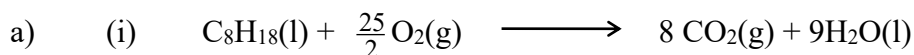


Worked solutions to the problems

Problem 1

The heat capacity of the calorimeter and its content is

$$C_s = 48 + (750 \times 4.184) = 3186 \text{ J K}^{-1}$$

The amount of heat released at constant volume is

$$q_v = -C_s \Delta T = -(3186 \text{ J K}^{-1})(8.220 \text{ K}) = -2.619 \times 10^4 \text{ J} = -26.19 \text{ kJ}$$

(Minus means exothermic reaction)

Hence, we obtain:

$$\Delta U^\circ = q_v = -26.19 \text{ kJ}$$

(ii) For the combustion of 1 mole of isooctane:

$$\Delta U^\circ = - \frac{(114.23 \text{ g mol}^{-1})(26.19 \text{ kJ})}{0.542 \text{ g}} = -5520 \text{ kJ mol}^{-1}$$

(iii) The enthalpy change (ΔH°) is related to ΔU° as follows:

$$\Delta H^\circ = \Delta U^\circ + \Delta n_{\text{gas}} (RT)$$

$$\text{From the reaction : } \Delta n_{\text{gas}} = 8 - \frac{25}{2} = -\frac{9}{2} \text{ mol}$$

$$\begin{aligned} \text{Thus, } \Delta n_{\text{gas}} (RT) &= \left(-\frac{9}{2}\right) (8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K}) \\ &= -11.15 \times 10^3 \text{ J} \end{aligned}$$

As ΔU° is given in kJ, we obtain

$$\Delta H^\circ = \Delta U^\circ - 11.15 = -5520 - 11.15 = -5531 \text{ kJ mol}^{-1}$$

(iv) Since $\Delta H^\circ = 8\Delta H_f^\circ, \text{CO}_2(\text{g}) + 9\Delta H_f^\circ, \text{H}_2\text{O}(\text{l}) - \Delta H_f^\circ, \text{C}_8\text{H}_{18}(\text{l})$

Therefore

$$\begin{aligned} \Delta H_f^\circ, \text{C}_8\text{H}_{18}(\text{l}) &= 8(-393.51) + 9(-285.83) - (-5531) \\ &= -190 \text{ kJ mol}^{-1} \end{aligned}$$

b) (i) From $\Delta G^\circ = -RT \ln K$, then

$$\ln K = -\frac{\Delta G^\circ}{RT} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

If the lower temperature, 298.15 K, is written as T_1 ,

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R}$$

Similarly, for the higher temperature 313.15 K

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R}$$

$$\text{Thus } \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\ln \frac{3.45 \times 10^3}{1.80 \times 10^3} = \frac{\Delta H^\circ \text{ J mol}^{-1}}{8.314} \cdot \frac{15.00 \text{ K}}{(298.15 \text{ K})(313.15 \text{ K})}$$

$$\Delta H^\circ = 33.67 \text{ kJ mol}^{-1}$$

For ΔS°

$$\ln 3.45 \times 10^3 = 8.146 = \frac{-33670 \text{ J mol}^{-1}}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(313.15 \text{ K})} + \frac{\Delta S^\circ \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\text{so that } \Delta S^\circ = 175.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

(ii) From the given equation, we obtain

$$K_p = \frac{P_{AB}}{P_A \cdot P_B}$$

From $PV = nRT$, then

$$K_p = \frac{[AB](RT)}{[A](RT)[B](RT)} = \frac{K_c}{RT}$$

At 298.15 K

$$K_p = \frac{(1.80 \times 10^3 \text{ L mol}^{-1})}{(8.314 \text{ atm L K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 0.726 \text{ atm}^{-1}$$

From $P_1 = X_1 P$, then

$$K_p = \frac{X_{AB}}{X_A \cdot X_B} \cdot P^{-1} = K_x \cdot P^{-1}$$

$$K_x = K_p \cdot P = (0.736 \text{ atm}^{-1})(1 \text{ atm}) = 0.726$$

c) From $\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$

Choose any two values of K at two different temperature, i.e. at 15.2°C (288.4 K) and 34.9°C (308.2 K).

$$\ln \frac{530}{840} = \frac{\Delta H^\circ}{8.314} \left(\frac{308.2 - 288.4}{288.4 \times 308.2} \right)$$

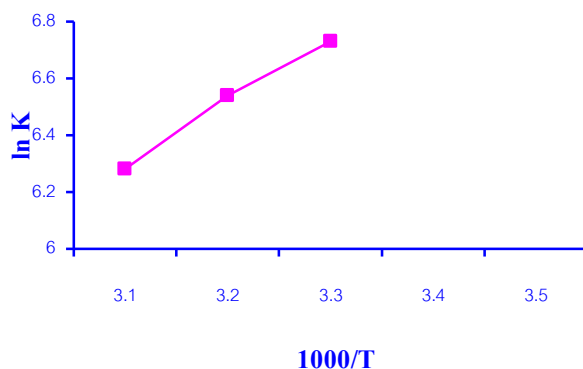
$$\Delta H^\circ = -1.72 \times 10^4 \text{ J} = -17.2 \text{ kJ}$$

OR

$$\text{From } \ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \cdot \frac{1}{T}$$

ΔH° and ΔS° are assumed to be constant. A plot of $\ln K$ against $1/T$ should be a straight line of slope equal to $-\Delta H^\circ/R$

T(Kelvin)	:	288.4	298.2	308.1
K	:	840	690	530
$10^3 / T$:	3.47	3.36	3.25
$\ln K$:	6.73	6.54	6.28



$$\text{Slope} = -\frac{\Delta H^\circ}{8.314} = 2.06 \times 10^3$$

$$\Delta H^\circ = -1.71 \times 10^4 \text{ J} = -17.1 \text{ kJ}$$

Problem 2

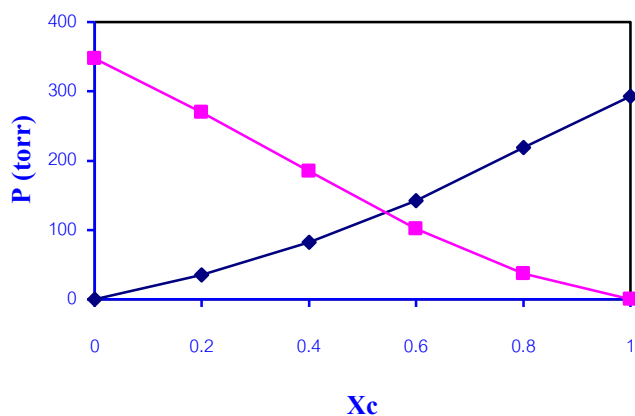
- a) (i) By calculation from the Raoult's law : $P_i = X_i P_i^\circ$, hence

X_C	: 0.20	0.40	0.60	0.80
$P_C = X_C P_C^\circ$ (torr)	: 59	117	176	234
P_C (measured)(torr)	: 35	82	142	219
$(P_C^\circ = 293 \text{ torr})$				

X_A	: 0.80	0.60	0.40	0.20
$P_A = X_A P_A^\circ$ (torr)	: 277	208	139	69
P_A (measured)(torr)	: 270	185	102	37
$(P_A^\circ = 347 \text{ torr})$				

It can be seen that the calculated vapor pressures of both acetone and chloroform are higher than the measured values at all proportions. Thus, the solutions deviated from ideal solution.

It can be shown, however, by plotting the pressure-composition diagram as follows:



- (ii) The solutions exhibit negative deviation from ideal behavior.

- (iii) From the data given, we can then calculate the activity of chloroform and acetone:

X_C	:	0.20	0.40	0.60	0.80
$a_C = P_C / P_C^\circ$:	0.12	0.28	0.48	0.75
X_A	:	0.80	0.60	0.40	0.20
$a_A = P_A / P_A^\circ$:	0.78	0.53	0.29	0.11

The activities of both chloroform and acetone are less than the mole fractions indicating negative deviation from ideal behavior.

- b) (i) From the Gibbs-Helmholtz equation,

$$\frac{d \ln X_1}{dT} = \frac{\Delta H_{\text{fus}}^\circ}{RT^2} \quad (1)$$

Where X_1 is the mole fraction of the liquid solvent and $\Delta H_{\text{fus}}^\circ$, the heat of fusion of pure solvent. If $\Delta H_{\text{fus}}^\circ$ is independent of T over a moderate range of temperature, we may integrate Eq.(1) from T_f° , the freezing point of pure solvent at $X_1 = 1$, to T , the temperature at which solid solvent is in equilibrium with liquid solvent of mole fraction X_1 . The result is

$$\ln X_1 = \frac{\Delta H_{\text{fus}}^\circ}{R} \left(\frac{1}{T_f^\circ} - \frac{1}{T} \right) \quad (2)$$

By expressing X_1 in terms of X_2 , the mole fraction of the solute:

$$\ln (1-X_2) = \frac{\Delta H_{\text{fus}}^\circ}{R} \left(\frac{T - T_f^\circ}{T \cdot T_f^\circ} \right) \quad (3)$$

If X_2 is small (corresponding to a solution), then

$$\ln (1-X_2) \sim -X_2$$

The freezing point depression is $T_f^\circ - T = \Delta T_f$. Since ΔT_f is small in comparison to T_f° , we may set the product $TT_f^\circ \sim T_f^{\circ 2}$. These changes convert Eq. (3) to

$$X_2 = \frac{\Delta H_{\text{fus}}^\circ}{R} \cdot \frac{\Delta T_f}{T_f^{\circ 2}} \quad (4)$$

In dilute solution, $X_2 = n_2/(n_1 + n_2) \sim n_2/n_1$.

