SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CHEMISTRY

9746/02

Preliminary Examination
Paper 2
Solutions

1 Potassium manganate (VII) is an oxidising agent used in redox titrations. A 50.0 cm^3 sample of iron (II) oxalate, FeC_2O_4, was dissolved in water and the solution made up to 250 cm^3. A 25.0 cm^3 portion of this solution was acidified and titrated with 20.80 cm^3 of 0.025 mol dm^{-3} potassium manganate (VII).

(a) **(i)** State the change in oxidation number for manganese.

The oxidation number of Mn **decreases from +7 in MnO_4^- to +2 in Mn^{2+}**.

(ii) Write an ionic equation for the oxidation of oxalate ion to carbon dioxide.

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e$$

(iii) Write an overall equation for the reaction between potassium manganate (VII) and iron (II) oxalate.

$$5Fe^{2+} + 5C_2O_4^{2-} + 3MnO_4^- + 24H^+ \rightarrow 5Fe^{3+} + 10CO_2 + 3Mn^{2+} + 12H_2O$$

(iv) Calculate the concentration of iron (II) oxalate in the original sample.

$5FeC_2O_4 \equiv 3MnO_4^-$

Amount of $Fe_2C_2O_4$ in 25.0 cm^3 portion = $\frac{5}{3} \times \frac{20.80}{1000} \times 0.025$

= 8.667×10^{-4} mol

Amount of $Fe_2C_2O_4$ in original sample = $\frac{250}{25.0} \times 8.667 \times 10^{-4}$

= 8.667×10^{-3} mol

Original [$Fe_2C_2O_4$] = $\dfrac{8.667 \times 10^{-3}}{50/1000}$ **= 0.173 mol dm^{-3}**

(v) State the colour change at the endpoint of the titration.

Purple to yellow or purple to colourless

In the above redox titration, carbon dioxide gas is produced. One of the uses of carbon dioxide is in the manufacture of carbonated drinks. Cola, a carbonated drink, was originally invented by chemist, John Pemberton, to stop headaches and calm nervousness.

Cylinders of pressurised carbon dioxide are used to produce cola. A commercial cola drink was manufactured using such cylinders, each with internal volume of 5 dm^3 and contains 2.58 kg of carbon dioxide. The pressure inside each of the cylinder was found to be 1.0×10^4 kPa at room temperature.

A glass of cola is fizzy because carbon dioxide has been dissolved in it under pressure. When 500 cm^3 of commercial cola drink is poured out from a bottle, the carbon dioxide is gradually released as bubbles of gas. On evolution of 1 dm^3 of carbon dioxide, the cola went flat, as the concentration of dissolved carbon dioxide decreases to its saturation level of 1.5 g dm^{-3} at room temperature.

(b) **(i)** Using the ideal gas equation pV = nRT, calculate the pressure the carbon dioxide would exert inside the cylinder at room temperature.

$$p = \frac{mRT}{MV}$$

$$= \frac{2.58 \times 10^3 \times 8.314 \times 298}{44.0 \times 5 \times 10^{-3}}$$

= $\underline{2.91 \times 10^7 \text{ Pa}}$

(ii) Suggest why the pressure you calculated in **b(i)** differs from the actual value.

CO_2 does not behave like an ideal gas at high pressure.

(iii) Calculate the total mass of carbon dioxide dissolved in the 500 cm^3 bottle of cola under pressure.

Mass of CO_2 at saturation level = $\frac{500}{1000} \times 1.5$
= 0.75 g

Mass of CO_2 evolved = $\frac{1}{24.0} \times 44.0$ = **1.833 g**

Total mass dissolved = 0.75 + 1.833 = <u>2.58 g</u>

(iv) Determine the number of 500 cm^3 bottles of cola that could be manufactured using one cylinder of pressurised carbon dioxide..

No. of bottled cola = $\frac{2.58 \times 10^3}{2.583}$ **= <u>998</u>**

[Total: 10]

2(a) Brine is water saturated or nearly saturated with sodium chloride salt, $NaCl$, and was historically used to preserve vegetables, fish, and meat.

Brine is electrolysed in the chloralkali process to make sodium hydroxide, chlorine and hydrogen, as well as the hypochlorite and chlorate salts on an industrial scale. In this case, the chloride ions are oxidised to chlorine, while water is reduced to hydrogen gas and hydroxide ions.

