



CHEMISTRY

2001 NATIONAL QUALIFYING EXAMINATION

SOLUTIONS GUIDE

Answers are a guide only and do not represent a preferred method of solving problems.

Section A

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

Section B**Q16**

- (a) (i) $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
 (ii) $\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{COOH} + 4\text{e}^- + 4\text{H}^+$
 (iii) $\text{CH}_3\text{CHO} + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{COOH} + 2\text{e}^- + 2\text{H}^+$
 (iv) $\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag(s)}$
 (v) $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{e}^-$
- (b) (i) $2\text{Cr}_2\text{O}_7^{2-} + 3\text{CH}_3\text{CH}_2\text{OH} + 16\text{H}^+ \longrightarrow 4\text{Cr}^{3+} + 3\text{CH}_3\text{COOH} + 11\text{H}_2\text{O}$ **1**
 (ii) $\text{Cr}_2\text{O}_7^{2-} + 3\text{CH}_3\text{CHO} + 8\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 3\text{CH}_3\text{COOH} + 4\text{H}_2\text{O}$ **2**
 (iii) $\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$ **3**
 (iv) $\text{CH}_3\text{CHO} + 2\text{Ag}^+ + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{COOH} + 2\text{Ag(s)} + 2\text{H}^+$ **4**
- (c) The overall equation contains protons on the left hand side. Hence, increasing the hydrogen ion concentration (by adding acid) pushes the equilibrium to the right.
- (d) First, the concentration of the Fe^{2+} solution is calculated:

$$n(\text{Fe}^{2+}) = \frac{m_{(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})}}{\text{MW}_{(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})}}$$

$$= \frac{7.43}{278.0} = 0.0267 \text{ mol}$$

$$\text{so } [\text{Fe}^{2+}] = \frac{n(\text{Fe}^{2+})}{V}$$

$$= \frac{7.43}{278.0} \times \frac{1000}{100} = 0.267 \text{ M}$$

$$\text{so } n(\text{Fe}^{2+} \text{ in } 50 \text{ mL aliquot}) = \frac{7.43}{278.0} \times \frac{1000}{100} \times \frac{25}{1000}$$

From equation **3** in (b) we see that $1 \text{ mol Cr}_2\text{O}_7^{2-} \equiv 6 \text{ mol Fe}^{2+}$

$$n(\text{Cr}_2\text{O}_7^{2-}) \text{ reacting with aliquot} = \frac{1}{6} \times \frac{7.43}{278.0} \times \frac{1000}{100} \times \frac{25}{1000} \text{ mol}$$

$$\text{so from titre } \left[\text{Cr}_2\text{O}_7^{2-} \right] = \frac{1}{6} \times \frac{7.43}{278.0} \times \frac{1000}{100} \times \frac{25}{1000} \times \frac{1000}{23.12}$$

$$= 0.0482 \text{ M}$$

- (e) From equation **4** in (b) we see that $1 \text{ mol CH}_3\text{CHO} \equiv 2 \text{ mol Ag (s)}$

$$n(\text{Ag(s)}) \text{ produced from } 50 \text{ mL} = \frac{m_{\text{Ag}}}{\text{AW}_{\text{Ag}}}$$

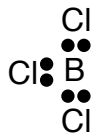
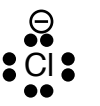
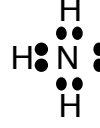
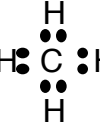
$$= \frac{0.234}{107.9} = 0.00217 \text{ mol}$$

$$\text{so } n(\text{ethanal}) \text{ in } 50 \text{ mL} = \frac{1}{2} \times \frac{0.234}{107.9} = 0.00108 \text{ mol}$$

