2023 Y6 Preliminary Examination
H2 Chemistry 9729 Paper 1
Suggested Solutions

Answer Key

1	2	3	4	5	6	7	8	9	10
C	**A**	**B**	**C**	**D**	**C**	**C**	**D**	**A**	**B**

11	12	13	14	15	16	17	18	19	20
D	**B**	**A**	**C**	**C**	**D**	**D**	**B**	**D**	**A**

21	22	23	24	25	26	27	28	29	30
B	**A**	**D**	**C**	**B**	**A**	**A**	**D**	**B**	**C**

1	**C**
	Since atomic radius of X is larger than that of sulfur, X is the element below sulfur in Group 16, selenium. Since atomic radius of Y is larger than that of X, Y precedes X in the same period and is arsenic. Its proton number is 33.

2	**A**
	Se: $[Ar]3d^{10}4s^24p^4$ Br: $[Ar]3d^{10}4s^24p^5$ Kr: $[Ar]3d^{10}4s^24p^6$ The 7th electron removed from Se is from an inner shell (n = 3) as compared to those removed from Br and Kr (n = 4). The inner shell electron is more strongly attracted to the nucleus and requires more energy for its removal. Kr has one more proton and a higher nuclear charge than Br. Since the additional electron in Kr is added to the same valence shell (n = 4), the valence electrons in Kr experience a shielding effect similar to those in Br. Thus, Kr has a higher effective nuclear charge than Br and more energy is required to remove the 7th electron from Kr.

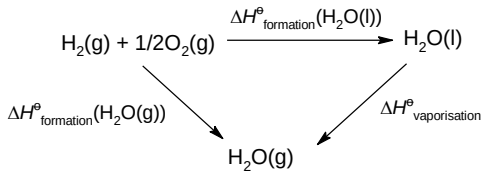
element	Se	Br	Kr
7th IE / kJ mol^{-1}	14990	9940	10710

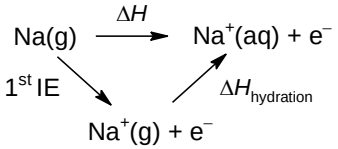
FYI:

3	**B**	
	Hexane molecule is non-polar and has id-id interactions between molecules. Water molecule is polar and has hydrogen bonds between molecules. Hence statement 2 is correct. Hexane and water molecules form weak id-id interactions which do not release sufficient energy to overcome the stronger hydrogen bonds between water molecules. Hence statement 4 is correct. As a result, hexane and water molecules do not mix well and hexane is immiscible with water.	
×	**1**	Hexane has a larger, more polarisable electron cloud than water, leading to stronger id-id interactions between hexane molecules. This statement is true but it does not help to explain the observation.
×	**3**	O–H bond has a larger bond energy than C–H bond so it is a true statement but it does not help to explain the observation as these covalent bonds are not broken or formed when hexane and water are mixed.

4	**C**	
×	**A**	Ice has a simple molecular structure with hydrogen bonds between water molecules. There are covalent bonds between atoms in the water molecules.
×	**B**	Iodine, I_2, has a simple molecular structure and is a non-polar molecule. There exists id-id interactions between molecules and covalent bond between iodine atoms in a molecule.
✓	**C**	Sodium sulfate, Na_2SO_4, has a giant ionic structure with ionic bonds between oppositely charged Na^+ and SO_4^{2-} ions. Within the SO_4^{2-} ion, there are covalent bonds between S and O atoms.
×	**D**	Copper has a giant metallic structure with metallic bonds between the positively charged metal cations and sea of delocalised electrons.

5	**D**
	pV = nRT $\Rightarrow M_r$ = mRT/(pV) $M_r = \frac{1.50\times8.31\times(227+273)}{(1.16\times10^5)\times(250\times10^{-6})} = 214.9$ If there are equal amounts of Al_2Cl_6(g) and $AlCl_3$(g), average $M_r = \frac{133.5+267}{2} = 200.25$ Since average M_r = 214.9 > 200.25, there are more moles of heavier Al_2Cl_6(g) than $AlCl_3$(g). Hence $\frac{\text{amount of } Al_2Cl_6(g)}{\text{amount of } AlCl_3(g)} > 1$

