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Mark Scheme (Results)
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GCE

GCE Chemistry Nuffield (6254) Paper 1

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General Marking Guidance

- All candidates must receive the same treatment. Examiners must mark the first candidate in exactly the same way as they mark the last.
- Mark schemes should be applied positively. Candidates must be rewarded for what they have shown they can do rather than penalised for omissions.
- Examiners should mark according to the mark scheme not according to their perception of where the grade boundaries may lie.
- There is no ceiling on achievement. All marks on the mark scheme should be used appropriately.
- All the marks on the mark scheme are designed to be awarded. Examiners should always award full marks if deserved, i.e. if the answer matches the mark scheme. Examiners should also be prepared to award zero marks if the candidate's response is not worthy of credit according to the mark scheme.
- Where some judgement is required, mark schemes will provide the principles by which marks will be awarded and exemplification may be limited.
- When examiners are in doubt regarding the application of the mark scheme to a candidate's response, the team leader must be consulted.
- Crossed out work should be marked UNLESS the candidate has replaced it with an alternative response.

Using the mark scheme

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.

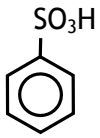
Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1.(a)	$\Delta S^{\ominus}_{system}$ = [202.9 + 2x192.3] – [99.7 + 2x94.6] = 587.5 – 288.9 = +299 J mol^{-1} K^{-1} Value **(1)** sign & units **(1)** Allow TE for internal error only if a failure to double one or both of the two energies: i.e. +106/+106.3 J mol^{-1} K^{-1} +393/+393.2 J mol^{-1} K^{-1} +201/+200.9 J mol^{-1} K^{-1} **(1 max)**	+298.6 J mol^{-1} K^{-1} **(2)** Correct answer with no working **(2)**	No credit for answer based on an inverse subtraction, i.e. -299/-298.6 J mol^{-1} K^{-1}	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1.(b)	$\Delta S^{\ominus}_{surroundings}$ = – ΔH/T or –21200/298 **(1)** = –71.1 J mol^{-1} K^{-1} **(1)** Only penalise units once in (a) & (b) Allow **one minor** slip in units, e.g. J mol^{-} K^{-1}	Correct answer with no working **(2)** -0.0711 kJ mol^{-1} K^{-1}	All other values	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1.(c)(i)	$\Delta S^{\ominus}_{total}$ = (+)227.5 (J mol^{-1} K^{-1}) / answer to (a) plus answer to (b), provided that value is positive. Since value is positive, (reaction is spontaneous) Must do the arithmetic **Both needed for the mark**	Rounded value e.g. (+)228 J mol^{-1} K^{-1} $\Delta S^{\ominus}_{system}$ is large and +ve $\Delta S^{\ominus}_{surroundings}$ is small and -ve so $\Delta S^{\ominus}_{total}$ must be positive (and reaction is spontaneous)	Any negative number	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1.(c)(ii)	Activation energy must be high / reaction must be kinetically hindered/reaction doesn't have to be fast	Poor contact between solids Few/no collisions between particles	ΔH is positive, so heat is needed to start the reaction	1

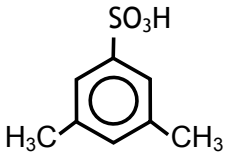
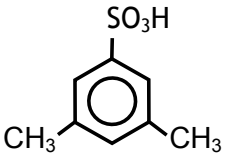
Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1.(c)(iii)	Dissolve solid(s) in water/solvent (before "mixing") **(1)** Particles/ions/"molecules" (**not** atoms) become mobile, so increasing chance of collisions, (hence interactions) **(1)** **mark independently**	Grind into a (fine) powder Which increases surface area so **improves chance of collisions**	Use of a catalyst	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2.(a)(i)	 Bond from benzene ring must be to the <u>sulphur</u> atom Hydrogen atom must be linked to oxygen	$C_6H_5SO_3H$ $C_6H_5SO_2OH$	$C_6H_5HSO_3$	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2.(a)(ii)	Fuming sulphuric acid / oleum / sulphur trioxide / SO_3 / sulphur trioxide or SO_3 in sulphuric acid	Concentrated sulphuric acid / $H_2S_2O_7$	H_2SO_4 / H_2SO_4(aq) / sulphuric acid / dilute sulphuric acid	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2.(a)(iii)	(aromatic) Electrophilic substitution	Electrophillic / Electrophylic / Eletrophilic substitution	Electrophic substitution	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2.(a)(iv)	SO_3/ SO_3H^+ Ignore name if given with formula	HSO_3^+	Sulphur trioxide / SO_3^+ / SO_3^-	1