The molality m_2 is related to the amount of n_2 of solute by $m_2 = \frac{n_2}{w_1} \times 1000$

where w_1 is the mass in grams of solvent.

For the solvent $n_1 = w_1/M_1$, where M_1 is its molar mass.

Then $X_2 = m_2 M_1 / 1000$.

Rearrangement of Eq. (4) and substitution for X_2 yields

$$\Delta T_f \sim \frac{M_1 R T_f^{\circ 2}}{\Delta H_{\text{fus}}^\circ \cdot 1000} \cdot m_2 \quad (5)$$

The freezing point depression or cryoscopic constant K_f defined as

$$K_f = \frac{M_1 R T_f^2}{\Delta H_f \cdot 1000} \quad (6)$$

Therefore,

$$\begin{aligned} K_f &= \frac{(147.01 \text{ g mol}^{-1})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(326.28 \text{ K})^2}{(17880 \text{ J mol}^{-1})(1000 \text{ g kg}^{-1})} \\ &= 7.26 \text{ K kg mol}^{-1} \end{aligned}$$

(ii) $\Delta T_f = 326.28 - 323.78 = 2.50 \text{ K}$

With the definition of K_f , Eq. (6) may be expressed as

$$\Delta T_f = K_f \cdot m_2 \quad (7)$$

$$\text{Since } m_2 = \frac{n_2}{w_1} \cdot 1000 = \frac{w_2 \cdot 1000}{w_1 \cdot M_2} \quad (8)$$

where M_2 is the molar mass of solute.

After rearrangement, we have

$$\begin{aligned} M_2 &= \frac{K_f \cdot w_2 \cdot 1000}{\Delta T_f \cdot w_1} \\ &= \frac{(7.26 \text{ K kg mol}^{-1})(1.50 \text{ g})(1000 \text{ g kg}^{-1})}{(2.50 \text{ K})(30.0 \text{ g})} \\ &= 145.6 \text{ g mol}^{-1} \end{aligned} \quad (9)$$

(iii) Using Eq. (2) we obtain

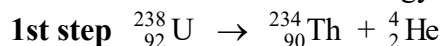
$$\ln X = \frac{17880}{8.314} \left(\frac{1}{326.28} - \frac{1}{298.15} \right) = -0.622$$

$$X = 0.537$$

The mole-fraction solubility of *p*-dichlorobenzene at 298.15 K in an ideal solution is, therefore, equal to 0.537.

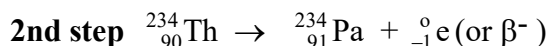
Problem 3

a) (i) Reaction and total kinetic energy



$$\begin{aligned} Q &= K_d + K_\alpha = [m({}^{238}\text{U}) - m({}^{234}\text{Th}) - m({}^4\text{He})]c^2 \\ &= [238.05079 \text{ u} - 234.04360 \text{ u} - 4.00260 \text{ u}]931.5 \text{ MeV u}^{-1} \\ &= (4.59 \times 10^{-3} \text{ u})(931.5 \text{ MeV u}^{-1}) = 4.28 \text{ MeV} \end{aligned}$$

K_d and K_α are KE of daughter and α -particle.



$$\begin{aligned} Q &= K_d + K_{\beta^-} = [m({}^{234}\text{Th}) - m({}^{234}\text{Pa})]c^2 \\ &= [234.04360 \text{ u} - 234.04332 \text{ u}]931.5 \text{ MeV u}^{-1} \\ &= (2.8 \times 10^{-4} \text{ u})(931.5 \text{ MeV u}^{-1}) = 0.26 \text{ MeV} \end{aligned}$$

(ii) At equilibrium (secular) $N_1\lambda_1 = N_2\lambda_2 = A$ (where A is activity)

$$\text{For } ^{226}\text{Ra}, \lambda_1 = \frac{0.693}{(1620 \text{ y})(365 \text{ d y}^{-1})} = 1.17 \times 10^{-6} \text{ d}^{-1}$$

$$\text{For } ^{222}\text{Rn}, \lambda_2 = \frac{0.693}{3.83} = 0.181 \text{ d}^{-1}$$

$$N_1 = \frac{1000 \text{ g} \times 6.022 \times 10^{23} \text{ mol}^{-1}}{226 \text{ g mol}^{-1}} = 2.66 \times 10^{24}$$

$$N_2 (0.181 \text{ d}^{-1}) = (2.66 \times 10^{24})(1.17 \times 10^{-6} \text{ d}^{-1})$$

$$N_2 = 1.72 \times 10^{19}$$

$$\text{Number of moles of } ^{222}\text{Rn} = \frac{1.72 \times 10^{19}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 2.86 \times 10^{-5} \text{ mol}$$

$$\begin{aligned} \text{Volume of } ^{222}\text{Rn} &= 2.86 \times 10^{-5} \text{ mol} \times 25.0 \text{ L mol}^{-1} \\ &= 7.15 \times 10^{-4} \text{ L} \end{aligned}$$

$$(iii) \quad N_1 = N_0 e^{-\lambda t}$$

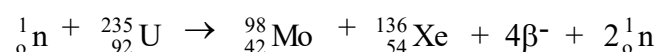
$$\text{Then } \frac{N_1}{N_2} = \frac{N_0 e^{-\lambda t_1}}{N_0 e^{-\lambda t_2}} = \frac{e^{-\lambda t_1}}{e^{-\lambda t_2}} = e^{\lambda(t_2 - t_1)}$$

$$\text{and } 10 = e^{\lambda(12.80 \text{ d})}$$

$$\lambda = \frac{\ln 10}{12.80 \text{ d}} = 0.181 \text{ d}^{-1}$$

$$t_{1/2} = \frac{0.693}{0.180 \text{ d}^{-1}} = 3.85 \text{ days}$$

- b) (i) On the reactant side there are 92 protons while on the product side there are 96 protons. There must be $4\beta^-$ and $2n$ on the product side.



The elementary particles released : $4\beta^-$ and $2n$

$$\begin{aligned} (ii) \quad \text{Input mass} &= 235.04393 \text{ u} + 1.00867 \text{ u} = 236.05260 \text{ u} \\ \text{Output mass} &= 97.90551 \text{ u} + 135.90722 \text{ u} + (2)(1.00867 \text{ u}) \\ &= 235.83007 \text{ u} \end{aligned}$$

Masses of $4\beta^-$ are included in the atomic mass of products., so they do not appear in the output mass.

$$\Delta m = 236.05260 \text{ u} - 235.83007 \text{ u} = 0.22253 \text{ u}$$

$$\text{Energy} = (0.22253 \text{ u})(931.5 \text{ MeV u}^{-1}) = 207.3 \text{ MeV}$$

$$\text{Energy} = (207.3 \text{ MeV})(1.602 \times 10^{-13} \text{ J MeV}^{-1}) = 3.32 \times 10^{-11} \text{ J}$$

which is the energy per fission.

$$(iii) \quad \text{Energy per gram} = \frac{6.022 \times 10^{23} \text{ mol}^{-1}}{235 \text{ g mol}^{-1}} \times 3.32 \times 10^{-11} \text{ J}$$

$$= 8.51 \times 10^{10} \text{ J g}^{-1}$$

$$1 \text{ W} = 1 \text{ J s}^{-1}$$

$$1 \text{ kW-hour} = (1000 \text{ W})(3600 \text{ s}) = 3.60 \times 10^6 \text{ Ws} \\ = 3.60 \times 10^6 \text{ J}$$

$$\text{Power in kW-hour} = \frac{8.51 \times 10^{10} \text{ J}}{3.60 \times 10^6 \text{ J/kW-hour}} \\ = 2.36 \times 10^4 \text{ kW-hour}$$

Problem 4

- (i) Average initial rate ($\text{M}^{-1} \text{ min}^{-1}$)

$$0.00330/25.0 = 0.000132$$

$$0.00390/15.0 = 0.000260$$

$$0.00770/7.50 = 0.00103$$

When [B] is doubled, the rate is doubled, hence the reaction is first order in B. When [A] is doubled, the rate is quadrupled, hence the reaction is second order in A.

$$\text{Rate} = k[\text{A}]^2[\text{B}]$$

- (ii)

Entry	$k = \frac{\text{rate}}{[\text{A}]^2[\text{B}]}$
1	$\frac{0.000132}{(0.100)^2(0.0500)} = 0.264$
2	$\frac{0.00026}{(0.100)^2(0.0100)} = 0.260$
3	$\frac{0.000103}{(0.200)^2(0.100)} = 0.258$

The average of k is $0.261 \text{ L}^2\text{mol}^{-2}\text{min}^{-1} = 4.34 \times 10^{-3} \text{ L}^2\text{mol}^{-2}\text{s}^{-1}$.

