Worked Solutions to Problems

1. Water

A. Phase diagram

a. The three phases of water coexist in equilibrium at a unique temperature and pressure (called the triple point):

T_{tr} = 273.16 K = 0.01 °C P_{tr} = 6.11 x 10^{-3} bar

b. If pressure decreases, boiling point decreases, but melting point increases (slightly).

c. Beyond this point, there is no distinction between liquid and vapour phases of water. Put alternatively, it is possible to have liquid to vapour transition by a continuous path going around the critical point. (In contrast, solid-liquid transition is discontinuous.)

d. T = 300K, P = 12.0 bar : liquid phase
T = 270K, P = 1.00 bar : solid phase

e. Below P = 6.11 x 10^{-3} bar, ice heated isobarically will sublimate to vapour.

f. If x_l and x_v are the mole fractions of water in liquid and vapour phases,

$$V = x_l \overline{V}_l + x_v \overline{V}_v = x_l \overline{V}_l + (1 - x_l)\overline{V}_v$$

$$\therefore \quad x_l = \frac{\overline{V}_v - V}{\overline{V}_v - \overline{V}_l} = 4.6 \times 10^{-1}$$

$$\frac{V_l}{V} = \frac{x_l \overline{V}_l}{V} = 0.140$$

$$\frac{V_v}{V} = 1 - 0.14 = 0.860$$

B. Clausius – Clapeyron equation

a. $\frac{dP}{dT} = \frac{\Delta\bar{H}}{T\Delta\bar{V}}$

$\Delta\bar{H}$ = molar enthalpy change in phase transition

$\Delta\bar{V}$ = molar change in volume in phase transition.

For ice-liquid water transition :

$\Delta\bar{H} > 0$ $\Delta\bar{V} < 0$, since ice is less dense than water.

$\therefore \frac{dP}{dT} < 0$

Since $|\Delta\bar{V}|$ is not large, the P-T curve for this transition is steep, with a negative slope. Thus decrease of pressure increases the melting point slightly.

For liquid water - vapour transition

$\Delta\bar{H} > 0$ $\Delta\bar{V} < 0$

$\therefore \frac{dP}{dT} > 0$

Decrease of pressure decreases the boiling point.

b. Clausius - *Clapeyron equation for (solid) liquid - vapour transition* is

$$\frac{dP}{dT} = \frac{P\ \Delta\bar{H}_{vap}}{RT^2}$$

This equation follows from the Clapeyron equation under the assumptions:

1. Vapour follows ideal gas law.
2. Molar volume of the condensed phase is negligible compared to molar volume of vapour phase.
3. If further $\Delta\bar{H}_{vap}$ is assumed to be constant (no variation with T), the eq. is integrated to give

$$\ln\frac{P_2}{P_1} = \frac{\Delta\bar{H}_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Here $P_1 = 1.01$ bar , $T_1 = 373.15$ K

$T_2 = 393.15$ K $\Delta\bar{H}_{vap} = 40.66$ kJ mol^{-1}

$R = 8.31$ J K^{-1} mol^{-1}

$\therefore \quad P_2 = 2.01$ bar

The estimate is based on assumptions 1, 2 and 3.

c. *For ice - liquid water equilibrium, use Clapeyron equation*

At $T_1 = 273.15$ K, $P_1 = 1.01$ bar

1. Assume that for a small change in T, $\frac{\Delta\bar{H}}{\Delta\bar{V}}$ is constant.

Integrating the Clapeyron equation above

$$P_2 - P_1 = \frac{\Delta\bar{H}}{\Delta\bar{V}} \ln\left(\frac{T_2}{T_1}\right)$$

$T_2 = 272.95$ K, $\Delta\bar{H}_{(fusion)} = 6008$ Jmol^{-1}

$$\Delta\bar{V} = \left(\frac{1}{1.00} - \frac{1}{0.917}\right) \times 18.015 = -1.63 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

$P_2 - P_1 = 27.0$ bar

$P_2 = 28.0$ bar

The estimate is based on assumption 1.

C. Irreversible condensation

a. On the P-T plane, this equilibrium state is a solid phase (ice). Water in liquid phase at this temperature and pressure is not an equilibrium state - it is a supercooled state that does not lie on the given P-T plane.

b. Treating the metastable state as equilibrium state, we can go from the supercooled liquid state to the solid state at the same temperature and pressure by a sequence of 3 reversible steps.

1. Supercooled liquid at -12.0°C to liquid at 0°C

q_1 = number of moles x $\bar{C}_p$ (liquid water) x change of temperature

$$\frac{28.5\,g}{18.015\,g\,mol^{-1}} \times 76.1\,J\,K^{-1}\,mol^{-1} \times 12.0\,K = 1445\,J$$

2. liquid at 0°C to ice at 0°C

$q_2 = 28.5\ g \times (-333.5)\ J\ g^{-1} = -9505\ J$

3. Ice at 0°C to ice at –12.0°C

q_3 = number of moles x $\bar{C}_p$ (liquid water) x change of temp.

$$= \frac{28.5}{18.015\,g\,mol^{-1}} \times 37.15\,J\,K^{-1}\,mol^{-1} \times (-12.0\,K)$$

$= -705.3\ J$

$\therefore \quad q = q_1 + q_2 + q_3 = -8765\ J$

Since all the steps are at the constant pressure of 1.00 bar,

$q = \Delta H$

But ΔH is independent of the path, i.e., it depends only on the end points. Thus for the irreversible condensation of supercooled liquid to ice

$q = \Delta H = -8765\ J$

c. The actual irreversible path between the two end states of the system is replaced by the sequence of three reversible steps, as above. For each reversible step, ΔS can be calculated.

$$\Delta S_1 = n \int_{T_1}^{T_2} \frac{\bar{C}_p}{T}\,dT = n\,\bar{C}_p \ln \frac{T_2}{T_1}$$

$$\Delta S_1 = \frac{28.5\,g}{18.015\,g\,mol^{-1}} \times 76.1\ J\ K^{-1}\,mol^{-1} \times \ln \frac{273.15}{261.15}$$

$= 5.41\ J\ K^{-1}$

$$\Delta S_2 = \frac{\Delta H_2}{T} = \frac{-9505}{273.15} = -34.79\ J K^{-1}$$

$$\Delta S_3 = \frac{28.5\ g}{18.015\ g\ mol^{-1}}\ 37.15\ J\ K^{-1} mol^{-1}\ \ln \frac{261.15}{273.15}$$

$$= -2.64\ J\ K^{-1}$$

$$\Delta S_{system} = \Delta S_1 + \Delta S_2 + \Delta S_3 = -32.02\ J\ K^{-1}$$

$$\Delta S_{sur} = \frac{q_{sur}}{T_{sur}} = \frac{8765}{261.15} = 33.56\ J K^{-1}$$

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{sur} = 1.54\ J K^{-1}$$

The entropy of the universe increases in the irreversible process, as expected by the Second Law of Thermodynamics.

2. van der Waals gases

a. For a van der Waals gas

$$Z = \frac{PV}{nRT} = 1 + \frac{bP}{RT} - \frac{na}{VRT} + \frac{n^2 ab}{V^2 RT}$$

The ratio of the magnitudes of the second and third terms on the right side is :

$$\frac{b}{na} PV \approx \frac{b}{a} RT, \quad \text{taking } PV = nRT \text{ up to zeroth order.}$$

The ratio of the magnitudes of the fourth and third terms on the right side is :

$$\frac{nb}{V} \approx \frac{bP}{RT}$$

i. From the ratios above, it follows that at sufficiently high temperature for any given pressure, the second term dominates the third and fourth terms. Therefore,

$$Z \cong 1 + \frac{bP}{RT} > 1$$

For small P, Z nearly equals unity.

ii. At lower temperatures, the third term can be greater (in magnitude) than the second term. It may be greater (in magnitude) than the fourth term also, provided P is not too large. Since the third term has a negative sign, this implies that Z can be less than unity.

iii. For a = 0

$$Z = 1 + \frac{b\,P}{R\,T}$$

which shows that Z increases linearly with P.

b. Helium has negligible value of a. Graph (1) corresponds to He and (2) corresponds to N_2.

c. Above $T > T_c$, only one phase (the gaseous phase) exists, that is the cubic equation in V has only one real root. Thus isotherm (2) corresponds to $T < T_c$.

d. At $T = T_c$, the three roots coincide at $V = V_c$ This is an inflexion point.

$$\left.\frac{dP}{dV}\right|_{V_c} = \left.\frac{d^2P}{dV^2}\right|_{V_c} = 0$$

The first condition gives

$$\frac{RT_c}{(V_c - nb)^2} = \frac{2\,n\,a}{V_c^{\,3}} \qquad (1)$$

The second condition gives

$$\frac{RT_c}{(V_c - n\,b)^3} = \frac{3\,n\,a}{V_c^{\,4}} \qquad (2)$$

These equations give

$$V_c = 3\,n\,b \text{ and } T_c = \frac{8a}{27b\,R}$$

For He, $T_c = 5.2\,K$

For N_2, $T_C = 128K$

Since, $T_c\,(N_2)$ is greater than $T_c\,(He)$, N_2 is liquefied more readily than He.

e.

$$W = \int_{V_1}^{V_2} P\,dV$$

$$= \int_{V_1}^{V_2} \left(\frac{RT}{V-b} - \frac{a}{V^2} \right) dV$$

$$= RT \ \ln \left(\frac{V_2 - b}{V_1 - b} \right) + \ a \left(\frac{1}{V_2} - \frac{1}{V_1} \right)$$

$$= 56.7 \quad \text{L bar mol}^{-1}$$

3. Rates and reaction mechanisms

a. Mechanism 1 :

$$\frac{1}{2}\frac{d[HI]}{dt} = \ k_1 [I]^2 [H_2]$$

Since the first step is fast, there is a pre - equilibrium :

$$K \ = \ \frac{[I]^2}{[I_2]}$$

$$\therefore \quad \frac{d[HI]}{dt} \ = \ 2 k_1 K [I_2][H_2] \ = \ k [H_2][I_2]$$

Mechanism 2 :

$$\frac{1}{2}\frac{d[HI]}{dt} \ = \ k_2 [I_2]_d [H_2]$$

$$K' = \ \frac{[I_2]_d}{[I_2]}$$

$$\therefore \quad \frac{d[HI]}{dt} \ = 2 k_2 K' [I_2][H_2] = k [H_2][I_2]$$

Both mechanisms are consistent with the observed rate law.

b. **i.**

$$k \ = \ A\, e^{-E_a / RT}$$

$$E_a \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = R \ln \frac{k_2}{k_1}$$

With the given numerical values,

$$E_a = 170 \ \text{kJ mol}^{-1}$$

ii. The activation energy is greater than the bond dissociation energy of I_2. Hence the second step is rate determining in both the mechanisms.

c. The activation energy $E_a^{'}$ for the reverse reaction is

$$E_a^{'} = E_a - \Delta U$$

$$= 170 + 8.2 = 178.2 \ \text{kJ mol}^{-1}$$

d. **i.**

$$\frac{d[I_2]}{dt} = k_3 [IAr][I]$$

$$K^{''} = \frac{[IAr][Ar]}{[I][Ar]^2}$$

$$\therefore \ \frac{d[I_2]}{dt} = K^{''} k_3 [I]^2 [Ar]$$

$$= k [I]^2 [Ar]$$

ii. A possible reason why this is negative is that Ea_3 is positive and less in magnitude than $|\Delta H^{\circ}|$, while ΔH^{o} is negative.

$$k = k_3 K^{''}$$

$$= A_3 e^{-E_{a3}/RT} \qquad e^{-\Delta G^{\circ}/RT}$$

$$\text{we know } \Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$\therefore k = A_3 \, e^{\frac{\Delta S^{\circ}}{R}} \, e^{-(E_{a3} + \Delta H^{\circ})/RT}$$

The activation energy for the overall reaction is $E_{a3} + \Delta H^{\circ}$

4. Enzyme catalysis

a. **i.** The differential rate equations for the Michaelis-Menten mechanism are

$$\frac{d[ES]}{dt} = k_1 [E][S] - k_1^{'} [ES] - k_2 [ES] \qquad (1)$$

$$\frac{d[P]}{dt} = k_2 [ES] \qquad (2)$$

In the steady-state approximation, $\frac{d[ES]}{dt} = 0$ (3)

Eq. (1) then gives $[ES] = \frac{k_1 [E][S]}{k_1' + k_2}$ (4)

Now $[E]_0 = [E] + [ES]$ (5)

where $[E]_0$ is the total enzyme concentration. Eqs. (4) and (5) gives

$$[ES] = \frac{[E]_0[S]}{K_m + [S]} \quad (6)$$

where $K_m = \frac{k_1' + k_2}{k_1}$ is the Michaelis-Menten constant.

From eq. (2), $$\frac{d[P]}{dt} = \frac{k_2 [E]_0 [S]}{K_m + [S]} \quad (7)$$

Since the backward rate is ignored, our analysis applies to the initial rate of formation of P and not close to equilibrium. Further, since the enzyme concentration is generally much smaller than the substrate concentration, [S] is nearly equal to $[S]_0$ in the initial stage of the reaction.

Thus, according to the Michaelis-Menten mechanism, the initial rate versus substrate concentration is described by eq. (7), where [S] is replaced by $[S]_0$.

For $[S] << K_m$,

$$\text{Initial rate} = \frac{k_2}{K_m} [E]_o [S] \quad (8)$$

i.e., initial rate varies linearly with [S].

For $[S] >> K_m$,

$$\text{Initial rate} = k_2 [E]_0 \quad (9)$$

i.e., for large substrate concentration, initial rate approaches a constant value $k_2 [E]_0$.

