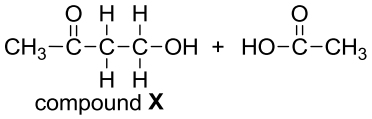
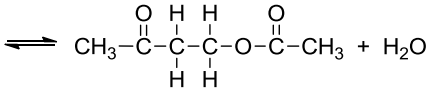
2014 JC2 H2 Chemistry Preliminary Examination
Paper 1 Detailed Answers

1	**D**	**2**	**D**	**3**	**B**	**4**	**C**	**5**	**D**
6	**C**	**7**	**C**	**8**	**B**	**9**	**C**	**10**	**A**
11	**D**	**12**	**C**	**13**	**D**	**14**	**A**	**15**	**D**
16	**C**	**17**	**B**	**18**	**A**	**19**	**D**	**20**	**B**
21	**C**	**22**	**B**	**23**	**A**	**24**	**A**	**25**	**A**
26	**D**	**27**	**D**	**28**	**C**	**29**	**B**	**30**	**C**
31	**B**	**32**	**B**	**33**	**D**	**34**	**A**	**35**	**C**
36	**B**	**37**	**A**	**38**	**B**	**39**	**A**	**40**	**C**

1 D



compound **X**



Molecular formula of compound **X** is $C_4H_8O_2$.

2 D

[O]: $Tl^+(aq) \rightarrow Tl^{3+}(aq) + 2e^-$
[R]: $VO_3^-(aq) + 6H^+(aq) + 3e^- \rightarrow V^{2+}(aq) + 3H_2O(l)$
Redox: $3Tl^+(aq) + 2VO_3^-(aq) + 12H^+(aq)$
$\rightarrow 2V^{2+}(aq) + 3Tl^{3+}(aq) + 6H_2O(l)$

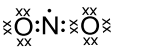
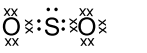
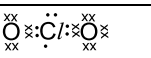
Add 2 mol of VO_3^- to the redox equation will lead to equal number of moles of $VO_3^-(aq)$ and $V^{2+}(aq)$:

$3Tl^+(aq) + \mathbf{4}VO_3^-(aq) + 12H^+(aq)$
$\rightarrow \mathbf{2VO_3^-(aq)} + 2V^{2+}(aq) + 3Tl^{3+}(aq) + 6H_2O(l)$

3 B

Option	Valence shell electronic configuration of ion	No. of unpaired e^-
A	ns^2np^2	2
B	ns^2np^5	1
C	ns^2np^3	3
D	ns^2np^2	2

4 C

Option	Molecule	No. of electrons on central atom
A		7
B		10
C		8
D		11

5 D

For **A**, $SnCl_2$: ~118° (2 bp, 1 lp), OCl_2: 105° (2 bp, 2 lp)

For **B**, both are bent in shape. The electronegativity of O atom is greater than that of S atom. Hence the bond pair of electrons is closer to the nucleus of O atom resulting in stronger bp–bp repulsion in H_2O and a larger bond angle for H_2O.

For **C**, both are linear in shape.

For **D**, both are trigonal pyramidal in shape. The electronegativity of F atom is greater than that of Cl atom. Hence the bond pair of electrons is further away from the N atom resulting in weaker bp–bp repulsion in NF_3 and a smaller bond angle for NF_3.

6 C

Weak dispersion forces between $CH_3CH_2CH_3$ molecules, dipole–dipole attractions between CH_3CHO molecules, hydrogen bonding between CH_3CH_2OH molecules and hydrogen bonding between HCO_2H molecules.
The stronger the attractive forces between the molecules, the greater the deviation from ideal gas behaviour.
HCO_2H is able to form more extensive hydrogen bonding between its molecules. Hence it has a greater deviation from ideal gas as compared to CH_3CH_2OH.

7 C

The same current flows through all the electrodes. Assuming 6 mol of e^- is passed, the reactions at the various electrodes are as shown.

E (oxidation): $2Al \rightarrow 2Al^{3+} + 6e^-$
F (reduction): $6H_2O + 6e^- \rightarrow 3H_2 + 6OH^-$
G (oxidation): $6Ag \rightarrow 6Ag^+ + 6e^-$
H (reduction): $3Cu^{2+} + 6e^- \rightarrow 3Cu$

Electrode **F** has no change in mass of electrode. Comparing the number of moles of electrode involved in the electrolysis, **G** has the greatest change in mass of electrode compared to **E** and **H**.