Problem 5

- (i) Mechanism I : rate = $k_1[\text{OCl}^-][\text{I}^-]$

Mechanism II :

$$\text{rate} = k_2[\text{HOCl}][\text{I}^-] \quad (\text{slow step}) \quad (1)$$

steady-state Approximation

$$\text{rate} = 0 = k_1[\text{OCl}^-] - k_2[\text{HOCl}][\text{I}^-]$$

$$[\text{HOCl}] = k_1[\text{OCl}^-]/k_2[\text{I}^-] \quad (2)$$

(2) in (1) ;
$$\text{rate} = \frac{d[\text{HOCl}]}{dt} = \frac{k_1 k_2 [\text{OCl}^-][\text{I}^-]}{k_2 [\text{I}^-]} = k_1 [\text{OCl}^-] \quad (3)$$

Mechanism III

$$\text{rate} = \frac{k_1 k_2 [\text{OCl}^-][\text{I}^-]}{k_{-1} [\text{OH}^-] + k_2 [\text{I}^-]} \quad (4)$$

if $k_2 \ll k_{-1}$

$$\text{rate} = \frac{k_1 k_2 [\text{OCl}^-][\text{I}^-]}{k_{-1} [\text{OH}^-]} \quad (5)$$

if $k_2 \gg k_{-1}$ $\text{rate} = k_1 [\text{OCl}^-] \quad (6)$

Therefore, Mechanism III is the most appropriate for observed kinetic behaviour when $k_2 \ll k_{-1}$

(ii) For Mechanism III

$$k = \frac{k_1 k_2}{k_{-1}}$$

$$E_a = E_{a1} + E_{a2} - E_{a-1}$$

$$A = \frac{A_1 A_2}{A_{-1}}$$

(iv) In a buffer solution, $[\text{OH}^-]$ is constant and $\text{rate} = k [\text{OCl}^-][\text{I}^-]$, therefore, the reaction is second order.

(iv) $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$; $[\text{OH}^-] = K_w / [\text{H}_3\text{O}^+]$

$$\text{rate} = \frac{k [\text{OCl}^-][\text{I}^-]}{[\text{OH}^-]} = \frac{k}{K_w} [\text{OCl}^-][\text{I}^-][\text{H}_3\text{O}^+]$$

(v) $\text{rate} = \frac{k}{K_w} \cdot [\text{OCl}^-][\text{I}^-][\text{H}_3\text{O}^+]$

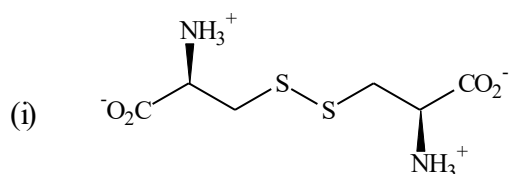
$$\text{rate} = k_{\text{cat}} [\text{OCl}^-][\text{I}^-]$$

$$k_{\text{cat}} = \frac{k}{K_w} [\text{H}_3\text{O}^+]$$

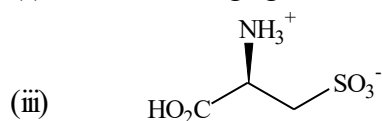
$$\log k_{\text{cat}} = \log \frac{k}{K_w} - \text{pH}$$

Problem 6

a)



(ii) reducing agent

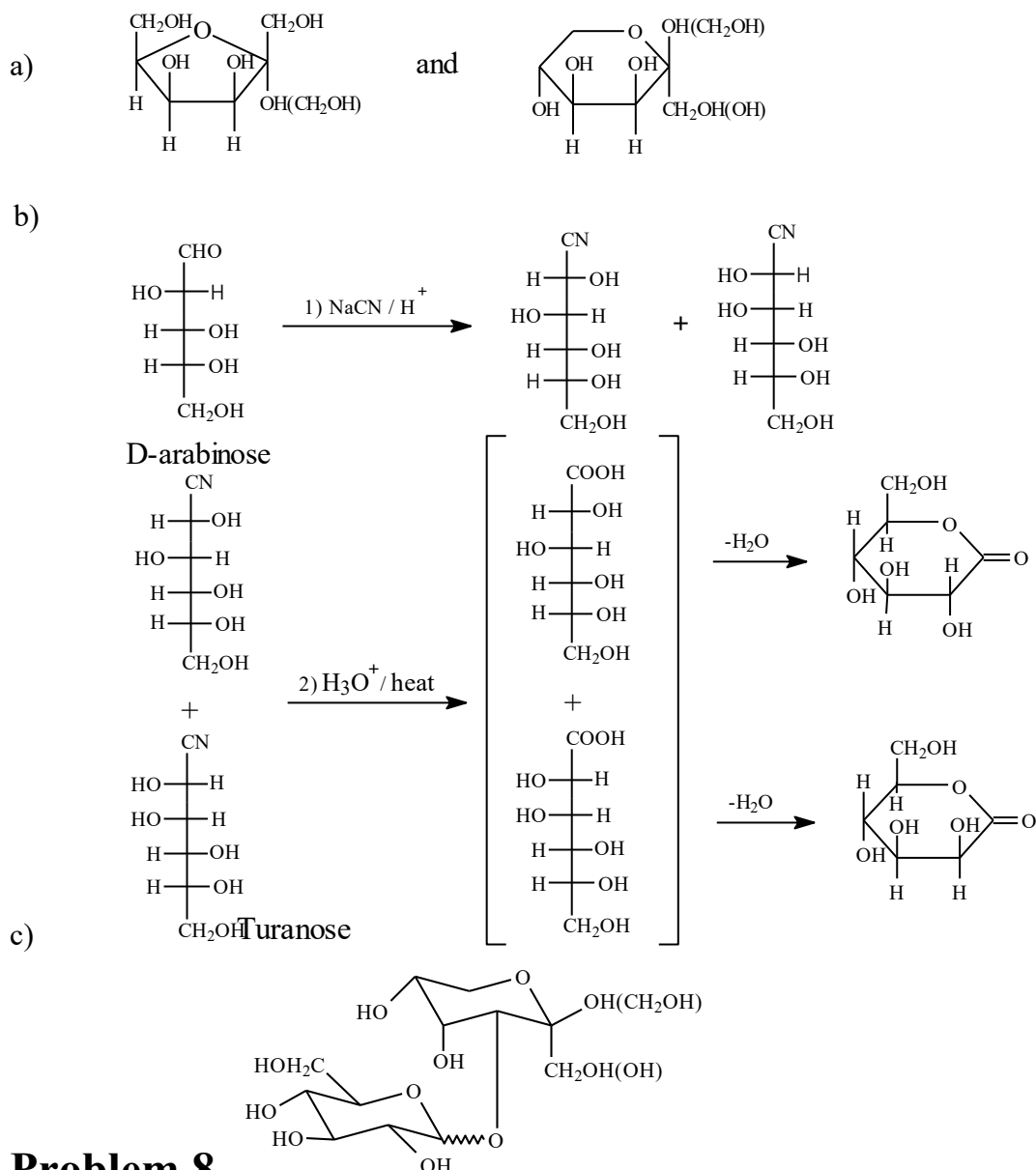


(iv) +4

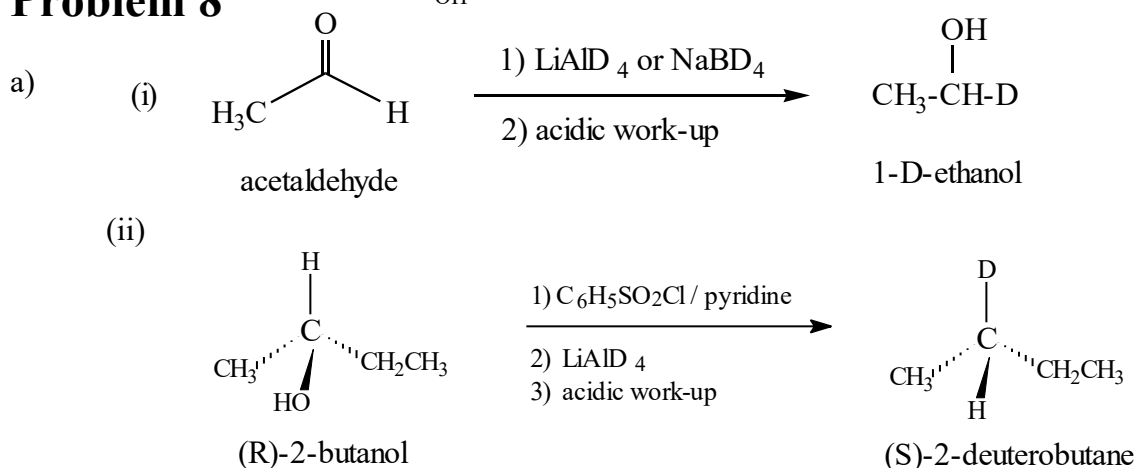
b) (i) Gly-Asn-Phe-Glu

(ii) < 7

Problem 7

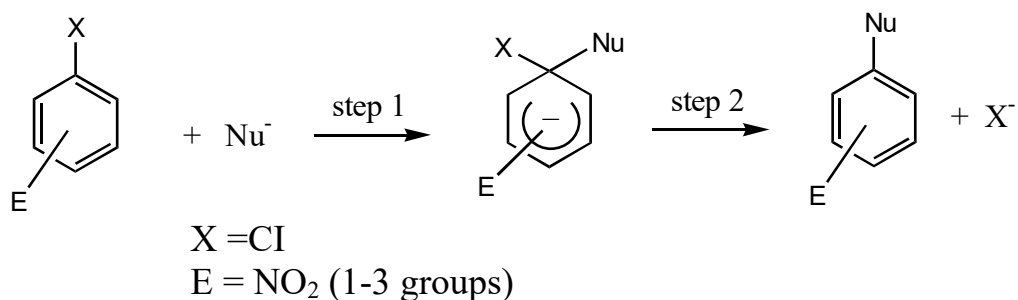


Problem 8

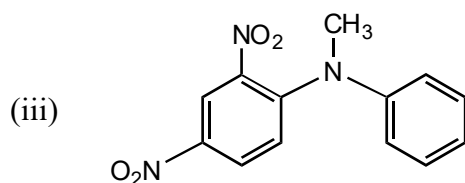


b)

