# ANGLO-CHINESE JUNIOR COLLEGE DEPARTMENT OF CHEMISTRY Preliminary Examination

CHEMISTRY 9729/01 Higher 2

Paper 1 Multiple Choice

24 August 2017

1 hour

Additional Materials:

**Optical Answer Sheet** 

Data Booklet

#### **READ THESE INSTRUCTIONS FIRST**

Write in soft pencil.

Do not use staples, paper clips, glue or correction fluids.

Write your name, index number and tutorial class on the Optical Answer Sheet in the spaces provided unless this has been done for you.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Optical Answer Sheet.

#### Read the instructions on the Optical Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

The use of an approved scientific calculator is expected, where appropriate.

This document consists of **14** printed pages, including this cover page.



For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

1 Carbon disulfide is a colourless volatile liquid with the formula CS<sub>2</sub>. The compound is used frequently as a building block in organic chemistry as well as an industrial solvent.

It reacts with nitrogen monoxide, NO, to form a yellow solid and two gases. These two gases are formed in equal amounts.

What are these two gases?

The yellow solid is sulfur.

You cannot balance the equation (with the two product gases in equal amounts) with the three other options.

Balanced equation:

 $CS_2 + 2NO \rightarrow CO_2 + N_2 + 2S$ 

2 Use of the Data Booklet is relevant to this question.

Which of the following ions will be deflected the **most** in an electric field?

**A** S<sup>2-</sup> **B** Br - **C** F - **D** O<sup>2-</sup>

You are to refer to the Data Booklet for the ionic radii (although it is not absolutely necessarily to do so; you can use the Group trend for ionic sizes).

The charge density of the oxide ion is the highest amongst the four.

**3** Use of the Data Booklet is relevant to this question.

Nuclear magnetic resonance (NMR) spectroscopy is an analytical technique that uses the magnetic properties of certain atomic nuclei in order to elucidate the structure of an organic molecule.

Atomic nuclei with an even number of protons and an odd number of neutrons (or vice versa) are most suitable for NMR spectroscopy.

Which of the following nuclei is **least** suitable for NMR spectroscopy?

**A** <sup>28</sup>Si **B** <sup>31</sup>P **C** <sup>103</sup>Rh **D** <sup>19</sup>F

A: no. of protons 14 no. of neutrons = 28 - 14 = 14

B: no. of protons 15 no. of neutrons = 31 - 15 = 16

C: no. of protons 45 no. of neutrons = 103 - 45 = 58

D: no. of protons 9 no. of neutrons = 19 - 9 = 10

A 25.00 cm<sup>3</sup> sample of a solution of 0.150 mol dm<sup>-3</sup>  $MoO_x^{2-}$  was passed through a Jones reductor (a column of zinc powder). It was reduced to  $Mo^{3+}$ . The filtrate required 22.50 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> acidified KMnO<sub>4</sub> (aq) to obtain back the original amount of  $MoO_x^{2-}$ .

What is the value of x?

**A** 4 **B** 3 **C** 2 **D** 1

Amt of electrons involved =  $(22.50 \times 0.100 / 1000) \times 5 = 0.01125$ 

Change in oxidation state in Mo =  $0.01125 / (25.00 \times 0.150 / 1000) = 3$ 

Original oxidation state of Mo = 3 + 3 = 6

Hence x = 4.

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

5 Neoxanthin is a major xanthophyll found in green leafy vegetables such as spinach.

Which of the following  $\sigma$  bonds are present in neoxanthin?

- 1 A  $\sigma$  bond formed by  $sp^2-sp^3$  overlap.
- **2** A  $\sigma$  bond formed by s-p overlap.
- 3 A  $\sigma$  bond formed by sp–sp<sup>2</sup> overlap.
- A 1 and 2 only
- **B** 1 and 3 only
- C 2 and 3 only
- **D** 1, 2 and 3

#### Recall:

Linear Carbon: sp (eg. =C= or −C≡)

Trigonal Planar Carbon: sp<sup>2</sup> Tetrahedral Carbon: sp<sup>3</sup>

Bent Oxygen (or Tetrahedral in terms of electron pair geometry) in C-O-C and C-O-H: sp<sup>3</sup>

Option 2 is wrong. For s-p overlap, it means that the s orbital belongs to hydrogen, whereas the p orbital (unhybridised) belong to carbon. But the overlaps in the following cases are:

$$-c - C - H = C - H = C - H = Sp^{3} = Sp^{3} = Sp^{3}$$

6 The enthalpy changes for the following reactions were measured experimentally:

$$\begin{array}{ll} \text{CH}_3\text{CH}_2\text{CH}_3(g) + 5\text{O}_2(g) \to 3\text{CO}_2(g) + 4\text{H}_2\text{O}(\textit{l}) & \Delta H = -2202 \text{ kJ mol}^{-1} \\ \text{H}_2(g) + \frac{1}{2} \text{ O}_2(g) \to \text{H}_2\text{O}(\textit{l}) & \Delta H = -286 \text{ kJ mol}^{-1} \\ \text{CH}_3\text{--}\text{C} \equiv \text{C} - \text{H}(g) + 2\text{H}_2(g) \to \text{CH}_3\text{CH}_2\text{CH}_3(g) & \Delta H = -310 \text{ kJ mol}^{-1} \\ \end{array}$$

What is the enthalpy change of combustion of propyne, CH<sub>3</sub>–C≡C–H, in terms of kJ mol<sup>-1</sup>?

