2012 DHS Preliminary Examination
H2 Chemistry 9647/01 Answer Key

Question Number	*Key*	*Question Number*	*Key*
1	**B**	21	**C**
2	**D**	22	**D**
3	**D**	23	**B**
4	**C**	24	**A**
5	**D**	25	**A**
6	**C**	26	**C**
7	**C**	27	**B**
8	**A**	28	**C**
9	**B**	29	**D**
10	**A**	30	**A**
11	**A**	31	**A**
12	**C**	32	**D**
13	**D**	33	**A**
14	**D**	34	**B**
15	**B**	35	**B**

2012 DHS Preliminary Examination
H2 Chemistry 9647/01 Solutions

Section A

1 **B**

$Ag^{+}_{unreacted} + SCN^{-} \rightarrow AgSCN$

Moles of $Ag^{+}_{unreacted}$
= No. of moles of SCN^{-}
$= \frac{3.64}{1000} \times 0.054 = 1.9656 \times 10^{-4}$ mol

$3Ag^{+}_{reacted} + AsO_4^{3-} \rightarrow Ag_3AsO_4$

Moles of $Ag^{+}_{reacted}$
$= (1.25 \times 10^{-3}) - 1.9656 \times 10^{-4}$
$= 1.053 \times 10^{-3}$ mol

Moles of As = Moles of AsO_4^{3-}
$= 1/3 \times 1.053 \times 10^{-3}$
Mass of As $= 1/3 \times 1.053 \times 10^{-3} \times 74.9$
= 0.026g

2 **D**

Extent of deflection $\propto \frac{q}{m}$

(charge is denoted by *q*; mass is denoted by *m*)

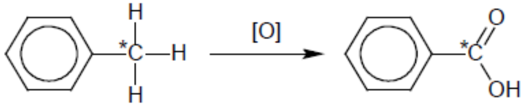
Cations will be deflected towards the negative plate and anions towards the positive plate.

Na^{+}	1/23.0 x (23 x 4.3)	4.3°
Be^{2+}	2/9.0 x (23 x 4.3)	22.0°
Ba^{2+}	2/137 x (23 x 4.3)	1.4°
S^{2-}	2/32.1 x (23 x 4.3)	6.2°
Br^{-}	1/79.9 x (23 x 4.3)	1.2°

3 **D**

Construct a half-equation for the oxidation of methylbenzene:
$C_6H_5CH_3 + 2H_2O \rightarrow C_6H_5COOH + 6H^{+} + 6e^{-}$

Alternatively,



O.S. of *C before oxidation = 4 – 7 = –3
O.S. of *C after oxidation = 4 – 1 = +3
Change in O.S. = +3 – (–3) = +6
∴ 6 electrons are removed during oxidation of methylbenzene to benzoic acid.

4 **C**

For options **A** and **B**,
$pV = nRT$
$pV = (m/M)RT =$ constant
⇒ Graph of P against pV should be a vertical line at a particular value of pV.

For options **C** and **D**,
$pV = nRT = (mR/M)T \Rightarrow pV \propto T$
⇒ Since the M_r of **I** is higher, the gradient of the line is gentler.

5 **D**

Heat absorbed by water
$= \frac{300 \times c \times \Delta T}{1000}$ kJ mol^{-1}

Moles of propan-1-ol burnt $= \frac{m}{60.0}$ mol

Heat released by burning *m* g of propan-1-ol = $\frac{m \times 2021}{60.0}$ kJ mol^{-1}

∴ Efficiency of heating process

$$= \frac{\frac{300 \times c \times \Delta T}{1000}}{\frac{m \times 2021}{60.0}} \times 100$$

$$= \frac{300 \times c \times \Delta T \times 60.0}{m \times 2021 \times 1000} \times 100\%$$

6 **C**

Calcium and chlorine form $CaCl_2$ rather than $CaCl$ because $\Delta H_f(CaCl_2)$ is more exothermic than $\Delta H_f(CaCl)$.

