Note to Head Mentors

Dear Mentors,

We are grateful for your time and effort that put into thorough reading of the 49th IChO preparatory problems. We valued and appreciated your suggestions and comments as they help us improve the preparatory problems. The suggestions and comments are carefully considered and addressed in this revised version.

The following are the list of preparatory problem topics and their solutions to the tasks that have been revised.

Tasks: 14 (14.1), 19 (structure of Perovskite), 27 (NMR data).

Solutions to the Tasks: 3 (3.1), 5 (5.2 and 5.3), 10 (10.5), 14 (14.1) and 19 (19.1).

For clarity, the corrections are highlighted in yellow.

Further comments and suggestions are always welcome. The revised version of the preparatory problems will be published by mid-March. We greatly appreciate your kind help and support.

We look forward to seeing you in Thailand.

Sincerely,

Task authors

Revised Preparatory Problems

Task 14. Spectrophotometric Determination of Iron

To study in vitro gastric digestion of iron, the following procedure is carried out. Dried and homogeneously ground supplement tablet of 0.4215 g is accurately weighed, mixed with 10 cm^3 of water, adjusted to pH 2.0 with 6 mol dm^{-3} HCl, 0.375 cm^3 of pepsin solution (16% w/v) added, and adjusted to 12.50 cm^3 with 0.01 mol dm^{-3} HCl. This mixture was quantitatively transferred into a dialysis bag of a fixed volume, which is further immersed for 2 hours in a 20.00 cm^3 solution containing 0.01 mol dm^{-3} HCl. Iron released by gastric digestion is dialyzed until the concentration of iron inside and outside the dialysis bag are equal.

0.01 mol dm^{-3} HCl of 20.00 cm^3

Magnetic stirrer

Dialysis bag

Dried sample of 0.4215 g, mixed with 10 cm^3 of water, adjusted to pH 2.0 with 6 mol dm^{-3} HCl, added with 0.375 cm^3 of pepsin solution, and adjusted to 12.50 cm^3 using with 0.01 mol dm^{-3} HCl
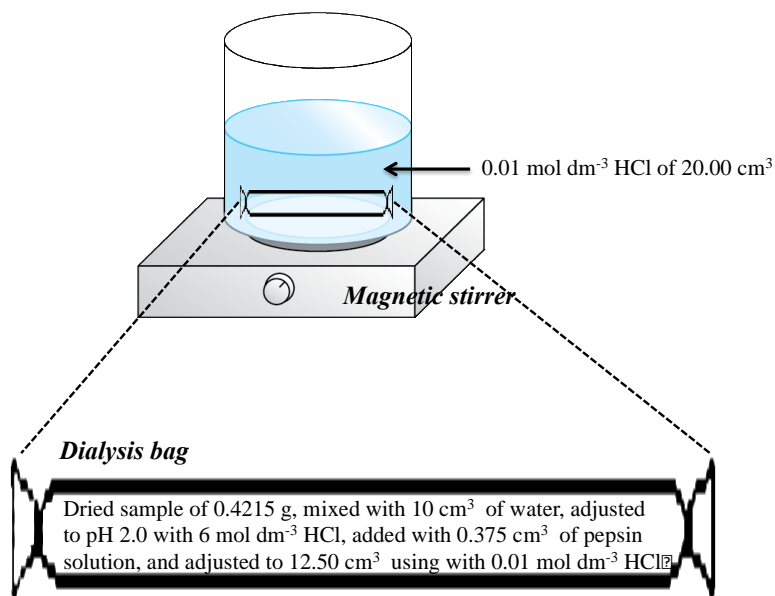
To determine the gastric digestible iron from the supplement tablet, colorimetric measurement after complex formation between ferrous ion (M) and complexing agent (L) is carried out at pH 5.0. The resulting ML$_3$ complex exhibits light absorption at 520 nm, whereas M and L do not absorb light at this particular wavelength.