**A** -2226 **B** -1940 **C** -1606 **D** -1320

$$\begin{array}{c} CH_{3}-C\equiv C-H(g)+4O_{2}(g)+2H_{2}(g)+O_{2}(g) & \xrightarrow{\Delta Hc(propyne)} & 3CO_{2}(g)+2H_{2}O(I)+2H_{2}(g)+O_{2}(g) \\ -310 & & & & & & & & \\ CH_{3}CH_{2}CH_{3}(g)+4O_{2}(g)+O_{2}(g) & & & & & & & \\ -2202 & & & & & & & & \\ & & & & & & & & \\ 3CO_{2}(g)+4H_{2}O(I) & & & & & & & \\ \end{array}$$

By Hess' Law,

$$\Delta$$
Hc(propyne) =  $-310 - 2202 - (2)(-286) = -1940 \text{ kJ mol}^{-1}$ 

- **7** 35 cm³ of 0.001 mol dm⁻³ nitric acid solution was added to 35 cm³ of sulfuric acid solution of the same concentration. What is the resulting pH of the combined solution?
  - **A** 1.5 **B** 2.5 **C** 2.8 **D** 3.0

Amount of H<sup>+</sup> from  $HNO_3 = (0.035)(0.001) = 0.000035$  mol

Amount of H<sup>+</sup> from  $H_2SO_4 = (2)(0.035)(0.001) = 0.000070$  mol

 $[H^+] = (0.000035 + 0.000070) \div (0.035 + 0.035) = 0.0015 \text{ mol dm}^{-3}$ 

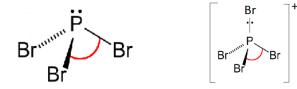
$$pH = -log [H^+] = 2.82$$

- In which of the following pairs is the bond angle in the first species smaller than that in the second species?
  - 1 PBr<sub>3</sub>, PBr<sub>4</sub><sup>+</sup>
  - 2 H<sub>2</sub>Se, H<sub>2</sub>O
  - 3 SF<sub>2</sub>, SC $l_2$
  - A 1 and 2 only
  - **B** 1 and 3 only
  - C 2 and 3 only
  - D 1, 2 and 3

Recall: VSEPR model dictates that

"Lone Pair – Lone Pair repulsion > Lone Pair – Bond Pair repulsion > Bond Pair – Bond Pair repulsion"

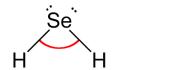
### Option 1



Lone pair on P in PBr<sub>3</sub> is closer to nucleus of P, compared to the Bond Pair in PBr<sub>4</sub><sup>+</sup>.

There is stronger repulsion between lone pair and bond pair in PBr<sub>3</sub>. Hence the bond angle will be smaller than that in PBr<sub>4</sub><sup>+</sup>.

# Option 2

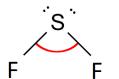


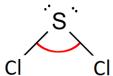


Selenium is larger atom than Oxygen. Selenium is also less electronegative than Oxygen. Electron density in Se—H bond is further away from Se, compared to electron density in O—H bond.

There is weaker repulsion between bond pairs in H<sub>2</sub>Se. Hence the bond angle will be smaller than that in H<sub>2</sub>O.

#### Option 3



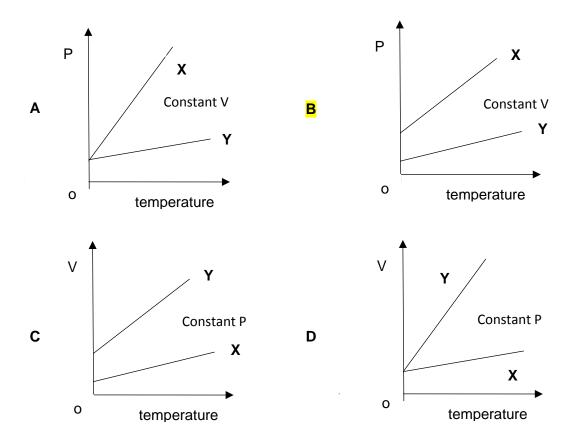


Fluorine is more electronegative than chlorine.

