ANDERSON SERANGOON JUNIOR COLLEGE

2024 JC2 PRELIMINARY EXAMINATION

NAME:__________________________ (   ) **CLASS:** 24 /____

CHEMISTRY **9729/01**

Paper 1 Multiple Choice

SUGGESTED SOLUTIONS

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

Which particle has more protons than electrons and more protons than neutrons?
(D represents deuterium, ^{2}H)

A NH_3 **B** NH_3D^+ **C** ND_4^+ **D** NHD^-

Ans: **B**

Approach

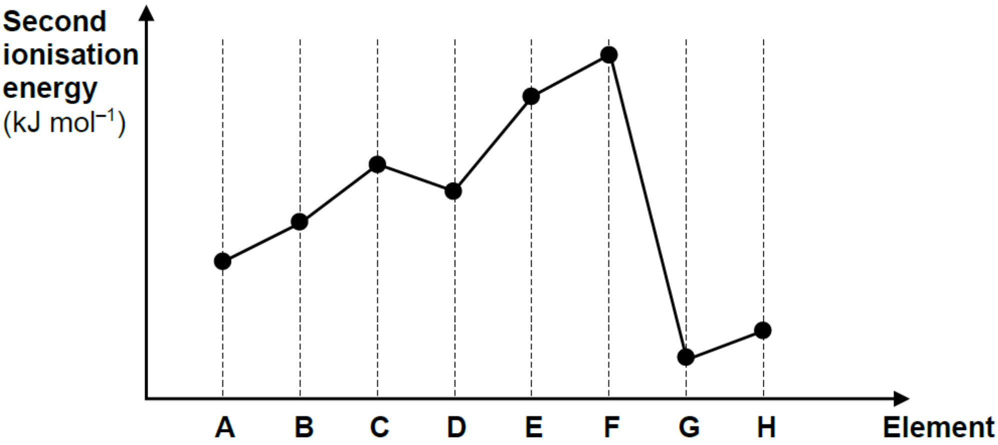
For a particle to contain more protons than electrons, it is likely to be a cation. Hence you should calculate the number of protons and neutrons for the particles in option **B** and **C**.

	NH_3	NH_3D^+	ND_4^+	NHD^-
number of protons	7 + 3(1) = 10	7 + 3(1) + 1 = 11	7 + 4(1) = 11	7 + 1 + 1 = 9
number of neutrons	7 + 0 = 7	7 + 0 + 1 = 8	7 + 4(1) = 11	7 + 0 + 1 = 8
number of electrons	10	10	10	10

From the table above, NH_3D^+ has 1 more proton than electron and 3 more protons than neutrons.

2 The graph shows the second ionisation energies of eight consecutive elements **A** to **H**, in Period 2 and 3 of the Periodic Table.

[Note that letters **A** to **H** are not the atomic symbols of the elements concerned.]



Which statements are correct?

1 **F** and **G** are in the same period in the Periodic Table.

2 The general increase from **A** to **F** is due to increasing atomic radius.

3 The small decrease from **C** to **D** is due to repulsion between paired electrons.

A 1 and 2 only **B** 1 and 3 only **C** 2 and 3 only **D** 3 only

Ans: **B**

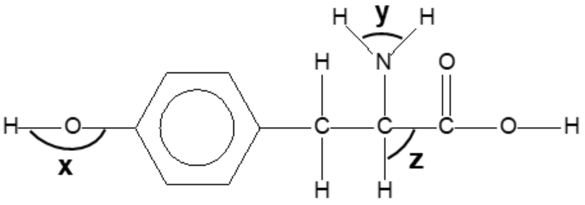
Statement 1 is correct.
The sharp dip in 2nd IE from **F** to **G** suggest that the second electron in **G** is removed from an electron shell which is further away / more shielded from the nucleus. The second electron removed from **F** is from the inner quantum shell. **F** is in group 1. **G** is in Group 2.

Statement 2 is incorrect.

- IE is not affected by atomic radius. IE is affected by nuclear charge, shielding effect and the distance of the valence electron from the nucleus.
- From **A**$^+$ to **F**$^+$, nuclear charge increases. Number of electron shells remains the same and shielding effect remains approximately constant. Electrostatic attraction between the valence electrons and the nucleus becomes stronger. More energy is required to remove a valence electron from an atom across a period.
- Due to the stronger attraction between the valence electrons and nucleus, atomic radius also decreases.

Statement 3 is correct.
C$^+$: $1s^22s^22p^3$ **D**$^+$: $1s^22s^22p^4$
The 2p electron to be removed from **D**$^+$ is a paired electron while that to be removed from **C**$^+$ is an unpaired electron. Due to inter-electronic repulsion between paired electrons in the same orbital, less energy is required to remove the 3p electron from **D**$^+$.

3 Tyrosine is an amino acid.



In which sequence is the bond angles arranged in decreasing order?

A ***x*** > ***y*** > ***z***

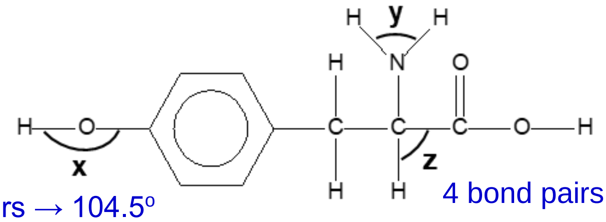
B **y** > **z** > **x**

C ***z*** > ***x*** > ***y***

D ***z*** > ***y*** > ***x***

Ans: **D**

3 bond pairs, 1 lone pair → 107°



2 bond pairs, 2 lone pairs → 104.5°

4 bond pairs, 0 lone pair → 109.5°

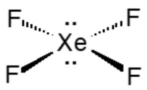
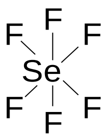
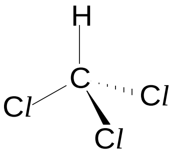
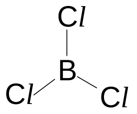
Hence the order is ***z*** > ***y*** > ***x***

4 The table identifies the shape and polarity of four molecules.

Which row is correct?

	molecule	molecular shape	polarity
A	xenon tetrafluoride	tetrahedral	non-polar
B	selenium hexafluoride	T-shaped	non-polar
C	trichloromethane	tetrahedral	polar
D	boron trichloride	trigonal planar	polar

Ans: **C**

	XeF_4	SeF_6	$CHCl_3$	BCl_3
No. of bp, lp on central atom	4 bp, 2 lp	6 bp, 0 lp	4 bp, 0 lp	3 bp, 0 lp
Molecular shape	Square planar 	octahedral 	tetrahedral 	trigonal planar 
polarity	non-polar	non-polar	polar	non–polar

5 A vessel is initially filled with argon gas at a particular temperature and pressure. The following changes are made to the vessel.

- the gas in the vessel was heated to 1.3 times the original temperature,
- the vessel was filled with an inert liquid such that the gas only occupied $\frac{1}{10}$ of the volume.

What is the number of times the gas pressure is built up in the vessel after the changes were made?

A 1.3 **B** 10 **C** 13 **D** 26

Ans: **C**

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Let P_1, V_1 and T_1 be the initial pressure, initial volume and initial temperature respectively and P_2 be the final pressure in the vessel after the changes were made.

