2020 RI H2 Chemistry Prelim Paper 2 – Suggested Solutions

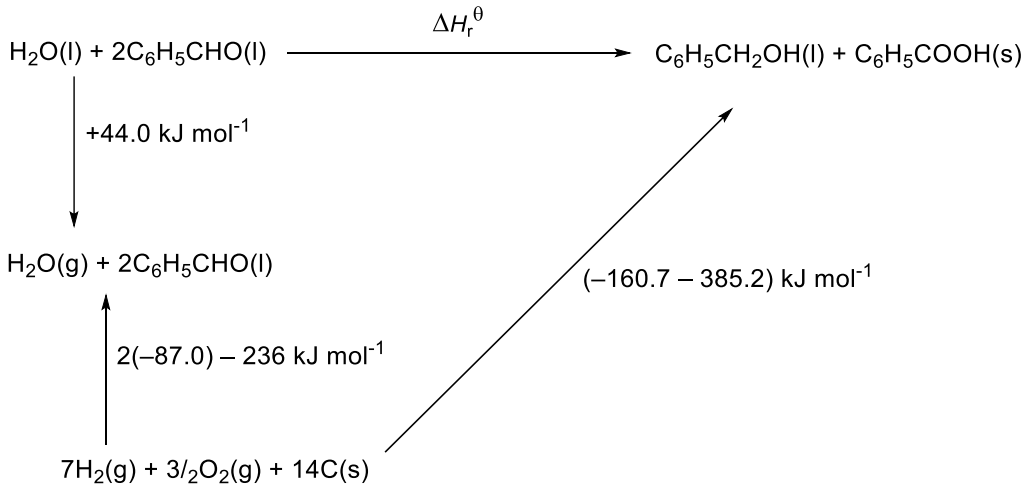
1(a)(i) oxidation number of C(1): +1
oxidation number of C(2): –1
oxidation number of C(3): +3

1(a)(ii) Disproportionation

1(b)(i) $H_2(g) + ½O_2(g) \longrightarrow H_2O(g)$

$\Delta H_f^{\ominus}(H_2O(g)) = BE(H–H) + ½\ BE(O=O) – 2BE(O–H)$
$= 436 + ½(496) – 2(460)$
$= –236\ kJ\ mol^{–1}$

1(b)(ii)



By Hess' Law,
$\Delta H_r^{\ominus} = +44 – 2(–87.0) – (– 236) –160.7 – 385.2 = –91.9\ kJ\ mol^{–1}$

1(b)(iii) equation 2 $2C_6H_5CHO(l) + H_2O(l) \longrightarrow C_6H_5CH_2OH(l) + C_6H_5COOH(s)$

$\Delta S^{\ominus} = 216.7 + 167.6 – 2(221.2) – 70 = –128.1\ J\ K^{–1}\ mol^{–1}$

$\Delta G^{\ominus} = \Delta H_r^{\ominus} – T\Delta S^{\ominus}$
$= –91.9 – 298(–128.1/1000) = –53.7\ kJ\ mol^{–1}$

$\Delta G^{\ominus} < 0$, hence the reaction is <u>feasible</u>.

2(a)(i) As the titration progresses, [$Ag^+(aq)$] decreases. If AgC*l* and AgBr are not filtered away before titration,
the ionic products of the silver halides fall below their respective K_{sp} values, causing the silver halide precipitates to dissolve and produce more Ag^+ ions.
OR
the position of equilibria (I) and (II) will shift to the left, causing the silver halide precipitates to dissolve and produce more Ag^+ ions.
$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$ ----- (I)
$Ag^+(aq) + Br^-(aq) \rightleftharpoons AgBr(s)$ ----- (II)

More SCN^- ions will be required to react with these additional Ag^+ ions (from the dissolution of silver halide precipitates) and the titre value will be larger than expected.