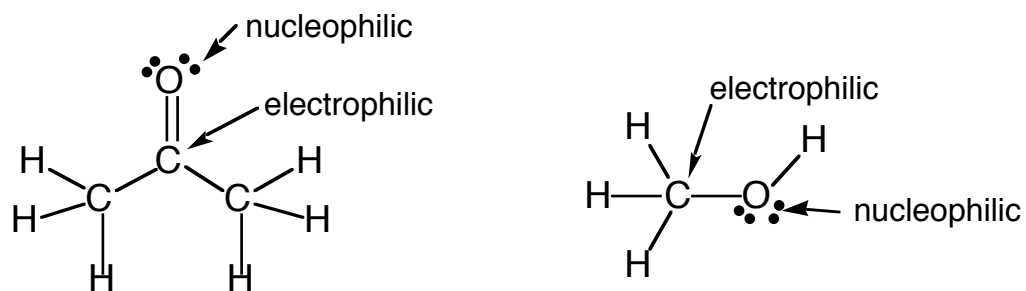
- (f) From equation 2 in (b) we see that 3 mol ethanal \equiv 1 mol $\text{Cr}_2\text{O}_7^{2-}$
- $$n_{(\text{Cr}_2\text{O}_7^{2-})} \text{ reacting just with ethanal in 50 ml} = \frac{1}{3} \times \frac{1}{2} \times \frac{0.234}{107.9} = 0.000361 \text{ mol}$$
- $$\text{total } n_{(\text{Cr}_2\text{O}_7^{2-})} \text{ used by ethanal/ethanol in 50 mL} = [\text{Cr}_2\text{O}_7^{2-}] \times V_{(\text{Cr}_2\text{O}_7^{2-})}$$
- $$= \left(\frac{1}{6} \times \frac{7.43}{278.0} \times \frac{1000}{100} \times \frac{25}{1000} \times \frac{1000}{23.12} \right) \times \frac{22.45}{1000}$$
- $$= 0.00108 \text{ mol}$$
- $$\text{so } n_{(\text{Cr}_2\text{O}_7^{2-})} \text{ reacting just with ethanol in 50 mL} = n_{(\text{Cr}_2\text{O}_7^{2-})_{\text{Total}}} - n_{(\text{Cr}_2\text{O}_7^{2-})_{\text{Ethanal}}}$$
- $$= 0.00108 - 0.000361$$
- $$= 0.000720 \text{ mol}$$
- (g) (i) From equation 1 in (b) we see that 3 mol ethanol \equiv 2 mol $\text{Cr}_2\text{O}_7^{2-}$
- $$n_{\text{ethanol}} \text{ in 50 mL} = \frac{3}{2} \times n_{(\text{Cr}_2\text{O}_7^{2-})_{\text{ethanol}}}$$
- $$\text{so } n_{\text{ethanol}} \text{ in 500 mL} = \frac{500}{50} \times \frac{3}{2} \times n_{(\text{Cr}_2\text{O}_7^{2-})_{\text{ethanol}}}$$
- $$= \frac{500}{50} \times \frac{3}{2} \times 0.000720 = 0.0108 \text{ mol}$$
- (ii) From equation 2 in (b) we see that 3 mol ethanal \equiv 1 mol $\text{Cr}_2\text{O}_7^{2-}$
- $$n_{\text{ethanal}} \text{ in 50 mL} = 3 \times n_{(\text{Cr}_2\text{O}_7^{2-})_{\text{ethanal}}}$$
- $$\text{so } n_{\text{ethanal}} \text{ in 500 mL} = \frac{500}{50} \times 3 \times n_{(\text{Cr}_2\text{O}_7^{2-})_{\text{ethanal}}}$$
- $$= \frac{500}{50} \times 3 \times \left(\frac{1}{3} \times \frac{1}{2} \times \frac{0.234}{107.9} \right) = 0.0108 \text{ mol}$$

Q17

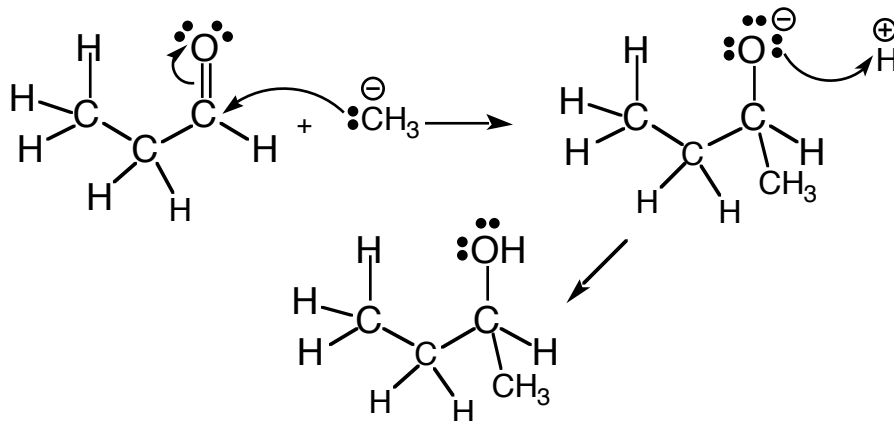
(a)

	electrophile
	nucleophile
	nucleophile
	neither

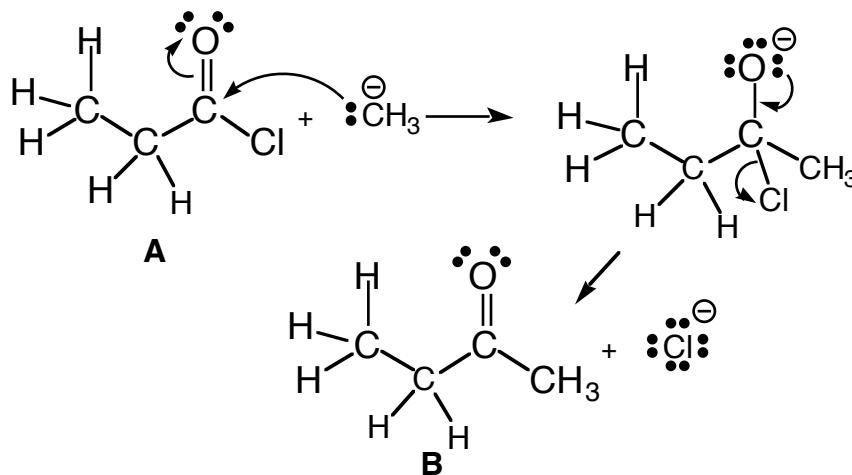
(b)