ΔH_f is the sum of enthalpy changes involved in a series of processes leading from the elements to the compounds:

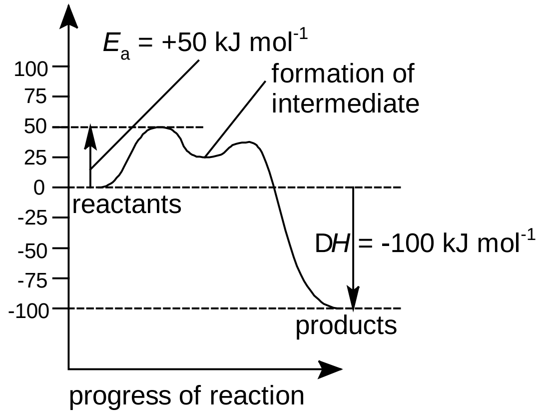
1. Forming separate atoms from elements (ΔH_{at})
2. Forming positive (from the metal atom) or negative (from the non-metal atom) ions. (Sum of I.E. or sum of E.A.)
3. Combining the ions together in an ionic lattice held together by the attraction between oppositely charged ions (LE).

For $CaCl$,

- less energy is required to ionise the Ca atom only once, to Ca^+
- only one Cl atom needs to be formed from Cl_2 and converted into a Cl^- ion
- lattice energy released by forming a 1:1 lattice of singly charged ions is less exothermic than that for $CaCl_2$, which involves Ca^{2+} ions.

Option **C** is the best answer.

7 **C**



8 **A**

In 1.0 mol dm^{-3} sulfuric acid, $[H^+]$ = 2.0 mol dm^{-3}. To make the electrode a standard hydrogen electrode, either change the acid to a 1.0 mol dm^{-3} monoprotic acid (option **A**), or halve the concentration of sulfuric acid used.

9 **B**

Since forward reaction is exothermic, higher temperatures will favour the backward reaction. This increases $[NH_3]$ and $[O_2]$ and decreases $[N_2]$ and $[H_2O]$ at higher temperatures. Thus the two downward–sloping graphs apply to either N_2 or H_2O.

At a higher pressure, backward reaction is favoured, and $[N_2]$ and $[H_2O]$ decreases. Thus, $z > y$.

10 **A**

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$
$K_w = [H^+][OH^-]$
$[H^+] = \sqrt{K_w}$

A	✓	At 25 °C, $[H^+] = 1.0 \times 10^{-7}$ mol dm^{-3} At 10 °C, $[H^+] = 0.5 \times 10^{-7}$ mol dm^{-3} At 0 °C, $[H^+] = 0.3 \times 10^{-7}$ mol dm^{-3}
B	✗	Ionic dissociation of water increases by a factor of 3.3 between 0 °C and 25 °C.
C	✗	Extent of hydrogen bonding cannot be deduced from the given information.
D	✗	$[H^+] = [OH^-]$ at 0 °C, 10 °C and 25 °C. Thus water remains a neutral liquid at these temperatures. However pH of neutral water is no longer 7.0, but increases with decreasing temperature.

11 A

Rate law is determined by slow step in proposed mechanism, i.e. Rate = $k'[O_3][O]$.
This rate law cannot be compared directly with the experimental rate equation because it contains the concentration of an intermediate, O. Thus we need to express rate law in a way that removes the intermediate O.

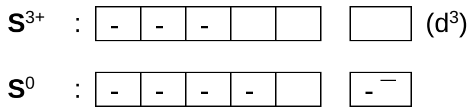
From Step 1, $K = \frac{[O_2][O]}{[O_3]}$ Þ $[O] = \frac{K[O_3]}{[O_2]}$
Assuming that Step 1 equilibrium is established quickly before O is reacted with O_3 in Step 2,

Rate = $k'[O_3][O] = \frac{k'K[O_3]^2}{[O_2]} = \frac{k[O_3]^2}{[O_2]}$
where $k = k'K$

12 C

$[\mathbf{S}(C_2O_4)_2(NH_3)_2]^-$

Let the oxidation number of **S** be x.
x + 2(–2) + 2(0) = –1
Þ x = +3



13 D

A	(Wrong) NH_3 acts as a weak base and a ligand in Reaction I.
B	(Wrong) **G** is $Cu(OH)_2$ and **H** is $[Cu(NH_3)_4]^{2+}$ Oxidation state of Cu remains at +2. \ It is not a redox reaction.
C	(Wrong) **H** is a deep blue solution containing $[Cu(NH_3)_4(H_2O)_2]SO_4$.
D	(Correct) When edta^{4-} binds to the Cu^{2+}during ligand exchange, 4 moles of NH_3 and 2 moles of H_2O is released. \ The entropy of the system increases when reaction III occurs.

