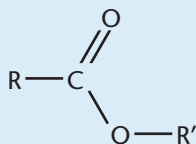ethanoic acid   methanol   methyl ethanoate
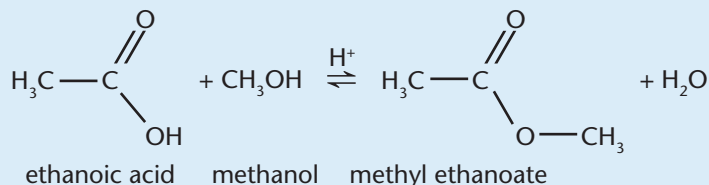
Using ammonia, a base, the initial reaction with a carboxylic acid is proton transfer to form the ammonium salt, but on heating, this salt decomposes to form an amide, $RCONH_2$.

$$CH_3CH_2CO_2H \ + \ NH_3 \ \longrightarrow \ CH_3CH_2CO_2^-NH_4^+ \ \xrightarrow{\text{heat}} \ CH_3CH_2CONH_2 \ + \ H_2O$$

propanoic acid   ammonium propanoate   propanamide

Using amines to form N-substituted amides:

$$CH_3CH_2CO_2H \ + \ CH_3NH_2 \ \xrightarrow{\text{heat}} \ CH_3CH_2CONHCH_3 \ + \ H_2O$$

Esters (alkyl alkanoates) – RCOOR'

Esters (alkyl alkanoates) are neutral in aqueous solution. They have a characteristic odour – often a fruity smell, but this can vary and some have unpleasant smells.

Esters are formed by condensation reactions

Rapid reaction of alcohol + acid chloride forming an ester + HCl:
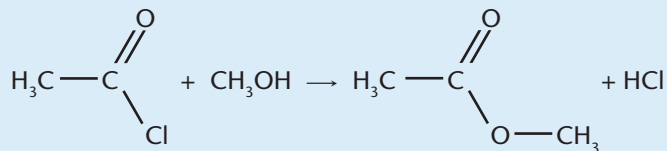
Acid catalysed reaction of alcohol + carboxylic acid to produce an ester + water:

butanoic acid   ethanol   ethyl butanoate
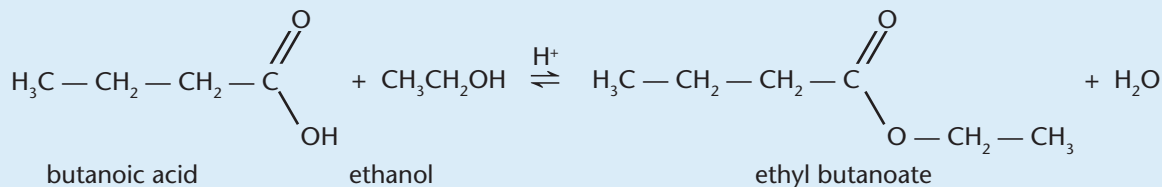
Equilibrium principles in aqueous systems

This chapter covers AS 91392 (Chemistry 3.6)

Equilibrium principles

When reactants are mixed, a reaction occurs to form products.

At any time, the reaction quotient, Q_c, is given by the expression $Q_c = \dfrac{[\text{products}]}{[\text{reactants}]}$

As the reaction proceeds, the concentration of reactants decreases and the concentration of products increases. When the concentrations of reactants and products are constant, and the rate of the forward reaction is equal to the rate of the backward reaction, the system is at equilibrium and the value of $Q_c = K_c$. Both Q_c and K_c have **no units**.

If the change in concentration of one of the components of the mixture is known, then the change for all other components is related by the mole ratio in the balanced equation for the reaction.

