CANDIDATE NAME	:			С	T GROUP	20\$		
CENTRE NUMBER					IDEX UMBER			
CHEMISTR	Y				<u> </u>		972	9/01
Paper 1 Multiple	e Choice					17 S	eptember	2021
Additional Mate	rials: Multiple Data Bo	Choice Answ	er Sheet				1	hour
READ THESE IN	ISTRUCTIONS	FIRST						
Write in soft pend	oil.							
Do not use staple	es, paper clips,	glue or corre	ction fluid.					
Complete the infe	ormation on the	Answer She	et as shown	below.				
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There are thirty of possible answers Choose the one y Sheet.	A, B, C and D	prect and reco	ord your cho	ice in so				
Read the instruc	tions on the A	Inswer Shee	t very caref	ully.				
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This document consists of 14 printed pages.

1 The successive ionisation energies of the gaseous ion, G<sup>+</sup>, are given in the table below:

1	2	3	4	5	6
				<u> </u>	
1907	2914	4964	6274	21 267	25 431
	1 1907	1 2 1907 2914	1 2 3 1907 2914 4964	1 2 3 4 1907 2914 4964 6274	1     2     3     4     5       1907     2914     4964     6274     21 267

Which group in the periodic table does G belong to?

A 14

**B** 15

**C** 16

**)** 17

2 In which of the following pairs of compounds would the second compound have a higher boiling point than the first compound?

1 HCHO, CH<sub>3</sub>OH

2 BF<sub>3</sub>, A/F<sub>3</sub>

3 CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, C(CH<sub>3</sub>)<sub>4</sub>

**A** 1 and 2

**B** 1 and 3

**C** 2 and 3

1, 2 and 3

D

3 Information about the properties of some compounds are given below.

ice water	density / g cm <sup>-3</sup> 0.931 0.997
	boiling point / °C
HF	19.5
$NH_3$	-33.3
2-nitrophenol	216
4-nitrophenol	279

Which statement about the hydrogen bonding in these compunds is incorrect?

- A HF has a higher boiling point than NH<sub>3</sub> because each HF molecule can form more hydrogen bonds on average compared to each NH<sub>3</sub> molecule.
- B Hydrogen bonds between molecules of H<sub>2</sub>O in ice causes the density of ice to be lower than that of water.
- When CH<sub>3</sub>CO<sub>2</sub>H is dissolved in benzene, hydrogen bonding between two molecules of CH<sub>3</sub>CO<sub>2</sub>H causes the *M<sub>r</sub>* to double from 60 to 120.
- **D** The boiling point of 2-nitrophenol is lower than 4-nitrophenol due to the presence of intramolecular hydrogen bonding in 2-nitrophenol.

Which graph will **not** have the same shape for a fixed mass of gas compared to the rest? (All values are measured in SI units.)

A pV against T

c pV against V at constant T

**B** p against density at constant T

**D** p against 1/V at constant T

When a liquid hydrocarbon was burnt in 100 cm³ of excess oxygen gas, the gaseous mixture contracted by 15 cm³. On passing the resultant gaseous mixture through aqueous sodium hydroxide, there was a further contraction of 60 cm³. What could be the molecular formula of the hydrocarbon? All volumes were measured at room temperature and pressure.

A C<sub>6</sub>H<sub>8</sub>

B C<sub>6</sub>H<sub>12</sub>

C C<sub>8</sub>H<sub>8</sub>

C<sub>8</sub>H<sub>12</sub>

6 The main isotopes of sulfur are summarised in the table below:

isotope	<sup>32</sup> S	<sup>33</sup> S	<sup>34</sup> S	<sup>36</sup> S
abundance	94.99	0.75	4.25	0.01

Which statements are correct?

1 The relative atomic mass of sulfur is 32.0929.

The relative isotopic mass of  $^{33}$ S is the mass of 1 atom of  $^{33}$ S relative to  $\frac{1}{12}$  of the mass of a  $^{12}$ C atom.

When unipositively charged ions of the isotopes of sulfur are passed through an electric field, the angle of deflection for <sup>32</sup>S<sup>+</sup> ion is the largest.

A 1 and 2

**B** 1 and 3

C 2 and 3

**D** 1, 2 and 3

When 13.1 g of zinc dust was added to 150 cm³ of 1.0 mol dm⁻³ aqueous copper(II) sulfate, the temperature of the solution rose by 15 °C.

What is the enthalpy change for the reaction:  $Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$ ?

Assume the specific heat capacity of the solution is  $4.20 \text{ J g}^{-1} \text{ K}^{-1}$  and the density of all solutions is  $1.00 \text{ g cm}^{-3}$ .

**A**  $-47.2 \text{ kJ mol}^{-1}$ 

 $C = -68.5 \text{ kJ mol}^{-1}$ 

 $B = -63.0 \text{ kJ mol}^{-1}$ 

**D** - 1210 kJ mol<sup>-1</sup>

8 Consider the following reactions:

$$2NaOH(aq) + H2SO4(aq) \rightarrow Na2SO4(aq) + 2H2O(l) \qquad \Delta H1$$

$$NaOH(aq) + CH3CO2H(aq) \rightarrow CH3CO2Na(aq) + H2O(l) \qquad \Delta H2$$

Which statements are correct?

- 1  $\Delta H_1$  represents the enthalpy change of neutralisation.
- 2 The pH of a solution of CH₃CO₂Na is greater than 7.
- 3 The magnitude of  $\Delta H_1$  is twice that of  $\Delta H_2$ .
- A 1 and 3
- B 3 only
- C 2 only
- **D** 1, 2 and 3

9 The equation for the reaction between bromate and bromide ions is shown below.

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + H_2O(I)$$

From initial rates experiments, the following rate equation was derived.

rate = 
$$k[BrO_3^-][Br^-][H^+]^2$$

The results of the initial rate experiments are shown.

initial [BrO <sub>3</sub> -] / mol dm <sup>-3</sup>	initial [Br <sup>-</sup> ] / mol dm <sup>-3</sup>	initial [H <sup>+</sup> ] / mol dm <sup>-3</sup>	initial rate, 1/t
0.004	0.04	0.40	0.10
0.004	0.04	0.80	×
0.004	0.08	0.40	у
0.008	z	0.80	1.60

What are the missing values, x, y, and z?

	x	у	z
Α	0.20	0.10	0.08
В	0.20	0.10	0.16
С	0.40	0.20	0.16
D	0.40	0.20	0.08

10 The mechanism for a given gaseous phase reaction is shown below.

$$2A \rightarrow C$$
 fast  $C + B \rightarrow D$  slow  $D + B \rightarrow E$  fast

Which statements are correct?

