Prelim 2009 H2 Chemistry P3 solutions

(a) Electronegativity is defined as the ability of an atom to attract **bonding pair of** electrons to itself in a covalent bond.

Oxygen atom is more electronegative than Nitrogen atom.

- Oxygen has a greater nuclear charge than Nitrogen atom.
- They have same screening effect.
- Effective nuclear charge of O atom is greater than that of N atom; it will attract the bonding electrons more strongly.
- (b) (i) Shape of N_2O is linear. Bond angle is 180° .
- (b) (ii) N₂O will require the highest temperature to behave like an ideal gas.
 - Ideal Gas Assumption: Negligible forces of attraction or repulsion between the particles.
 - N₂O exhibit permanent dipole-dipole interactions while the other 2 are exhibit temp dipole-induced dipole interactions.
 - Since pd-d is stronger than td-id; a higher temperature is required to overcome the intermolecular bonds between N₂O molecules for it to be ideal.
- (c)(i) By plotting a graph partial pressure against time; it was found that the half life is constant at **3500 s**; hence reaction is first order with respect to N₂O.

$$t_{1/2} = \frac{\ln 2}{k}$$

- (d) (i) Electrophilic substitution
 - (ii) Lone pair on oxygen atom of phenol is delocalized into the benzene ring, making it more reactive (more activated). more able to attract the electrophile, the diazonium ion.

(e) (i)

$$(H) \longrightarrow (H) \longrightarrow ($$

2 (i)(I) Minimum $[Ag^+] = 8.52 \times 10^{-14} \text{ moldm}^{-3}$

- (II) Minimum [Ag⁺] = $3.17 \times 10^{-5} \, moldm^{-3}$
- (ii) $[I^-] = 2.69 \times 10^{-12} \text{ moldm}^{-3}$

(b)(i) The reaction mixture must be titrated quickly or else the position of equilibrium will shift This will cause the measured amount of thiosulfate used to be inaccurate.

(ii) $K_c = 3.98 \times 10^{-3}$

(c) Electrophilic addition



carbocation intermediate B

Carbocation **A** is more stable than carbocation **B**, and **A** would lead to the major product.

(d) $CH_3COI + H_2O \rightarrow HI + CH_3COOH$

A undergoes complete hydrolysis, resulting in the formation of a strong acid HI, which completely dissociates in H^+ .

 $CH_2ICOOH + H_2O \Leftrightarrow H_3O^+ + CH_3COO^-$

B is a weak acid that undergoes partial dissociation, resulting in lesser moles of H^+ than in the case of **A** and therefore **A** would have pH 0.5 and **B** pH 3.0.



- 3(a) pH = 2.375
- (bi) Heat energy released by the neutralization process to complete the dissociation of CH_3COOH .
- (bii) $\Delta H_{neut} = -57.3 \text{ kJ mol}^{-1}$
- (ci) $CH_3COOH hydrogen bonding$ $CH_3COSH \& CH_3COSeH - td-id$ Energy required : H-bonding > td-id $CH_3COSeH - larger$ electron cloud
- (cii) $\Delta H_{\text{formation}}(\text{H-bonding}) = -24.5 \text{ kJ mol}^{-1}$



- II Enthalpy of dimerisation = -59 kJmol⁻¹
- III At low temperature, $\Delta G < O$, dimerisation is spontaneous.



- (dii) In the presence of NaOH, the phenol group is deprotonated to give O⁻/ phenoxide ion, which is a stronger nucleophile.
- (diii) Reagents: Add neutral iron(III) chloride / FeCl₃ Observations: Ethanoic acid – solution remains yellow

но СH₂OH

- An intense purple complex is formed.

4 a

$$\left[\operatorname{Ca}\right]^{2+} 2 \left[\begin{array}{c} \operatorname{Ca} \operatorname{C$$

b i Calcium iodate is white as the electronic transitions are between different principal quantum shells.

In the presence of ligands, the degenerate d-orbitals of Fe ions undergo dsplitting. An electron in the lower energy d-orbital undergoes d-d transition by absorbing visible light.

ii Fe has more protons than Ca, thus has a higher nuclear charge. The inner 3d electrons of Fe are poor shielding compared to the inner 3s and 3p electrons of Ca. Thus, the valence electrons of Fe experience greater attraction to the nucleus and require more energy to remove compared to Ca.

c i
$$2 \operatorname{Ca}(IO_3)_2(s) \rightarrow 2 \operatorname{CaO}(s) + 2 I_2(g) + 5 O_2(g)$$

ii The charge density of the ions given by $\frac{\text{charge}}{\text{ionic radius}}$ decreases down the group.

Hence, polarizing power of the ions decreases and the electron cloud of the iodate ion is polarized to a smaller extent.

The iodine-oxygen bonds in the iodate ion becomes less weakened and more energy is required to break the bonds. Thus, thermal stability of the group II iodates increase.

> $E^{o}_{cell} = 0.44 + 0.54$ = + 0.98 V

Thus, Fe is oxidized to Fe^{2+} .

Thus, the brown solution of iodine is decolourised and a pale green solution of Fe^{2+} formed. Fe metal dissolves.

e Ca²⁺ although cationic is unable to act as a catalyst. Thus the reaction still takes one day.

 Co^{2+} is cationic and shows variable oxidation states. Hence, Co^{2+} is able to act as a homogeneous catalyst as shown by the equations below. The reaction speeds up and only takes ten minutes.



5(b)(i)

- double bond character present in the C-CI bond present due to the overlapping of the p-orbital on CI atom with those of the C atoms of the ring resulting in a stronger C-CI bond.
- C-Cl bond in chloroethane is a single bond hence weaker and easier to cleave.

5(b)(ii)

- Chlorobenzene has a larger larger electron cloud size than chloroethane resulting in its stronger temporary dipole-induced dipole interactions.
- The energy at room temperature is insufficient to break all the forces between the chlorobenzene molecules but sufficient to break all the forces between the chloroethane molecules, causing chlroethane to exist in vapour form.

5(c)(i)

The product formed still has a lone pair present to act as a nucleophile to compete with NH_3 for chloroethane.

The yield can be increased by making NH_3 in excess.

5(c)(ii)





$$\Delta Hr^{\theta} = -57.3 - (-50.1) = -7.2 \text{ kJ mol}^{-1}$$

5(e)(ii)