(i) Write the reactions that occur at the anode and the cathode and hence the overall equation for the electrolysis of brine.

Anode : $\mathbf{2Cl^- \rightarrow Cl_2 + 2e^-}$

Cathode : $\mathbf{2H_2O + 2e^- \rightarrow H_2 + 2OH^-}$

Overall : $\mathbf{2NaCl\ (aq) + 2H_2O\ (\mathit{l}) \rightarrow Cl_2\ (g) + H_2\ (g) + 2NaOH(aq)}$ or
$2Cl^- + 2H_2O \rightarrow Cl_2 + H_2 + 2OH^-$

(ii) During a random sampling it was found that sodium chlorate (I) was detected. Write a chemical equation to illustrate a possible reaction that causes this observation.

$\mathbf{Cl_2\ (g) + 2NaOH\ (aq) \rightarrow NaClO\ (aq) + NaCl\ (aq) + H_2O\ (l)}$

(iii) The volume of chlorine gas collected 3 hours after the chloralkali process was 2700 cm^3. Assuming there is no contamination to the chlorine gas collected and the process efficiency was 80%, Calculate the current required to produce the specify quantity of chlorine gas at room temperature.

Amount of Cl_2 collected = $\dfrac{\frac{2700}{1000}}{24}$ = **0.1125 mol**

$2Cl^- \rightarrow Cl_2 + 2e$

Amount of Faraday required = 2 x 96500 C

$0.1125 = \dfrac{Q'}{2 \times 96500}$

Q' = **21712.5 C**

Actual charge required = $\dfrac{100}{80}$ x 21712.5= **27140 C**

$Q = I \times t$

$21740 = I \times 3 \times 3600 \rightarrow I =$ **2.51 A**

(b) Sedoneural is sodium bromide salt and was widely used as an anticonvulsant and a sedative. When concentrated sulphuric acid is warmed with sodium bromide, 3 different gases were released. Write equations for the reaction:

$NaBr\ (s) + H_2SO_4\ (aq) \rightarrow NaHSO_4\ (aq) + HBr\ (g)$

$2HBr\ (g) + H_2SO_4\ (aq) \rightarrow Br_2\ (g) + 2H_2O\ (l) + SO_2\ (g)$

(c) Hydrogen halides are formed from the chemical reaction of hydrogen with one of the halogen elements (fluorine, chlorine, bromine, iodine), which are found in Group VII of the periodic table. Hydrogen halides can be abbreviated as HX where H represents a hydrogen atom and X represents a halogen (fluorine, chlorine, bromine or iodine). Upon dissolving the hydrogen halides in water, acids are formed.

(i) With reference from the *Data Booklet*, explain and rank the pK_a of the following acids: HI, HBr and HC*l*.

Down the group,

- **Bond length of H-X increases**
- There is an **decrease in H-X bond strength**
- Hence increase in ease of breaking the H-X bond
  - ⇒ **H^+ (H_3O^+) can be formed more easily**

$$H\text{—}X + H_2O \rightarrow H_3O^+ + X^-$$

- **pKa: HI < HBr < HC*l***

From *Data Booklet,*

H-C*l*	431 kJ mol^{-1}
H-Br	366 kJ mol^{-1}
H-I	299 kJ mol^{-1}

(ii) What would you expect to see when hydrobromic acid reacts with aqueous silver nitrate followed by concentrated ammonia?

HBr reacts with $AgNO_3$: **Cream ppt is formed**

On addition of concentrated NH_3: **Cream ppt dissolved**

(iii) Explain your observation made in **c(ii)** when concentrated ammonia was added. Include equations in your answer.

When HBr reacts with $AgNO_3$, cream AgBr is formed

$$AgBr\ (s) \rightleftharpoons Ag^+\ (aq) + Br^-\ (aq) \text{ ------------------ } (1)$$

$$Ag^+\ (aq) + 2NH_3\ (aq) \rightleftharpoons [Ag(NH_3)_2]^+\ (aq) \text{ ------------- } (2)$$

On addition of **concentrated NH_3, diamminesilver (I) complex** is formed. **$[Ag^+]$ in (1) decreases**, by Le Chatelier's Principle, **equilibrium position in (1) will shift right** so that **solubility of AgBr increases** or (and as such AgBr dissolved since **ionic product of AgBr < K_{sp} of AgBr**)

[Total: 12]

3(a) Copper and iron are in the same period with chromium and are essential in all plants and animals. Most mollusks (such as mussels and scallops) and some arthropods (such as horseshoe crab and blue crab) use the copper-containing pigment hemocyanin rather than iron-containing haemoglobin for oxygen transport.

