Suggested Answers for 9746/H2 Chemistry Preliminary Examination Paper 3

- 1. (a) (i) forward reaction is exothermic
 - low temperature \Rightarrow high yield of SO₃
 - but equilibrium reached at a lower rate
 - a moderately high temperature is used to achieve equilibrium more rapidly

(ii)		2SO ₂ (g) +	O ₂ (g)	=	2SO ₃ (g)
	Initial partial pressure / atm	2	1		-
	Eqm partial pressure / atm	0.02(2) = 0.04	0.02(1) = 0.02		0.98(2) = 1.96

$$K_{\rm p} = \frac{(1.96)^2}{(0.04)^2(0.02)} = 1.20 \times 10^5 \, {\rm atm}^{-1}$$

- (iii) (effect on yield)
 - when volume is reduced, pressure is increased
 - equilibrium position shifts right to the side with fewer gaseous molecules
 - percentage conversion of SO₂ into SO₃ increases

(effect on K_p)

- no change in temperature so K_p remain unchanged
- (b) (i) (high melting points of Na_2O and Al_2O_3)
 - giant ionic structure
 - strong electrostatic attraction between oppositely charged ions in Na₂O and Al₂O₃

(low melting point of SO₂)

- simple molecular structure
- weak van der Waals' forces (or weak permanent dipole-permanent dipole interactions) between molecules

 $(Al_2O_3$ has higher melting point than Na₂O)

- stronger ionic bond
- Al³⁺ has higher charge density than Na⁺

- **1.** (b) (ii) (Na₂O)
 - reacts vigorously with water
 - solution with pH = 13-14
 - Na₂O + H₂O \rightarrow 2NaOH

 (Al_2O_3)

• insoluble in water

 (SO_2)

- reacts with water
- solution with pH = 1-3
- $SO_2 + H_2O \rightarrow H_2SO_3$





- (ii) an electron-deficient species which attacks electron-rich benzene ring
- (iii) acid

 $HNO_3 + H_2SO_4 = NO_2^+ + H_2O + HSO_4^-$

(iv) phenol has an electron-donating –OH group which strongly activates the benzene ring

2. (a) (i) $Ag(s) + \frac{1}{2}N_2(g) + \frac{3}{2}O_2(g) \rightarrow AgNO_3(aq)$

(ii)
$$\Delta H_{rxn} = [4(+106) + 4(-207) + 90 + 33 + 3(-286)] - 6(-207)$$

= +103 kJ mol⁻¹

- (iii) $\Delta G = \Delta H T\Delta S$
 - Since $\Delta H>0$ and $\Delta G<0$ (i.e. spontaneous), T ΔS must be as positive as ΔH , so $\Delta S>0$
 - increase in disorder because disorder achieved in breaking the lattice into ions is greater than the ordering of water molecules around the ions

(b) Amount of silver produced = $\frac{1.44}{108}$ = 1.33 × 10⁻² mol Since Ag = e, amount of e = 1.33 × 10⁻² mol

 $\begin{array}{l} \mathsf{Q} = \mathsf{I} \times \mathsf{time} = \mathsf{n} \times \mathsf{F} \\ \mathsf{10} \times (\mathsf{t} \times 60) = \mathsf{1.33} \times \mathsf{10}^{-2} \times \mathsf{96500} \ \Rightarrow \mathsf{t} = \mathsf{2.14} \ \mathsf{mins} \end{array}$

Since **X** = 3e, Amount of **X** produced = $1.33 \times 10^{-2} \div 3$ $A_{\rm r}$ of **X** = $\frac{0.120}{(1.33 \times 10^{-2} \div 3)}$ = 27.0

- (c) (i) white ppt of AgCl when AgNO₃ is added
 - dissolves to form a colourless solution of Ag(NH₃)₂⁺ when excess NH₃ is then added.