- (i) Nucleophilic Aromatic Substitution
General mechanism:



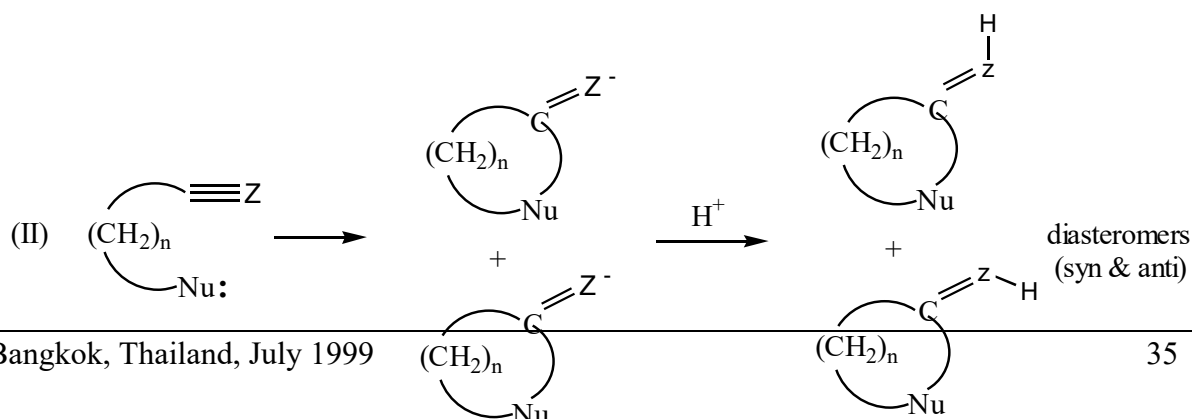
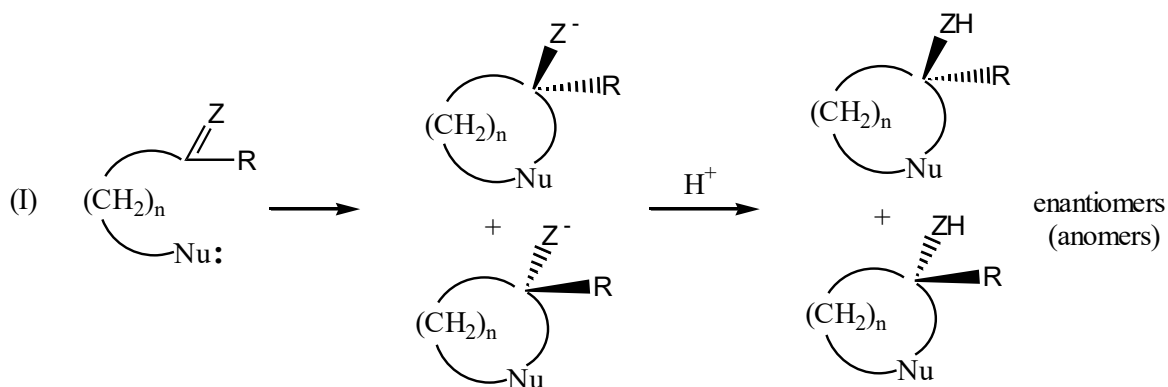
- (ii) s
l
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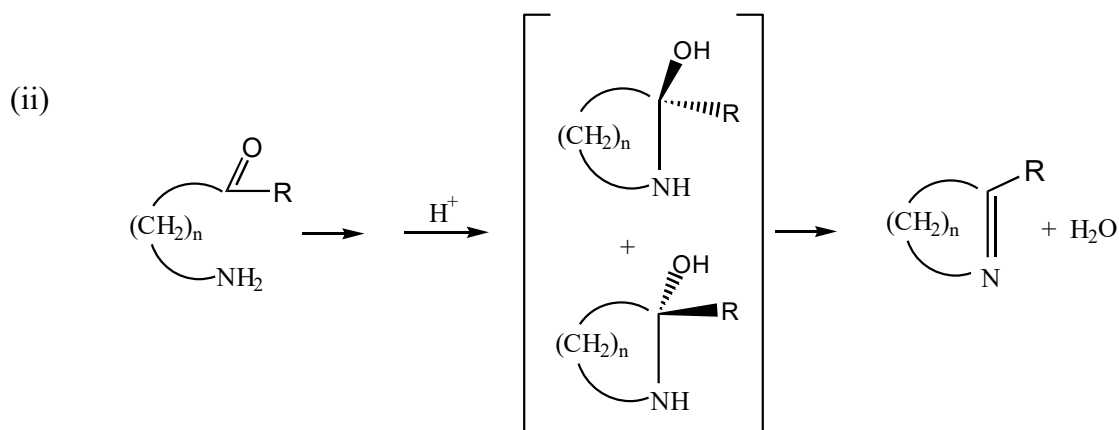


- (iv) According to mechanism in (i), step 1 is slower than step 2, and step 1 is the rate determining step.

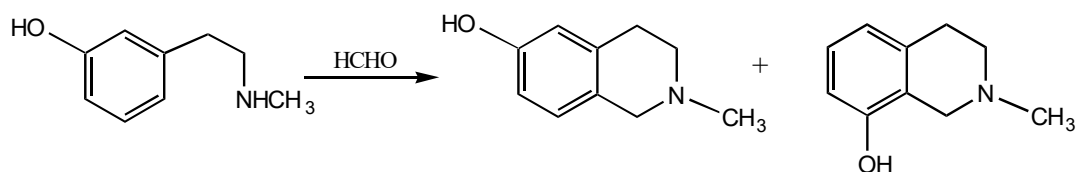
Problem 9

a) (i)



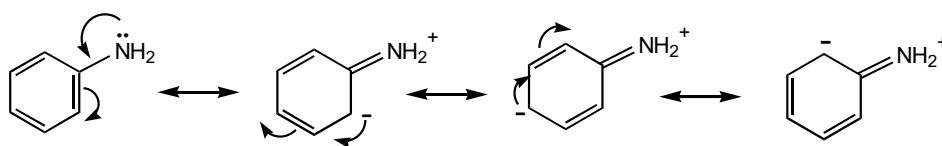


b)

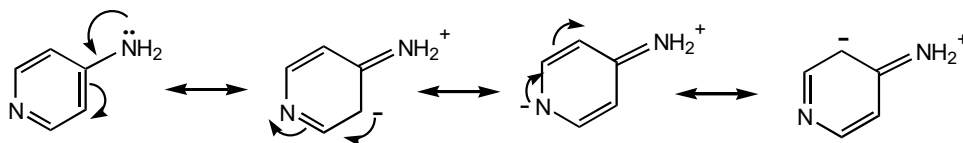


Problem 10

- a)
- Pyridine is less basic than piperidine because the pair of electrons that gives pyridine its basicity occupies an sp^2 orbital; it is held more tightly and is less available for sharing with acids than the pair of electrons of piperidine, which occupies an sp^3 orbital.
 - Pyridine has a pair of electrons (in an sp^2 orbital) that is available for sharing with acid; pyrrole has not, and can accept a proton only at the expense of the aromatic character of the ring.
 - There are two reasons behind this observation. First, the nitrogen of aniline is bonded to an sp^2 -hybridized carbon atom of the aromatic ring, which is more electronegative than the sp^3 -hybridized carbon atom of cyclohexylamine. Second, the non-bonding electron can be delocalized to the aromatic ring. Resonance contributions indicate that it has decreased electro density at the nitrogen. Therefore, cyclohexylamine is more basic than aniline.