(i) Comment on values of the first ionisation energy of copper and iron as given in the *Data Booklet* with the aid of appropriate electronic configuration.

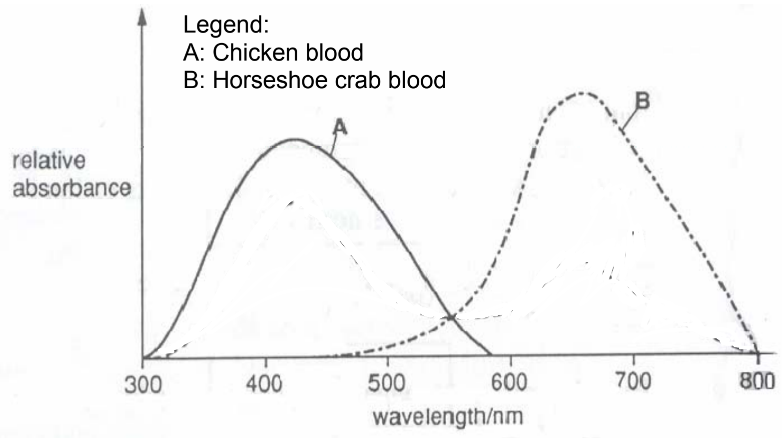
From the Data Booklet:
$Fe \rightarrow Fe^{+} + e$ 1st IE : +762 kJ mol^{-1}
$[Ar]3d^{6}4s^{2}$ $[Ar]3d^{6}4s^{1}$

$Cu \rightarrow Cu^{+} + e$ 1st IE: +745 kJ mol^{-1}
$[Ar]3d^{10}4s^{1}$ $[Ar]3d^{10}$

- 1st IE of Cu < 1st IE of Fe
- **Cu has a greater shielding effect since it has 10 3d electrons thus less energy is required to remove the 4s electron**.

Alternative:
- Removal of one electron from Cu result in **stable electronic configuration/stable d^{10} configuration/fully filled d sub-shell.**
- **Less energy** is required to remove the first electron from Cu than from Fe

(ii) A sample of oxygenated horseshoe crab blood and chicken blood was analysed and the absorption spectrum was observed.



Colour	Wavelength (nm)
Violet	380 – 450
Blue	450 – 495
Green	495 – 570
Yellow	570 – 590
Orange	590 – 620
Red	620 – 750

Suggest from the spectrum and the data available the colour of the oxygenated horseshoe blood and explain why this colour arises.

- **Blue or violet or indigo**
- The **d orbitals in copper ion are split into two groups** due to the ability of the ligands to split them into the energy levels as shown.
- The d electron undergoes **d-d electron transition** and is **promoted to a higher energy** d **orbital**.
- During the transition, the d electron **absorbs the red light (longer wavelength of light)** from the visible region of the electromagnetic spectrum and **transmits the blue light (shorter wavelength of light)** which appears as the colour observed.

(iii) Explain, with aid of appropriate equations, what you will observe when dilute ammonia is gradually added until in excess to an extract of oxygenated horseshoe crab blood containing Cu^{2+}(aq) ions.

$NH_3(aq) + H_2O\,(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \longrightarrow Cu(OH)_2\,(s) + 6H_2O\,(l)$

$Cu(OH)_2\,(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$ ----- (1)

When NH_3(aq) is added gradually, [OH^-] will increase

☑ **Equilibrium position in (1) shifts right.**

☑ **Ionic product of $Cu(OH)_2$ > K_{sp} of $Cu(OH)_2$**

☑ Pale **blue ppt**, $Cu(OH)_2$ is formed

$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$ -----(2)

When NH_3 is added in excess,

☑ Stronger **NH_3 ligands** replaces the **H_2O** ligands, forming a **deep blue $[Cu(NH_3)_4(H_2O)_2]^{2+}$** complex

☑ **[Cu^{2+}(aq)] decreases** as it is being used to form the complex

⇒ equilibrium position in **(1)** shifts **left to increase [Cu^{2+}(aq)]**

OR **Ionic product of $Cu(OH)_2$ < K_{sp} of $Cu(OH)_2$**

☑ **Pale blue ppt dissolves.**

(b) Iron is an important component of several biological molecules especially in haemoglobin. What is the function of haemoglobin in the body and explain how it carries out this function?