8 B

Mass of water = 150.00 – 50.00 = 100.00 g
Change in temperature of water = 53 – 20 = 33 °C
Heat gained by water = $mc\Delta T$
= (100)(4.18)(33)
= 13800 J

9 C

For **A** and **B**, forward endothermic reaction is favoured at higher temperature, leading to higher K_c and increase in partial pressure of NO_2.
For **C**, enthalpy change (ΔH) does not change with temperature.
For **D**, activation energy is unchanged unless in the presence of a catalyst.

10 A

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

For **A**, $BaSO_4$ or its ions do not react with $NH_3(aq)$.
For **B**, AgCl reacts with $NH_3(aq)$ to give $[Ag(NH_3)_2]^+Cl^-$. Thus equilibrium is affected.
For **C**, increase in $[OH^-]$ will cause equilibrium position to shift left.
For **D**, decrease in $[Cu(H_2O)_6^{2+}]$ due to $Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s)$ will cause equilibrium position to shift left.

11 D

For **A**, excess sodium hydrogencarbonate with hydrochloric acid will produce the buffer consisting of a mixture of H_2CO_3 and HCO_3^-.

For **B**, $[H^+] = 10^{-pH} = 3.98 \times 10^{-8}$ mol dm^{-3}
$K_a = [H^+][HCO_3^-] / [H_2CO_3]$
$[HCO_3^-] / [H_2CO_3] = (7.90 \times 10^{-7}) \div (3.98 \times 10^{-8})$
≈ 20

For **C**, dilution with water affects the $[HCO_3^-]/[H_2CO_3]$ equally. Hence there is no change in its pH value.

For **D**, pH = pK_a when $[HCO_3^-] = [H_2CO_3]$, i.e. maximum buffer capacity. Since $[HCO_3^-] / [H_2CO_3] \approx 20$, pH ≠ p$K_a$.

12 C

Step 2 is the rate–determining step and rate = $k'[CHCl_3][Cl]$.

Since C*l* is an intermediate, it cannot be in the rate equation and [C*l*] is dependent on [Cl_2] in step 1.

$K_c = \dfrac{[Cl]^2}{[Cl_2]} \Rightarrow [Cl] = (K_c)^{1/2}\,[Cl_2]^{1/2}$

Thus, rate = $k'[CHCl_3]\,(K_c)^{1/2}\,[Cl_2]^{1/2} = k[CHCl_3]\,[Cl_2]^{1/2}$ where $k = k'(K_c)^{1/2}$.

13 D

For **A**, Mg has the highest 1st IE among the three elements but its melting point is not the lowest.

For **B**, A*l* has the lowest 1st IE among the three elements and its melting point is higher than Mg.

For **C**, Si has a lower 1st IE than P and its melting point is the highest.

For **D**, P has the highest 1st IE among the three elements and its melting point is the lowest. Si has the highest melting point due to strong covalent bonds in a giant molecular structure. S_8 has a higher melting point than P_4 as it has a greater number of electrons leading to stronger dispersion forces.

14 A

From *Data Booklet*, ionic radii of Be^{2+} is 0.031 nm, Mg^{2+} is 0.065 nm and Al^{3+} is 0.050 nm. Hence Be^{2+} has the highest charge density and Mg^{2+} has the lowest charge density. The higher the charge density, the greater the distortion of the electron cloud of nitrate ion leading to lower thermal decomposition temperature. Thus, decomposition temperature of $Mg(NO_3)_2 > Al(NO_3)_3 > Be(NO_3)_2$.

15 D

Y_2 can undergo displacement reactions with **X^-** and **Z^-**. **X_2** can undergo displacement reaction with **Z^-** only. Hence on going down Group VII it will be **Y**, **X** and **Z** as oxidising power of halogen decreases down the group.

Ag**Y** is expected to be the most soluble in aqueous ammonia and Ag**Z** the least soluble in aqueous ammonia.

16 C

For **A** (incorrect), addition of acid (such as H_2SO_4(aq)) instead of NaOH(aq) to K_2CrO_4(aq) will produce an orange solution of $K_2Cr_2O_7$.

For **B** (incorrect), the redox reaction between Fe^{3+}(aq) and I^-(aq) is feasible from the *Data Booklet*:
$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

For **C** (correct), $[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons CuCl_4^{2-} + 6H_2O$, yellow solution of $H_2[CuCl_4]$ is produced.

For **D** (incorrect), Na_2CO_3(aq) hydrolyses to form HCO_3^-(aq) and OH^-(aq), and $CrCl_3$(aq) hydrolyses to form $Cr(H_2O)_5(OH)^{2+}$(aq) and H_3O^+(aq). Effervescence of CO_2 and green ppt of $Cr(OH)_3$ instead of $Cr_2(CO_3)_3$ are produced when Na_2CO_3(aq) is added to $CrCl_3$(aq).