2(a)(ii) Amount of remaining Ag^+ ions in 10.0 cm^3 filtrate
= Amount of SCN^- ions
$= 14.25/1000 \times 0.100$
$= 1.425 \times 10^{-3}$
$= 1.43 \times 10^{-3}$ mol

2(a)(iii) Amount of remaining Ag^+ ions in 40 cm^3 of mixture after precipitation
$= 40.0/10.0 \times 1.425 \times 10^{-3}$
$= 5.70 \times 10^{-3}$ mol

Initial amount of Ag^+ ions added = $0.700 \times 15.0/1000 = 1.05 \times 10^{-2}$ mol

Amount of Ag^+ ions that reacted with the halide ions = $(10.5 - 5.70) \times 10^{-3}$
$= 4.80 \times 10^{-3}$ mol

Total concentration of halide ions = $4.80 \times 10^{-3} \div 25.0/1000 = 0.192$ mol dm^{-3}

Since sample **X** contains equimolar amounts of Cl^- and Br^- ions,
concentration of Cl^- ions = 0.192 / 2 = 0.0960 mol dm^{-3} (shown)

2(b)(i) At the end of the separation, a saturated solution of AgC*l* is formed. Hence,
$[Ag^+][Cl^-] = K_{sp} = 1.77 \times 10^{-10}$
$[Ag^+] = 1.77 \times 10^{-10} \div 0.0960 = 1.844 \times 10^{-9}$
$= 1.84 \times 10^{-9}$ mol dm^{-3}

2(b)(ii) At the end of the separation, the solution is still a saturated solution of AgBr. Hence,
$[Ag^+][Br^-] = K_{sp} = 5.35 \times 10^{-13}$
$[Br^-] = 5.35 \times 10^{-13} \div (1.844 \times 10^{-9}) = 2.90 \times 10^{-4}$ mol dm^{-3}

2(b)(iii) Amount of Ag^+ ions in solution = $1.844 \times 10^{-9} \times 25.0/1000 = 4.61 \times 10^{-11}$ mol

Amount of Ag^+ ions used to precipitate AgBr = $(0.0960 - 2.90 \times 10^{-4}) \times 25.0/1000$
$= 2.39 \times 10^{-3}$ mol

Total amount of Ag^+ ions added = $(2.39 \times 10^{-3}) + (4.61 \times 10^{-11}) = 2.39 \times 10^{-3}$ mol

Mass of $AgNO_3$ added = $2.39 \times 10^{-3} \times 169.9 = 0.407$ g

2(c)(i) Let the solubility of Ag_2CrO_4 in water be s mol dm^{-3}.

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$$

eqm conc	2s	s

$K_{sp} = 1.12 \times 10^{-12} = [Ag^+]^2 [CrO_4^{2-}] = 4s^3$

$s = 6.54 \times 10^{-5}$ mol dm^{-3}

2(c)(ii) Let the solubility of Ag_2CrO_4 in K_2CrO_4 solution be s' mol dm^{-3}.

$[K_2CrO_4] = 0.100 / 0.500 = 0.200$ mol dm^{-3}

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$$

eqm conc	2s'	s' + 0.2

$K_{sp} = 1.12 \times 10^{-12} = (2s')^2(s' + 0.200)$
Due to common ion effect, the solubility is reduced.
Hence, assume $(s' + 0.200) \approx 0.200$
$1.12 \times 10^{-12} = (2s')^2(0.200)$
$s' = 1.18 \times 10^{-6}$ mol dm^{-3}

2(c)(iii) Difference in solubility = $(6.54 \times 10^{-5}) - (1.18 \times 10^{-6}) = 6.42 \times 10^{-5}$ mol dm^{-3}

