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Mark Scheme (Results)
Summer 2007

GCE

GCE Chemistry Nuffield (6254) Paper 01

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General Guidance on Marking

Examiners should look for qualities to reward rather than faults to penalise. This does NOT mean giving credit for incorrect or inadequate answers, but it does mean allowing candidates to be rewarded for answers showing correct application of principles and knowledge.

Examiners should therefore read carefully and consider every response: even if it is not what is expected it may be worthy of credit.

Crossed out work should be marked UNLESS the candidate has replaced it with an alternative response.

Using the mark scheme

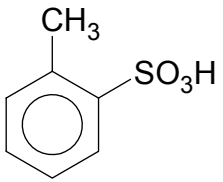
The mark scheme gives you:

- an idea of the types of response expected
- how individual marks are to be awarded
- the total mark for each question
- examples of responses that should NOT receive credit.

Candidates must make their meaning clear to the examiner to gain the mark. Make sure that the answer makes sense. Do not give credit for correct words/phrases which are put together in a meaningless manner. Answers must be in the correct context.

1 / means that the responses are alternatives and either answer should receive full credit.
2 ( ) means that a phrase/word is not essential for the award of the mark, but helps the examiner to get the sense of the expected answer.
3 [ ] words inside square brackets are instructions or guidance for examiners.
4 Phrases/words in **bold** indicate that the meaning of the phrase or the actual word is **essential** to the answer.
5 ecf/TE/cq (error carried forward) means that a wrong answer given in an earlier part of a question is used correctly in answer to a later part of the same question.

6254/01

	EXPECTED ANSWER			ACCEPT	REJECT	MARK
1.	(a)	(i)	methylbenzene/phenylmethane			**(1)**
		(ii)		Alternative substitution products with $-SO_3H$ group on other ring positions $SO_3^- H^+$ Multiple substitutions Displayed Formulae	Bonding to ring through H or O atom	**(1)**
	(b)	(i)	(conc.) nitric acid **(1)** (conc.) sulphuric acid **(1)** Mark independently	HNO_3 H_2SO_4	Incorrect formula in conjunction with name Dilute, HNO_3 (aq) H_2SO_4(aq)	**(2)**
		(ii)	NO_2^+		$NO_2^{\delta+}$	**(1)**
	(c)	(i)	Substitution **(1)** Electrophilic / electrophile **(1)**	Either way round	Incorrect type or mechanism in conjunction with correct response	**(2)**
		(ii)	the ring is more susceptible to attack by electrophiles/ more nucleophilic/ ring has greater electron density **(1)** as methyl group pushes electrons into ring/ toluene has a dipole moment **(1)**			**(2)**
	(d)	Oxidation		Partial oxidation	Redox Full oxidation	**(1)**

	EXPECTED ANSWER		ACCEPT	REJECT	MARK
	(e)	sodium/ potassium dichromate((VI)) **(1)** sulphuric acid **(1)** or Potassium manganate ((VII)) **(1)** Sulphuric acid **(1)**	$Na_2Cr_2O_7$/ $K_2Cr_2O_7$ H_2SO_4 dil. or conc. 'acidified dichromate' = 1 or $KMnO_4$ H_2SO_4 'acidified manganate' = 1 OR Potassium manganate ((VII)) **(1)** Sodium hydroxide **(1)**	Incorrect oxidation numbers Incorrect Formula in conjunction with correct name	**(2)**