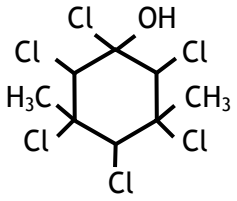
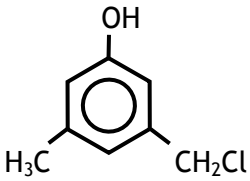
Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2.(b)(i)	 Allow TE from 2(a)(i)	 Formula for 2,6-dimethyl benzene sulphonic acid		1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2.(b)(ii)	Reagent X: CH_3Cl **(1)** Catalyst Y: $AlCl_3$ **(1)** Allow TE from (b)(i) e.g. CH_3CH_2Cl if an ethylbenzene	CH_3Br / CH_3I **(1)** Al_2Cl_6/$AlBr_3$/AlI_3**(1)** **One correct name and one correct formula (2)** Names for <u>both</u> answers **(1 max)**		2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2.(b)(iii)	Hydrogen chloride / HCl	Answer consequential on (b)(ii), e.g. HBr	Hydrochloric acid	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2.(c)(i)	It contains a phenol group	OH attached to benzene ring / phenyl OH group It is **a** phenol	hydroxyl / OH / alcohol / hydroxide / OH^- It is phenol It contains a phen**yl** group	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2.(c)(ii)	Water / H_2O	Named alcohol/ any named metal hydroxide or correct formula		1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2.(c)(iii)	 Ring hydrogen atoms may be included Must be complete addition of Cl_2 to the ring (as above) OR substitution in the methyl groups OR both	 Allow any further substitution into the methyl groups	Substitution of Cl_2 into ring	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2.(d)(i)	4-chloro-3,5-**di**methylphenol 3,5-**di**methyl-4-chlorophenol	Accept no/wrong punctuation Allow name based on hydroxybenzene Allow "cloro" or "methly"		1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2.(d)(ii)	Hydrogen bonding interactions between dettol and water are weaker than those between water molecules OR Hydrogen bonding interactions between dettol and water are weaker thatn the van der Waals' forces in dettol Look for good use of scientific language. Answer must include a specific type of intermolecular force	Hydrogen bonding between dettol and water is weak Dettol can only form **one** H-bond with water/only has **one** OH group to H-bond with water	Dettol molecule is too big Arguments based on lone pairs of electrons on OH group being delocalised into the ring	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3.(a)(i)	Hydroxide ions / OH^- / OH^- (aq)		Sodium hydroxide /NaOH	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3.(a)(ii)	**A**: $\frac{8.0 \times 10^{-4}}{33}$ = 2.4(2)×10^{-5} (mol dm^{-3} s^{-1}) **(1)** **B**: $\frac{8.0 \times 10^{-4}}{16}$ = 5.0(0)×10^{-5} (mol dm^{-3} s^{-1}) **(1)**			2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3.(a)(iii)	(Comparing **A** and **B**), rate (approximately) doubles/time halves when concentration (of 2-bromo-2-methylpropane) doubles, so reaction is 1st order (wrt 2-bromo-2-methylpropane)		Because $[C_4H_9Br] \propto$ rate of reaction OR there is a steady increase in rate when $[C_4H_9Br]$ increases/is doubled	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3.(a)(iv)	(Rate of reaction in **B** = 5.0 × 10^{-5} mol dm^{-3} s^{-1}) Rate of reaction in **C** = 1.2 × 10^{-3} /24 = 5.0 × 10^{-5} (mol dm^{-3} s^{-1}) **(1)** Focus on the value 5.0 x 10^{-5} for 1st mark (Comparing **B** and **C**), rate remains <u>constant</u> when concentration of NaOH changes (by 50 %), so reaction is **zero order** wrt NaOH **(1)** **Mark independently**	Rate for C calculated to be the same as that calculated for **B** in (a)(ii)		2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3.(a)(v)	Rate = k$[CH_3C(Br)(CH_3)CH_3]^{(1)}$ $([OH^-]^0)$ Allow transferred error, but answer must be consistent with (iii) & (iv) **Look for inclusion of rate constant, k**	$[NaOH]^0$ instead of $[OH^-]^0$ Rate = k$[C_4H_9Br]^{(1)}([OH^-]^0)$		1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3.(a)(vi)	slow $CH_3C(Br)(CH_3)CH_3 \longrightarrow CH_3C^+(CH_3)CH_3 + Br^-$ **(1)** Positive charge must be on carbon shown (fast) $CH_3C^+(CH_3)CH_3 + OH^- \rightarrow CH_3C(OH)(CH_3)CH_3$ **(1)** Identification of the rate determining step/RDS **(1)** Only allow this S_N1 mechanism if consistent with 1st order reaction in (a)(v)	$CH_3C^+(CH_3)CH_3 + H_2O \longrightarrow CH_3C(OH)(CH_3)CH_3 + H^+$ Allow S_N2 mechanism **consequential on 2nd order rate equation in** (a)(v): OH^- attacks C-Br forming C-OH as C-Br breaks to form Br^-, Or can be shown in diagram, e.g. with transition state using dotted bonds or with curly arrows in one concerted step **(max 2)**		3

