AUSTRALIAN SCIENCE OLYMPIADS

2005 National Qualifying Exam – Chemistry

Solutions

1. E
2. D
3. D
4. C
5. B
6. E
7. B
8. D
9. A
10. B
11. C
12. D
13. D
14. D
15. B

Question 16

(a) [2 marks each]

(i) $Zn \rightarrow Zn^{2+} + 2e^-$ oxidation
(ii) $Fe^{2+} \rightarrow Fe^{3+} + e^-$ oxidation
(iii) $U^{4+} + 2H_2O \rightarrow UO_2^{2+} + 4H^+ + 2e^-$ oxidation

(b) [2 marks each]

(i) $2\ H_2O + U + 2\ \underline{H^+} \rightarrow UO_2^{2+} + 3\ H_2$
(ii) $4\ H^+ + \underline{UO_2^{2+}} + Zn \rightarrow Zn^{2+} + U^{4+} + 2\ H_2O$
(iii) $2\ H_2O + U^{4+} + 2\ \underline{Fe^{3+}} \rightarrow 2\ Fe^{2+} + UO_2^{2+} + 4\ H^+$
(iv) $Fe^{2+} + \underline{Ce^{4+}} \rightarrow Ce^{3+} + Fe^{3+}$

(c)

$n(Ce^{4+}) = c(Ce^{4+}) \times v(Ce^{4+})$
$= 0.375 \times .02069$
$= 0.007759$ moles [1 mark]
$n(Fe^{2+}) = n(Ce^{4+}) = 0.007759$ moles [1 mark]
$n_1(U) = ½ \times n(Fe^{2+}) = ½ \times 0.007759 = 0.003879$ moles [1 mark]
$m_1(U) = n(U) \times M_r(U) = 0.003879 \times 238 = 0.92329$ g [1 mark]

% (U) = 92.3 % (92.1 – 92.5 acceptable) [1 mark]

(d) Higher [1 mark]

(e)

$n(Ce^{4+}) = c(Ce^{4+}) \times v(Ce^{4+})$ [1 mark]

$= 0.375 \times 0.01862$

$= 0.0069825$ moles

$n(Fe^{2+}) = n(Ce^{4+}) = 0.0069825$ moles [1 mark]

$n_2(U) = ½ \times n(Fe^{2+}) = ½ \times .0069825 = 0.0034913$ moles [1 mark]

$m_2(U) = n(U) \times M_r(U) = 0.0034913 \times 238 = 0.83092$ g [1 mark]

% (U) = 83.1 % (82.9 – 83.3 acceptable) [1 mark]

(f)

$m(U)$ extra = $m_1(U) – m_2(U) = 0.92329 – 0.83092 = 0.09237$ g [1 mark]

$n(U)$ extra = $m(U)$ extra / $M_r(U)$ = 0.9237 / 238 = 3.8811E-4 moles [1 mark]

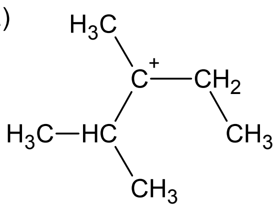
$n(Nb) = n(U)$ extra = 3.8811E-4 moles [1 mark]

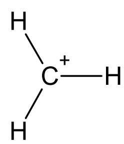
$m(Nb) = n(Nb) \times M_r(Nb)$ = 3.8811E-4 x 92.9 = 0.036055 g [1 mark]

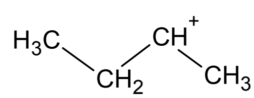
% (Nb) = 3.61 % (3.59 – 3.63 acceptable) [1 mark]

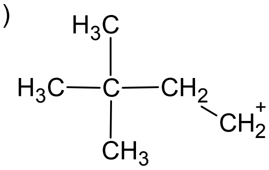
Question 17

(a)

(a)


(b)


(c)


(d)