C_M, mol dm^{-3}	C_L, mol dm^{-3}	Abs (at 520 nm), pathlength (b) = 1 cm
6.25×10^{-5}	2.20×10^{-2}	0.750
3.25×10^{-5}	9.25×10^{-5}	0.360

In an excess of L, all of iron is in the form of ML_3.

a) Calculate the molar absorptivity (ε) of ML_3 complex

b) Calculate the formation constant (K_f) of ML_3 complex

14.2) The CHN analysis shows that the complexing agent (L) contains 80% C, 4.44% H, and 15.56% N. The molar mass of this compound is 180 g. Determine the molecular formula of L.

14.3) The Fe^{2+} complex, ML_3, adopts the octahedral structure (assume perfect octahedral geometry for each isomer of these three complexes). Sketch the d-orbital splitting diagram for ML_3. Draw all possible isomers of Fe^{2+} complex. Order the magnitudes of Δ_o (crystal field splitting) of these three complexes and explain.(Spectrochemical series: $I^- < Br^- < Cl^- \approx SCN^- < F^- \approx$ urea $< ONO^- \approx OH^- < H_2O < NCS^- <$ pyridine $\approx NH_3 <$ en $<$ bipy $< o$-phen $< NO_2^- < CN^- \approx CO$)

14.4) To determine the dialyzable iron concentration (iron outside the dialysis bag), 5.00 cm^3 of the solution outside the dialysis bag is added with a reducing agent to ensure that all of dissolved iron is in the ferrous ion form. Then, the solution is adjusted to the suitable pH, followed by addition of excess amount of complexing agent (L) and deionized water added to make up the volume to 50.00 cm^3 in a volumetric flask. The absorbance measured at 520 nm is 0.550. Calculate the concentration of dialyzable iron (in unit of mg dm^{-3}).

14.5) Presumable, all of iron in the supplement tablet is completely digestible in the gastric condition. Determine in mg the iron in 1.0000 g of supplement tablet.

Task 19. Perovskite Structure

A mineral perovskite crystallizes in the cubic unit cell in which Ca^{2+} and O^{2-} ions constitute a ccp arrangement and Ti^{4+} ion occupies an interstitial hole as shown here.
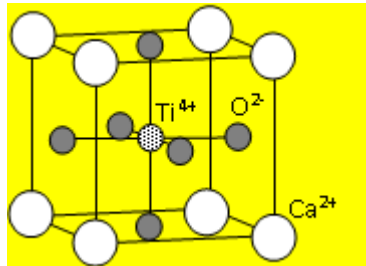
19.1) Based on the unit cell above, what is the empirical formula of perovskite?

19.2) Name types of interstitial holes present in the ccp unit cell. How many holes are there, for each type, within the unit cell?

19.3) From your answer in 19.2, which type of interstitial hole is occupied by Ti^{4+} ion?

Task 27. Atropine

Atropine is an organic compound used to treat certain types of nerve agent and pesticide poisonings. This compound can be synthesized from tropine and tropic acid in one step.

27.1) Tropine can be prepared as shown in the diagram below. The first step of this synthesis is "double Mannich reaction" (Robinson, 1917).