6	**C**	
✓	**1**	$\Delta H^{\ominus}_{formation}$ ($H_2O(l)$) and $\Delta H^{\ominus}_{combustion}$ ($H_2(g)$) are represented by the same equation: $H_2(g) + ½O_2(g) \rightarrow H_2O(l)$
×	**2**	Bond energy values apply to covalent bonds in the **gaseous** molecules. $\Delta H^{\ominus}_{formation}$ ($H_2O(l)$) ≠ [BE(H–H) + $\frac{1}{2}$BE(O=O) − 2BE(O–H)] because the enthalpy change of vaporisation of $H_2O(l)$ has not been taken into account. FYI: $\Delta H^{\ominus}_{formation}$ ($H_2O(g)$) = BE(H–H) + $\frac{1}{2}$BE(O=O) − 2BE(O–H)
×	**3**	 $\Delta H^{\ominus}_{formation}$ ($H_2O(g)$) = $\Delta H^{\ominus}_{formation}$ ($H_2O(l)$) + $\Delta H^{\ominus}_{vaporisation}$ ($H_2O(l)$)

7	**C**
	$\Delta H^{\ominus}_{solution}$ = −LE + $\Delta H^{\ominus}_{hydration}$ ($Na^+(g)$) + $\Delta H^{\ominus}_{hydration}$ ($Cl^-(g)$) 4 = 786 + $\Delta H^{\ominus}_{hydration}$ ($Na^+(g)$) −363 $\Delta H^{\ominus}_{hydration}$ ($Na^+(g)$) = −419 kJ mol^{-1}  ΔH = 494 + −419 = **+75 kJ mol^{-1}**

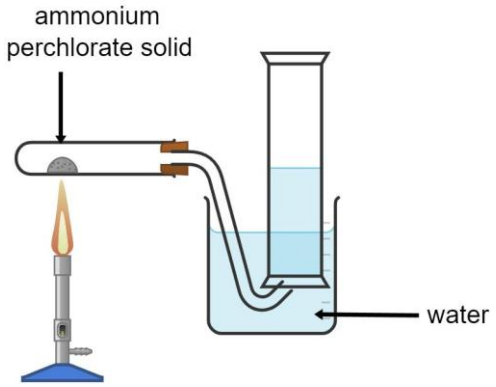
8	**D**	
×	**A**	A*l* is a metal which conducts electricity in both the solid and molten state. P exists as P_4, a simple molecule, which does not conduct electricity in any state.
×	**B**	Al_2O_3 is an ionic compound with partial covalent character due to the high charge density of the Al^{3+} ion. The oxide of P is P_4O_{10} which is a solid at room temperature.
×	**C**	A*l*C*l*$_3$ reacts rapidly (not slowly) with (limited) cold water to produce white fumes of HC*l*(g): A*l*C*l*$_3$(s) + 3H_2O(l) → A*l*(OH)$_3$(s) + 3HC*l*(g) PC*l*$_5$ reacts rapidly with (limited) water to produce white fumes of HC*l*(g): PC*l*$_5$(s) + H_2O(l) → POC*l*$_3$(l) + 2HC*l*(g)
✓	**D**	A*l*C*l*$_3$ reacts rapidly (not slowly) with (limited) cold water to produce white fumes of HC*l*(g): A*l*C*l*$_3$(s) + 3H_2O(l) → A*l*(OH)$_3$(s) + 3HC*l*(g) When PC*l*$_5$ is added to water, a strongly acidic solution is formed: PC*l*$_5$(s) + 4H_2O(l) → H_3PO_4(aq) + 5HC*l*(aq) Both observations are correct.

9	**A**	
✓	**1**	$MCO_3(s) \rightarrow MO(s) + CO_2(g)$ where M = Ca, Ba For the same mass of MCO_3, $CaCO_3$ has a smaller M_r and a larger amount which leads to more moles of CO_2(g) formed.
✓	**2**	$\|LE\| \propto \left\|\frac{q_+ q_-}{r_+ + r_-}\right\|$ q_+, q_- and r_- are constant Since Ca^{2+} has a smaller r_+ than Ba^{2+}, $CaCO_3$ has a larger magnitude of LE than $BaCO_3$.
✓	**3**	Since Ca^{2+} has a smaller r_+ than Ba^{2+}, Ca^{2+} has a higher charge density and polarising power than Ba^{2+}.
×	**4**	Since Ca^{2+} has a higher polarising power than Ba^{2+}, the CO_3^{2-} electron cloud is more polarised and the covalent bonds are weakened to a greater extent in $CaCO_3$. Hence $CaCO_3$ requires less energy and a lower temperature for thermal decomposition.