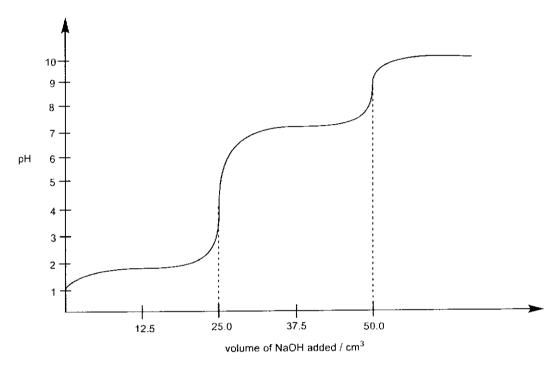
- 1 The overall equation is  $2\mathbf{A} + 2\mathbf{B} \rightarrow \mathbf{E}$ .
- 2 The units of the rate constant is  $atm^{-2} s^{-1}$ .
- The initial rate of formation of **E** is directly proportional to the square of the initial partial pressure of **A**.
  - **A** 1 and 2 **B** 1 and 3 **C** 2 and 3 **D** 1, 2 and 3
- What is the effect on decreasing temperature on the rate constants,  $k_f$  for the forward reaction and  $k_b$  for the backward reaction, and on the equilibrium constant  $K_c$ , for a reversible reaction where the forward reaction is exothermic?

	k <sub>f</sub>	$k_{\mathrm{b}}$	Kc
Α	decrease	decrease	increase
В	decrease	decrease	no effect
С	increase	decrease	increase
D	increase	increase	decrease

When an acid is titrated with a strong base, the equivalence point is reached when the amount of base added is equal to the amount of H<sup>+</sup> dissociated.

Sulfurous acid,  $H_2SO_3$ , a dibasic acid, has p $K_a$  values of 1.9 and 7.1.

The curve for the titration of 25.0 cm<sup>3</sup> of 0.10 mol dm<sup>-3</sup> sulfurous acid against a standard solution of sodium hydroxide, NaOH, is shown below.



The pH ranges of colour changes for thymol blue indicator are 1.2 - 2.8 and 8.0 - 9.6.

Which statement is correct?

- A The initial pH of 0.10 mol dm<sup>-3</sup> sulfurous acid is 1.20 if the effect of the second  $pK_a$  is ignored.
- B The concentration of sodium hydroxide is 0.05 mol dm<sup>-3</sup>.
- C Thymol blue is a suitable indicator to detect the first and second equivalence points.
- **D** HSO<sub>3</sub><sup>-</sup> has p $K_a$  value of 7.1 and p $K_b$  value of 12.1.
- 13 Phosphoric acid,  $H_3PO_4$ , a tribasic weak acid, has p $K_a$  values of 2.1, 7.2 and 12.4.

What are the major species present in a solution of phosphoric acid buffered at pH 7?

- A H<sub>3</sub>PO<sub>4</sub> and HPO<sub>4</sub><sup>2-</sup>
- B H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>
- C  $H_2PO_4$  and  $HPO_4^{2-}$
- **D**  $HPO_4^{2-}$  and  $PO_4^{3-}$

A solution contains  $Cu^{2+}(aq)$ ,  $Ni^{2+}(aq)$ , and  $Zn^{2+}(aq)$ , each of concentration 0.0010 mol dm<sup>-3</sup>. To selectively precipitate the cations present, H<sub>2</sub>S was bubbled into the solution until the concentration of S<sup>2-</sup>(aq) in the solution reaches 1 × 10<sup>-19</sup> mol dm<sup>-3</sup>.

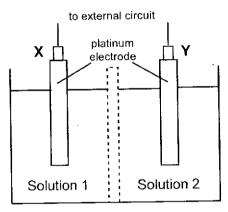
The value of the solubility product of each of the sulfides is given below.

salt	K <sub>sp</sub> / mol <sup>2</sup> dm <sup>-6</sup>
CuS	6.3 × 10 <sup>-36</sup>
ZnS	1.6 × 10 <sup>-24</sup>
NiS	4.0 × 10 <sup>-21</sup>

Which statement describes what happens in the solution?

- A CuS and ZnS only are precipitated
- B CuS only is precipitated
- c ZnS and NiS only are precipitated
- **D** NiS only is precipitated
- 15 Use of the Data Booklet is relevant to this question.

An electrochemical cell set-up is shown below:



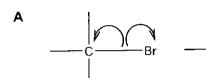
porous membrane

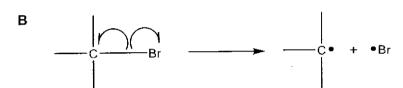
Which combination will cause electrons to flow in the external circuit from X to X2

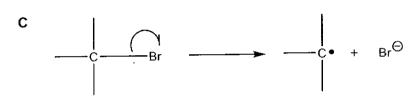
	solution 1	solution 2
Α	Cr³+	H <sub>2</sub> O <sub>2</sub> , H⁺
В	H₂O₂, H⁺	C <i>I</i> -
С	Co <sup>3+</sup>	Fe <sup>2+</sup>
D	Co²⁺	Fe <sup>3+</sup>

- An electric current is passed through two cells connected in series. One cell contains gold(III) chloride and the other contains aqueous copper(II) sulfate. If 4.00 g of gold is formed in the cell containing gold(III) chloride, what is the mass of copper deposited in the other cell?
  - **A** 0.64 g
- **B** 0.86 g
- **C** 1.29 g
- **D** 1.93 g

17 Which equation is correct?

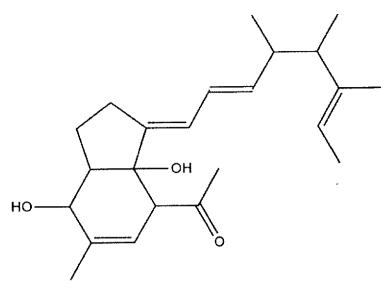








18 The compound below is reacted with an excess of hydrogen gas in the presence of a platinum catalyst.



How many additional chiral centres will each molecule of the product have after the reaction?

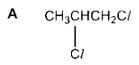
- **A** 3
- B 4
- **D** 9
- 19 Catalytic converters are used to convert the toxic gases emitted from exhausts of vehicles using internal combustion engines to less harmful compounds.

