NEW ZEALAND QUALIFICATIONS AUTHORITY
MANA TOHU MĀTAURANGA O AOTEAROA

Scholarship, 2004

Chemistry (93102)

National Statistics

Assessment Report

Assessment Schedule

Chemistry, Scholarship, 2004

General Comments

Candidates awarded Scholarship had the following skills:
- analytical
- critical thinking
- evaluation
- flair and innovation
- interpretation
- problem-solving skills: flexible thinking in unfamiliar/complex situations
- communication skills: organisation, development and articulation of ideas
- sophistication in approaches, performances or solutions.

Candidates awarded scholarships demonstrated:
- a thorough grounding in the subject
- an outstanding understanding of content knowledge
- an ability to make deductions: apply, integrate and synthesise knowledge
- high subject-specific literacy skills.

National Statistics

Number of	Percentage		
Results	Not Achieved	Scholarship	Outstanding
1,012	90.0%	9.2%	0.8%

Assessment Report

Candidates awarded Scholarship in Chemistry showed a thorough knowledge of Chemistry at this level, the ability to apply this knowledge to a range of different situations, and communicate their ideas in a logical cohesive manner using the correct chemical terms. Key factors in good performances were the careful reading of questions, correct assessment of the amount of information required in an answer, and the evaluation of outcomes in the light of the chemistry involved.

Questions One (a) and (b) required problem-solving skills and a thorough knowledge of aspects of organic chemistry. Candidates who were successful in answering (a), recognised that there was more than one possible isomer for compound A and checked all the criteria listed to choose the correct answer.

Question One (c) required a depth of understanding of intermolecular forces and the ability to explain these using the correct terms and ideas. Some indication of the relationship between the intermolecular forces and the boiling point was also necessary. Hydrogen bonds between molecules of compounds 2 and 3 were correctly described, and the effect of the packing of the branched chain in compound 2 was explained in terms of the temporary induced dipoles between the molecules (other equivalent terms were acceptable). Similarly, the effect of the increased size of the molecules of compound 4 was explained in terms of the size of the electron cloud and the temporary induced dipoles. The term van der Waals force was only accepted if the nature of the attractions were described in more detail.

Question Two (a) required candidates to demonstrate understanding of titration calculations and titration curves. To calculate the two pH values successfully, required the pK_a of the ethanolamine to be determined from the graph and, for part (ii), the dilution factor at equivalence point to be taken into account. To successfully discuss the shape of the curve in relation to the species present, equations

needed to be written to show the species present at significant parts of the curve. These included the ethanolamine solution before any acid was added, the buffer region, the equivalence point and the region after the equivalence point. The initial pH was discussed in terms of the species present in a weak base, the buffer region in terms of the base and increasing amounts of the conjugate acid being formed, the equivalence point in terms of the presence of the conjugate acid of the weak base, and the pH after equivalence point is related to the concentration of HCl present in the titration flask. Successful discussions recognised that the flat part of the curve (between 10 and 30 mL of added acid) is a buffer region because both a base and its conjugate acid are present. The concentrations of these are only equal at the mid point of this region and at this point pH = pK_a. Too often candidates confused the buffer region and the point in the titration when the base and conjugate acid concentrations were equal. It is surprising how few candidates wrote equations or discussed actual species present at different parts of the titration curve.

Question Two (b) appeared to be a straightforward solubility calculation which lead to a pH value of 5.62. However, this answer was unacceptable given the basic nature of the hydroxide; hence the assumptions usually made about the contribution of the water dissociation were not valid, and this had to be taken into account in the final answer.

Scholarship candidates are expected to show knowledge of experimental procedures. In Question Three, the steps in the each procedure used in the alcohol investigation needed to be explained in terms of the chemistry of the compounds used. Candidates were required to discuss reasons for distilling the blood, heating the alcohol and dichromate, using a back titration and adding starch near to the end point. The comparison of the results for the home brew experiment required an understanding of the experimental error introduced when small titres are obtained. Formulating an alternative method to overcome this problem needed an understanding of the whole procedure. This was also demonstrated in the correct calculation being carried out.