> ### *Example*
>
> 2 mol $N_2(g)$ and 2 mol $H_2(g)$ are placed in a 1 L flask at 250 °C. They are allowed to react according to the equation below. If, at any time, the change in concentration of N_2 is x mol L^{-1}, then the new concentration of species in the mixture is calculated as follows.
>
> | | $N_2(g)$ | + | $3H_2(g)$ | $\longrightarrow$ | $2NH_3(g)$ |
> |---|---|---|---|---|---|
> | Initial concentration / mol L^{-1} | 2 | | 2 | | 0 |
> | Change in conc / mol L^{-1} | –x | | –3x | | +2x |
> | Final concentration / mol L^{-1} | 2 – x | | 2 – 3x | | +2x |

Each reaction has its own characteristic value of K_c, **which can only be changed by changing the temperature**.

A large value of K_c indicates a higher concentration of products compared with reactants at equilibrium. The value of K_c can also be related to the relative stability of the species present at equilibrium. The higher the value of K_c, the more stable the products relative to the reactants.

## Predicting the direction of a reaction

To decide whether a reaction mixture is at equilibrium or not, the reaction quotient, Q_c, needs to be calculated and compared with the value of K_c.

- If $Q_c < K_c$, then the reaction moves to form **more** products.
- If $Q_c > K_c$, then the products decompose to form **more** reactants.
- If $Q_c = K_c$, the reaction is at equilibrium, and **no change** occurs.

Questions:
Equilibrium principles

NCEA practice

Question One

The Boudouard reaction is the name given to the oxidation-reduction reaction involving a mixture of carbon (graphite), carbon dioxide and carbon monoxide at equilibrium, at a given temperature. The reaction is an important process inside a blast furnace in the production of metals from metal oxides.

The graph below shows how the reaction mixture composition of the gases present changes with changing temperature at atmospheric pressure (101 kPa).

Boudouard equilibrium
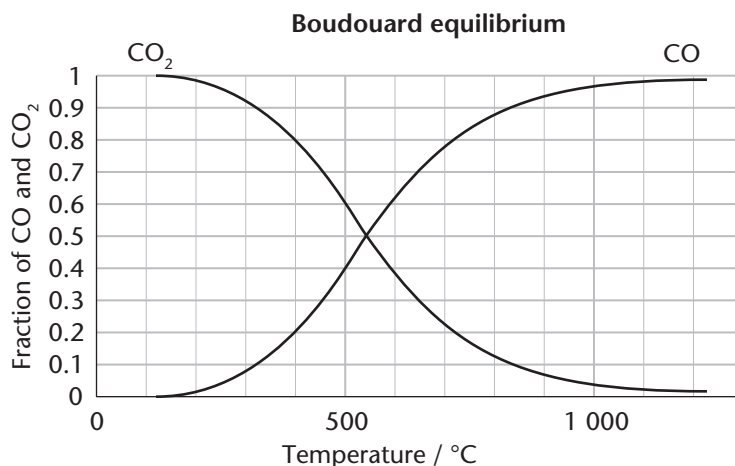
a. Identify, with justification, the product of the exothermic process in the Boudouard reaction.

Use your answer to discuss the reaction products when the hot gases from a blast furnace reach the cooler air at the top of the chimney.

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Chapter 4

b. A large, heat-proof syringe with a freely moveable airtight piston initially contained 50 mL of carbon dioxide at 101 kPa and 25 °C, plus 1 g of granular carbon. The apparatus was heated and maintained at a certain constant temperature until equilibrium was reached. The pressure of the system remained constant at 101 kPa throughout. The apparatus was then cooled rapidly to 25 °C. (At this temperature any further change in composition was negligible.) A total of 60 mL of gas was then present.

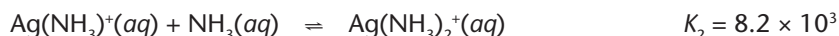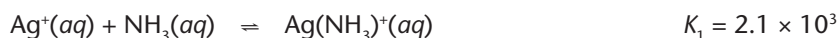Determine the temperature at which the reaction was carried out.

Note:

*   the same conditions apply to this experiment and to that represented by the graph at the start of this question

*   the volume of a substance in its gas phase at a particular temperature and pressure is directly proportional to the amount in moles of the substance present.

Question Two

0.746 g of a mixture of sodium chloride and potassium chloride was dissolved in water and made up to 250 mL of solution in a volumetric flask. A 50.00 mL portion of this solution required 25.6 mL of 0.0970 mol L^{-1} silver nitrate solution for titration to the endpoint.