10	**B**	
×	**A**	No observable change because there is no reaction between NH_3(aq) and the halide ions. No Ag^+ ions was added.
✓	**B**	Brown I_2(aq) is added in excess to colourless solution containing the halide ions. Hence the colourless solution turns brown.
×	**C**	Br_2 is a stronger oxidising agent than I_2. Hence Br_2(aq) is reduced to Br^-(aq) while I^-(aq) is oxidised to brown I_2(aq). Since excess Br_2(aq) is added, the resulting solution is brown, a mixture of orange Br_2(aq) and brown I_2(aq).
×	**D**	White ppt of AgC*l* and yellow ppt of AgI will be formed.

11	**D**	
✓	**1**	No. of mol of N_2 molecules $= 16.3 \div (2 \times 14.0) = 0.582\ mol$ No. of N_2 molecules $= 0.582 \times 6.02 \times 10^{23} = 3.50 \times 10^{23}$
✓	**2**	No. of mol of MgO_2 $= 2.43 \div [24.3 + (2 \times 16.0)]$ $= 0.0431\ mol$ Each mol of MgO_2 contains 1 mol of Mg^{2+} cations and 1 mol of O_2^{2-} anions. No. of moles of ions in 2.43 g of MgO_2 $= 2 \times 0.0431 = 0.0862\ mol$
×	**3**	Sodium carbonate has the formula Na_2CO_3. Hence there are 6 mol of atoms in 1 mol of

		Na_2CO_3.

12	B
	When the hot gaseous product mixture is cooled to room temperature and pressure, water vapour condenses to form liquid water. HCl dissolves readily in water. Only N_2 (g) and O_2 (g) are collected under experimental conditions. M_r of NH_4ClO_4 $= 12.4 + (4 \times 1.0) + 35.3 + (4 \times 16.0) = 117.5$ No. of mol of NH_4ClO_4 used $= 0.235 \div 117.5 = 2.00 \times 10^{-3}\ mol$ No. of mol of gases collected $= \frac{7}{4} \times 2.00 \times 10^{-3} = 3.50 \times 10^{-3}\ mol$ Volume of gases collected $= 3.50 \times 10^{-3} \times 24000 = 84.0\ cm^3$ FYI: the experimental setup is shown in the diagram below 

13	A
	$n(BrO_3^-) = (0.02)(0.02) = 0.0004$ mol $n(NH_2OH) = (0.08)(0.01) = 0.0008$ mol $BrO_3^- \equiv 2NH_2OH \equiv 6e^-$ $\Rightarrow$ Every 1 mol of NH_2OH lose 3 mol of e^- O.N. of N in $NH_2OH = 3(-1) + 2 = -1$ O.N. of N in product $= -1 + 3 = +2$ $\Rightarrow$ Product is NO (O.N. of N = +2)

14	C
	Step 2 is the rate–determining step. Therefore, rate = $k'[CHCl_3][Cl]$. Since Cl is an intermediate, it cannot be present in the rate equation and $[Cl]$ is dependent on $[Cl_2]$ in step 1. $K_c = \frac{[Cl]^2}{[Cl_2]} \Rightarrow [Cl] = (K_c)^{1/2}\,[Cl_2]^{1/2}$ Thus, rate = $k'[CHCl_3]\,(K_c)^{1/2}\,[Cl_2]^{1/2}$

