## YJC 2014 Prelim Paper 3 answers

1 (a) Na<sub>2</sub>O : dissolves readily in H<sub>2</sub>O to form a strongly alkaline solution with pH = 13(accept 11 - 14).

 $Na_2O + H_2O \rightarrow 2NaOH$  $SO_3$ : dissolves in H<sub>2</sub>O forming a strongly acidic solution with pH = 2 (accept 0 -3).

$$SO_3 + H_2O \rightarrow H_2SO_4$$

- (b) (i) Buffer solutions resist pH changes when a small amount of acid or alkali is added.
  - (ii) Small amount of H<sup>+</sup>:

 $CO_3^{2^-} + H^+ \text{ (or } H_3O^+) \rightarrow HCO_3^- (+H_2O)$ The H<sup>+</sup> added is removed by the large reservoir of  $CO_3^{2^-}$ . Small amount of OH<sup>-</sup>:  $HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$ 

The OH<sup>-</sup> added is removed by the large reservoir of HCO<sub>3</sub><sup>-</sup>

(iii) Buffer most effective when  $[HCO_3^-] = [CO_3^{2^-}]$  (maximum buffering capacity), using Hasselbalch equation,

$$pH = pK_a = -lg (5.61 \times 10^{-11}) = 10.3$$

Range of effectiveness =  $pK_a \pm 1 = 9.3$  to 11.3

(iv) By Hasselbalch equation,  $pH = pK_a + lg \frac{[CO_3^{2^-}]}{[HCO_2^{-}]}$ When  $\frac{[CO_3^{2^-}]}{[HCO_2^{-}]}$  increases from 0.50 to 0.85, pH change = lg (0.85) – lg (0.50) = -0.0706 - (-0.301)= +0.230OR ratio 0.5, pH = 9.95 ratio 0.85, pH = 10.18

Difference = 10.18 - 9.95 = 0.230

(c) (i)  $M_r AlCl_3 = [27 + 3(35.5)] = 133.5$  $M_r (AlCl_3)_n = 267, n = 2$ Molecular formula is  $Al_2Cl_6$ .



(ii) Al<sub>2</sub>O<sub>3</sub>

(iii) When large amount of water added, aluminium chloride forms  $A/(H_2O)_6^{3+}$ .  $A/(H_2O)_6^{3+}$  (+  $H_2O$ )  $\Rightarrow A/(H_2O)_5(OH)^{2+}$  +  $H^+$  (or  $H_3O^+$ ) **pH = 3.0** 

(d) (i) Electrophilic substitution

(ii) Step 1:

$$Cl_2 + AlCl_3 \rightarrow Cl^+ + AlCl_4^-$$

Step 2:











For (iii) and (iv), accept if Br/OH is in 3<sup>rd</sup> position of cyclic ring instead of 2<sup>nd</sup>.

(c) (i) 
$$E^{e}_{cell} = E_{PbO2/Pb2+} - E_{Pb2+/Pb}$$
  
= +1.47 - (-0.13)  
= +1.60 V

- (ii) 2 PbSO<sub>4</sub>(s) + 2 H<sub>2</sub>O(l)  $\rightarrow$  Pb(s) + PbO<sub>2</sub>(s) + H<sub>2</sub>SO<sub>4</sub>(aq) + HSO<sub>4</sub><sup>-</sup>(aq) + H<sup>+</sup>(aq) OR 2 PbSO<sub>4</sub>(s) + 2 H<sub>2</sub>O(l)  $\rightarrow$  Pb(s) + PbO<sub>2</sub>(s) + 2 H<sub>2</sub>SO<sub>4</sub>(aq) OR 2 PbSO<sub>4</sub>(s) + 2 H<sub>2</sub>O(l)  $\rightarrow$  Pb(s) + PbO<sub>2</sub>(s) + 2 HSO<sub>4</sub><sup>-</sup>(aq) + 2 H<sup>+</sup>(aq)
- (iii) As time passes, more of the reactants are being used up, causing the concentration of the reactants (H<sub>2</sub>SO<sub>4</sub>) to decrease. As a result, E<sup>e</sup><sub>cell</sub> decreases.
- (iv) Hydrogen fuel cell . The reactants are constantly replenished as it is supplied from the air, thus e.m.f. remains constant. .