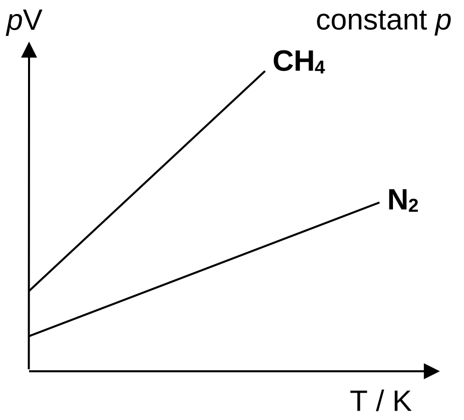
$$\frac{P_1V_1}{T_1} = \frac{P_2 \times 0.1V_1}{1.3T_1}$$

$$\frac{P_2}{P_1} = \frac{1.3}{0.1} = 13$$

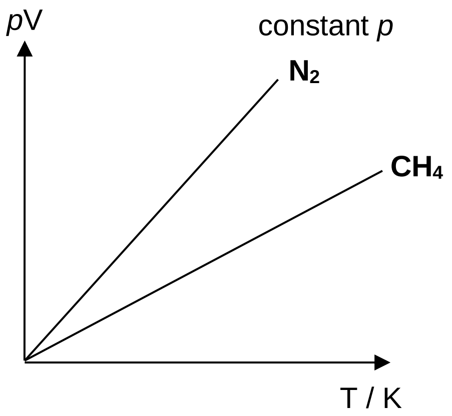
6 *Use of the Data Booklet is relevant to this question.*

Which graph correctly describes the behaviour of fixed masses of N_2 and CH_4? The gases behave as ideal gases under the conditions chosen.

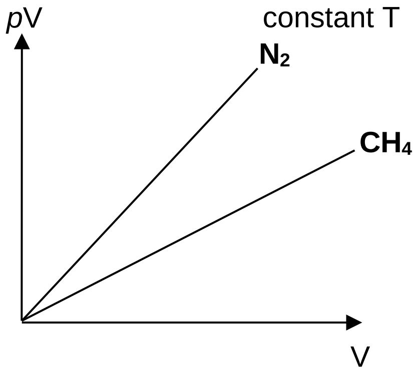
A



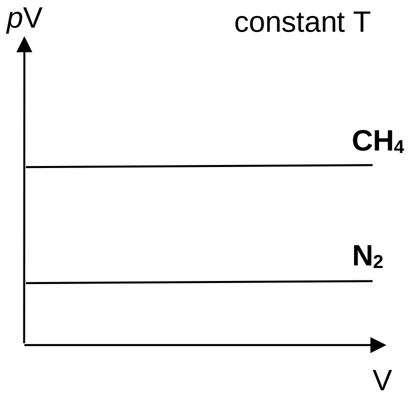
B



C



D



Ans: **D**

$pV = nRT$

$pV = \frac{m}{M}RT$

Gas	N_2	CH_4
Molar mass	28.0	16.0

Option **A**: Shape of graph is wrong. Graph should start from origin.

Option **B**: Shape of graph is correct. $\frac{m}{M}R$ is the gradient. From above, since N_2 has a larger M_r, its gradient should be less steep. Hence graph is wrong.

Option **C**: A graph of pV against V at constant T will give a constant value (i.e. horizontal line). Hence, graph is wrong.

Option **D**: The gas with the smaller molar mass (CH_4) will give the plot with the largest pV value while the gas with the larger molar mass (N_2) will give the smaller pV value. Graph is correct.

7 The properties of the oxides of four Period 3 elements **E, F, G** and **H** are given in the table below.

oxide of element	melting point	electrical conductivity when molten	reaction with H_2O
E	2850 °C	good	very little
F	1720 °C	poor	none
G	1280 °C	good	exothermic
H	580 °C	poor	exothermic

Which of the following is in the correct order of increasing proton number?

A **E**, **F**, **G**, **H**

B **E**, **G**, **F**, **H**

C **G**, **F**, **E**, **H**

D **G**, **E**, **F**, **H**

Ans: **D**

E and **G** forms metal oxides with giant ionic structure since the presence of mobile ions allows these oxides to conduct electricity in the molten state.

Since oxides of **E** has a higher melting point and is only sparingly soluble in H_2O, oxides of **E** should be MgO. Oxides of **G** should be NaO which reacts completely and vigorously with water to form a strongly alkaline solution.

F and **H** forms non-metal oxides with giant covalent structure or simple molecular structure. This results in the absence of mobile ions or delocalised electrons in the molten oxides and makes them poor electrical conductors.

Since oxides of **F** has high melting point and does not dissolve in water, it has a giant covalent structure with strong and extensive covalent bonds between its atoms, which require a large amount of energy to overcome. Oxides of **F** is likely to be SiO_2.

H most likely forms an oxide with simple molecular structure like SO_3 or P_4O_{10}. Small amount of energy is needed to overcome the weak instantaneous dipole-induced dipole of attraction between the molecules, thus accounting for its relatively low melting point. It reacts completely and vigorously in water to form a strongly acidic solution.

In the order of increasing proton number:
Na(**G**), Mg(**E**), Si(**F**), P/S(**H**)

8 Theoretical values have been obtained for the two compounds CuCl(s) and TlCl(s) as shown below.

Compound	CuCl(s)	TlCl(s)
Lattice energy / kJ mol^{-1}	−979	−748
Sum of enthalpies of hydration of separate ions / kJ mol^{-1}	−996	−709

Which statements are correct?

1 Enthalpy change of solution, $\Delta H_{solution}$ of CuCl is more exothermic than that of TlCl.

2 The strength of interaction with water molecules is greater for the ions of CuCl compared to that of TlCl.

3 $\Delta G^{\ominus}_{soln}$ of TlCl is negative at all temperatures.

A 2 and 3 only **B** 1 and 2 only **C** 1 and 3 only **D** 1, 2 and 3

Ans: **B**

$\Delta H^{\ominus}_{soln} = -LE + \Delta H^{\ominus}_{hyd}$

ΔH_{sol} CuCl (s) = −17 kJ mol^{-1}
ΔH_{sol} TlCl. (s) = +39 kJ mol^{-1}

Option 1 is correct.

Option 2 is correct. The more exothermic ΔH_{hyd} suggests a stronger interaction of the ions with water.

Option 3 is incorrect.
- Using $\Delta G^{\ominus}_{soln} = \Delta H_{sol} - T\Delta S^{\ominus}_{sol}$
- If $\Delta S^{\ominus}_{sol} > 0$, $-T\Delta S^{\ominus}_{sol} < 0$. Since $\Delta H_{sol} > 0$, $\Delta G^{\ominus}_{soln} < 0$ when $-T\Delta S^{\ominus}_{sol}$ is more negative than ΔH_{sol} at high temperature.
- If $\Delta S^{\ominus}_{sol} < 0$, $-T\Delta S^{\ominus}_{sol} > 0$. Since $\Delta H_{sol} > 0$, $\Delta G^{\ominus}_{soln}$ will be always positive.