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

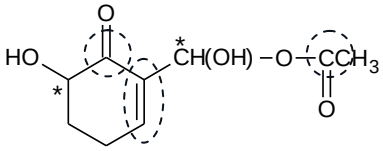
15	C	
✓	1	$X_2 \rightarrow 0.5\ X_2 \rightarrow 0.25\ X_2$ 25 min 25 min 75% of X_2 converted means 25% of X_2 remained. This happens after two half-lives so a total of 25 × 2 = 50 minutes have elapsed.
×	2	<table><tr><td></td><td>$X_2(g) \rightarrow$</td><td>2X(g)</td></tr><tr><td>Initial moles</td><td>1</td><td>0</td></tr><tr><td>Change in moles</td><td>–0.75</td><td>+1.5</td></tr><tr><td>Final moles</td><td>0.25</td><td>1.5</td></tr></table> Total moles in the mixture = 0.25 + 1.5 = 1.75 mol Mole fraction of X = $\frac{1.5}{1.75}$ = 0.857 <u>Note:</u> 1.5 mol of X have been formed but mole fraction of X is 0.857!!
✓	3	At constant temperature and volume (sealed vessel), $p \propto n$. $\frac{p_i}{n_i} = \frac{p_f}{n_f}$ $p_f = \frac{p_i}{n_i} \times n_f = \frac{p}{1} \times (0.25 + 1.5) = \frac{7p}{4}$

16	D
	<u>Thinking process</u>: Based on a quick scan of the given options, there is a need to determine $[H_2O]$ using density (0.997 g cm^{-3}) and M_r (18.0) of water.
	Since density of water = 0.997 g cm^{-3} Mass of water in 1 dm^3 = 0.997 × 1000 = 997 g $[H_2O] = \frac{\text{mass}}{M_r} = \frac{997}{18.0}$ mol dm^{-3} $K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$ $[H_3O^+] = [OH^-]$, $K_c = [H_3O^+]^2 / [H_2O]^2$ $[H_3O^+]^2 = [H_2O]^2\,K_c$ $[H_3O^+] = [H_2O]\sqrt{K_c}$ Moles of H_3O^+ in 1 dm^3 $= [H_3O^+] = [H_2O]\sqrt{K_c}$ Number of H_3O^+ in 1 dm^3 $= [H_2O]\sqrt{K_c} \times L$ $= \frac{997}{18} L\sqrt{K_c}$ where L = Avogadro constant

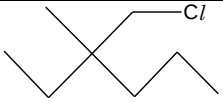
17	D
	As the forward reaction is exothermic, an increase in the temperature at t_1 will favour the endothermic backward reaction to absorb heat hence position of equilibrium shifts to the left. [NO] increases while [NO_2] decreases at new equilibrium. At t_2, there is a sudden increase in both [NO] and [NO_2]. This is due to increase in the pressure of the vessel (by decreasing the volume of the system). Partial pressure of each gas component increases. Position of equilibrium shift the to the right to reduce the number of gaseous molecules. More NO_2 is formed at new equilibrium.

18	B	
✓	1	H_2SO_3 is a dibasic acid. $H_2SO_3 \equiv 2NaOH$ Complete neutralisation to form SO_3^{2-} occurs at the <u>second</u> pH jump i.e. at **50 cm^3** of NaOH. n(NaOH) = 0.1 × (50.0/1000) = 5.0 × 10^{-3} mol n(H_2SO_3) ½ (5.0 × 10^{-3}) = 2.5 × 10^{-3} mol vol of H_2SO_3 = (2.5 × 10^{-3}) ÷ 0.10 mol dm^{-3} = 25.0 cm^3 <u>Note:</u> A faster method is by observation. Since concentrations of both acid and base used in the titration are the same, volume ratio between the acid and base will give the reacting mole ratio. Note that volume of base (NaOH) required is 50 cm^3. Hence, base on mole ratio, volume of H_2SO_3 is 25 cm^3.
×	2	<u>First equivalence point:</u> 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. OR pH transition range of thymol blue (≈ 1.2 to 2.8) does not lie within the rapid pH change (≈ 3 to 5) over the equivalence point. <u>Second equivalence point:</u> The working range of thymol blue does 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. OR pH transition range of thymol blue (≈ 8.0 to 9.6) lies within the rapid pH change (≈ 8 to 9) over the equivalence point.
✓	3	HSO_3^- can act as a Bronsted acid as well as a Bronsted base. The question gave two pK_a values: $H_2SO_3 \rightleftharpoons HSO_3^- + H^+$ pK_a = 1.9 $HSO_3^- \rightleftharpoons SO_3^{2-} + H^+$ pK_a = 7.2 Hence the second pK_a value for H_2SO_3 is the pK_a value of HSO_3^- i.e. 7.2. HSO_3^- is the conjugate base of H_2SO_3, Hence pK_b of HSO_3^- = 14 – (pK_a of H_2SO_3) = 14 – 1.9 = 12.1. [Note: for conjugate acid−base pair at 25 °C, pK_a + pK_b = 14 OR $K_a.K_b = K_w$ $H_2SO_3 \rightleftharpoons HSO_3^- + H^+$ pK_a = 1.9 $HSO_3^- + H_2O \rightleftharpoons H_2SO_3 + OH^-$ pK_b = 14 – 1.9

