CHEMISTRY

2002 NATIONAL QUALIFYING EXAMINATION

SOLUTIONS GUIDE

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

Section A

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

Section B

Q16

(a) (i) Fe^{2+} (aq) $\rightleftharpoons$ Fe^{3+} (aq) + e^-

(ii) $4H^+$ (aq) + $4e^-$ + O_2 (g)) $\rightleftharpoons$ $2H_2O$ (l)

(b) $4Fe^{2+}$ (aq) + $4H^+$ (aq) + O_2 (g) $\rightleftharpoons$ $4Fe^{3+}$ (aq) + $2H_2O$ (l)

(c)   Yes – the presence of H^+ ions on the LHS means the more acidic the solution, the more oxidation will occur.

(d)   6+

(e) Fe^{2+} (aq) $\rightleftharpoons$ Fe^{3+} (aq) + e^- **(1)**

$Cr_2O_7^{2-}$ (aq) + $14H^+$ (aq) + $6e^-$ $\rightleftharpoons$ $2Cr^{3+}$ (aq) + $7H_2O$ (l)   **(2)**

6x**1 + 2** $6Fe^{2+}$ (aq) + $Cr_2O_7^{2-}$ (aq) + $14H^+$ (aq) $\rightleftharpoons$ $6Fe^{3+}$ (aq) + $2Cr^{3+}$ (aq) + $7H_2O$ (l)   **(3)**

(f)   The persistence of the blue-green colour at the titration end point indicates the presence of free ligand (H_3L).

(g) Fe^{3+} (aq) + $2H_3L$ (aq) $\rightleftharpoons$ $[FeL_2]^{3-}$ (aq) + $6H^+$ (aq)

$\therefore$ 1 mol Fe^{3+} $\equiv$ 2 mol H_3L

Because the stoichiometry for the reaction of H_3L and Cr^{3+} is the same as that for the reaction with Fe^{3+} we can say that:

1 mol (Fe^{3+} + Cr^{3+}) $\equiv$ 2 mol H_3L

thus   mol H_3L in titre $= \frac{0.3182 \times 30.20}{1000} = 9.61 \times 10^{-3}$

and   mol (Fe^{3+} + Cr^{3+}) in aliquot $= \frac{0.3182 \times 30.20}{1000} \times \frac{1}{2} = 4.81 \times 10^{-3}$

so   mol Fe^{3+} in aliquot $= \frac{0.3182 \times 30.20}{1000} \times \frac{1}{2} \times \frac{6}{8} = 3.60 \times 10^{-3}$

and   mol Fe^{2+} in original solution $= \frac{0.3182 \times 30.20}{1000} \times \frac{1}{2} \times \frac{6}{8} \times \frac{10}{1} = 3.60 \times 10^{-2}$

$[Fe^{2+}]$ in original solution $= \frac{0.3182 \times 30.20}{1000} \times \frac{1}{2} \times \frac{6}{8} \times \frac{10}{1} \times \frac{1000}{200} = 0.1802 M$

(h) $Fe(ClO_4)_2 \cdot xH_2O$

Molecular mass $= 55.85 + (35.45 + 4 \times 16) \times 2 + x(18.06)$

$= 254.75 + x(18.06)$

now molecular mass $= \frac{mass}{moles} = \frac{13.4}{0.03601}$

so $254.75 + x(18.06) = \frac{13.4}{0.03601}$

and   x = 6.5

(i)   There was no appreciable Fe^{3+} content in the solution. Kesan sees indication of free ligand upon addition of only one drop.

