

Markscheme

May 2019

Chemistry

Higher level

Paper 2

18 pages

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Question			Answers	Notes	Total
1.	a		$\text{C}_2\text{H}_2(\text{g}) + 2.5\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$ OR $2\text{C}_2\text{H}_2(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ ✓		1
1.	b	i	$\text{H:C}\equiv\text{C:H}$ / $\text{H}-\text{C}\equiv\text{C}-\text{H}$ ✓	Accept any valid combination of lines, dots and crosses.	1
1.	b	ii	«ethyne» shorter AND a greater number of shared/bonding electrons OR «ethyne» shorter AND stronger bond ✓		1
1.	b	iii	London/dispersion/instantaneous dipole-induced dipole forces ✓	<i>Do not accept just “intermolecular forces” or “van der Waals’ forces”.</i>	1
1.	c	i	ethanal ✓		1
1.	c	ii	«sum of bond enthalpies of reactants =» $2(\text{C-H}) + \text{C}\equiv\text{C} + 2(\text{O-H})$ OR $2 \times 414 \text{ «kJ mol}^{-1}» + 839 \text{ «kJ mol}^{-1}» + 2 \times 463 \text{ «kJ mol}^{-1}»$ OR 2593 «kJ» ✓ «sum of bond enthalpies of A =» $3(\text{C-H}) + \text{C=C} + \text{C-O} + \text{O-H}$ OR $3 \times 414 \text{ «kJ mol}^{-1}» + 614 \text{ «kJ mol}^{-1}» + 358 \text{ «kJ mol}^{-1}» + 463 \text{ «kJ mol}^{-1}»$ OR 2677 «kJ» ✓ «enthalpy of reaction = 2593 kJ – 2677 kJ» = –84 «kJ» ✓	Award [3] for correct final answer. 3	

(continued...)

(Question 1c continued)

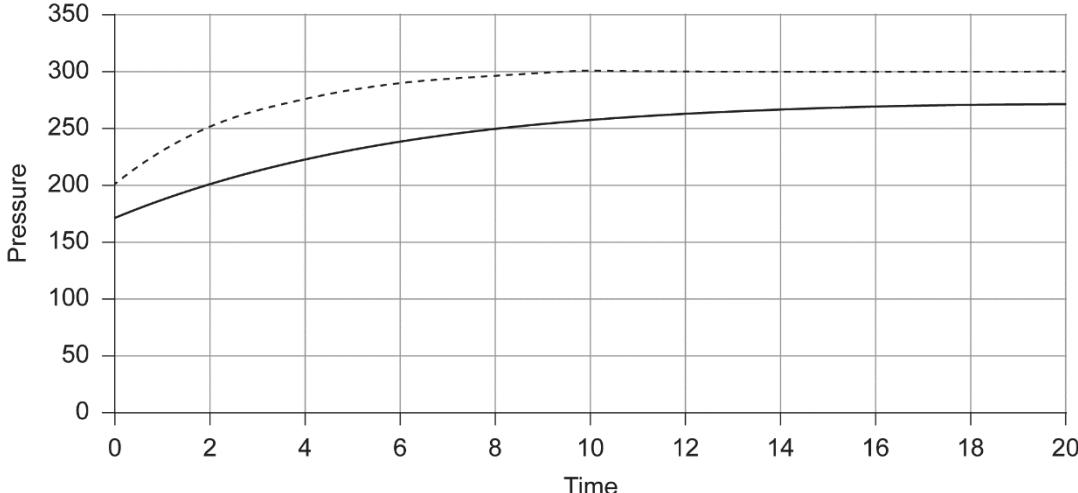
Question			Answers	Notes	Total
1.	c	iii	B AND it has a more negative/lower enthalpy/«potential» energy OR B AND more exothermic «enthalpy of reaction from same starting point» ✓		1
1.	c	iv	<p><i>Identity of product: «B»</i></p> <p><i>IR spectrum:</i> 1700–1750 «cm⁻¹ band» AND carbonyl/CO group present OR no «band at» 1620–1680 «cm⁻¹» AND absence of double bond/C=C OR no «broad band at» 3200–3600 «cm⁻¹ » AND absence of hydroxyl/OH group ✓</p> <p><i>¹H NMR spectrum:</i> «only» two signals AND A would have three OR «signal at» 9.4–10.0 «ppm» AND «H atom/proton of» aldehyde/–CHO present OR «signal at» 2.2–2.7 «ppm» AND «H atom/proton of alkyl/CH next to» aldehyde/CHO present OR «signal at» 2.2–2.7 «ppm» AND «H atom/proton of» RCOCH₂- present OR no «signal at» 4.5–6.0 «ppm» AND absence of «H atom/proton next to» double bond/C=C ✓</p>	Accept a specific value or range of wavenumbers and chemical shifts. Accept “two signals with areas 1:3”.	2