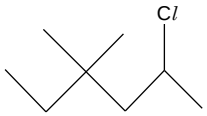
19	D
	A saturated solution formed from ZnF_2(s) is shown below: $ZnF_2(s) \rightleftharpoons Zn^{2+}(aq) + 2F^-(aq)$ s 2s $[Zn^{2+}][F^-]^2 = 4s^3 = 8.7 \times 10^{-2}$ $s = 2.8 \times 10^{-1}$ mol dm^{-3} $\therefore [F^-] = 2s = 5.6 \times 10^{-1}$ mol dm^{-3} $BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-(aq)$ y $2y + 5.6 \times 10^{-1}$ where 5.6×10^{-1} >> 2y since K_{sp} of ZnF_2 >> BaF_2. Hence $[Ba^{2+}][F^-]^2 = y(5.6 \times 10^{-1})^2 = 1.8 \times 10^{-7}$ $y = \frac{1.8 \times 10^{-7}}{(5.6 \times 10^{-1})^2} = 5.7 \times 10^{-7}$ mol dm^{-3}

20	A	
×	1	There is no cis-trans isomer in Compound P. C=C in the ring cannot exhibit cis-trans isomerism as the trans isomer is too strained to be formed.
×	2	 Compound P There are altogether four sp^2 carbon atoms. They are circled above.
✓	3	There are altogether 2 chiral centres in Compound P, as indicated by *.
×	4	A π bond is formed via the side-on overlap of p-orbitals. Hybridised atomic orbitals overlap head-on to form σ bonds.

21 **B**



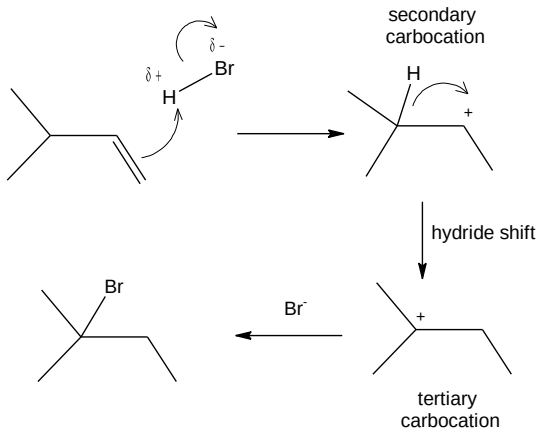
To form , there are a total of 6 equivalent H atoms on primary carbons to substitute from.

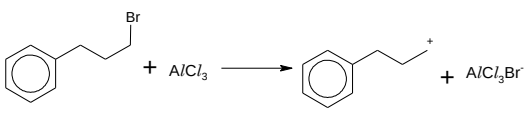


To form , there are a total of 2 equivalent H atoms on a secondary carbon to substitute from.

ratio $= 6 : 2 \times 4.5$
$= 6 : 9 = 2 : 3$

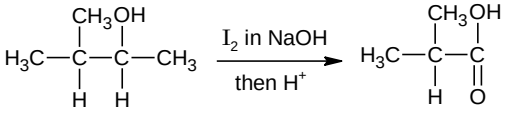
22 **A**

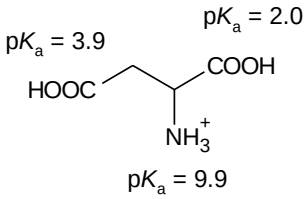
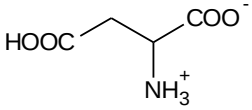


23	**D**	
×	**A**	AlCl_3 will undergo hydrolysis in the presence of water and hence will not be able to act as a Lewis acid catalyst to generate the CH_3^+ electrophile required.
×	**B**	$CH_2CH{=}CH_3$ will undergo strong oxidation when heated with $KMnO_4$ and the diol will not be formed. *Note:* Cold condition is required to form diol from alkene.
×	**C**	Concentrated sulfuric acid is used to convert alcohol to alkene. Ethanolic NaOH is the reagent used to convert halogenoalkane to alkene.
✓	**D**	In the first step, alkyl side chain undergoes free radical substitution with limited Br_2 to form bromoalkane. The bromoalkane reacts with AlCl_3 to generate electrophile and substitutes into the benzene ring. 