17 B

Step 1: redox
$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2 \quad E^\ominus_{cell} = +0.77 - (+0.54) > 0$ V
Step 2: ligand exchange
$Fe(H_2O)_6^{2+} + 6CN^- \rightarrow Fe(CN)_6^{4-} + 6H_2O$
Step 3: redox
$Fe(CN)_6^{4-} + \tfrac{1}{2}Cl_2 \rightarrow Fe(CN)_6^{3-} + Cl^-$
$E^\ominus_{cell} = +1.36 - (+0.36) > 0$ V

For **A**, step 3 is incorrect as SO_2 cannot be reduced by $Fe(CN)_6^{4-}$.
For **C**, step 2 is incorrect as Fe^{2+} is oxidised to Fe^{3+} while I^- cannot be reduced.
For **D**, step 1 is incorrect as reaction is not feasible since $E^\ominus_{cell} = +0.77 - (+0.80) < 0$ V. Step 2 is incorrect as Fe^{2+} is oxidised to Fe^{3+} while I^- cannot be reduced.

18 A

Compound **E** contains nitrile, ketone and carboxylic acid.

For **A**, $NaBH_4$ is a weaker reducing agent than $LiAlH_4$ and will reduce nitrile and ketone to sp^3 hybridised carbon atoms, leaving behind the C=O of the carboxylic acid as the only sp^2 hybridised carbon atom in the product.

For **B**, $LiAlH_4$ will reduce all the functional groups to sp^3 hybridised carbon atoms, leaving no sp^2 hybridised carbon atom in the product.

For **C**, nitrile undergoes hydrolysis in the presence of HC*l*(aq) to give carboxylic acid. There are three sp^2 hybridised carbon atoms in the product.

For **D**, carboxylic acid reacts with $SOCl_2$ to give acid chloride. There are two sp^2 hybridised carbon atoms in the product.

19 D

For **A** (correct), propan–2–ol is a proton acceptor in step 1 and hence it acts as a base.

For **B** (correct), H_2SO_4 is a catalyst as it is regenerated at the end of step 3.

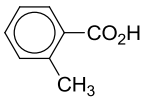
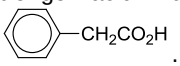
For **C** (correct), the reactants in step 3 can undergo addition reaction to give $CH_3CH(OSO_3H)CH_3$.

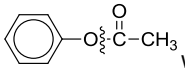
For **D** (incorrect), the formation of carbocation in step 2 is not likely for primary alcohols as compared to tertiary alcohols since primary carbocation is less stable than tertiary carbocation.

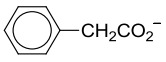
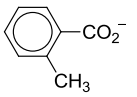
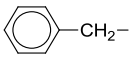
20 B

Option	Products
A	CH_3CO_2H $CH_3COCH_2CH_2COCH_3$ $CH_2(CO_2H)_2$
B	CH_3COCH_3 $CH_3COCH_2CH_2CO_2H$ $CH_2(CO_2H)_2$
C	CH_3COCH_3 $CH_2(CO_2H)CH_2COCO_2H$ $CH_3CH_2CO_2H$
D	CH_3COCH_3 $CH_3COCH_2COCH_3$ $CH_2(CO_2H)_2$

21 C

P is  which is a stronger acid with a smaller pK_a value compared to **Q**,  .

R is  which undergoes base hydrolysis to form $C_6H_5O^-Na^+$ and $CH_3CO_2^-Na^+$.

 is a less stable anion than  as the electron donating inductive effect of  is greater than that of  , intensifying the negative charge on $-CO_2^-$.

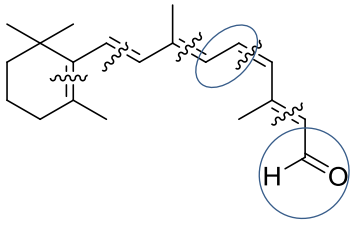
22 B

For **A** (incorrect), five C=C and one RCHO reduced by 6 mol of H_2(g).

For **B** (correct), 1 1–*cis*–retinal and NH_2–opsin undergo condensation reaction to form 1 mol of H_2O.

For **C** (incorrect), C=C is not reduced by Li*A*lH_4. RCHO is reduced to a primary alcohol which does not have a chiral centre.

For **D** (incorrect), only three different organic products are formed. Hot $H^+/KMnO_4$ will cleave the C=C bonds to form five products. However, the 2 mol of ethanedioic acid (see circled) will be further oxidised to CO_2 and H_2O.



