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Mark Scheme (Results)
January 2007

GCE

GCE Chemistry (Nuffield) (6254/01)

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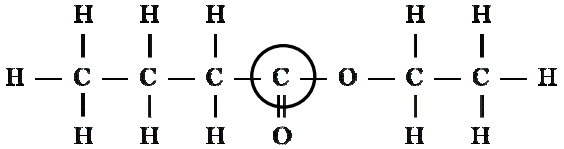
1.	(a)	(i)	NO_2 is a gas (whereas BaO is a solid) **(1)** $Ba(NO_3)_2$ has a more complicated structure than BaO **(1)** Allow 2nd mark if a correct statement is combined with a "neutral" wrong statement	$Ba(NO_3)_2$ "molecule" has more electrons / is larger than BaO "molecule" **(1)** More atoms/ions/particles More complicated/complex compound	$Ba(NO_3)_2$ has a larger molar mass than BaO More molecules/elements	**(2 marks)**
		(ii)	$\Delta S^{\ominus}_{system}$ = 70.4 + (2×240.0) + (½×205.0) — 213.8 **(1)** = +439.1 J mol^{-1} K^{-1} **(1)** -1 per error	+439 J mol^{-1} K^{-1} J/ mol /K		**(2 marks)**
	(b)		$\Delta S^{\ominus}_{surroundings}$ = $-\frac{\Delta H}{T}$ **(1)** = $-\frac{505\times1000}{298}$ = — 1700 J mol^{-1} K^{-1} (3 s.f.) **(1)** Penalise wrong units in (a)(ii) and (b) once only	—1690 J mol^{-1} K^{-} —1695 J mol^{-1} K^{-1} Answers in kJ mol^{-1} K^{-1}	—1694 J mol^{-1} K^{-1} —1694.6 J mol^{-1} K^{-1} —1694.63 J mol^{-1} K^{-1}	**(2 marks)**
	(c)		$\Delta S^{\ominus}_{total}$ = +439.1 — 1695 = — 1260 (J mol^{-1} K^{-1}) **(1)** *Allow TE [follow through working from (a)(ii) and (b)]* Mark consistently with (a)(ii) and (b) The reaction isn't spontaneous / doesn't "go" (at 298K) **(1)** Must be consistent with sign in calculation	—1256 J mol^{-1} K^{-1} —1261 J mol^{-1} K^{-1} —1255.5 J mol^{-1} K^{-1}		**(2 marks)**
	(d)		When just spontaneous, $\Delta S^{\ominus}_{total}$ = 0 or implied by calculation i.e 505 OR 505000 a(ii) **(1)** $\Rightarrow$ $\Delta S^{\ominus}_{surroundings}$ = —439.1 J mol^{-1} K^{-1} $\Rightarrow$ T = $\frac{505\times1000}{439.1}$ = 1150 (K) **(1)** ignore ^{0}K Allow full marks for an answer without working	1150.1 K 877 °C 1151K with no working (1 max)	1151K for 2nd mark any negative value for T (in K): no 2nd mark 1150^{0}C	**(2 marks)**
						(Total 10 marks)

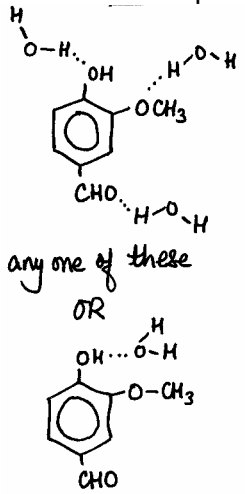
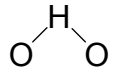
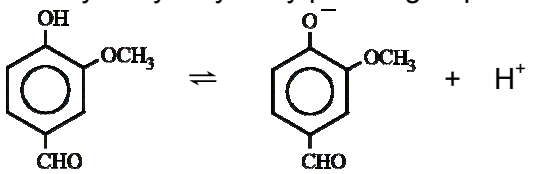
2.	(a)	Yellow/orange solid/precipitate/crystals formed			Red	**(1 mark)**
	(b)	**F** : $CH_3CH(CH_3)CHO$ **(1)** **G** : $CH_3CH_2COCH_3$ **(1)** **H** : e.g. $CH_2(=)CHCH_2CH_2OH$ **(1)**		**H** : other alkenols and cyclic alcohols, e.g. cyclobutanol / correct enols / cyclic ethers **(1)** Allow displayed formulae		**(3 marks)**
	(c)	(i)	Prevents **reagents**/**products** from **boiling**/**volatilising** /**evaporating** away/being lost to the surroundings Reactants have greater chance of reacting since they condense and rejoin the mixture	Reduces the risk of fire; **(1)** Prevents potentially harmful vapours from entering the lab **(1)**		**(1 mark)**
		(ii)	Ethyl butanoate			**(1 mark)**
		(iii)	Ethanol **(1)** Sodium butanoate **(1)**	T.E. from (ii)	Butanoic acid	**(2 marks)**
		(iv)	Hydrolysis / saponification		Hydration	**(1 mark)**
		(v)	 **(1)** The carbon atom is (electrophilic, since it is) attached to (two) oxygen atom(s) which draw away its electron density **(1)** OWTTE	(the C=O/C—O bond is polarized) with $\delta+$ charge on carbon **(1)** (providing the "carbon" is obviously referring to the carbonyl carbon)	Carbon 'molecule' oxygen 'molecule'	**(2 marks)**
						(Total 11 marks)