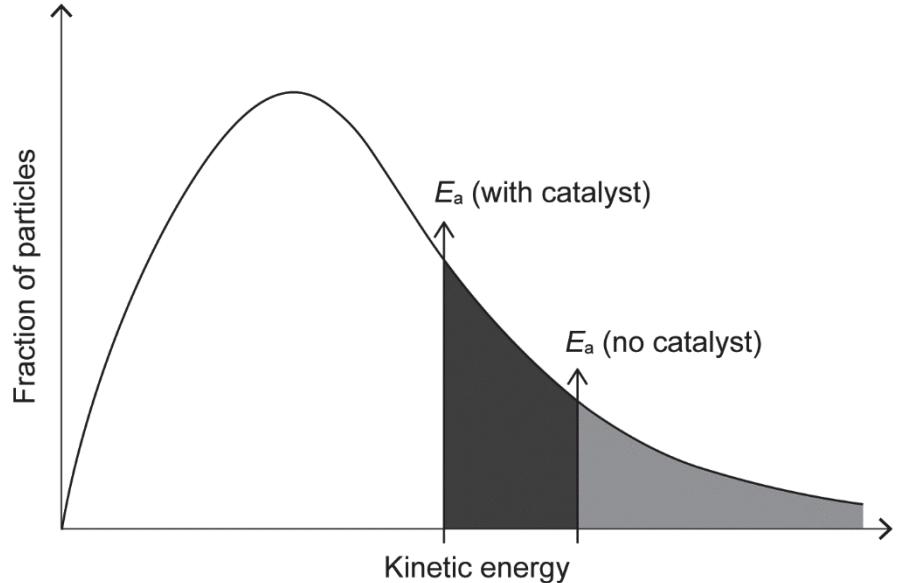
(continued...)

(Question 1c continued)

Question			Answers	Notes	Total
1.	c	v	2.3 ppm: doublet ✓ 9.8 ppm: quartet ✓		2
1.	d	i	<i>Reagents:</i> acidified/H ⁺ AND «potassium» dichromate(VI)»/K ₂ Cr ₂ O ₇ /Cr ₂ O ₇ ²⁻ ✓ <i>Conditions:</i> distil «the product before further oxidation» ✓	Accept “«acidified potassium» manganate(VII)/KMnO ₄ /MnO ₄ ⁻ /permanganate”. Accept “H ₂ SO ₄ ” or “H ₃ PO ₄ ” for “H ⁺ ”. Accept “more dilute dichromate(VI)/manganate(VII)” or “excess ethanol”. Award M1 if correct reagents given under “Conditions”.	2
1.	d	ii	–1 ✓		1
1.	d	iii	<i>Any three of:</i> has an oxygen/O atom with a lone pair ✓ that can form hydrogen bonds/H-bonds «with water molecules» ✓ hydrocarbon chain is short «so does not disrupt many H-bonds with water molecules» ✓ «large permanent» dipole-dipole interactions with water ✓		3 max

Question			Answers	Notes	Total
2.	a		increase in the amount/number of moles/molecules «of gas» ✓ from 2 to 3/by 50 % ✓		2
2.	b		«rate of reaction decreases» concentration/number of molecules in a given volume decreases OR more space between molecules ✓ collision rate/frequency decreases OR fewer collisions per unit time ✓	<i>Do not accept just “larger space/volume” for M1.</i>	2
2.	c	i	half «of the initial rate» ✓	Accept “lower/slower «than initial rate»”.	1
2.	c	ii	1 slower than 2 OR 1 rate determinant step/RDS ✓ 1 is unimolecular/involves just one molecule so it must be first order OR if 1 faster/2 RDS, second order in N ₂ O OR if 1 faster/2 RDS, first order in O ✓		2

Question		Answers	Notes	Total
2.	d	 <p>smaller initial gradient ✓</p> <p>initial pressure is lower AND final pressure of gas lower «by similar factor» ✓</p>		2
2.	e	<p>no AND it is a systematic error/not a random error OR no AND «a similar magnitude» error would occur every time ✓</p>		1

Question			Answers	Notes	Total
2.	f		 <p>catalysed and uncatalysed E_a marked on graph AND with the catalysed being at lower energy ✓</p> <p>«for catalysed reaction» greater proportion of/more molecules have $E \geq E_a$ / $E > E_a$ OR</p> <p>«for catalysed reaction» greater area under curve to the right of the E_a ✓</p>	Accept “more molecules have the activation energy”.	2
2.	g	i	$\Delta S^\ominus = 2(S^\ominus(N_2)) + S^\ominus(O_2) - 2(S^\ominus(N_2O))$ OR $\Delta S^\ominus = 2 \times 193 \text{ «J mol}^{-1} K^{-1} \text{»} + 205 \text{ «J mol}^{-1} K^{-1} \text{»} - 2 \times 220 \text{ «J mol}^{-1} K^{-1} \text{»} \checkmark$ « $\Delta S^\ominus = +» 151 \text{ «J K}^{-1} \text{»} \checkmark$	Award [2] for correct final answer.	2

(continued...)