 $AgCl(s) = Ag^{+}(aq) + Cl^{-}(aq) -----(*)$

- due to formation of complex Ag(NH₃)₂⁺, [Ag⁺(aq)] decreases
- equilibrium position in (*) shift right, increasing solubility of AgCI
- (ii) AgI

 $K_{sp}(AgI)$ is smaller than $K_{sp}(AgCl)$

2. (d) (i) nucleophilic addition

(ii) optical isomerism



acidified K₂Cr₂O₇, heat under reflux

3. (a) (i) a solution which resists pH change when a small amount of acid or base is added

(ii)
$$K_s = \frac{[HCO_3][H^*]}{[H_2CO_3]}$$

 $pH = 7.4 \Rightarrow [H^*] = 10^{-7.4} \mod 4m^{-3}$
 $= 3.98 \times 10^8 \mod 4m^3$
 $7.90 \times 10^{-7} = \frac{[HCO_3](10^{-7.40})}{[H_2CO_3]}$
 $\frac{[HCO_3]}{[H_2CO_3]} = \frac{7.90 \times 10^{-7}}{3.98 \times 10^{-8}} = 19.8$
• ratio is high
• HCO_3⁻ is needed to remove lactic acid in the blood
(iii) H⁺(aq) + HCO_3⁻(aq) \rightarrow H₂CO₃(aq)
(iv) When lactic acid is removed,
H₂CO₃(aq) = CO₂(aq) + H₂O(*l*) ----- (1)
[H₂CO₃] increases \Rightarrow equilibrium position in (1) shifts right, forming
more CO₂(aq)
CO₂(aq) = CO₂(g) ----- (2)
[CO₂(aq)] increases \Rightarrow equilibrium position in (2) shifts right, forming
more CO₂(g) and thus resulting in higher rate of breathing
(i) $K_{sp}(CaCO_3) = [Ca^{2*}][CO_3^{2-}]$
(ii) $CaCO_3(s) = Ca^{2*}(aq) + CO_3^{-2-}(aq) ------ (3)$
At eqm: $-x \times x$
where *x* mol dm⁻³ is the solubility of CaCO_3.
[Ca²⁺] = [CO_3^{2-}] = 9.35 \times 10^{-5} mol dm^{-3},
 $K_{sp}(CaCO_3) = (9.35 \times 10^{-5})^2$
 $= 8.74 \times 10^9 mol^2 dm^{-6}$
(iii) BeCO₃ is not stable due to
• high charge density of Be²⁺
• Be²⁺ has a high polarising power
Be(OH)₂ is relatively more stable as

(b)

(b)

OH⁻ is smaller than CO₃²⁻
OH⁻ is less polarisable by Be²⁺



Q

- Q decolourises Br₂
 ⇒ Q contains a C=C bond/is an alkene and Q undergoes electrophilic addition
- Q does not react with 2,4-DNPH
 ⇒ Q is not a carbonyl compound/ not an
 aldehyde or ketone. (or not an enol,
 CH₃CH=CH(OH) or CH₃(OH)C=CH₂ which
 can be rearranged to give carbonyl group)
- Q undergoes vigorous oxidation with hot conc. acidified KMnO₄ to gives only CO₂ ⇒ Q is CH₂=CHCH₂OH. Q is oxidised to CO₂ and (COOH)₂ which then further oxidises to CO₂ and H₂O

- 4. (a) (i) A homogeneous catalyst
 - is in the same phase as the reactants and products
 - increases the rate of reaction by providing an alternative reaction pathway/mechanism of a lower activation energy than that of the uncatalysed reaction
 - (ii) iron is able to vary its oxidation states in its compounds or Fe can exist as Fe^{2+} or Fe^{3+}
 - (iii) Step 1: $2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$ $E_{cell} = (+0.77) - (+0.54) = +0.23 V > 0$ (energetically feasible)

Step 2: $S_2O_8^{2^-}(aq) + 2Fe^{2^+}(aq) \rightarrow 2SO_4^{2^-}(aq) + 2Fe^{3^+}(aq)$ $E_{cell} = (+2.01) - (+0.77) = +1.24 \text{ V} > 0$ (energetically feasible)

(iv) $[Fe(CN)_6]^{3-} + e^- = [Fe(CN)_6]^{4-}$ E = +0.36 V E value not within +0.54 V and +2.01 V so the intermediate compound, $[Fe(CN)_6]^{4-}$, cannot be formed

 $[Fe(CN)_6]^{3-}$ is negatively charged so activation energy is high due to electrostatic repulsion between like charges

- (v) ligands causes the d orbitals to split into 2 sets of different energies
 - difference in energies between these 2 sets of d orbitals is so small
 - such that radiation from the visible region of the electromagnetic spectrum
 - when an electron moves from a d orbital of lower energy to another unfilled/partially filled d orbital of higher energy
 - Hence, complexes are coloured as the colour seen is the complement of the colours absorbed
- (b) $I_2 + 2e = 2I^-$ E = +0.54 V $Cr_2O_7^{2^-} + 14H^+ + 6e = 2Cr^{3^+} + 7H_2O$ E = +1.33 V