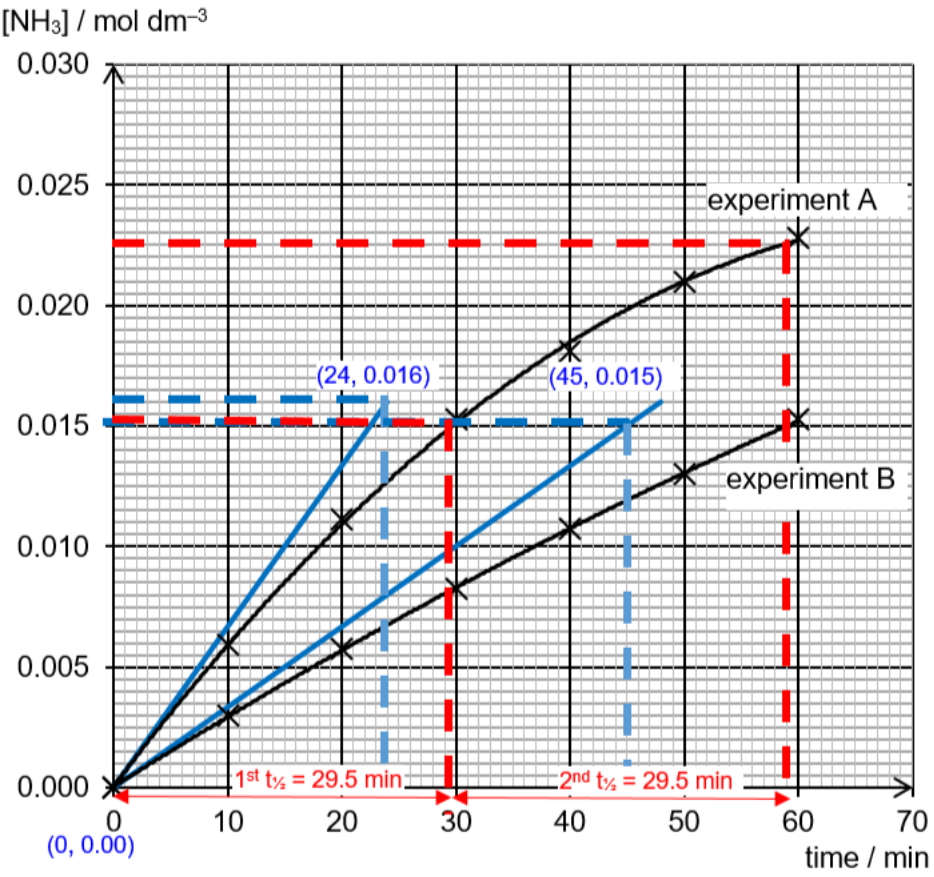
Amount of Ag_2CrO_4 precipitated = $6.42 \times 10^{-5} \times 0.500 = 3.21 \times 10^{-5}$ mol
Mass of Ag_2CrO_4 precipitated = $3.21 \times 10^{-5} \times 331.8 = 0.0107$ g

3(a)(i) $CO(NH_2)_2 + 2OH^- \longrightarrow 2NH_3 + CO_3^{2-}$

Since the initial concentration of $CO(NH_2)_2$ (limiting reagent) is 0.015 mol dm^{-3} for experiment A,

$[NH_3]$ when the reaction goes to completion = $2 \times 0.015 = 0.0300$ mol dm^{-3}

3(a)(ii)



From the graph of expt A,
First $t_{1/2}$ (from 0.0 → 0.015 mol dm^{-3}) = 29.5 min;
Second $t_{1/2}$ (from 0.015 → 0.0225 mol dm^{-3}) = 29.5 min
⇒ $t_{1/2}$ is constant

∴ reaction is first order with respect to $CO(NH_2)_2$.
(Note: Show all construction lines and label at least two $t_{½}$ on the graph)

For expt A,

initial rate = ½ x $\frac{0 - 0.016}{0 - 24}$ = 3.333 x 10^{-4} ≈ 3.33 x 10^{-4} mol dm^{-3} min^{-1}

For expt B,

initial rate = ½ x $\frac{0 - 0.015}{0 - 45}$ = 1.666 x 10^{-4} ≈ 1.67 x 10^{-4} mol dm^{-3} min^{-1}

(Note: On the graph, label coordinates used to obtain the initial rates.)