(Question 2g continued)

Question			Answers	Notes	Total
2.	g	ii	<p>exothermic decomposition OR $\Delta H_{(decomposition)} < 0 \checkmark$</p> <p>$T\Delta S^\ominus > \Delta H^\ominus$ OR $\Delta G^\ominus «= \Delta H^\ominus - T\Delta S^\ominus» < 0 «at all temperatures» \checkmark$</p> <p>reaction spontaneous at all temperatures ✓</p>		3

Question			Answers	Notes	Total
3.	a	i	absorbs <u>UV/ultraviolet light</u> «of longer wavelength than absorbed by O ₂ » ✓		1
3.	a	ii	NO(g) + O ₃ (g) → NO ₂ (g) + O ₂ (g) ✓ NO ₂ (g) + O ₃ (g) → NO(g) + 2O ₂ (g) ✓	<i>Ignore radical signs.</i> <i>Accept equilibrium arrows.</i> Award [1 max] for NO ₂ (g) + O(g) → NO(g) + O ₂ (g).	2
3.	b	i	mass spectrometry/MS ✓		1
3.	b	ii	« $\frac{(98 \times 14) + (2 \times 15)}{100} =\!\!> 14.02$ ✓ « $M_r = (14.02 \times 2) + 16.00 =\!\!> 44.04$ ✓		2
3.	b	iii	Any two: same AND have same nuclear charge /number of protons/Z _{eff} ✓ same AND neutrons do not affect attraction/ionization energy/Z _{eff} OR same AND neutrons have no charge ✓ same AND same attraction for «outer» electrons ✓ same AND have same electronic configuration/shielding ✓	Accept “almost the same”. “Same” only needs to be stated once.	2 max

Question			Answers	Notes	Total
3.	c		<p><i>Nitrogen and carbon:</i> N has greater nuclear charge/«one» more proton «and electrons both lost from singly filled p-orbitals» ✓</p> <p><i>Nitrogen and oxygen:</i> O has a doubly filled «p->orbital OR N has only singly occupied «p->orbitals ✓</p>	Accept “greater e ⁻ – e ⁻ repulsion in O” or “lower e ⁻ – e ⁻ repulsion in N”. Accept box annotation of electrons for M2.	2
3.	d	i	delocalization OR delocalized π -electrons ✓	Accept “resonance”.	1
3.	d	ii	linear AND 2 electron domains OR linear AND 2 regions of electron density ✓	Accept “two bonds AND no lone pairs” for reason.	1
3.	d	iii	sp ✓		1

Question			Answers	Notes	Total
4.	a		$^{185}_{75}\text{Re}$ ✓		1
4.	b	i	gap in the periodic table OR element with atomic number «75» unknown OR break/irregularity in periodic trends ✓ «periodic table shows» regular/periodic trends «in properties» ✓		2
4.	b	ii	electrolyze «a solution of /molten» rhenium salt/ Re^{n+} ✓ graphite as cathode/negative electrode OR rhenium forms at cathode/negative electrode ✓	Accept “using rhenium anode” for M1.	2
4.	b	iii	Any two of: variable oxidation states ✓ forms complex ions/compounds ✓ coloured compounds/ions ✓ «para»magnetic compounds/ions ✓	Accept other valid responses related to its chemical metallic properties. Do not accept “catalytic properties”.	2 max
4.	c		place «pieces of» Re into each solution ✓ if Re reacts/is coated with metal, that metal is less reactive «than Re» ✓	Accept other valid observations such as “colour of solution fades” or “solid/metal appears” for “reacts”.	2

Question			Answers	Notes	Total
4.	d	i	rhenium(III) chloride OR rhenium trichloride ✓		1
4.	d	ii	« $M_r \text{ ReCl}_3 = 186.21 + (3 \times 35.45) \Rightarrow 292.56$ ✓» « $100 \times \frac{186.21}{292.56} = 63.648 \text{ «\%»}$ ✓»		2
4.	e	i	same group as Mn «which forms MnO_4^- » OR in group 7/has 7 valence electrons, so its «highest» oxidation state is +7 ✓		1
4.	e	ii	$\text{ReO}_4^- (\text{aq}) + 6\text{H}^+ (\text{aq}) + 3\text{e}^- \rightleftharpoons [\text{Re}(\text{OH})_2]^{2+} (\text{aq}) + 2\text{H}_2\text{O} (\text{l})$ ✓		1
4.	e	iii	no AND ReO_4^- is a weaker oxidizing agent than Fe^{3+} OR no AND Fe^{3+} is a stronger oxidizing agent than ReO_4^- OR no AND Fe^{2+} is a weaker reducing agent than $[\text{Re}(\text{OH})_2]^{2+}$ OR no AND $[\text{Re}(\text{OH})_2]^{2+}$ is a stronger reducing agent than Fe^{2+} OR no AND cell emf would be negative/–0.41 V ✓		1