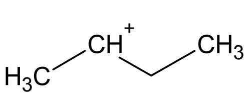
tertiary, 3°	methyl	secondary, 2°	primary, 1°
most stable	least stable	2nd most stable	3rd most stable

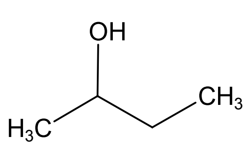
(order of stability: a>c>d>b)

Total = 6: 1 mark for each correct designation of methyl, 1° etc
2 for correct order of stability, 1 for reverse order

(b)

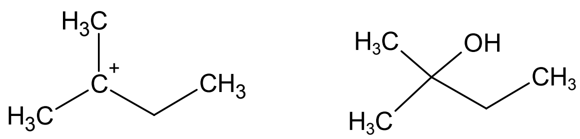
(i)





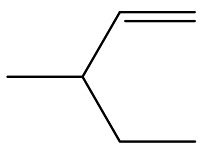
Total = 2: 1 mark for each correct structure

(ii)



Total = 2: 1 for each correct structure

(c)



3-methylpent-1-ene

Total = 2

(d)

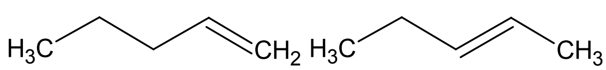
The H^+ adds to the carbon containing more hydrogens already (the less substituted carbon)

The OH^- adds to the carbon containing fewer hydrogens (the more substituted carbon)

Total = 2

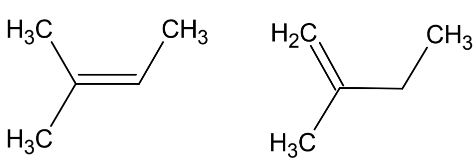
- **1 mark for just stating that Markovnikov's rule is involved**

(e)



Total = 4: 2 marks for each correct structure

(f)



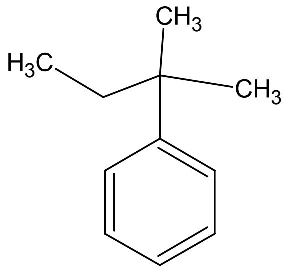
Total = 4: 2 marks for each correct structure

(g)

There is no such compound – the primary carbocation is too unstable, so won't form the primary alcohol.

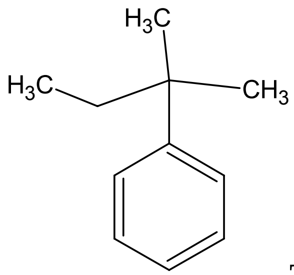
Total 2

(h)



Total 3

(i)



Total 3

- 1 only for giving the non-rearranged product

Question 18

(a) For example, HCl and NaOH [1 mark each]

(b) Yes [1 mark]

(c) Must contain an electron pair. [1 mark]

(d) pH = $-\log_{10} 1.5 \times 10^{-3} = 2.82$ [2 marks]

(e) $[H_3O^+] = [OH^-] = (5.19 \times 10^{-14})^{1/2} = 2.278 \times 10^{-7}$ [1 mark]
pH = $-\log_{10} 2.278 \times 10^{-7} = 6.642$ [1 mark]

(f) Still neutral, since $[H_3O^+] = [OH^-]$. pH = 6.642 is defined as the neutral pH at 50°C.
[1 marks for the answer, 2 marks for the explanation] [3 marks]

(g) $HCN + H_2O \rightleftharpoons CN^- + H_3O^+$ [2 marks]

(h) $K_a = ([CN^-] \times [[H_3O^+]) / [HCN]$ [1 mark]

(i) $CN^- + H_2O \rightleftharpoons HCN + OH^-$ [2 marks]

(j) $K_b = ([HCN] \times [[OH^-]) / [CN^-]$ [1 mark]

(k) $K_a(HCN) \times K_b(CN^-) = K_w$ [1 mark]

(l) pH = $-\log_{10}0.011 = 1.96$ [1 mark]