Comparing expt A and expt B, when $[OH^-] \times 2$, initial rate $\times 2$.

∴ reaction is first order with respect to OH^- ions.

[Alternative method to find order of reaction with respect to OH^- ions]

$t_{1/2}$ of expt A = 29.5 min
$t_{1/2}$ of expt B = 59.0 min

Since OH^- is in large excess, $[OH^-]$ remains effectively constant during the reaction. Hence the reaction follows pseudo first-order kinetics.

rate = $k'[CO(NH_2)_2]$, where $k' = k[OH^-]^x$

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[OH^-]^x}$$

By comparing expt A and expt B and their $t_{1/2}$ values, <u>when $[OH^-]$ is halved then $t_{1/2}$ is doubled.</u>
$\Rightarrow$ x = 1 and reaction is first order with respect to OH^- ions.

3(a)(iii) From expt A, $3.333 \times 10^{-4} = k(0.015)(2.0)$
$\therefore k = 0.01111 \approx 0.0111$ mol^{-1} dm^3 min^{-1}

OR

$$t_{½} = \frac{\ln 2}{k\,[OH^-]}$$

From expt A, $29.5 = \frac{\ln 2}{k\,(2.0)}$
$k = 0.0117$ mol^{-1} dm^3 min^{-1}

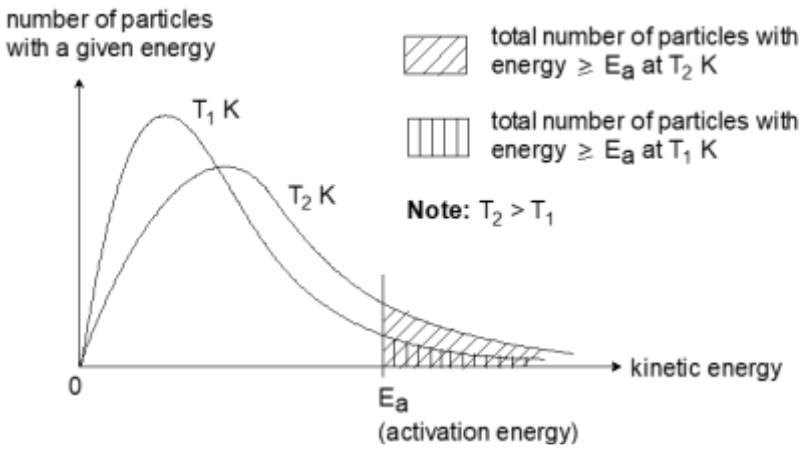
3(a)(iv) Since <u>OH^- is in large excess</u>, $[OH^-]$ remains effectively constant during the reaction. The reaction follows pseudo first-order kinetics.

rate = $k'[CO(NH_2)_2]$, where $k' = k[OH^-]$

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[OH^-]}$$

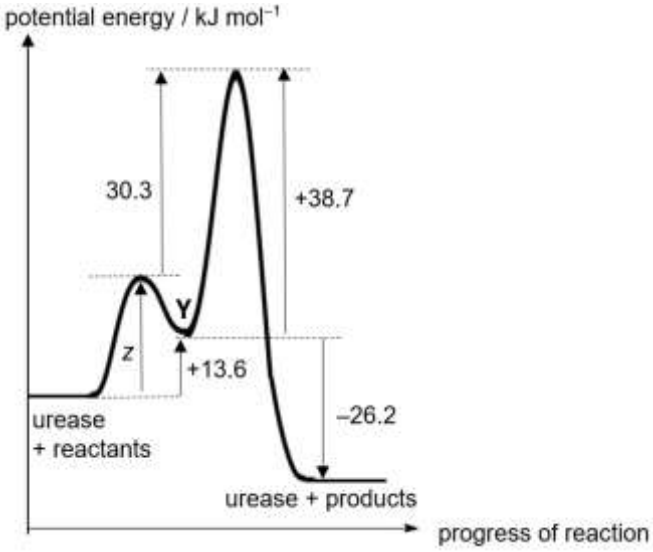
Since $[OH^-]$ in expt C is twice that of expt A *(or four times that of expt B)*,
$t_{1/2} = 29.5 \times ½ = 14.8$ min *(or $t_{1/2} = 59 \times ¼ = 14.8$ min)*
OR
$t_{1/2} = \ln 2 \div 0.0111(4.00) = 15.6$ min