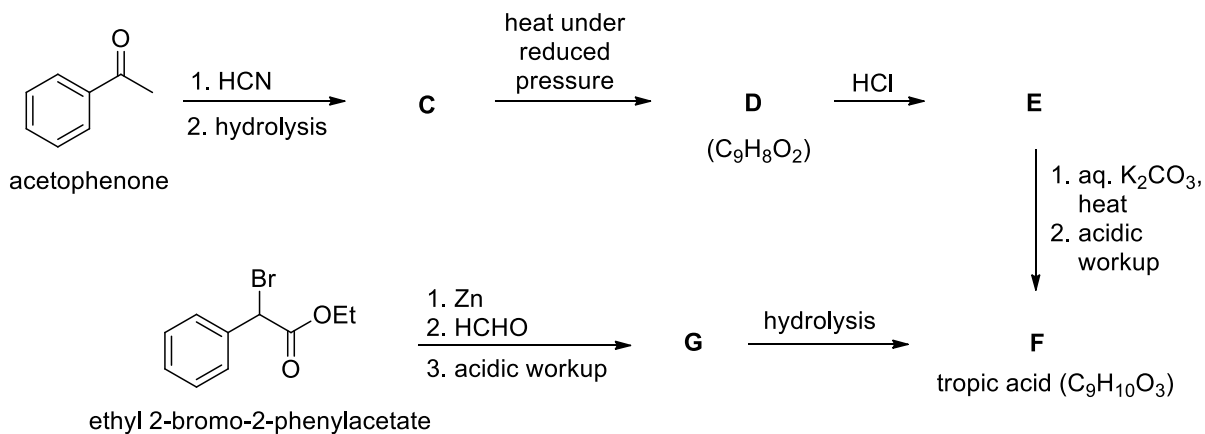Write down the structural formulae of compounds **A** and **B**.
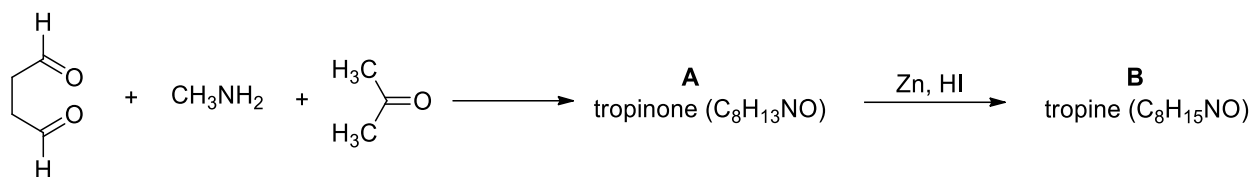
27.2) Tropic acid can be prepared from the reaction of acetophenone and HCN followed by hydrolysis, elimination, addition and nucleophilic substitution (Mackenzie and Ward, 1919). In this synthesis, it should be noted that the electrophilic addition by HCl did not follow Markovnikov's Rule, and the anti-Markovnikov product (**E**) was obtained.

Tropic acid (**F**) can also be prepared in only three steps from ethyl 2-bromo-2-phenylacetate and paraformaldehyde (Pernot, 1950). NMR data of tropic acid (**F**) are provided below.
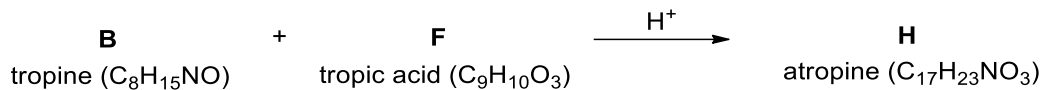
^{1}H NMR (400 MHz, d-DMSO): δ 12.35 (br, s, 1H), 7.34-7.25 (m, 5H), 4.91 (br s, 1H), 3.91 (dd, J = 10.0, 8.4 Hz, 1H), 3.64 (dd, J = 8.4, 6.0 Hz, 1H), 3.56 (dd, J = 10.0, 6.0 Hz, 1H).