(d) (i) 
$$K_{sp} = [Pb^{2+}][CrO_4^{2-}]$$
  
=  $s^2$   
= 1.69 × 10<sup>-14</sup> mol<sup>2</sup> dm<sup>-6</sup>  
(where s is the solubility of PbCrO\_4.)  
s = 1.30 × 10<sup>-7</sup> mol dm<sup>-3</sup>

(ii) Precipitation occurs when ionic product >  $K_{sp}$ , so the maximum ionic product before precipitation =  $K_{sp}$ .

 $[Pb^{2+}][0.01] = 1.69 \times 10^{-14}$  $[Pb^{2+}]_{saturation} = 1.69 \times 10^{-12} \text{ mol dm}^{-3}$ 

(iii)  $2CrO_4^{2^-} + 2H^+ \rightleftharpoons Cr_2O_7^{2^-} + H_2O$ In the presence of acid, the H<sup>+</sup> concentration increases, causing the equilibrium to shift to the right by Le Chatelier's Principle, with  $CrO_4^{2^-}$  forming  $Cr_2O_7^{2^-}$ . In the presence of alkali, [H<sup>+</sup>] decreases as it is neutralized by OH<sup>-</sup>, resulting in the equilibrium shifting left to replenish the H<sup>+</sup> by LCP, thus more  $CrO_4^{2^-}$  is formed.

(e) (i) 
$$Pb(OH)_2 PbCO_3(s) \rightarrow 2PbO(s) + H_2O(g) + CO_2(g)$$

(ii) 
$$M_r Pb(OH)_2 PbCO_3 = [2(207) + 5(16.0) + 2(1) + 12.0]$$
  
= 508  
1 mole white lead produces 1 mole CO<sub>2</sub> and 1 mole H<sub>2</sub>O, so...  
Mass (in g) loss per mole white lead =  $M_r CO_2 + M_r H_2O$   
= 62.0  
Hence, % loss in mass = (62.0 / 508) × 100%  
= **12.2%**

- (iii) Decomposition temperature of Ca(OH)<sub>2</sub>.CaCO<sub>3</sub> would be **lower** than that of white lead, as...
  - Ionic radius of Ca<sup>2+</sup> (0.099 nm) < Ionic radius of Pb<sup>2+</sup> (0.120 nm) (students need not state values)
  - Charge density of Ca<sup>2+</sup> > charge density of Pb<sup>2+</sup>
  - Ca<sup>2+</sup> polarizes OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup> electrons cloud to a greater extent
  - Bond energy of O-H and O-C bond weakened
  - Less energy needed to overcome the bond energies to decompose.

Penalised if  $OH^{-}/CO_{3}^{2-}$  not mentioned in decomposition.

- **3 (a) (i)** k =  $(\ln 2) / t_{\frac{1}{2}}$ =  $(\ln 2) / 5$ = 0.139 min<sup>-1</sup>
  - (ii) Final [R-Br] =  $(6.25 / 100) \times 1.6$ = 0.1 mol dm<sup>-3</sup>  $1.6 \rightarrow 0.8 \rightarrow 0.4 \rightarrow 0.2 \rightarrow 0.1$ 4 t<sub>½</sub> must be drawn.



(b) (i)  $S_N 2$  reaction occurs because the 2 methyl groups do not pose much stearic hindrance, while  $S_N 1$  may occur as the 2 electron-donating methyl groups can stabilize the carbocation.

OR

 $S_{\rm N}1$  reaction occurs because the 2 methyl groups pose significant stearic hindrance, while  $S_{\rm N}2$  may occur as the 2 electron-donating methyl groups may not stabilize the carbocation.

(ii)



(iii) For  $[OH^-] = 0.01 \text{ mol dm}^{-3}$ , % rate =  $\frac{4.7 \times 0.01}{4.7 \times 0.01 + 0.24} \times 100\% = 16.4\%$  For  $[OH^{-}] = 0.1 \text{ mol } dm^{-3}$ , % rate =  $\frac{4.7 \times 0.1}{4.7 \times 0.1 + 0.24} \times 100\%$  = **66.2%** For  $[OH^{-}] = 1.0 \text{ mol } dm^{-3}$ , % rate =  $\frac{4.7}{4.7 + 0.24} \times 100\%$  = **95.1%** 

(iv) The higher the concentration of OH<sup>-</sup>, the higher the percentage rate for S<sub>N</sub>2, as the second order kinetics rate is dependent / proportional to [OH<sup>-</sup>].