23 A

$CH_3CH_2CO_2Na$ exists as ions in solution and form strong ion–dipole interactions with water, making it the most soluble. $CH_3CH_2CH_2NH_2$ molecules form hydrogen bonds with water which are weaker than ion–dipole interactions but stronger than dipole–dipole interactions formed between $CH_3CH_2CH_2C$*l* molecules and water.

24 A

For **A**, the C=C bond is cleaved by hot $H^+/KMnO_4$. However, the strong oxidation will oxidise $(CO_2H)_2$ to CO_2 and H_2O.

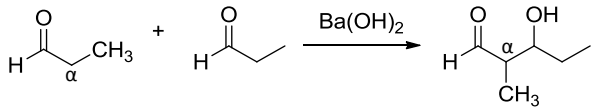
For **B**, compound can be formed by reducing fumaric acid using H_2/Pt catalyst.

For **C**, compound can be formed by oxidising fumaric acid using cold acidified $KMnO_4$.

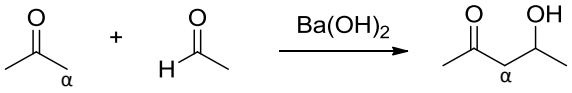
For **D**, compound can be formed by hydrating fumaric acid using cold concentrated H_2SO_4 followed by warming with water, and then oxidising the 2^o alcohol to ketone using hot $H^+/KMnO_4$.

25 A

From given pattern,



Thus,



26 D

Aliphatic alcohols undergo nucleophilic substitution with both SOC*l*$_2$ and HC*l*. Carboxylic acids undergo nucleophilic substitution with only SOC*l*$_2$. Phenol does not undergo nucleophilic substitution with either SOC*l*$_2$ or HC*l*.

27 D

HBr(aq) acts as an acid. It hydrolyses the amide linkage and neutralises the amine groups to form salts.

28 C

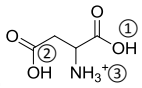
For **A**, phenol with Br_2 in CC*l*$_4$ will result in monosubstitution instead of trisubstitution.

For **B**, ethene is a gas and hence setup is unsuitable.

For **C**, ethanamide is a liquid at rtp and can be placed in the conical flask while lithium aluminium hydride in dry ether (liquid) can be added dropwise from the funnel to the conical flask at cold temperature.

For **D**, formation of ester from alcohol and carboxylic acid in the presence of concentrated sulfuric acid catalyst requires reflux, not cold temperature.

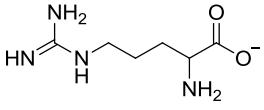
29 B

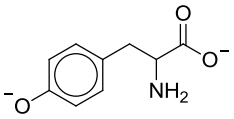
The fully protonated form of aspartic acid,  , is a tribasic acid. Deprotonation occurs when the given pH is above the pK_a value. At pH 7, deprotonation occurs at ① (α–CO_2H) where pK_a = 2.10 and ② (–CO_2H at R group) where pK_a = 3.86. No deprotonation at ③ (α-amino group) where pK_a = 9.82.

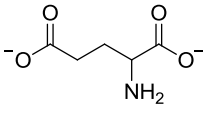
30 C

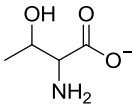
At pH 10, the acidic carboxylic and phenolic groups will be deprotonated. **B** and **C** both have a charge of –2 but **C** will move more readily to the positive anode as the R group has a smaller molecular mass.

At pH 10:

A: 

B: 

C: 

D: 

31 B

Based on the given electronic configurations, **X** is Co and **Y** is Cu.

For **1**, the maximum oxidation state of **X** is +5 (no. of unpaired 3d + 4s electrons) and does not exist as $K_2\mathbf{X}_2O_7$ with an oxidation state of +6.

For **2**, $\mathbf{Y}^{3+}$ lies further down the period compared to $\mathbf{X}^{3+}$ and has a higher effective nuclear charge. Hence $\mathbf{Y}^{3+}$ is less stable than $\mathbf{X}^{3+}$ and has a higher tendency to be reduced compared to $\mathbf{X}^{3+}$. $E^{\ominus}$ value of $\mathbf{Y}^{3+}/\mathbf{Y}^{2+}$ should be more positive.

For **3**, $\mathbf{Y}^{2+}$ in $\mathbf{Y}Cl_2(aq)$ has an incomplete 3d subshell in which d–d transition can occur while $\mathbf{Y}^{+}$ in $[\mathbf{Y}Cl_2]^-(aq)$ has a complete 3d subshell in which d–d transition cannot occur. Hence $[\mathbf{Y}Cl_2]^-(aq)$ is colourless.