Satisfactory answers to Question Four (a) contained a logical systematic discussion of the sizes of the atoms and the ions of the three elements using the correct terminology. Candidates were required to demonstrate their understanding of the structure of atoms and ions by the completeness and accuracy of their answers. Comparisons of the size of the atoms recognised the effect of different numbers of energy levels or the size of the nuclear charge when the number of energy levels was the same. Comparisons of the size of an atom to its ion recognised the effect of the valence electrons being in a lower energy level in the case of a cation, or the repulsive effect of the added electrons when an anion was formed. Comparisons of the sizes of the ions took into account the number of energy levels occupied or the size of the nuclear charge. Explanations that used 'effective nuclear charge' without explaining this term, or used proton:electron ratios to account for differences without any further explanation, were unacceptable.

Question Four (b) required a logical 'proof' to support the answer. It was not intended that the data for Question Four (d) be used. Successful answers began with equations to represent the enthalpy of combustion and used Hess's Law to show the difference in the two values. Discussions involving bond making and breaking were not conclusive without more information about bond strengths.

The calculation for Question Four (c) was straightforward, but the interpretation required an understanding of the term 'neutral' and the temperature dependence of K_w and hence the pH scale.

For Question Four (d) a scholarship answer successfully completed both parts of the calculation. It was intended that this included the recognition of liquid water as the product of the combustion reaction, but answers that used the correct process without taking this into account were accepted.

Question Five required problem solving skills using an understanding of the relationship between pK_a and the relative strength of conjugate bases and electrode potential data. The scheme devised needed to use only litmus paper and an acidified solution of I^-. The scheme was justified correctly in relation to the data given. Answers which met the criteria, linked the colour change of red litmus paper in solutions of the salts to the basic nature of the solution as determined by the pK_a values. The reaction of a solution of the solid with acidified aqueous iodide was discussed in terms of the $E°$ values given. Answers which

included a calculation of the net cell potential for the reaction of the anions with I⁻, usually offered a more comprehensive discussion. Answers which simply stated that 'it is spontaneous because the $E°$ value is greater', were unacceptable unless the oxidant was identified.

Candidates awarded Scholarship with Outstanding Performance consistently performed as described above for Scholarship. In addition, the analysis and discussion of problems from a chemical perspective was coherent and well-reasoned. Explanations given covered all possible aspects using the correct chemical ideas and principles, including an explanation of the chemical terms used. This was particularly apparent in the questions discussing intermolecular forces, titration curves, relative atomic and ionic radii and the justification for the scheme provided to identify the given white solids in Question Five.

Assessment Schedule

Scholarship Chemistry (93102)

Evidence Statement

Question	Evidence	Scholarship	Outstanding
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	Either 1(a) all correct OR 1(b) all correct	

Question	Evidence	Scholarship	Outstanding
1(b)	X = propanoic acid or ethyl methanoate or methyl ethanoate or 2,3,dihydroxypropene (propen-2,3-diol) or hydroxypropanone or 1,1, dihydroxypropene (propen-1,1-diol) or 3-hydroxypropanal, Y = propen-1,2 diol or cyclopropandiol or propen-1,3,diol Z = 2-hydroxypropanal		
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.	2 out of 3 of: Significance of size on intermolecular force Effect of H-bonding in 2 and 3 Effect of packing	All ideas correct

Question	Evidence	Scholarship	Outstanding
2(a)(i)	$c(HOCH_2CH_2NH_2) = 0.0150$ mol L^{-1} $\qquad$ $pK_a = 9.5$ $K_a = 3.16 \times 10^{-10}$ $\left[H_3O^+\right]^2 = \dfrac{K_w \times K_a}{c_{(base)}} = \dfrac{1 \times 10^{-14} \times 3.16 \times 10^{-10}}{0.0150}$ $[H_3O^+] = 1.45 \times 10^{-11}$ pH = 10.8	Both correct	
2(a)(ii)	Equation for titration: $HOCH_2CH_2NH_2 + HCl \quad OCH_2CH_2NH_3^+ + Cl^-$ $[HOCH_2CH_2NH_3^+] = \dfrac{0.0250 \times 0.0150}{0.0600} = 6.25 \times 10^{-3}$ From graph: $pK_a = 9.5 \quad K_a = 3.16 \times 10^{-10}$ $[H_3O^+]^2 = 3.16 \times 10^{-10} \times 6.25 \times 10^{-3}$ $[H_3O^+] = 1.40 \times 10^{-6}$ pH = 5.85		
2(a)(iii)	**Initial pH 10.8** Ethanolamine is a weak base, so partial dissociation in water $HOCH_2CH_2NH_2 + H_2O \quad HOCH_2CH_2NH_3^+ + OH^-$ **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^+ : $HOCH_2CH_2NH_3^+ + H_2O \quad HOCH_2CH_2NH_2 + H_3O^+$ So pH < 7 **Beyond 35 mL** pH is dependent on $[H_3O^+]$ from excess HCl added.	3 regions discussed	All correct with comprehensive discussion
2(b)	For the dissolving reaction $\qquad Hg(OH)_2 \rightarrow Hg^{2+} + 2OH^-$ $\qquad$ If solubility = s $\qquad K_s = [Hg^{2+}] \times [OH^-]^2 = 4s^3 = 3.6 \times 10^{-26}$ $\qquad s = 2.08 \times 10^{-9}$ mol L^{-1} $\qquad [OH^-] = 4.16 \times 10^{-9} \qquad$ pH = 5.62 Assumption: $[OH^-]$ from water dissociation is negligible. Since pH is acidic assumption is not valid. ie $[OH^-]$ from the dissolving $\ll [OH^-]$ from the water $\qquad [OH^-] = 4.16 \times 10^{-9} \ll 10^{-7}$ 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 $[OH^-]$ with recognition of contribution of water dissociation	