 (c) (i) Boiling point increases from C<sub>2</sub>H<sub>5</sub>Cl → C<sub>2</sub>H<sub>5</sub>Br → C<sub>2</sub>H<sub>5</sub>I. As size of molecule (HX) increases, number of electrons increases, leading to greater tendency to polarize and instantaneous-dipole-induced-dipole attraction strength increases.

Thus more energy is required to overcome to id-id.

- (ii) Atomic radius: I > Br > Cl. Thus bond energy: C - I < C - Br < C - Cl Thus C<sub>2</sub>H<sub>5</sub>I would react with nucleophile more readily than C<sub>2</sub>H<sub>5</sub>Br (than C<sub>2</sub>H<sub>5</sub>Cl) as the bond is more easily overcome.
- (d) (i) Electrode I.
  - (ii)  $Ti^{x+} + xe^- \rightarrow Ti$

$$\frac{zF}{It} = \frac{M}{m}$$

$$\frac{x(96500)}{(0.5)(5400)} = \frac{47.9}{0.45}$$

x = 2.98 ≈ 3

## <u>OR</u>

 $n_{Ti} = \frac{0.45}{47.9} = 9.39 \times 10^{-3} \text{ mol}$ Q = It = (0.5A)(90 × 60s) = 2700C

If  $9.39 \times 10^{-3}$  mol Ti requires 2700C, 1 mol Ti would require  $\frac{2700}{9.39 \times 10^{-3}} = 287\ 400\ C$ x = Amount of electrons per mole of Ti =  $\frac{287400}{96500} = 2.98 \approx 3$ 



$$\Delta H_{f} = 6(-394) + 3(-286) + 3054$$
  
= -168 kJ mol<sup>-1</sup>

(ii) 
$$\Delta G = \Delta H - T\Delta S = -168 - (298)(-0.384) = -53.6 \text{ kJ mol}^{-1}$$

- (b) (i) 2,4,6-trichlorophenol has a larger K<sub>a</sub> value than phenol.
   3 electron withdrawing Cl further disperses the negative charge of the phenoxide ion, hence stabilizing the phenoxide ion to a larger extent, thus acidity (and K<sub>a</sub>) increases.
  - (ii) Add aqueous Br<sub>2</sub> (or conc HNO<sub>3</sub>). Phenol will decolourise brown Br<sub>2</sub> to colourless while forming a white precipitate (or for conc HNO<sub>3</sub>, yellow precipitate), while 2,4,6-tricholorophenol would not.

Full mark given only for correct test and results.



- (ii) Sn, conc HCl, heat, followed by NaOH(aq).
- (iii) Q may form intramolecular hydrogen bonding between OH and NH<sub>2</sub>, which would make unavailable the lone pairs or hydrogen for hydrogen bonding with water.
   1-napthol will only form intermolecular bonding with H<sub>2</sub>O.





More accurate if ionic bond indicated between  $O^-$  and  $Cu^{2+}$ . Penalised if phenol instead of phenoxide.

- (ii)  $Cu(NH_3)_4(H_2O)_2^{2+}$  or  $Cu(NH_3)_4^{2+}$
- (e) (i) Cu<sup>2+</sup> contains partially filled 3d orbitals. In the presence of ligands, the 3d orbitals are split into 2 groups of different energies (d and d\*). When a lower energy d electrons absorbs light to be promoted to the higher energy d\* orbital, it absorbs light of a particular wavelength in the visible region, allow the complementary colour to be observed.
  - (ii) This is due to ligand exchange. Different ligands of differing strengths cause the d-orbitals to be split to different extent, which would alter the d-d\* energy gap and cause a different wavelength of light to be absorbed, hence a different complementary colour.
  - (iii) Cu<sup>2+</sup> ions disrupts the disulfide bonds in keratin by reducing the sulfur in disulfide / by attracting the lone pair of electrons on S.
     (Ionic bonding ignored here as question specified S-S bonds in story).
  - (iv) Dilute acid / alkali and heat. Accept 6 mol  $dm^{-3} H_2SO_4$ .
- 5 (a) (i) At equilibrium, 2.0 moles  $NH_3$  remaining, thus 3.0 moles of  $N_2$  and 9.0 moles of  $H_2$  in the vessel.