Calculate the percentage of sodium chloride in the mixture.

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Year 2009
Ans. p. 135 **Question Three**

When silver ions are dissolved in an aqueous ammonia solution, complex ions of $Ag(NH_3)_2^+(aq)$ form. The formation of $Ag(NH_3)_2^+(aq)$ occurs in two steps that are represented by the equations below, together with the corresponding equilibrium constant for each reaction.

$$Ag^+(aq) + NH_3(aq) \rightleftharpoons Ag(NH_3)^+(aq) \qquad K_1 = 2.1 \times 10^3$$

$$Ag(NH_3)^+(aq) + NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \qquad K_2 = 8.2 \times 10^3$$

0.15 mol of $AgNO_3(s)$ is dissolved in 1.00 L of a 1.00 mol L^{-1} solution of aqueous ammonia.

Use the values of the equilibrium constants to identify the major species in this solution at equilibrium, and hence calculate the concentrations in mol L^{-1} of the Ag^+, $Ag(NH_3)^+$ and $Ag(NH_3)_2^+$ ions.

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Question Four

The concentrations of the species present in a system at equilibrium can be altered by applying a variety of stresses to the system.

Typically these involve:

- increasing or decreasing pressure (by changing the total volume of the system), or
- addition or removal of heat, or
- addition or removal of one (or more) of the reactants or products.

The graph following shows changes in the concentration of the species present in a system involving the following reaction at equilibrium. The reaction is endothermic in the forward direction.

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

Discuss the nature of the stresses applied to the system at positions **W**, **X**, **Y** and **Z**, and how these stresses result in the changes in the concentrations of the species present in the system.

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Answers and explanations

Chapter 1: Quantitative analysis AS 91387 (Chemistry 3.1)

Ch 1 Oxidation-reduction titrations

Question One p. 3
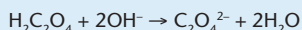
Reaction with permanganate determines both oxalate and oxalic acid

$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2\,Mn^{2+} + 10CO_2 + 24H_2O$
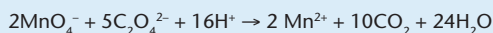
$n(MnO_4^-) = 0.01803$ mol $L^{-1} \times 0.02335$ L $= 4.210 \times 10^4$ mol

$n(C_2O_4^{2-}) = n(MnO_4^-) = 0.001053$ mol

Total $n(C_2O_4^{2-}) = 20 \times 0.001053 = 0.02106$ mol

Reaction with OH^- determines oxalic acid

$H_2C_2O_4 + 2OH^- \rightarrow C_2O_4^{2-} + 2H_2O$

$n(OH^-) = 0.1040$ mol $L^{-1} \times 0.01730$ L $= 0.001799$ mol

$n(H_2C_2O_4) = \frac{1}{2}n(OH^-) = 8.996 \times 10^{-4}$ mol

Total $n(H_2C_2O_4) = 10 \times 8.996 \times 10^{-4} = 0.008996$ mol

m(oxalic acid) $= 0.008996 \times 90.04 = 0.810$ g

n(oxalate) $= 0.02105 - 0.008996 = 0.01205$ mol

m(sodium oxalate) $= 0.01205 \times 134.02 = 1.615$ g

Or: m(oxalate ion) $= 0.01205 \times 88 = 1.060$ g

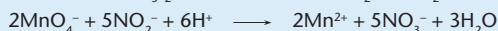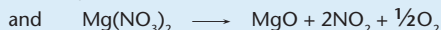mass fraction oxalic acid $= \dfrac{0.810\text{ g}}{2.496\text{ g}} = 0.325$

mass fraction sodium oxalate $= \dfrac{1.615\text{ g}}{2.496\text{ g}} = 0.647$

Or: mass fraction oxalate ion $= \dfrac{1.060\text{ g}}{2.496\text{ g}} = 0.425$

mass fraction impurity $= 0.028$

Question Two p. 4

$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$

and $\quad Mg(NO_3)_2 \longrightarrow MgO + 2NO_2 + \frac{1}{2}O_2$

$2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

$n(H_2C_2O_4) = 5.125 \times 10^{-4}$ mol and

$n(MnO_4^-)_{excess} = \frac{2}{5} \times n(H_2C_2O_4) = 2.05 \times 10^{-4}$ mol