9 Consider the following reactions:

$\mathrm{Zn(s) + 2HC}l\mathrm{(aq)} \longrightarrow \mathrm{ZnC}l_2\mathrm{(aq) + H_2(g)}$ $\Delta H = -80.7\ \mathrm{kJ\ mol^{-1}}$

$\mathrm{ZnO(s) + 2HC}l\mathrm{(aq)} \longrightarrow \mathrm{ZnC}l_2\mathrm{(aq) + H_2O(l)}$ $\Delta H = -168.3\ \mathrm{kJ\ mol^{-1}}$

$\mathrm{H_2(g) + \tfrac{1}{2}O_2(g)} \longrightarrow \mathrm{H_2O(l)}$ $\Delta H = -285.0\ \mathrm{kJ\ mol^{-1}}$

What is the enthalpy change for the following reaction?

$$\mathrm{2Zn(s) + O_2(g)} \longrightarrow \mathrm{2ZnO(s)}$$

A $-109.8\ \mathrm{kJ\ mol^{-1}}$

B $-197.4\ \mathrm{kJ\ mol^{-1}}$

C $-394.8\ \mathrm{kJ\ mol^{-1}}$

D $-1068.0\ \mathrm{kJ\ mol^{-1}}$

Ans: **C**

Method 1

$$\begin{tikzcd}
\mathrm{4HC}l\mathrm{(aq) + 2Zn(s) + O_2(g)} \arrow[r, "\Delta H_r"] \arrow[d, "2 \times -80.7"] & \mathrm{2ZnO(s) + 4HC}l\mathrm{(aq)} \arrow[d, "2 \times -168.3"] \\
\mathrm{2ZnC}l_2\mathrm{(aq) + 2H_2(g) + O_2(g)} \arrow[r, "2 \times -285.0"] & \mathrm{2ZnC}l_2\mathrm{(aq) + 2H_2O(l)}
\end{tikzcd}$$

$\Delta H_r = (2 \times -80.7) + (2 \times -285.0) - (2 \times -168.3)$
$= -394.8\ \mathrm{kJ\ mol^{-1}}$

Method 2
Given

$\mathrm{Zn(s) + 2HC}l\mathrm{(aq)} \longrightarrow \mathrm{ZnC}l_2\mathrm{(aq) + H_2(g)}$ $\Delta H = -80.7\ \mathrm{kJ\ mol^{-1}}$

$\mathrm{ZnO(s) + 2HC}l\mathrm{(aq)} \longrightarrow \mathrm{ZnC}l_2\mathrm{(aq) + H_2O(l)}$ $\Delta H = -168.3\ \mathrm{kJ\ mol^{-1}}$

$\mathrm{H_2(g) + \tfrac{1}{2}O_2(g)} \longrightarrow \mathrm{H_2O(l)}$ $\Delta H = -285.0\ \mathrm{kJ\ mol^{-1}}$

Rearranging the 2nd equation and multiplying with a factor of 2 to all, you will get

$\mathbf{2}\mathrm{Zn(s)} + \mathbf{4}\mathrm{HC}l\mathrm{(aq)} \longrightarrow \mathbf{2}\mathrm{ZnC}l_2\mathrm{(aq)} + \mathbf{2}\mathrm{H_2(g)}$ $\Delta H = \mathbf{2}(-80.7)\ \mathrm{kJ\ mol^{-1}}$

$\mathbf{2}\mathrm{ZnC}l_2\mathrm{(aq)} + \mathbf{2}\mathrm{H_2O(l)} \longrightarrow \mathbf{2}\mathrm{ZnO(s)} + \mathbf{4}\mathrm{HC}l\mathrm{(aq)}$ $\Delta H = \mathbf{2}(\mathbf{+}168.3)\ \mathrm{kJ\ mol^{-1}}$

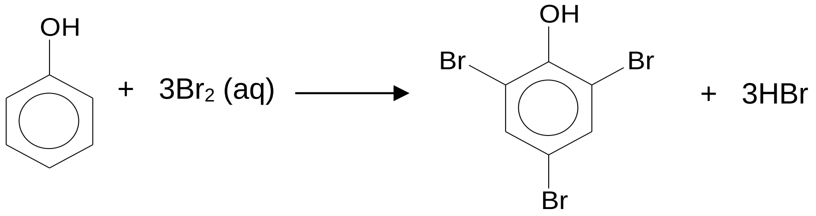
$\mathbf{2}\mathrm{H_2(g) + O_2(g)} \longrightarrow \mathbf{2}\mathrm{H_2O(l)}$ $\Delta H = \mathbf{2}(-285.0)\ \mathrm{kJ\ mol^{-1}}$

Summing up the 3 equations above, you will get
$\mathbf{2Zn(s) + O_2(g) \longrightarrow 2ZnO(s)}$

Hence, $\Delta H_r = 2(-80.7) + 2(+168.3) + 2(-285.0)$
$= -394.8\ \mathrm{kJ\ mol^{-1}}$

10 The initial rate of the reaction between potassium bromate(V) and potassium bromide under acidic conditions can be studied using phenol. The equations for the reactions are as follows.

$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$ reaction 1



reaction 2

A small amount of phenol and three drops of methyl red indicator was added into each experiment mixture to study the progress of reaction. The bromine produced by reaction 1 will immediately react with phenol, until all the phenol is consumed. Any additional bromine that is produced will bleach the indicator completely. The time taken, t, for the complete disappearance of the red colour of the indicator is measured.

Expt no	Volume of $KBrO_3$ / cm^3	Volume of KBr / cm^3	Volume of HC*l* / cm^3	Volume of phenol / cm^3	Volume of water / cm^3	Time, t / s
1	5	25	30	2	40	80
2	5	25	60	2	10	20
3	10	25	60	2	5	10
4	5	50	15	2	30	160
5	10	100	30	4	60	**x**

Which of the following statements is correct?

A The value of **x** is 10.

B The overall order of reaction is 3.

C The units of the rate constant are $mol^{-3}\,dm^9\,s^{-1}$.

D Increasing the concentration of phenol added will result in a smaller value of t.

Ans: **C**

Since the total volume of the reaction mixture for expt 1 to expt 4 is kept constant at 100 cm^3, the initial [reactant] in the reaction mixture is directly proportional to volume of reactant used.

t is the time taken for the complete disappearance of the indicator i.e. the time taken for a fixed and small amount of Br_2 to be formed in reaction 1. Since the reaction proceeded to the same extent for expt 1 to expt 4, initial rate is directly proportional to $\frac{1}{t}$.

Expt no	Volume of $KBrO_3$ / cm^3	Volume of KBr / cm^3	Volume of HC*l* / cm^3	Volume of phenol / cm^3	Volume of water / cm^3	Time, t / s	1/t / s^{-1}
1	5	25	30	2	40	80	0.01250
2	5	25	60	2	10	20	0.05000
3	10	25	60	2	5	10	0.10000
4	5	50	15	2	30	160	0.00625

To determine the order of reaction w.r.t. HC*l*:
Compare Experiment 1 and 2, when [HC*l*] doubles, rate increases by a factor of 4. Since rate is directly proportional to $[HCl]^2$, the reaction is **<u>second order</u>** with respect to H^+.

