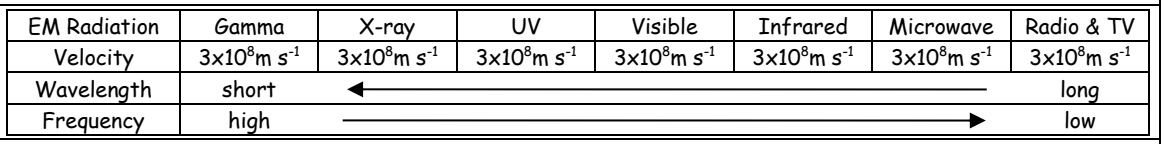
Past Papers Advanced Higher Chemistry

2001

Marking Scheme

2001 Adv Higher Chemistry Marking Scheme

MC Qu	Correct Answer	% Correct	Reasoning
1	D	67	☒A Wavenumber is $^1/_\lambda$ ∴ increase in wavelength gives decrease in wavenumber ☒B velocity (c) is constant ($3x10^8$ m s^{-1}) ☒C As $\lambda = {}^c/_f$ ∴ increase in wavelength gives decrease in frequency ☑D Purple/Blue end of EM Spectrum is 450nm and red end is 700nm
2	C	88	green light is absorbed ∴ red & blue light is transmitted → red+blue = purple (magenta)
3	A	65	Colour in compounds of transition metals is caused by d→d electron transitions
4	B	53	Most covalent character ∴ smallest electronegativity difference ∴ P and H both 2.2
5	C	85	☒A 4xO = -8 & ion has 1- charge ∴ Mn=+7 ☒B 4xO = -8 & ion has 2- charge ∴ Mn=+6 ☑C 4xO = -8 & ion has 3- charge ∴ Mn=+5 ☒D 6xCN^- ions = 6- charge & complex has overall 3- charge ∴ Mn=+3
6	B	66	☒A $C_4H_9Br + OH^- \rightarrow C_4H_9OH + Br^-$ and $C_2H_5Br + C_2H_5O^- \rightarrow C_2H_5OC_2H_5 + Br^-$ ☑B ether molecules form hydrogen bonds with water molecules but not other ether molecules ☒C Both alkanols and ethers are used as solvents ☒D Both alkanols and ethers are flammable carbon-based compounds
7	C	49	Rate Determining Step is the slow reaction ∴ 3 reactant molecules involved in RDS ∴ order of reaction = 3
8	A	71	1 mol reactant gas molecules → 2 mol gas product molecules ∴ <u>low pressure</u> favours forward reaction Forward reaction is endothermic ∴ <u>high temperature</u> favours forward reaction
9	C	64	2 mol of Cl^- ions are part of complex and 1 mol of Cl^- ions are free ions (outside complex) $[Cr(H_2O)_4Cl_2]^+Cl^-.2H_2O$ meets above criteria
10	B	63	❶ $2C + O_2 \rightarrow 2CO$ ΔG^o= -475 kJ ❷x-1 $2ZnO \rightarrow 2Zn + O_2$ ΔG^o= +340 kJ add $2C + 2ZnO \rightarrow 2CO + 2Zn$ ΔG^o= -135 kJ divide by 2 $C + ZnO \rightarrow CO + Zn$ ΔG^o= – 67.5kJ mol^{-1}
11	B	75	Nickel atoms have 28 electrons with electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$ ☒A $3d^8$ means no empty d-orbitals (three pairs and two unpaired) ☑B $2p^6 + 3p^6$ = 12 electrons ☒C $3d^8$ is not full as d-orbitals hold a maximum of 10 electrons. ☒D $3d^8$ contains 3 pairs of electrons and 2 unpaired electrons
12	A	69	From question: $MnO_4^- + 4H^+ + 2e^- \rightarrow MnO_2 + 2H_2O$ E^o= +2.26V -1x equation (from data book) $SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$ E^o= -0.17V add equations $MnO_4^- + 2H^+ + SO_3^{2-} \rightarrow MnO_2 + H_2O + SO_4^{2-}$ E^o= +2.09V
13	A	61	Ammonia solution + hydrochloric acid ⟶ ammonium chloride + water Ammonium chloride is acidic so pH range of indicator must be below 7
14	D	77	The reaction becomes thermodynamically feasible when $\Delta G^o = 0$ $\Delta G^o = \Delta H^o - T\Delta S^o = 0 \quad \therefore T\Delta S^o = \Delta H^o \quad \therefore T = \frac{\Delta H^o}{\Delta S^o} = \frac{178 \times 1000 \text{ J mol}^{-1}}{161 \text{ J K}^{-1} \text{ mol}^{-1}} = 1106K$
15	D	50	$FeCl_3$ polarises Cl_2 molecule and δ+ end of the Cl_2 molecule is electrophilically substituted onto the benzene ring and a hydrogen leaves the ring to form a molecule of HCl with the negative end of the chlorine molecule.