Thus the indicated features of the graph are consistent with Michaelis-Menten mechanism.

ii. The asymptotic value of initial rate is $k_2\,[E]_0$

From the graph,

$k_2\,[E]_0 = 3.0 \times 10^{-6}\ M\ s^{-1}$

With $[E]_0 = 1.5 \times 10^{-9}\ M$

we get $k_2 = 2.0 \times 10^{3}\ s^{-1}$

iii. From eq. (7), for $[S] = K_m$, the initial rate is half the asymptotic value. From the graph, therefore,

$K_m = 5.0 \times 10^{-5}\ M$

For $[S] = 1.0 \times 10^{-4}\ M$, using eq. (7) again,

$$\text{Initial rate} = \frac{[2.0 \times 10^{3}\ s^{-1}] \times [1.5 \times 10^{-9}\ M] \times [1.0 \times 10^{-4}]M}{[5.0 \times 10^{-5}]M + [1.0 \times 10^{-4}]M}$$

$$= 2.0 \times 10^{-6}\ M\ s^{-1}$$

iv. We have $K_m = \dfrac{k_1^{|} + k_2}{k_1} = 5.0 \times 10^{-5}\ M$

The enzyme equilibrates with the substrate quickly, that is the first step of equilibration between E, S and [ES] is very fast. This means that $k_1^{|}$ is much greater than k_2. Therefore, neglecting k_2 above,

$$\frac{k_1^{|}}{k_1} = 5.0 \times 10^{-5}\ M$$

The equilibrium constant K for the formation of ES from E and S is,

$$\frac{K}{1M} = \frac{k_1}{k_1^{|}} = 2.0 \times 10^{-5}$$

b. From the graph at the new temperature, $k_2\,[E]_0 = 6.0 \times 10^{-6}\ M\ s^{-1}$

i.e., $$k_2 = \frac{6.0 \times 10^{-6}\ M\,s^{-1}}{1.5 \times 10^{-9}\ M} = 4.0 \times 10^{3}\ s^{-1}$$

Using Arrhenius relation for temperature dependence of rate constant :

$$k = A\ e^{-\frac{E_a}{RT}} \qquad (10)$$

where E_a is the molar activation energy.

$$\frac{k(T_1)}{k(T_2)} = e^{-\frac{E_a}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]}$$

$$\text{i.e.} \qquad E_a = R\frac{\ln\frac{k(T_2)}{k(T_1)}}{\left(\frac{1}{T_1}-\frac{1}{T_2}\right)} \qquad (11)$$

Now $\frac{k_2(310)}{k_1(285)} = 2.0$, $\qquad R = 8.31\ J\ K^{-1}\ mol^{-1}$

$\therefore \qquad E_a = 20.4\ kJ\ mol^{-1}$

c. **i.** The fraction of the enzyme that binds with the substrate is, from eq. (6):

$$\frac{[ES]}{[E]_0} = \frac{[S]}{K_m + [S]} \qquad (12)$$

where [S] is nearly equal to $[S]_0$ in the initial stage of the reaction.

Now $[S]_0 = \frac{3.0 \times 10^{-6}\ mol}{1 \times 10^{-3} L} = 3.0 \times 10^{-3}\ M$

and $K_m = 5.0 \times 10^{-5}\ M$

$$\therefore \quad \frac{[ES]}{[E]_0} = \frac{3.0 \times 10^{-3} M}{(5.0 \times 10^{-5} + 3.0 \times 10^{-3})M} = 0.98$$

Nearly the whole of the enzyme is bound with the substrate.

ii. From eq. (7),

Integrating the equation gives,

$$\frac{d[S]}{dt} = -\frac{k_2 [E]_0 [S]}{K_m + [S]}$$

$$K_m \ln\frac{[S]}{[S]_0} + [S] - [S]_0 = - k_2 [E]_0 t \quad (13)$$

If at $t = T$, $[S] = 1/2[S]_0$,

$$T\ k_2 [E]_0 = K_m \ln 2 + \frac{1}{2} [S]_0 \quad (14)$$

Here $[E]_0 = \frac{2.0 \times 10^{-12}\ \text{mol}}{1.0 \times 10^{-3}\ \text{L}} = 2.0 \times 10^{-9}\ \text{M}$

$k_2 = 2.0 \times 10^3\ \text{s}^{-1}$, $K_m = 5.0 \times 10^{-5}\ \text{M}$,

$[S]_0 = 3.0 \times 10^{-3}\ \text{M}$

Substituting these values in eq. (14) gives

$T = 384\ \text{s}$

Thus 50% of the antibiotic dose is inactivated in 384 s.

d. i. The differential rate equations for the situation are :

$$\frac{d}{dt}[ES] = k_1 [E][S] - k_1^{|} [ES] - k_2 [ES] \quad (15)$$

$$\frac{d}{dt}[EI] = k_3 [E][I] - k_3^{|} [EI] \quad (16)$$

$$\frac{d}{dt}[P] = k_2 [ES] \quad (17)$$

where k_3 and $k_3^{|}$ are the forward and backward rate constants for the enzyme-inhibitor reaction.

Applying steady-state approximation to [ES] and [EI],

$$[ES] = \frac{k_1 [E][S]}{k_1^{|} + k_2} \quad (18)$$

and $$[EI] = \frac{k_3 [E][I]}{k_3^{|}} \quad (19)$$

Now $$[E]_0 = [E] + [ES] + [EI] \quad (20)$$

Eliminating [E] and [EI] from eqs. (18) to (20) gives :

$$[ES] = \frac{[E]_0\,[S]}{[S] + K_m\left(1 + \frac{[I]}{K_I\,(1M)}\right)} \qquad (21)$$

$$\frac{d[P]}{dt} = \frac{k_2\,[E]_0\,[S]}{[S] + K_m\left(1 + \frac{[I]}{K_I\,(1M)}\right)} \qquad (22)$$

Here, $K_I(1M) = \frac{k_3^I}{k_3}$ is the equilibrium constant for the dissociation of EI to E and I.

The degree of inhibition is $i = 1 - \frac{r}{r_0}$

Using eq. (22), $i = \frac{\frac{K_m}{K_I}\,\frac{[I]}{(1M)}}{[S] + K_m\left(1 + \frac{[I]}{K_I\,(1M)}\right)}$ (23)

For fixed [I], i decreases with increase in [S] *(competitive inhibition).*

and for large [S], $i \rightarrow 0$, i.e., the inhibitor ceases to play any role.

ii. For small [S] $i = \frac{[I]}{K_I\,(1M) + [I]}$

If $r = \frac{1}{4}\,r_{0,}$ $i = \frac{3}{4}$

i.e., $[I] = 3\,K_I \times (1M) = 1.5 \times 10^{-4}$ M

The inhibitor concentration required to reduce the rate of inactivation by a factor of 4 is 1.5×10^{-4} M; i.e., 0.15 μmol in a volume of 1.00 mL.

5. Schrödinger equation

a.

i. One-dimensional Schrödinger equation for a free particle of mass m:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \qquad \hbar = \frac{h}{2\pi}$$

where E stands for the energy of the particle and ψ its wave function.

ii. The boundary conditions are :

$\psi(0) = \psi(L) = 0$

Only $\psi_n(x) = \sin\frac{n\pi x}{L}$ satisfies the required boundary conditions.

Other functions are not possible wave functions of the electron in a one-dimensional rigid box.

iii.

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\sin\frac{n\pi x}{L} = \frac{\hbar^2\pi^2}{2mL^2}n^2\sin\frac{n\pi x}{L}$$

$$\therefore \quad E_n = \frac{\hbar^2\pi^2}{2mL^2}n^2 = \frac{h^2n^2}{8mL^2}$$

iv. Ground state (n = 1)

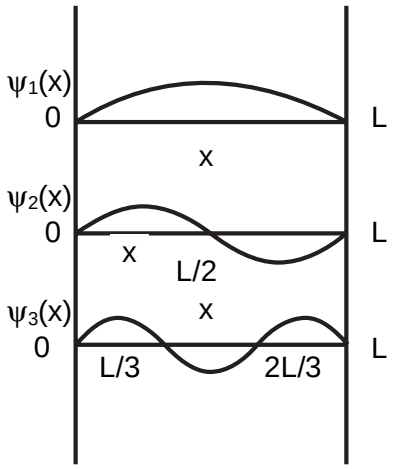
$$\psi_1(x) = \sin\frac{\pi x}{L}$$

First excited state (n = 2)

$$\psi_2(x) = \sin\frac{2\pi x}{L}$$

Second excited state (n = 3)

$$\psi_3(x) = \sin\frac{3\pi x}{L}$$



Number of nodes in ψ_n = n –1, apart from the nodes at the end points.

v.

$$\psi_1^N(x) = N \sin \frac{\pi x}{L}$$

$$1 = \int_{-\infty}^{\infty} \left|\psi_1^N(x)\right|^2 dx$$

$$= N^2 \int_0^L \sin^2 \frac{\pi x}{L} dx = \frac{N^2}{2} \int_0^L \left(1 - \cos \frac{2\pi x}{L}\right) dx$$

$$= N^2 \frac{L}{2}$$

$$\therefore \quad N = \sqrt{\frac{2}{L}} \qquad (N \text{ is chosen to be real})$$

$$\psi_1^N(x) = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L}$$

b. In the example

$L = 5 \times 1.4 \times 10^{-10}$ m $= 7.0 \times 10^{-10}$ m

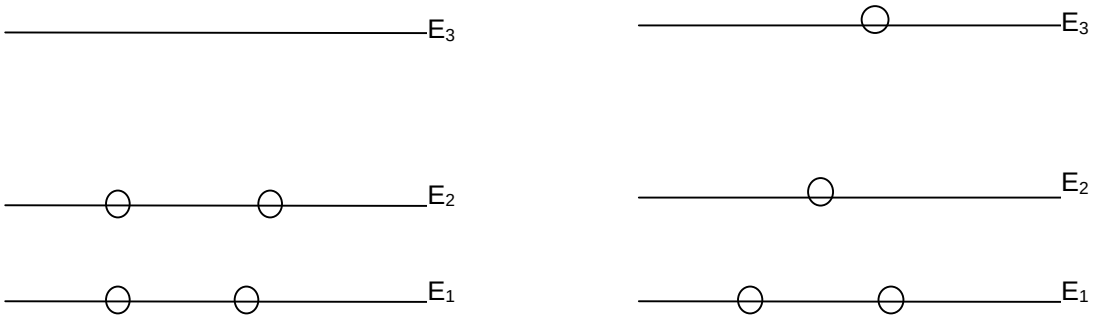
The first three energy levels are:

$$E_1 = \frac{h^2}{8mL^2} = 1.22 \times 10^{-19} \text{ J}$$

$E_2 = 4 E_1 = 4.88 \times 10^{-19}$ J

$E_3 = 9 E_1 = 10.98 \times 10^{-19}$ J

In the ground state, the four electrons will occupy the levels E_1 and E_2, each with two electrons.



Ground state Lowest excited state

The lowest excitation energy

$E_3 - E_2 = 6.10 \times 10^{-19}$ J

c. The condition that $\psi(\phi)$ is single valued demands that

$\Psi(\phi) = \Psi(\phi + 2\pi)$

$e^{i\lambda\phi} = e^{i\lambda(\phi+2\pi)}$

$e^{i\,2\pi\lambda} = 1$

i.e. $\lambda = m$, where $m = 0, \pm1, \pm2, \pm3, \ldots\ldots$

This shows that angular momentum projection (L_z) cannot be an arbitrary real number but can have only discrete values: $m\hbar$, where m is a positive or negative integer (including zero).

6. Atomic and molecular orbitals

A. Atomic orbitals

a.

i. $$\psi_{1s}^{N} = N e^{-\frac{r}{a_o}}$$

$$1 = \int \left|\psi_{1s}^{N}\right|^2 dv = 4\pi a_o^3 N^2$$

$$= 4\pi N^2 \times \frac{a_o^3}{4} = \pi a_o^3 N^2 \qquad \text{(N chosen to be real)}$$

$$\therefore \quad N = \left[\pi a_o^3\right]^{-\frac{1}{2}}$$

$$\psi_{1s}^{N} = \left[\pi a_o^3\right]^{-\frac{1}{2}} e^{-\frac{r}{a_o}}$$

ii. Probability of finding an electron between r and r + dr

$$= 4\pi r^2 \times \left[\pi a_0^3\right]^{-1} e^{-\frac{2r}{a_0}} dr$$

This is a maximum at $r = r_{max}$, given by

$$\frac{d}{dr}\left(r^2 e^{-\frac{2r}{a_0}}\right)_{r=r_{max}} = 0$$

This gives

$$r_{max} = a_0$$

The 1s electron is most likely to be found in the neighborhood of $r = a_0$.

b. $\psi_{2s} = 0$ at $r = 2a0$

Nodal surface is a sphere of radius $2a_0$

$\psi_{2p_z} = 0$ at $\theta = \frac{\pi}{2}$

Nodal surface is the xy plane.

$\psi_{3d_{z^2}} = 0$ at $3\cos^2\theta - 1 = 0$, i.e., $\theta = \cos^{-1}\left(\pm\frac{1}{\sqrt{3}}\right)$

Nodal surfaces are cones with these values of half-angle, one above the xy plane and the other below it.

(Note: all three wave functions vanish as $r \to \infty$. At $r = 0$, ψ_{ls} does not vanish, but the other two wave functions vanish.)

c. Each electron in n = 1 shell of helium atom has energy $-Z^2_{eff} \times 13.6$ eV

Helium ground state energy $= -Z^2_{eff} \times 27.2$ eV

Energy of He^+ ground state $= -4 \times 13.6 = -54.4$ eV

Ionization energy $= (-54.4 + Z^2_{eff} \times 27.2)$ eV $= 24.46$ eV

This gives $Z_{eff} = 1.70$

B. Molecular orbitals

a. ψ_1 and ψ_2 are bonding orbitals

$\tilde{\psi}_1$ and $\tilde{\psi}_2$ are antibonding orbitals

Bonding orbital

No nodal surface between the nuclei. Electronic energy has a minimum at a certain internuclear distance. Qualitative reason: electron has considerable probability of being between the nuclei and thus has attractive potential energy due to both the nuclei.

Antibonding orbital

Nodal surface between the nuclei. Electronic energy decreases monotonically with internuclear distance. Hence bound state is not possible.

b. $R_e = 1.32 \times 10^{-10}$ m

D = –1.36 – (–15.36) = 1.76 eV

c. It will dissociate to a hydrogen atom in 2s state and a bare hydrogen nucleus (proton).

d. The two electrons occupy the same molecular orbital with the lowest energy. By Pauli's principle, their spins must be antiparallel. Hence the total electronic spin is zero.

e. In the first excited state of H_2, one electron is in ψ_1 (bonding orbital) and the other in ψ_1 (antibonding orbital). It will dissociate into two hydrogen atoms.

f. Using the aufbau principle, in the ground state two electrons of He_2 are in ψ_1 (bonding orbital) and two in ψ_1 (antibonding orbital). The bond order is

½ (2 –2) = 0

Therefore, bound He_2 is unstable and difficult to detect. However, if one or more electrons are elevated from the antibonding orbital to (higher energy) bonding orbitals, the bond order becomes greater than zero. This is why it is possible to observe He_2 in excited states.

7. Fission

a.

$$^{235}_{92}U + n \rightarrow {}^{94}_{38}Sr + {}^{140}_{54}Xe + 2n$$

$$^{235}_{92}U + n \rightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3n$$

b. The net nuclear reaction is

$$^{235}_{92}U + n \rightarrow {}^{94}_{40}Zr + {}^{140}_{58}Ce + 2n + 6e^- + (Q)$$

The energy released is

$$Q = [m_N(^{235}U) - m_N(^{94}Zr) - m_N(^{140}Ce) - m_n - 6m_e]\, c^2$$

where the small energy of the initial thermal neutron has been ignored. (m_N denotes the nuclear mass.) Now

$$m_N(^{235}U) = m(^{235}U) - 92m_e$$

ignoring the small electronic binding energies compared to rest mass energies. Similarly for other nuclear masses.

$$Q = [m(^{235}U) - m(^{94}Zr) - m(^{140}Ce) - m_n]\, c^2$$

Using the given data,

$$Q = 213.3 \text{ MeV}$$

c. $1 \text{ MWd} = 10^6 \text{ Js}^{-1} \times 24 \times 3600 \text{ s} = 8.64 \times 10^{10} \text{ J}$

$$\text{No. of atoms of } ^{235}U \text{ fissioned} = \frac{8.64 \times 10^{10}}{213.3 \times 1.60 \times 10^{-13}} = 2.53 \times 10^{21}$$

$$\text{Mass of } ^{235}U \text{ fissioned} = \frac{2.53 \times 10^{21} \times 235}{6.02 \times 10^{23}} = 0.99 \text{ g}$$

Mass of ^{235}U in 1 kg uranium removed from the reactor $= 7.2 - 0.99 = 6.2$ g

Abundance of ^{235}U is 0.62 %

8. Radioactive decay

a. $1\mu Ci = 3.7 \times 10^4$ disintegrations per second (dps).