To determine the order of reaction w.r.t. BrO_3^-:
Compare Experiment 2 and 3, when $[BrO_3^-]$ doubles, rate doubles. Since rate is directly proportional to $[BrO_3^-]$, the reaction is **<u>first order</u>** with respect to BrO_3^-.

Let the order of reaction w.r.t. Br^- be x.
Rate = $k[Br^-]^x[BrO_3^-][HCl]^2$

To determine the order of reaction w.r.t. Br^-,
Compare Experiment 1 and 4,

$$\frac{\text{rate 4}}{\text{rate 1}} = \frac{k(50)^x(5)^1(15)^2}{k(25)^x(5)^1(30)^2}$$

$$\frac{0.00625}{0.01250} = \frac{(2)^x}{(1)^x}\left(\frac{1}{2}\right)^2$$

$$2 = (2)^x$$
$$x = 1$$

The reaction is **<u>first order</u>** with respect to Br^-.

$$\text{rate} = k[Br^-][BrO_3^-][HCl]^2$$

$$\text{units of k} = \frac{\text{units of rate}}{\text{units of }[Br^-][BrO_3^-][H^+]^2}$$

$$= \frac{\text{mol dm}^{-3}\text{ s}^{-1}}{(\text{mol dm}^{-3})^4}$$

units of k = <u>$\text{mol}^{-3}\text{dm}^9\text{s}^{-1}$</u> (Option **C** is correct)

Overall order of reaction = <u>4</u> (Option **B** is incorrect)

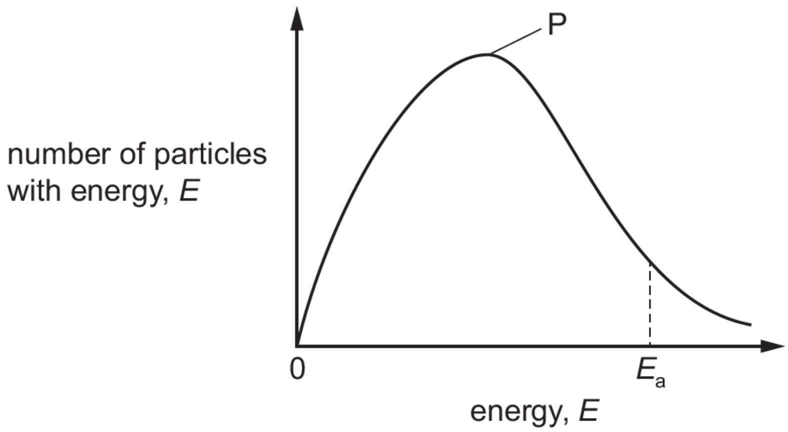
Option **A** is incorrect because value would be 160 s (same as Expt 4). Since total volume in Expt 5 is twice that of Expt 4, the volumes of solutions in Expt 5 are equivalent to,

Expt no	Volume of $KBrO_3$ / cm^3	Volume of KBr / cm^3	Volume of HC*l* / cm^3	Volume of phenol / cm^3	Volume of water / cm^3	Time, t / s
4	5	50	15	2	30	160
5	10	100	30	4	60	**x**
5'	5	50	15	2	30	**x**

The volumes used is similar to expt 4. Hence, the initial concentration for each reactant used in Expt 5 is identical to that in Expt 4. As a result, the rate will be the same and the time taken for the complete disappearance of red colour will be the same as expt 4.

Option **D** is incorrect. Increasing the concentration of phenol added means more moles of phenol is added. This means more Br_2 will need to be produced to react with the increased amount of phenol before the disappearance of the red colour is observed. Hence, t will be larger.

11 The diagram shows the Boltzmann distribution for one mole of a gas. The gas takes part in an uncatalysed reaction with an activation energy, E_a.



The table identifies the changes to the distribution curve and the number of molecules with energy than E_a in response to a change in condition i.e. temperature or catalyst.

Which row is correct?

	Change in condition	Position of Peak P	Position of E_a	Number of molecules with energy greater than E_a
A	Addition of catalyst	no change	shift left	decreases
B	Increasing temperature	shift right	shift left	increases
C	Addition of catalyst	shift right	no change	no change
D	Decreasing temperature	shift left	no change	decreases

Ans: **D**

	Change in condition	Position of Peak P	Position of E_a	No. of molecules with energy greater than E_a
A	Addition of Catalyst	no change	shift left	~~decreases~~ increases
B	Increasing temperature	shift right	~~shift left~~ no change	increases
C	Addition of Catalyst	~~shift right~~ no change	~~no change~~ shift left	~~no change~~ increases

12 The diagram shows a gas syringe with a free-moving piston. The syringe contains a gaseous mixture of carbon disulfide, hydrogen, methane and hydrogen sulfide at equilibrium.

$$CS_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2S(g) \qquad \Delta H > 0$$

The following changes are applied separately to the system at equilibrium.

1 Increasing the temperature.

2 Decreasing the volume by pushing the piston further into the syringe.

3 Increasing the total pressure by adding an inert gas and keeping the volume constant.

Which changes will increase the amount of methane and hydrogen sulfide present at equilibrium?

A 1, 2 and 3 **B** 1 and 2 only **C** 1 and 3 only **D** 2 and 3 only

Ans: **B**

To increase the amount of methane and hydrogen sulfide present equilibrium, the change will need to case position of equilibrium to shift to the right.

Option 1: Increase in temperature will favour the forward endothermic reaction. Position of equilibrium will shift to the right to absorb the extra heat.

Option 2: This will increase the pressure and position of equilibrium will shift to the right to decrease the pressure by producing fewer gaseous molecules.

Option 3: Increase in total pressure by introduction of inert gas at constant volume will not shift the position of equilibrium since partial pressures of all gases remained unchanged.

13 Silver chloride dissolves in $NH_3(aq)$ whereas silver iodide remains insoluble in $NH_3(aq)$.

The following equations represent the equilibria involved.

$$AgCl(s) \rightleftharpoons AgCl(aq) \qquad K_{sp}$$

$$AgCl(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2Cl(aq) \qquad K_{c1}$$

$$AgI(s) \rightleftharpoons AgI(aq) \qquad K_{sp}$$

$$AgI(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2I(aq) \qquad K_{c2}$$

Which of the following statements explains the observation?

A Equilibrium constant, K_{c1} is equal to K_{c2}.

B Equilibrium constant, K_{c1} is numerically smaller than K_{c2}.

C Solubility product of silver iodide is numerically smaller than that of silver chloride.

D Ionic product of silver iodide in the mixture containing silver iodide and ammonia is smaller than the solubility product of silver iodide.

Ans: **C**

Statement **A** and **B** are incorrect.
Since AgC*l* is more soluble than AgI in aq. NH_3, the equilibrium position for the above reaction lies more to the right for AgC*l*. Since $K_c = \frac{[Ag(NH_3)_2X]}{[NH_3]^2[AgX]}$, K_c is numerically greater for $X = Cl$ than for $X = I$.

Statement **D** is incorrect.

