GCE 2004
June Series

AQA

ASSESSMENT and
QUALIFICATIONS
ALLIANCE

Mark Scheme

Chemistry
(Subject Code CHM4)

Mark schemes are prepared by the Principal Examiner and considered, together with the relevant questions, by a panel of subject teachers. This mark scheme includes any amendments made at the standardisation meeting attended by all examiners and is the scheme which was used by them in this examination. The standardisation meeting ensures that the mark scheme covers the candidates' responses to questions and that every examiner understands and applies it in the same correct way. As preparation for the standardisation meeting each examiner analyses a number of candidates' scripts: alternative answers not already covered by the mark scheme are discussed at the meeting and legislated for. If, after this meeting, examiners encounter unusual answers which have not been discussed at the meeting they are required to refer these to the Principal Examiner.

It must be stressed that a mark scheme is a working document, in many cases further developed and expanded on the basis of candidates' reactions to a particular paper. Assumptions about future mark schemes on the basis of one year's document should be avoided; whilst the guiding principles of assessment remain constant, details will change, depending on the content of a particular examination paper.

CHM 4 Further Physical and Organic Chemistry

SECTION A

Question 1

(a)   (i)   Experiment 2 2.60×10^{-3} 1
            Experiment 3 0.60×10^{-2} 1
            Experiment 4 11.4×10^{-2} 1

(ii) $k = \dfrac{10.4 \times 10^{-3}}{(4.80 \times 10^{-2})(6.60 \times 10^{-2})^2}$ 1

       $= 49.7$ 1
       (Allow 49.8 and 50)

       $\text{mol}^{-2}\,\text{dm}^6\,\text{s}^{-1}$ 1

(b)   No change   1

                                                                                                        Total 7

Question 2

(a) $K_a = \dfrac{[H^+][A^-]}{[HA]}$ 1

      *(All three sets of square brackets needed, penalise missing brackets or
      missing charge once in the question)*
      (Don't penalise extra $[H^+]^2/[HA]$)

(b) $K_a = \dfrac{[H^+]^2}{[HA]}$ or $[H^+] = [A^-]$ 1

      $[H^+] = \sqrt{(1.45 \times 10^{-4}) \times 0.25}$ 1

          $= 6.02 \times 10^{-3}$ 1

      pH $= 2.22$ 1
      (must be to 2dp)
      (allow 4th mark consequential on their $[H^+]$)

(c)   (i)   pH (almost) unchanged   1
            (Must be correct to score explanation)

            H^+ removed by A^- forming HA   1
            or acid reacts with salt
            or more HA formed

      (ii) $[H^+] = 10^{-3.59} = 2.57 \times 10^{-4}$ or 2.6×10^{-4} 1

            $[A^-] = \dfrac{K_a[HA]}{[H^+]}$ 1

            $= \dfrac{(1.45 \times 10^{-4}] \times 0.25}{2.57 \times 10^{-4}}$ 1

            $= 0.141$ (mol dm^{-3})   1
            (Allow 0.139 to 0.141 and allow 0.14)
            (If not used 3.59, to find [H⁺] can only score M2 for working)
            (If 3.59 used but [H⁺] is wrong, can score M2 for correct method
            and conseq M4)
            If wrong method and wrong expression, can only score M1)

      (ii) *Alternative scheme for first three marks of part (c)(ii)*
            $pH = pK_a - \log\dfrac{[HA]}{[A^-]}$ (1)

            $pK_a = 3.84$ (1)

            $3.59 = 3.84 - \log\dfrac{0.250}{[A^-]}$ (1)

                                                                          Total 11

Question 3

(a)   12 (kPa)   1

pp = mole fraction $\times$ total pressure   **or**   mole fraction = 12/104   1

= 0.115   1
(allow 0.12)

(b)   68 (kPa)   1

(c)   1
$$K_p = \frac{(pSO_3)^2}{(pSO_2)^2 \times (pO_2)}$$
(If K_p wrong, allow consequential units only)
(penalise square brackets in expression but then mark on)

$$= \frac{68^2}{24^2 \times 12}$$ 1

= 0.669   1
(Allow 0.67)
(A*llow full marks in calculation consequential on their values in (a) and*
(b))

kPa^{-1} 1

(d) T_2 1
(Must be correct to score any marks in this section)

Exothermic   1

Reduce T to shift equilibrium to the right   1
or forward reaction favoured by low T
or K_p increases for low T
or low T favours exothermic reaction