Initial β –activity $= 3.7 \times 10^6$ dps

$$\left.\frac{-dN_1}{dt}\right|_{t=0} = N_1^o \lambda_1 = 3.7 \times 10^6 \text{ dps}$$

where N_1^o is the number of atoms of ^{210}Bi at $t = 0$ and λ_1 is its decay constant .

$$\frac{0.693}{5.01 \times 24 \times 3600} N_1^0 = 3.7 \times 10^6$$

$$N_1^0 = 2.31 \times 10^{12}$$

$$\text{Intial mass of } {}^{210}\text{Bi} = 2.31 \times 10^{12} \times \frac{210}{6.02 \times 10^{23}} \text{ g}$$

$$= 8.06 \times 10^{-10} \text{ g}$$

b. Number of atoms of ^{210}Bi at time t is given by

$$N_1 = N_1^0 e^{-\lambda_1 t}$$

The number of atoms of ^{210}Po, N_2, is given by equation

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2$$

where λ_2 is the decay constant of ^{210}Po.

$$\frac{dN_2}{dt} = \lambda_1 N_1^0 e^{-\lambda_1 t} - \lambda_2 N_2$$

Using the integrating factor $e^{\lambda_2 t}$

$$e^{\lambda_2 t} \frac{dN_2}{dt} + \lambda_2 N_2 e^{\lambda_2 t} = \lambda_1 N_1^0 e^{(\lambda_2 - \lambda_1)t}$$

$$\frac{d}{dt}(N_2 e^{\lambda_2 t}) = \lambda_1 N_1^0 e^{(\lambda_2 - \lambda_1)t}$$

Integrating

$$N_2 e^{\lambda_2 t} = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 e^{(\lambda_2 - \lambda_1)t} + C$$

To calculate C, use the condition that at t = 0, $N_2 = 0$

$$C = -\frac{\lambda_1 N_1^0}{\lambda_2 - \lambda_1}$$

This gives

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 (e^{-\lambda_1 t} - e^{-\lambda_2 t})$$

The time t = T when N_2 is maximum is given by the condition

$$\left.\frac{dN_2}{dt}\right|_{t=T} = 0$$

which gives

$$T = \frac{\ln \frac{\lambda_1}{\lambda_2}}{\lambda_1 - \lambda_2} = 24.9 \text{ d}$$

At t = T, N_2 can be calculated from above.

$N_2 = 2.04 \times 10^{12}$

Mass of ^{210}Po at t = T,

$= 7.11 \times 10^{-10}$ g

c. α-disintegration rate of ^{210}Po at t = T

$= 1.18 \times 10^5$ dps

At t = T

β - disintegration rate of ^{210}Bi

= α-disintegration rate of ^{210}Po = 1.18×10^5 dps

9. Redox reactions

a.

i. Over-all reaction

$$Sn^{2+} + 2Fe^{3+} \rightarrow Sn^{4+} + 2Fe^{2+} \qquad E^\circ = +0.617 \text{ V}$$

$$\Delta G^\circ = -nFE^\circ = -2FE^\circ$$
$$= -2 \times 96485 \times 0.617 \text{ V}$$
$$= -119 \text{ KJ}$$

ii. $$E^{\circ} = \frac{0.0592}{n} \log K$$

$$\log K = \frac{(2 \times 0.617)}{0.0592} \cong 20.84$$

$$K = 6.92 \times 10^{20}$$

b. Before the equivalence point, E of the cell is given by following equation

$$E_{cell} = {}_{ox}E^{o}_{S.C.E} + {}_{red}E^{o}_{Sn^{4+}/Sn^{2+}} - \frac{0.0592}{2} \log \frac{[Sn^{2+}]}{[Sn^{4+}]}$$

$$= - 0.242 + 0.154 - \frac{0.0592}{2} \log \frac{[Sn^{2+}]}{[Sn^{4+}]}$$

i. The addition of 5.00 mL of Fe^{3+} converts 5.00/20.00 of the Sn^{2+} to Sn^{4+}; thus

$$\frac{[Sn^{2+}]}{[Sn^{4+}]} = \frac{15.0/20.0}{5.0/20.0} = 3.00$$

$E_{cell} = - 0.102$ V.

ii. At the equivalence point, add the two expressions corresponding to Sn^{4+}/Sn^{2+} and Fe^{3+}/Fe^{2+}.

$$2 \quad E_{cell} = 2\ {}_{ox}E^{\circ}_{S.C.E} + 2 \quad {}_{red}E^{\circ}_{Sn^{4+}/Sn^{2+}} - 0.0592 \quad \log \frac{[Sn^{2+}]}{[Sn^{4+}]}$$

$$1 \quad E_{cell} = {}_{ox}E^{\circ}_{S.C.E} + \quad {}_{red}E^{\circ}_{Fe^{3+}/Fe^{2+}} - 0.0592 \quad \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

to get

$$3 \quad E_{cell} = 3\ {}_{ox}E^{\circ}_{S.C.E} + 2\ {}_{red}E^{\circ}_{Sn^{4+}/Sn^{2+}} + {}_{red}E^{\circ}_{Fe^{3+}/Fe^{2+}} - 0.0592 \log \frac{[Sn^{2+}][Fe^{2+}]}{[Sn^{4+}][Fe^{3+}]}$$

At the equivalence point, $[Fe^{3+}] = 2\,[Sn^{2+}]$ and $[Fe^{2+}] = 2\,[Sn^{4+}]$

Thus,

$$E_{cell} = {}_{ox}E^{\circ}_{S.C.E} + \frac{2\,{}_{red}E^{\circ}_{Sn^{4+}/Sn^{2+}} + {}_{red}E^{\circ}_{Fe^{2+}/Fe^{3+}}}{3}$$

$$= -\ 0.242\ + \frac{(2)(0.154) + 0.771}{3} = +\ 0.118\ V$$

Beyond the equivalence point, E of the cell is given by following equation

$$E_{cell} = {}_{ox}E^{o}_{S.C.E} + {}_{red}E^{o}_{Fe^{3+}/Fe^{2+}} - 0.0592\ \log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

When 30 mL of Fe^{3+} is added , 10 mL of Fe^{3+} is in excess. i.e.

$$\frac{[Fe^{2+}]}{[Fe^{3+}]} = \frac{20.0}{10.0} = 2.00$$

$E_{cell} = 0.511$ V

c.

i. $\Delta G^{\circ} = -RT \ln K_{sp}$

$= 68.27$ K J

$\Delta G^{\circ} = -nFE^{\circ}, \quad n = 1$

$E^{\circ} = -\ 0.707$ V

ii. $Cu^{+} + I^{-} = CuI_{(s)}$ $\quad E^{\circ} = 0.707$ V

$Cu^{2+} + e^{-} = Cu^{+}$ $\quad E^{\circ} = 0.153$ V

The overall reaction for reduction of Cu^{2+} by I^{-} is

$Cu^{2+} + I^{-} + e^{-} = CuI_{(s)}$ $\quad E^{\circ} = 0.86$ V

The E° value for the reduction of Cu^{2+} by I^{-} can now be calculated

$2 \times Cu^{2+} + I^{-} + e^{-} = CuI_{(s)}$ $\quad E^{\circ} = 0.86$ V

$I_2 + 2e^{-} = 2I^{-}$ $\quad E^{\circ} = 0.535$ V

The over-all reaction is

$2Cu^{2+} + 4I^- \rightarrow 2CuI_{(s)} + I_2 \qquad E^\circ = 0.325\ V$

The positive value of effective E° indicates that the reduction reaction is spontaneous. This has come about since in this reaction, I^- is not only a reducing agent, but is also a precipitating agent. Precipitation of Cu^+ as CuI is the key step of the reaction, as it practically removes the product Cu^+ from the solution, driving the reaction in the forward direction.

iii. $\Delta G^o = -nFE^o$

Here $n = 1, \quad E^o = 0.325V$

$\Delta G^o = -31.3\,kJ$

$\Delta G^o = -RT\ln K$

$\log K = 5.47$

$K = 2.9 \times 10^5$

10. Solubility of sparingly soluble salts

a. $Ag_2C_2O_{4\,(s)} = 2\,Ag^+ + C_2O_4^{2-}$

The solubility product Ksp is given by

$K_{sp} = [Ag^+]^2\ [C_2O_4^{2-}]$

If S is the solubility of $Ag_2C_2O_4$

$[Ag^+] = 2S \qquad (1)$

The total oxalate concentration, denoted by C_{ox}, is

$C_{ox} = S = [C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4] \qquad (2)$

The dissociation reactions are:

$H_2C_2O_4 = H^+ + HC_2O_4^- \qquad K_1 = 5.6 \times 10^{-2} \qquad (3)$

$HC_2O_4^- = H^+ + C_2O_4^{2-} \qquad K_2 = 6.2 \times 10^{-5} \qquad (4)$

Eqs. (2), (3) and (4) give

$$C_{ox} = S = [C_2O_4^{2-}] + \frac{[C_2O_4^{2-}][H^+]}{K_2} + \frac{[C_2O_4^{2-}][H^+]^2}{K_1K_2}$$

$$\therefore \quad [C_2O_4^{2-}] = \alpha C_{ox} = \alpha S$$

$$\text{where} \qquad \alpha = \frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2} \qquad (5)$$

At pH = 7, $[H^+] = 10^{-7}$ and $\alpha \cong 1$

$K_{sp} = 4S^3 = 3.5 \times 10^{-11}$

At pH = 5.0, $[H^+] = 10^{-5}$

From the values of K_1, K_2 and $[H^+]$, we get

$\alpha = 0.861$ (6)

$K_{sp} = [2S]^2 [\alpha S]$

$$\therefore \quad S = \left(\frac{K_{sp}}{4\alpha}\right)^{\frac{1}{3}} = 2.17 \times 10^{-4}$$

b. $[NH_3] = 0.002$

At pH = 10.8, $[H^+] = 1.585 \times 10^{-11}$

Eq. (5) implies

$\alpha = 1$

i.e $C_{ox} = S = [C_2O_4^{-2}]$ (7)

The total silver ion in the solution is given by

$C_{Ag} = 2S = [Ag^+] + [AgNH_3^+] + [Ag(NH_3)_2^+]$ (8)

The complex formation reactions are

$Ag^+ + NH_3 = AgNH_3^+$ $\quad K_3 = 1.59 \times 10^3$ (9)

$AgNH_3^+ + NH_3 = Ag(NH_3)_2^+$ $\quad K_4 = 6.76 \times 10^3$ (10)

From eqs. (8), (9) and (10)

$C_{Ag} = 2S = [Ag^+]\{1 + K_3[NH_3] + K_3K_4[NH_3]^2\}$

$\therefore \quad [Ag^+] = \beta \times C_{Ag} = \beta \times 2S$

where $\beta = \dfrac{1}{1 + K_3[NH_3] + K_3K_4[NH_3]^2}$

Using the values of K3, K_4 and $[NH_3]$,

$\beta = 2.31 \times 10^{-4}$

$K_{sp} = [Ag^+]^2 [C_2O_4^{2-}]$

$= [\beta \times 2S]^2 [S]$

$\therefore \quad S = \left(\dfrac{K_{sp}}{4\beta^2}\right)^{\frac{1}{3}}$

$= 5.47 \times 10^{-2}$

11. Spectrophotometry

a. Denote the molar absorptivity of MnO_4^- at 440 nm and 545 nm by ε_1 and ε_2 and that of $Cr_2O_7^-$ by $\in_3$ and $\in_4$:

$\in_1 = 95 \ \text{Lmol}^{-1}\text{cm}^{-1}$, $\quad \in_2 = 2350 \ \text{Lmol}^{-1}\text{cm}^{-1}$

$\in_3 = 370 \ \text{Lmol}^{-1}\text{cm}^{-1}$, $\quad \in_4 = 11 \ \text{Lmol}^{-1}\text{cm}^{-1}$

The absorbance A is related to % transmittance T by

$A = 2 - \log T$

From the values given for the sample solution

$A_{440} = 2 - \log 35.5 = 0.45$

$A_{545} = 2 - \log 16.6 = 0.78$

Now if one denotes the molar concentrations of MnO_4^- and $Cr_2O_7^{2-}$ in the steel sample solution by C_1 and C_2 respectively, we have

$A_{440} = \in_1 x\, C_1 x\, 1 + \in_3 x\, C_2 x\, 1$

$A_{545} = \in_2 x\, C_1 x\, 1 + \in_4 x\, C_2 x\, 1$

Using the given data, we get

$C_1 = 0.0003266$ M

$C_2 = 0.001132$ M

Amount of Mn in 100 mL solution

$= 0.0003266 \text{ molL}^{-1} \times 54.94 \text{ gmol}^{-1} \times 0.1$ L

$= 0.001794$ g

$$\%\,\text{Mn in steel sample} = \frac{0.001794 \times 100}{1.374} = 0.13\%$$

Amount of Cr present in 100 mL solution

$= 0.001132 \text{ mol L}^{-1} \times 2 \times 52.00 \text{ g mol}^{-1} \times 0.1$ L

$= 0.0118$ g

$$\%\,\text{Cr in steel sample} = \frac{0.0118 \times 100}{1.374} = 0.86\%$$

b. In solution 1, since all the ligand is consumed in the formation of the complex,

$$[CoL_3^{2+}] = \frac{2 \times 10^{-5}}{3} = 0.667 \times 10^{-5}$$

Absorptivity of the complex CoL_3^{2+} is

$$\in = \frac{0.203}{0.667 \times 10^{-5} \text{ mol L}^{-1} \times 1.0 \text{ cm}} = 3.045 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$$

If the concentration of the complex CoL_3^{2+} in solution 2 is C,

$$C = \frac{0.68}{3.045 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1} \times 1.0 \text{ cm}}$$

$$= 2.233 \times 10^{-5} \text{ M}$$

$[Co^{2+}] = [Co^{2+}]_{total} - [CoL_3^{2+}]$

$= 3 \times 10^{-5} - 2.233 \times 10^{-5} = 0.767 \times 10^{-5}$

Similarly, $[L] = [L]_{total} - 3[CoL_3^{2+}]$

$= 7 \times 10^{-5} - 3 \times 2.233 \times 10^{-5} = 0.300 \times 10^{-5}$

The complex formation reaction is

$Co^{2+} + 3L = [CoL_3^{2+}]$

The stability constant K is given by

$$K = \frac{[CoL_3^{2+}]}{[Co^{2+}][L]^3}$$

$$= 1.08 \times 10^{17}$$

12. Reactions in buffer medium

$RNO_2 + 4H^+ + 4e \rightarrow RNHOH + H_2O$

$HOAc = H^+ + OAc^-$

$$K_a = \frac{[H^+]\,[OAc^-]}{[HOAc]}$$

i.e

$$pK_a = pH + \log \frac{[HOAc]}{[OAc^-]}$$

$$4.76 = 5.0 + \log \frac{[HOAc]}{[OAc^-]}$$

$$\frac{[HOAc]}{[OAc^-]} = 0.5715$$

$$[HOAc] + [OAc^-] = 0.500$$

$$[OAc^-] = 0.3182$$

$$[HOAc] = 0.5 - 0.3182 = 0.1818$$

mmoles of acetate (OAc^-) present initially in 300 mL

= 0.3182 x 300 = 95.45

mmoles of acetic acid (HOAc) present initially in 300 mL

= 0.1818 x 300 = 54.55

mmoles of RNO_2 reduced

= 300 x 0.0100 = 3

From the stoichiometry of the equation, 3 mmoles of RNO_2 will consume 12 moles of H^+ for reduction. The H^+ is obtained from dissociation of HOAc.