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq) \qquad (1)$$

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) \qquad (2)$$

In the presence of dilute $NH_3(aq)$, $[Ag^+]$ decreases as a soluble $[Ag(NH_3)_2]^+$ complex is formed. Even though $[Ag^+]$ is being decreased and ionic product of AgI decreases, ionic product of AgI is still greater than the K_{sp} of AgI. Hence AgI remains insoluble.

Statement **C** is correct.
Since AgC*l* and AgI have the same formulae unit and AgC*l* is more soluble in aq. NH_3 than AgI, it means that the K_{sp} of AgC*l* is larger than that of AgI as the solubility of AgC*l* is higher than AgI.

14 The following equations are some reactions that ammonia is involved.

Which pair of equations does ammonia act as a Lewis base in one and a Brønsted-Lowry acid in the other?

1 $NH_3 + CH_3Br \longrightarrow CH_3NH_2 + HBr$

2 $NH_3 + HNO_2 \longrightarrow N_2 + 2H_2O$

3 $NH_3 + BF_3 \longrightarrow H_3NBF_3$

4 $NH_3 + NaH \longrightarrow NaNH_2 + H_2$

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

Ans: **D**

A Lewis base is defined as an electron pair donor. A Brønsted–Lowry acid is defined as a proton (H^+) donor.

1: NH_3 is a Lewis base as it donates the lone pair of electrons on N to C in CH_3Br to form a dative bond.

2: NH_3 acts as a reducing agent in this redox reaction. The oxidation number of N in NH_3 increases from −3 to 0 in N_2.

3: NH_3 is a Lewis base it donates the lone pair of electrons on N to B in BF_3 to form a dative bond.

4: NH_3 is a Brønsted-Lowry acid where it donates a proton to the H^- ion in NaH to form H_2.

The pairs of equations are

Lewis base	Brønsted-Lowry acid
1	4
3	4

15 The ionic product of water, K_w, at different temperatures is given below.

temperature / °C	K_w / $mol^2\,dm^{-6}$
25	1.00×10^{-14}
50	5.50×10^{-14}

Which statement describes what happens as the temperature of water is increased from 25 °C to 50 °C.

A pH of water increases and $[H^+]$ is less than $[OH^-]$.

B pH of water increases and $[H^+]$ is equal to $[OH^-]$.

C pH of water decreases and $[H^+]$ is more than $[OH^-]$.

D pH of water decreases and $[H^+]$ is equal to $[OH^-]$.

Ans: **D**

$H_2O \rightleftharpoons H^+ + OH^- \quad \Delta H > 0$
$K_w = [H^+][OH^-]$

When temperature of water increases, K_w also increases. This shows that the position of equilibrium has shifted to the right and more H^+ and OH^- ions are produced.

$pH = -\log_{10}[H^+]$
$\therefore$ pH of water decreases

Since the stoichiometric coefficients of H^+ and OH^- ions are equal in the above equation, the number of H^+ and OH^- ions will be the same.
$\therefore [H^+] = [OH^-]$

16 25.0 cm^3 of 0.100 mol dm^{-3} phosphoric acid, H_3PO_4, is titrated against 0.100 mol dm^{-3} NaOH. The following pH values are recorded.

Volume of NaOH added/ cm^3	pH
25.00	4.70
50.00	9.65

The table below shows the pH range for colour change for some acid-base indicators.

indicator	pK_a	range of pH for colour change
bromocresol green	4.7	3.8 – 5.4
phenol red	7.9	6.8 – 8.4
phenolphthalein	9.3	8.3 – 10.0

Which suitable indicators can be used to identify the titration end-points?

A Bromocresol green, phenol red and phenolphthalein

B Bromocresol green and phenol red

C Bromocresol green and phenolphthalein

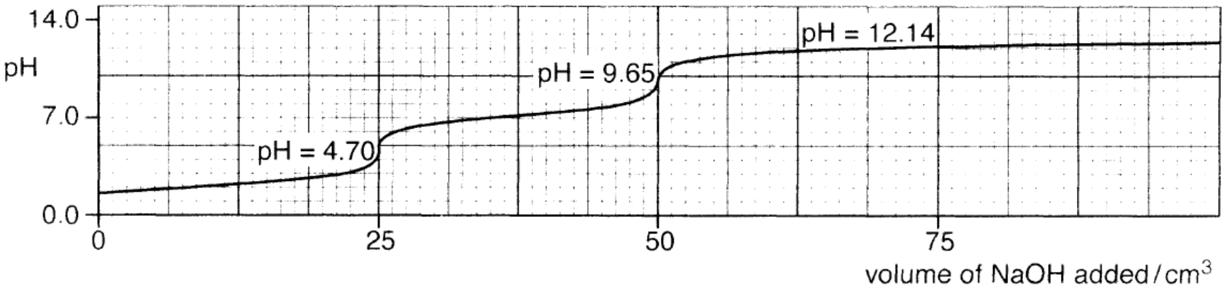
D Phenol red and phenolphthalein

Ans: **C**

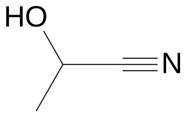
Based on the equivalence point pH values, the suitable indicators are bromocresol green for the first equivalence point and phenolphthalein for the second equivalence point as the pH at equivalence point for the titration occurs within the working pH range of these indicators respectively.

In reality, we have performed this titration before, and the indicators used are screened methyl orange and thymolphthalein. Notice screened methyl orange values below. Why does it still work during our titration? You may see the titration curve below to think of the reason.

indicator	colour in acid	colour in alkali	pK_a	range of pH colour change
screened methyl orange	grey-violet	green	3.5 (estimated)	3.2 – 4.2



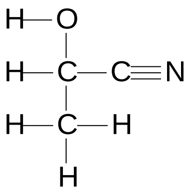
17 How many σ bonds and π electrons are there in a molecule of the following cyanohydrin?



	σ bonds	π electrons
A	4	2
B	7	4
C	8	2
D	9	4

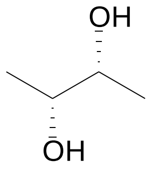
Ans: **D**

Draw out the full displayed formula to count the number of σ bonds and π electrons.

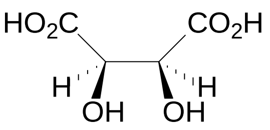


18 Which molecules rotate plane polarised light?

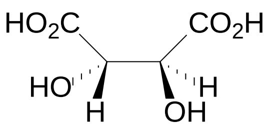
1



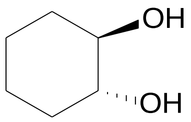
2



3



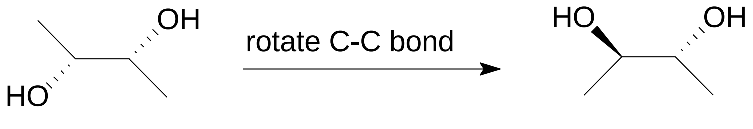
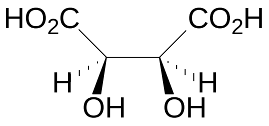
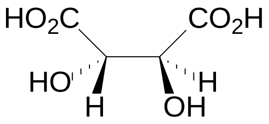
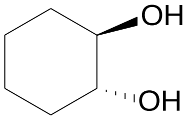
4



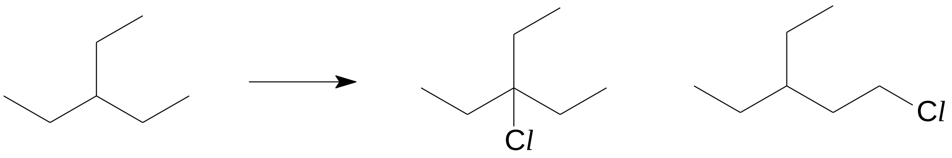
A 1, 3 and 4 **B** 1 and 2 **C** 3 and 4 **D** 2 only

Ans: **A**

For a molecule to rotate the plane of polarised light, it must have at least a chiral carbon and no internal plane of symmetry.