14 D

Z has a greater atomic radius than ***W***
Þ ***Z*** is earlier on in the period (***Z*****…..*****W*****…..**)
W has greater electrical conductivity than ***Y*** and ***Y*** has higher boiling point than ***W***
Þ ***Y*** is in Group **IV** and hence ***W*** is a metal (not Si)

15 B

First trace of precipitate appears when ionic product = K_{sp}.

$ZnCO_3(s)$ Ý $Zn^{2+}(aq) + CO_3^{2-}(aq)$
$K_{sp} = [Zn^{2+}][CO_3^{2-}] = 1.4$ ´ 10^{-11}
\ $[CO_3^{2-}]$ at which first trace of $ZnCO_3$ appears = $\frac{1.4´\ 10^{-11}}{0.2}$ = 7 ´ 10^{-11} mol dm^{-3}

$Ag_2CO_3(s)$ Ý $2Ag^2(aq) + CO_3^{2-}(aq)$
$K_{sp} = [Ag^+]^2[CO_3^{2-}] = 8.1$ ´ 10^{-12}
\ $[CO_3^{2-}]$ at which first trace of Ag_2CO_3 appears = $\frac{8.1´\ 10^{-12}}{0.1^2}$ = 8 ´ 10^{-10} mol dm^{-3}

Thus $ZnCO_3$ will precipitate first when $[CO_3^{2-}]$ reaches 7 ´ 10^{-11} mol dm^{-3}. When $[CO_3^{2-}]$ reaches 8 ´ 10^{-10} mol dm^{-3}, Ag_2CO_3 will precipitate next.

16 B

A	(Wrong) Down the group, oxidising power decreases.
B	(Correct) Down the group, K_{sp} value decreases.
C	(Wrong) Down the group, lattice energy of AgX becomes less exothermic due to the increasing anionic radius of halides.
D	(Wrong) Down the group, the hydration energy decreases due to the increasing anionic radius of halides.

17 C

n	formula	distribution of C*l* atoms		no. of chloroethanes
		C1	C2	
1	C_2H_5Cl	1	0	1
2	$C_2H_4Cl_2$	2	0	2
		1	1	
3	$C_2H_3Cl_3$	3	0	2
		2	1	
4	$C_2H_2Cl_4$	3	1	2
		2	2	
5	C_2HCl_5	3	2	1
6	C_2Cl_6	3	3	1

Total no. of different chloroethanes = 9

18 A

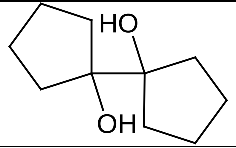
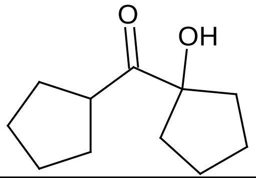
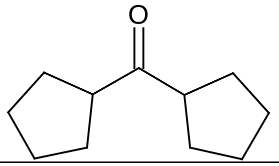
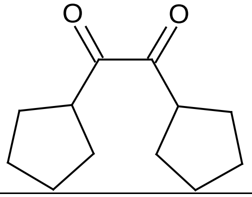
The stronger an acid, the lower the pK_a value. The following lists the four acids used in the options:

- CH_3CO_2H
- CCl_3CO_2H
- C_2H_5OH
- C_6H_5OH

Increasing acid strength:
$C_2H_5OH < C_6H_5OH < CH_3CO_2H < CCl_3CO_2H$

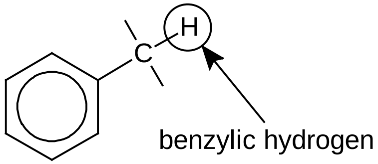
Decreasing pK_a value:
$C_2H_5OH > C_6H_5OH > CH_3CO_2H > CCl_3CO_2H$

19 D

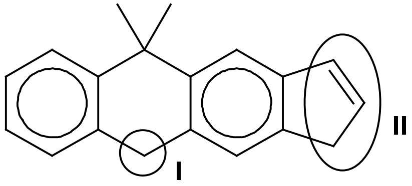
		product(s) of oxidation
A	O	
B	O	
C	O	 + CO_2
D	P	

20 B

Alkyl side-chains on a benzene ring are susceptible to oxidative degradation if they possess at least one benzylic hydrogen atom.



Thus, side-chains on **Z** which can be oxidised are:



I : It is only possible to oxidise the carbon atom in $–CH_2$ to a lower oxidation state of +2 in –C=O, rather than +3 in –COOH. There is only 1 C atom connecting both benzene rings. If **I** is oxidised to –COOH, one of the benzene rings has to be reduced by replacing the oxidised carbon with a hydrogen atom.