On complete electrolytic reduction of RNO_2,

mmoles of HOAc = 54.55 – 12.00 = 42.55

mmoles of OAc^- = 95.45 + 12.00 = 107.45

$$4.76 = pH + \log \frac{42.55}{107.45}$$

$$pH = 5.16$$

13. Identification of an inorganic compound

a. The white gelatinous precipitate in group (III) obtained by qualitative analysis of solution **B** indicates the presence of Al^{3+} ions. The white precipitate with $AgNO_3$ indicates the presence of Cl^- ions.

From the above data the compound **A** must be a dimer of aluminium chloride Al_2Cl_6.

b. The reactions are as follows

$$Al_2Cl_6 \xrightarrow{H_2O} 2[Al.6H_2O]^{3+} + 6Cl^-$$

$$6Cl^- + 6AgNO_3 \longrightarrow 6AgCl_{(s)} + 6NO_3^-$$

$$AgCl_{(s)} + NH_4OH_{(aq)} \longrightarrow Ag(NH_3)^+ \text{ or } Ag(NH_3)_2^+ + H_2O + Cl^-$$

$$Al^{3+} + NH_4OH_{(aq)} \longrightarrow Al(OH)_{3(s)} + NH_4^+$$

$$Al(OH)_{3(s)} + NaOH_{(aq)} \longrightarrow [Al(OH)_4]^- + Na^+$$

$$[Al(OH)_4]^- + CO_2 \longrightarrow Al(OH)_{3(s)} + HCO_3^-$$

$$Al_2Cl_6 + LiH \longrightarrow (AlH_3)_n \xrightarrow{\text{excess of LiH}} Li[AlH_4]$$

14. Ionic and metallic structures

a.

i. The lattice of NaCl consist of interpenetrating *fcc* lattices of Na^+ and Cl^-

ii. The co-ordination number of sodium is <u>six</u> since, it is surrounded by six nearest chloride ions.

iii. For NaCl, the number of Na^+ ions is: twelve at the edge centres shared equally by four unit cells thereby effectively contributing 12 x 1/4 =

$3Na^+$ ions per unit cell and one at body center. Thus, a total of 3 + 1 = 4 Na^+ ions per unit cell.

Number of Cl^- ions is: six at the center of the faces shared equally by two unit cells, thereby effectively contributing $6 \times 1/2 = 3$ Cl^- ions per unit cell and eight at the corners of the unit cell shared equally by eight unit cells thereby effectively contributing $8 \times 1/8 = 1$ Cl^- ion per unit cell. Thus, a total of 3+ 1 = 4 Cl^- ions per unit cell.

Hence, the number of formula units of NaCl per unit cell = $4Na^+ + 4Cl^-$ = <u>4NaCl</u>

iv. The face diagonal of the cube is equal to $\sqrt{2}$ times 'a' the lattice constant for NaCl. The anions/anions touch each other along the face diagonal. The anion/cations touch each other along the cell edge.

Thus, $a = 2 (r_{Na^+} + r_{Cl^-})$ ……..(1)

Face diagonal $\sqrt{2}\, a = 4\, r_{Cl^-}$ ……..(2)

Substituting for 'a' from (1) into (2) we get :

$\sqrt{2} \times 2 (r_{Na^+} + r_{Cl^-}) = 4\, r_{Cl^-}$ from which,

the limiting radius ratio r_{Na^+} / r_{Cl^-} = <u>0.414</u>

v. The chloride ion array is expanded to make the octahedral holes large enough to accommodate the sodium ions since, the r_{Na^+}/ r_{Cl^-} ratio of 0.564 is larger than the ideal limiting value of 0.414 for octahedral six coordination number.

vi. As the cation radius is progressively increased, the anions will no longer touch each other and the structure becomes progressively less stable. There is insufficient room for more anions till the cation / anion radius ratio equals 0.732 when, eight anions can just be grouped around the cation resulting in a cubic eight coordination number as in CsCl.

vii. Generally, the *fcc* structure with a six coordination number is stable in the cation/anion radius ratio range 0.414 to 0.732. That is, if $0.414 < r^+/r^- < 0.732$ then, the resulting ionic structure will generally be NaCl type *fcc.*

b.

i. Bragg's law states $\lambda = 2d_{hkl}\,Sin(\theta)$

$$154\ pm = 2 \times d_{200} Sin(15.8^\circ)$$

$$d_{200} = \frac{154\,pm}{2 \times Sin(15.8^\circ)} = \frac{154\ pm}{2 \times 0.272} = 283\ pm$$

Thus, the separation between the (200) planes of NaCl is 283 pm.

ii. Length of the unit cell edge, $a = d_{100} = 2 \times d_{200}$

$a = 2 \times 283pm =$ 566 pm.

iii. Since it is an *fcc* lattice,

cell edge, $a = 2(r_{Na}^+ + r_{Cl}^-)$

radius of sodium ion $r_{Na+} = \frac{a - 2}{2}\, r_{Cl}^- = \frac{566 - 362}{2} = 102\ pm$

c.

i. The difference in an *hcp* and a *ccp* arrangement is as follows:

The two 'A' layers in a *hcp* arrangement are oriented in the same direction making the packing of successive layers ABAB.. and the pattern repeats after the second layer whereas, they are oriented in the opposite direction in a *ccp* arrangement resulting in a ABCABC… packing pattern which repeats after the third layer.

The unit cell in a *ccp* arrangement is based on a cubic lattice whereas in a *hcp* arrangement it is based on a hexagonal lattice.

ii. Packing fraction = $\frac{\text{Volume occupied by 4 atoms}}{\text{Volume of unit cell}}$

Let 'a' be the length of the unit cell edge

Since it is an *fcc* lattice, face diagonal = $\sqrt{2}a = 4r$ ……..(1)

Volume of the unit cell = a^3

$$\text{Packing fraction} = \frac{4 \times 4 \ \pi \ r^3}{3 \times a^3} \text{.....(2)}$$

Substituting for 'a' from (1) into (2), we get

$$\text{Packing fraction} = \frac{4 \times 4 \ \times 22 \times (\sqrt{2})^3 \times r^3}{3 \times 7 \times (4r)^3} = 0.74$$

Thus, packing fraction in a *ccp* arrangement = 0.74

iii. The coordination number(12) and the packing fraction (0.74) remain the same in a *hcp* as in a *ccp* arrangement.

d.

i. For an *fcc*, face diagonal = $\sqrt{2}a = 4r_{Ni}$

where a = lattice constant

r_{Ni} = radius of the nickel atom

$$r_{Ni} = \frac{\sqrt{2} \times a}{4} = \frac{\sqrt{2} \times 352.4 \text{ pm}}{4} = 124.6\text{pm}$$

ii. Volume of unit cell = $a^3 = (3.524 \text{ Å})^3 = 43.76 \text{Å}^3$

iii. Density of Nickel, $\rho_{Ni} = \frac{Z \times M/N}{V}$

No. of Ni atoms, Z = 4 for an *fcc* lattice

Avogadro constant

$$N = \frac{Z \times M}{\rho_{Ni} \ V} = \frac{4 \times 58.69 \text{ g mol}^{-1}}{8.902 \text{ g cm}^{-3} \times 43.76 \times 10^{-24} \text{ cm}^3}$$

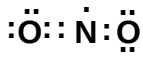
$$N = 6.02 \times 10^{23} \text{ mol}^{-1}$$

15. Compounds of nitrogen

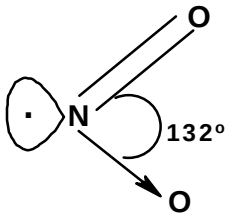
a.

i. NO_2 : No. of electrons in the valence shell around nitrogen
= 5 + 0 + 2 = 7

The Lewis structure for NO_2 is as shown below.

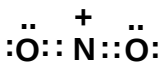


According to VSEPR, the molecule ideally should have linear geometry. However, this molecule has one single unpaired electron present on nitrogen. Due to the repulsion between the unpaired electron and the other two bonded pairs of electrons, the observed bond angle is less than 180 (132^o). Thus, the shape of the molecule is angular as shown below.

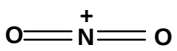


ii. NO_2^+: No. of electrons in the valence shell around nitrogen
= (5 + 2 + 2 –1) = 8

The Lewis structure is as shown below



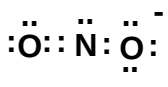
Thus, there are no non-bonded electrons present on nitrogen. The two σ - bonds will prefer to stay at 180^o to minimize repulsion between bonded electron pairs giving a linear geometry (180^o). The π-bonds do not influence the shape.

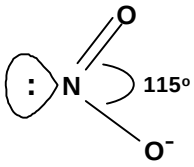


NO_2^-: No. of electron in the valence shell around nitrogen

= 5 + 2 + 1 = 8

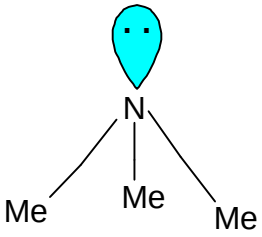
The Lewis structure is as shown below

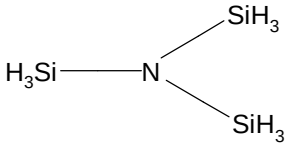




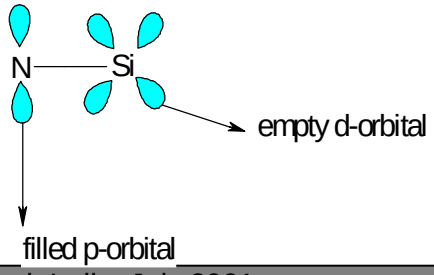
In case of NO_2^-, there is a lone pair of electrons present on nitrogen. Due to strong repulsion between the lone pair of electrons and the bonded pairs of electrons the angle between the two bond pairs shrinks from the ideal 120° to 115°.

b. In case of trimethylamine, the shape of the molecule is pyramidal with a lone pair present on nitrogen. Due to the lone pair Me-N-Me angle is reduced from 109°4′ to 108°.

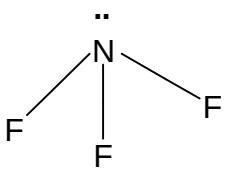


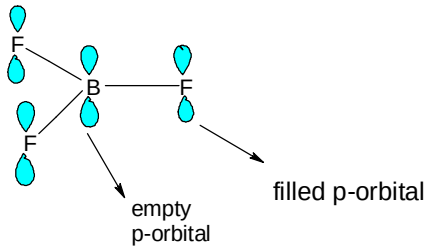


However, in case of trisilylamine, d orbital of silicon and p orbital of nitrogen overlaps giving double bond character to the N-Si bond. Thus, delocalisation of the lone electron pair of nitrogen takes place and the resultant molecule is planar with 120° bond angle.



c. Both N and B are tricovalent. However, NF_3 is pyramidal in shape. In case of BF_3, the B-F bond gets double bond character due to the overlapping of p orbitals present on boron and fluorine. The observed bond energy is, therefore, much greater in BF_3





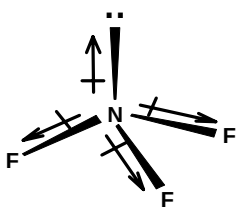
d.

i. The difference in boiling points of NF_3 and NH_3 is due to hydrogen bonding which is present in ammonia.

High electronegativity of fluorine decreases the basicity of nitrogen in NF_3. Thus, NF_3 does not act as a Lewis base.

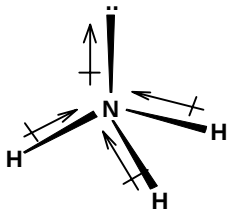
ii. In NF_3, the unshared pair of electrons contributes to a dipole moment in the direction opposite to that of the net dipole moment of the

N-F bonds. See figure (a).



NF_3

(a)



NH_3

(b)

In NH_3, the net dipole moment of the N-H bonds and the dipole moment due to the unshared pair of electrons are in the same direction. See figure (b).

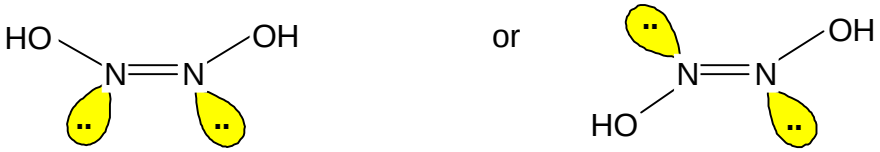
e.

$$2NaNO_3 + 8Na(Hg) + 4H_2O \rightarrow Na_2N_2O_2 + 8NaOH + 8Hg$$

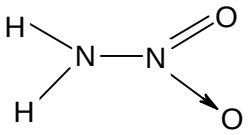
$$NH_2OH + EtNO_2 + 2NaOEt \rightarrow Na_2N_2O_2 + 3EtOH$$

$Na_2N_2O_2$ is the salt of $H_2N_2O_2$ (Hyponitrous acid).

Structure :

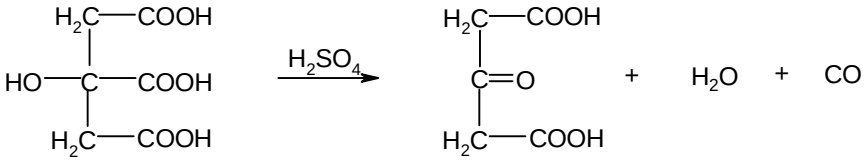


Isomer is: $H_2N—NO_2$ (Nitramide)



16. Structure elucidation with stereochemistry

a.