3(a)(v)



As temperature increases from T_1 to T_2 K, the average kinetic energy of the reactant particles also increases. As such, significantly more reactant particles have energy greater than or equal to the activation energy of the reaction. Consequently, the frequency of effective collisions increases accordingly, and hence the reaction rate increases. Also, an increase in temperature results in a larger rate constant, and hence an increase in the reaction rate.

3(b)(i)



3(b)(ii) z = 13.6 + (38.7 – 30.3) = +22.0

3(b)(iii) At low $[CO(NH_2)_2]$, not all of the active sites on urease are occupied. In this case, rate $\propto$ $[CO(NH_2)_2]$ or reaction is first-order with respect to $CO(NH_2)_2$.

At high $[CO(NH_2)_2]$, all the active sites on urease become saturated / are fully occupied by molecules of $CO(NH_2)_2$. The reaction is zero order with respect to $CO(NH_2)_2$ or rate is independent of $[CO(NH_2)_2]$.

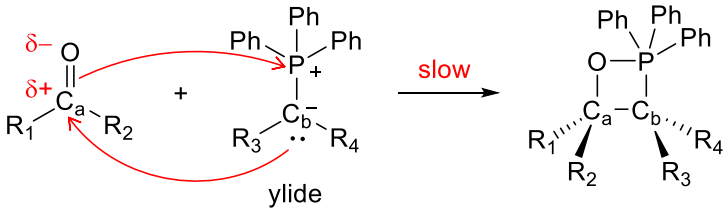
4(a) Nucleophilic addition

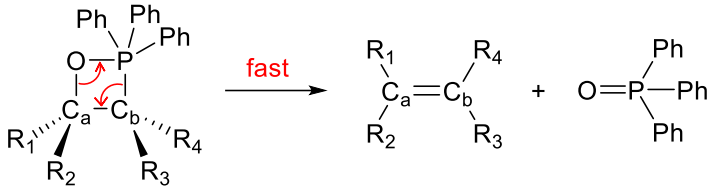
4(b)(i) sp^3

4(b)(ii) The O−C_a−C_b bond angle in the intermediate is 90° and deviates greatly from the <u>ideal bond angle of 109.5°</u>. Hence, the <u>orbital overlap is less effective / the bonds are weakened / reaction in step 2 will open the ring and relieve ring strain</u>.
Thus the reaction happens readily.

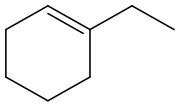
4(c) An alkene <u>does not have an electron-deficient carbon atom</u> for the nucleophilic ylide to attack.

4(d)

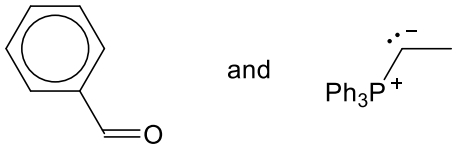




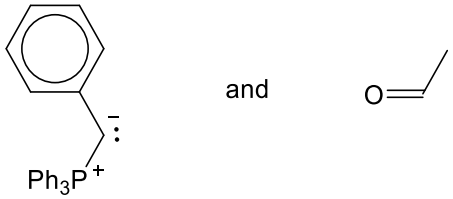
4(e)(i)



4(e)(ii)



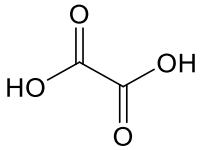
OR



4(f)(i) $K_2Cr_2O_7$(aq), H_2SO_4(aq), heat (under reflux)

4(f)(ii) Oxidation would lead to two ketone functional groups, which will lead to the formation of <u>a compound with two alkene functional groups (diene)</u> after the Wittig reaction.