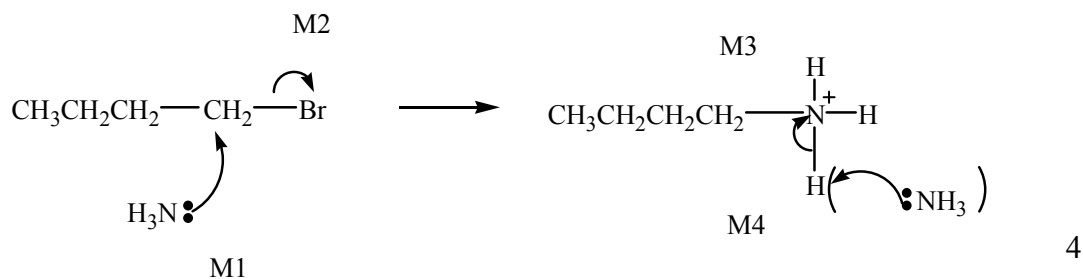(e)   Increase   1

None   1

                                                                                          Total 13

Question 4

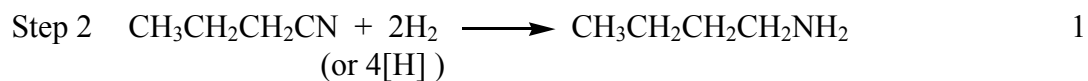(a)   Nucleophilic substitution   1

M1, M2 and M4 for arrows, M3 for structure of cation   4
(Allow M2 alone first, i.e. SN1 formation of carbocation)
(Penalise M4 if Br⁻ used to remove H⁺)

(b)   Step 1 $CH_3CH_2CH_2CN$ 1
              $CH_3CH_2CH_2Br + KCN \longrightarrow CH_3CH_2CH_2CN + KBr$ balanced   1
                            (or CN^-)   (or Br^-)
              (not HCN)

        Step 2 $CH_3CH_2CH_2CN + 2H_2 \longrightarrow CH_3CH_2CH_2CH_2NH_2$ 1
                     (or 4[H])

(c)   (i)   Lone pair (on N) (in correct context)   1
              R group increases electron density / donates electrons /pushes   1
              electrons / has positive inductive effect

        (ii)   Any strong acid (but not concentrated)   1
              or any amine salt or ammonium salt of a strong acid

(d) $CH_3CH_2N(CH_3)_2$ 1

                                                                                                              Total 12

Question 5

(a) (i)

$$\begin{array}{cc} H & H \\ | & | \\ -C-C- \\ | & | \\ H & CN \end{array}$$

         1

(Ignore n or brackets, but trailing bonds are essential)

    (ii)   Addition or radical   1

(b) (i)   2-aminobutanoic (acid)   1

    (ii)

$$\begin{array}{cc} & CH_2CH_3 \\ \overset{+}{H_3}N- & \overset{|}{C}-COOH \\ & \overset{|}{H} \end{array}$$

         1

(c) (i) $C_3H_4O_2$ 1

    (ii)

$$\begin{array}{ccc} HO-C-CH_2CH_2-C-OH \\ \parallel \qquad\qquad\quad \parallel \\ O \qquad\qquad\qquad O \end{array}$$

         1

(1,4-)butan(e)dioic (acid)   1
(allow succinic, but not dibutanoic nor butanedicarboxylic acid)

    (iii) Can be hydrolysed / can react with acid or base or water /   1
can react with nucleophiles

                                            Total 8

Question 6

(a)   Pentan-2-one   1

(b)   (i) $1680 - 1750$ (cm^{-1}) 1

      (ii) $3230 - 3550$ or $1000 - 1300$ (cm^{-1}) 1

      (iii)   4   1

(c)

Reagent	$K_2Cr_2O_7/H^+$	$KMnO_4/H^+$	Na	$CH_3COOH/$ H_2SO_4
with **C**	no reaction	no reaction	no reaction	no reaction
with **D**	goes green	goes colourless	effervescence	smell

1

1

1

(penalise incomplete reagent e.g. $K_2Cr_2O_7$ or $Cr_2O_7{}^{2-}/H^+$ then mark on)

(d)

Reagent	Tollens	Fehlings or Benedicts
with **E**	silver (mirror)	red ppt or goes red *(not red solution)*