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3.(b)	1-bromobutane is a primary halogenoalkane / 2-bromo-2-methylpropane is a tertiary halogenoalkane **(1)** Primary carbonium ion intermediate cannot easily be stabilised / tertiary carbonium ion intermediate can be stabilised **(1)** **Mark independently**	Arguments based on relative activation energies of formation of primary vs tertiary carbonium ion intermediates / steric hindrance in the tertiary compound		2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4.(a)(i)	$K_p = \frac{(p_{NO})^2}{p_{N_2} \times p_{O_2}}$ Allow answer with brackets and/or "x" omitted Ignore (g) and eq	$K_p = \frac{p^2_{NO}}{p_{N_2} \times p_{O_2}}$	Anything in [ ]	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4.(a)(ii)	Same number of moles on each side of the equation OR The (partial pressure) units all cancel out (in the expression for K_p)			1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4.(b)(i)	$(p_{NO})^2 = 0.87 \times 0.23 \times 5.0 \times 10^{-31}$ **(1)** $= 1.0 \times 10^{-31}$ $p_{NO} = \sqrt{(1.0 \times 10^{-31})}$ $= 3.2 \times 10^{-16}$ (atm) **(1)** Ignore sig fig Mark consequentially only if based on reciprocal of correct expression in (a)(i)	3.16×10^{-16} (atm) **(1)**		2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4.(b)(ii)	$0.87 + 0.23 (+ 3.2 \times 10^{-16}) = 1.10 / 1.1$ (atm) Allow TE from (b)(i)		Answer based on adding **2 x** p_{NO}	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4.(b)(iii)	p_{NO} doubles/will become 6.4×10^{-16} atm **(1)** K_p remains constant/is (still) 5.0×10^{-31} **(1)** Ignore any "neutral" qualifications to these answers	p_{NO} will increase	More than double Answers with incorrect reasoning	2