- five coordination sites are occupied by nitrogen
- **H_2O ligand** at the 6th site is **replaced by O_2 ligand** which is **reversibly** bonded to Fe^{2+} **via dative bonding**

  Thus enables haemoglobin to **carry oxygen** to all parts of the body in the form of **oxyhaemoglobin.**

(c)(i) A half-cell containing copper electrode and copper (II) solution was connected to another half-cell containing iron(III) and iron (II) solution with platinum electrode. Determine the $E^{\ominus}_{cell}$ of the reaction.

$Cu^{2+} + 2e \rightleftharpoons Cu$	+0.34 V	$E^{\ominus}_{oxd}$
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	+ 0.77 V	$E^{\ominus}_{red}$

$E^{\ominus}_{cell} = +0.77 - (+0.34)$
$= \mathbf{+0.43\ V}$

(ii) Deduce the direction of electron flow in the set-up mentioned in **c(i)**.

Electron flows from the **Cu^{2+}/Cu half cell to the Fe^{3+}/Fe^{2+} half cell**

Or (electrons flow from the **copper electrode to the platinum electrode**)

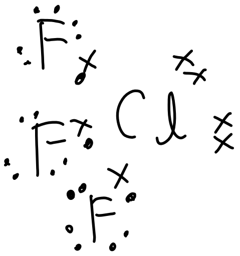
(iii) Suggest what will happen to the $E^{\ominus}_{cell}$ when sodium hydroxide was added to the half-cell containing copper and copper (II) solution.

- **$Cu(OH)_2$ will be precipitated**
- **$[Cu^{2+}]$ will decrease**
- By Le Chatelier's Principle,
  $Cu^{2+} + 2e \rightleftharpoons Cu$
  Equilibrium position will shift left to increase the $[Cu^{2+}]$
- Oxidation is favoured
- $E^{\ominus}_{oxd}$ will become less positive
- **$E^{\ominus}_{cell}$ will become more positive**

[Total: 16]

4(a) Chlorine triflouride, ClF_3, is one of the most reactive compounds known and was used in incendiary bombs in World War II. ClF_3 reacts explosively with water and many organic compounds.

(i) Draw a 'dot-and-cross' diagram of the ClF_3 molecule. Hence, predict the shape of this molecule.



T-shaped

(ii) Suggest a value of F-C*l*-F bond angle in the ClF_3 molecule.

< **90°** **(87.5° is the actual bond angle)**

(b) ClF_3 is also a powerful fluorination agent and it reacts with MgO as follows:

$$4\,ClF_3(g) + 6MgO(s) \rightarrow 6MgF_2(s) + 2Cl_2(g) + 3O_2(g)$$

(i) Use the data given below to calculate the standard enthalpy change of the above reaction.

Compound	ΔH^{θ}_{f} / kJ mol^{-1}
ClF_3	-158.87
MgO	-601.24
MgF_2	-1124.24

ΔH^{θ}_{rxn} = ΔH^{θ}_{f} (products) - ΔH^{θ}_{f} (reactants)

= 6(-1124.24) – [4(-158.87) + 6(-601.24)]

= -2502.52 kJ mol^{-1}

= **-2500 kJ mol^{-1}** or **(-2503 kJ mol^{-1})**

(ii) Using relevant data from ***(b)(i)*** and the *Data Booklet*, estimate the average bond energy of the C*l*-F bond.

$$\frac{1}{2}Cl_2(g) + \frac{3}{2}F_2(g) \rightarrow ClF_3\,(g)$$

$\Delta H^{\theta}_{f}(ClF_3)$ = Σ BE of bonds broken in rxts - Σ BE of bonds formed in pdts