Molecule 1 	There are 2 chiral carbons and no internal plane of symmetry → it can rotate plane polarised light
Molecule 2 	This a meso compound since there are 2 chiral carbon atoms and an internal plane of symmetry. → it cannot rotate plane polarised light
Molecule 3 	There are 2 chiral carbons and no internal plane of symmetry → it can rotate plane polarised light
Molecule 4 	There are 2 chiral carbons and no internal plane of symmetry → it can rotate plane polarised light

19 When 3-ethylpentane is reacted with chlorine, it forms the two monochlorinated products in the following mole ratio.



L **M**

2 : 1

Which statement about 3-ethylpentane helps to explain the mole ratio?

A The C−H bond at the tertiary carbon atom is half as strong as the C−H bond at primary carbon atom.

B The carbocation intermediate that forms product **L** is more stable than the one that forms product **M**.

C There are 2 times as many hydrogen atoms that can be substituted to form product **L** than to form product **M**.

D The hydrogen atom at the tertiary carbon atom is substituted 18 times faster than the hydrogen atom at the primary carbon atom.

Ans: **D**

Option **A**: The bond strength of C-H single bonds on different atoms while not identical, should not differ so much as to explain for the 2:1 ratio of products.

Option **B**: The reaction goes through via free radical substitution mechanism and should not have carbocations.

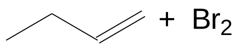
Option **C**: There should be 9 times as many hydrogen atoms that can be substituted to form product **M** than to form product **L**.

Option **D**: Combined with the ratio of H atoms to be substituted as explained for option C, it explains for the eventual 2:1 mole ratio for L : M.

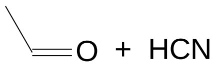
	L	:	**M**
Number of H atoms =	1	:	9
Relative rate of subt =	18	:	1
Overall ratio =	18	:	9
=	2	:	1

20 Which reaction will **not** produce a mixture of two enantiomers?

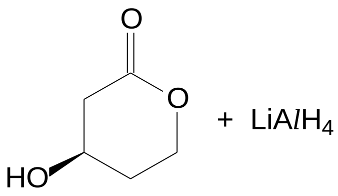
A



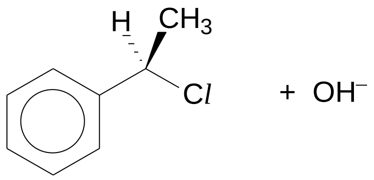
B



C



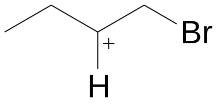
D



Ans: **C**

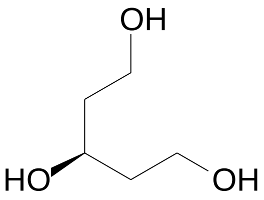
Option **A** Reaction goes through trigonal planar shape carbocation intermediate. Br^- ion can attack from either side of the carbocation intermediate.

Carbocation intermediate:

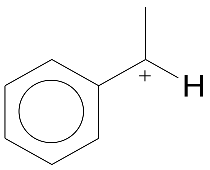


Option **B** Reaction goes through trigonal planar shape carbonyl carbon. CN^- nucleophile attacks from either side with equal probability.

Option **C** Upon reduction, the ester forms 2 –OH groups. There is absence of chiral center.

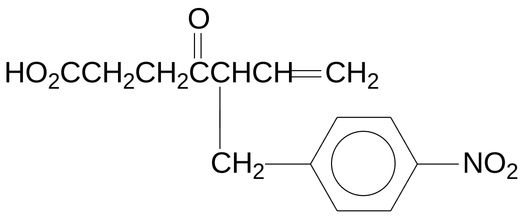


Option **D** Reaction proceeds via S_N1 as the carbocation intermediate is resonance stabilised. OH^- nucleophile attacks from either side with equal probability.



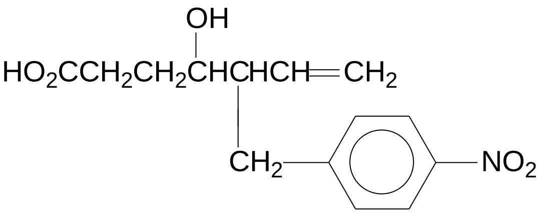
Carbocation intermediate:
See also N2022 P1 Q22.

21 Compound **Y** has the following structure.

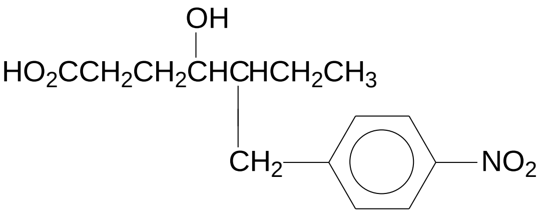


When **Y** is treated with sodium borohydride, what is the final product obtained?

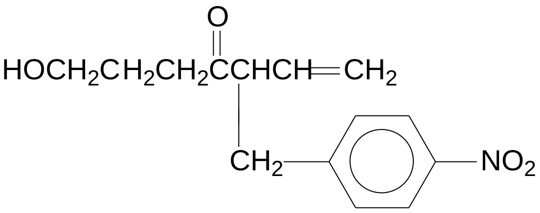
A



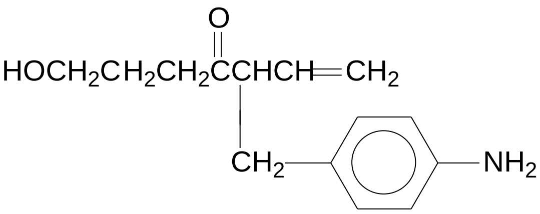
B



C



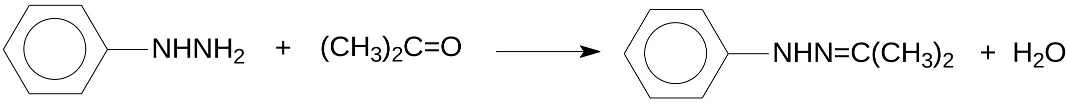
D



Ans: **A**

$NaBH_4$ only reduces carbonyl compounds. The ketone group in **Y** will be reduced to secondary alcohol.