	CH_3COOH +	H_2O $\rightleftharpoons$	$CH_3CO_2^-$ +	H_3O^+
Initial conc (M):	0.020		0	$10^{-7} \approx 0$
Equil conc (M):	0.020-x		x	x
Approx conc (M):	0.020		x	x

$K_a = 1.76 \times 10^{-5} = x^2 / 0.020$

$x = [H_3O^+] = 5.93 \times 10^{-4}$ mol L^{-1}

pH = $-\log_{10}\ 5.93 \times 10^{-4} = 3.23$

[4 marks]

Combination is: 1-96-3-23 [1 mark]

(m) All Bronsted-Lowry bases can be Lewis acids and vice versus. A Lewis base is an electron pair donor and a Bronsted-Lowry Base is an H^+ acceptor.
[2 marks]

(n) $FeCl_3(s) + 6\ H_2O \rightleftharpoons Fe(H_2O)_6^{3+} + 3\ Cl^-$ [1 mark]

$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons Fe(H_2O)_5(OH)^{2+} + H_3O^+$ [1 mark]

(o) The Fe^{3+} salt is more acidic. [1 mark]
The Fe^{3+} can better polarise the OH bond in water. [1 mark]

Question 19

(a) 6.6 MPa *[**1.0 mark** for ±0.2 MPa; subtract 0.5 marks for more than 2 sf or missing or incorrect units.]*

(b) All three phases (solid, liquid, gas) coexist at this point. *[**2.0 marks –** 1 each for the mention of 3 phases and for the idea of coexistence (although you don't have to use this wording to get the marks)]*

(c)

Temperature	**Observation**
194 K	Solid sublimes (or turns to gas)

*[**0.5 marks** for temperature ±1 K; subtract 0.5 marks for more than 3 sf or missing or incorrect units; **0.5 marks** for correct observation.]*

(d)

Temperature	Observation
217 K	Solid melts (or turns to liquid)
220 K	Liquid evaporates (vaporises, turns to gas)

*[**1 mark** for temperatures: 0.5 mark each for ±1 K; subtract 0.5 marks for more than 3 sf or missing or incorrect units;*
***1 mark**, 0.5 each for correct observations. In general, whenever this sort of question turns up, all the detail I give in these solutions is not required: a sensible observation is enough to get the marks.]*

(e) Take P_1 = 75 kPa, T_1 = 190 K, P_2 = 520 kPa, T_2 = 217 K. Then substituting in gives

$$\Delta_{sub}H = \frac{R\ln\left(\frac{P_2}{P_1}\right)}{\frac{1}{T_1}-\frac{1}{T_2}} = 25\ \text{kJ mol}^{-1}.$$

*[**1 mark** for sensible values from graph or elsewhere, 0.5 per pair,*

***1.0 mark** for rearranging equation & working,*

***1.0 mark** for final result within ±2 kJ mol^{-1}; subtract 0.5 marks for more than 3 sf or missing or incorrect units]]*