Electron density in S—F bond is further away from S, compared to electron density in S—Cl bond. There is weaker repulsion between bond pairs in  $SF_2$ . Hence the bond angle will be smaller than that in  $SC_{l_2}$ .

9 X and Y are both ideal gases. X has the smaller molecular mass.

Which of the following diagrams correctly describe the behaviour of equal masses of these gases? All temperatures are measured in °C.



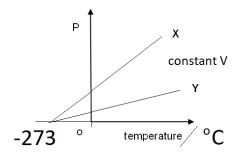
For Ideal Gas, PV = nRT

 $PV = (m / M_r) RT$ 

At constant Volume,  $P = (m R / VM_r) T$ 

where Gradient of Line =  $(m R / VM_r)$ 

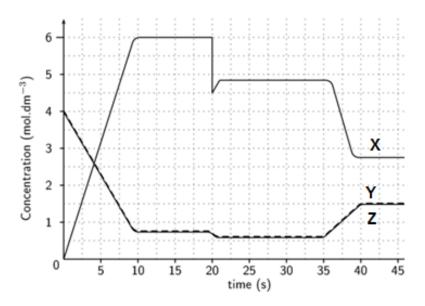
X has smaller M<sub>r</sub> than Y. Hence the line for X has a steeper gradient than Y.



10 X exists in equilibrium with Y and Z.

$$2X(g) \rightleftharpoons Y(g) + Z(g)$$

The concentrations of **X**, **Y** and **Z** varies across time as shown below. Note that the dotted line refers to both concentrations of **Y** and **Z**.



Which of the following statements is false?

- A The equilibrium constant is dimensionless.
- **B** X(g) was taken out of the system at 20 s.
- Given that the temperature was decreased at 35 s, it can be concluded that the forward reaction is endothermic.
- **D** Temperature has no effect on the spontaneity of this reaction.

#### Option A

 $Kp = (P_v P_z) / P_x^2$  atm . atm / atm<sup>2</sup>

Hence Kp is dimensionless.

# Option B

Sudden decrease in [X], but [Y] and [Z] both decrease over time at t = 20s.

This implies that X(g) is taken out of the system at t = 20s.

# Option C

If  $\Delta H_{\text{forward}} = +ve$ , temperature must increase for the POE to shift right.

## Option D

$$\Delta G = \Delta H - T\Delta S$$

 $\Delta S$  = 0 because there is no change in total amount of gaseous particles in the system, regardless of the system shifting left or right.

Assumption: Temperature is not low enough for liquefaction of gases to occur.

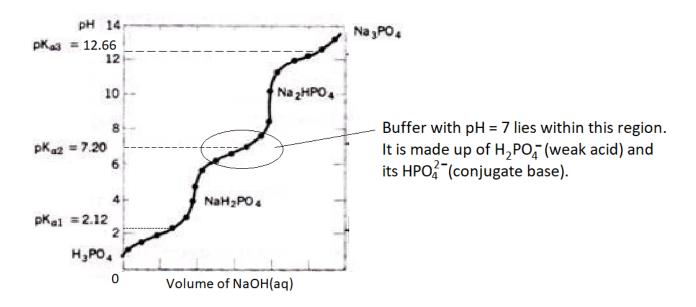
11 The stepwise dissociation equations of phosphoric acid and the corresponding equilibrium constants are shown below.

$$\begin{array}{lll} H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ & K_a = 7.50 \times 10^{-3} \, mol \, dm^{-3} \\ H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ & K_a = 6.20 \times 10^{-8} \, mol \, dm^{-3} \\ HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+ & K_a = 2.20 \times 10^{-13} \, mol \, dm^{-3} \end{array}$$

A phosphate buffer with pH 7 needs to be prepared.

Which is the best way to prepare such a solution?

- A Dissolving Na<sub>3</sub>PO<sub>4</sub> alone in water.
- **B** Dissolving H<sub>3</sub>PO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub> in water.
- C Dissolving Na<sub>2</sub>HPO<sub>4</sub> and Na<sub>3</sub>PO<sub>4</sub> in water.
- Dissolving Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub> in water.



12 An equilibrium can be represented by the equation below.

$$W$$
 (aq) +  $X$  (aq)  $\rightleftharpoons Y$  (aq) +  $Z$  (aq)

In 0.50 dm<sup>3</sup> of a certain mixture, the concentrations of these substances at equilibrium were as shown:

Species	W	Х	Υ	Z
Concentration / mol dm <sup>-3</sup>	1.00	2.00	2.00	1.00

A certain amount of Y was added to this equilibrium mixture.

What is the number of moles of **Y** added such that the new equilibrium [**W**] is 1.20 mol dm<sup>-3</sup>?

Assume that the temperature remained constant throughout.