3-oxo-1,3-pentanedioic acid

α - Hydroxy carboxylic acids undergo similar reaction.

b. Molecular weight of **A** = 236

20 mL 0.05 M KOH ≡ 118 mg **A**

1000 mL 1 M KOH ≡ 118 g **A**

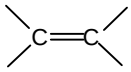
∴ The acid is dibasic

Molecular weight of **A** = 236

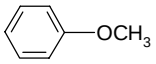
80 mg Br_2 ≡ 118 mg **A**

160 gm Br_2 ≡ 236 g **A**

A contains one double bond



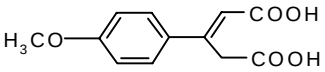
It has anisole ring in the molecule



It is formed from HOOC– CH_2–CO–CH_2–COOH

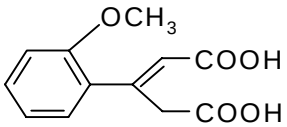
It has molecular formula **$C_{12}H_{12}O_5$**

Due to steric hindrance the attachment of the aliphatic portion on the anisole ring will be para with respect to -OCH_3. Hence the structure will be

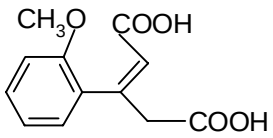


As **A** forms anhydride the two COOH groups should be on the same side of the double bond.

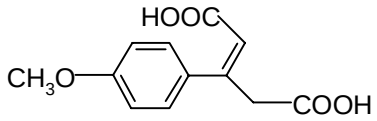
c. Isomers of **A**



(E) 3-(2-methoxyphenyl)-2-pentenedioic acid

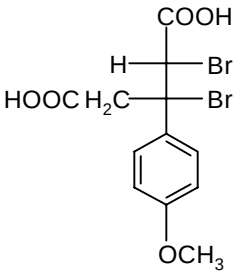


(Z) 3-(2-methoxyphenyl)-2-pentenedioic acid

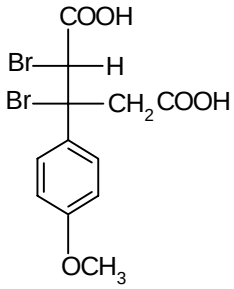


(Z) 3-(4-methoxyphenyl)-2-pentenedioic acid

d. Two products are possible when compound **A** reacts with bromine.



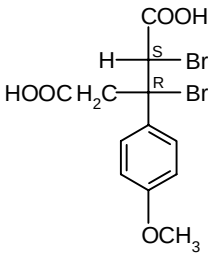
[1]

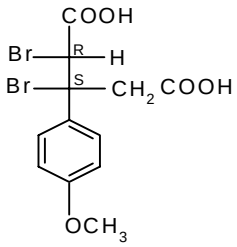


[2]

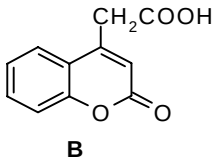
Structures 1 and 2 are enantiomers.

e.



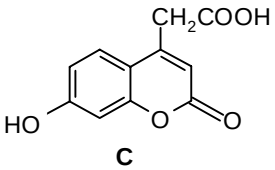


f.



B

Product obtained by reaction with phenol



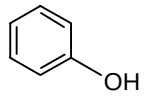
C

Product obtained by reaction with resorcinol

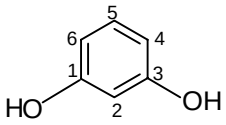
g. In the formation of compound **A** from anisole, the attack takes place at the *p*-position of the **OCH_3** group. However, when compound **B** is formed from phenol, the attack takes place at the *o*-position of the **OH** group. Steric

hindrance of **OCH_3** group favours the attack at the *para* position. Steric hindrance of the **OH** group is comparatively less. Thus, the attack is possible at the *ortho* or *para* positions. However, addition at *ortho* position is favoured as it leads to cyclization of the intermediate acid to stable **B**.

h. Phenol has only one **OH** group on the phenyl ring whereas resorcinol has two **OH** groups on the phenyl ring at the m-positions. Hence, position 4 is considerably more activated (i.e, electron rich) in the case of resorcinol.



Phenol

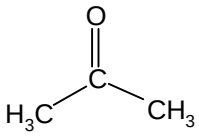


Resorcinol

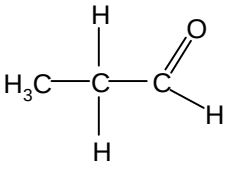
Therefore, under identical reaction conditions, the yield of compound **C** is much higher than that of **B.**

17. Organic spectroscopy and structure determination

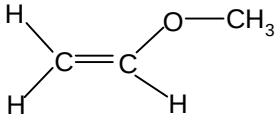
a. The given Molecular formula is **C_3H_60.** Therefore, the possible structures are:



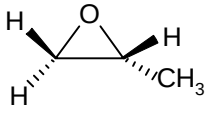
I



II

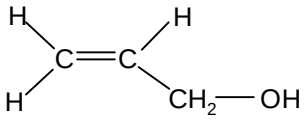


III



IV

V

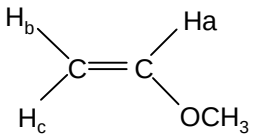


VI

The NMR spectrum of compound **A** shows a single peak which indicates that all the protons in **A** are equivalent. This holds true only for structure I. The IUPAC name of this compound is 2-propanone.

The NMR spectrum of compound **B** shows four sets of peaks, which indicate the presence of four non-equivalent protons**.** This holds true for structures III and IV. However, for structure IV, no singlet peak (see peak at $\delta = 3$) will be observed. So, compound **B** must have structure III. The IUPAC name is 1-methoxyethene.

b.



Three doublets of doublets centred at 6.5 ppm, 3.9 ppm, 3.5 ppm are seen in the spectrum. The assignments in the spectrum are

H_a : 6.5 ppm
H_b : 3.5 ppm
H_c : 3.9 ppm

Due to the presence of electron donating **OCH_3**, the trans proton H_b has higher electron density and thus more shielded than H_c. Thus, H_b appears upfield as compared to H_c. There is also a singlet line at δ=3. This corresponds to the **H** in **OCH_3**.

c. Coupling constants

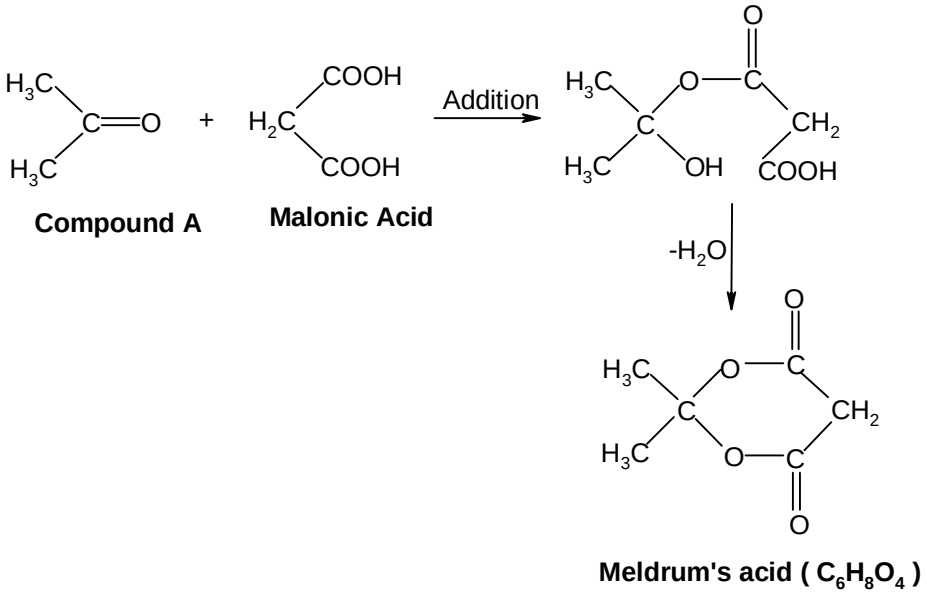
H_a	:	12, 16 Hz	J (H_a, H_b) = 12 Hz
			J (H_a, H_c) = 16 Hz
H_b	:	8, 12 Hz	J (H_a, H_b) = 12 Hz
			J (H_b, H_c) = 8 Hz
H_c	:	8, 16 Hz	J (H_b, H_c) = 8 Hz
			J (H_c, H_a) = 16 Hz

Note: J = (difference in two lines in ppm) x (Instrument frequency)
Geminal coupling < *cis*-vicinal coupling < *trans*-vicinal coupling

d.

Peak positions in Hz (for 400 MHz instrument)	Peak positions in Hz (for 600 MHz instrument)
2614	3921
2602	3903
2598	3897
2586	3879

e. Compound **A** will react with malonic acid in the following manner

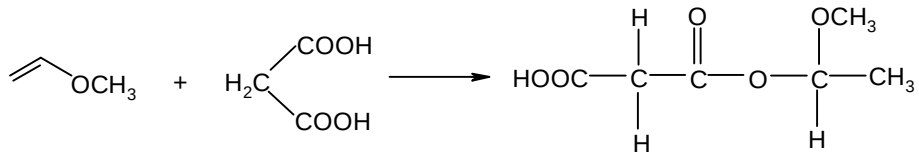


Compound A **Malonic Acid**

Meldrum's acid ($C_6H_8O_4$)

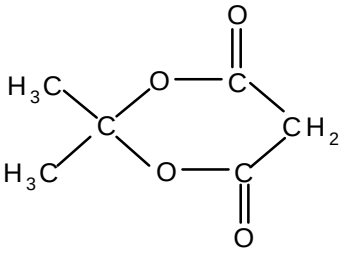
The structure of Meldrum's acid is consistent with the ^{1}H-NMR and IR data. The peak in the IR spectrum at 1700 –1800 cm^{-1} is because of the C=O stretching. The presence of peaks only between 0 – 7 δ in the ^{1}H-NMR spectrum indicates that the compound doesn't have any acidic group like COOH or OH.

If compound B reacts, the only possibility is that it will add across the double bond giving a product with molecular formula equal to **$C_6H_{10}O_5$**. This molecular formula does not match with the one stated in the problem.



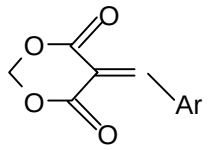
Compound B **Malonic Acid**

f. The increased acidity is due to active $–CH_2$ group of Meldrum's acid flanked by two – CO groups. The carbanion formed at $–CH_2$ will be stabilised by these –CO groups, which are coplanar.



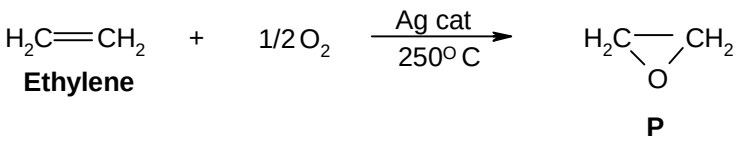
Meldrum's acid ($C_6H_8O_4$)

g. The condensation product of Meldrum's acid with an aromatic aldehyde has the structure

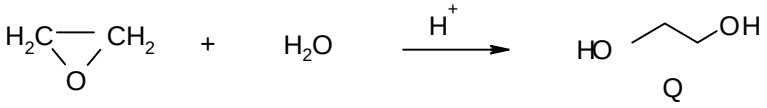


18. Polymer synthesis

a.

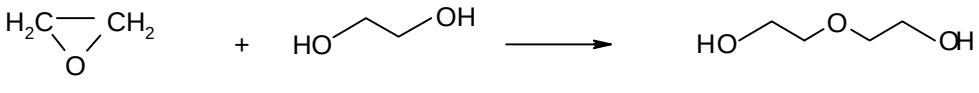


Ethylene **P**

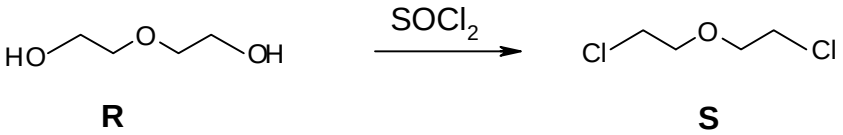


Q

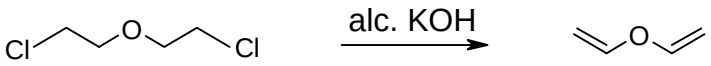
b.



P **Q** **R**

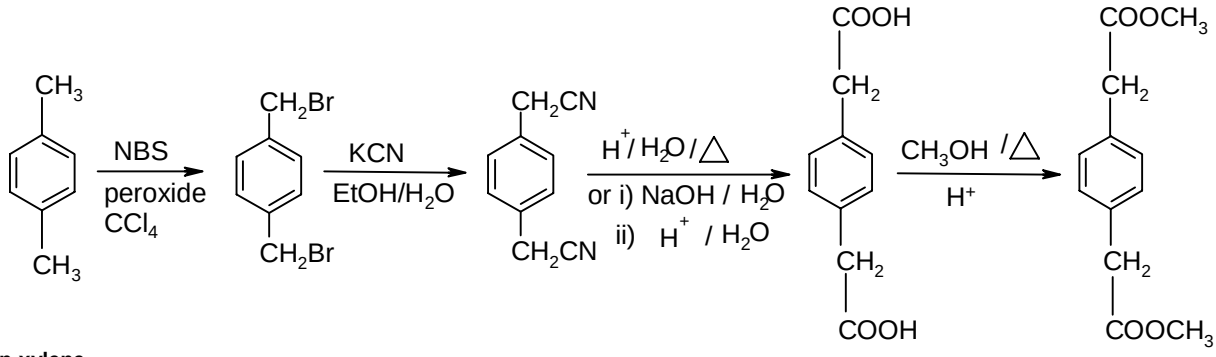


R **S**



S **T**

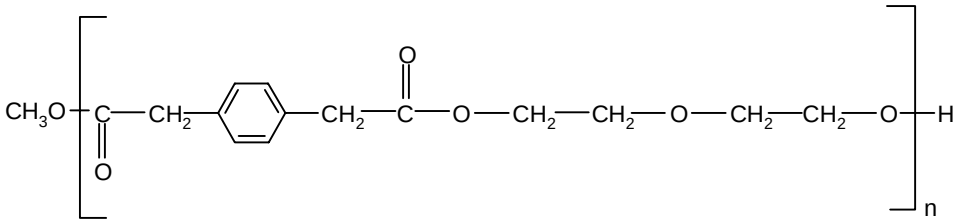
c.



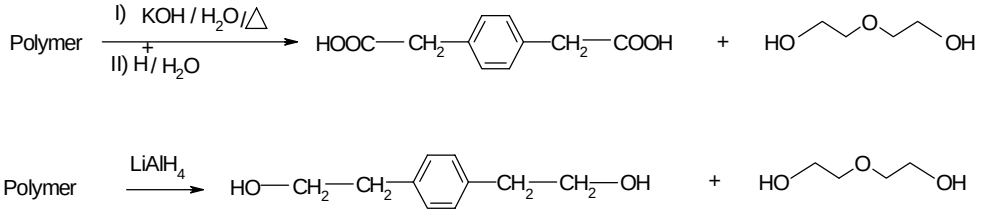
p-xylene **dimethyl benzene-1,4-*bis*(acetate)**

d. Three signals (three singlets for $-CH_3$, $-CH_2$ and aromatic protons)

e. Structure of polymer

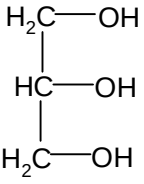


f.