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 iodine, 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 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(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 $n(\text{dichromate remaining}) = \dfrac{1}{6} \times n(S_2O_3^{2-}) = 3.122 \times 10^{-4}$ 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 $n(\text{alcohol})$ in 100 mL $= 2.70 \times 10^{-3}$ mol *(> 0.0174 mol L^{-1})* $m(\text{alcohol})$ 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.	All correct	

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.
		Discussion shows understanding of process – should include 3 correct points from 3(a) and 3(c)	

Question	Evidence		Scholarship	Outstanding
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.	Any two sets correctly discussed	All aspects of comparisons discussed correctly
	$Mg^{2+}<Mg$ $S^{2-}>S$ and $O^{2-}>O$	entire E level of e^- lost when ion is formed 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.		
4(b)	$CH_3CH_3 + 3\frac{1}{2}O_2 \rightarrow 2CO_2 + 3H_2O$ $CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$ $\Delta_cH = \Delta_fH(\text{products}) - \Delta_fH(\text{reactants})$ Since products same for both reactions $\Delta_cH(\text{ethanol}) = X - (-235)\ kJ\ mol^{-1}$ $\Delta_cH(\text{ethane}) = X - (-84)\ kJ\ mol^{-1}$ Hence $\Delta_cH(\text{ethane}) < \Delta_cH(\text{ethanol})$ and $\Delta_cH(\text{ethane})$ is more negative.		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 and reason for neutrality	
4(d)	$C_{12}H_{22}O_{11} + 12O_2 \rightarrow 12CO_2 + 11H_2O(\ell)$ $\Delta H = 12(-393.5) + 11(-285.8) - (-2222.0)$ $\quad = -5643.8\ kJ\ mol^{-1}$ $H_2O(\ell) \rightarrow H_2O(g) \quad \Delta H = 44\ kJ\ mol^{-1}$ 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 = $\dfrac{2445}{5644} \times 342 = 148.1$ g			

Question	Evidence	Scholarship	Outstanding
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 $E°(I_2/I^-)$ (0.62 V). Therefore I^- reacts with IO_3^- ($E°(IO_3^-/I_2)$ = 1.2 V) and HOCl (arising from OCl^- at low pH) ($E°(HOCl/Cl^-)$ = 1.51 V) but does not react with Br^- because it is a reductant only. OR Reaction of I^- with SO_3^{2-} $E°_{cell} = E°(H_2SO_3/S) - E°(I_2/I^-) = 0.45 - 0.62 = 0.17 < 0$ so reaction not spontaneous so no reaction observed. Reaction of OCl^- with I^- $E°_{cell} = E°(HOCl/Cl^-) - E°(I_2/I^-) = 1.51 - 0.62 = 0.89 > 0$ so reaction spontaneous so reaction observed. Reaction of IO_3^- with I^- $E°_{cell} = E°(IO_3^-/I_2) - E°(I_2/I^-) = 1.20 - 0.62 = 0.58 > 0$ so reaction spontaneous so reaction observed.	Correct results for litmus with reasons linked to pK_a Correct results for iodide with reasons linked to $E°$ values	All correct and concisely explained

Judgement Statement:

Scholarship: 8 out of 13 Scholarship criteria

8 × S

Outstanding: 2 of Outstanding criteria and at least 10 Scholarship criteria

2 × O + 10 × S