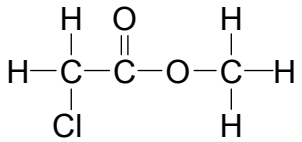
	EXPECTED ANSWER		ACCEPT	REJECT	MARK
	(f)	**Test:** (Heat with) Benedicts solution **(1)** Fehlings Solution **Result with benzaldehyde:** red (ppt) **(1)** **Result with benzoic acid:** remains blue **(1)** } Dependant on 1st mark OR **Test:** Add Brady's Reagents/2,4 dinitrophenylhydrazine **(1)** **Result with benzaldehyde** : orange/yellow **ppt (1)** **Result with benzoic acid:** remains orange (solution) **(1)** } Dependent on 1st mark OR **Test:** Add sodium carbonate **solution /**sodium hydrogencarbonate solution **(1)** **Result with benzaldehyde:** no gas evolved **(1)** **Result with benzoic acid**: bubbles of (colourless) gas evolved **(1)**	green/ yellow/ brown/ orange Tollens Regent: Result with benzaldehyde : silver ppt Results with benzoic acid : stays colourless orange-red Na_2CO_3 **(aq)** If a test is carried out with an insoluble carbonate then 1 max if its clearly added to benzoic acid **solution**	red 2,4 DNP no reaction no change Test with litmus/UI or other acid-base indicators	**(3)**
					Total 15 marks

	EXPECTED ANSWER			ACCEPT	REJECT	MARK
2.	(a)	measuring the time taken **(1)** for the potassium manganate(VII) to become colourless/go brown **(1)** OR measuring the time taken **(1)** for a measured volume of CO_2 to be collected **(1)** OR Take sample at a given time **(1)** (Quench and) titrate with $Fe^{2+}(aq)$ **(1)**		measuring the time taken for the potassium manganate(VII) to change colour = 1 Other suitable reducing agents		**(2)**
	(b)	(i)	Glucose = 0 **(1)** potassium manganate (VII) = 1 - because when the concentration of (potassium manganate (VII)) doubles so does the rate/because the rate in experiment 1 is double the rate in experiment 2 (and $[KMnO_4^-]$ is double but $[C_6H_{12}O_6]$ and $[H^+]$ are constant) **(1)** hydrogen ions = 1 because order wrt $[MnO_4^-]$ = 1 so when $[MnO_4^-]$ & $[H^+]$ double, rate is quadrupled / when $[Mn0_4^-]$ is quadrupled and $[H^+]$ is doubled rate goes up by a factor of 8 OWTTE **(1)**			**(3)**
		(ii)	rate = $k[MnO_4^-][H^+]$ OR rate = $k[KMn0_4][H^+]$	correct names expressions including $[C_6H_{12}O_6]^0$ TE from (b)(i)		**(1)**

	EXPECTED ANSWER			ACCEPT	REJECT	MARK
		(iii)	4×10^{-3} **(1)** $dm^3\ mol^{-1}\ s^{-1}$ **(1)** unit mark independent of 1st mark but must be consistent with rate equation	 units in any order allow TE from (b)(i) & (b) (ii)		**(2)**
	(c)	(i)	3.22×10^{-3} -4.00 both needed for the mark	0.00322 -4		**(1)**
		(ii)	labelled axes including units and sensible scale **(1)** correct plotting of points and line of best fit **(1)**		$/10^{-3}$	**(2)**
		(iii)	gradient = - 10823(K) **(1)** Ea = 10823 x 8.31 = + 89939 J mol^{-1} = (+) 90 **kJ mol^{-1}** / (+) 90 000 **J mol^{-1}** **(1)**	gradient range = -11200 to -10400 TE from gradient to Ea (+) 93 to (+) 86 kJ mol^{-1} but must be consistent with gradient		**(2)**
						Total 14 marks