1

1

Total 9

SECTION B

Question 7

X is methyl propanoate   1

M2 (left structure label)   M3 = structure

M4 = 3 arrows

M1 (left structure label)
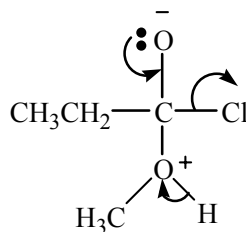
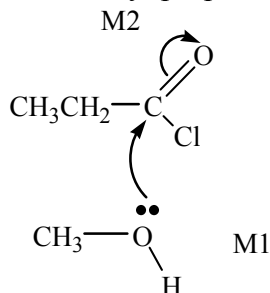M1 for arrow and lone pair,   4
M2 for arrow
addition-elimination   1

Spectrum 2   1
if thinks Spectrum 1 = X can only score for structure of Y
Y is CH_3COOCH_2CH3 1
The two marks for explanation are awarded for discussing one or more of the   2
four peaks (not those for the CH_3 of the ethyl groups)
for stated δ values the integration or the splitting should be related to the
structure: e.g. structure of **X** shows that
      at δ 3.7 – 4.1 (1) spectrum of **X** should have integration 3 / singlet (1)
or
      at δ 2.1 – 2.6 (1) spectrum of **X** should have integration 2 / quartet (1)
Spectrum 2 has these
[OR Spectrum 1 has
      at 3.7 – 4.1 (1)   quartet / integration 2 (1)   so not **X**
      at 2.1 – 2.6 (1)   singlet / integration 3 (1)   so not **X**]
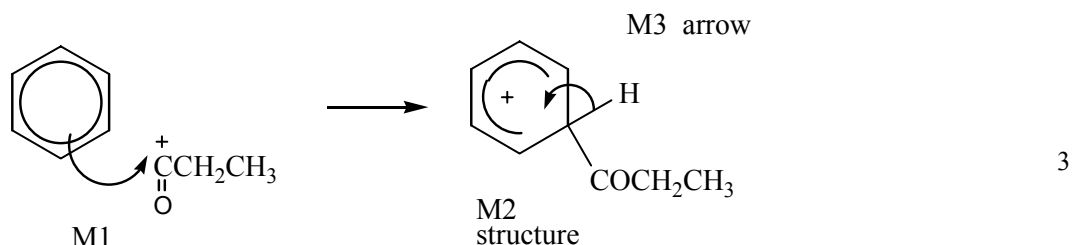
                                                                                                                    Total 10

Question 8

(a) $[CH_3CH_2CO]^+$ 1
        $CH_3CH_2COCl + AlCl_3 \longrightarrow [CH_3CH_2CO]^+ + AlCl_4^-$ 1
        (Penalise wrong arrows in the equation or lone pair on Al
        In the equation, the position of the + on the electrophile can be on O or C or
        outside square brackets,
        Can score electrophile mark in mechanism if not previously gained)

        M3 arrow

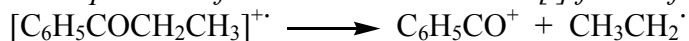   3

        (Arrow for M1 must be to C or to the + on C
        penalize + in intermediate if too close to C1 ;
        horseshoe should extend from C2 to C6)

(b) $m/z = 105$ $C_6H_5CO^+$ 1
        $m/z = 77$ $C_6H_5^+$ *(not Wheland intermediate)*   1
        (Penalise missing + once)
        Allow position of + on O or C of CO or outside [ ] for the fragment ion
        $[C_6H_5CO]^+$
        Allow position of + on H or C or outside [ ] for the fragment ion $[C_6H_5]^+$
        $[C_6H_5COCH_2CH_3]^{+\cdot} \longrightarrow C_6H_5CO^+ + CH_3CH_2{\cdot}$
        (${\cdot}$ must be on H or C of CH₂ or outside bracket)
         [1] for molecular ion   [1] for RHS   2
        Allow molecular formulae, i.e. $C_9H_{10}O^{+\cdot} \longrightarrow C_7H_5O^+ + C_2H_5{\cdot}$

(c)   Nucleophilic addition   1

        1 Q contains asymmetric carbon or chiral centre or are chiral molecules
        2 with 4 different groups/atoms attached (stated)   *not molecules attached*
        3 planar C=O
        4 attack from each side
        5 equally likely or equal amounts of each isomer formed
        6 Racemic mixture or racemate (Q of L)
        7 of mirror images or enantiomers or d/l or +/– or R/S or drawn   max 6

(d)   Conc H_2SO_4 or conc H_3PO_4 or Al_2O_3 or iron oxides   Not HCl or HBr   1
        Geometrical or cis-trans   1
        Double bond or C=C   not just π cloud *(stated not just drawn)*   1
        2 Different atoms/groups on each C (not molecules) *(stated not just drawn)*   1

                                                                                                                     Total 20