II : **II** may be regarded as 2 separate alkyl groups, with each being oxidised to –COOH.

21 C

A	(Account is correct) Electrophilic substitution of phenol by bromine in aqueous medium yields a tri-substituted product, rather than a mono-substituted one.
B	(Account is correct) Ppt is 2,4,6-tribromophenol, which is white.
C	(Account is wrong) Resultant solution contains 2,4,6-tribromophenol, which is acidic.
D	(Account is correct) Resultant solution is yellow, due to the presence of excess dissolved bromine.

22 D

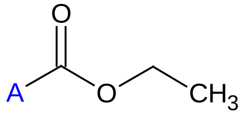
A	O	1 mol –COOH reacts with 1 mol PCl_5, and 1 mol –OH group reacts with 1 mol PCl_5. \ 1 mol citric acid reacts with 4 mol PCl_5.
B	O	3 mol tribasic acid reacts with 1 mol Na_2CO_3. (Alcohols are neutral, and do not react with Na_2CO_3.) \ 1 mol citric acid reacts with $\frac{1}{3}$ mol Na_2CO_3.
C	O	1 mol –COOH reacts with 1 mol NaOH. (Alcohols are neutral, and do not react with NaOH.) \ 1 mol citric reacts with 3 mol NaOH.
D	P	1 mol –COOH reacts with 1 mol Na, and 1 mol –OH group reacts with 1 mol Na. \ 1 mol citric acid reacts with 4 mol Na.

23 B

Nitrile groups on CS are hydrolysed to either salts of carboxylic acids (alkaline hydrolysis) or carboxylic acids (acid hydrolysis).

24 A

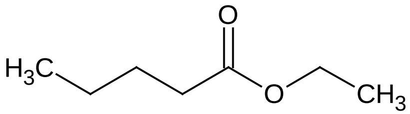
Product of Claisen condensation of ethyl esters must be an ethyl b-keto ester:



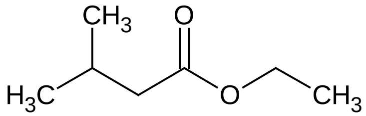
Þ Options **B** and **D** are not possible.

4th member of series has 2 isomers:

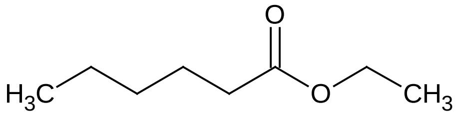
I :



II :

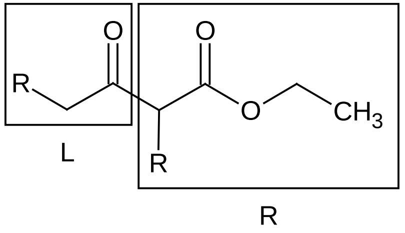


Þ Option **C** is not possible, since it is derived from an isomer of the 5th member:



<u>Explanation for option **A**</u>:

Option **A** is one of four possible products resulting from the condensation of two different esters, i.e. ethyl ethanoate and isomer **II**:



source	
segment L	segment R
ethyl ethanoate	ethyl ethanoate
ethyl ethanoate	**II**
II	**II**
II	ethyl ethanoate

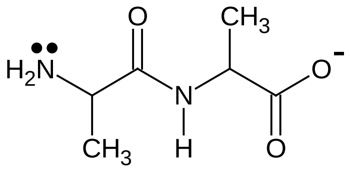
® **A**

25 A

A substituent group (fluorine atom), and not a hydrogen, is substituted without disruption to the aromaticity of the benzene ring. This is therefore not an electrophilic substitution reaction.

F is highly electronegative. The C atom to which F atom is attached is d+, and can attract a nucleophile.

This reaction is therefore a nucleophilic substitution reaction, with



being the nucleophile, and F atom being the leaving group.