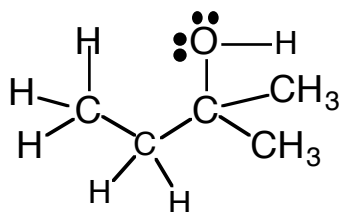
(c)



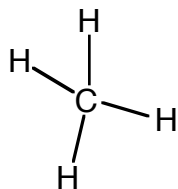
(d)



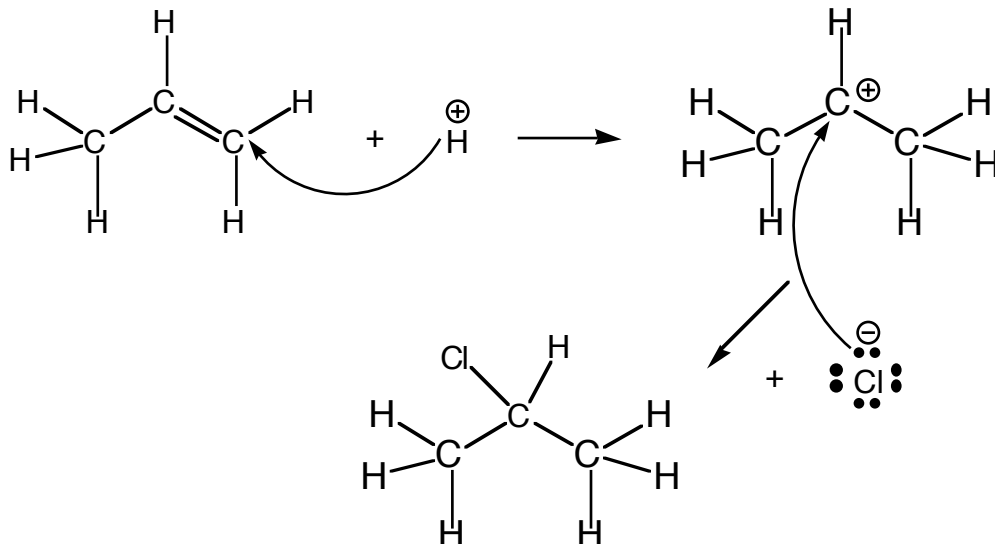
(e) The structure of compound X is



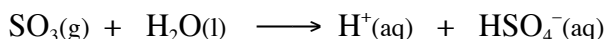
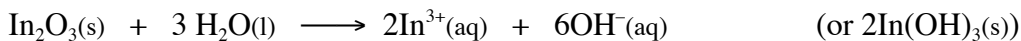
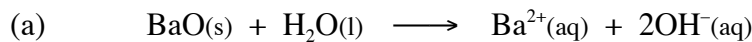
(f) The gas evolved was methane



(g)



Q18



(c) SO_3 is the more acidic oxide and hence forms the stronger acid, H_2SO_4 .

For a given series the acid strength increases with an increase in the number of oxygen atoms attached to the central atom. Zumdahl suggests that this happens because the very electronegative O atoms are able to draw electrons away from the central atom and the O-H bond, the net effect is to both polarise and weaken the O-H bond and is more important as the number of attached O atoms increases.

An **alternative explanation** is: S is in the +6 oxidation state in SO_3 and H_2SO_4 compared with the +4 state in SO_2 and H_2SO_3 . In the +6 state S will more strongly attract electron density from the neighbouring O atoms in turn weakening the O-H interaction in the acid and hence leading to a stronger acid.



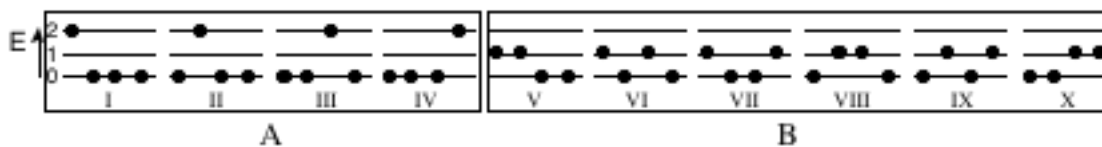
(e) SnO is the more basic oxide.

