UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS

GCE Advanced Level and GCE Advanced Subsidiary Level

MARK SCHEME for the May/June 2006 question paper

9701 CHEMISTRY

9701/04   **Paper 4**

Maximum raw mark 60

This mark scheme is published as an aid to teachers and students, to indicate the requirements of the examination. It shows the basis on which Examiners were initially instructed to award marks. It does not indicate the details of the discussions that took place at an Examiners' meeting before marking began. Any substantial changes to the mark scheme that arose from these discussions will be recorded in the published *Report on the Examination*.

All Examiners are instructed that alternative correct answers and unexpected approaches in candidates' scripts must be given marks that fairly reflect the relevant knowledge and skills demonstrated.

Mark schemes must be read in conjunction with the question papers and the *Report on the Examination*.

The minimum marks in these components needed for various grades were previously published with these mark schemes, but are now instead included in the Report on the Examination for this session.

*   CIE will not enter into discussion or correspondence in connection with these mark schemes.

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1 (a) (i) order w.r.t. NO = 2   [1]
order w.r.t. O_2 = 1   [1]

(ii) rate = $k[NO]^2[O_2]$ [1]

taking the first row: k   =   rate/$([NO]^2[O_2])$
           = $0.020/(0.005^2 \times 0.005)$
           =   **1.6 x 10^5**   ecf [1]
   units =   **$mol^{-2}dm^6sec^{-1}$**   ecf [1]

(iii) rate   = $k[NO]^2[O_2]$
       = $1.6 \times 10^5 \times 0.0025^2 \times 0.0025$
       =   **2.5 x 10^{-3}** (mol dm^{-3} s^{-1})   ecf [1]

                                                   [6]

(b) (i) homogeneous   [1]

(ii) $NO + \frac{1}{2} O_2 \longrightarrow NO_2$
$SO_2 + NO_2 \longrightarrow SO_3 + NO$
$(SO_3 + H_2O \longrightarrow H_2SO_4)$ [2]

                                                   [3]

                                                  [Total: 9]

2 (a) (i) $K_{sp} = [Ca^{2+}][SO_4^{2-}]$ [1]

units are: mol^2dm^{-6} ecf [1]

(ii) $[CaSO_4] = \sqrt{K_{sp}} = $ **5.5 x 10^{-3}** (5.477×10^{-3})(mol dm^{-3})   ecf [1]

(iii) $n(CaSO_4)$ in 100 dm^3 = $5.5 \times 10^{-3} \times 100$ = 0.55 moles   ecf from **(ii)** [1]

$M_r(CaSO_4)$ = 136.1

Thus mass$(CaSO_4)$ = 0.55 x 136.1 = **74.8g** *(0.55 x M_r)*   [1]
(if the accurate $[CaSO_4]$ is held throughout the calculation, ans = **74.5g**)

                                                   [5]

(b) (i) down the group: the $\Delta H_{solution}$ becomes more endothermic;
both lattice energy **and** $\Delta H_{hydration}$ become less (exothermic);
due to **ionic** radius (of M^{2+}) increasing;
but $\Delta H_{hydration}$ changes more than lattice energy *any three points*   [3]

(ii) $K_{sp} = [Ba^{2+}][SO_4^{2-}] = (9 \times 10^{-6})^2 = $ **8.1 x 10^{-11}**   **NO** ecf [1]

                                                   [4]

(c) (i) LE is the energy change when **1 mole** of (ionic) solid   [1]

is formed from its **gaseous ions**   [1]

(ii) LE$(BaSO_4)$ < LE$(MgSO_4)$, due to larger radius of Ba^{2+} both points   [1]

                                                   [3]

                                                  [Total: 12]

3 (a) (i) +2, +3, +4, +5   (ignore 0 and +1)   *all four* [1]

(ii) $[Ar]3d^2$ [1]

[2]

(b) (i) take a fixed amount/aliquot/pipette-full of the Fe^{2+} solution   [1]

titrate with $KMnO_4$ in **the burette**   [1]

until the first permanent pink colour (*or* change from colourless to pink) [1]

repeat until two titres are within 0.1 cm^3 [1]

$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$ [1]
(*or* molecular equn.)

(ii) $n(MnO_4^-) = 0.02 \times 14/1000 = 2.8 \times 10^{-4}$ moles   [1]

$n(Fe^{2+})$ in 25 cm^3 = $2.8 \times 10^{-4} \times 5$ (*x 5*) [1]
(= 1.4×10^{-3} moles)
$n(Fe^{2+})$ in 100 cm^3 = $1.4 \times 10^{-3} \times 4$ (*x 4*) [1]
(= 5.6×10^{-3} moles)
mass of Fe in 2.0 g ore = $5.6 \times 10^{-3} \times 55.8$
= 0.31 g
percentage = $100 \times 0.31/2$ = **15.6%**   (*use of 55.8 or 56 and %*)   [1]

[9]

(c) (i) $Cu^{2+}(aq)$ or $[Cu(H_2O)_6]^{2+}$ [1]