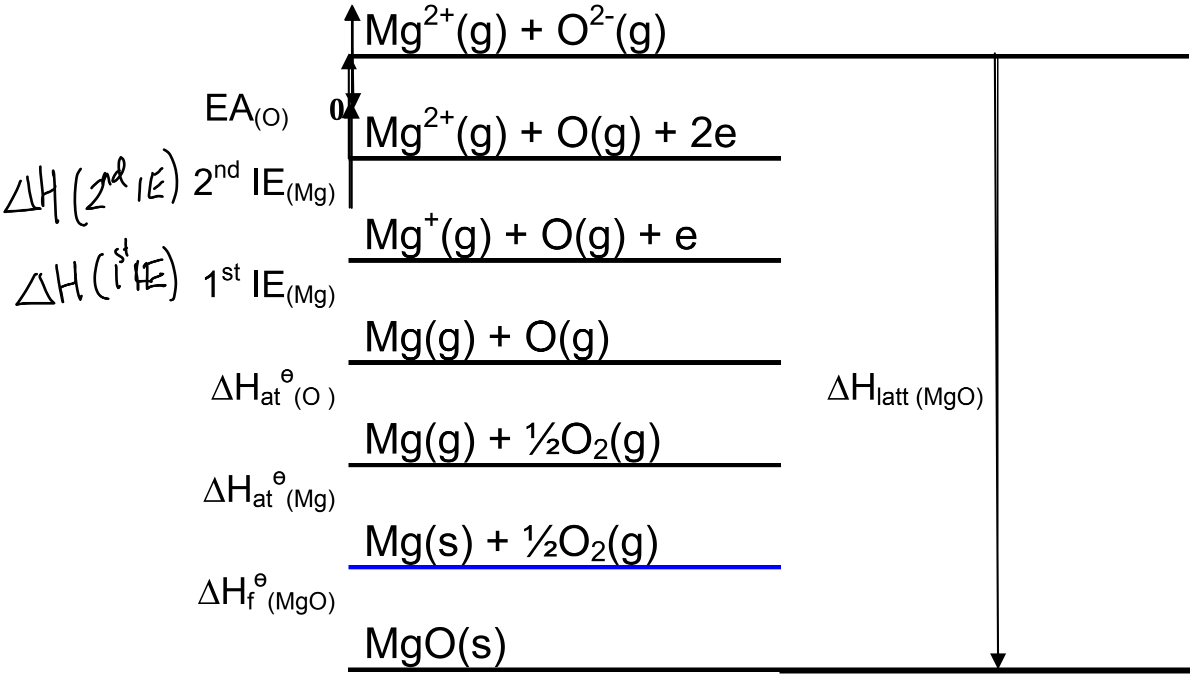
-158.87 = ½ (244) + 3/2 (158) – 3BE(C*l*-F)

3BE(C*l*-F) = 517.87 kJ mol^{-1}

BE(C*l*-F) = **+173 kJ mol^{-1}** **or (+172.6 kJ mol^{-1})**

(c) Use the following data, together with relevant data from the *Data Booklet* and ***(b)(i),*** calculate a value for the lattice energy of MgO(s).

Enthalpy change of atomisation of Mg	+150 kJ mol^{-1}
Sum of the first two electron affinities of oxygen atoms	+702 kJ mol^{-1}



By Hess' law,

$\Delta H_f^{\ominus}(MgO) = \Delta H_{at}^{\ominus}(Mg) + \Delta H_{at}^{\ominus}(O) + 1^{st}\ IE(Mg) + 2^{nd}\ IE(Mg) + EA(O)\ \Delta H_{latt}\ (MgO)$

$\Rightarrow \Delta H_{latt\ (MgO)} = -602 - [150 + 248 + 736 + 1450 + 702] = -3888$

$= \mathbf{-3890\ kJ\ mol^{-1}}$

(d) Suggest and explain how you would expect the magnitude of lattice energy of MgS to compare with the value you obtained in **(c)**.

Magnitude of $\Delta H_{latt} \propto \dfrac{q_+ q_-}{r_+ + r_-}$ for ionic compound

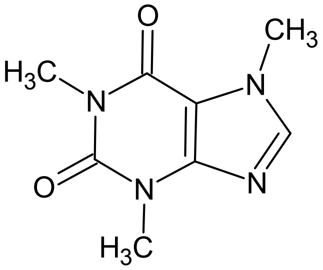
Ionic radius, r_-: $\mathbf{S^{2-} > O^{2-}}$

|lattice energy| for MgS < MgO

[Total: 10]

5 Caffeine, a stimulant found in coffee and tea, was discovered by a German chemist, Friedrich Ferdinand Runge, in 1819.

The structure of caffeine is given below.