**A** 0.10 **B** 0.20 **C** 0.75 **D** 1.50

At initial equilibrium,  $Kc = [Y(aq)][Z(aq)] \div [W(aq)][X(aq)]$ 

$$Kc = (2.00)(1.00) \div (1.00)(2.00)$$

$$Kc = 1$$

 $W (aq) + X (aq) \rightleftharpoons Y (aq) + Z (aq)$ 

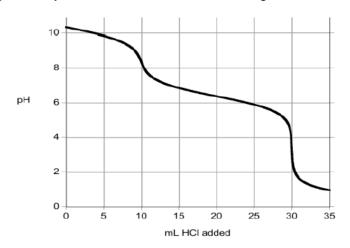
Initial Conc	1.00	2.00	2.00 + a	1.00
Change	+0.20	+0.20	-0.20	-0.20
Egm Conc	1.20	2.20	1.80 + a	0.80

For the new equilibrium,  $Kc = (1.80 + a)(0.80) \div (1.20)(2.20) = 1$ 

Upon solving,  $a = 1.5 \text{ mol dm}^{-3}$ 

Since it is  $0.5 \text{ dm}^3$  solution, therefore the amount added = (1.5)(0.5) = 0.75 mol

13 A sample of washing powder which contains a mixture of Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> was titrated with aqueous hydrochloric acid and the following titration curve was obtained.



What is the mole ratio of HCO<sub>3</sub> to CO<sub>3</sub><sup>2</sup> in the washing powder?

1:1

2:1

D 3:1

The first 10 cm<sup>3</sup> of HCl is used for:

 $H^+(aq) + CO_3^{2-}(aq) \rightarrow HCO_3^-(aq)$ 

The next  $(30 - 10) = 20 \text{ cm}^3$  of HCl is used for:

1:2

 $H^+(aq) + HCO_3^-(aq) \rightarrow H_2CO_3(aq)$ 

But this HCO<sub>3</sub><sup>-</sup>(aq) comes from the original sample, and from the first reaction.

Hence the  $HCO_3^-(aq)$  from original sample should correspond to (20 - 10) = 10 cm<sup>3</sup> of HCl.

Amount of HCO<sub>3</sub><sup>-</sup>(aq): Amount of CO<sub>3</sub><sup>2-</sup>(aq)

■ Volume of HCl reacting with HCO<sub>3</sub><sup>-</sup>(aq) in original sample : Volume of HCl reacting with

CO<sub>3</sub><sup>2-</sup>(aq) in sample

 $= 10 \text{ cm}^3 : 10 \text{ cm}^3$ 

= 1:1

14 The table below contains the standard reduction potential values for some cobalt and mercury species.

half-equation	E°/ V
$Co^{3+}$ (aq) + e $\rightleftharpoons$ $Co^{2+}$ (aq)	+1.82
$Co^{2+}(aq) + 2e \rightleftharpoons Co(s)$	-0.28
$Hg^{2+}(aq) + e \rightleftharpoons Hg^{+}(aq)$	+0.91
$Hg^+(aq) + e \rightleftharpoons Hg(l)$	+0.80

Which one of the following predictions is correct?

- A Both Co<sup>2+</sup> and Hg<sup>+</sup> will disproportionate.
- **B** Neither Co<sup>2+</sup> nor Hg<sup>+</sup> will disproportionate.
- C Only Co<sup>2+</sup> will disproportionate.
- **D** Only Hg<sup>+</sup> will disproportionate.

For 
$$Co^{2+} \rightarrow Co^{3+} + Co$$
  
 $E^{\Theta}_{cell} = E^{\Theta}_{red} + E^{\Theta}_{ox} = (-0.28) + (-1.82) = -2.10 \text{ V}$   
Since  $E^{\Theta}_{cell} < 0$ , the reaction is NOT spontaneous.

For 
$$Hg^+ \rightarrow Hg^{2+} + Hg$$
  
 $E^{\Theta}_{cell} = E^{\Theta}_{red} + E^{\Theta}_{ox} = (+0.80) + (-0.91) = -0.11 \text{ V}$   
Since  $E^{\Theta}_{cell} < 0$ , the reaction is NOT spontaneous.

15 Use of the Data Booklet is relevant to this question.

> The reaction between iodide and peroxydisulfate (S<sub>2</sub>O<sub>8</sub><sup>2</sup>-) is slow due to its high activation energy.

> Which of the following cannot function as a catalyst for the above mentioned reaction?