32 B

For **1**, both graphs are horizontal lines, i.e. Y = constant.
For **2**, both graphs are straight lines passing through the origin, i.e. $Y = kX$.
For **3**, T against 1/P (at constant V) has the shape of $Y = k/X$ while T against V (at constant P) is a straight line passing through the origin, i.e. $Y = kX$.

33 D

Reaction is first order with respect to **P** and zero order with respect to **Q**.
Hence rate is dependent on temperature (doubles for every 10 ^oC rise) as well as [**P**].

Let the rate of [**P**] = 0.10 mol dm^{-3} at 20 ^oC be **r**.
Condition 1: T increases by 20 ^oC, rate = $(2)^2\mathbf{r} = 4\mathbf{r}$
Condition 2: [**P**] doubles and T increases by 10 ^oC, rate = $(2)^2\mathbf{r} = 4\mathbf{r}$
Condition 3: [**P**] increases by 3 times, rate = $(2)^3\mathbf{r} = 8\mathbf{r}$

34 A

For **1**, at the anode Sn is oxidised to Sn^{2+}, leaving behind the pink copper metal as $E^{\ominus}(Sn^{2+}/Sn)$ is less positive than $E^{\ominus}(Cu^{2+}/Cu)$.

For **2**, at the cathode: $2H^+ + 2e^- \rightarrow H_2$
$Q = I \times t = 2 \times 10 \times 60 = 1200$ C
No. of moles of electrons = $1200 \div 96500 = 0.0124$ mol
Volume of H_2 gas = $0.0124 \div 2 \times 22400 \approx 140$ cm^3

For **3**, since current is steady at 2 A, the mass of anode will decrease at a constant rate.

35 C

Solid **P**: **M**O, solution of **Q**: **M**$(OH)_2$, solid **R**: **M**O
Solution of **W**: **M**$(OH)_2$, solid **X**: **M**O,
solution of **Y**: **M**SO_4

36 B

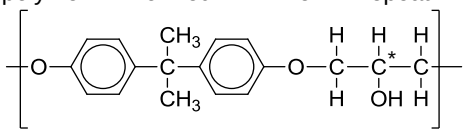
For **1**, H–At has a weaker covalent bond than H–C*l* due to larger atomic size of At. Hence HAt is a stronger acid than HC*l* as it undergoes dissociation more readily to produce a larger $[H^+]$.

For **2**, since I_2 disproportionates in hot dilute sodium hydroxide to yield IO_3^- and I^- as major products, At_2 which is below I_2 in Group VII would also behave likewise.

For **3**, solubility of AgX in dilute aqueous ammonia solution decreases down Group VII. Since AgI is insoluble in dilute aqueous ammonia solution, AgAt would also be insoluble in dilute aqueous ammonia solution.

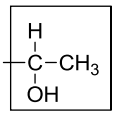
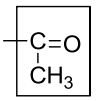
37 A

Condensation reaction takes place between **P** and **Q** to form the polymer and HC*l* molecules. One HC*l* molecule is removed for each repeat unit of the polymer formed. The repeat unit is



and each repeat unit contains one chiral centre.

38 B

To have a positive iodoform test, the molecule must contain either alcohol with  group or carbonyl with  group.

For **3**, the ester is hydrolysed by NaOH(aq) to form CH_3OH and $CHI_2CO_2^-Na^+$. CH_3OH does not undergo positive iodoform test. $CHI_2CO_2^-Na^+$ can undergo nucleophilic substitution with NaOH(aq) to form $CH(OH)_2CO_2^-Na^+$ which then eliminate water to form  .

39 A

For **1**, ester group in **X** undergoes acid hydrolysis to form 3^o alcohol which cannot be oxidised by $K_2Cr_2O_7$. There is no change in the colour of solution. However, the acid hydrolysis of **Y** formed 2^o alcohol which can be oxidised by $K_2Cr_2O_7$. The colour of solution changes from orange to green.

For **2**, both the ester groups in **X** and **Y** undergo base hydrolysis. However, only **Y** shows a positive iodoform test due to presence of $CH_3CH(OH)$– group after hydrolysis.

For **3**, base hydrolysis of R–Br in **X** followed by excess $HNO_3(aq)$ and $AgNO_3(aq)$ results in a cream ppt of AgBr. No cream ppt is observed for **Y** as the Br atom is bonded to C=C bond where the p orbital of Br interacts with the p orbital of C in C=C, resulting in partial double bond character in the C–Br bond.

40 C

Since 2–bromo–2–methylbutane is a tertiary bromoalkane, it undergoes S_N1 mechanism.