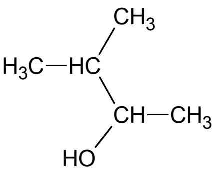
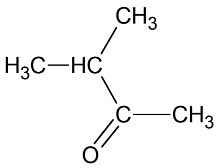
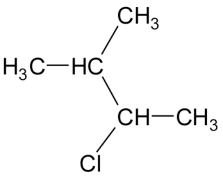
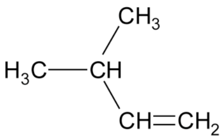
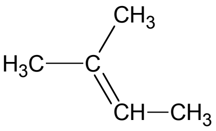
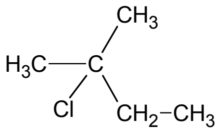
NEW ZEALAND SCHOLARSHIP 2004

ASSESSMENT SCHEDULE FOR CHEMISTRY

Evidence Statement

Question	Evidence	C answer	B answer	A answer
1(a)	 A 3-methyl butan-2-ol  B methyl butan-2-one  C 2-chloro-3-methylbutane  D 3-methylbut-1-ene  E 3-methylbut-2-ene  F	Sequence of functional groups correct but incorrect carbon skeleton	Either 1(a) all correct OR 1(b) all correct	
1(c)	Compounds **1** and **4** have the same forces between molecules (no H-bonds). Higher boiling point in larger molecule due to increased size of e^- cloud, which results in increased instantaneous induced dipoles between molecules. Compounds **2** and **3** same size of e^- cloud as **1**, but higher boiling points than **1** due to added intermolecular force exerted by H-bonds between molecules. **2** and **3** have same number of H-bonds between molecules, but **3** has greater boiling point than **2** due to straight hydrocarbon chain. Branched chains in **2** mean induced dipole forces between chains are reduced, hence lowering boiling point.	Answer shows understanding of effect of size of e^- cloud on intermolecular force between all molecules and also shows understanding of H-bonding between molecules for primary **or** secondary amines	2 out of 3 of: Significance of size of e^- cloud on intermolecular force Effect of H-bonding in 2 **and** 3 Effect of packing	All ideas correct

Q	Evidence	C answer	B answer	A answer
2(a)(i)	$c(HOCH_2CH_2NH_2) = 0.0150$ mol L^{-1} $pK_a = 9.5$ $K_a = 3.16 \times 10^{-10}$ $[H_3O^+]^2 = \frac{K_w \times K_a}{c_{(base)}} = \frac{1\times10^{-14}\times3.16\times10^{-10}}{0.0150}$ $[H_3O^+] = 1.45 \times 10^{-11}$ pH = 10.8	Correct process for both calculations but incorrect values of pK_a and/or $[HOCH_2CH_2NH_3^+]$ determined using data from titration	Both correct	
2(a)(ii)	Equation for titration: $HOCH_2CH_2NH_2 + HCl \rightarrow OCH_2CH_2NH_3^+ + Cl^-$ $[HOCH_2CH_2NH_3^+] = \frac{0.0250\times0.0150}{0.0600} = 6.25 \times 10^{-3}$ From graph: $pK_a = 9.5$ $K_a = 3.16 \times 10^{-10}$ $[H_3O^+]^2 = 3.16 \times 10^{-10} \times 6.25 \times 10^{-3}$ $[H_3O^+] = 1.40 \times 10^{-6}$ pH = 5.85			
2(a)(iii)	**Initial pH 10.8** Ethanolamine is a weak base, so partial dissociation in water $HOCH_2CH_2NH_2 + H_2O \rightleftharpoons HOCH_2CH_2NH_3^+ + OH^-$ **Addition of HCl** $HOCH_2CH_2NH_2$ converted to $HOCH_2CH_2NH_3^+$ While *both acid and conjugate base are present,* a 'buffer' region exists represented by the relatively flat region of the graph. In this region pH only changes by small amount even though acid is being added. **At 35 mL** all the base has been neutralised (equivalence point) to produce $HOCH_2CH_2NH_3^+Cl^-$ solution. This reacts with water to produce H_3O^+ : $HOCH_2CH_2NH_3^+ + H_2O \rightleftharpoons HOCH_2CH_2NH_2 + H_3O^+$ So pH < 7 **Beyond 35 mL** pH is dependent on $[H_3O^+]$ from excess HCl added.	2 regions discussed with reference to relevant species present	3 regions discussed	All correct with comprehensive discussion
2(b)	For the dissolving reaction $Hg(OH)_2 \rightarrow Hg^{2+} + 2OH^-$ If solubility = s $K_s = [Hg^{2+}] \times [OH^-]^2 = 4s^3 = 3.6 \times 10^{-26}$ $s = 2.08 \times 10^{-9}$ mol L^{-1} $[OH^-] = 4.16 \times 10^{-9}$ pH = 5.62 Assumption: $[OH^-]$ from water dissociation is negligible. Since pH is acidic assumption is not valid. ie $[OH^-]$ from the dissolving « $[OH^-]$ from the water $[OH^-] = 4.16 \times 10^{-9} << 10^{-7}$ so pH is neutral as it only depends on H_2O dissociation OR $[OH^-] = 1 \times 10^{-7} + 4.16 \times 10^{-9}$ and pH = 7.02	Calculation of pH =5.62 but failure to recognize importance of dissociation of water and that this calculated pH is impossible for a basic solution.	Calculation of $[OH^-]$ with recognition of contribution of water dissociation	