V<sup>2+</sup>

Mn<sup>2+</sup> В

Mn<sup>3+</sup>

Co3+

From Data Booklet,  $V^{2+} + 2e \rightleftharpoons V$ 

$$V^{2+} + 2e \rightleftharpoons V$$

-1.20 V

$$V^{3+} + e \rightleftharpoons V^{2+}$$

-0.26 V

$$I_2 + 2e \rightleftharpoons 2I^-$$

+0.54 V

$$S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{2-}$$

+2.01 V

Case 1: S<sub>2</sub>O<sub>8</sub><sup>2</sup>-react first with V<sup>2+</sup>.

$$S_2O_8^{2-} + 2V^{2+} \rightarrow 2SO_4^{2-} + 2V^{3+}$$

$$E_{cell}^{\Theta} = E_{red}^{\Theta} + E_{ox}^{\Theta} = (+2.01) + (+0.26) = +2.27 \text{ V}$$

Since  $E^{\Theta}_{cell} > 0$ , the reaction is spontaneous.

Subsequently, V<sup>3+</sup> must react to form V<sup>2+</sup> again, for V<sup>2+</sup> to function as a catalyst.

$$2I^- + 2V^{3+} \rightarrow I_2 + 2V^{2+}$$

$$E_{cell}^{\Theta} = E_{red}^{\Theta} + E_{ox}^{\Theta} = (-0.26) + (-0.54) = -0.80 \text{ V}$$

Since  $E_{cell}^{\Theta}$  < 0, the reaction is NOT spontaneous.

Hence V<sup>2+</sup> cannot function as a catalyst in this reaction.

Case 2: I- react first with V2+.

$$2l^{-} + V^{2+} \rightarrow l_{2} + V$$

$$E_{cell}^{\Theta} = E_{red}^{\Theta} + E_{ox}^{\Theta} = (-1.20) + (-0.54) = -1.76 \text{ V}$$

Since  $E_{cell}^{\theta}$  < 0, the reaction is NOT spontaneous.

16 The decomposition of hydrogen peroxide is a first order reaction.

It takes 20 minutes for a 0.140 mol dm<sup>-3</sup> solution of hydrogen peroxide to halve its concentration.

How much time (in minutes) does it take for a 0.280 mol dm<sup>-3</sup> solution of hydrogen peroxide to halve its concentration?

Α

80

R 40

20

D

10

**Half-life** is the time required for a quantity to reduce to half its initial value.

"Half its initial value" means that it is 50% of its initial value. It is about percentage or ratio, not about the absolute amount.

For 1st order reaction, k t<sub>2</sub> = ln 2. Since temperature is constant, the rate constant (k) will be constant, and hence the half-life ( $t_{1/2}$ ) will be constant.

17 The reaction mechanism between  $O_2$  and HBr is as proposed:

$$HBr + O_2 \rightarrow HO_2Br (slow)$$

$$HOBr + HBr \rightarrow Br_2 + H_2O$$

Which of the following statements is true?

- A The bromine in  $HO_2Br$  is oxidised in the second step.
- B The overall equation is  $O_2 + 4HBr \rightarrow 2Br_2 + 2H_2O$ .
- **C** The half-life of this reaction is constant.
- $\mathbf{D}$  HO<sub>2</sub>Br is the only intermediate.

#### Option A

$$H-O-O-Br + H-Br \rightarrow 2H-O-Br + 1 + 1$$

Option B: Add up all the elementary steps to get the overall equation.

# Option C

Rate = 
$$k [HBr]^{1} [O_{2}]^{1}$$

This is not a first-order reaction.

Note: We need to assume that the HBr is NOT in large excess. Otherwise, Rate =  $k'' [O_2]^1$ 

This is a pseudo first-order reaction. Then the half-life will be constant.

Similarly, we assume that  $O_2$  is NOT in large excess.

#### Option D

HOBr is another intermediate.

The numerical values of the solubility products at 25 °C for PbC $l_2$  and PbI $_2$  are 1.70 x 10<sup>-5</sup> and 9.80 x 10<sup>-9</sup> respectively.

What is the value of the equilibrium constant for the reaction below?

$$PbI_2(s) + 2Cl^-(aq) \Longrightarrow PbCl_2(s) + 2I^-(aq)$$

- **A** 3.01 x 10<sup>6</sup>
- **B** 1.73 x 10<sup>3</sup>
- C 5.76 x 10<sup>-4</sup>
- **D**  $3.32 \times 10^{-7}$

$$K_{\rm sp}$$
 of PbC $l_2 = [{\rm Pb^{2+}}][{\rm C}l^{-}]^2 = 1.70 \times 10^{-5} \rightarrow [{\rm C}l^{-}]^2 = 1.70 \times 10^{-5} / [{\rm Pb^{2+}}]$ 

$$K_{sp}$$
 of PbI<sub>2</sub> = [Pb<sup>2+</sup>][I<sup>-</sup>]<sup>2</sup> = 9.80 x 10<sup>-9</sup>  $\rightarrow$  [I<sup>-</sup>]<sup>2</sup> = 9.80 x 10<sup>-9</sup> / [Pb<sup>2+</sup>]

$$K_c = [I^{-1}]^2 / [Cl^{-1}]^2 = (9.80 \times 10^{-9}) / (1.70 \times 10^{-5}) = 5.76 \times 10^{-4}$$

Mohr's salt is named after the German chemist Karl Friedrich Mohr, who made many important advances in the methodology of titration in the nineteenth century.