3.	(a)	(i)	$(5.0/1000) \times 0.010 = 5.0 \times 10^{-5}$ (mol)			**(1 mark)**
		(ii)	½ × 5.0×10^{-5} = 2.5×10^{-5} (mol) **(1)** TE from (i)			**(1 mark)**
		(iii)	$2.5 \times 10^{-5} \times (1000/40.0) = 6.25 \times 10^{-4}$ mol dm^{-3} **(1)** $6.25 \times 10^{-4} / 5 = 1.25 \times 10^{-4}$ (mol dm^{-3} s^{-1}) **(1)** Allow T.E.	(ii) X5: 2 marks (ii) ÷5: 1st mark		**(2 marks)**
	(b)	(i)	First			**(1 mark)**
		(ii)	First **(0)** Comparing experiments 2& 3 $[I^-]$ doubles, so from (b)(i) rate should also double yet rate is 6 times greater, so extra trebling of rate must be caused by trebling of $[S_2O_8^{2-}]$ ⇨ Rate ∝ $[S_2O_8^{2-}]^1$ **(1)** Or other valid argument			**(1 mark)**
		(iii)	Rate = k $[S_2O_8^{2-}]$ $[I^-]$ **(1)**	T.E. from (i) + (ii)		**(1 mark)**
		(iv)	k = rate / ($[S_2O_8^{2-}]$ $[I^-]$) = $2.74 \times 10^{-5} / (0.01 \times 0.02)$ = $\underline{0.137\ dm^3\ mol^{-1}\ s^{-1}}$ numerical answer (1) units (1) Mark independently	T.E. from (iii)		**(2 marks)**
						(Total 9 marks)

4.	(a)	(i)	pH = 3.5 **(1)** $\log_{10}[H^+] = -3.5$ $\Rightarrow [H^+] = 3.16 \times 10^{-4}$ (mol dm^{-3}) **(1)** 2.5(1)x10^{-4} (mol dm^{-3}) based on pH=3.6 (2 marks)	T.E. from wrong pH providing < 7 3.2X10^{-4} (mol dm^{-3}) 3X10^{-4}(mol dm^{-3}) allowed if evidence of rounding being applied		**(2 marks)**
		(ii)	$K_a = \frac{[H^+][CH_3CH_2CH_2CO_2^-]}{[CH_3CH_2CH_2CO_2H]}$ **(1)**	Accept version with $[H_3O^+]$ Molecular formulae $\frac{[H^+]\,[C_4H_7O_2^-]}{[C_4H_8O_2]}$		**(1 mark)**
		(iii)	$K_a = \frac{[H^+]^2}{[CH_3CH_2CH_2COOH]}$ **(1)** $= \frac{(3.16\times10^{-4})^2}{0.00660}$ (1^{st} mark can be scored here) $= 1.5 \times 10^{-5}$ (mol dm^{-3}) **(1)** Ignore units Only 2 sig. fig. allowed	TE from (i) Allow any number of s.f. provided consistent with calculation	TE from (ii)	**(2 marks)**
	(b)	(i)	$CH_3CH_2CH_2CO_2H$ ((aq)) + NH_3 ((aq)) → $CH_3CH_2CH_2CO_2(^-)NH_4(^+)$ ((aq)) Molecular formulae acceptable	eqn via NH_4OH $\rightarrow CH_3CH_2CH_2CO_2^- + NH_4^+$	Any amide product	**(1 mark)**
		(ii)	Ammonium butanoate **(1)** (Excess) butanoic acid **(1)** no TE from (b)(i)	Ammonium ions and butanoate ions (1)	Butanoate ions alone Formulae	**(2 marks)**
		(iii)	A buffer (mixture) **(1)** There is a relatively small **rise /change in pH** (as aqueous ammonia is added) OWTTE **(1)** Mark independently		Sharp neutralisation point/**no** change in pH	**(2 marks)**
		(iv)	There is no large increase in pH / vertical shape to the graph (at the end-point) OWTTE	No sudden change in pH	No indicator has the required pH range	**(1 mark)**