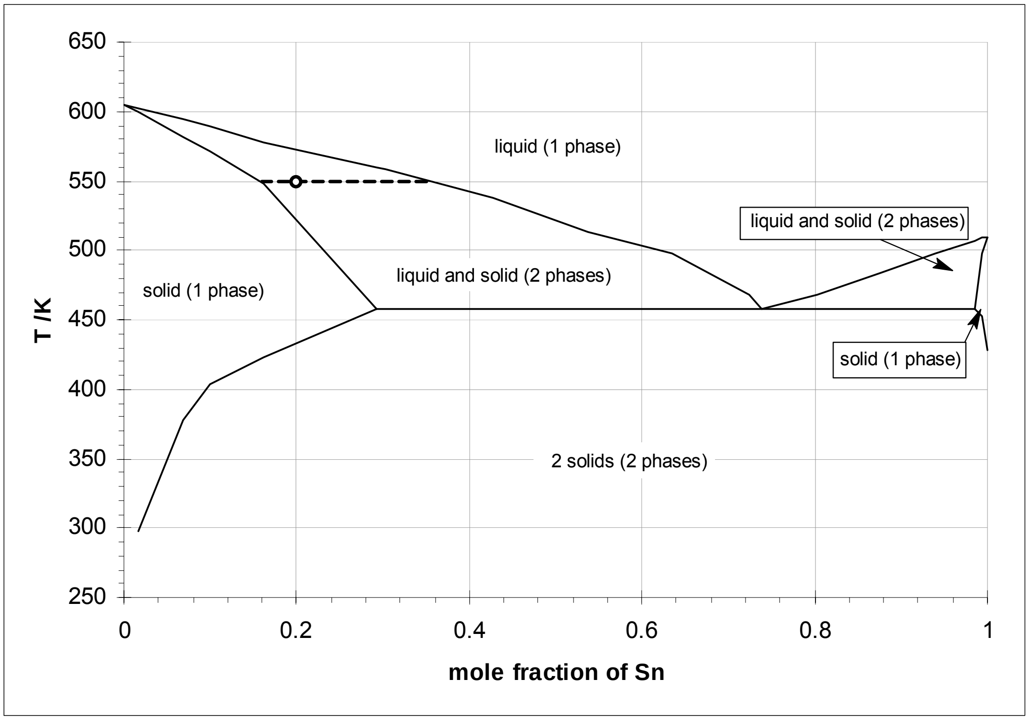
(f) Suppose that a fraction *f* of the mixture is solid. Then the mole fraction of Sn present is $0.2f + 0.5(1 - f) = 0.5 - 0.3f = 0.4$, which gives $f = 0.33$.

(This is just the lever rule; although they're not going to know the rule itself they should be able to perform the simple algebra above which gives the specific result I asked for.)

*[**1 mark** for algebraic setup ("a fraction f is solid"), **1 mark** for deciding to calculate fraction of Sn [or Pb] present, **1 mark** for correctly relating fraction of solid and liquid to fraction of Sn [Pb],*

***1 mark** for determining f. Subtract 0.5 marks for more than 2 sf and for minor arithmetic errors like percentages of solid and liquid not adding up to 100.]*

(g)



Solid phase containing about 16% Sn, liquid phase containing about 34% Sn.
*[**1 mark** for line in correct position; **2 marks** for phases, 0.5 each for correct phase with composition ±3%, 0.5 each for phase descriptions [solid, liquid].]*

(h)

Temperature	Observation
525 K	Solid begins to melt
525–570 K	Solid continues to melt gradually; both solid and liquid present
570 K	Solid melts completely; liquid only present

*[**1.5 marks** for temperatures ±10 K, 0.5 each;*

***1.5 marks** for observations, 0.5 each.]*

(i) 74% Sn, 26% Pb. *[**1 mark** for ±3%.]*

(j)

Temperature	Observation
960 K	Some zeta alloy begins to convert to silver-rich alloy
960–1020 K	Zeta alloy continues to convert to silver-rich alloy; both phases present
1020 K	Remaining zeta alloy melts; still some solid silver-rich alloy present
1020–1150 K	Silver-rich alloy gradually melts; 1 solid and 1 liquid phase present
1150 K	Alloy melts completely; 1 liquid phase present

*[**2.5 marks** for temperatures ±20 K, 0.5 each;*

***2.5 marks =** 1.5+0.5+0.5 for observations.]*

(k)

Temperature	Observation
760 K	Some **X** converts to zeta alloy; the rest melts
760–960 K	Zeta alloy gradually melts; 1 solid and one liquid phase present
960 K	Zeta alloy melts completely; 1 liquid phase present

*[**1.5 marks** for temperatures ±20 K, 0.7 for each significant T;*

***2.5 marks** = 0.8+0.6+0.6 for observations. At most 2 marks total if incorrect observations also made.]*

(l) **X** = Ag_3Sn. *[**1 mark**]*