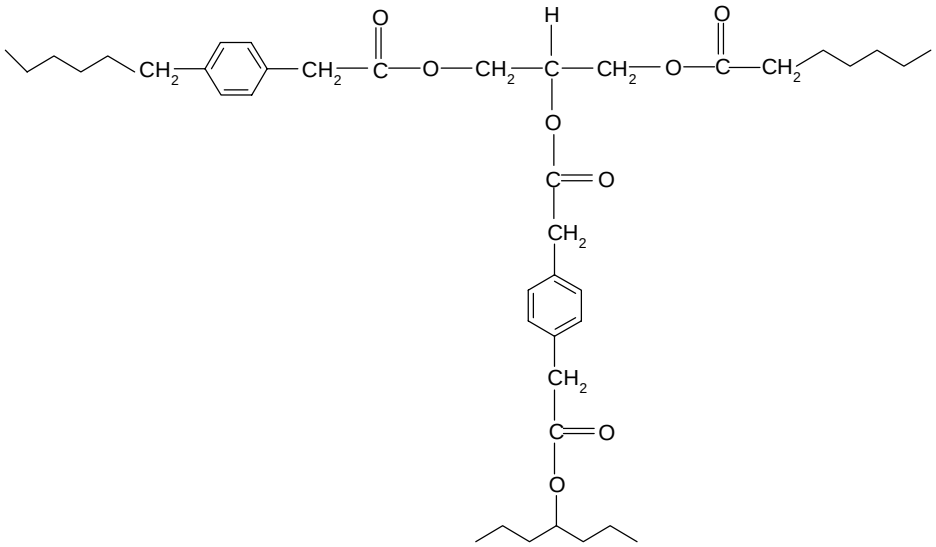


g. With Glycerol (being a triol), cross-links between the polymer chains involving

the secondary hydroxyl group will form giving a three-dimensional network polymer is possible.



Glycerol

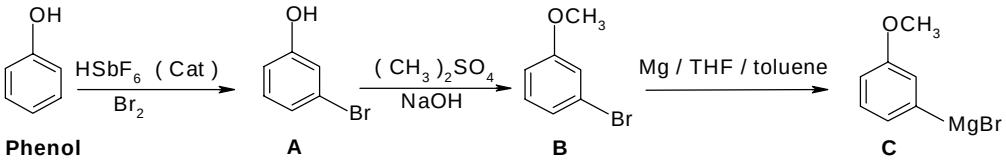


The polymer is unsuitable for drawing fibers because of its cross-linked, resin-like property.

19. Organic synthesis involving regioselection

a. The product obtained in the presence of catalyst $HSbF_6$ is *m*-bromophenol. From the mass spectra given in the problem, direct bromination of phenol gives o/p–bromo derivatives as OH group present in phenol is *o*/*p*- directing.

b.

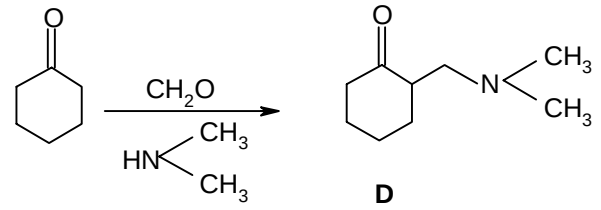


Phenol **A** **B** **C**

Compound **B** may undergo nucleophilic reaction at the carbon bearing bromine. Compound **C** contains a carbanion and hence functions as a

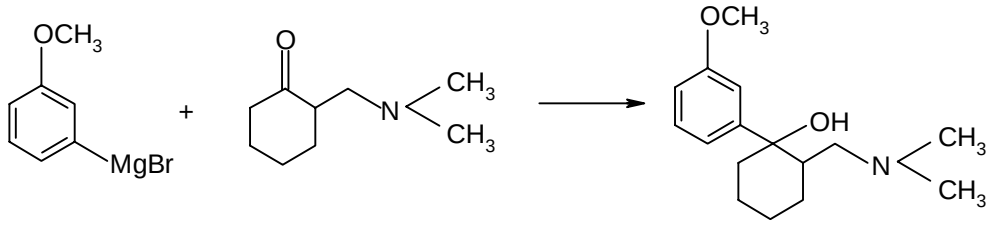
nucleophile and will attack an electrophile. Thus, reactivity of **B** is reversed on its conversion to **C** (umpolung).

c.



D

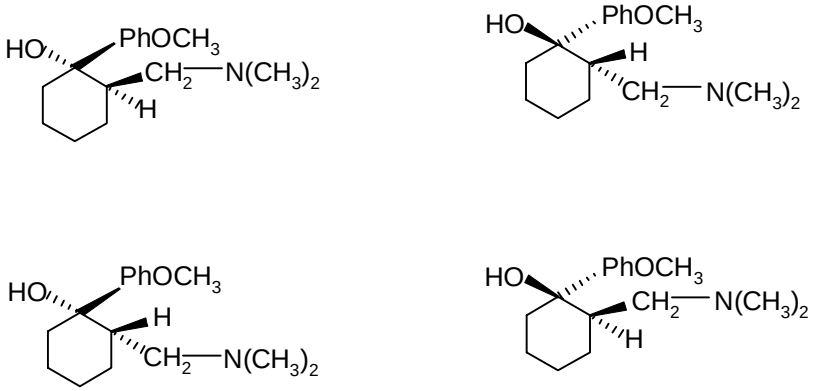
Cyclohexanone



C **D**

Tramadol

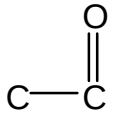
d.



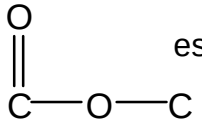
Tramadol has two asymmetric carbon atoms. It has two pairs of enantiomers .

20. Carbon acids

a. The molecular formula of the keto ester is **$C_5H_8O_3$**. Since **X** and **Y** are keto esters, they must have the following units-



keto group



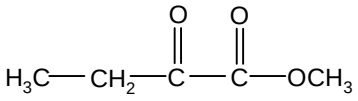
ester group

This accounts for C_4O_3 .The remaining part comprises of CH_8. Thus, only two types of ester groups are possible, methyl or ethyl.

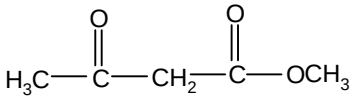
For a methyl ester: **CH_3** will be a part of the ester moiety. This leaves CH_5 to be attached.

For an ethyl ester: **CH_2CH_3** will be a part of the ester group. Therefore H_3 unit needs to be accounted for.

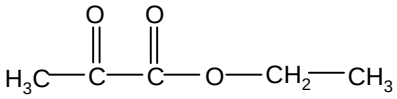
Therefore, possible structures of the keto esters are:



Structure I



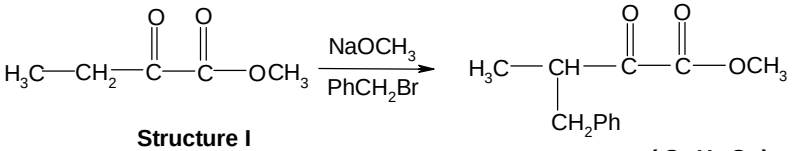
Structure II



Structure III

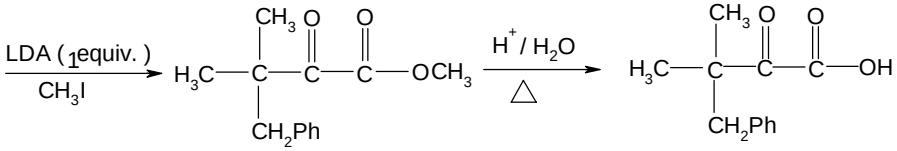
b. Reaction sequence for keto esters

*



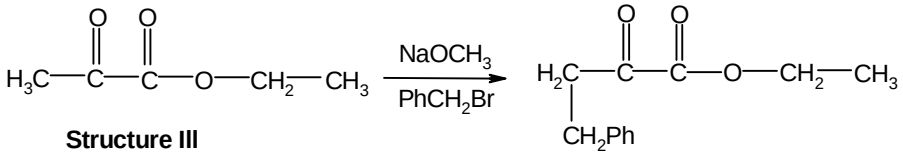
Structure I

Keto acid ($C_{12}H_{14}O_3$)

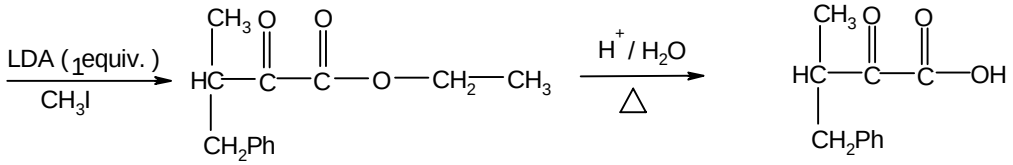


Keto acid ($C_{12}H_{14}O_3$)

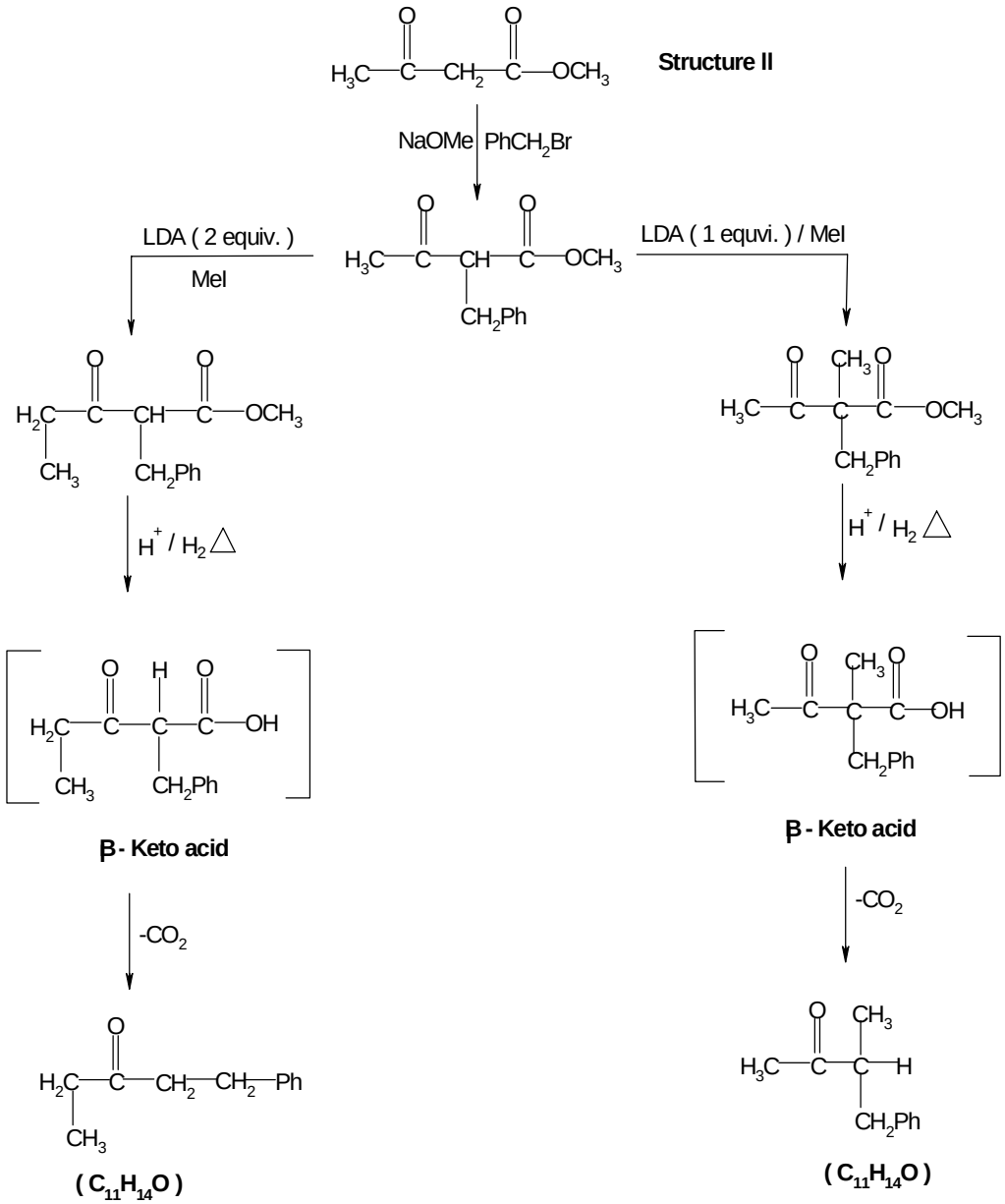
*



Structure III

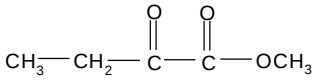


Keto acid ($C_{11}H_{12}O_3$)



- Structure I gives a keto acid with molecular formula **$C_{12}H_{14}O_3$** which matches with the formula of the keto acid obtained from **Y.** ∴ Structure I is **Y**.
- Structure II gives a neutral compound with molecular formula **$C_{11}H_{14}O$** that matches with the molecular formula of the neutral acid stated for **X**. ∴ Structure II is **X**.
- Structure III gives a keto acid with molecular formula **$C_{11}H_{12}O_3$** that also does not match with any given molecular formula.

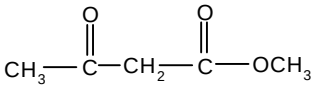
Hence the two keto esters are :



Compound **Y**

(Structure I)

α-keto ester

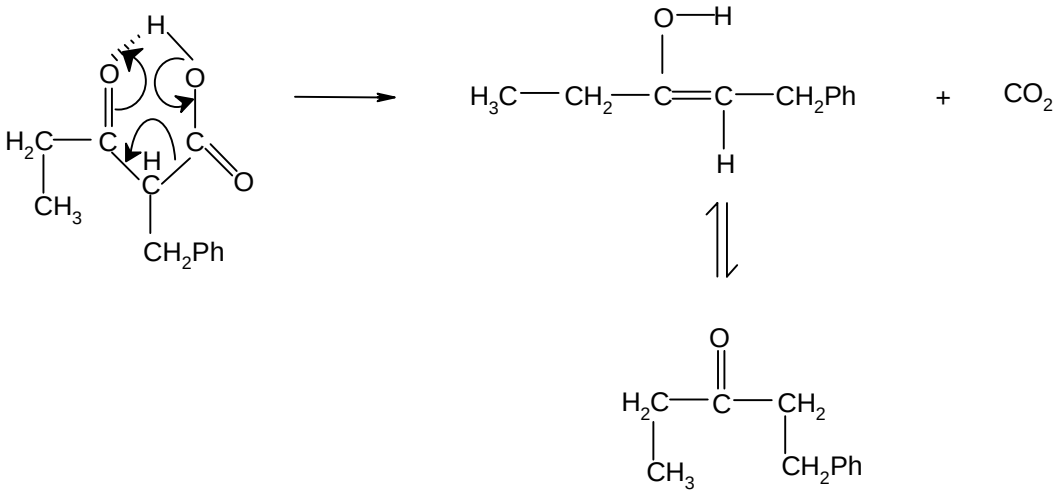


Compound **X**

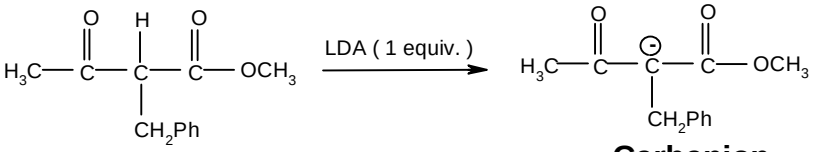
(Structure II)

β-keto ester

c. The β-keto ester gives on hydrolysis a β-keto acid. This acid readily undergoes decarboxylation involving a 6-membered transition state, giving a neutral product (Ketone).