It is a double salt because it contains two cations and an anion.

Heating solid Mohr's salt with sodium hydroxide liberated a colourless gas. A green precipitate is also formed. It was insoluble in excess sodium hydroxide. On standing in air the solid turned brown.

What is the formula of Mohr's salt?

- A AgCr( $CO_3$ )<sub>2</sub>
- **B**  $Ag_2Fe(CO_3)_2$
- $\mathbf{C}$  Fe(NH<sub>4</sub>)(SO<sub>4</sub>)<sub>2</sub>
- D Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>

Heating the solid with NaOH liberated a colourless gas of ammonia, thus NH<sub>4</sub><sup>+</sup> is present.

The green precipitate of  $Fe(OH)_2$  was formed, which was insoluble in excess sodium hydroxide and turned brown due to oxidation by air to  $Fe(OH)_3$ , thus  $Fe^{2+}$  is present.

Given the above deduction, the answer can be narrowed down to options C or D. To ensure that the overall compound is electrically neutral, there must be one mole of  $Fe^{2+}$ , two moles of  $NH_4^+$  and two moles of  $SO_4^{2-}$  per mole of the salt. Hence,  $Fe(NH_4)_2(SO_4)_2$  must be the salt.

20 Photographic film contains silver halides, which absorb light to form silver metal and halogens are formed. Different silver halides have different sensitivity to light and will undergo this process to a different extent.

During the development of the film, a solution of aqueous ammonia or sodium thiosulfate is used to dissolve the unreacted silver halides. However, sodium thiosulfate is preferred, as some silver halides are not soluble in aqueous ammonia.

Which statements concerning the above processes are correct?

- 1 Metallic silver forms a very stable complex with thiosulfate, hence silver halides are soluble.
- The decomposition of the silver halide to metallic silver and the respective halogen is easier for AgBr than for AgCl because bromide is more reducing than chloride.
- 3 AgBr is less soluble than AgCl in aqueous ammonia, as solubility product of AgCl is of a higher value.
- A 1 and 2 only
- B 1 and 3 only
- C 2 and 3 only
- **D** 1, 2 and 3
- 1: False. It is silver ion (Ag<sup>+</sup>), not metallic silver, that complexes with thiosulfate.
- **2:** True. Going down Group 17, the reducing power of the halides increases. It is true that bromide is more reducing than chloride.
- **3:** True. Given that both AgCl and AgBr are binary salts, their  $K_{sp}$  values can be compared directly to determine which is more soluble. Since AgBr is less soluble than AgCl in aqueous ammonia, its  $K_{sp}$  value must be lower than that of AgCl.

Hence, statements 2 and 3 only are correct.

21 Use of the Data Booklet is relevant to this question.

Which of the following statements about the above complex is **false**?

- A There are no 4s electrons in manganese in this complex.
- B This complex contains five ligands.
- **C** The coordination number of this complex is 5.
- **D** The oxidation number of manganese in this complex is +2.

**A:** True. Mn<sup>2+</sup>: [Ar]3d<sup>5</sup>. The two 4s electrons have been removed in the formation of Mn<sup>2+</sup> from Mn.

**B:** False. The complex **does not contain five ligands**. There is only one polydentate ligand.

**C:** True. As there are five dative covalent bonds formed into the Mn<sup>2+</sup> ion, the coordination number is 5.

**D:** True. As the complex is electrically neutral overall, the central metal ion must be Mn<sup>2+</sup> as it is bonded to two O<sup>-</sup>.

22 Cobalt forms many coloured complexes with ligands such as H<sub>2</sub>O and SCN<sup>-</sup>.

A 100 cm<sup>3</sup> solution of Co<sup>2+</sup>(aq) turns from pink to bright blue when 10 cm<sup>3</sup> of NaSCN(aq) is added to the solution.

$$[Co(H_2O)_6]^{2+}(aq) + 4SCN^-(aq) \rightleftharpoons [Co(SCN)_4]^{2-}(aq) + 6H_2O(l)$$
  
pale pink bright blue

At equilibrium,  $[Co(H_2O)_6]^{2+}$  and  $[Co(SCN)_4]^{2-}$  are found to be present in a mole ratio of 1:10.

Given that  $\lg K_c$  for the equilibrium is 3.00, which of the following statements is **false**?

- A At equilibrium,  $[SCN^-] = 3.16 \times 10^{-1} \text{ mol dm}^{-3}$ .
- **B**  $[Co(SCN)_4]^{2-}$  is more stable than  $[Co(H_2O)_6]^{2+}$ .
- **C** The units of  $K_c$  is mol<sup>-4</sup> dm<sup>12</sup>.
- D Dilution of the reaction mixture decreases the ratio of  $[Co(H_2O)_6]^{2+}$  to  $[Co(SCN)_4]^{2-}$  at equilibrium.