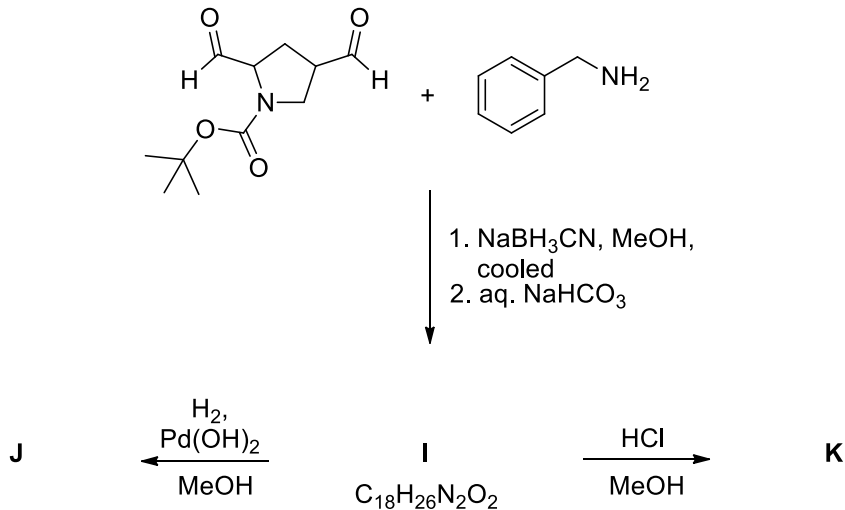^{13}C NMR (101 MHz, d-DMSO) δ 173.7, 137.1, 128.4, 128.0, 127.1, 63.4, 54.3

Write down the structural formulae of compounds **C**-**G** in the diagram below. t

27.3) When tropine was combined with tropic acid under acidic conditions, atropine was produced. Write down the structural formula of atropine.

$$\text{B} \quad + \quad \text{F} \quad \xrightarrow{\;H^+\;} \quad \text{H}$$

tropine ($C_8H_{15}NO$)   tropic acid ($C_9H_{10}O_3$)   atropine ($C_{17}H_{23}NO_3$)

27.4) Predict the major products of the reactions shown below. ^{13}C NMR spectrum of compound **I** shows nine signals in the range of 0-80 ppm, four signals in the range of 120-140 ppm, and one signal at 155 ppm. ^{13}C NMR spectrum of compound **J** shows eight signals in the range of 0-80 ppm and one signal at 155 ppm. ^{13}C NMR spectrum of compound **K** shows seven signals in the range of 0-80 ppm and four signals in the range of 120-140 ppm.

1. NaBH$_3$CN, MeOH, cooled
2. aq. NaHCO$_3$

$$\text{J} \xleftarrow[\text{MeOH}]{\begin{array}{c}H_2,\\ Pd(OH)_2\end{array}} \quad \underset{C_{18}H_{26}N_2O_2}{\textbf{I}} \quad \xrightarrow[\text{MeOH}]{\text{HCl}} \quad \text{K}$$

Revised Solution to the Tasks

Task 3. Expansion of Ideal Gas and Thermodynamics of Liquid Mixing

3.1) $\Delta U = 0, \quad q = -w$

$w = -P\Delta V = -(1.00 \text{ atm})(2.42\text{-}0.200 \text{ dm}^3)(101.325 \text{ J dm}^{-3} \text{ atm}^{-1})$

$= -225 \text{ J}$

$q = 225 \text{ J}$

$\Delta S_{surr} = -225 \text{ J}/295.4 \text{ K} = -0.762 \text{ J K}^{-1}$

$\Delta S_{sys} = (0.100 \text{ mol})(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \ln(2.42/0.200) = 2.07 \text{ J K}^{-1}$

$\Delta S_{univ} = 2.07 + (-0.762) = 1.31 \text{ J K}^{-1}$

3.2) $\Delta H^{mix} = \Delta V^{mix} = 0$

The other functions are given by these equations:

$\Delta G^{mix} = RT \sum_i x_i \ln x_i$ and $\Delta S^{mix} = -R \sum_i x_i \ln x_i$.

The mole fraction of **A** is $3.00/(3.00+5.00) = 0.375$.

The mole fraction of **B** is $1.000\text{-}0.375 = 0.625$.

$\Delta G^{mix} = (8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298.0 \text{ K})\{0.375\ln(0.375)+0.625\ln(0.625)\} = -1639 \text{ J mol}^{-1}$

$\Delta S^{mix} = -(8.314 \text{ J mol}^{-1} \text{ K}^{-1})\{0.375\ln(0.375)+0.625\ln(0.625)\} = 5.50 \text{ J K}^{-1} \text{ mol}^{-1}$

Task 5. Water-gas-shift Reaction

5.1) The mole fraction of H_2 in the reactor, $X_{H_2} = \dfrac{n_{H_2}}{n_{H_2} + n_{CO_2} + n_{H_2O} + n_{CO}} = \dfrac{0.475}{1.0} = 0.475$.