Q	Evidence	C answer	B answer	A answer
3(a)	• Back titration used because reaction is too slow, end point difficult to determine, mixture of products. • Distillation used to remove red colour which would obscure end point / remove other components of blood which may also be oxidised by $Cr_2O_7^{2-}$. • Mixture heated to ensure all ethanol is oxidised to ethanoic acid by $Cr_2O_7^{2-}$. • Unused $Cr_2O_7^{2-}$ determined by reaction with acidified iodide, which produces iodine which is titrated with thiosulfate. • Starch is added to make a sharper end point. Add near end point, otherwise it binds with I_2.	Discussion shows limited understanding of either process – should include 2 points from 3(a) or 2 points from 3(c)	Discussion shows understanding of process – should include 3 correct points from 3(a) and 3(c)	5 points from 3(a) and (c) discussed including error associated with 1 mL titre
3(c)	• Titre values are too small and will lead to a higher experimental error (% error in each reading higher than for larger titre values). • Titre values can be increased by: - decreasing the concentration of the $S_2O_3^{2-}$ solution - increasing the amount of $Cr_2O_7^{2-}$ initially added (either by increasing its volume or concentration) - decreasing the amount of alcohol added by either decreasing the volume or diluting the sample.			
3(b)	Average value of concordant titres is 17.84 mL $n(S_2O_3^{2-}) = 0.01784 \times 0.105 = 1.873 \times 10^{-3}$ mol $n(\text{dichromate remaining}) = \frac{1}{6} \times n(S_2O_3^{2-})$ $= 3.122 \times 10^{-4}$mol $n(\text{dichromate originally added}) = 0.0492 \times 0.010 = 4.92 \times 10^{-4}$ mol $n(\text{dichromate used up}) = (4.92 - 3.12) \times 10^{-4}$ mol $= 1.80 \times 10^{-4}$ mol $n(\text{alcohol}) = 3/2 \times n(\text{dichromate used up})$ $= 2.70 \times 10^{-4}$ mol present in 10 mL sample n(alcohol) in 100 mL = 2.70×10^{-3} mol *(> 0.0174 mol L^{-1})* m(alcohol) in 100 mL = $2.70 \times 10^{-3} \times 46 = 0.124$ g or 124 mg The amount of alcohol present in the blood sample is over the legal limit.	Calculation shows basic understanding of principles of back titration calculation with minor mathematical errors.	All correct	