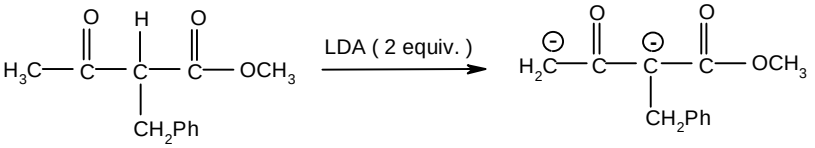


d. **i.** When 1 equivalent of LDA is used compound **X** produces a carbanion (monoanion) as shown below.



Compound X **Carbanion (monoanion)**

ii. Use of 2 equivalents of LDA leads to the formation of a dianion .



Compound X **Dianion**

21. Amino acids and enzymes

a. The protonated amino group has an electron withdrawing effect. This enhances the release of proton from the neighboring –COOH, by stabilizing the conjugate base $–COO^-$. This effect is greater when the $–COO^-$ is physically closer to $–NH_3^+$. As $–NH_3^+$ group is present on the α-carbon, the effect is greater on α-COOH than on the γ-COOH. So the pKa value of α-COOH is lower than that of γ-COOH.

b. The ratio of ionized to unionized γ-COOH group is obtained by using Henderson-Hasselbalch equation,

$$pH = pK_a + \log\frac{[COO^-]}{[COOH]}$$

The pH = 6.3 and pKa of γ-COOH group is 4.3. Substituting these values in the above equation we get,

$$6.3 = 4.3 + \log\frac{[COO^-]}{[COOH]}$$

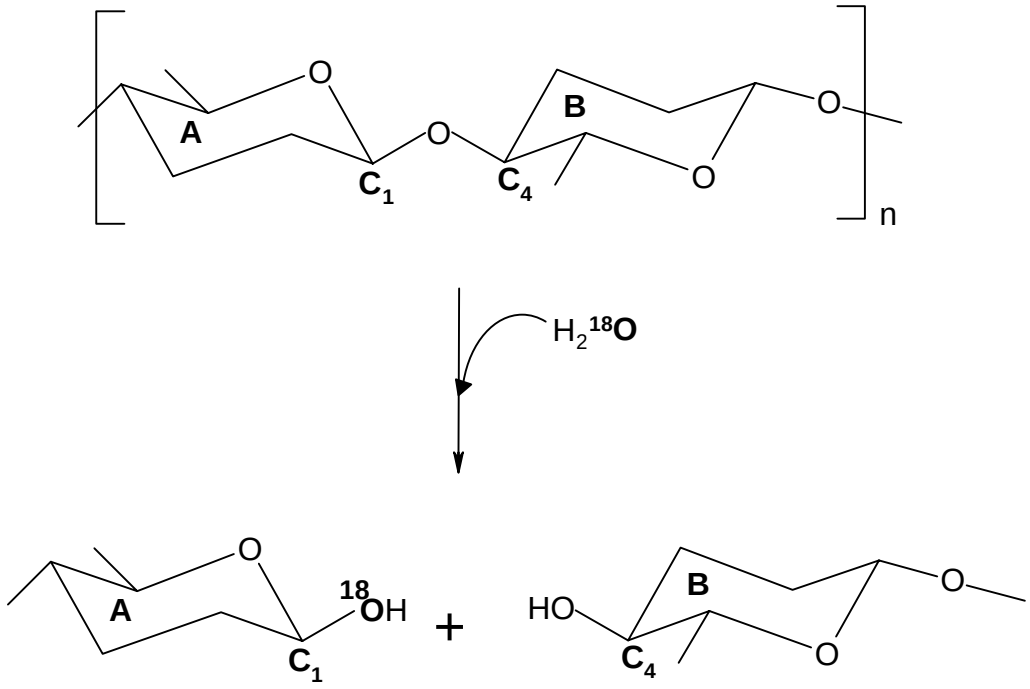
$$\therefore [COOH] = \frac{100}{101} = 0.99\% \text{ at pH } 6.3$$

c. Glutamic acid has two pKa values lower than 7.0 and one pKa value higher than 7.0. Thus, the isoelectric point (pI) for glutamic acid will lie between the two acidic pKa values.

pI = (2.2 + 4.3)/ 2 = 3.25

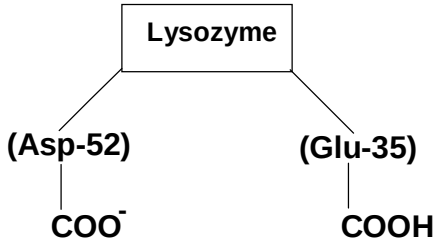
At pH = 3.25, net charge on glutamic acid will be zero since this pH coincides with pI of glutamic acid. Hence, glutamic acid will be stationary at pH 3.25.

d. In the hydrolysis of the glycosidic bond, the glycosidic bridge oxygen goes with C_4 of the sugar **B**. On cleavage, ^{18}O from water will be found on C_1 of sugar **A**.



NOTE: The reaction proceeds with a carbonium ion stabilized on the C_1 of sugar **A**.

e. Most glycosidases contain two carboxylates at the active site that are catalytically important. Lysozyme is active only when one carboxylate is protonated and the other is deprotonated. A descending limb on the alkaline side of the pH profile is due to ionization of -COOH. An ascending limb on the acidic side is due to protonation of -COO^-. Thus the enzyme activity drops sharply on either side of the optimum pH. The ideal state of ionization at pH = 5 will be,



NOTE: It is desirable to study the amino acid side chains (R-groups) and their ionization properties. The pKa values of these groups significantly determine the pH dependence of enzyme activity.

f. Answers 2 and 4 are correct. Ionization of –COOH leads to generation of a negatively charged species, $–COO^-$. This charged species is poorly stabilized by diminished polarity and enhanced negative charge. Hence ionization of –COOH group is suppressed and the pKa is elevated.

g. The ratios of pseudo-first order rate constant (at 1M CH_3COO^-) in (a) to the first order rate constants in (b) and (c) provide the effective local concentrations.

For example, (2) (0.4) / (0.002) = 200

i.e the effective concentration = 200 M

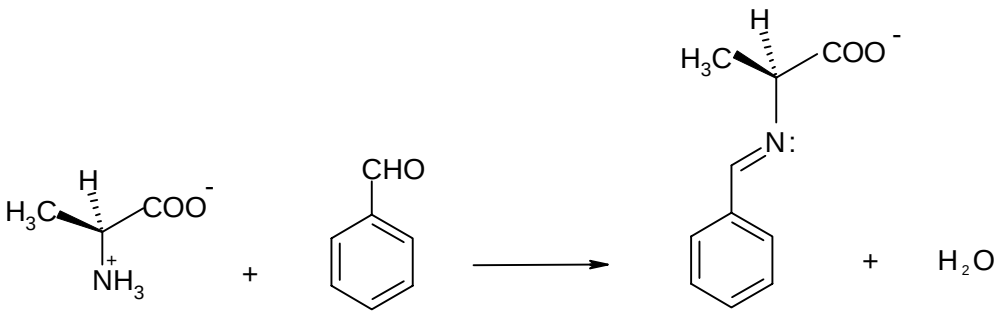
(3) (20) / (0.002) = 10,000

i.e. the effective concentration = 10,000 M

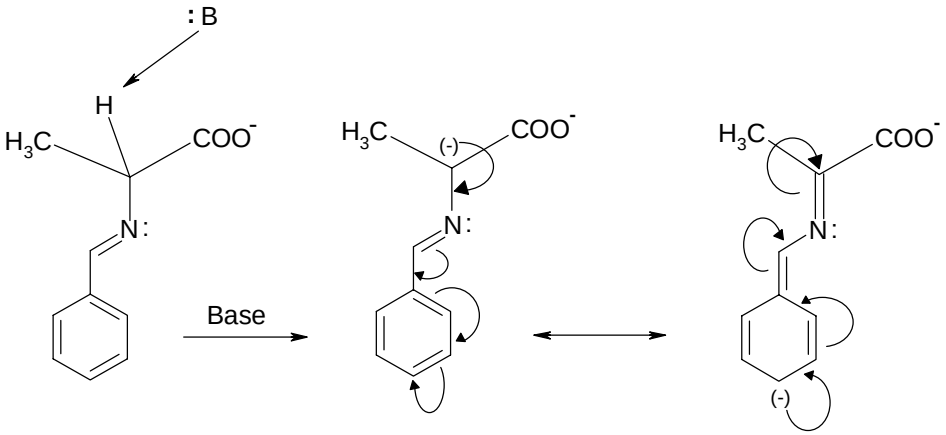
h. In addition to the enhanced local concentration effect, the COO^- group in (3) is better oriented to act in catalysis. The double bond restricts the motion of COO^- and thus reduces the number of unsuitable orientation of $–COO^-$, thereby enhancing the reaction rate.

22. Coenzyme chemistry

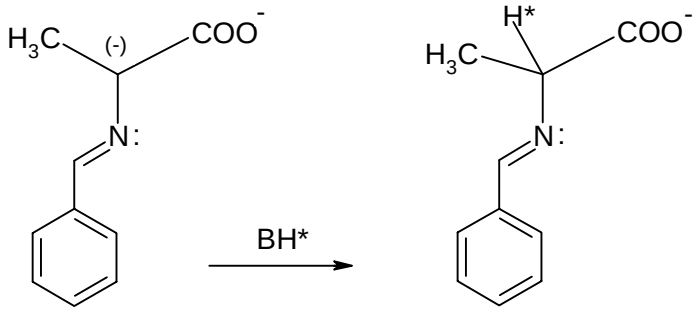
a. Step 1: Schiff base formation



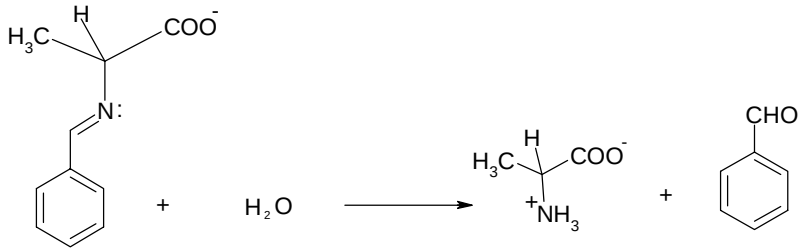
Step 2: Proton abstraction



Step 3: Reprotonation



Step 4: Hydrolysis



b. From the information stated in the problem, the following conclusions can be drawn:

Structure 2: Removal of the phosphate group does not hamper the activity. This indicates that the phosphate is not critical for the activity of PLP.

Similarly,

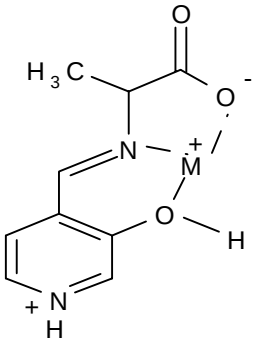
Structure 3: CH_2-OH is not critical.

Structure 4: Phenolic OH is needed in the free form.

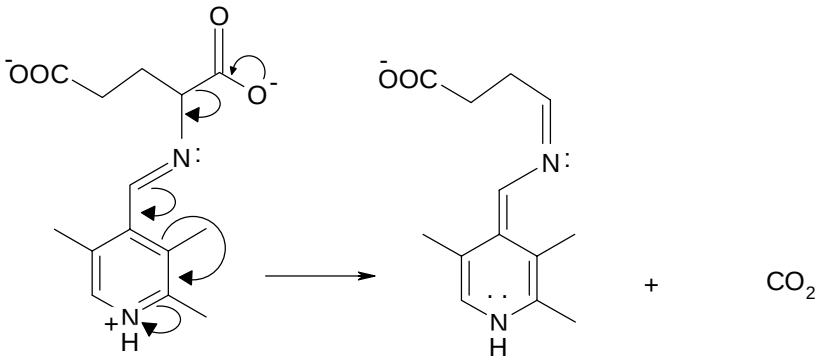
Structure 5: NO_2, a well-known electron withdrawing group, causes benzaldehyde to become activated. Hence positively charged nitrogen in structure 3 must be also important for its electron withdrawing effect.

Structure 6: Electron withdrawing effect of NO_2 is only effective from the *para* position. Introduction of this group at *meta* position leads to an inactive analog.

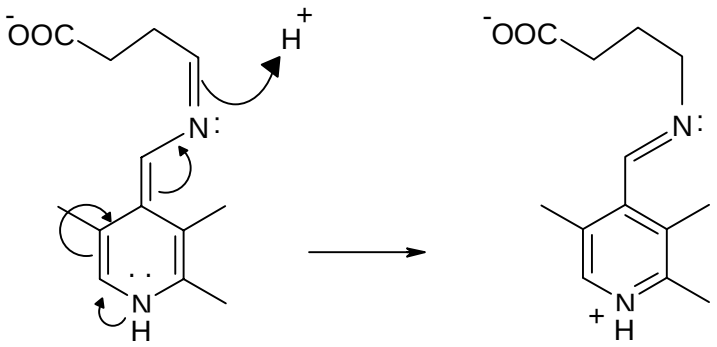
c. **Role of metal ion**: The metal ion is involved in a chelation, as shown below, and provides an explanation for the critical role of the phenolic OH. The planar structure formed due to chelation assists in the electron flow.



