Raffles Institution 2015 Year 6 Preliminary Examination Suggested Answers to H2 Chemistry Paper 2

(a) H_2O_2 acts as an oxidizing agent to oxidise Co(II) to Co(III) and itself reduced to H_2O_2 .

(b) Preparation of the 100 cm³ crude mixture

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- 1. Weigh out accurately about 1.45 g of $Co(NO_3)_2$ using an electronic balance and transfer this to a 250 cm³ beaker.
- 2. Measure out 45 cm³ of concentrated ammonia using a 50 cm³ measuring cylinder and add this to the beaker. Stir with a glass rod to mix.
- 3. Measure out 25 cm³ of hydrogen peroxide using a separate 50 cm³ measuring cylinder and using a dropper, add this to the mixture dropwise/slowly.
- 4. Cool the mixture in an ice bath or carry out step 5 in an ice bath.
- 5. Measure out 30 cm³ of concentrated nitric acid using a separate 50 cm³ measuring cylinder and using a dropper, add this to the mixture dropwise/slowly with stirring.
- 6. Remove the mixture from the ice bath, allow the mixture to sit for 10 mins for complete reaction.

Precipitate the product from the crude mixture

- 7. Using a 100 cm³ measuring cylinder, transfer 100 cm³ of ethanol to the 250 cm³ beaker containing the crude mixture.
- 8. Allow the mixture to sit for 10 mins for complete precipitation.

Separate the precipitated product from the mixture

9. Filter the precipitated product using vacuum filtration/gravity filtration and wash the residue with ethanol to remove the impurities.

Recrystallisation

10. Transfer the residue into a 50 cm³ (or 100 cm³) conical flask with 2 boiling chips.

- 11. Add about 5 cm³ (small amount) of ammonium nitrate solution into the conical flask and place it on the heating plate. (or a hot ammonium nitrate solution can be prepared prior to addition by placing it on a heating plate)
- 12. When the mixture is boiling and the solid does not dissolve, add ammonium nitrate slowly to the mixture until the solid just dissolves.
- 13. Remove from heating plate and allow it to cool to room temperature slowly before cooling in an ice bath. Crystals will grow as the mixture is cooled.
- 14. Filter the cooled mixture using vacuum filtration/gravity filtration and wash the residue with cold ethanol.
- 15. Dry the residue under the infra-red lamp.

(c) The concentrated nitric acid (or concentrated ammonia) is corrosive. Wear gloves and goggles when handling the chemical / do the experiment in a fumehood.

OR

Inhaling the corrosive fumes of concentrated ammonia. Carry out the experiment in a fumehood.

OR

Ethanol is flammable. Any heating should be done using a water bath and not with a naked flame.

2 (a)(i) sp

(ii) The σ bond in C=O bond of R-N=C=O is made up of sp-sp² head-on overlap whereas the σ bond in C=O of CH₃COCH₃ is made up of sp²-sp² head on overlap.

The sp–sp² σ bond in C=O bond of R-N=C=O therefore has a higher s–character, hence leading to more effective overlap of orbitals and shorter bond length.

- (iii) Geometric (cis-trans) isomerism
- (iv) 3 stereoisomers
- **(b)** [Ag(NCO)₂]⁻



 $[Ag(OCN)_2]^-$



- (a)(i) HBr and HCl readily dissolve in water to form acids containing H_3O^+ , Br⁻ and Cl⁻.
 - (ii) HBr is a stronger reducing agent than HCl. HCl does not reduce concentrated H_2SO_4 .

HBr reduces concentrated H₂SO₄ to SO₂ in which the oxidation state of S decreases from +6 (in H_2SO_4) to +4 (in SO_2). HBr is oxidised to Br_2 in which the oxidation state of Br increases from -1 (in HBr) to 0 (in Br₂).

(iii)
$$\frac{PV}{T}$$

SO₂
HF
Ideal gas

 $2HBr(g) + H_2SO_4(l) \longrightarrow Br_2(l) + SO_2(g) + 2H_2O(l)$

HF forms strong intermolecular hydrogen bonding while SO₂ forms slightly weaker permanent dipole-permanent dipole interaction.

HF, with stronger intermolecular forces of attraction deviate from ideality to a larger extent, than SO₂.

- (b)(i) N≡N bond is strong and the reaction has a high activation energy.
 - (ii) As temperature increases, K_p increases. The position of equilibrium shifts to the right. An increase in temperature favours the endothermic forward reaction.

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(iii) In this reaction, 2 moles of gaseous molecules react to form 2 moles of gaseous products, $\Delta n=0. \Delta S^{\theta}$ is very small.

For the reaction to be feasible at high temperature, $\Delta G^{\theta} < 0$. Thus, $\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta} < 0$. Since ΔH^{θ} is positive, ΔS^{θ} must be slightly positive for ΔG^{θ} to be negative.