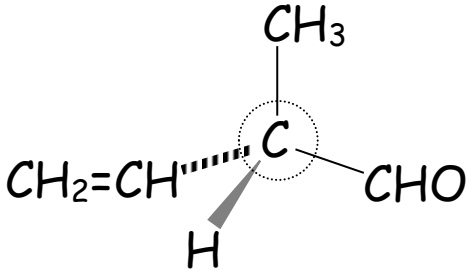
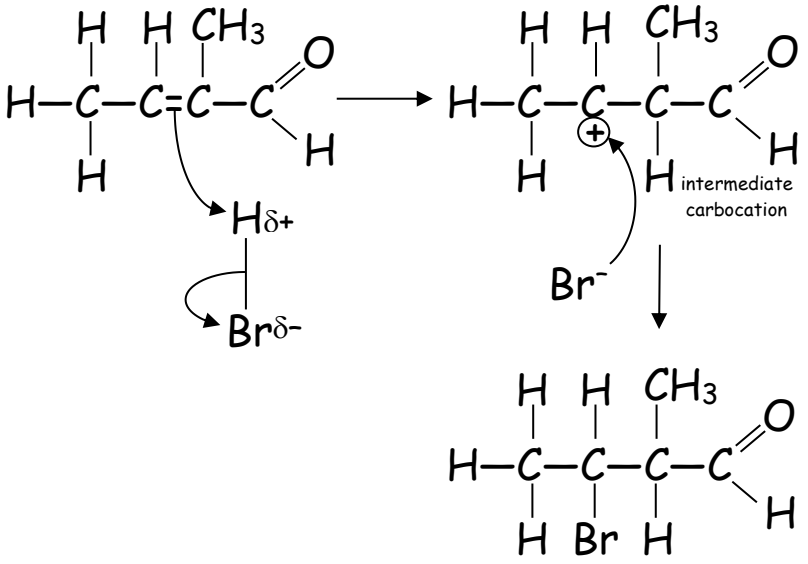
16	D	34	569 kJ of energy released ∴ bond forming is exothermic Forming 1 mole of H-F bonds would produce 569kJ of energy. ☒A bond breaking and bond forming in this reaction ☒B bond breaking ∴ endothermic reaction ☒C bond breaking and bond forming in this reaction ☑D $H_{(g)} + F_{(g)} \longrightarrow HF_{(g)}$ forms 1mol of H-F bonds from free gaseous H & F atoms
17	C	65	In Ellingham diagrams, upper line is reversed $2Zn + O_2 \rightarrow 2ZnO$ needs to be upper line to be reversed $2Zn + O_2 \rightarrow 2ZnO$ is upper line at temperatures above 1300°C
18	D	64	☒A 2nd Ionisation energy of Ca ∴ endothermic ☒B Bond breaking step ∴ endothermic ☒C 1st Electron Affinity is exothermic but not as big as Lattice enthalpy ☑D Lattice Enthalpy of $CaBr_2$ is much more exothermic than electron affinity
19	A	60	E^o = -0.26V + 0.37V = +0.11V n=1 as 1mol of electrons transferred in equation $\Delta G^o = -nFE^o$ = -1 x 96500 x 0.11 = negative value. Feasible reactions have a equilibrium constant K greater than 1
20	B	72	☒A Reactants are not elements in natural state ☑B Formation of 1 mole of a substance from its elements in their natural state. ☒C Ca(g) is not the natural state of calcium at 298K ☒D Reactants are not elements in natural state
21	C	91	6 x Reaction ❶: $6C + 6O_2 \longrightarrow 6CO_2$ ΔH= -2364kJ mol^{-1} 7 x Reaction ❷: $7H_2 + 3\frac{1}{2}O_2 \longrightarrow 7H_2O$ ΔH= -2002kJ mol^{-1} -1 x Reaction ❸: $6CO_2 + 7H_2O \longrightarrow C_6H_{14} + 9\frac{1}{2}O_2$ ΔH= +4160 kJ mol^{-1} Add ❶'+❷'+❸' $6C + 7H_2 \longrightarrow C_6H_{14}$ ΔH= -206 kJ mol^{-1}
22	C	71	
23	A	61	$C_2H_5O^-$ is negative ion so nucleophilic attack nucleophilic substitution as $C_2H_5O^-$ joins as Br^- leaves molecule.
24	A	52	☑A methanoic acid has lowest pK_a value ∴ most acidic ☒B alkanols are not acidic (they are neutral) ☒C phenol has a higher pK_a value than methanoic acid (p13 data booklet) ☒D propanoic acid has a higher pK_a value than methanoic acid (p13 data booklet)
25	B	83	Decreased volatility as increased chain length increase London Dispersion Forces Decreased solubility in water as hydrocarbon chain length increases
26	D	87	☒A Forms derivative with both which then needs to be separately checked for melting point ☒B Lithium aluminium hydride would reduce both an aldehyde and a ketone ☒C Hydrogen cyanide would react with both across the C=O double bond. ☑D Tollen's Reagent would give a silver mirror with an aldehyde but not a ketone
27	C	86	IR absorption at 2725cm^{-1} indicates aldehyde –CHO group present (p14 data booklet)
28	D	61	Carbonyl (C=O) group properties changed as COOH group does not react with 2,4-dinitrophenylhydrazine Hydroxyl (-O-H) group properties changed as group dissociates and releases H^+ ions (i.e. acidic)
29	D	40	-OH groups do not normally release H^+ ions but proximity to benzene ring allow dissociation $-NH_2$ groups accept H^+ ions by forming dative covalent bond at the N lone pair of electrons. Proximity to benzene ring makes this less likely to happen.
30	A	92	☑A Agonists produce the biological response of the natural substrate ☒B Antagonists bind with the binding site of the receptor but do not produce the biological response ☒C Pharmacophore is the shape which fits the binding site of the receptor ☒D A receptor binds to the drug/natural substrate