24	**C**	
✓	**1**	Electrophilic addition of an alkene fulfills both criteria. A carbocationic intermediate is formed in the slow step. The planar sp^2 carbon can be attacked by a nucleophile from either face with equal probability, leading to the formation of a racemic mixture if a chiral carbon is formed.
×	**2**	Nucleophilic addition of a carbonyl involves an anionic intermediate, not a carbocation.
×	**3**	Bimolecular nucleophilic substitution (S_N2) involves a pentavalent transition state, but no intermediate.
✓	**4**	Unimolecular nucleophilic substitution (S_N1) fulfills both criteria. The nucleophile approaches the trigonal planar carbocation intermediate from either face with equal probability, leading to the formation of a racemic mixture if a chiral carbon reacts.

25	**B**	
		All four structures of S are correct. Due to the overlap of halogen p-orbital and the π system of a benzene ring or C=C bond, aryl and vinyl halides exhibit partial double bond character in the C–X bond. The C–F bond is very strong hence fluoroalkanes are resistant towards hydrolysis. In addition, AgF is soluble in water and no ppt will be observed. As such, these compounds are resistant towards hydrolysis.
×	**A**	Iodoalkanes undergo hydrolysis more readily compared to bromoalkanes as the C–I bond is longer and weaker than the C–Br bond.
✓	**B**	The primary bromoalkane will undergo hydrolysis to form the AgBr ppt that is insoluble in dilute ammonia. This is the only viable answer. *Note:* Since the primary bromoalkane reacts more slowly than the secondary bromoalkane, the reaction occurs by S_N1 mechanism.
×	**C**	Chloroalkanes undergo hydrolysis less readily compared to bromoalkanes as the C–Cl bond is shorter and stronger than the C–Br bond. As such, the AgCl ppt takes a longer time to appear compared to the AgBr ppt. However, AgCl ppt dissolves in dilute ammonia.
×	**D**	Aryl halides are resistant towards hydrolysis.

26	**A**	
✓	**A**	The alcohol undergoes mild oxidation with alkaline aqueous iodine to form CHI_3 and the correct carboxylic acid. 
×	**B**	The amide undergoes a hydrolysis reaction to form the acid.
×	**C**	The secondary alcohol undergoes oxidation to form a ketone, not a carboxylic acid. It also has 1 fewer carbon atom.
×	**D**	The nitrile undergoes a hydrolysis reaction to form the acid.

27	**A**
	The pK_a value of each group is shown below.  Each acidic group is protonated when pH < pK_a, and deprotonated when pH > pK_a. The zwitterionic form of aspartic acid is shown below:  It is the major species when 2.0 < pH < 3.9.

28	**D**	
×	**1**	Temperature should be 298K.
×	**2**	The partial pressure of O_2 should be 1 bar.
×	**3**	A platinum (Pt) electrode should be used instead of a palladium (Pd) electrode.
×	**4**	At pH 1, $[H^+]$ = 0.100 mol dm^{-3}. For $E^{\ominus}$ to be measured, $[H^+]$ should be 1.00 mol dm^{-3}.

29	**B**
	Mg^{2+} and H_2O migrate to the cathode. Since $E^{\ominus}_{H_2O/H_2}$ is less negative than $E^{\ominus}_{Mg^{2+}/Mg}$, water will be preferentially reduced at the cathode to form H_2. NO_3^- and H_2O migrate to the anode. Since nitrogen is at its maximum oxidation state and can no longer be further oxidised, water will be preferentially oxidised at the anode to form O_2. The reactions occurring at each electrode are: (-) cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (+) anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ Since H_2 and O_2 are formed in a 2:1 ratio, Mass ratio $= \frac{2\times2}{32} = \frac{1}{8}$

30	**C**
	The three circled data points correspond to transition elements. They have higher melting points and densities compared to main group metals.