Thus 
$$p_{NH3} = \frac{2}{14} p$$
,  $p_{N2} = \frac{3}{14} p$ ,  $p_{H2} = \frac{9}{14} p$   
 $K_p = \frac{p_{NH_3}^2}{p_{N_2} \cdot p_{H_2}^3}$   
 $= \frac{(\frac{2}{14}p)^2}{(\frac{3}{14}p) \cdot (\frac{9}{14}p)^3}$   
 $= 5.33 \text{ atm}^{-2}$ 

Solving, p = 0.259 atm.



- (iii) At lower temperatures which favour the exothermic forward reaction to produce ammonia, the reaction would be too slow. Thus, a catalyst is used to increase the rate so that the yield of ammonia can remain high and rate of production is reasonable.
- (b) (i) Carbon monoxide contains a lone pair of electrons on C which forms a dative (coordinate) bond to Fe<sup>2+</sup>.
  - (ii) Vanadium and iron are both transition elements, with **partially filled d orbitals** that can accept dative bonds.
  - (iii) Mass of V in sea squirt =  $100 \times 10^{-3}$  mol dm<sup>-3</sup> x 0.300 dm<sup>3</sup> x 50.9 g mol<sup>-1</sup> = 1.527 g

Volume of seawater needed =  $1.527 \text{ g} / 7.1 \times 10^{-6} \text{ g} \text{ L}^{-1}$ =  $2.15 \times 10^5 \text{ L}$ 

Mass of seawater needed =  $2.15 \times 10^5 \text{ L} \times 1.03 \text{ kg} \text{ L}^{-1}$ =  $2.22 \times 10^5 \text{ kg}$ 

(c)	Reactions	Deductions
	<b>S</b> : $C_{10}H_{14}O + 2Br_2 \rightarrow T$ : $C_{10}H_{14}OBr_4$	Electrophilic addition. <b>S</b> has 2 C=C bonds.
	Br <sub>2</sub> decolourised	
	<b>S</b> insoluble in NaOH.	<b>S</b> does not contain phenol or COOH.
	<b>S</b> and <b>T</b> + Tollen's $\rightarrow$ Ag(s)	Both <b>S</b> and <b>T</b> has aldehydes.
	<b>S</b> + hot KMnO <sub>4</sub> $\rightarrow$ <b>U</b> : C <sub>3</sub> H <sub>4</sub> O <sub>3</sub> + <b>V</b> : C <sub>7</sub> H <sub>10</sub> O <sub>5</sub>	Oxidative cleavage of both C=C in S. At
		least 1 C=C in cyclic structure.
	$\mathbf{U} + \mathbf{I}_2 / \mathbf{OH}^- \rightarrow \mathbf{CHI}_3$	U contains CH <sub>3</sub> -C=O ketone group.
		<b>U</b> is CH <sub>3</sub> C(O)COOH (by structure).
	$U + CO_3^{2^-} \rightarrow CO_2$	<b>U</b> contains COOH. <b>U</b> is $CH_3C(O)COOH$ .
	$V + \text{LiAlH}_4 \rightarrow \overset{HO}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H}{\overset{H}}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_3C}{\overset{H_{}}{\overset{H_{}}{\overset{H_{}}{\overset{H_{}}{\overset{H_{}}{\overset{H}{H$	

S can be one of



And **T** the corresponding tetra-brominated product (add Br<sub>2</sub> across each C=C).

(d) (i) Aq NaOH, heat.

Phenylamide would produce effervescence, the gas turning moist red litmus blue, while N-phenyl methylamide would not.

 (ii) Either PCI<sub>5</sub> (white fumes for 1<sup>st</sup> compound) or Na metal (effervescence for 1<sup>st</sup> compound).