		(v)	EITHER End-point = 30 cm^3 **(1)** $\Rightarrow$ $[NH_3] = (10/30) \times 0.00660 = 0.00220\ (mol\ dm^{-3})$ **(1)** OR 10 cm^3 of butanoic acid contain 6.60×10^{-5} mol From equation this requires 6.60×10^{-5} mol NH_3 From graph, end-point = 30 cm^3 **(1)** $\Rightarrow$ $[NH_3] = 6.60 \times 10^{-5} \times (1000/30)$ $= 2.20 \times 10^{-3}$ / 0.00220 (mol dm^{-3})**(1)** Allow internal TE for 2nd mark based on an incorrect equivalence point i.e. $\frac{0.0660}{V}$ (mol dm^{-3})	Allow T.E. from (b)(i)		**(2 marks)**
						(Total 13 marks)

5.	(a)	(i)	Conc(entrated) / fuming sulphuric acid / sulphur trioxide / SO_3 **(1)**	Oleum **(1)**	Sulphuric acid / H_2SO_4	**(1 mark)**
		(ii)	Substitution **(1)** Electrophilic **(1)**			**(2 marks)**
	(b)	(Warm) with a lump of sodium **(1)** Effervescence with 2-methoxyphenol (but not with methoxybenzene) **(1)** **OR** Add NaOH **(1)** 2-methoxyphenol more "soluble" in NaOH(aq) /Seen to dissolve /legitimate use of indicator to follow neutralisation **(1)** **OR** Add $FeCl_3$(aq) /Fe^{3+}(aq) **(1)** Purple coloration with 2-methoxyphenol **(1)** In all cases 2nd mark dependent on 1st		Dissolve in water & measure pH; pH<7 for the phenol **(1 max)** 2-methoxyphenol forms a salt/ is neutralised by Na0H (1 max) Only 2-methoxyphenol decolourises Br_2(aq) (1 max) Only 2-methoxyphenol reacts with $HN0_3$(aq) to give a coloured mixture (1 max)	Na_2 CO_3 (0) IR spectroscopy	**(2 marks)**

	(c)	(i)	$C_8H_8O_3$			**(1 mark)**
		(ii)	Opportunities for hydrogen bonding exist **(1)**; diagram shown with intermolecular bonding between H of water molecule and O of phenol/methoxy/carbonyl group or O of water and H of phenol group  any one of these OR Intermolecular bonding must not be shown as a Solid Line **(1)**	H-bonding	Any illegitimate hydrogen bonding (e.g. to methyl group) even if in combination with correct hydrogen bonding 	**(2 marks)**
		(iii)	The hydroxyl / hydroxy/phenol group/ OH /–OH (group) **(1)**  Organic ionic product can show negative change delocalised over whole structure Allow molecular formulae **(1)**	Bronsted-Lowry version involving H_2O and H_3O^+; Allow → instead of ⇌ Allow equation where vanillin is neutralised by an alkali / OH^- ions	Hydrox**ide** group Alcohol group OH^-/ ^-OH	**(2 marks)**

	(d)	(i)	To avoid losing too much vanillin (in the filtrate when crystallisation occurs) OWTTE	To maximise the yield	Answer only referring to saturation	**(1 mark)**
		(ii)	Insoluble impurities removed by **hot**/ **first** filtration **(1)** Soluble impurities remain in solution **(1)**			**(2 marks)**
		(iii)	Measure mpt **(1)** Compare with data OR sharp melting point **(1)**	bpt. method can only score 2nd mark		**(2 marks)**
	(e)	Vanillin is likely to be a product since …….. IR spectrum of product shows an absorption for aldehyde C=O stretching /vibration **(1)**… …… at about 1740-1720 cm^{-1} /any value within this range **(1)** (This is absent in the 2-methoxyphenol IR spectrum)				**(2 marks)**
						(Total 17 marks)