	EXPECTED ANSWER			ACCEPT	REJECT	MARK
3.	(a)	(i)	[6 x 188.7 + 4 x 210.7] – [4 x 192.3 + 5 x 205] **(1)** +180.8 J mol^{-1} K^{-1} **(1)** -1 for missing + sign/missing or incorrect units but penalise only once in part (a) [IGNORE sig fig]	+181 J mol^{-1} K^{-1}	Internal TE	**(2)**
		(ii)	yes, as **9 molecules of gas** are being changed to **10 molecules of gas** (therefore increase in disorder)	TE from (i)	Not just 9 molecules going to 10 molecules	**(1)**
		(iii)	--905.6 x 1000 /1123 **(1)** + 806.4 J mol^{-1} K^{-1} / 0.8064 kJ $mol^{-1}K^{-1}$ **(1)** [IGNORE SF]	+ 806 J mol K^{-1}		**(2)**
		(iv)	+987.2 J mol^{-1} K^{-1}	+987 J mol^{-1} K^{-1} allow TE from (i) & (iii)	No TE if J mol^{-1} K^{-1} added to kJ $mol^{-1}K^{-1}$	**(1)**
		(v)	All products/reaction goes to completion because ΔS_{tot} > 200 J $mol^{-1}K^{-1}$/ΔStot is **very** large [Needs to be consistent with (iv)]			**(1)**
		(vi)	catalysed pathway should have lower E_a than uncatalysed pathway and the peak of the curve should be above the energy level of the reactants **(1)** Energy of products should be lower than energy of reactants **(1)**			**(2)**

	EXPECTED ANSWER			ACCEPT	REJECT	MARK
	(b)	(i)	$K_p = \frac{pNO_2^{\,2}}{pNO^2 \times pO_2}$	$\frac{p^2NO_2}{p^2NO \times pO_2}$	**[ ]**	**(1)**
		(ii)	mole fraction NO_2 = $\frac{4.95}{5}$ or 0.99 **(1)** mole fraction NO = $\frac{0.025}{5}$ or 0.005 OR mole fraction O_2 = $\frac{0.025}{5}$ or 0.005 **(1)** $K_p = \frac{(0.99)^2\,(1.5)^2}{(0.005)^3\,(1.5)^3}$ = 5227200 / 5.2 x 10^6 **(1)** atm^{-1} **(1)** unit mark independent but consistent with expression used in calculation. IGNORE SF	Correct answer for K_p alone = 3 max		**(4)**
		(iii)	Equilibrium lies to RHS/products side as K_p is large OR reaction won't go to completion as $K_p < 10^{10}$ Must be consistent with (ii)	Allow TE from b(ii)		**(1)**
		(iv)	K_p remains unchanged as pressure does not affect it / only temperature affects K_p **(1)** partial pressure of NO_2 increases as eqm moves to side of fewest (gas) molecules/RHS **(1)** or Partial pressure of NO_2 increases as pp = mole fraction × total pressure	justification in terms of entropy		**(2)**
						Total 16 marks

	EXPECTED ANSWER			ACCEPT	REJECT	MARK
4.	(a)	(i)	$K_a = \frac{[CH_2ClCO_2^-][H^+]}{[CH_2ClCO_2H]}$	$[H_3O^+]$ in place of $[H^+]$ allow one set of sq brackets to be missing		**(1)**
		(ii)	$[H^+]^2 = 1.3 \times 10^{-3} \times 0.001$ **(1)** $= 1.3 \times 10^{-6}$ $[H^+] = \sqrt{1.3 \times 10^{-6}}$ 1.14×10^{-3} **(1)** pH = - log 1.14×10^{-3} = 2.9(4) **(1)** [IGNORE SF]			**(3)**
		(iii)	Trichloroethanoic, as it has the largest K_a value **(1)** and has (3 electron withdrawing) chlorine atoms to stabilise the anion formed (on dissociation). **(1)**			**(2)**
	(b)	(i)	 ester group **(1)** rest of molecule **(1)** dependent on first mark (must be fully displayed) methyl chloroethanoate **(1)**		No transferred error for name	**(3)**

	EXPECTED ANSWER			ACCEPT	REJECT	MARK
		(ii)	ester(s)		ether	**(1)**
		(iii)	nucleophile, **(1)** as it has a lone pair (of electrons) on the (hydroxyl) oxygen **(1)** which can attack the **positive carbonyl carbon** on the acid **(1)**	2nd and 3rd marks could be obtained by use of a diagram	Attack by CH_3O^-	**(3)**
		(iv)	(reflux) heat with NaOH(aq) **(1)** (cool) and add HCl(aq) **(1)** OR reflux **(1)** [must be in context] with HCl **(1)**			**(2)**
						Total 15 marks