Thus, $P_{H_2} = X_{H_2} P_{total} = (0.475)(1.00 \text{ atm}) = 0.475 \text{ atm}$.

And likewise, $P_{CO_2} = 0.475 \text{ atm}$ and $P_{H_2O} = P_{CO} = 0.025 \text{ atm}$

$K = \dfrac{P_{H_2} P_{CO_2}}{P_{H_2O} P_{CO}} = \dfrac{(0.475)(0.475)}{(0.025)(0.025)} = 3.6 \times 10^2$

Therefore, $\Delta G^o = -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(273 \text{ K}) \ln(3.6 \times 10^2) = -13.4 \text{ kJ mol}^{-1}$.

5.2) The kinetics data given reflects the forward rate of the WGS reaction. The only rate law that is consistent with the given data is $r_f = k_f P_{CO} P_{H_2O}$, and $k_f = 4.4 \times 10^{-3}$ atm^{-1} s^{-1}.

Thus, X = $(4.4 \times 10^{-3}$ atm^{-1} s$^{-1})(0.28$ atm$)(0.72$ atm$) = 8.9 \times 10^{-4}$ atm s^{-1}.

5.3) $k_b = k_f/K = (4.4 \times 10^{-3}$ atm^{-1} s$^{-1})/(3.6 \times 10^2) = 1.2 \times 10^{-5}$ atm^{-1} s^{-1}.
So during the normal course of the reaction,
$r = r_f - r_b = k_f P_{CO} P_{H_2O} - k_b P_{CO_2} P_{H_2} = (4.4 \times 10^{-3}$ atm^{-1} s$^{-1})(0.14$ atm$)(0.14$ atm$) - (1.2 \times 10^{-5}$ atm^{-1} s$^{-1})(0.36$ atm$)(0.36$ atm$) = 8.44 \times 10^{-5}$ atm s^{-1}.

5.4) $\Delta G = \Delta G^o + RT \ln Q = (-13.4$ kJ mol$^{-1}) + (8.314$ J mol^{-1} K$^{-1})(273$ K$) \ln\left(\dfrac{(0.36)(0.36)}{(0.14)(0.14)}\right) = -9.1$

kJ mol^{-1}

5.5) The reaction $CO_2H(ads) \rightarrow CO_2(ads) + H(ads)$ is first-order, whose rate can be expressed as rate $= k[CO_2H] = k\theta S_0 = k'\theta$, where S_0 denotes the maximum number of adsorbed intermediates for this surface.
Thus, $\theta = $ rate$/k' = (1.0 \times 10^{11}$ molecules s^{-1} cm$^{-2})/(2.0 \times 10^{12}$ molecules s^{-1} cm$^{-2}) = 0.050$.
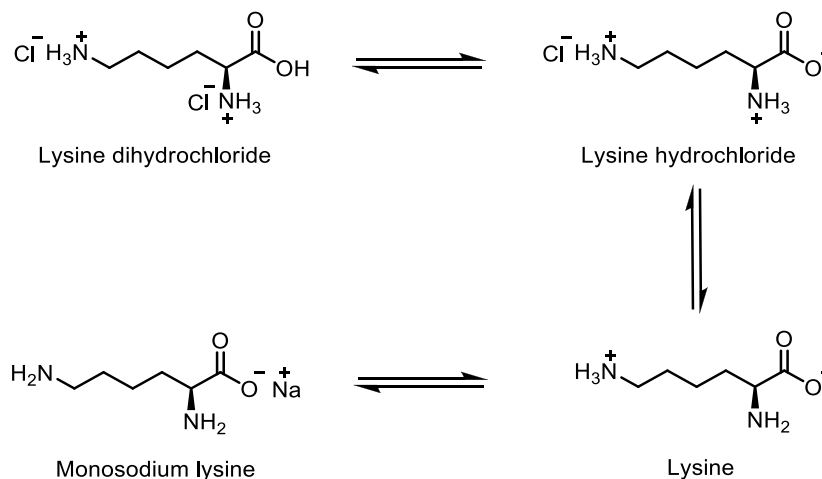
Task 10. Buffer from Biological Acid: Lysine