26 C

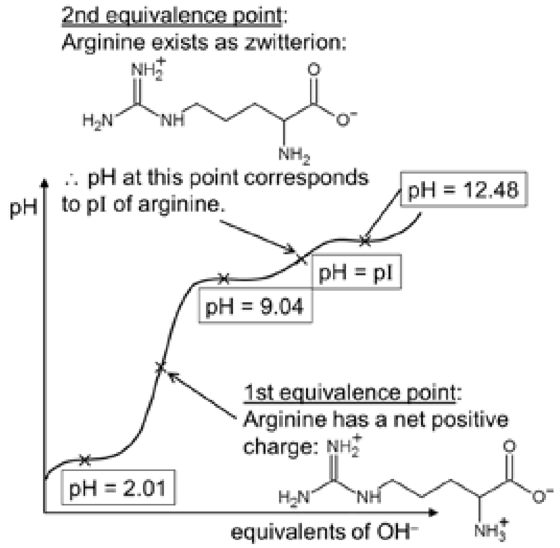
Mechanism **C** involves the electrophilic addition of Br_2 to methylbenzene. This destroys the aromaticity of the benzene ring and is energetically not favourable.

27 B

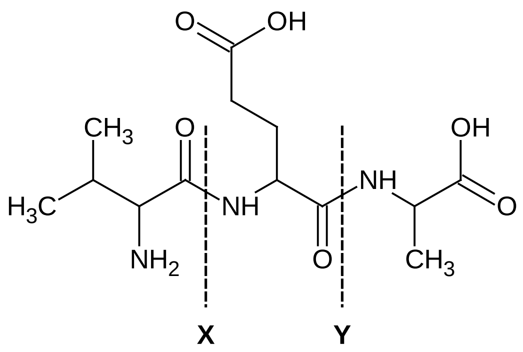
In arginine, pK_a of side-chain $=NH_2^+$ group is higher than pK_a of a–NH_3^+ group. Thus a–NH_3^+ group will be de-protonated first before zwitterion is formed.

28 C

Since an acidic solution of arginine is used, there are three groups, i.e. a-COOH, a-NH_2, and protonated basic side group, to be neutralised.
\ This reaction may be regarded as a triprotic acid whose neutralisation takes place in three stages. This eliminates pH titration graphs for diprotic acids (options **A** and **B**).
a-COOH is neutralised first, followed by a-NH_3^+, and finally the protonated basic side group.
At half-equivalence point for each neutralisation stage, pH = pK_a of each respective acidic group.



29 D



Hydrolysis of this tripeptide will break the amide linkage at **X** and / or **Y**.

30 A

Amino acid residue at N terminus: alanine (Ala)
Amino acid residue at C terminus: valine (Val)
Thus **P** is (N) Ala-Pro-Lys-Leu-Ileu-Val (C).

Section B

31 A

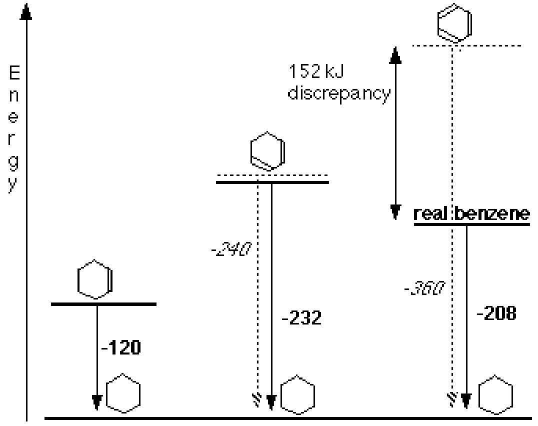
1	P	Over time, the amalgam filling is oxidised by dissolved oxygen in the saliva. $(E^{\ominus})_{cell}$ = $E^{\ominus}$ (O_2/H_2O) – $E^{\ominus}$ (Sn_8Hg/Sn^{2+}) = +1.23 – (–0.13) = +1.36 V > 0 An acidic medium results in $E^{\ominus}$ (O_2/H_2O) and $(E^{\ominus})_{cell}$ becoming more positive. Corrosion becomes thermodynamically more feasible.
2	P	Contact between aluminum foil and amalgam filling short-circuits the cell in Statement **1**. A*l* reduces Sn^{2+} to Sn, and amalgam becomes the cathode.
3	P	$E^{\ominus}$ (Sn_8Hg/Sn^{2+}) is more negative than $E^{\ominus}$ (Au^{3+}/Au). When Au is in contact with the amalgam, a galvanic cell is set up with the amalgam filling as the anode and gold inlay as the cathode. Tin in the amalgam is oxidised to Sn^{2+} and releases electrons to the gold cathode where oxygen is reduced preferentially. [$E^{\ominus}$ (O_2/H_2O) is less positive than $E^{\ominus}$ (Au^{3+}/Au). Thus O_2 is reduced.]