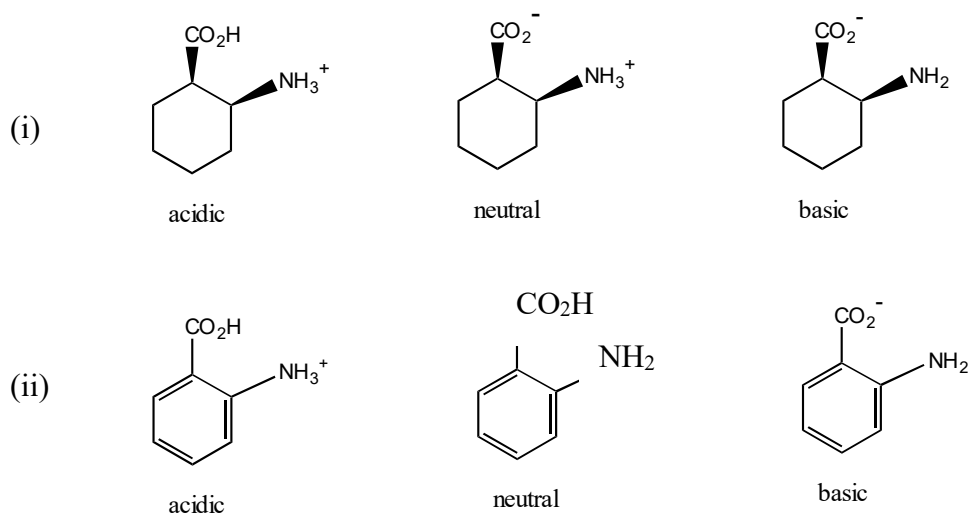


- (iv) Delocalization of lone pair of electrons of the NH_2 group into the ring is possible. This results in an increase electro density on the heterocyclic nitrogen atom, hence, an increase in basicity at this site.



- (v) Piperidine is more basic than morpholine. The oxygen atom in morpholine is more electronegative than methylene group (at the same position) of piperidine so there is less electron density on nitrogen atom of morpholine than that of piperidine.

b)



- (iii) isoelectric point = $(\text{pK}_{a1} + \text{pK}_{a2}) / 2 = 6.88$

Problem 11

a) Substitution of benzene by auxochromes, chromophores, or fused rings has different effects on the absorption spectrum.

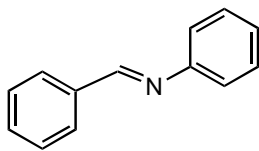
- (i) Introduction of polar substituents such as $-\text{NH}_2$, $-\text{OH}$, OCH_3 cause marked spectral changes. The nonbonding electrons of the $-\text{OH}$ group can conjugate with the π system of the ring. Since the energy of the π^* system is lowered by delocalization over the entire conjugated system, the $n-\pi^*$ absorption occurs at longer wavelength than in benzene.
- (ii) Conversion of phenol to the phenolate anion makes an additional pair of nonbonding electrons available to the conjugated system, and both the

wavelengths and the intensities of the absorption bands are increased. A suspected phenolic group may be determined by comparison of the uv spectrum of the compound in neutral and in alkaline (pH 13) solution.

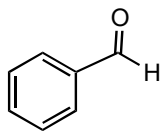
- (iii) Conversion of aniline to the anilinium cation involves attachment of a proton to the nonbonding electron pair, removing it from conjugation with the π

electrons of the ring. The absorption of this ion closely resemble those of benzene.

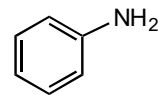
b)



compound (I)

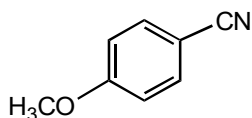


compound (II)

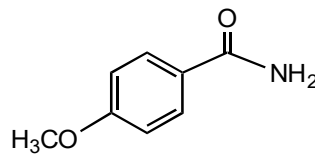


compound (III)

c)



compound (IV)



compound (V)

d) (i) allyl alcohol

 $\delta \approx 5.1$ ppm, dd, 1H

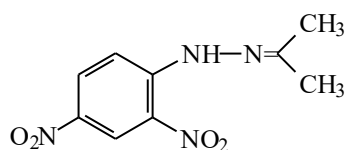
 s, 1H, disappeared on shaking with D₂O
 $\delta \approx 6$ ppm, m, 1H $\delta \approx 5.3$ ppm, dd, 1H

(ii) cyclopropanol

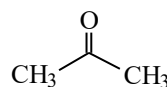
 $\delta \approx 4$ ppm, m, 1H

 s, 1H, disappeared on shaking with D₂O
CH₂ $\delta \approx 1$ ppm, m, 4H

e)



2,4-DNP-derivative



compound (VI)

Problem 12

(i) “Zeolite (I)”

Zeolite (I) (Si/Al = 1) contains more aluminium than zeolite (II) (Si/Al = 2), consequently it possess relatively higher number of exchangeable cation sites.

(ii) “Zeolites with high Si/Al”

In high silica zeolites, there is fewer number of acid sites than the lower one. In addition, electronegativity of Si is slightly higher than Al. Therefore, the more Si in the framework, the more electronegative the framework.

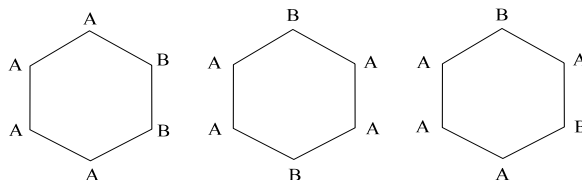
Accordingly, strength of an acid site in such framework is markedly stronger than that of the other.

(iii) “Zeolite containing Li”

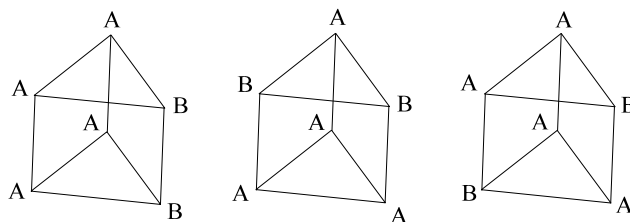
Li is the smallest alkali cation. Its charge density is very high, so it would strongly interact with water.

Problem 13

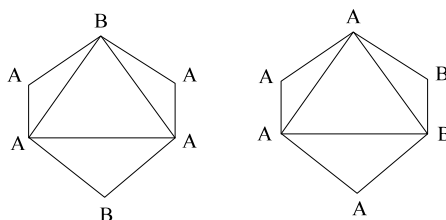
a) (i) For A1, there are three possible geometrical isomers.



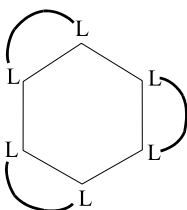
For A2, there are also three possible geometrical isomers.



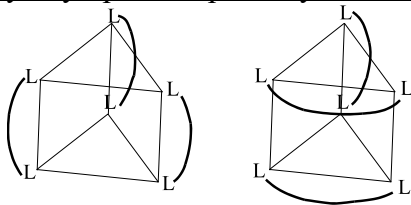
For A3, only two geometrical isomers are possible.



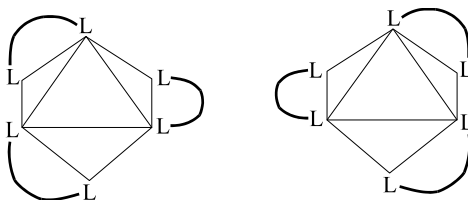
(ii) For A1, there is only one geometrical isomer but no optical isomer.



For A2, there are two geometrical isomers with no optical isomers.

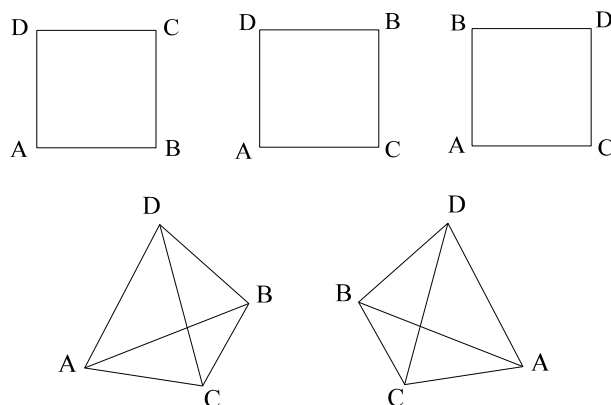


For A3, two optical isomers existing in an enantiomeric pair.

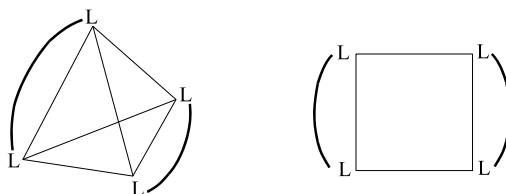


e)

(i) For the square planar geometry, there are three geometrical isomers, none has optical isomer. For the tetrahedral geometry there is only one geometrical arrangement which can exist as a pair of enantiomers.

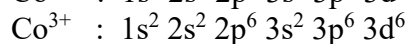
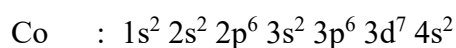


(ii) Both geometries can exist in one geometrical arrangement but no optical isomer.