Acid Dissociation Constants

10.1)
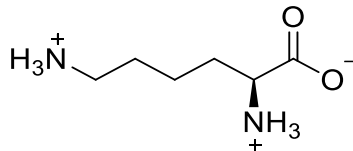
No, the correct form is shown:

10.2)

Lysine dihydrochloride	Lysine hydrochloride

Monosodium lysine	Lysine

10.3) *Given that* H_3L^{2+} : *the most acidic form*

                 H_2L^+ : *the first intermediate form*
                 HL : *the second intermediate form*
 L^-: *the most basic form*

    To prepare buffer solution at pH 9.5, the conjugate acid H_2L^+ is mixed with conjugate base HL.

    Starting with the most acidic form H_3L^{2+}, all of H_3L^{2+} is converted to H_2L^+.
    Number of moles of KOH used to convert H_3L^{2+} to H_2L^+:
         $nKOH_i = (0.100$ mol dm$^{-3})(0.1$ dm$^3) = 0.01$ mol KOH
    Then some of H_2L^+ is converted to HL to create a buffer solution by reacting with x mol of KOH ($nKOH_{ii}$):

	H_2L^+ +	OH^- ⇌	HL +	H_2O
(i)	*0.01 mol*	*x mol*	*0*	
(ii)	*-x*	*-x*	*+x*	
(iii)	*0.01-x*	*0*	*+x*	
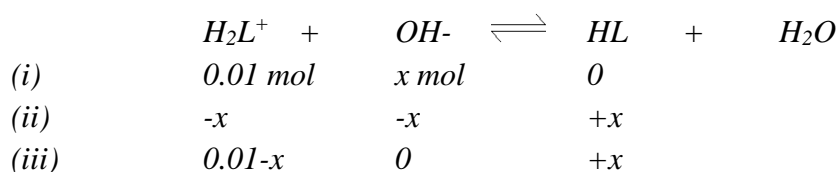
From Handerson-Hasselbalch equation:

$$pH = pK_a - log\frac{[H_2L^+]}{[HL]}$$

$$pH = pK_a - log\frac{0.01-x}{x}$$

$$9.5 = 9.06 - log\frac{0.01-x}{x}$$

$x = 0.0073$ *which is the number of mole of KOH used to convert* H_2L^+ *to HL*

Total KOH $= nKOH_i + nKOH_{ii} = 0.01 + 0.0073$ *mole* $= 0.0173$ *mole*
Volume of 0.5 mol dm^{-3} *KOH that is used* $= (\frac{1000\ cm3}{0.5\ mole})(0.0173\ mole) = 34.6\ \ $ cm^3

10.4) In this case, K_{a1} is carboxylic acid K_a, K_{a2} is ammonium K_a, and K_{a3} is substituent K_a.

HL is the second intermediate form

$$[H^+] = \sqrt{\frac{K_{a2}K_{a3}[HL]+K_{a2}K_w}{K_{a2}+[HL]}}$$

Since K_{a2} and K_{a3} are small;

$$[HL] = \frac{(5.00\ g)(\frac{1\ mol}{146.19\ g})}{0.100\ \text{dm}^3} = 0.342\ \text{mol dm}^{-3}$$

$$[H^+] = \sqrt{\frac{[10^{-9.06}10^{-10.54}(0.342)]+[10^{-9.06}10^{-14})}{10^{-9.06}+0.342}} = 1.59x10^{-10}\ \text{mol dm}^{-3}$$

pH = 9.80

The alternative calculation is pH = (pK$_{a2}$ + pK$_{a3}$)/ 2 = (9.06 + 10.54)/2 = 9.80.