Question			Answers	Notes	Total
5.	a	i	<p><i>Weak acid:</i> partially dissociated/ionized «in aqueous solution/water»</p> <p>AND</p> <p><i>Strong acid:</i> «assumed to be almost» completely/100 % dissociated/ionized «in aqueous solution/water» ✓</p>		1
5.	a	ii	CO ₃ ²⁻ ✓		1
5.	b		shifts to left/reactants AND to increase amount/number of moles/molecules of gas/CO ₂ (g) ✓	Accept “shifts to left/reactants AND to increase pressure”.	1
5.	c		<p>«K_a =» 10^{-6.36}/4.37 × 10⁻⁷ = $\frac{[H^+]^2}{[CO_2]}$</p> <p>OR</p> <p>«K_a =» 10^{-6.36}/4.37 × 10⁻⁷ = $\frac{[H^+]^2}{0.200}$ ✓</p> <p>[H⁺] «= $\sqrt{0.200 \times 4.37 \times 10^{-7}}$ » = 2.95 × 10⁻⁴ «mol dm⁻³» ✓</p> <p>«pH =» 3.53 ✓</p>	Award [3] for correct final answer.	3

Question			Answers	Notes	Total
5.	d	i	<p><i>Between sodium and hydrogencarbonate:</i> ionic ✓</p> <p><i>Between hydrogen and oxygen in hydrogencarbonate:</i> «polar» covalent ✓</p>		2
5.	d	ii	<p>«additional HCO_3^-» shifts position of equilibrium to left ✓</p> <p>pH increases ✓</p>	<i>Do not award M2 without any justification in terms of equilibrium shift in M1.</i>	2
5.	d	iii	<p>«molar mass of $\text{NaHCO}_3 = \gg 84.01 \text{ g mol}^{-1}$» ✓</p> <p>«concentration = $\frac{3.0 \times 10^{-2} \text{ g}}{84.01 \text{ g mol}^{-1}} \times \frac{1}{0.100 \text{ dm}^3} = \gg 3.6 \times 10^{-3} \text{ mol dm}^{-3}$» ✓</p>	<i>Award [2] for correct final answer.</i>	2
5.	d	iv	« $1.0 - 0.6 = \pm$ » 0.4 «%» ✓		1
5.	e		<p><i>Equation (3):</i> OH^- donates an electron pair AND acts as a Lewis base ✓</p> <p><i>Equation (4):</i> OH^- accepts a proton/H^+/hydrogen ion AND acts as a Brønsted–Lowry base ✓</p>		2

Question		Answers	Notes	Total
5.	f	<p>S-shaped curve from ~7 to between 12 and 14 ✓ equivalence point at 5 cm³ ✓</p>	Accept starting point >6~7.	2

Question		Answers	Notes	Total
6.	a	<p style="text-align: center;">/ -CH₂CH(C₆H₅) - ✓</p>	<p><i>Do not penalize the use of brackets and "n".</i></p> <p><i>Do not award the mark if the continuation bonds are missing.</i></p>	1
6.	b	$\ln k \ll = -\frac{10000}{8.31 \times 298} \gg = -4.04 \quad \checkmark$ $k = 0.0176 \quad \checkmark$	Award [2] for correct final answer.	2
6.	c	<p><i>Similarity:</i> «both» involve an electrophile OR «both» electrophilic ✓</p> <p><i>Difference:</i> first/reaction of ring/with NO₂⁺ is substitution/S_E AND second/reaction of C=C/with HBr is addition/A_E ✓</p>	<p><i>Answer must state which is substitution and which is addition for M2.</i></p>	2

Question			Answers	Notes	Total
6.	d	i	<p><i>Two forms:</i> chiral/asymmetric carbon OR carbon atom attached to 4 different groups ✓</p> <p><i>Relationship:</i> mirror images OR enantiomers/optical isomers ✓</p>	<p>Accept appropriate diagrams for either or both marking points.</p>	2
6.	d	ii	benzene ring «of the $C_6H_5-CH_2$ » and the bromine «on the CH_2-Br » can take up different relative positions by rotating about the «C–C, $\sigma-$ »bond ✓	<p>Accept “different parts of the molecule can rotate relative to each other”.</p> <p>Accept “rotation around σ-bond”.</p>	1
6.	e		$C_6H_5-CH_2-CH_2OH$ ✓		1