(j)

moles H_3L reacting $= 0.3182 \times \frac{11.35}{1000} = 3.61 \times 10^{-3}$

so   moles of Fe^{3+} $= 0.3182 \times \frac{11.35}{1000} \times \frac{1}{2} = 1.81 \times 10^{-3}$

and $[Fe^{3+}] = 0.3182 \times \frac{11.35}{1000} \times \frac{1}{2} \times \frac{1000}{20} = 9.03 \times^{-2} M$

(k)

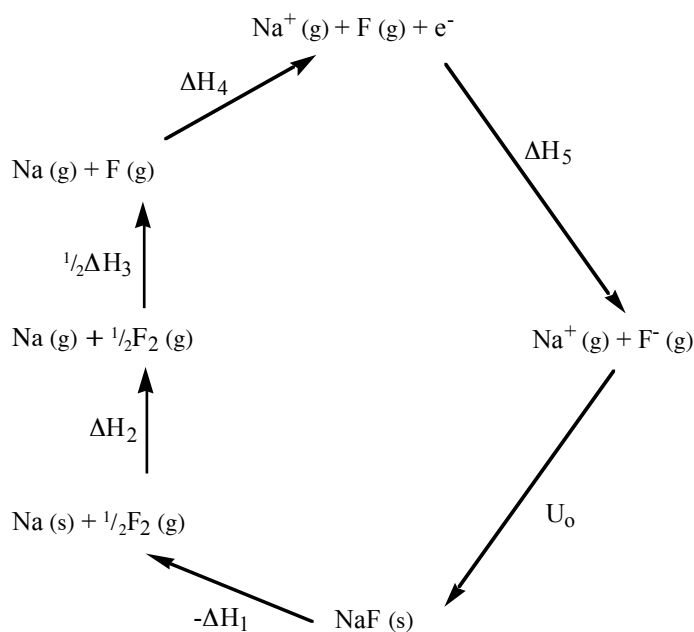$$[Fe(II)]_{used} = [Fe^{3+}]_{in\ sample\ 2} = 9.03 \times^{-2} M$$

$$(Fe(II))_{fraction\ remaining} = \frac{[Fe(II)]_{original} - [Fe(II)]_{used}}{[Fe(II)]_{original}}$$

$$= \frac{0.1802 - 0.0903}{0.1802}$$

$$= 0.4988$$

$$\approx 0.5\ (50\%)$$

(l)   The titre should be less than 22.7 mL. The rate of oxidation will depend on $[Fe^{2+}]$ which has already been reduced after one week compared to the original concentration.
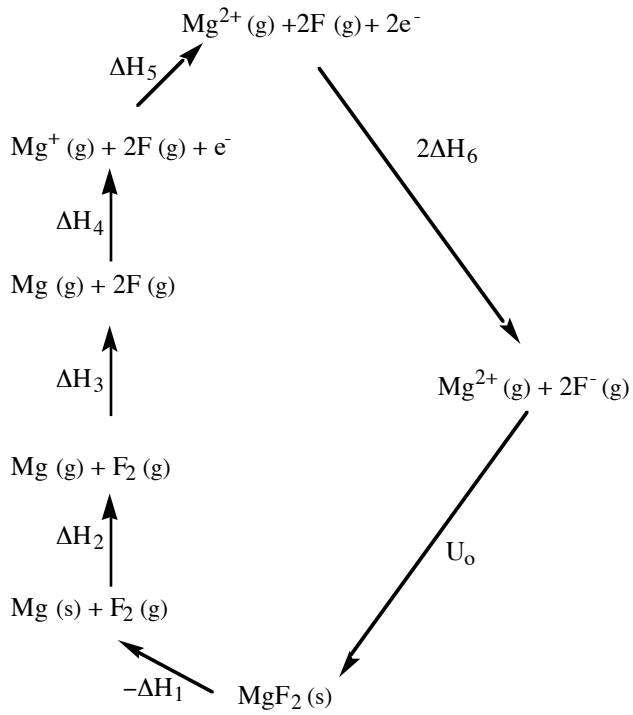
Q17

(a)

(b) $\Sigma\ \Delta H = 0$

ie $-\Delta H_1 + \Delta H_2 + \frac{1}{2}\Delta H_3 + \Delta H_4 + \Delta H_5 + U_o = 0$

ie $561.5 + 108 + \frac{1}{2}(155) + 496 - 332 + U_o = 0$

ie $U_o = -911\ kJ\ mol^{-1}$ for NaF (s)

(c)