Which equations represent reactions that will take place in the catalytic converter?

- 1 Oxides of nitrogen + carbon monoxide → nitrogen + carbon dioxide
- 2 Unburnt hydrocarbons + carbon monoxide → carbon dioxide + water
- 3 Carbon monoxide + oxygen  $\rightarrow$  carbon dioxide
- A 3 only
- **B** 1 and 2
- **C** 1 and 3
- **D** 2 and 3

20 Hydrogen bromide undergoes an addition reaction with propene forming 2-bromopropane. When propene is bubbled through bromine monochloride, BrC/, dissolved in a suitable solvent, a similar reaction occurs.

Which product would be present in the greatest yield?



- 21 Which statement about benzene and cyclohexene is correct?
  - A Benzene and cyclohexene have delocalised  $\pi$  electrons.
  - **B** Benzene and cyclohexene decolourises aqueous bromine in the presence of finely divided iron.
  - C Benzene and cyclohexene undergo complete combustion to give the same products.
  - D Benzene and cyclohexene are planar molecules.
- The glucose molecule undergoes polymerisation to form carbohydrate chains of different lengths under suitable conditions. A short carbohydrate chain comprising 10 units of glucose molecules is shown below.

How many moles of H<sub>2</sub> gas will form when 1 mole of the carbohydrate chain above is reacted with excess sodium metal?

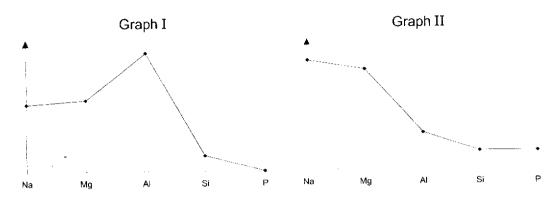
- **A** 3
- B 11
- **C** 16
- **D** 32

- Which compound will give a yellow precipitate with alkaline aqueous iodine and also gives a brick red precipitate with Fehling's reagent?
  - A HO
  - в н 0
  - c HO
  - D HO HO
- 24 How may the ester phenyl butanoate be made in the laboratory?
  - A  $CH_3(CH_2)_2CO_2H + C_6H_5OH$   $\xrightarrow{conc. H_2SO_4}$  ester +  $H_2O$
  - B  $C_6H_5CO_2H + CH_3(CH_2)_2CH_2OH$  conc.  $H_2SO_4$  ester +  $H_2O$
  - C  $CH_3(CH_2)_2COC_l + C_6H_5OH$  ester +  $HC_l$
  - **D**  $C_6H_5COC_l + CH_3(CH_2)_2CH_2OH$  ester +  $HC_l$

- 25 Which statement about the relative basicity of methylamine, dimethylamine and trimethylamine in the gas phase is correct?
  - A The lone pair of electrons on the nitrogen atom of trimethylamine delocalises over three methyl groups, making trimethylamine most basic.
  - B The lone pair of electrons on the nitrogen atom of trimethylamine is most available for donation, making trimethylamine the strongest Lewis base.
  - C Three electron-withdrawing methyl groups increase the electron density of the nitrogen atom of trimethylamine, making trimethylamine most basic.
  - **D** Three methyl groups disperse the negative charge on the nitrogen atom of trimethylamine, making trimethylamine the strongest Bronsted base.
- 26 Which reagents can be used to distinguish between compounds Y and Z?

- 1 2,4-dinitrophenylhydrazine
- 2 Hot acidified potassium dichromate
- 3 Hot aqueous sodium hydroxide
- **A** 1 and 2 **B** 1 and 3 **C** 2 and 3 **D** 2 only

27 The graphs below show the variation in two properties of the elements Na to P and their compounds.



Which properties are illustrated in Graphs I and II?

Graph I

- A electrical conductivity of the element
- B electrical conductivity of the element
- **C** melting point of the element
- **D** melting point of the element

## Graph II

pH of the chloride when added to water pH of the oxide when added to water pH of the chloride when added to water pH of the oxide when added to water

- Which statement explains the variation in the type of bonding of oxides and chlorides across Period 3?
  - A The number of valence electrons available for bonding increases due to the ability of P, S and C*I* to expand their octets.
  - **B** Effective nuclear charge increases as the proton number increases but shielding effect remains relatively constant.
  - C The magnitude of the electron affinity of oxygen is greater than that of chlorine.
  - **D** Difference in electronegativity between each element and oxygen or between each element and chlorine decreases.
- 29 Use of the Data Booklet is relevant to this question.

Some properties of fluorine and its compounds are compared with those of chlorine and bromine.

Property  ${\bf Q}$  for fluorine is lower than that for chlorine and bromine.

Which could be property Q?

- 1 The bond dissociation energy of the halogen-halogen bond.
- 2 The thermal stability of the hydrogen halide.
- 3 Reducing power of the halide ion.
- **A** 1 and 2
- **B** 1 and 3
- **C** 2 and 3
- D 1 only

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

An excess of zinc powder, Zn, is added into a solution containing  $VO_3^-$  ions.

What will be the final oxidation state of vanadium?

**A** 0

)

**B** +2

С

+3

D +4

**END OF PAPER** 



# HWA CHONG INSTITUTION 2021 C2 H2 CHEMISTRY PRELIMINARY EXAM SUGGESTED SOLUTIONS

## ANSWERS:

11	2	3	4	5	6	7	8	9	10
В	Α	Α	C	С	D	В	С	D	D
11	12	13	14	15	16	17	18	19	20
		HER SECTION OF THE PARTY OF THE	Total Control of the						25577 2000000000000000000000000000000000
Α	D	С	Α	Α	D	В	В	С	D
A 21	D 22	C 23	A 24	A 25	D 26	B 27	B 28	C 29	D (30)

### Comments

#### 1 B

In order to find the number of valence electrons in the  $G^+$  ion, we take the difference between all the successive ionisation energies to find the one with the greatest difference.

No of electrons removed	1	2	3	4	5	6
Ionisation energy/ kJ mol <sup>-1</sup>	1907	2914	4964	6274	21 267	25 431
Difference in IE		1007	2050	1310	14993	4164

After analysing the table, we can see that the greatest jump in ionisation energy is when the 5<sup>th</sup> electron is removed. This means that the **G**<sup>+</sup> ion has 4 electrons in its valence shell.

Therefore, **G** would have 5 electrons in the valence shell, and belong to group 15.