32 D

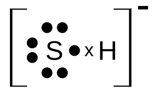
$2N_2(g) + 3H_2(g)$ Ý $2NH_3(g)$ D*H* = –ve

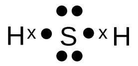
1	P	D*G* = D*H* –TD*S* D*S* < 0 Þ –TD*S* is always positive. D*G* < 0 only if |D*H*| > |TD*S*| At high temperatures, |D*H*| < |TD*S*| and D*G* > 0. \ Reaction becomes less feasible as temperature increases.
2	O	At higher pressures, by LCP, equilibrium position lies more to the right to favour the side of the reaction with fewer gas molecules, i.e. formation of NH_3. \ Yield of NH_3 increases. Higher pressures increase rate of reaction between gaseous reactants.
3	O	Presence of a catalyst does not affect yield. However a catalyst increases both the forward and backward reaction.

33 A

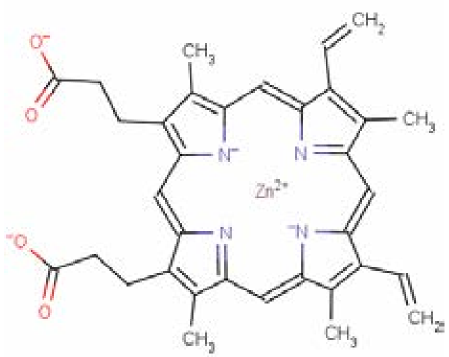


34 B



1	P	No. of lone pairs around S atom = 3
2	P	SH^- accepts an H^+ ion to become its conjugate acid, H_2S.  No. of electrons from S atom = 16 No. of electrons from H atoms = 2 Charge = 0 \ Total no. of electrons on H_2S = 16 + 2 = 18
3	O	O.S. of S = 6 – 8 = –2

35 B

1	P	Protoporphyrin molecule is a chelate. Each N atom / ion shares a lone pair with central Zn^{2+} ion to form a dative bond.
2	P	Each Zn–N bond is a s-bond.
3	O	Structure of ligand before bonding:  Thus Zn has an oxidation state of +2.

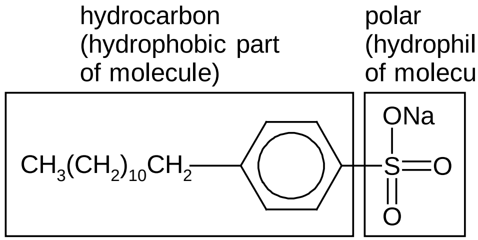
36 C

1	O	Oxidation number of chlorine changes from 0 in Cl_2 to –1 in $Cl^–$ and to +5 in $ClO_3^–$.
2	P	$6OH^–(aq) + 3X_2(aq)$ ® $5\ X^–(aq) + XO_3^–(aq) + 3\ H_2O(l)$ 2**r** mol of KOH was required and $\frac{5}{3}$**r** mol of KC*l* was produced.
3	P	A disproportionation reaction occurred. However, the final products obtained included <u>chloride</u> and potassium chlorate (V).

37 C

1	O	The pH of the solution from the reaction of the metal oxides with water increases down the group.
2	P	The reactivity of the elements with water increases down the group.
3	P	The decomposition temperature of the carbonates increases down the group due to the decrease in the polarising effect on the carbonate ion.

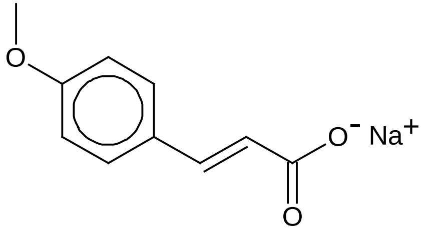
38 A



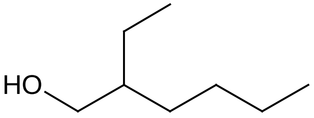
1	P	Ionic portion of SDBS is attracted to polar solvents like water – *hydrophilic*
2	P	Hydrocarbon portion of SDBS is soluble in organic solvents – *hydrophobic*
3	P	There are 4 bond pairs and 0 lone pair around S atom.

39 D

The ester is hydrolysed by NaOH(aq) to form the following products:



and



40 B

1	P	Bromoethane is more volatile than ethanol, and propanal is more volatile than propanol. Thus both products will distil over as they are being produced while the other substances remain in the flask.
2	P	
3	O	Propene is a gas at r.t.p.