10.5) $HL \rightleftharpoons L^- + H^+$ $\qquad\qquad\qquad$ $K_{a3} = 10^{-10.54}$

$\quad$ $HL + H_2O \rightleftharpoons H_2L^+ + OH^-$ $\qquad$ $K_{b2} = \frac{K_W}{K_{a2}} = \frac{10^{-14}}{10^{-9.06}} = 1.15 \times 10^{-5}$

From question 10.4; [H$^+$] $= 1.59x10^{-10}$ mol dm^{-3}

[OH$^-$] $= \frac{K_W}{[H^+]} = \frac{10^{-14}}{1.59x10^{-10}} = 6.29 \times 10^{-5}$ mol dm^{-3}

At equilibrium;

[HL] $= C_{HL}(\frac{K_1K_2[H^+]}{[H^+]^3+K_1[H^+]^2+K_1K_2[H^+]+K_1K_2K_3})$

$\qquad\qquad$ Where; C$_{HL}$=0.342 M

==[HL] = 0.250 M==

$$K_{a3} = \frac{[L^-][H^+]}{[HL]}$$

$$\rightarrow [L^-] = \frac{K_{a3}[HL]}{[H^+]} = \frac{10^{-10.54}(0.250)}{1.59x10^{-10}} = \boxed{0.0453} \text{ mol dm}^{-3}$$

$$K_{b2} = \frac{[H_2L^+][OH^-]}{[HL]}$$

$$\rightarrow [H_2L^+] = \frac{K_{b2}[HL]}{[OH^-]} = \frac{1.15\times10^{-5}(0.25)}{6.29x10^{-5}} = \boxed{0.0457} \text{ mol dm}^{-3}$$

$$H_2L^+ + H_2O \rightleftharpoons H_3L^{2+} + OH^- \qquad K_{b3} = \frac{K_W}{K_{a1}} = \frac{10^{-14}}{10^{-2.16}} = 1.45 \times 10^{-12}$$
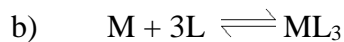
$$K_{b3} = \frac{[H_3L^{2+}][OH^-]}{[H_2L^+]}$$

$$\rightarrow [H_3L^{2+}] = \frac{K_{b3}[H_2L^+]}{[OH^-]} = \frac{1.45\times10^{-12}(0.0457)}{6.29x10^{-5}} = \boxed{1.05 \times 10^{-9}} \text{ mol dm}^{-3}$$

Task 14. Spectrophotometric Determination of Iron

14.1)

a) At ==C_L== $= 2.20 \times 10^{-2}$ mol dm^{-3}, $[ML_3] = 6.25 \times 10^{-5}$

A = εbC, therefore ε = A/bC = $0.750/6.25 \times 10^{-5}$ = 12,000 L mol^{-1} cm^{-1}

b) $M + 3L \rightleftharpoons ML_3$

$K_f = [ML_3] / [M] [L]^3$ \qquad\qquad (1)

at ==C_L== $= 9.25 \times 10^{-5}$ M, $[ML_3] = 0.360 / 12000$

$[ML_3] = 3.0 \times 10^{-5}$ mol dm^{-3} \qquad (2)

therefore, $[M] = (3.25 \times 10^{-5}) - (3.0 \times 10^{-5})$

$[M] = 0.25 \times 10^{-5}$ mol dm^{-3} \qquad (3)

$[L] = (9.25 \times 10^{-5}) - 3 \times (3.0 \times 10^{-5})$

$[L] = 0.25 \times 10^{-5}$ mol dm^{-3} \qquad (4)

Hence $K_f = (3.0 \times 10^{-5}) / (0.25 \times 10^{-5}) (0.25 \times 10^{-5})^3$