#### 2 A

# 1 HCHO, CH₃OH

	НСНО	CH₃OH	
	о н. <sup>с</sup> .н	H, O	
Intermole	cular force:	Intermolecular Force:	
Permaner dipole inte	nt dipole-permanent eractions	Hydrogen bonding	.2
	# 2 To the title	and the second s	,et ,

CH<sub>3</sub>OH has the higher boiling point. (strength of dispersion forces similar since number of electrons for each molecule is similar.)

**2** BF<sub>3</sub>: Simple covalent compound. Dispersion forces present between the non-polar molecules of BF<sub>3</sub>.

A/F<sub>3</sub>: Ionic compound. Ionic bonds present between oppositely charged ions.

AlF<sub>3</sub> has the higher boiling point.

# 3 CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, C(CH<sub>3</sub>)<sub>4</sub>

Both compounds are simple non-polar covalent molecules, with same number of electrons. However, C(CH<sub>3</sub>)<sub>4</sub> is a branched chain hydrocarbon while CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> is a straight chain hydrocarbon. CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> has linear shape and greater surface area of contact between molecules, hence more extensive dispersion forces. CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> has the higher boiling point.

## 3 A

Option **A**: Both NH<sub>3</sub> and HF can form only one hydrogen bond on average per molecule. Hence while it is true that HF has a higher boiling point than NH<sub>3</sub>, it is because the hydrogen bonds between HF molecules are stronger than the hydrogen bonds between NH<sub>3</sub> molecules. F more electronegative than N, so there is higher partial positive charge on the H of HF, hence the hydrogen bonds between HF molecules are stronger.

Option **B**: In the solid state, H<sub>2</sub>O molecules are held at fixed positions and arranged in an orderly manner to form a regular lattice such that hydrogen bonding is maximised to four per molecule. The hydrogen bonding between water molecules in ice are positioned in a roughly tetrahedral shape around each O atom. This produces an open lattice, with empty spaces between the H<sub>2</sub>O molecules. The more random arrangement of hydrogen bonding in liquid water results in H<sub>2</sub>O molecules packing much more closely and, together, take up less space. So the lattice structure of ice occupies a larger volume for the same mass of liquid water, hence ice has a lower density than liquid water.

Option **C**: CH<sub>3</sub>CO<sub>2</sub>H dimerises in non-aqueous solvents as shown in the following diagram.

Option **D**: In 2-nitrophenol, the –OH and –NO<sub>2</sub> groups can form intramolecular hydrogen bonding, so there is less extensive intermolecular hydrogen bonding between 2-nitrophenol molecules compared to between 4-nitrophenol molecules. Therefore, less energy is needed to overcome the intermolecular hydrogen bonding for 2-nitrophenol to boil, hence its lower boiling point. (The words 'less extensive'

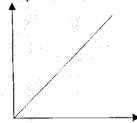
refers to lower average number of hydrogen bonds present in the same mass of 2-nitrophenol molecules as compared to 4-nitrophenol molecules.)

intramolecular hydrogen bonding

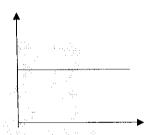
Refer to Section 8.3 on hydrogen bonding in Chemical Bonding Lecture Notes.

## 4 C

For options A, B and D, the graph is a straight line passing through the origin.



For option C, the graph is a horizontal line parallel to the x axis.



In order to derive the shape of the graph, start from the ideal gas equation: pV = nRT

For each of the options, find the relationship the different terms have based on the ideal gas equation. E.g. for option B

pV= nRT

Since density =  $\frac{mass}{V}$ 

 $pV = \frac{mass}{M_r} RT$   $p = \frac{mass}{V} \frac{RT}{M_r}$ 

Since  $\frac{RT}{M_r}$  is constant, p is directly proportional to density.

	C <sub>x</sub> H <sub>y</sub> (l)	+	$(x+\frac{y}{4}) O_2 (g)$	$\rightarrow$	xCO <sub>2</sub> (g)	+	$\frac{y}{2}$ H <sub>2</sub> O ( <i>l</i> )
Initial gas volume/ cm <sup>3</sup>	-		100		-		-
Final gas volume/ cm <sup>3</sup>	<del>-</del>		25		60		
Reacting volume/ cm <sup>3</sup>			75		60		

Since the gaseous mixture contracted by 15 cm $^3$  after the reaction, the total volume of excess  $O_2$  and  $CO_2 = 85$ cm $^3$ 

When the gaseous mixture was passed through NaOH (aq), the volume of gas contracted another 60cm<sup>3</sup>. This implies that the volume of CO<sub>2</sub> is **60 cm<sup>3</sup>**.

The volume of excess oxygen is therefore  $25\text{cm}^3$ . Hence  $100-25=75\text{ cm}^3$  of  $O_2$  reacted with the hydrocarbon.

The ratio of vol of  $O_2$  reacted: vol of  $CO_2$  produced =  $x + \frac{y}{4}$ : x = 75: 60

Hence the ratio of x: y = 1:1.

Any hydrocarbon with C:H of 1:1 could be the answer.

#### 6 D

1 Relative atomic mass = 0.9499 × 32 + 0.0075 × 33 + 0.0425 × 34 + 0.0001 × 36

2 This is a correct definition.

3 The angle of deflection in an electric field is directly proportional to the charge/ mass ratio. Since the charges of the isotopes are the same (all +1), the lightest isotope will have the largest angle of deflection.

## 7 B

No. of moles of zinc = 13.1/65.4 = 0.200 mol No. of moles of  $Cu^{2+} = \frac{150}{1000} \times 1 = 0.150$  mol

Cu<sup>2+</sup> is the limiting reagent.

 $q=m_{solution}c\Delta T = 150 \times 4.20 \times 15 = 9450 J$ 

 $\Delta H_{\text{rxn}} = -\frac{9450}{0.15} = -63\ 000\ \text{J mol}^{-1} = -63.0\ \text{kJ mol}^{-1}$ 

1 The enthalpy change of neutralisation is defined as the energy evolved when one mole of water is formed from a reaction between an acid and a base. This equation shows the formation of 2 moles of water. Hence this equation is twice that of the enthalpy change of neutralisation.

**2** As ethanoic acid is a weak acid, its conjugate base is a weak base that is able to hydrolyse partially in water to give OH<sup>-</sup> ions.

$$CH_3CO_2^- + H_2O \rightleftharpoons CH_3CO_2H + OH^-$$

As such the pH of a solution of CH<sub>3</sub>CO<sub>2</sub>Na is greater than 7.