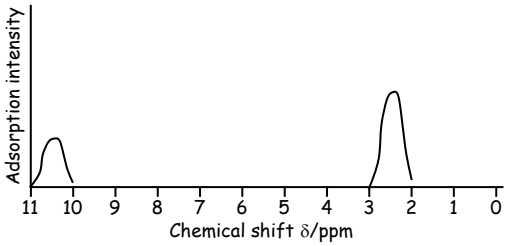
The style of question in Q31-33 has been abandoned but the content of the questions is still relevant.		
31a	C+E (Both for 1 mark)	☑C Melting increases the disorder → increase in disorder increases the ΔS^o ☑E melting is an endothermic process hence a positive ΔH^o.
31b	B	Equilibrium constant is greater than 1 (or =1) in feasible reactions
31c	F	ΔG equals zero when a system is in equilibrium. Both forward and reverse reactions happen at equal rate and a positive value of ΔG for either reaction would make that reaction not feasible.
31d	D	k is the constant in the kinetics equation
32a	D+F (Both for 1 mark)	☑D CuO is insoluble metal oxide (NB: soluble metal oxides dissolve in water to form alkalis) ☑F Hydrides react with water to form hydrogen and alkali ($H^- + H_2O \rightarrow H_2 + OH^-$)
32b	B	☒A linear ☑B trigonal bipyrimidal ☒C trigonal ($AlCl_3$ is covalent) ☒D ionic ☒E trigonal ☒F ionic
32c	A	☑A linear ☒B trigonal bipyrimidal ☒C trigonal (NB: $AlCl_3$ is covalent) ☒D ionic ☒E trigonal ☒F ionic
32d	F	$LiAlH_4$ is an reducing agent which reduces alkanals to primary alkanols, etc.
33	C+D (Both for 1 mark)	☒A $C_6H_5 - \mathbf{CH_2} - CHO$ ☒B $CH_3 - CH_2 - \mathbf{CH_2} - CHO$ ☑C $C_6H_5 - CHO$ ☑D $H - CHO$ ☒E $CH_3 - \mathbf{CH_2} - CHO$ ☒F $CH_3 - CH(CH_3) - \mathbf{CH_2} - CHO$