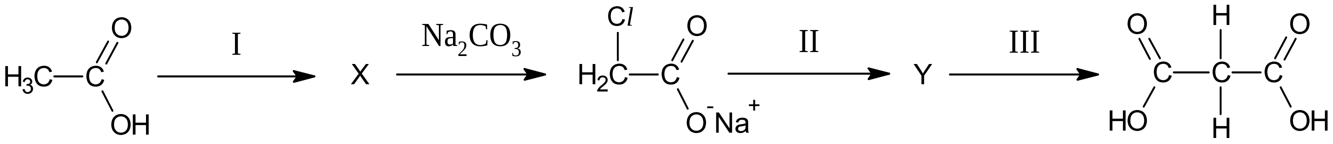
(a) State the number of carbon atoms with the following hybridisations in caffeine.

sp^2: **5**

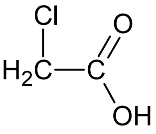
sp^3: **3**

(b) Caffeine can be synthesized in the laboratory using dimethyl urea, $(CH_3)NHCONH(CH_3)$ and malonic acid, $HOOC(CH_2)COOH$.

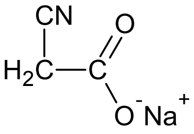
Malonic acid is usually prepared from ethanoic acid as follows:



(i) Draw the structures of the intermediates **X** and **Y**.



X



Y

(ii) For steps **I**, **II** and **III**, in the reaction sequence, give reagent(s) and conditions.

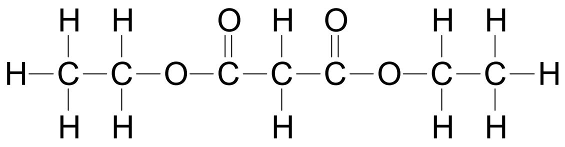
Step **I**
reagent(s): **Cl_2**
conditions: **ultraviolet light**

Step **II**
reagent(s): **alcoholic KCN**
conditions: **reflux / heat**

Step **III**
reagent(s): **dilute HCl or H_2SO_4**
conditions: **reflux / heat**

(c) Malonic acid on reaction with an alcohol under appropriate condition forms a sweet smelling liquid of molecular formula $C_7H_{12}O_4$.

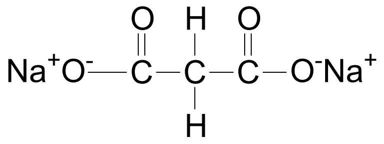
(i) Draw the displayed formula of this sweet smelling liquid.



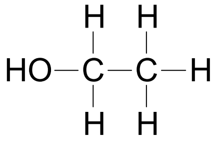
$CH_3CH_2OCOCH_2COOCH_2CH_3$

(ii) The sweet smelling liquid was heated with aqueous sodium hydroxide. State the type of reaction and draw the two organic products formed.

Type of reaction: **basic hydrolysis / nucleophilic substitution / hydrolysis**

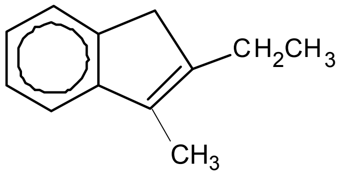


$Na^+{}^-OOCCH_2COO^-Na^+$

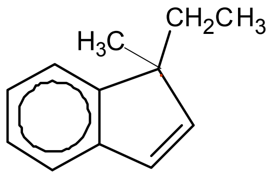


$HOCH_2CH_3$

(d) Describe a chemical test that would distinguish the following two compounds.



A



B

Test:
Add $KMnO_4$ in H_2SO_4(aq) to both compounds separately and heat. To the oxidised products, add 2,4-DNPH and warm.

A: orange ppt
B: no ppt

Alternative:
(1) Use alkaline aqueous iodine, warm.
(2) Cold alkaline $KMnO_4$, followed by $Cr_2O_7^{2-}$
(3) H_3PO_4, 300°C, 70atm, followed by $Cr_2O_7^{2-}$
(4) $KMnO_4$ in H_2SO_4, passed CO_2 gas produced into $Ca(OH)_2$(aq), white ppt for A.

[Total: 12]

~~END OF CORRECTIONS~~