 $E_{\text{cell}} = (+1.33) - (+0.54) = +0.79 \text{ V} > 0$ (energetically feasible)

Overall eqn: $Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

(c) (i) brown $I_2(aq)$ decolourises and pale yellow ppt forms



- 4. (c) (ii) R undergoes substitution with PCI_5
 - \Rightarrow **R** contains –OH group / is an alcohol
 - R undergoes ester formation/esterification with ethanoyl chloride ⇒ R contains –OH group/ is an alcohol
 - R undergoes oxidation with alkaline aq. I₂
 ⇒ R contains –CH(OH)CH₃ group
 - R undergoes oxidation with conc. KMnO₄ in acid solution to give two organic products
 ⇒ R contains a C=C bond/is an alkene and it undergoes oxidation

 \Rightarrow R contains a C=C bond/is an alkene and it undergoes (with cleavage of the C=C

- Both S and T undergo oxidation with alkaline aq. I₂ \Rightarrow S and T contain –COCH₃ group
- Structure of **S**: CH₃COCH₃
- Structure of **R**: $CH_3C = CHCHCH_3$



• Structure of **T** O $C - C - CH_3$ HO O

When V_{HCl} /[HCl] increases by 1.5 times \Rightarrow rate increases by $\frac{0.00188}{0.00125}$ = 1.5 times first order wrt HCl (Compare Expts 2 and 3) When V_{sucrose}/[sucrose] decreases by half/ 0.5 times ⇒ rate decreases by $\left(\frac{0.000938}{0.00188} = 0.499 \approx 0.5\right)$ by half/ 0.5 times OR When V_{sucrose}/[sucrose] increases by 2 times \Rightarrow rate increases by $(\frac{0.00188}{0.000938} = 2.00)$ by 2 times first order with respect to sucrose rate = k[sucrose][HCl] From Expt 1, $[sucrose] = 0.79 \times 20/50 = 0.316 \text{ mol } dm^{-3}$ $[HCl] = 1.25 \times 20/50 = 0.500 \text{ mol dm}^{-3}$ $\therefore k = \frac{0.00125}{0.316 \times 0.500} = 7.91 \text{ x } 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$ or From Expt 2, $[sucrose] = 0.79 \times 20/50 = 0.316 \text{ mol } dm^{-3}$ $[HCl] = 1.25 \times 30/50 = 0.750 \text{ mol dm}^{-3}$ $\therefore k = \frac{0.00188}{0.316 \times 0.750} = 7.93 \text{ x } 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$ or From Expt 3, $[sucrose] = 0.79 \times 10/50 = 0.158 \text{ mol } dm^{-3}$ $[HCl] = 1.25 \times 30/50 = 0.750 \text{ mol dm}^{-3}$ $\therefore k = \frac{0.000938}{0.158 \times 0.750} = 7.92 \text{ x } 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$ From Expt 4, $[sucrose] = 0.79 \times 40/70 = 0.451 \text{ mol dm}^{-3}$ $[HCl] = 1.25 \times 20/70 = 0.357 \text{ mol dm}^{-3}$:. Initial rate = $7.91 \times 10^{-3} \times 0.451 \times 0.357$ = 1.27×10^{-3} mol dm⁻³ min⁻¹

(b) (i) Initial rate Zero order Page 9 of 11 Graph 1

(ii)

5.

(b) At low [sucrose], reaction is first order wrt sucrose (ii)

As [sucrose] increases,

- more active sites of enzyme molecules occupied by sucrose • molecules
- reaction is no longer first order wrt sucrose

At high [sucrose],

- all active sites of enzyme molecules occupied by sucrose molecules
- reaction is zero order wrt to sucrose
- (b) (iv) • Ag⁺ forms ionic interactions with COO⁻ and disrupts ionic interactions
 - Ag⁺ binds tightly to SH group and disrupts disulphide bridges
 - small proportion of the enzyme is denatured
- (C) (i) • exists as zwitterions
 - giant ionic structure in solid form •
 - · can form ion-dipole interactions with water
 - soluble

(ii)

5.	(c)	(iii)	Type of interaction	Diagram illustrating interaction