Sn is in the +2 oxidation state in SnO and the +4 state in SnO_2 . In the +2 state Sn will less strongly attract electron density from the neighbouring O atoms leading to a more ionic and hence more basic oxide.

- (f) $\text{BeO(s)} + 2\text{H}^+(\text{aq}) \longrightarrow \text{Be}^{2+}(\text{aq}) + \text{H}_2\text{O(l)}$
 $\text{BeO(s)} + 2\text{OH}^-(\text{aq}) + \text{H}_2\text{O(l)} \longrightarrow [\text{Be}(\text{OH})_4]^{2-}(\text{aq})$
 $\text{As}_2\text{O}_3(\text{s}) + 6\text{H}^+(\text{aq}) \longrightarrow 2\text{As}^{3+}(\text{aq}) + 3\text{H}_2\text{O(l)}$
 $\text{As}_2\text{O}_3(\text{s}) + 6\text{OH}^-(\text{aq}) \longrightarrow 2\text{AsO}_3^{3-}(\text{aq}) + 3\text{H}_2\text{O(l)}$
- (g) $\text{BaO}_2(\text{s}) + 2\text{H}_2\text{O(l)} \longrightarrow \text{Ba}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) + \text{H}_2\text{O}_2(\text{aq})$
 $2\text{KO}_2(\text{s}) + 2\text{H}_2\text{O(l)} \longrightarrow 2\text{K}^+(\text{aq}) + 2\text{OH}^-(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) + \text{O}_2(\text{g})$
- (h) NH_3
 $\text{Mg}_3\text{N}_2(\text{s}) + 6\text{H}_2\text{O(l)} \longrightarrow 3\text{Mg}^{2+}(\text{aq}) + 6\text{OH}^-(\text{aq}) + 2\text{NH}_3(\text{aq})$
- (i) PH_3
 $\text{Na}_3\text{P(s)} + 3\text{H}_2\text{O(l)} \longrightarrow 3\text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq}) + \text{PH}_3(\text{g})$
- (j) NH_3 is the stronger base. N is more electronegative than P and hence the N atom in NH_3 will attract/bind a proton more strongly than the P atom in PH_3 .

Q19

(a)



- (b) (i) There are 10 microstates.
(ii) There are 2 different configurations.

(c) (i) For $N = 3, E = 3$

Configuration	Occupation Numbers	Number of Microstates
A	$n_0 = 2, n_3 = 1$	3
B	$n_0 = 1, n_1 = 1, n_2 = 1$	6
C	$n_1 = 3$	1

(ii) For $N = 4, E = 2$

A	$n_0 = 3, n_2 = 1$	4
B	$n_0 = 2, n_1 = 2$	6

(d) (i) for A

$$W = \left(\frac{N!}{n_0! \times n_1! \times n_2! \times \dots} \right)$$

$$= \frac{4!}{n_0! \times n_2!}$$

$$= \frac{4!}{3! \times 1!}$$

$$= \frac{24}{6 \times 1}$$

$$= 4 \text{ microstates}$$

for B

$$\begin{aligned}
 W &= \left(\frac{N!}{n_0! \times n_1! \times n_2! \times \dots} \right) \\
 &= \frac{4!}{n_0! \times n_1!} \\
 &= \frac{4!}{2! \times 2!} \\
 &= \frac{24}{2 \times 2} \\
 &= 6 \text{ microstates}
 \end{aligned}$$

(ii) and (iii)

Configuration	Occupation Numbers	Number of Microstates
A	$(n_0 = 9, n_3 = 1)$	10
B	$n_0 = 8, n_1 = 1, n_4 = 1$	90
C	$n_0 = 8, n_2 = 1, n_3 = 1$	90
D	$n_0 = 7, n_1 = 2, n_3 = 1$	360
E	$n_0 = 7, n_1 = 1, n_2 = 2$	360
F	$n_0 = 6, n_1 = 3, n_2 = 1$	840
G	$(n_0 = 5, n_1 = 5)$	252

(iv) Total number of microstates = 2002

Most probable configuration = F ($n_0 = 6, n_1 = 3, n_2 = 1$)

$$\begin{aligned}
 \text{Probability of adopting most probable configuration} &= \frac{840}{2002} \\
 &= 0.420 \\
 &= 42\%
 \end{aligned}$$

(e) (i)

$$\begin{aligned}
 W &= \frac{10!}{3! \times 3! \times 2! \times 1! \times 1!} \\
 &= 50,400
 \end{aligned}$$

(ii) $N_X = 5, N_Y = 5$

(f) (i)

$$\begin{aligned}
 W &= \frac{10!}{2! \times 6! \times 1! \times 1!} \\
 &= 2,520
 \end{aligned}$$

(ii) Now $N_Y = 7, N_X = 3$, ie more Y than X. This is what you might expect given that Y is lower in energy than X or Y is more stable than X.