$K_f = 7.68 \times 10^{17}$ dm^9 mol^{-3}

14.2)   mole of C : mole of H : mole of N   =   80/12 : 4.44/1 : 15.56/14

                                           =   6.67 : 4.44 : 1.11
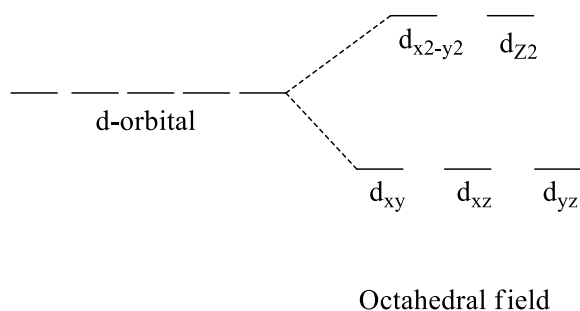
                                           =   6 : 4 : 1

therefore, the empirical formula of L is C_6H_4N

The empirical molar mass = (6 x 12) + (4 x 1) + (1 x 14) = 90
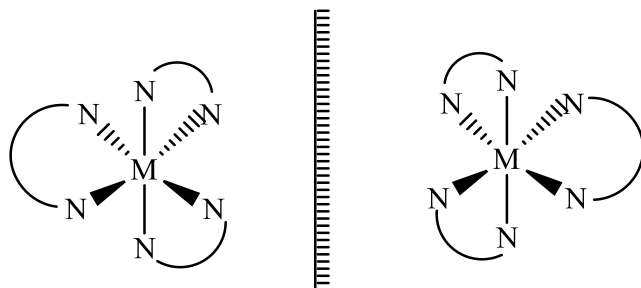
molar mass/ empirical molar mass = 180 / 2

Therefore, the molecular formula of L is $C_{12}H_8N_2$.

14.3)   **d-orbital splitting diagram for ML_3**

Octahedral field

Possible isomers of Fe^{2+} complexes

ML_3 :

Δ_o of $ML < ML_2 < ML_3$ ∵ H_2O is a weaker field ligand as compared with bipyridine.

14.4)

$A = \varepsilon bC$, therefore $C = A/\varepsilon b = 0.550/12000 = 4.58 \times 10^{-5}$ mol dm^{-3}

The concentration of dialyzable iron is

4.58×10^{-5} mol dm^{-3} x 50.00/5.00 $= 4.58 \times 10^{-4}$ mol dm^{-3}

4.58×10^{-4} mol dm^{-3} x 55.845 g mol^{-1} x 1000 mg g^{-1} $= 2558$ mg dm^{-3}

14.5)

From 14.4), the concentration of dialyzable iron is 2557.7 mg dm^{-3} which is also equal to the concentration of iron inside the dialysis bag.

The total volume is 12.50 cm^3 (inside the dialysis bag) + 20.00 cm^3 (outside the bag)

$= 32.50$ cm^3.

Therefore, the total amount of digestible iron is

(2557.7 mg dm^{-3} x 32.50 cm^3) / (1000 cm^3 dm^{-3}) = 83.125 mg

For the supplement of 0.4215 g, the iron content is 83.125 mg

For the supplement of 1.0000 g, the iron content is 83.125 mg x 1.0000 g / 0.4215 g

$= 197.2$ mg

Task 19. Perovskite Structure

19.1)   Number of Ca^{2+} ions: 8 corners x 1/8 Ca^{2+} ion/corner = 1

Number of O^{2-} ions: 6 cube faces x 1/2 O^{2-} ion/cube face = 3

Number of Ti^{4+} ions: one Ti^{4+} ion in the cube center = 1

Therefore, the empirical formula is CaTiO$_3$.

19.2)   (1) octahedral hole (4 per unit cell), (2) tetrahedral hole (8 per unit cell)

19.3)   Octahedral hole