Problem 14

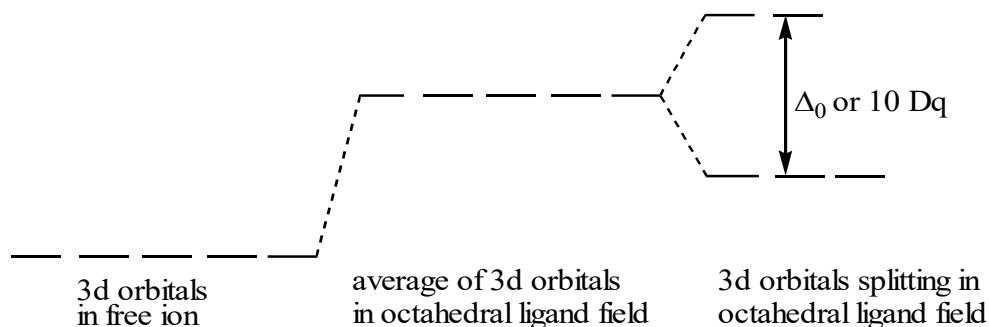
a) The electronic configuration of Co and Co^{3+} are as follows.



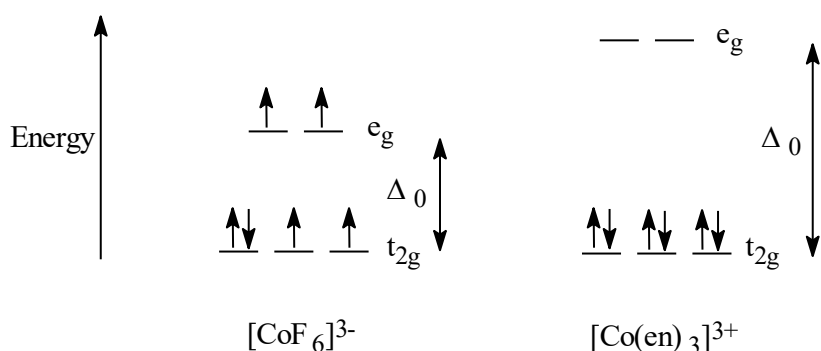
Co^{3+} ion is in octahedral crystal field. The electrons in d orbitals will be repelled by the field from the surrounding ligands. As a result, the $d_{x^2-y^2}$ and d_{z^2} orbitals, which point direct and

head-on toward the ligands will be repelled strongly and raised in energy. The rest of the d orbitals, d_{xy} , d_{xz} and d_{yz} , point into the space between the ligands, their energies are thus

relatively unaffected by the field. These two sets of d orbitals are designated as e_g and t_{2g} , respectively, and their energy difference is designated as Δ_0 or $10 Dq$. The crystal field splitting diagram is shown below.



Different ligands split the d-orbital energies to different extents. Strong field ligands lead to a larger crystal field splitting energy (larger Δ_0); weak field ligands lead to a smaller splitting energy (smaller Δ_0). In the case of $[\text{CoF}_6]^{3-}$ ion, Δ_0 is smaller than that of $[\text{Co}(\text{en})_3]^{3+}$ ion. The splitting energy (Δ_0) and the orbital occupancy for these two complexes are shown below.



The complex ion $[\text{CoF}_6]^{3-}$ has all its six electrons distributed in the high spin configuration, as a result there are four unpaired electrons so it is paramagnetic. Its magnetic moment, μ , can be estimated from the 'spin-only' formula.

$$\mu = \sqrt{n(n+2)} \quad \text{B.M.}$$

where n is the number of unpaired electron. For $[\text{CoF}_6]^{3-}$, $n = 4$, therefore, $\mu = 4.89$ B.M.

While in $[\text{Co}(\text{en})_3]^{3+}$ ion all electrons are paired in the low spin configuration leading to a diamagnetic property. Since, for $[\text{Co}(\text{en})_3]^{3+}$, $n = 0$, therefore, $\mu = 0$ B.M.

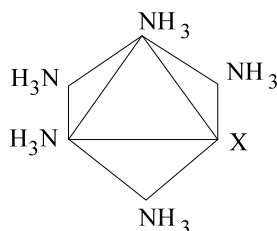
The complex ion $[\text{CoF}_6]^{3-}$ has smaller Δ_0 , so it should absorb at longer λ .

b) The information contained in the table of relationship of wavelengths to colors in Problem 14 is useful in working out for the answers.

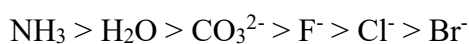
Table Rewritten formula and color of complexes.

Complexes	λ_{max} , nm	Color
1. $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ Hexaamminecobalt(III) chloride	475	Yellowish red
2. $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5](\text{NO}_3)_3$ Aquo pentaamminecobalt(III) nitrate	495	Red
3. $[\text{Co}(\text{CO}_3)(\text{NH}_3)_5]\text{NO}_3$ Carbonatopentaamminecobalt(III) nitrate	510	Red
4. $[\text{CoF}(\text{NH}_3)_5](\text{NO}_3)_2$ Fluoropentaamminecobalt(III) nitrate	515	Red
5. $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$ Chloropentaamminecobalt(III) chloride	534	Reddish violet
6. $[\text{CoBr}(\text{NH}_3)_5]\text{Br}_2$ Bromopentaamminecobalt(III) bromide	552	Violet

- (i) The IUPAC formula and the complex parts are shown in [] in the Table above.
- (ii) All these complexes can be written in the general form as $[\text{Co}(\text{NH}_3)_5\text{X}]^{(3-n)+}$ where $n = 0, 1$ or 2 depending on X groups. (X = NH_3 , H_2O , CO_3^{2-} , F^- , Cl^- , Br^-).



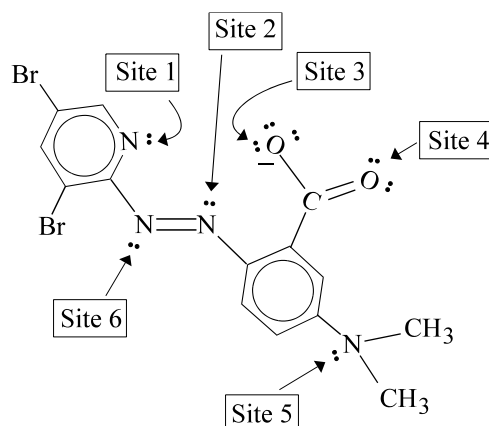
The different in λ_{max} arise from the nature of different X groups which exert repulsion on the electrons of the d orbitals. The stronger the X group bonds to the central metal atom the stronger repulsion would be, rendering shift of λ_{max} to the lower nm (higher energy) or larger Δ_0 as described in a). From the λ_{max} shift, we can arrange the strength of X as follows.



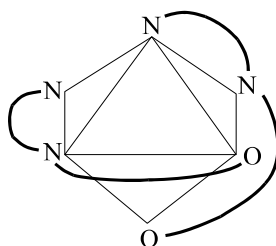
c)

- (i) Referring to the wavelength absorbed and the color, free BBDAB absorbs at 428 nm (curve A), so the color of free BBDAB should be yellow. For Co-BBDAB complex (curve B) the absorption appears at 540 nm, so the color of the complex would be red-violet.
- (ii) The structure of 3,5-diBr-PAMB is rewritten to expose the lone pair electrons it possesses. The atoms with lone pair electrons are the potential sites that can bond to the metal atom. There are six sites altogether, but only some of them will be available to bonding. Of these, sites 1, 2, and 3 can bond

simultaneously leading to the chelate complex which is more stable compared with the other sites. The rest, sites 4, 5, and 6, can bond one at a time as a monodentate ligand which is less stable. Sites 3 and 4 can be used together as a bidentate ligand, too, but is also less stable.



One form of the tentative complex is shown, by using sites 1, 2, and 3 to form a chelate complex. The complex consists of one metal atom and two molecules of 3,5-diBr-PAMB.



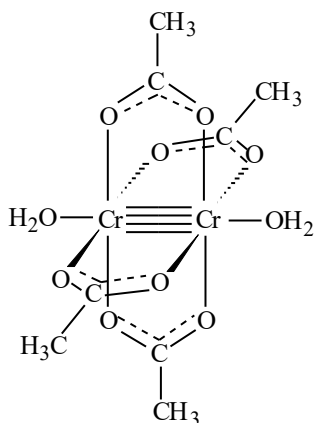
- (iii) The color of the complexes can be deduced as follows.
- Complex with reagent 1 : red violet
 - Complex with reagent 2 : blue green
 - Complex with reagent 3 : red violet
 - Complex with reagent 4 : red violet
 - Complex with reagent 5 : violet
 - Complex with reagent 6 : blue green

Problem 15

- (i)
- | | Cr | C | H | O | |
|-----------------------|------|------|------|-------|------------|
| Elemental composition | 27.1 | 25.2 | 4.25 | 43.45 | % by mass. |
| Atomic weight | 52 | 12 | 1 | 16 | |
| Number of moles | 0.52 | 2.1 | 4.25 | 2.71 | |
| Moles ratio | 1 | 4.04 | 8.17 | 5.21 | |
- From the mole ratio, the empirical formula would be $\text{CrC}_4\text{H}_8\text{O}_5$.