(ii) pale blue ppt. (of $Cu(OH)_2(s)$)   *[ignore any refs. to iron hydroxides]*   [1]
(which dissolves to give....)
a **deep blue solution**   [1]

which contains $[Cu(NH_3)_4]^{2+}$ ions   (*can be read into equn, below*)   [1]

formed by ligand displacement   [1]
or an equation such as
$Cu(OH)_2 + 4NH_3 \longrightarrow [Cu(H_2O)_4]^{2+} + 2OH^-$
or $[Cu(H_2O)_6]^{2+} + 4NH_3 \longrightarrow [Cu(H_2O)_4]^{2+} + 6H_2O$

[5]

[Total: 16 max 14]

4 **(a)** HCl or H_2SO_4 or H^+ or acid   [1]

conc(if HCl only)/dilute/aqueous + heat   [1]
                                                                                                                                    [2]

(b) **two** rings only (1 ring around the α-C of tyrosine & 1 around the α-C of lysine) [1]
                                                                                                                                    [1]

(c) $^+NH_3CH_2CO_2^-$ (*or* displayed formula)   [1]
                                                                                                                                    [1]

(d) **(i)** $NH_2CH_2CO_2^-$ (Na$^+$)   (*either* -CO$_2^-$Na$^+$ *or* -CO$_2$Na but NOT –CO-O-Na)   [1]

(ii) (Na$^+$) $^-$O-C$_6$H$_4$-CH$_2$CH(NH$_2$)CO$_2^-$ (Na$^+$)   [1] + [1]

(iii) (Cl)$^+$NH$_3$(CH$_2$)$_4$CH(NH$_3^+$)CO$_2$H (Cl)   [1] + [1]

(iv) HO-C$_6$H$_2$Br$_2$-CH$_2$CH(NH$_2$)CO$_2$H (if shown, Br at 2,6 to OH group)   [1]
                                                                                                                                    [6]

(e)

structure [1]
at least one peptide group identified [1]
                                                                                                                                    [2]

(f) **(i)** e.g.

[1]

(ii)

or ClCO-------------COCl [1]
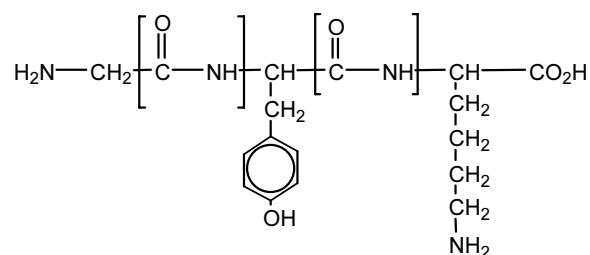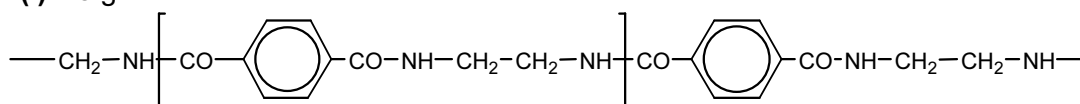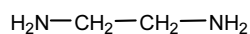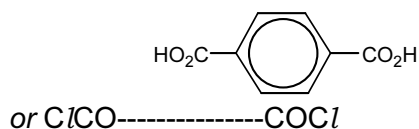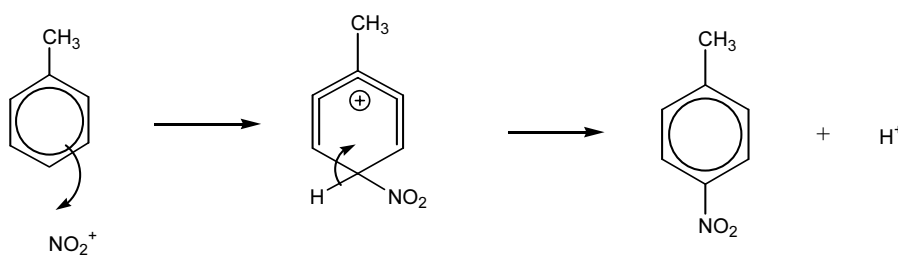   [1]
                                                                                                                                    [3]

[Total: 15 max 14]

5 **(a)** I: $HNO_3 + H_2SO_4$ (*or* names)   [1]

       (both) conc. and at $50^oC < T < 60^oC$ ✓   [1]

    II: $KMnO_4$ $(+OH^-)$ + heat   [1]

    III: Sn + (conc) HCl [1]

    IV: CH_3CH_2OH (*or* name)   [1]

       + c. H_2SO_4 + heat   [1]

                                                                        [6]

(b)

    intermediate, including ⊕   [1]
    NO_2^+ at start and H^+ at finish   [1]
    (no marks for curly arrows, but if present, they must be in correct direction)

                                                                        [2]

(c) (i)   ester and (primary) amine   [2]

    (ii) **more** basic: amine group is *not* adjacent to benzene ring   **both** points [1]
          (*or* lone pair (on N) is not delocalised)

                                                                           [3]

                                                                    [Total: 11]