2001 Adv Higher Chemistry Marking Scheme

Long Qu	Answer	Reasoning
1a	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$	or [Ne] $3s^2 3p^6 3d^6$ ([Ar]$3d^6$ not acceptable)
1b	Orbitals are equal in energy	All five d-orbitals are of equal energy in isolated atoms. In the presence of ligands, the d-orbitals split into two levels.
1c(i)	in isolated Fe^{2+} ions	Degenerate means the electron orbitals are of equal energy
1c(ii)	Ligands split d-orbitals into two levels	Ligands pull the d_{z^2} and $d_{x^2-y^2}$ orbitals apart from the remaining d-orbitals
1c(iii)	Light energy excites electron from lower level to upper level	Visible light wavelength is absorbed by electron in lower d-orbital to excite/promote electron to upper d-orbital level (a d-d transition). This wavelength of visible is removed and the complimentary colour is observed.
2a	Iodine will react with any unsaturated fat present	I_2 reacts with C=C bonds in unsaturated fats/oils. This method will extract the sulphite so that it can be titrated more accurately.
2b	starch	Starch turns blue/black in the presence of Iodine
2c(i)	3.04×10^{-5} mol	No of mol = volume x concentration = 0.0152 x 0.002 = 0.0000304mol
2c(ii)	0.0383%	$SO_3^{2-} + H_2O + I_2 \rightarrow 2I^- + 2H^+ + SO_4^{2-}$ 1mol 1mol 3.04×10^{-5}mol 3.04×10^{-5}mol 1 mol of Na_2SO_3 = (2x23)+(1x32.1)=(3x16) = 46+32.1+48 = 126.1g **m**ass = **n**o. of mol x **gfm** = 3.04×10^{-5} mol x 126.1g mol^{-1} = 3.83×10^{-3}g $\%mass = \frac{\text{mass of } Na_2SO_3}{\text{total mass}} = \frac{3.83\times10^{-3}}{10} \times 100 = 0.0383\%$
3a(i)	$2F^-(l) \rightarrow F_2(g) + 2e^-$	
3a(ii)	Fluorine is below MnO_4^- in the electrochemical series	Upper half-reaction in electrochemical series reverses in a redox reaction.
3b	(Cl_2) X = 0 (Cl^-) Y = -1 (ClO^-) Z = +1	Oxidation numbers for all *elements* is zero ClO^- : as O is -2 so Cl must be +1
4a	$K_w = [H^+][OH^-]$	$K_w = \frac{[H^+][OH^-]}{[H_2O]}$ But $[H_2O] = 1$ as water is also the solvent $K_w = [H^+][OH^-]$
4b	K_w increases as water dissociates more as temp increases	K_w increases because $[H^+]$ and $[OH^-]$ are increasing. $[H^+]$ and $[OH^-]$ increase as there is more dissociation of H_2O
4c	6.6	$K_w = [H^+][OH^-] = [H^+]^2 = 5.48\times10^{-14}$ NB $[H^+] = [OH^-]$ $[H^+] = \sqrt{(5.48\times10^{-14})} = 2.34\times10^{-7}$ mol l^{-1} $\log_{10}[H^+] = -6.6$ $-\log_{10}[H^+] = 6.6$ pH = 6.6

5a	Benzene does not react with Br_2	or C to C bond length in benzene in equal but C=C double bonds is shorter than C–C single bonds.
5b	-164 kJ mol^{-1}	Bond Breaking / Bond Forming 3xH-H = 3x436 =1308kJ 3xC=C = 3x612 =1836kJ 3xC-C = 3x348 =1044kJ 6xC-C = 6x348 =2088kJ 6xC-H = 6x412 =2472kJ 12xC-H = 12x412 =4944kJ total endothermic =6660kJ total exothermic =7032kJ ΔH_1 = Σendothermic steps - Σexothermic steps = +6660kJ - 7032kJ = -372kJ stability factor = $\Delta H_1 - \Delta H_2$ = -372 – (-208) = -164kJ mol^{-1}
5c	6 delocalised electrons in ring	The 3 delocalised electrons above 6 carbon ring and the 3 delocalised electrons below the carbon ring flatten the carbon ring and stabilise the structure.
6a	CH_3COO^-	$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$ Acid (Donates H^+) Base (Accepts H^+) Conjugate Acid (Formed when Base accepts H^+) Conjugate Base (Formed when Acid loses H^+)
6b(i)	0.456mol l^{-1}	1 mol $Na^+CH_3COO^-$ = 23 + 24 + 3 + 32 = 82g no. of mol = $\frac{\text{mass}}{\text{gfm}} = \frac{3.74}{82} = 0.0456\text{mol}$ concentration = $\frac{\text{no. of mol}}{\text{volume}} = \frac{0.0456\text{mol}}{0.1\text{ litres}} = 0.456\text{mol l}^{-1}$
6b(ii)	5.12	$pH = pK_a - \log\frac{[\text{acid}]}{[\text{salt}]} = 4.76 - \log\frac{0.2}{0.456} = 4.76 - \log(0.439)$ $= 4.76 - (-0.358)$ $= 5.12$
6b(iii)	Answer to include:	OH^- ions added will react with H^+ ions present. H^+ ions then replaced as equilibrium shifts to replace H^+ ions by dissociation of acid molecules ($CH_3COOH \rightleftharpoons CH_3COO^- + H^+$)
7a	$K=\frac{[I_2]_{\text{cyclohexane}}}{[I_2]_{\text{water}}}$	$K=\frac{[\text{solute}]_{\text{product solvent}}}{[\text{solute}]_{\text{reactant solvent}}}$
7b(i)	0.01 - x	no. of mol = v x c = 0.1l x 0.10 mol l^{-1} = 0.01mol I_2 (in aqueous layer at start) x mol left in aqueous layer after equilibrium formed $\therefore$ (0.01 – x) mol I_2 in cyclohexane layer.
7b(ii)	7.14x10^{-3} mol l^{-1}	$0.4 = \frac{[0.01 - x]}{[x]}$ $\therefore$ 0.4 [x] = [0.01 – x] $\therefore$ 1.4[x] =0.01 $\therefore [x] = \frac{0.01}{1.4} = 7.14\text{x}10^{-3}$ mol l^{-1}
7c(i)	No change	Partition coefficient is independent of the volume of either solvent.
7c(ii)	No change	The concentration of the iodine in the cyclohexane is the same as half the volume of cyclohexane would extract less iodine from the aqueous layer.
8a	Answer must include:	Nucleophiles contain either a negative charge or a lone pair of electrons and attack a centre of positive charge on a molecule. (1mark) Nucleophile attacks a carbon with a δ+ charge and replaces (substitutes) the atom/group with the δ- charge which leaves the molecule under attack (1mark)