- (ii) From the empirical formula $\text{CrC}_4\text{H}_8\text{O}_5$, the compound is $[\text{Cr}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})]$. Therefore, the ligands are acetate groups. Since the acetate group (CH_3COO) has a charge of -1, therefore, the oxidation state of Cr is 2^+ .

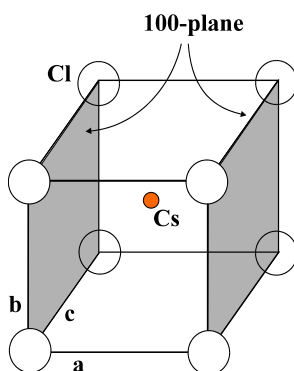
- (iii) Cr^{2+} ion is a d^4 system, i.e., having 4 electrons in the d orbitals. The distribution of four electrons should be in the high spin type due to the low strength of the ligands. This alone would make $[\text{Cr}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})]$ a paramagnetic species. However, from the experimental result this compound is, in fact, a diamagnetic compound. This is because the compound exists in the dimer form as shown.



In this structure, the two Cr atoms form a quadruple bond consisting of one sigma, two pi, and one delta bonds, giving a total bond order of four. The formation of the quadruple bond requires that all the d orbital electrons must be paired up. Therefore, in term of magnetic property, the compound in the dimer form is diamagnetic.

Problem 16

- (i) P
 (ii) The simplest (or empirical) formula is CsCl .
 Number of Cs atom (at the center) = 1
 Number of Cl atoms = $(1/8) \times 8 = 1$
 $\text{Cs} : \text{Cl} = 1 : 1$
 (iii) Coordination number is 8.
 (iv) From the given information , the distance between the (100)plane can be calculated by using Bragg's Law.



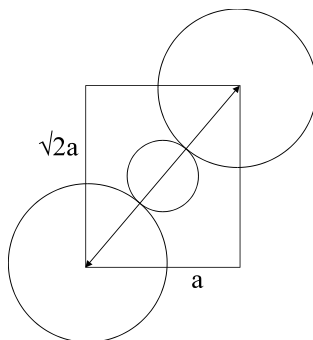
$$\begin{aligned}
 \frac{2d \sin \theta}{d} &= n \lambda \\
 &= n \lambda / 2 \sin \theta \\
 &= (1)(1.542) / (2)(0.1870) \\
 &= 4.123 \text{ \AA}
 \end{aligned}$$

That is the distance between (100)-planes, a , is 4.123 \AA .

For the cubic cell, $a = b = c$, therefore the volume of the cell $= (4.123)^3$
 $= 70.09 \text{ \AA}^3$.

$$\begin{aligned} \text{(v)} \quad \text{Density} &= w/v = Z.M/v \\ &= (1 \times 168.36 \text{ g.mol}^{-1}) / [(6.02 \times 10^{23} \text{ mol}^{-1})(4.123 \times 10^{-8} \text{ cm})^3] \\ &= 3.99 \text{ g.cm}^{-3} \end{aligned}$$

(vi) The diagonal plane of the unit cell can be shown below.



$$\begin{aligned} a^2 + (\sqrt{2}.a)^2 &= (2.r_{Cs} + 2.r_{Cl})^2 \\ 3.a^2 &= (2.r_{Cs} + 2(1.81))^2 \\ \sqrt{3}.a &= 2.r_{Cs} + 3.62 \\ r_{Cs} &= (\sqrt{3}.a - 3.62) / 2 \\ &= (\sqrt{3} \times 4.123 - 3.62) / 2 \\ &= 1.76 \text{ \AA}. \end{aligned}$$

Problem 17

a)

(i) Here, a buffer of H_3PO_4 and H_2PO_4^- is present

$$\begin{aligned} [\text{H}_3\text{PO}_4] &= [\text{H}_2\text{PO}_4^-] \\ [\text{H}^+] &= K_1 \frac{[\text{H}_3\text{PO}_4]}{[\text{H}_2\text{PO}_4^-]} \\ &= K_1 = 7.1 \times 10^{-3} \text{ M} \\ \text{pH} &= -\log(7.1 \times 10^{-3}) = 2.15 \end{aligned}$$

(ii) At the 2nd equivalent point, HPO_4^{2-} is present therefore

$$\begin{aligned} [\text{H}^+] &= (K_2 K_3)^{1/2} \\ &= [(6.2 \times 10^{-8})(4.4 \times 10^{-13})]^{1/2} \\ &= 1.7 \times 10^{-10} \text{ M} \\ \text{pH} &= -\log(1.7 \times 10^{-10}) = 9.77 \end{aligned}$$

(iii) HPO_4^{2-} ($K_3 = 4.4 \times 10^{-13}$) is not really a much stronger acid than H_2O

($K_w = 1.00 \times 10^{-14}$). Addition of strong base to HPO_4^{2-} solution is similar to addition of a strong base to water.

- b) Since the formation constant for $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$, $K_f = \frac{1}{K_d} = 1.667 \times 10^{13}$ is very large, therefore most of the added Ag^+ forms complex with $\text{S}_2\text{O}_3^{2-}$ and

$$[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}] = \frac{20 \text{ mmol}}{200 \text{ ml}} = 0.100 \text{ M}$$

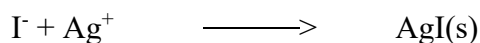
$$\text{mmol of free } \text{S}_2\text{O}_3^{2-} = 530 - (2 \times 20) = 490 \text{ mmol}$$

$$[\text{S}_2\text{O}_3^{2-}] = \frac{490 \text{ mmol}}{200 \text{ ml}} = 2.450 \text{ M}$$

concentration of free Ag^+ calculated from K_d

$$K_d = \frac{[\text{Ag}^+][\text{S}_2\text{O}_3^{2-}]^2}{[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}]} = 6.0 \times 10^{-14}$$

$$[\text{Ag}^+] = \frac{6.0 \times 10^{-14} [\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}]}{[\text{S}_2\text{O}_3^{2-}]^2} = \frac{6.0 \times 10^{-14} (0.100)}{(2.450)^2} = 1.0 \times 10^{-15}$$



$$\begin{aligned} K_{sp} &= [\text{Ag}^+][\text{I}^-] = 8.5 \times 10^{-17} \\ (1 \times 10^{-15})(\text{I}^-) &= 8.5 \times 10^{-17} \end{aligned}$$

$$[\text{I}^-] = \frac{8.5 \times 10^{-17}}{1.0 \times 10^{-15}} = 8.5 \times 10^{-2} \text{ M}$$

$$\begin{aligned} \text{mmol KI} &= (8.5 \times 10^{-2})(200) \\ &= 17.0 \text{ mmol} \end{aligned}$$

Problem 18

- a) **Ans:** *p*-nitro-di-Bolane is suitable indicator but not di-Bolane
For di-Bolane,

$$E_{\text{solution}} = E_{\text{dip}}^{\circ} + \frac{0.059}{2} \log \frac{[\text{In}_{\text{ox}}]}{[\text{In}_{\text{red}}]}$$

$$\text{When } [\text{In}_{\text{ox}}] / [\text{In}_{\text{red}}] = 10$$

$$E_{\text{solution}} = 0.76 + \frac{0.059}{2} \log 10 = 0.79$$

At 0.79 V, calculate $[\text{Fe}^{3+}] / [\text{Fe}^{2+}]$

$$E_{\text{solution}} = E_{\text{Fe}}^{\circ} - \frac{0.059}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

$$0.79 = 0.77 + 0.059 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$$\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = 2.2$$

Di-Bolane is not suitable indicator because $[\text{Fe}^{3+}]$ is 2.2 times $[\text{Fe}^{2+}]$

For *p*-nitro-di-Bolane

$$E_{\text{solution}} = E_{\text{pn}}^{\circ} + \frac{0.059}{2} \log \frac{[\text{In}_{\text{ox}}]}{[\text{In}_{\text{red}}]}$$

When $[\text{In}_{\text{ox}}] / [\text{In}_{\text{red}}] = 10$

$$E_{\text{solution}} = 1.01 + \frac{0.059}{2} \log 10 = 1.04 \text{ V}$$

At 1.04 V, calculate $[\text{Fe}^{3+}] / [\text{Fe}^{2+}]$

$$E_{\text{solution}} = E_{\text{Fe}}^{\circ} + \frac{0.059}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

$$1.04 = 0.77 + 0.059 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$$\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = 3.80 \times 10^4$$

b)

(i) Sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$

(ii) $\text{MnO}_4^- (\text{aq}) + 8\text{H}^+ (\text{aq}) + 5\text{e}^- \longrightarrow \text{Mn}^{2+} (\text{aq}) + 4\text{H}_2\text{O} (\text{l})$

$E^{\circ} = +1.51 \text{ V}$

The Nernst equation is

$$E = E^{\circ} - \frac{RT}{5F} \ln \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-] \cdot [\text{H}^+]^8}$$

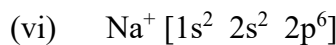
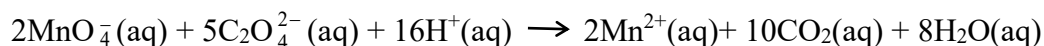
or

$$E = 1.51 - \frac{(257 \times 10^{-3})}{5} \ln \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-] \cdot [\text{H}^+]^8}$$

or

$$E = 1.51 - \frac{(59.2 \times 10^{-3})}{5} \log \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-] \cdot [\text{H}^+]^8}$$

- (iii) One mole of electron is required for one mole of the gaseous product.
Half reaction is $\text{C}_2\text{O}_4^{2-}(\text{aq}) \longrightarrow 2\text{CO}_2(\text{g}) + 2\text{e}^-$
- (iv) Ten moles of electron is involved in overall reaction.
- (v) The overall or net reaction of compound A and potassium permanganate.