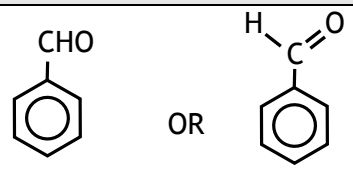
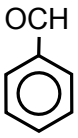
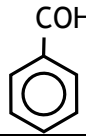
Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4.(c)(i)	Reaction will occur, but (very) **little** NO is formed OR the equilibrium mixture is mainly (unreacted) N_2 and O_2	Reaction occurs, but equilibrium lies (very much) to the left	"Reaction is more likely to occur from right to left" OR "Reverse reaction is favoured", unless included with acceptable answer	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4.(c)(ii)	No change of state of any of the components is involved (as the gases are heated up) OWTTE OR All components are gases (at these temperatures) IGNORE Any reference to the number of particles involved			1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4.(c)(iii)	(Δ*H* is positive so) $-\frac{\Delta H}{T} = \Delta S_{surroundings}$ will be negative No mark for "negative" alone	Negative, since for an endothermic reaction energy is taken from the surroundings causing a decrease in disorder / reduction in entropy		1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4.(c)(iv)	(As T increases) $\Delta S_{surroundings}$ becomes greater/less negative/more positive, so ΔS_{total} (also) becomes greater/less negative/more positive/increases	$\Delta S_{surroundings}$ becomes "smaller", <u>if qualified</u>, e.g. becomes closer to zero		1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4.(d)	Equilibrium might not have been reached (in the very short time the gases are present in the engine) Ignore references to the fact that the system is not "closed"	Other gases are present in the air (apart from N_2 and O_2) Temperature inside engine may be <u>less</u> than 1500K Actual (total) pressure may be less than that assumed		1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
5.(a)(i)	 OR	C_6H_5CHO 	If bond from benzene ring points clearly to H or O  C_6H_5COH	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
5.(a)(ii)	Sodium/potassium dichromate((VI)) **(1)** Oxidation number not needed, but if given must be correct (concentrated/dilute) Sulphuric acid **(1)** In each case, correct name, but incorrect formula (**0**) **Mark independently**	$Na_2Cr_2O_7$ / $K_2Cr_2O_7$ H_2SO_4	 Hydrochloric acid	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
5.(b)	The carboxyl group/$C^{\delta+}$ must **deactivate** (the ring) / **draw electrons** (from the ring) **(1)** The ring is less reactive/negative towards **electrophiles / NO_2^+ (1)** **Mark independently**	Electrons are pulled towards the oxygen(s) (of COOH group)	Carbon atom of COOH group deactivates the ring, unless qualified	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
5.(c)(i)	$C_6H_5CO_2Na$: Sodium hydroxide/sodium carbonate/Sodium hydrogencarbonate (solution) **(1)** $C_6H_5CO_2CH_3$: Methanol **(1)** (Concentrated) sulphuric acid **(1)** **Mark all chemicals independently** If a choice is given in each case, then all must be correct	$NaOH/Na_2CO_3/ NaHCO_3$ ((aq)) Sodium/Na/sodium oxide/Na_2O CH_3OH H_2SO_4 Hydrochloric acid / HCl	 Any <u>dilute</u> acid	

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
5.(c)(ii)	Sodium benzoate is a solid / has a higher mpt/bpt / has no smell, whereas methyl benzoate is a liquid / has a smell OR Sodium benzoate is likely to be soluble in (hot) water, whereas methyl benzoate is probably only sparingly soluble **(1)** **Must be a comparison for 1st mark** Sodium benzoate is ionic/contains ionic bonds, (whereas methyl benzoate is covalent) OR Methyl benzoate is covalent, (whereas sodium benzoate is ionic/contains ionic bonds) **(1)** **Mark independently**	Sodium benzoate has a high**er** mpt/bpt Sodium benzoate is **more** soluble in (hot) water	Answers based on IR spectra	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
5.(c)(iii)	Delocalisation occurs / charge spread out with the carboxylate ion / CO_2^- (but not with the covalent linkage) **(1)** Illustration with two appropriate diagrams i.e.  **(1)** **(**no need to show that C=O is shorter than C-O)	If diagram not given for methyl benzoate, answer should say that C=O is different from / shorter than C-O		2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
5.(d)	$[C_6H_5CO_2H]$ = ($^1/_5$ x 0.010 =) 0.002(0) mol dm^{-3} $[C_6H_5CO_2^-]$ = ($^4/_5$ x 0.020 =) 0.016 mol dm^{-3} Both correct **(1)** $[H^+]$ (= K_a x $[C_6H_5CO_2H]$ / $[C_6H_5CO_2^-]$ = 6.3 x 10^{-5} x 0.0020 / 0.016) = 7.875 x 10^{-6} **(1)** Do not penalise SF for the first two marks pH = -log$[H^+]$ = 5.1 / 5.10 **(1)** Mark for final answer must be dependant on valid working e.g. correct [acid]/[base] ratio. Correct answer with no working **(1)**	pK_a = 4.20 **(1)** $\frac{0.002}{0.016}$ **(1)** pH = (4.20 + 0.90) = 5.1 / 5.10 **(1)** **Allow internal TE** e.g. an $^{[acid]}/_{[base]}$ ratio of $^{0.010}/_{0.020}$ leads to a pH of 4.50 **(2)**	5.104 or 5 1 or >3 sig.fig.	3