8b	Rate = $k[CR_3Br]$	Rate Determining Step (RDS) is always the slow step. Only species which appear in the slow step appear in the rate equation. (S_N1 reaction)
8c	x = 2 y = 0.5	S_N2 reaction ∴ Rate = $k[CR_3Br][OH^-]$ ∴ order of both reactants = 1 In Experiment 2: doubling $[OH^-]$ while double relative rate ∴ x=2 In Experiment 3: Doubling $[CR_3Br]$ will double relative rate from 1 → 2 Relative rate increase from 2 → 10 must result from increasing $[OH^-]$ x5
8d	Answer should include:	Bulky aromatic rings on molecule will hinder the nucleophilic attack of OH^- ions towards the $\delta+$ on the C atom in the C-Br bond.
9a	4	Each of the four P atoms has one lone pair of electrons
9b	60°	As each bond is equal in size each triangle of P atoms must be an equilateral triangle.
9c	2	triple bonds contain: 1 sigma (σ) bond and 2 pi (π) bonds double bonds contain: 1 sigma (σ) bond and 1 pi (π) bond
9d	2 mol of $P_2(g)$ molecules is more disordered than 1 mol of $P_4(g)$ molecules	An increase in entropy means an increase in disorder.
10a	Molecule C	In compound C, both bonds off the left carbon in the C=C bond are C-H bonds. These bonds need to be different to have geometric isomerism (i.e. cis- and trans- versions)
10b	Molecule C	
10c(i)	Diagram showing:	
10c(ii)	Compound D	Markovnikov's Rule: Hydrogen tends to add to the carbon in the C=C bond which has the most hydrogens already attached to it. In molecule C, C_1 had 2H and C_2 has 1H atom so hydrogen in H-Br tends to add to C_1 and Br adds to C_2 forming compound D
11a	methylpropanedioic acid	Or 2-methylpropanedioic acid but methyl must be on C_2

11b(i)	$[COOH]^+$	$COOH$: m=(1x12)+(2x16)+(1x1) = 12+32+1 = 45 $[COOH]^+$: $^{m}/_{z} = {}^{45}/_{1} = 45$
11b(ii)	2xH atoms 1xO atom	Molecule A has mass=118 (heaviest peak) 118 – 100 = 18 → H and OH or 2H and 1O have mass = 18
11c	$COOH$ – peak at δ=10→ CH_2 –peak at δ=2.1→2.8 CH_2 peak double size of $COOH$ peak	
12a	8	$CsCl$ has 8:8 co-ordination and NaCl has 6:6 co-ordination
12b(i)	0.96	Radius Ratio of $CsCl$ = (Cs^+ radius)÷(Cl^- radius) = $^{174pm}/_{181pm}$ = 0.96
12b(ii)	KF will have same ionic structure as $CsCl$	Radius Ratio of KF = (K^+ radius)÷(F^- radius) = $^{133pm}/_{133pm}$ = 1.00
12c(i)	Diameter of K^+ ion too big to fit into [15]-crown-5-ether	Diameter of K^+ = 2x radius of K^+ ion = 2x133pm = 266pm Diameter of in [15]-crown-5-ether is 170-220pm
12c(ii)	[18]-crown-6-ether	*[18]* → 18 Carbon and Oxygen atoms in ether -6- → 6 oxygens in ether