Mg^{2+} (g) + 2F (g) + 2e$^-$

ΔH_5

Mg$^+$ (g) + 2F (g) + e$^-$

$2\Delta H_6$

ΔH_4

Mg (g) + 2F (g)

ΔH_3

Mg^{2+} (g) + 2F$^-$ (g)

Mg (g) + F$_2$ (g)

ΔH_2

U_o

Mg (s) + F$_2$ (g)

$-\Delta H_1$ MgF$_2$ (s)

(d) $\Sigma \Delta H = 0$

ie $-\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + 2\Delta H_6 + U_o = 0$

ie $1090 + 141 + 155 + 738 + 1450 - 2(332) + U_o = 0$

i.e. $U_o = -2910$ kJ mol^{-1} for MgF$_2$ (s)

Q18

(a)

4

(b)

(c)

mirror

(R)-1-bromo-1-chloroethane   (S)-1-bromo-1-chloroethane

(d)

mirror

(R)-2-chlorobutane   (S)-2-chlorobutane

(e)

mirror

(R)-propane-1,2-diol   (S)-propane-1,2-diol

(f) (i)

(2R,3S)-   (2R,3R)-   (2S,3S)-   (2S,3R)-
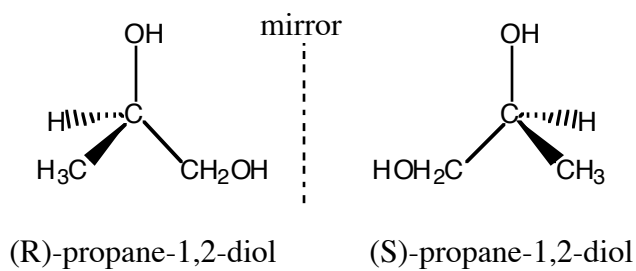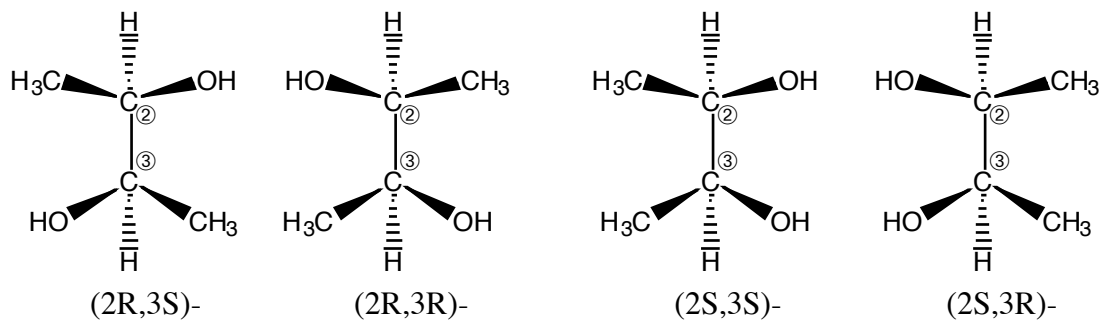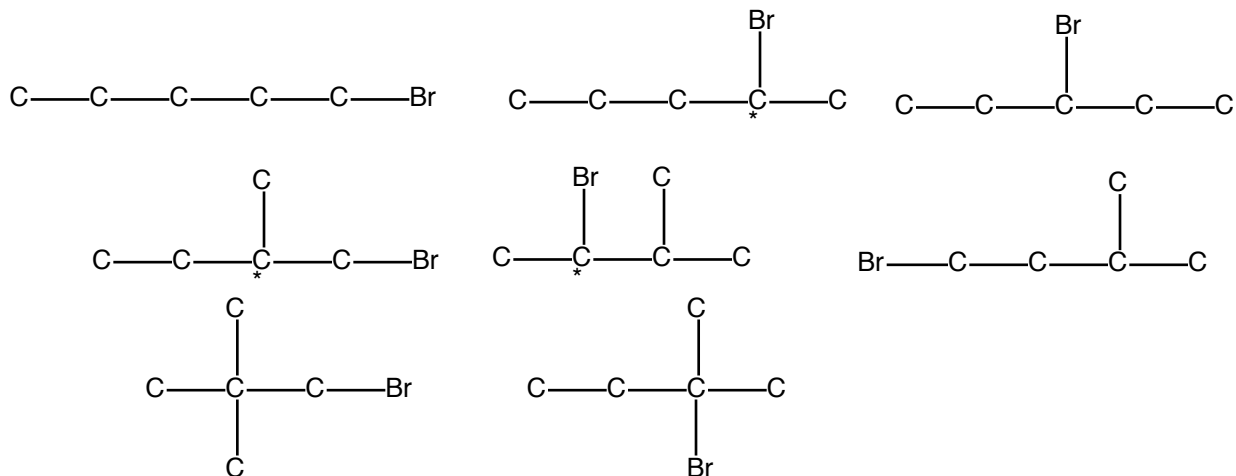
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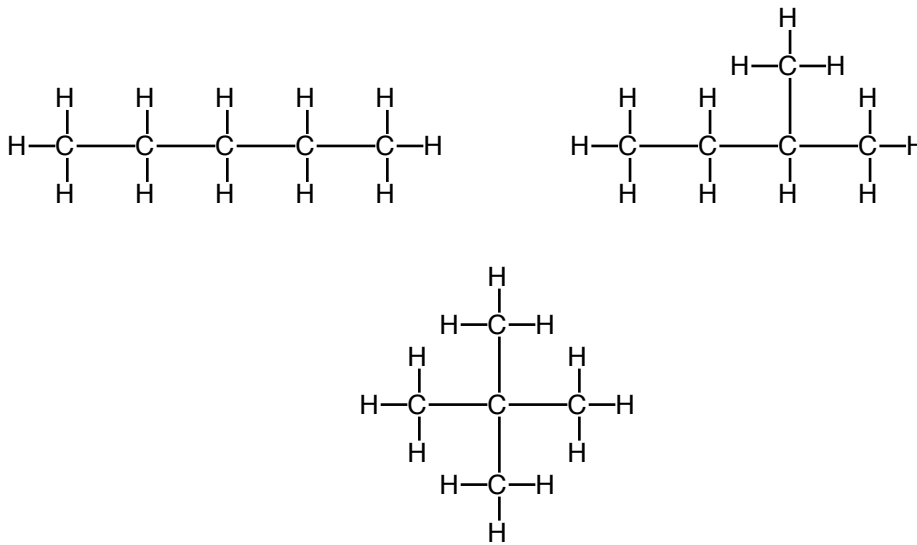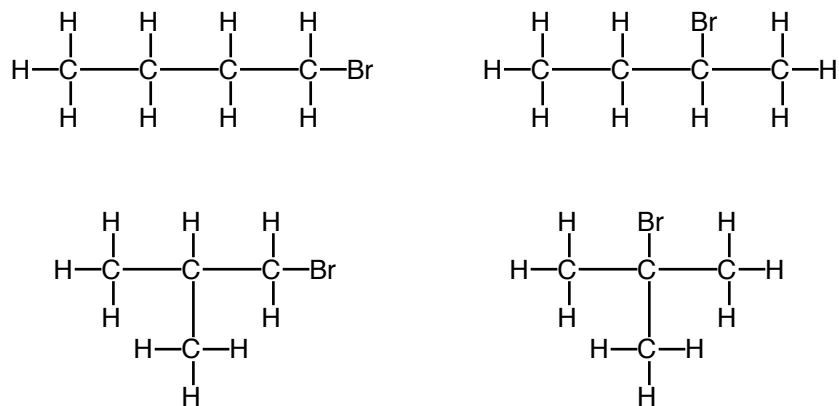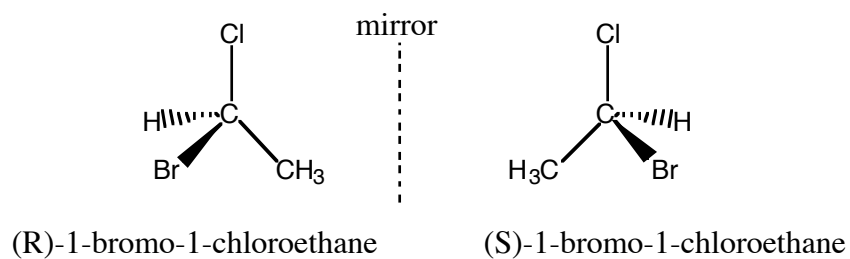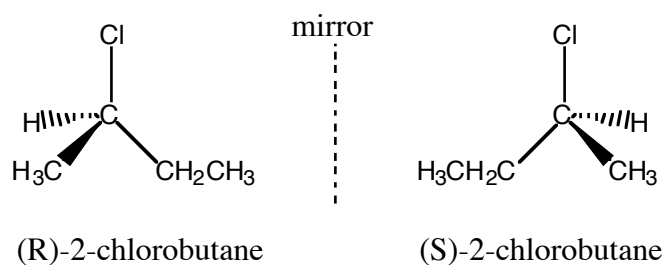
(ii) The (2R,3S)- and (2S,3R)- forms are in fact identical. They are not mirror images of one another due to the molecules having a plane of symmetry.