(iv)
$$\stackrel{xx}{*} \stackrel{\cdot}{O} \stackrel{\cdot}{*} : \stackrel{\cdot}{N} : \stackrel{xx}{\underset{xx}{O}} \stackrel{xx}{*}$$

- (v) NO and NO₂ are free radicals/have an unpaired electron. They will propagate a chain reaction to cause rapid and extensive ozone depletion.
- (vi) Step 1:



Step 2:



(c)(i)		$SCl_2(g)$	+ 2CH ₂ =CH ₂ (g)	\rightarrow	$C_4H_8SCl_2(g)$
	Initial / mol	0.258	0.592		0
	Change/ mol	-0.0350	-0.070		+0.0350
	Eqm / mol	0.223	0.522		0.0350

Total no. of moles of gas at equilibrium = 0.223 + 0.522 + 0.0350 = 0.780 mol

(ii) pV = nRT $p (5 \times 10^{-3}) = 0.780 \times 8.31 \times (20 + 273)$

(iii)
$$P_{SC12} = \frac{0.223}{0.780} \times 3.80 \times 10^5 = 1.086 \times 10^5 Pa$$

 $P_{CH2=CH2} = \frac{0.522}{0.780} \times 3.80 \times 10^5 = 2.543 \times 10^5 Pa$
 $P_{C4H8SC12} = \frac{0.035}{0.780} \times 3.80 \times 10^5 = 1.705 \times 10^4 Pa$
 $K_p = \frac{1.705 \times 10^4}{1.086 \times 10^5 \times (2.543 \times 10^5)^2} = 2.43 \times 10^{-12} Pa^{-2}$

(iv) With a larger flask, the volume of the system is greater, and the concentrations (or pressures) of all the gases are lower. The position of equilibrium will shift to the left with more gaseous molecules to increase the concentration (or pressure) of the gases.

OR

When volume increases, partial pressures of all the gases decreases

$$Q_{\rm p} = \frac{P_{C4H8SC12}}{P_{SC12} \times P_{C2H4}^{2}} > K_{\rm p}$$

Hence, the position of equilibrium will shift to the left to decrease Q_{p} .

AND

As the temperature of the system remains the same, and K_p is only affected by temperature, the K_p value is unchanged.

- (v) Addition
- (vi) Mustard gas: $ClCH_2CH_2SCH_2CH_2Cl$
- 4 (a)(i) Sn, conc HC*l*, heat then NaOH(aq)



(iii) AlBr₃

- (iv) A/ has a energetically low-lying empty p-orbital which can accept a pair of electrons.
- (v) The –NH₂ group activates the benzene ring due to the partial delocalisation of the lone pair of electrons on N into the pi electron cloud of the benzene ring. Hence the benzene ring is more susceptible to electrophilic attack in phenylamine and only mild conditions are required for reaction.
- (b)(i) Mechanism: Electrophilic substitution

Generation of electrophile: $2H_2SO_4 + HNO_3 \rightleftharpoons NO_2^+ + 2HSO_4^- + H_3O^+$

Step 1: Electrophilic attack by NO₂⁺



Step 2: Loss of a proton from carbocation





reaction co-oramate

(c)(i) The rate determining step (slow) in the nitration of benzene does not involve the breaking of the C-H bond.

Hence the deuterium isotopic effect is not present.

- (ii) Since $\frac{k_H}{k_D}$ = 6, the rate-determining step involves breaking of a C–H bond. Hence the rds is step 2.
- (iii) Rate = $k'[CH_3C(OH)CH_3^+] = k[CH_3COCH_3][H^+]$
- (iv) The rate-determining step does not involve the breaking of an I-I bond, so the rate of reaction does not depend on the concentration of iodine.
- 5 (a) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$
 - (b) The presence of H₂O ligands causes the splitting of the five 3d orbitals in Cu²⁺ ion into two sets of slightly different energy levels.

Since these 3d orbitals are partially filled, electrons from the lower-energy d orbitals can absorb energy corresponding to certain wavelengths (OR red/orange/yellow) from the visible spectrum and get promoted to the higher-energy d orbitals

The colour observed is the complement of the colour absorbed.

- (c)(i) $[Cu(NH_3)_4]^{2+}$ or $[Cu(NH_3)_4(H_2O)_2]^{2+}$
 - (ii) Fe(OH)₃

(d)(i)

(iii) $[Cu(NH_3)_4]^{2+}(aq) + 2H_2O(I) + 2H^+(aq) \longrightarrow Cu(OH)_2(s) + 4NH_4^+(aq)$



By Hess' Law, $\Delta H_f = +339 + \frac{1}{2} (+496) + 745 + 1960 + (-141) + 790 + \Delta H_{LE} = -155$ $\Delta H_{LE} = -4096 \text{ kJ mol}^{-1} = -4100 \text{ kJ mol}^{-1} (3 \text{ s.f.})$

(ii) Black CuO dissolves in concentrated HCl to form the yellow-coloured complex $[CuCl_4]^{2-}$.

When water is added in excess, a ligand exchange reaction occurs as the H_2O ligands replace the Cl^- ligands to form the blue-coloured complex $[Cu(H_2O)_6]^{2+}$. The following equilibrium is established:

 $[CuCl_4]^{2-}(aq) + 6H_2O(l) \approx [Cu(H_2O)_6]^{2+}(aq) + 4C\Gamma(aq)$