3 When a weak acid is neutralised by a base, the enthalpy change of neutralisation will be slightly less exothermic as energy is absorbed to ionise the un-ionised weak acid.

## 9 D

Given the rate equation, rate =  $k[BrO_3^-][Br^-][H^+]^2$ 

To determine x:

Since the order with respect to [H<sup>+</sup>] is 2, when the [H<sup>+</sup>] is doubled from 0.40 to 0.80 mol dm<sup>-3</sup> in experiment 1 to 2, 1/t will be four times its original value. Hence  $\mathbf{x} = 0.10 \times 4 = 0.40 \text{ s}^{-1}$ .

To determine y:

Since the order with respect to [Br] is 1, when the [Br] is doubled from 0.04 to 0.08 mol dm<sup>-3</sup> in experiment 1 to 3, 1/t will be double its original value. Hence  $y = 0.10 \times 2 = 0.20 \text{ s}^{-1}$ .

To determine z:

When [H<sup>+</sup>] and [BrO<sub>3</sub><sup>-</sup>] are both doubled from experiment 1 to 4, if there is no change to [Br<sup>-</sup>], then 1/t would be 0.10 x 2 x  $2^2 = 0.80$ . Since actual 1/t is 1.60 s<sup>-1</sup>, the [Br<sup>-</sup>] must also be higher resulting in a faster rate of reaction.

Compare the initial rate of 0.10 s<sup>-1</sup> and 1.60 s<sup>-1</sup>: Let the multiplication factor of [Br<sup>-</sup>] be  $\mathbf{a}$  $\mathbf{a} \times 2 \times 2^2 = (1.60 \div 0.10)$  $\mathbf{a} = 2$ 

$$z = 2 \times 0.04 = 0.08 \text{ mol dm}^{-3}$$

### 10 D

The overall equation is the sum of all individual steps:

 $2A \rightarrow C$   $C + B \rightarrow D$  $D + B \rightarrow E$ 

 $2A + 2B + C + D \rightarrow C + D + E$ 

Overall: 2A + 2B → E Statement 1 is correct.

The rate equation of the slow step is: rate =  $k_2P_BP_C$ Since the concentration of intermediates do **not** appear in the rate equation, the  $P_C$  is replaced by the  $P_A$  (assuming step is a fast equilibrium) i.e  $P_C = K_1P_A^2$ Hence, rate =  $kP_A^2P_B$  where  $k = k_2K_1$ 

This suggests that the initial rate of formation of **E** is proportional to the initial partial pressure of **A**, raised to the power of 2. Thus, statement 3 is correct.

Analysis of the units of the rate constant: atm  $s^{-1} = (Units of k) \times atm^2 \times atm$ Units of  $k = atm^{-2} s^{-1}$ Therefore statement 2 is correct.

#### 11 A

Decreasing the temperature will cause <u>both</u> forward and backward reactions to slow down, hence <u>both</u> rate constants  $k_f$  and  $k_b$  will decrease. Hence either option **A** or **B** is correct.

Decreasing the temperature will change  $K_c$  since  $K_c$  is dependent on temperature. Hence option  $\boldsymbol{B}$  is incorrect and  $\boldsymbol{A}$  is the answer.

To deduce *how*  $K_c$  has changed (whether increase or decrease), we can look at the equilibrium shift. Since the forward reaction is exothermic, based on LCP, a decrease in temperature will favour the forward reaction, and the position of equilibrium will shift to the right. This means that  $K_c$  must have increased (such that Q becomes < K when T decreases, and a shift in POE to the right will re-establish the equilibrium.)

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## 12 D

 $pK_{a1} = 1.9$  $K_{a1} = 0.0126$ 

 $K_{a1} = \frac{[H^+][HSO_3^-]}{[H_2SO_3]}$ 

 $[H^+]^2 = K_{a1}[H_2SO_3]$   $[H^+]^2 = 0.0126 \times 0.1$  (assuming that  $[H^+] << [H_2SO_3]_{initial}$ )  $[H^+] = 0.0355$  mol dm<sup>-3</sup> pH = 1.45 Statement **A** is incorrect.  $n(H_2SO_3) = 0.1 \times (25.0/1000) = 2.5 \times 10^{-3} \text{ mol}$ 

Since 1 mol of H<sub>2</sub>SO<sub>3</sub> reacts with 2 mol of NaOH to form SO<sub>3</sub><sup>2</sup>, n(NaOH) required for complete neutralisation to form SO<sub>3</sub><sup>2</sup> = 5.0 × 10<sup>-3</sup> mol

Complete neutralisation to form SO<sub>3</sub><sup>2</sup>- occurs at the <u>second</u> pH jump i.e. at **50 cm**<sup>3</sup> of NaOH.

Hence, [NaOH] =  $5.0 \times 10^{-3} \div 50.0/1000 = 0.10 \text{ mol dm}^{-3}$ Statement **B** is incorrect.

From the graph, the region of rapid pH change for the first equivalence point is between pH 3 and 5. However, the working range of thymol blue does not coincide with this range.

Statement C is incorrect.

(Note that the working range of thymol blue does in fact coincide with the region of rapid pH change between 8 and 9, so thymol blue would be a suitable indicator for the second equivalence point.)

HSO<sub>3</sub><sup>-</sup> can act as a Bronsted acid as well as a Bronsted base.

The question gave two pKa values:

 $H_2SO_3 \rightleftharpoons HSO_3^- + H^+ pK_a = 1.9$ 

 $HSO_3^- \rightleftharpoons SO_3^{2-} + H^+ pK_a = 7.1$ 

Hence the second p $K_a$  value for H<sub>2</sub>SO<sub>3</sub> is the p $K_a$  value of HSO<sub>3</sub>-i.e. 7.1.

HSO<sub>3</sub><sup>-</sup> is the conjugate base of H<sub>2</sub>SO<sub>3</sub>,

hence  $pK_b$  of  $HSO_3^- = 14 - (pK_a \text{ of } H_2SO_3) = 14 - 1.9 = 12.1.$ 

Statement **D** is correct.