(vii) Stoichiometric ratio $= \frac{\text{mol KMnO}_4}{\text{mol Na}_2\text{C}_2\text{O}_4} = \frac{2}{5}$

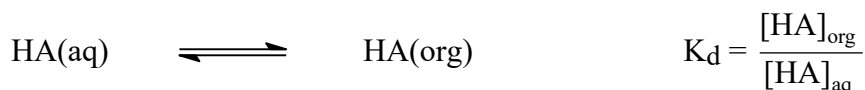
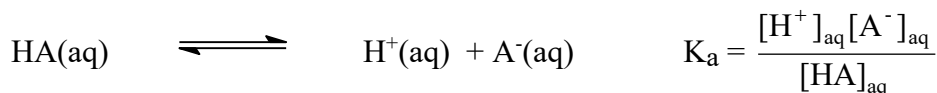
Therefore, the molarity of the potassium permanganate solution is 0.00146 M.

- (viii) No, since $E^\circ(\text{M}^+, \text{M}) = +1.69 \text{ V}$ is higher than the standard potential of potassium permanganate.
- (ix) The biological standard potential (at pH 7) of the half reaction is 1.69 V.

Problem 19

a)

- (i) From



Distribution ratio (D) can be estimated as

$$\begin{aligned} D &= \frac{[\text{HA}]_{\text{org}}}{[\text{HA}]_{\text{aq}} + [\text{A}^-]_{\text{aq}}} \\ &= \frac{[\text{HA}]_{\text{org}} / [\text{HA}]_{\text{aq}}}{[\text{HA}]_{\text{aq}} / [\text{HA}]_{\text{aq}} + [\text{A}^-]_{\text{aq}} / [\text{HA}]_{\text{aq}}} \\ &= \frac{K_d}{1 + K_a / [\text{H}^+]} \end{aligned}$$

- (ii) From answer (i)

$$\log D = \log K_d - \log (1 + K_a / [\text{H}^+])$$

at low pH: $[\text{H}^+] \gg K_a$

$$\log D = \log K_d = \text{constant}$$

$$D = K_d; K_d = 5.190 \text{ (average of 5.200, 5.180 and 5.190)}$$

at high pH: $[\text{H}^+] \ll K_a$

therefore

$$\log D = \log K_d - \log K_a / [\text{H}^+]$$

$$\log D = \log K_d - \log K_a - \text{pH}$$

$$\text{Therefore, } \log K_d - \log K_a = 6.70$$

$$K_a = 1.02 \times 10^{-6}$$

b)

$$\begin{aligned} \text{(i) Resolution, } R_s &= 2[(t_R)_B - (t_R)_A] / (W_A + W_B) \\ &= 2[(17.63 - 16.40)] / (1.11 + 1.21) \\ &= 1.06 \end{aligned}$$

$$\begin{aligned} \text{(ii) The number of theoretical plates, } N &= 16(t_R/W)^2 \\ \text{For the first peak, } N &= 16(16.40/1.11)^2 = 3493 \\ \text{for the second peak, } N &= 16(17.63/1.21)^2 = 3397 \\ \text{The average number of plates, } N_{av} &= (3493 + 3397)/2 = 3495 \sim 3.4 \times 10^3 \end{aligned}$$

$$\begin{aligned} \text{(iii) The plate height (H) can be calculated from } L/N \\ \text{when } L = \text{column length and } N = \text{number of theoretical plates.} \\ H = 30.0 \text{ cm} / 3445 = 8.7 \times 10^{-3} \text{ cm} \end{aligned}$$

$$\text{(iv) } N = 16 R_s^2 \left(\frac{\alpha}{\alpha - 1} \right)^2 \left(\frac{1 + k'_B}{k'_B} \right)^2$$

The capacity factor (k') and the selectivity factor (α) do not change with N or L , therefore

$$(R_s)_1 / (R_s)_2 = \sqrt{N_1} / \sqrt{N_2}$$

where subscripts 1 and 2 refer to the original and the longer columns, respectively.

$$\begin{aligned} 1.06/1.5 &= \sqrt{3.4 \times 10^3} / \sqrt{N_2} \\ N_2 &= 6.9 \times 10^3 \\ L &= N.H = 60 \text{ cm} \end{aligned}$$

Problem 20

a) For peaks in the molecular ion cluster, three peaks are expected from two chlorine atoms. The intensities can be calculated from $(a+b)^n$

where a = relative abundance of the light isotope (^{35}Cl)
 b = relative abundance of the heavy isotope (^{37}Cl)
 n = number of halogen atoms present.

Since the relative abundance of $^{35}\text{Cl} = 75.77$ and that of $^{37}\text{Cl} = 24.23$, it can be assumed then that their relative abundances are $^{35}\text{Cl} = 3$ and $^{37}\text{Cl} = 1$ for purpose of convenience.

$$\begin{aligned} \text{(i) Relative intensities of the peaks at } m/z \text{ 84, 86 and 88} &= a^2 + 2ab + b^2 \\ &= 3^2 + 2 \times 3 \times 1 + 1^2 \end{aligned}$$

That is, the relative intensities for m/z 84:86:88 = 9:6:1

$$\begin{aligned} \text{(ii) As for the peaks at } m/z \text{ 49 and 51, corresponding to the loss of one chlorine} \\ \text{atom from the molecular ion, the two peaks are due to } \text{CH}_2 \text{ } ^{35}\text{Cl}^+ \text{ and} \\ \text{CH}_2 \text{ } ^{37}\text{Cl}^+, \text{ respectively.} \end{aligned}$$

$$\begin{aligned} \text{Relative intensity of the peak at } m/z \text{ 49 and 51} &= a + b \\ &= 3 + 1 \end{aligned}$$

$$\text{That is, the relative intensities for } m/z \text{ 49:51} = 3:1$$

- b) In terms of the relative abundance, $^{79}\text{Br} : ^{81}\text{Br} = 50.69 : 49.31 \approx 1:1$.
Relative intensities of the isotopic peaks can be calculated from $(a+b)^n$
where a = relative intensity of $^{79}\text{Br} = 1$
 b = relative intensity of $^{81}\text{Br} = 1$
 n = number of halogen atoms present = 3

$$\text{Relative intensities} = a^3 + 3a^2b + 3ab^2 + b^3$$

$$M : (M+2) : (M+4) : (M+6) = 1^3 : 3 \times 1^2 \times 1 : 3 \times 1 \times 1^2 : 1^3 = 1:3:3:1$$

Problem 21

- (i) From Beer's Law, $A = \epsilon bc$

$$\epsilon_X^{440} = \frac{0.096}{1.00 \times 8.00 \times 10^{-5}} = 1.2 \times 10^3 \quad \text{cm}^{-1} \text{ mol}^{-1} \text{ L}$$

$$\epsilon_X^{660} = \frac{0.373}{1.00 \times 8.00 \times 10^{-5}} = 4.67 \times 10^3 \quad \text{cm}^{-1} \text{ mol}^{-1} \text{ L}$$

$$\epsilon_Y^{440} = \frac{0.600}{1.00 \times 2.00 \times 10^{-4}} = 3.00 \times 10^3 \quad \text{cm}^{-1} \text{ mol}^{-1} \text{ L}$$

$$\epsilon_Y^{660} = \frac{0.030}{1.00 \times 2.00 \times 10^{-4}} = 1.50 \times 10^2 \quad \text{cm}^{-1} \text{ mol}^{-1} \text{ L}$$

- (ii) At 520 nm

$$\begin{aligned} \text{Absorbance} &= A_X + A_Y \\ &= \frac{3.00 \times 10^{-5}}{8.00 \times 10^{-5}} \times 0.113 + \frac{5.00 \times 10^{-4}}{2.00 \times 10^{-4}} \times 0.433 \\ &= 1.125 \end{aligned}$$

At 600 nm

$$\begin{aligned} \text{Absorbance} &= A_X + A_Y \\ &= \frac{3.00 \times 10^{-5}}{8.00 \times 10^{-5}} \times 0.264 + \frac{5.00 \times 10^{-4}}{2.00 \times 10^{-4}} \times 0.100 \\ &= 0.349 \end{aligned}$$

- (iii) At 440 nm

$$0.400 = 1.2 \times 10^3 C_X + 3.0 \times 10^3 C_Y$$

At 660 nm

$$0.500 = 4.67 \times 10^3 C_X + 1.5 \times 10^2 C_Y$$

The above two equations can be solved for C_X and C_Y

$$C_X = 1.04 \times 10^{-4} \text{ M}$$

$$C_Y = 9.17 \times 10^{-5} \text{ M}$$