A: True.

$$K_c = 1000 = [Co(SCN)_4]^{2-}] = (10 / 0.11)$$

$$[[Co(H_2O)_6]^{2+}][SCN^{-}]^4 (1 / 0.11)[SCN^{-}]^4$$

$$\therefore [SCN^{-}] = 0.316 \text{ mol dm}^{-3}$$

**B:** True. SCN<sup>-</sup> is a stronger ligand than  $H_2O$ , thus  $[Co(SCN)_4]^{2-}$  is more stable than  $[Co(H_2O)_6]^{2+}$ . This can also be concluded from the fact that at equilibrium, the mole ratio  $[Co(SCN)_4]^{2-}$ :  $[Co(H_2O)_6]^{2+} = 10:1$ .

**C:** True. 
$$K_c = \frac{[[Co(SCN)_4]^{2-}]}{[[Co(H_2O)_6]^{2+}][SCN^{-1}]^4}$$
 (mol dm<sup>-3</sup>)<sup>-4</sup>  $\rightarrow$  mol<sup>-4</sup> dm<sup>12</sup>

**D:** False. By Le Chatelier's Principle, dilution of the reaction mixture causes the position of equilibrium to shift to the left, resulting in an <u>increase in the ratio of  $[Co(H_2O)_6]^{2+}$  to  $[Co(SCN)_4]^{2-}$  at equilibrium.</u>

Carbon disulfide,  $CS_2$ , can be electrolysed into carbon subsulfide,  $C_3S_2$ , an unusual compound.

The boiling points of these two compounds are 46.2 °C and 90.0 °C respectively.

$$CS_2(l)$$
  $\xrightarrow{I}$   $ZnS(l)$  +  $S=C=C=C=S$   $(l)$   $\xrightarrow{Br_2}$   $\xrightarrow{Br}$   $\xrightarrow{Br$ 

Which of the following statements are **false**?

- 1 Bromine is acting as a reducing agent in II.
- **2** C<sub>3</sub>S<sub>2</sub> has the higher boiling point because there are more covalent bonds to be broken than in CS<sub>2</sub>.
- 3 The carbon atoms in  $C_3S_2$  do not share a common oxidation state.
- A 2 and 3 only
- **B** 1 and 3 only
- C 1 and 2 only
- **D** 1, 2 and 3
- 1: False. Bromine is acting as an oxidising agent in II.
- **2:** False. The boiling point of a simple covalent molecule depends on the intermolecular forces of attraction, not the number or strength of the covalent bonds.
- **3:** True. Each of the carbon atoms directly bonded to sulfur is +3, while the other carbon not directly bonded to sulfur is +2.

Hence, statements 1 and 2 only are false.

24 L-lyxose and D-xylose are monosaccharides.

Which of the following statements are true?

- 1 They have the same melting point.
- 2 The same volume of hydrogen gas is produced when excess sodium is added to equal amounts of each of them under the same conditions.
- 3 Both compounds undergo intramolecular nucleophilic substitution to form cyclic esters.
- A 1 and 2 only
- **B** 1 and 3 only
- C 2 and 3 only
- D 2 only
- **1:** False. L-xylose and D-xylose are not enantiomers (they are diastereomers), thus they have different physical properties, such as melting point.
- **2:** True. Both L-xylose and D-xylose have four hydroxyl groups each. One mole of the monosaccharide produces two moles of hydrogen gas when reacted with sodium.
- **3:** False. Ester is formed from the reaction between a carboxylic acid (or acyl halide) and an alcohol functional group. There is no carboxylic acid functional group in either monosaccharides.

Hence, statement 2 only is correct.

25 Cyproterone acetate (abbreviated as CPA) is a drug that is used in the treatment of androgen-related conditions like acne and prostate cancer.

Which of the following statements about CPA are correct?

- 1 One mole of CPA undergoes condensation with three moles of 2,4-dinitrophenylhydrazine.
- 2 Two moles of yellow precipitate is formed when one mole of CPA is warmed with alkaline iodine solution.
- 3 CPA does not cause a colour change in hot acidified potassium dichromate(VI).
- A 1 and 3 only
- B 1 and 2 only
- C 2 and 3 only
- D 3 only
- 1: False. One mole of CPA undergoes condensation with only two moles of 2,4-DNPH.
- 2: False. Only one mole of yellow precipitate is formed when one mole of CPA is subjected to iodoform test.
- **3:** True. Alkenes can only be oxidised by hot acidified potassium manganate(VII), while the alcohol formed from the cleavage of the ester bond is a tertiary alcohol and thus cannot be oxidised.