(g) 2^n

(h) (i) There are 8 constitutional isomers. (See the diagrams below that show only the carbon skeleton.)

(ii) Three of the constitutional isomers exist as enantiomeric pairs. (the three below that have a C atom marked with *.)

C—C—C—C—C—Br

C—C—C—C(Br)*—C

C—C—C(Br)—C—C

C—C—C*—C—Br with C above and C below (side chains)

C—C(Br)*—C(C)—C

Br—C—C—C(C)—C

C—C(C)(C)—C—Br

C—C—C(C)(Br)—C

Q19

(a) (i) The forces are attractive, because it takes energy to break the attraction by moving more molecules to the surface.

(ii) Water will have higher surface tension as the intermolecular forces involve significant hydrogen-bonding and are therefore stronger, so that the force needed to increase the surface area will be greater.

(b) Because it takes energy to create an interface on the bubble, surface tension will act to decrease surface of bubble until it vanishes (by redissolving gas, etc.)

(c) Air will move from bubble C to bubble B, such that C practically disappears and B becomes as large as possible. $r_B > r_C$. By equation (**1**), the pressure inside C is therefore greater than the pressure inside B. By Le Chatelier's principle, pressure will try to equalise, which means that molecules will move from C to B, which makes C even smaller and the pressure difference greater, and so accelerating to the end result.

(d) When small droplets do spontaneously form, they will be under high pressure as within a spherical curve. This means the vapour pressure is higher than normal and so, if small enough, they will evaporate again. 'Seeding' means that enough particles will condense at the surface to form a particle large enough that pressure difference still leaves vapour pressure below boiling point, so that evaporation doesn't occur.

(e)
$$\gamma = \rho g h r / 2$$
$$= 997.1 kg m^{-3} \times 9.81 ms^{-2} \times 0.0736 m \times 2.0 \times 10^{-4} m / 2$$
$$= 0.072 Nm^{-1}$$

(f) In this case the forces between liquid molecules are stronger than the forces of attraction between the side walls and the liquid: curving inward lowers energy by preserving as much liquid-

liquid force as possible. By the equation given, the LHS becomes negative, which means the height term on the right must be negative: the liquid in the tube is lower than the bulk surface.

(g)

$$2\gamma \cos\theta / r = 2\times 0.072 Nm^{-1} \times \cos 105° / (20\times 10^{-6}\, m)$$

$$= -1863.5 Pa$$

So, that much pressure is needed to make the pressure on the bulk water the same as that existing below the curve, which means it will stay at the same level. Any greater pressure will start to force the meniscus up into the capillary. Given the surface tensions for the other interfaces you can calculate energy change to make the water touch the walls instead of air, but this turns out to be negligible: increased surface area = $2\pi rh$.