$n(MnO_4^-)_{total} = 4.00 \times 10^{-4}$ mol

$n(MnO_4^-)_{reacted\ with\ nitrite} = n(MnO_4^-)_{total} - n(MnO_4^-)_{excess}$

$\quad = 1.95 \times 10^{-4}$ mol in 10.0 mL or 1.95×10^{-2} mol in 1 litre

$n(NO_2^-) = \frac{5}{2} \times 0.0195$ mol $= 0.04875$ mol $= n(NaNO_3)$

$m(NaNO_3) = 0.04875$ mol $\times 85.0$ g mol$^{-1} = 4.14$ g

$m(Mg(NO_3)_2) = 11.21$ g

Question Three p. 4

a. $HOCH_2CH(OH)CH_2OH + 3H_2O \longrightarrow 3HCOOH + 8H^+ + 8e^-$

$Ce^{4+} + 2e^- \longrightarrow Ce^{2+}$

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$
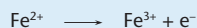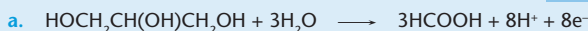
$n(Ce^{4+})_r = 0.050$ L $\times 0.0837$ mol L$^{-1} - \frac{1}{2} \times 0.01211 \times 0.0448$

$\quad = 0.004185 - 0.0002712 = 0.003914$

n(glycerol) $= \dfrac{n(Ce^{4+})}{4} = 9.785 \times 10^{-4}$

m(glycerol) $= 92.0$ g mol$^{-1} \times 0.0009785 = 90.0$ mg

% glycerol $= \dfrac{90.0\text{ mg}}{100\text{ mg}} \times 100 = 90.0\%$

b. Titration reactions need to be fast. The reaction between glycerol and cerium(IV) needed heating for 15 minutes so was too slow for a direct titration to be used. The titration between Ce^{4+} and Fe^{2+} is fast and hence suitable for titration *or* in a back titration there is an extra error introduced as there are two measurements needed, each of which has its own uncertainty.

Question Four p. 5

a. • Vigorous swirling can introduce species in the air into solution (e.g. O_2 or CO_2). In this case, reaction with oxygen gas could result in oxidation of I^- to I_2, which would affect the amount of thiosulfate needed in the titration (and hence the accuracy of the experimental value for the vitamin C concentration). More thiosulfate suggests more iodine unreacted in solution, and, in the calculation, this would result in less vitamin C calculated as being present.

• Allowing solutions to stand could result in some of the iodine being lost, as it is a volatile solid. Less iodine present in the solution would mean the calculation would result in showing a higher amount of vitamin C having reacted with iodine.

• The addition of excess iodide ions to produce I_3^- means that there is less I_2 in solution (or present as solid), and therefore the problems identified above are less likely to occur. As an equilibrium exists between the I_2 and I_3^- ion, then, as the I_2 reacts, the triiodide ion will dissociate until all iodine has been made available for reaction with thiosulfate ions.

b. $n(KBrO_3) = \dfrac{1.33\text{ g}}{167\text{ g mol}^{-1}} = 7.96 \times 10^{-3}$ mol

$c(BrO_3^-)$ in diluted solution $= \frac{1}{5} \times \dfrac{7.96 \times 10^{-3}\text{ mol}}{0.500\text{ L}}$

$\quad = 3.19 \times 10^{-3}$ mol L^{-1}

$n(S_2O_3^{2-}) = 0.00238$ mol L$^{-1} \times 0.00236$ L $= 5.62 \times 10^{-6}$ mol

$n(I_2) = \frac{1}{2} \times n(S_2O_3^{2-}) = 2.81 \times 10^{-6}$ mol