#### 13 C

At low	pH =	1 <sup>st</sup>	pH =	2 <sup>nd</sup>	pH =	3 <sup>rd</sup>	At high
рH	2.1	equival	7.2	equival	12.4	equival	pН
814-i-1-1-4-94		ence	1.0	ence		ence	
		point		point		point	
Mainly	H <sub>3</sub> PO <sub>4</sub>	Mainly	H <sub>2</sub> PO <sub>4</sub> -	Mainly	HPO <sub>4</sub> <sup>2</sup> -	Mainly	Mainly
H <sub>3</sub> PO <sub>4</sub>	and	H <sub>2</sub> PO <sub>4</sub> -	and	HPO4 <sup>2</sup> -	and	PO <sub>4</sub> 3-	PO <sub>4</sub> 3-
	H <sub>2</sub> PO <sub>4</sub> -		HPO <sub>4</sub> <sup>2-</sup>		PO <sub>4</sub> 3-		
	in a 1:1	1	in a 1:1	17	in a 1:1		
	ratio		ratio	::-	ratio		·

At pH 7, only the first deprotonation would have taken place, and the major species present would be  $H_2PO_4^-$  and  $HPO_4^{2-}$ .

#### 14 A

 $IP = 0.0010 \times 1 \times 10^{19} = 1 \times 10^{-22} \,\text{mol}^2 \,\text{dm}^{-6}$ 

IP >  $K_{sp}$  of CuS, CuS will precipitate.

 $IP > K_{sp}$  of ZnS, ZnS will precipitate.

 $IP < K_{sp}$  of NiS, NiS will **not** precipitate.

## 15 A

Solution 1:  $Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O$  (+1.33 V) Oxidation Solution 2:  $H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O$  (+1.77 V) Reduction  $E^e_{cell} > 0$ , electrons flow from X to Y.

Solution 1:  $H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O$  (+1.77 V) Reduction Solution 2:  $Cl_2 + 2e \rightleftharpoons 2Cl^-$  (+1.36 V) Oxidation  $E^{\theta}_{cell} > 0$ , electrons flow from Y to X.

Solution 1:  $Co^{3+} + e \rightleftharpoons Co^{2+}$  (+1.89 V) Reduction Solution 2:  $Fe^{3+} + e \rightleftharpoons Fe^{2+}$  (+0.77 V) Oxidation  $E^e_{cell} > 0$ , electrons flow from Y to X.

Solution 1:  $Co^{3+} + e \rightleftharpoons Co^{2+} (+1.89 \text{ V})$ Solution 2:  $Fe^{3+} + e \rightleftharpoons Fe^{2+} (+0.77 \text{ V})$  $E^{9}_{cell} < 0$ , there is no reaction (or electron flow).

# 16 D

For electrolytic cells connected in series, the same number of electrons will pass through each cell.

n(Au) deposited =  $4.0 \div 197.0 = 0.0203$  mol n(e) transferred =  $0.0203 \times 3 = 0.0609$  mol

Since 0.0609 mol of electrons was transferred, and 1 mol of Cu<sup>2+</sup> requires 2 mol of electrons for reduction, 0.0305 mol of Cu was deposited.

Mass of Cu deposited =  $0.0305 \times 63.5 = 1.93 g$ 

#### 17 B

This question tests understanding of homolytic and heterolytic fission and their representations in the form of full or half curved arrows.

Homolytic fission should be represented by half curved arrows. They should always occur in pairs, hence option **C** is incorrect.

Heterolytic fission should be represented by a single full curve arrow, hence option **A** is wrong This single full arrow should also point towards the more electronegative atom in a covalent bond, hence option **D** is incorrect.

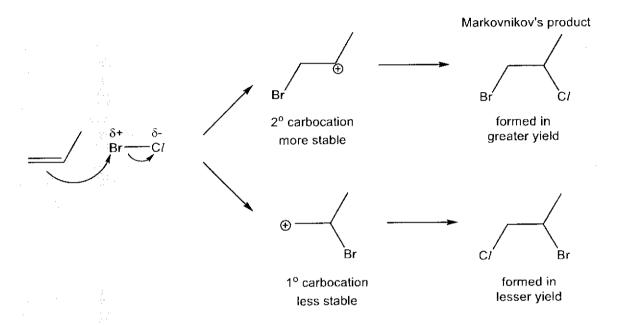
19 C

The catalytic converter gets rids of unwanted gases in exhaust fumes in cars by catalysing redox reactions between these gases which ordinarily cannot happen at the temperatures found in the car engine or exhaust systems.

Options 1 and 3 are redox reactions that are catalysed in the converter. Option 2 shows both the hydrocarbon and carbon monoxide on the left side of the equation becoming oxidised which is not possible as there is no species being reduced (i.e. lack of redox couple).

Electrophilic addition occurs between BrCI and propene (an unsymmetical alkene). Hence Markovnikov's rule must be applied to deduce the major product (present in greatest yield).

Since C/ is more electronegative than Br, the partial positive charge is found on Br and when the electron-deficient Br bonds to the propene, it should bond to the carbon atom of the C=C which gives the more substituted carbocation which is more stable due to the larger number of electron-donating alkyl groups.



21 C

> Option A: Only benzene has delocalised electrons where the six  $\pi$  electrons are delocalised over the six carbon atoms in the structure. The two  $\pi$  electrons in cyclohexene are localised between two sp<sup>2</sup>-hybridised carbon atoms.

> Option B: Cyclohexene decolorises yellow-orange aqueous bromine at room temperature but benzene decolorises reddish-brown liquid bromine upon warming with Fe(s) or FeBr<sub>3</sub>(s) under anhydrous conditions (absence of moisture or water).

Option C: Carbon dioxide and water will be formed from complete combustion.

Option D: Cyclohexene is not planar, it has four sp<sup>3</sup>-hybridised carbon atoms which are tetrahedral about each of them.

Each OH group will give only ½ mole of hydrogen gas. Since there are 8 x 3 OH groups in the 8 repeat units in the glucose polymer,  $8 \times 3 \div 2 = 12$  moles of hydrogen gas will be formed. The two ends of the polymer have 4 OH groups each, which gives  $4 \times 2 \div 2 = 4$  moles of hydrogen gas. Hence the total amount of hydrogen gas given off = 16 moles.

#### 23 D

The following compounds (R = H or alkyl) will be oxidised by alkaline aqueous iodine to give a yellow precipitate  $CHI_3$ , this is also known as a positive iodoform test.

Only an aliphatic aldehyde will be oxidised by Fehling's reagent to give a brick red precipitate Cu<sub>2</sub>O, benzaldehyde (aromatic aldehyde) will give a negative test with Fehling's reagent.

Option A is incorrect. Both the primary alcohol and ketone groups will give a negative iodoform test and a negative test with Fehling's reagent.

Option **B** is incorrect. The aliphatic aldehyde group will give a positive test with Fehling's reagent but the ester -OCOCH<sub>3</sub> group will give a negative iodoform test.