22 Which transformations involve a nucleophile?

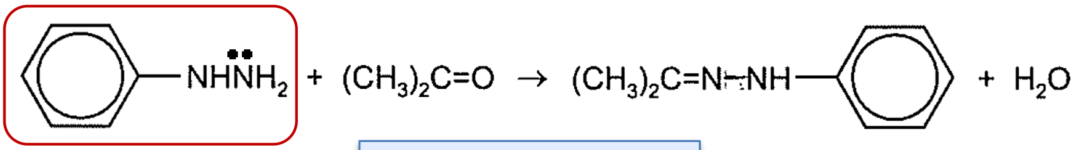
1 

2 $(CH_3)_2C{=}O \;+\; HCN \xrightarrow{NaCN} (CH_3)_2C(OH)CN$

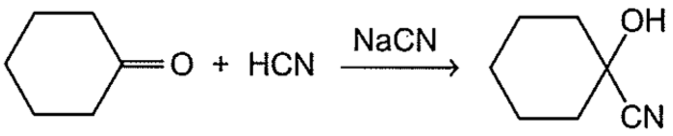
3 $CH_3COCl \;+\; NH_3 \longrightarrow CH_3CONH_2 \;+\; HCl$

A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 3 only

Ans: **A**

1 

nucleophilic addition–elimination

2 

:CN⁻ (nucleophile)

nucleophilic addition of ketone

3 $CH_3CH_2COCl + \boxed{\ddot{N}H_3} \rightarrow CH_3CH_2CONH_2 + HCl$

nucleophilic acyl substitution of acyl chloride

23 Which reaction forms an organic product containing deuterium, D? (D represents deuterium, ^2H)

A $CH_3CH_2COOCH_3 \xrightarrow{\text{NaOD, } D_2O\text{, heat}}$

B $CH_3CH_2CN \xrightarrow{\text{NaOD, } D_2O\text{, heat}}$

C $CH_3CH_2COOH \xrightarrow{D_2\text{, Ni, heat}}$

D $CH_3CH_2COOD \xrightarrow{\text{NaOD}}$

Ans: **A**

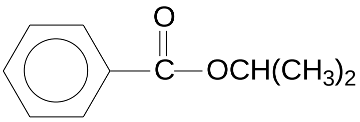
A: $CH_3CH_2COO^-$ and CH_3OD

B: $CH_3CH_2COO^- + ND_4^+$

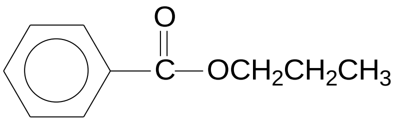
C: No reaction

D: $CH_3CH_2COO^-$ and D_2O

24 Which of the following describes the correct chemical test and observations to differentiate between compounds **X** and **Y**?



X



Y

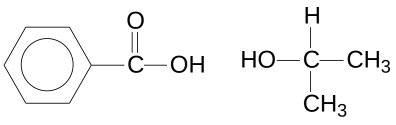
	Test	Observations
A	Tollens', warm	Silver mirror will be observed for **Y**.
B	Fehling's, warm	Red-brown ppt will be observed for **X**.
C	Aqueous alkaline I_2, warm	Yellow ppt will be observed for **X**.
D	Acidified $K_2Cr_2O_7$, warm	Orange solution turns green observed for **X**.

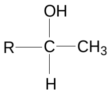
Ans: **C**

A: Both **X** and **Y** will give not silver mirror for Tollen's reagent.

B: Only aliphatic aldehyde reacts with Fehling's, thus **Y** should give a red-brown ppt.

C: Hydrolysis of the esters occurred. **X** will give



Since the alcohol product has the structure  , yellow ppt is observed.

D: Hydrolysis of the esters occurred. A secondary alcohol is obtained from **X** and a primary alcohol is obtained from **Y**. Hence both will turn acidified $K_2Cr_2O_7$ from orange to green.

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 methylamine delocalises over one methyl group, making it the least basic.

B Three electron-donating methyl groups intensifies the negative charge on the nitrogen atom of trimethylamine, making it the most basic.

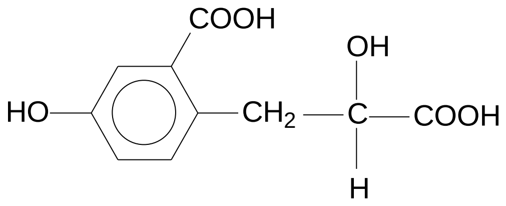
C Methylamine is the least basic because of one electron-withdrawing methyl group that increases the availability of lone pair of electrons on the nitrogen atom to accept a proton.

D Trimethylamine is the most basic because of three electron-donating methyl groups that increases the availability of lone pair of electrons on the nitrogen atom to accept a proton.

Ans: **D**

The extra alkyl groups in secondary and tertiary amine exerts a greater electron donating effect and increase the electron density on N atom. This increases the availability of the lone pair of electrons on N atom to accept a proton.

26 Which reagent reacts in stoichiometric ratio with 1 mol of compound **Z** in a complete reaction?



Compound **Z**

A 2 mol of $SOCl_2$

B 2 mol of aqueous Na_2CO_3

C 3 mol of Na

D 3 mol of aqueous NaOH

Ans: **D**

A is **incorrect**. Alcohol and carboxylic acid functional groups are all able to react with $SOCl_2$ to form RCl and RCOCl respectively. Hence 3 mol of $SOCl_2$ will react with 1 mol of **Z**.

B is **incorrect**. Only the 2 carboxylic acid functional groups are all able to react with Na_2CO_3. As shown in the equation below, 2 mol of RCOOH will react with 1 mol of Na_2CO_3.

$$2RCOOH + CO_3^{2-} \rightarrow CO_2 + 2RCOO^- + H_2O$$

C is **incorrect**. All 4 alcohol, phenol and carboxylic acid functional groups are all able to react with Na. Hence 4 mol of Na will react with 1 mol of **Z**.

D is **correct**. Only carboxylic acid and phenol will react with aqueous NaOH. Hence 3 mol of NaOH will react with 1 mol of **Z**.

27 Montreal Protocol in 1987 banned the use of chlorofluorocarbons, CFCs, for their role in ozone depletion and hydrofluorocarbons, HFCs, were used to replace them.

Which statement explains why HFCs do not release radicals?

A The F• radical is too reactive to survive in the stratosphere.

B C−H and C−F bonds are very strong and not broken by UV light.

C They are lighter than CFCs and do not accumulate in the stratosphere.

D The C−F bonds are highly polarised and undergo heterolytic fission.

Ans: **B**

C−F bonds are stronger than C−C*l* bonds and thus not broken by uv light.

28 When a standard copper electrode is joined to a standard hydrogen electrode, the $E^\ominus_{cell} = +0.34$ V.

Which change to the cell conditions will lead to a higher cell potential?

A increasing the hydrogen ion concentration of the hydrogen electrode

B decreasing the pressure of the hydrogen gas of the hydrogen electrode

C using 1.0 mol dm^{-3} copper(II) nitrate solution instead of copper(II) sulfate solution

D using 1.0 mol dm^{-3} ethanoic acid instead of hydrochloric acid in the hydrogen electrode

Ans: **D**

$Cu^{2+} + 2e \rightleftharpoons Cu$ --- (1) $E^\ominus = +0.34$ V
$2H^+ + 2e \rightleftharpoons H_2$ --- (2) $E^\ominus = +0.00$ V

$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox}$
$= E^\ominus(Cu^{2+}/Cu) - E^\ominus(H^+/H_2)$

Option **A**: Increasing $[H^+]$ will shift POE of (2) to the right, causing $E^\ominus(H^+/H_2)$ to be more positive and $E^\ominus_{cell}$ to be less positive (i.e. lower).