Q	Evidence	C answer	B answer	A answer
4(a)	O<S<Mg O and S in the same group so same number of valence e^- but S has extra E level so larger. Mg in same period as S so outer e^- have same shielding but nuclear attraction less in Mg due to fewer protons, so less attraction between outer e^- and nucleus hence larger atom. $Mg^{2+} < Mg$ entire E level of e^- lost when ion is formed $S^{2-} > S$ and $O^{2-} > O$ e^-s are added when ions form and increased repulsion between valence e^- means larger radius. $S^{2-} > O^{2-} > Mg^{2+}$ S^{2-} has one more E level than O^{2-} , O^{2-} and Mg^{2+} have same number of outer shell e^-s but Mg^{2+} has greater nuclear charge, hence e^-s are held more closely.	Answer shows understanding of fact that relative radius of atoms and ions depends on the charge in the nucleus and the energy level in which valence electrons are placed, and links to relevant electrostatic attraction or repulsion	Any two sets correctly discussed	All aspects of comparisons discussed correctly
4(b)	$CH_3CH_3 + 3\frac{1}{2}O_2 \rightarrow 2CO_2 + 3H_2O$ $CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$ $\Delta_c H = \Delta_f H(\text{products}) - \Delta_f H(\text{reactants})$ Since products same for both reactions $\Delta_c H(\text{ethanol}) = X - (-235)$ kJ mol^{-1} $\Delta_c H(\text{ethane}) = X - (-84)$ kJ mol^{-1} Hence $\Delta_c H(\text{ethane}) < \Delta_c H(\text{ethanol})$ and $\Delta_c H(\text{ethane})$ is more negative.	Answer identifies that $\Delta_c H$(ethane) is more negative, with valid reasoning that is not supported by numerical data	Logical reasoning based on data given (reference to bond breaking and making not acceptable)	
4(c)	pH = 6.8 Solution is neutral because $[H_3O^+] = [OH^-]$	Correct pH calculated	Correct pH and reason for neutrality	
4(d)	$C_{12}H_{22}O_{11} + 12O_2 \rightarrow 12CO_2 + 11H_2O(\ell)$ $\Delta H = 12(-393.5) + 11(-285.8) - (-2222.0)$ $= -5643.8$ kJ mol^{-1} $H_2O(\ell) \rightarrow H_2O(g) \quad \Delta H = 44$ kJ mol^{-1} 1L of water is 1000 g i.e. 1000 g /18 g mol^{-1} = 55.6 mol 55.6 mol requires 44 × 55.6 = 2445 kJ mass required = $\frac{2445}{5644} \times 342 = 148.1$ g	Enthalpy change $\Delta H = -5643.8$ kJ mol^{-1} correct OR Calculation of mass sucrose required is calculated correctly using incorrect value of ΔH	Both answers correct	

Q	Evidence	C answer	B answer	A answer
5	SO_3^{2-} turns litmus blue no reaction with I^- OCl^- turns litmus blue reacts with I^- to give dark I_2 precipitate Br^- no change to litmus no reaction with I^- IO_3^- no change to litmus reacts with I^- to give dark I_2 precipitate HBr and HIO_3 are both strong acids. Their conjugates (Br^- and IO_3^-) are weaker bases than water and hence would not turn red litmus blue. HOCl and HSO_3^- are both weak acids. Their conjugate bases (OCl^- and SO_3^{2-}) are therefore more basic than water and react to generate excess OH^- thus turning red litmus blue. I^- is a reductant and reacts with oxidants in couples that have E° higher than $E^\circ(I_2/I^-)$ (0.62 V). Therefore I^- reacts with IO_3^- ($E^\circ(IO_3^-/I_2) = 1.2$ V) and HOCl (arising from OCl^- at low pH) ($E^\circ(HOCl/Cl^-) = 1.51$ V) but does not react with Br^- because it is a reductant only. OR Reaction of I^- with SO_3^{2-} $E^\circ_{cell} = E^\circ(H_2SO_3/S) - E^\circ(I_2/I^-) = 0.45 - 0.62 = 0.17 < 0$ so reaction not spontaneous so no reaction observed. Reaction of OCl^- with I^- $E^\circ_{cell} = E^\circ(HOCl/Cl^-) - E^\circ(I_2/I^-) = 1.51 - 0.62 = 0.89 > 0$ so reaction spontaneous so reaction observed. Reaction of IO_3^{--} with I^- $E^\circ_{cell} = E^\circ(IO_3^-/I_2) - E^\circ(I_2/I^-) = 1.20 - 0.62 = 0.58 > 0$ so reaction spontaneous so reaction observed.	Correct results for all anions with litmus but reasons not clearly linked to pK_a of acid or basicity of anion OR Results for 2 species clearly linked to pK_a of acid or basicity of anion	Correct results for litmus with reasons linked to pK_a	All correct and concisely explained
		Correct results for reaction (or lack of reaction) of 3 anions with iodide but reasons not clearly linked to E° values	Correct results for iodide with reasons linked to E° values	