Option **C** is incorrect. The –CH(OH)(CH<sub>3</sub>) group will give a positive iodoform test but the benzaldehyde group will give a negative test with Fehling's reagent.

Option **D** is correct. The –CH(OH)(CH<sub>2</sub>I) group will give a positive iodoform test while the aliphatic aldehyde group will give a positive test with Fehling's reagent.

Option **A** is incorrect as there will be **no** condensation (nucleophilic acyl substitution) reaction due to phenol being a weak nucleophile. Due to the delocalisation of the lone pair of electrons on the oxygen atom of phenol into the benzene ring, the lone pair of electrons on the oxygen atom of phenol is thus less available (and unable) to attack the electron-deficient carboxyl carbon of the carboxylic acid (the electrophile) to form the ester. Refer to Carboxylic Acids Lecture Notes Section 4.5.1.

Option **B** is incorrect as butyl benzoate will be formed instead. Note that this reaction of alcohol and carboxylic acid with conc. acid is slow and reversible, so a lower yield of butyl benzoate will be obtained as compared to option **D**.

Option **C** is correct as phenyl butanoate will be formed from the condensation reaction between the acyl chloride and phenol at room temperature. This nucleophilic acyl substitution reaction is possible because acyl chloride is a stronger electrophile as compared to carboxylic acid in option **A** despite phenol being a weak nucleophile. The acyl carbon in acyl chloride is more electron-deficient than the carboxyl carbon of the carboxylic acid due to the highly electronegative C*I* atom which withdraws electrons through inductive effect from the C=O group, making the acyl chloride more susceptible to nucleophilic attack by phenol. In addition, the chloride ion, C*I*<sup>r</sup>, is a better leaving group than hydroxide ion, OH<sup>-</sup>. Refer to Carboxylic Acids Lecture Notes Section 5.4.

Option **D** is incorrect as butyl benzoate will be formed instead from the condensation reaction between the acyl chloride and alcohol at room temperature.

Option **A** is incorrect. There is **no** delocalisation of the lone pair of electrons on the nitrogen atom of trimethylamine since there are no 3 or more adjacent p orbitals in the molecule. The electron density on the nitrogen atom of trimethylamine is localised on the nitrogen atom.

triethylamine

Option B is correct.

A Lewis base is a species that donates an electron pair. The following equation shows trimethylamine (Lewis base) donating a lone pair to a proton (H<sup>+</sup>) which acts as the Lewis acid (electron pair acceptor).

$$(CH_3)_3N + HCl \rightarrow (CH_3)_3NH^+ + Cl^-$$

The increasing number of electron-donating methyl groups from methylamine (1 methyl group) to trimethylamine (3 methyl groups) attached to the nitrogen atom increases the electron density about the nitrogen atom, causing the lone pair on the nitrogen atom to be more available for donation to a proton, making trimethylamine the strongest Lewis base.

Option **C** is incorrect. Methyl groups are electron-donating, not electron-withdrawing. Electron-withdrawing groups would decrease the electron density about the nitrogen atom, causing the lone pair on the nitrogen atom to be less available for donation to a proton, making the base a weaker base.

Option **D** is incorrect. Trimethylamine has no net charge, there is **no** negative charge on the nitrogen atom of trimethylamine. Nitrogen is more electronegative than carbon, hence nitrogen has a partial negative charge ( $\delta$ –), but **not** a negative charge. The concept of the negative charge on an oxygen atom being dispersed by an electron-withdrawing group, hence stabilising the conjugate base, thus making an organic acid dissociate to a larger extent, can be applied, for example, to explain why 4-chlorophenol is more acidic than phenol.

$$CI$$
  $\longrightarrow$   $OH$   $\longrightarrow$   $CI$   $\longrightarrow$   $O^{\ominus}$  +  $H^{+}$  4-chlorophenol conjugate base

### 26 B

Compound Y has the following functional groups: alkene, aldehyde and chloroalkane

Compound Z has the following functional groups: 2° alcohol and amide

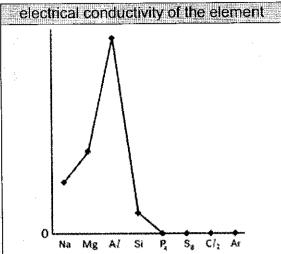
Option 1: 2,4-DNPH reacts with aldehydes and ketones. Compound Y (contains aldehyde) will give an orange ppt while compound Z will not.

Option **2**: Hot acidified  $Cr_2O_7^{2-}$  can oxidise 1° alcohols, 2° alcohols and aldehydes. Compound Y will get oxidised as it contains an aldehyde. Compound Z will also get oxidised as it contains a 2° alcohol.

Option 3: Hot aqueous NaOH can react with halogenoalkanes, esters, amides and nitriles. Compound Y (contains chloroalkane) will react via nucleophilic substitution to give C/r but this does not give an observable change unless AgNO<sub>3</sub> is added. Compound Z (contains amide) reacts via hydrolysis to form gaseous NH<sub>3</sub> which can be detected with moist red litmus paper turning blue.

Hence only options 1 and 3 may distinguish between compounds Y and Z.

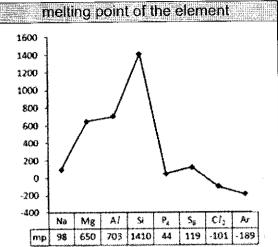
This is a recall question, testing knowledge of the trends below:



Na, Mg and A/ have giant metallic structures. From Na to A/, the number of valence electrons that can be contributed per atom increases. Therefore, electrical conductivity increases.

Si has a giant molecular structure. As a metalloid, it is a semiconductor.

In the **simple covalent molecules**  $P_4$ ,  $S_8$  and  $C_{12}$ , outer electrons are held strongly in covalent bonds and are not free to move about. Ar exists as neutral discrete **atoms**. All four do not contain mobile charge carriers and therefore do not conduct electricity.



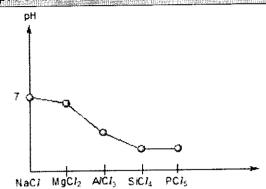
Na, Mg and A/ have giant metallic structures. From Na to A/, there is an **increase in the number of valence electrons** that can be **contributed per atom**. In addition, from Na<sup>+</sup> to A/3<sup>+</sup>, charge increases but ionic radius decreases so **charge density increases**. Hence, the strength of metallic bonding increases and melting point increases.