4(g)(i)



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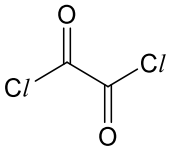

$C_2O_2Cl_2$

4(g)(ii) I_2(aq), NaOH(aq), heat

4(h) H_2O

5(a) Although Group 2 ions have the same charge, their ionic radii increase down the group. Hence charge density and polarising power of the ions decreases down the group.

Consequently, the electron cloud of the NO_3^- anion is distorted to a smaller extent and hence the covalent bonds within the NO_3^- anion is weakened to a smaller extent.

Thus, more heat energy is required to break the covalent bonds within the NO_3^- anion, causing temperature required to decompose Group 2 nitrates to increase down the group.

5(b)(i) Be is from Period 2 and does not have low lying (or energetically accessible) vacant d orbitals to expand its octet. Hence Be^{2+} can only form bonds with 4 H_2O.

OR

Be is from Period 2 and the vacant orbitals available in Be^{2+} to accept lone pair of electrons from O in H_2O are from the n=2 shell.
Since the n=2 shell has only one 2s and three 2p orbitals (or 4 orbitals), Be^{2+} can only accept 4 lone pairs of electrons from 4 H_2O molecules.
Hence only a maximum of 4 H_2O molecules can be coordinated to Be^{2+} in the aqua complex of Be^{2+}.

5(b)(ii) The higher the pK_a, the lower the K_a and the weaker the acid.

Having a smaller charge and a larger ionic radius, Mg^{2+} has a lower charge density / polarising power than Al^{3+} and thus polarises/distorts the electron cloud of H_2O coordinated to it to a lesser extent.

As a result, the extent of hydrolysis to form H^+ ions is lesser / O-H bond in water is polarised to a smaller extent for $[Mg(H_2O)_6]^{2+}$ resulting in its lower acidity and hence higher pK_a.

5(b)(iii) The gas produced is CO_2.

To liberate CO_2 from CO_3^{2-}, the reagent added must be a stronger acid than HCO_3^- and H_2CO_3.

As $[Al(H_2O)_6]^{3+}$ is a stronger acid (as shown by its smaller pK_a value) than HCO_3^- and H_2CO_3, it reacts with CO_3^{2-} to form H_2CO_3. H_2CO_3 then decomposes to form CO_2 and H_2O, resulting in effervescence being observed.

5(b)(iv)

precipitate formed between Na_2CO_3(aq) and Mg^{2+}(aq)	$MgCO_3$
precipitate formed between Na_2CO_3(aq) and Al^{3+}(aq)	$Al(OH)_3$

5(c)(i) $Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq)$
OR
$Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2[Al(OH)_4]^-(aq)$

5(c)(ii) $PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$

pH of resultant solution = 1 or 2

5(d)(i) Electronic configuration of calcium: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Electronic configuration of copper(I) ion, Cu^+: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

5(d)(ii) Graph Y showed the variation in successive ionisation energies (IE) for Ca.
This is because there is a large jump between the 2nd and 3rd IE showing that the 3rd electron is removed from an inner shell and the atom has 2 valence electrons.

5(d)(iii) $E^{\ominus}[Cu^{2+}(aq) \mid Cu(s)] = +0.34V$
$E^{\ominus}[H_2O(l) \mid H_2(g)] = -0.83V$
$E^{\ominus}[Ca^{2+}(aq) \mid Ca(s)] = -2.87V$

As Cu^{2+} has the most positive $E^{\ominus}$ value, Cu^{2+} will be (preferentially) discharged at the cathode to form Cu(s).

Hence, the method works as Cu(s) will be separated from the Ca^{2+} ions remaining in the solution.