Hence, statement 3 only is correct.

26 Xantocillin was first isolated from *Penicillium notatum* in the 1950s. It is used as an antibiotic.

$$\begin{array}{c} \ominus \\ C \\ \boxplus \\ N \oplus \\ \\ N \oplus \\ C \\ \ominus \\ \end{array} \\ OH$$

xantocillin

Which of the following statements about xantocillin is false?

- A It is a nitrile.
- **B** It exists as three cis-trans isomers.
- **C** There are four sp hybridised atoms.
- **D** It gives a violet colouration on adding neutral iron(III) chloride.

A: False. It is **not a nitrile** (-CN), but rather contains isocyanide (-NC) functional groups.

**B:** True. As xantocillin is symmetrical and there are two C=C double bonds, there are the cis-cis, cistrans (or trans-cis) and trans-trans isomers.

**C:** True. Each of the two isocyanide (–NC) functional groups contains one sp carbon atom and one sp nitrogen atoms. Hence, there are four sp hybridised atoms in total.

**D:** True. Phenol reacts with neutral iron(III) chloride to give a violet colouration.

27 Ketenes are important reagents in organic synthesis. They can be formed from carboxylic acids via the synthetic route below.

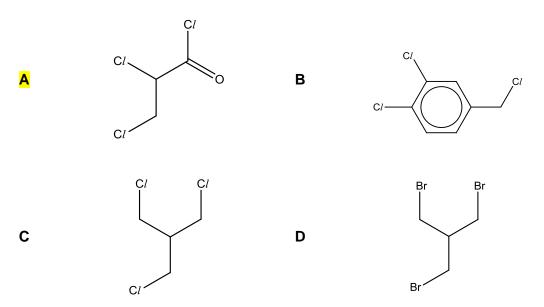
$$H \longrightarrow \begin{array}{c} R_1 \\ C \longrightarrow CO_2H \end{array} \longrightarrow \begin{array}{c} step I \\ R_2 \end{array} \longrightarrow \begin{array}{c} R_1 \\ C \longrightarrow COCl \end{array} \longrightarrow \begin{array}{c} R_1 \\ C \longrightarrow COCl \end{array} \longrightarrow \begin{array}{c} R_1 \\ R_2 \end{array} \longrightarrow \begin{array}{c} R_$$

Which of the following statements about the above reaction are correct?

- 1 The ketene will always be non-chiral, no matter which **Z** is used as the starting reactant.
- 2 Hydrochloric acid can be used as the reagent in step I.
- 3 The ketene can be converted back into **Z** by using water under suitable conditions.
- A 1 and 2 only
- **B** 1 and 3 only
- C 2 and 3 only
- **D** 1, 2 and 3
- 1: True. There is no chiral carbon in the ketene (C=C=O) functional group.
- **2:** False. Such conversion can be achieved through the use of  $PCl_3$ ,  $PCl_5$  or  $SOCl_2$  instead of HCl.
- 3: True. Water acts as a nucleophile to convert ketene back into Z.

Hence, statements 1 and 3 only are correct.

Aqueous silver nitrate can be used to test for the presence of halogens in organic compounds. Which of the following compounds produces a precipitate most readily when aqueous silver nitrate is added?



As acyl chloride is the easiest to hydrolyse, the compound in option **A** will produce a precipitate most readily upon the addition of aqueous silver nitrate.

The Reimer–Tiemann reaction is a chemical reaction used for the orthoformylation of phenols, with the simplest example being the conversion of phenol to salicylaldehyde.

salicylaldehyde

Which of the following types of reaction are involved in the above reaction scheme?

- 1 Nucleophilic substitution
- 2 Electrophilic substitution
- 3 Elimination
- A 1 and 2 only
- **B** 1 and 3 only
- C 2 and 3 only
- **D** 1, 2 and 3
- **1:** True. Step 3 involves nucleophilic substitution of –Cl to –OH.
- 2: True. Step 2 involves electrophilic substitution on the 2-position of the phenyl ring.
- **3:** True. Step 4 involves elimination of C*l*<sup>-</sup>.

Hence, statements 1, 2 and 3 are correct.

30 Hydroboration is one of the many methods to hydrate alkenes to alcohols. An example is shown below.

Which of the following alcohols cannot be formed via hydroboration?

- A Butan-2-ol from but-1-ene
- B 2-methylpropan-1-ol from 2-methylpropene
- **C** 3-methylpentan-2-ol from 3-methylpent-2-ene
- **D** 4-methylhexan-3-ol from 3-methylhex-3-ene

As seen from the example, hydroboration is an anti-Markovnikov electrophilic addition reaction. It means a hydrogen atom is added to the more substituted carbon atom instead of the less substituted carbon atom.

As such, subjecting but-1-ene to hydroboration should result in the formation of butan-1-ol instead of butan-2-ol.