Si has a very high melting point due to its giant molecular structure. A lot of energy is needed to overcome the many strong covalent bonds between Si atoms during melting.

 $P_4$ ,  $S_8$  and  $C_{12}$  are non-polar simple covalent molecules with weak dispersion forces between molecules. Ar is monoatomic with weak dispersion forces between atoms.

S<sub>8</sub> has the **largest number of electrons** *I* **electron cloud**, followed by P<sub>4</sub>, then C*I*<sub>2</sub>, then Ar. Therefore, strength of dispersion forces decreases in that same order, energy needed to overcome dispersion forces during melting decreases. So S<sub>8</sub> has the highest melting point.

# pH of the chloride when added to water



Na\* has **low charge density**, and hence no hydrolysis occur. The solution thus remains neutral at pH 7.

Due to the higher charge density of Mg<sup>2+</sup> compared to Na<sup>+</sup>, the hydrated magnesium ion undergoes **slight hydrolysis** to form an acidic solution around **pH 6.5**.

$$[Mg(H_2O)_6]^{2+}(aq) + H_2O(l)$$
  
 $\Rightarrow [Mg(H_2O)_5OH]^{+}(aq) + H_3O^{+}(aq)$ 

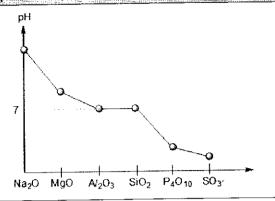
Due to the **higher charge density** of A/3+ compared to Mg<sup>2+</sup>, the hydrated aluminium complex undergoes **hydrolysis to a further extent** than Mg<sup>2+</sup>(aq), resulting in an acidic solution around **pH 3**.

$$[A/(H_2O)_6]^{3+}(aq) + H_2O(I)$$
  
 $\Rightarrow [A/(H_2O)_5OH]^{2+}(aq) + H_3O^{+}(aq)$ 

Complete hydrolysis occurs to result in a strongly acidic solution (pH 1) containing hydrochloric acid.

$$SiC/_4(I) + 4H_2O(I) \rightarrow SiO_2.2H_2O(s) + 4HC/(aq)$$
  
 $PCI_5(s) + 4H_2O(I) \rightarrow H_3PO_4(aq) + 5HC/(aq)$ 

# pH of the oxide when added to water



Na<sub>2</sub>O dissolves in water and forms a strong alkaline solution around **pH 13**.

$$Na_2O(s) + H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq)$$

MgO has very slow reaction and limited solubility in water. Some magnesium hydroxide is formed but is only sparingly soluble, hence forms an alkaline solution of around **pH 9**.

$$MgO(s) + H2O(I) \rightarrow Mg(OH)2(s)$$
  
 $Mg(OH)2(s) \rightleftharpoons Mg2+(aq) + 2OH-(aq)$ 

 $Al_2O_3$  and  $SiO_2$  are **insoluble in water** hence **pH is 7**. Too much energy is needed to overcome the strong ionic bonding in  $Al_2O_3$  and the extensive covalent bonding in  $SiO_2$ .

 $P_4O_{10}$  and  $SO_3$  react violently with water to give an acidic solution around **pH 2** and **pH 1**, respectively.

$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$$
  
 $SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq)$ 

Option **A** is incorrect. This statement does not explain the variation in type of bonding. Instead, it explains why the highest oxidation number of the elements in oxides and chlorides increases across Period 3.

Option **B** is incorrect. This statement does not explain the variation in type of bonding. Instead, it explains why the atomic radius of the elements generally decreases across Period 3. This statement also explains why the first ionisation energy of the elements generally increases across Period 3.

Option **C** is incorrect. This statement is irrelevant.

Option **D** is correct. The difference in electronegativity between the elements in a compound explains why the bonding of oxides and chlorides changes from ionic to covalent across Period 3.

### 29 B

Option 1 is correct as bond energy of F—F is lower.

From Data Booklet.

	F∸F	C/-C/	Br—Br
Bond energy / kJ mol <sup>-1</sup>	158	244	193

Option **2** is incorrect. Bond energy of H—F is higher, hence more energy is needed to break a H—F bond, thus HF has a higher thermal stability.

From Data Booklet,

	H–F	H–C/	H—Br
Bond energy / kJ mol <sup>-1</sup>	562	431	366

Option 3 is correct. E<sup>e</sup>(F<sub>2</sub>/F<sup>-</sup>) is higher, hence F<sup>-</sup> has a lower tendency to undergo oxidation, hence F<sup>-</sup> has a lower reducing power.

# 144 	F-	СГ	Br <sup>-</sup>
$E^e / V$ for $X_2 + 2e^- \rightleftharpoons 2X^-$	+2.87	+1.36	+1.07
Reducing power of halide ion	Lowest		Highest

Reduction of VO<sub>3</sub><sup>-</sup> to form V<sup>2+</sup> in three steps as follows:

 $E^{9} = -0.76 \text{ V } [O]$  $Zn^{2+} + 2e^- \rightleftharpoons Zn$ 

 $VO_3^- + 4H^+ + e^- \rightleftharpoons VO^{2+} + 2H_2O E^0 = + 1.00 V [R]$ 

ON of V changes from +5 to +4

Reduction of VO<sub>3</sub><sup>-</sup> to VO<sup>2+</sup> by Zn,

 $E^{\theta}_{cell}$  = + 1.00 - (-0.76) = + 1.76 V > 0, hence reaction is spontaneous.

 $VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$   $E^0 = + 0.34 \text{ V [R]}$ 

ON of V changes from +4 to +3

Further reduction of VO<sup>2+</sup> to V<sup>3+</sup> by Zn,

 $E_{\text{cell}}^{\text{e}} = +0.34 - (-0.76) = +1.10 \text{ V} > 0$ , hence reaction is spontaneous.

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

 $E^{\circ} = -0.26 \text{ V [R]}$  ON of V changes from +3 to +2

Further reduction of  $V^{3+}$  to  $V^{2+}$  by Zn,

 $E^{\theta}_{cell} = -0.26 - (-0.76) = +0.50 \text{ V} > 0$ , hence reaction is spontaneous.

Further reduction of V<sup>2+</sup> to V by Zn is **not** spontaneous.

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

 $E^{\circ} = -1.20 \text{ V [R]}$ 

ON of V changes from +2 to 0

 $E^{\theta}_{cell} = -1.20 - (-0.76) = -0.44 \text{ V} < 0$ , hence reaction is **not** spontaneous.