Option **B**: Decreasing pressure of H_2 gas will shift POE of (2) to the right, causing $E^\ominus(H^+/H_2)$ to be more positive and $E^\ominus_{cell}$ to be less positive (i.e. lower cell potential).

Option **C**: There will be no change in concentration of Cu^{2+} ions and hence no effect on POE.

Option **D**: $[H^+]$ is less than 1 mol dm^{-3}, POE will shift to the left to produce more H^+. This will cause $E^\ominus(H^+/H_2)$ to be less positive and $E^\ominus_{cell}$ to be more positive (i.e. higher).

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

Which properties of transition elements are **not** shown by s-block elements such as calcium?

1 They have variable oxidation states.

2 Their ionic radii are smaller than their atomic radii.

3 Their ions can act as oxidising agents in aqueous solution.

A Only 1 is correct.

B Only 1 and 2 are correct.

C Only 1 and 3 are correct.

D 1, 2 and 3 are correct.

Ans: **C**

Statement 1 is correct.

- s–block elements have **fixed oxidation states** (identical to their Group no.)

Statement 2 is incorrect.

- Ions formed from both transition elements and s–block elements have a **smaller ionic radius** than their respective atomic radius.
- Nuclear charge remains the same for both the cation and atom. The cation has one electronic shell less than the atom. The valence electrons in the cation are closer to the nucleus and less shielded. Hence, the stronger electrostatic forces of attraction between the nucleus and the valence electrons in cation resulted in a smaller ionic radius.

Statement 3 is correct.

- s–block elements are good reducing agents as the $E^\ominus$ values tends to be more negative. Hence tendency for the elements to be oxidised to be cations is higher. Therefore, the cations do not undergo reduction easily and hence their cations are poor oxidising agent.
  e.g. $Ca^{2+} + 2e \rightleftharpoons Ca$ $E^\ominus = -2.87$ V

- However, ions of transition element can act as oxidising agent as $E^\ominus$ values tends to be more positive. Therefore, the cations undergo reduction easily.
  e.g. $Fe^{3+} + 2e \rightleftharpoons Fe^{2+}$ $E^\ominus = +0.77$ V
  e.g. $Mn^{3+} + 2e \rightleftharpoons Mn^{2+}$ $E^\ominus = +1.54$ V

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

An acidic solution of $VO_2^+(aq)$ is reacted separately with an excess of zinc metal and with an excess of tin metal. What is the oxidation number of vanadium in each resulting solution after the reaction?

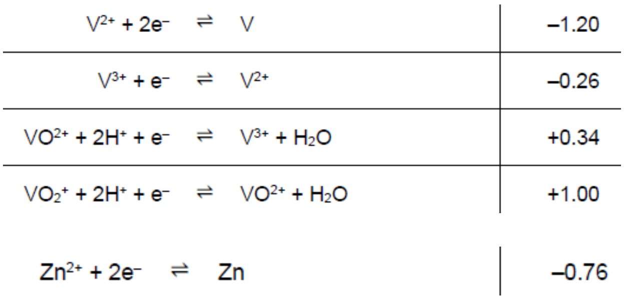
	with zinc metal	with tin metal
A	+4	+2
B	+4	+3
C	+2	+3
D	+2	+4

Ans: **C**

This is a question on the successive reduction of the vanadium species by Zn and Sn into lower oxidation states. We need to compare E^θ values to determine if the redox reactions will be spontaneous.

For excess Zn and VO_2^+

From *Data Booklet:*



$V^{2+} + 2e^- \rightleftharpoons V$	–1.20
$V^{3+} + e^- \rightleftharpoons V^{2+}$	–0.26
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.34
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	+1.00
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	–0.76

Compare $E^\theta(Zn^{2+}/Zn)$ with the E^θ of the vanadium species in order, starting from $E^\theta(VO_2^+/\ VO^{2+})$. Since Zn is to undergo oxidation, the reaction between Zn and the vanadium species will be spontaneous as long as $E^\theta(Zn^{2+}/Zn)$ is less positive/more negative than that of the vanadium species. Notice that $E^\theta(Zn^{2+}/Zn)$ is only less negative than $E^\theta(V^{2+}/V)$, meaning it will be able to reduce $VO_2^+ \rightarrow VO^{2+} \rightarrow V^{3+} \rightarrow V^{2+}$ (but not to V metal).

[You may also see the calculated E_{cell} below for further proof.]

Between Zn and VO_2^+ : $E^\theta_{cell} = E^\theta_{red} - E^\theta_{oxid} = 1.00 - (-\ 0.76) = +\ 1.76$ V (spontaneous)

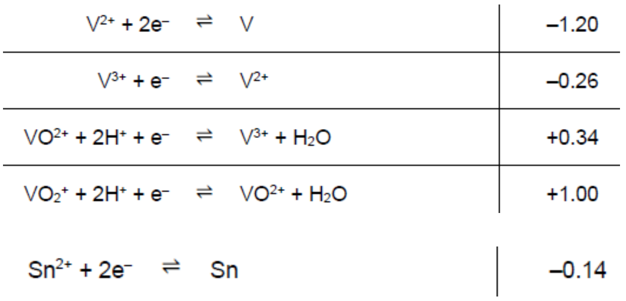
Between Zn and VO^{2+} : $E^\theta_{cell} = E^\theta_{red} - E^\theta_{oxid} = 0.34 - (-\ 0.76) = +\ 1.10$ V (spontaneous)

Between Zn and V^{3+} : $E^\theta_{cell} = E^\theta_{red} - E^\theta_{oxid} = -0.26 - (-\ 0.76) = +\ 0.50$ V (spontaneous)

Between Zn and V^{2+} : $E^\theta_{cell} = E^\theta_{red} - E^\theta_{oxid} = -1.20 - (-\ 0.76) = -0.44$ V (Non-spontaneous)

Hence, VO_2^+ will be reduced to $\mathbf{V^{2+}}$ by Zn.

For excess Sn and VO_2^+
From *Data Booklet:*



$V^{2+} + 2e^- \rightleftharpoons V$	-1.20
$V^{3+} + e^- \rightleftharpoons V^{2+}$	-0.26
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	$+0.34$
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	$+1.00$
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	-0.14

Between Sn and VO_2^+ : $E^\theta_{cell} = E^\theta_{red} - E^\theta_{oxid} = 1.00 - (-0.14) = +1.14$ V (spontaneous)

Between Sn and VO^{2+} : $E^\theta_{cell} = E^\theta_{red} - E^\theta_{oxid} = +0.34 - (-0.14) = +0.48$ V (spontaneous)

Between Sn and V^{3+} : $E^\theta_{cell} = E^\theta_{red} - E^\theta_{oxid} = -0.26 - (-0.14) = -0.12$ V (Not spontaneous)

Hence, VO_2^+ will be reduced to $\mathbf{V^{3+}}$ by Sn.