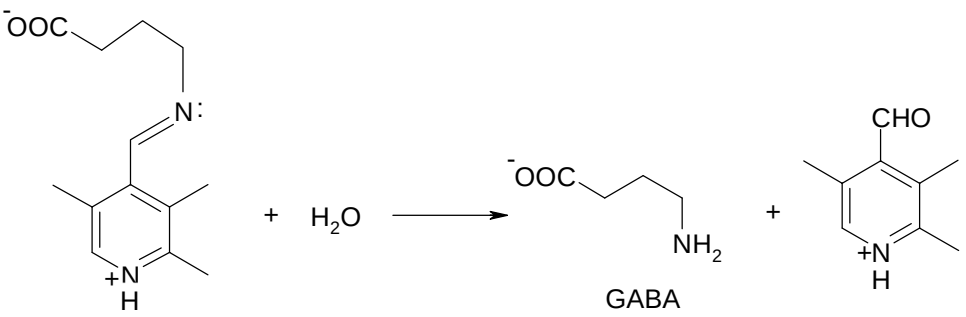
d. Step 1: Schiff base formation and decarboxlyation



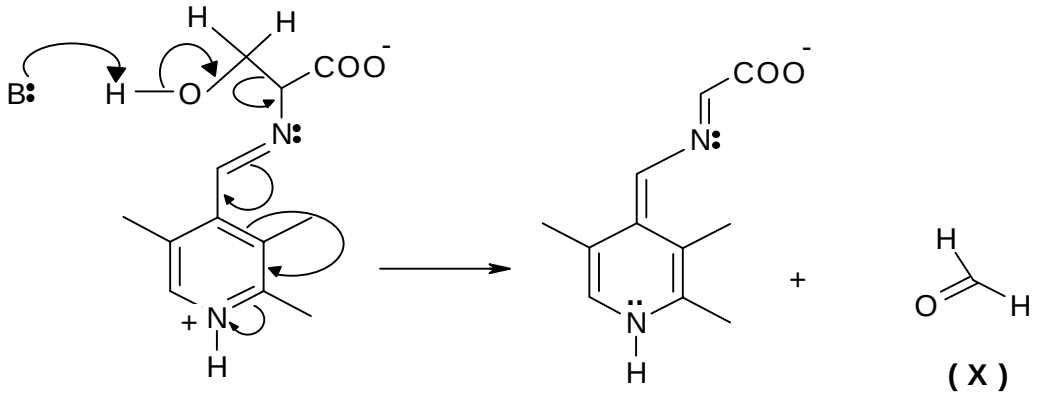
Step 2: Tautomerization



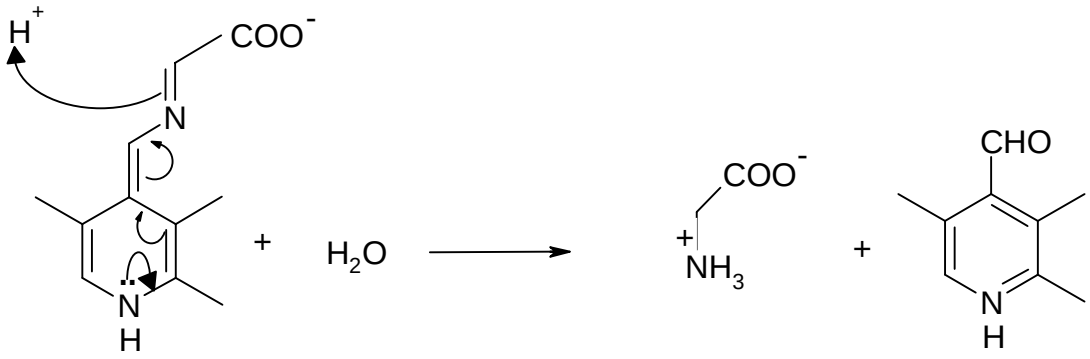
Step 3: Hydrolysis



e. Step 1: Schiff base formation followed by carbon- carbon bond scission.

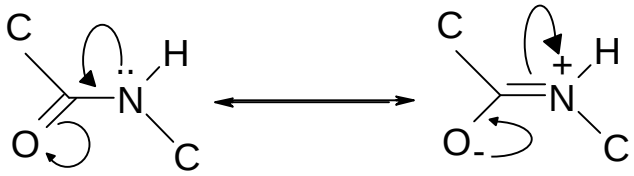


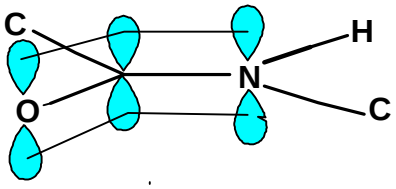
Step 2: Tautomerization followed by hydrolysis



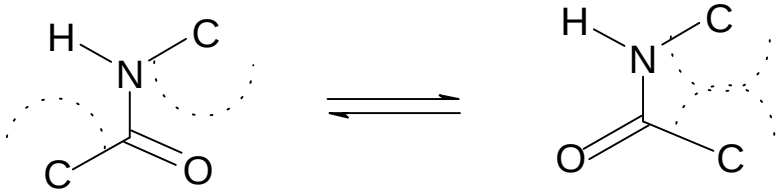
23. Protein folding

a. The planar amide group, that is, C_α, O, H and the next C_α are in a single plane - is stabilized by resonance. The C-N bond of the amide assumes partial double bond character and the overlap between p orbitals of O, C and N is maximized. The C_α's across this partial double bond can assume *cis* or *trans* arrangement.

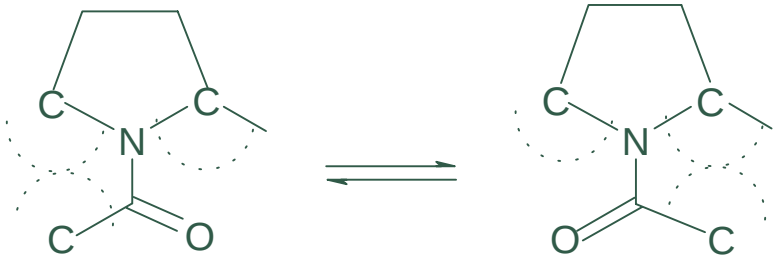




b. With nineteen of the amino acids, the *trans* arrangement is sterically favoured (i. e. it is comparatively less crowded). In the case of <u>proline</u>, *cis* and *trans* arrangements are almost equally crowded.



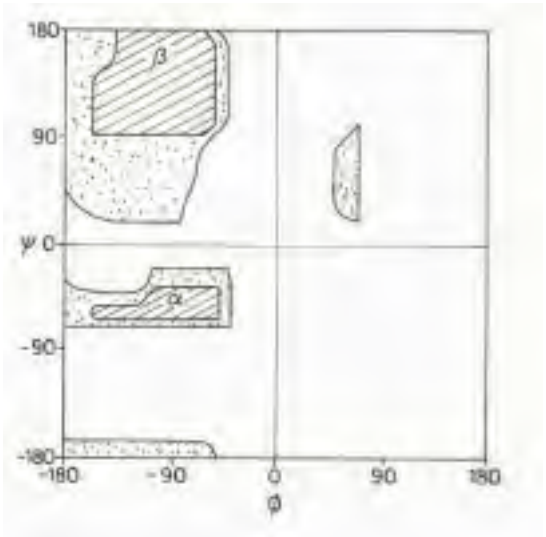
trans – amide *cis* - amide



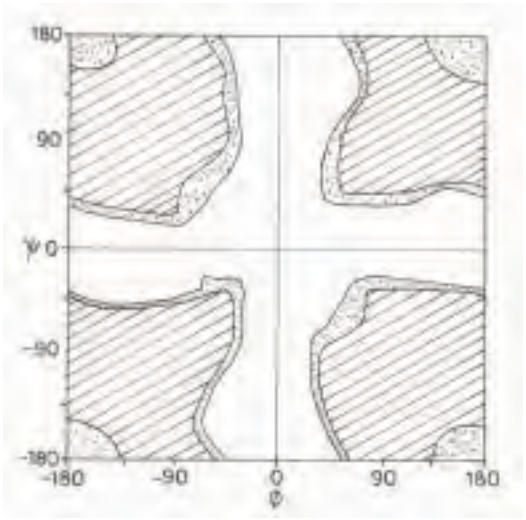
trans – amide *cis* - amide

c. **Note about Ramchandran diagram**: In a polypeptide, the amide units are planar (partial double bond character across the N-C bond) but the bonds connecting N and C_α, and the carbonyl carbon and C_α are free to rotate. These rotational angles are defined as ϕ and ψ, respectively. The conformation of the main chain is completely defined by these angles. Only some combinations of these angles are allowed while others are disallowed due to steric hindrance. The allowed range of ϕ and ψ angles are visualised as a steric contour diagram, shown below, known as the Ramachandran diagram.

For nineteen amino acids, the conformational choice is largely restricted to the so-called α and β regions on left half of the Ramachandran diagram (Panel A). This is due to the L - chiral nature of amino acids and the steric effects of their R groups. Glycine is an achiral residue with H as the R group. Therefore, much larger conformational regions on both left and right halves of Ramachandran diagram are accessible to this residue (Panel B).

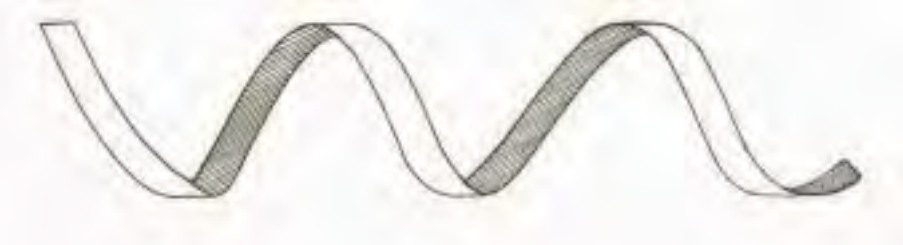


Panel A



Panel B

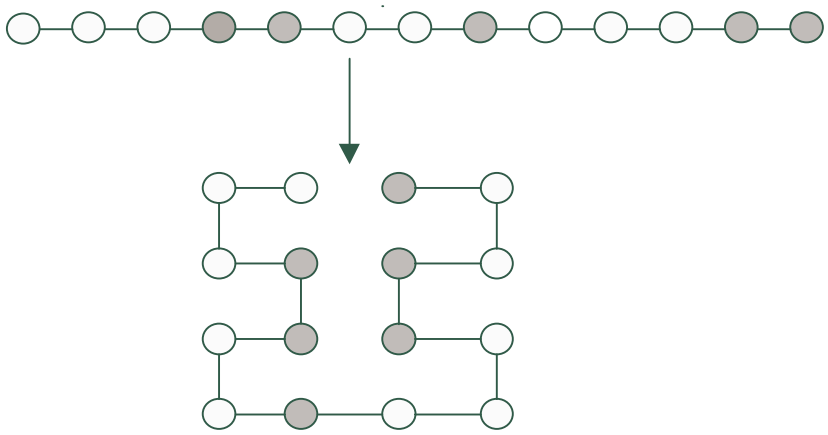
d. Consecutive residues in α conformation form the α-helix. Similarly, consecutive residues in β conformation form the β-sheet. Both α-helix and β-sheet structures feature extensive networks of hydrogen bonds which stabilise them. Thus random combinations of α and β conformations are rarely found.



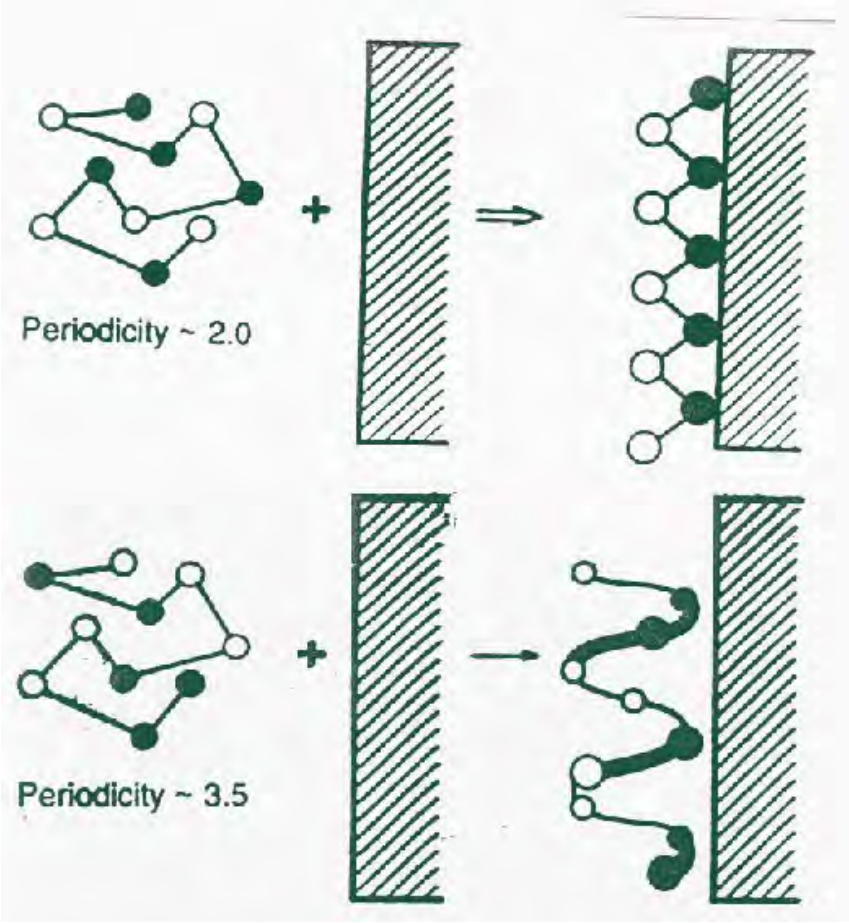
α - helix

β - sheet

e. For a polypeptide to fold in an aqueous environment, nearly half the R groups should be nonpolar (water hating) and the other half polar (water loving). Upon folding to form a globular protein, the nonpolar R groups are packed inside (away from water) while the polar groups are positioned on the surface (in contact with water). The phenomenon is similar to the hydrophobic aggregation of a micellar structure in water. If all the R groups are either polar or non-polar, no hydrophobic segregation is possible, and no folding will occur.



f. Alternating polar/nonpolar periodicity of R groups favors β-sheets. All the non-polar groups will face the apolar surface while the polar groups will be exposed to water. So the net folding will be like a β-sheet. On the other hand, a complex periodic pattern of R group polarities is needed in forming the α-helix.



Hydrophobic periodicity (primary sequence) + **Apolar surface (interface)** ⇒ **Induced (secondary structure)**

24. Protein sequencing

The sequence of amino acids in a protein or polypeptide is expressed starting from the N-terminal amino acid. From Edman degradation method the N-terminal amino acid is Asp. In the N-terminal fragment generated by trypsin or CNBr this amino acid should, therefore, be in position1. All other peptides generated by CNBr cleavage will

be preceded by Met on their N-terminal side. Likewise, all peptides generated by trypsin should be preceded by Arg or Lys. As we proceed from N-terminal amino acid to C-terminal amino acid, we carefully examine the different amino acids in each position shown in Table1(a) and 1(b)

For the first fragment starting from N-terminal Asp in position 1, we look for residues common in each position to CNBr and trypsin cleaved peptides. This gives

Position 1 2 3 4 5 6

Residue Asp -Pro/Tyr - Tyr -Val -Ile/Leu -Arg .....(1)

At position 6 Arg will render the polypeptide susceptible to trypsin. Therefore, 7th residue of this CNBr fragment (Table1a) should be same as residue1 in another peptide generated by trypsin and 8th residue of this CNBr fragment will be same as residue 2 in Table 1(b). Therefore we get

7 8

Gly/Phe - Tyr .....(2)

Since 8 will be Tyr, Pro will be assigned to position 2 of the polypeptide .....(3)

Residue 9 in the polypeptide should be at position 3 in the Table1(b) and residues 10,11,12,13 and 14 should be at positions 4,5,6,7 and 8 respectively in Table1(b). The same residues should be in positions 1 onwards in Table1(a).

None of the residues in position 3 (Table1b) is same as in position 1 in Table 1(a). However, positions 4 to 8 in Table 1(b) have residues common with positions 1 to 5 in Table 1(a). Further Glu in position 1 (Table 1a) will be preceded by Met (since it is a part of CNBr cleaved peptide). And position 3 in Table 1(b) has Met. Therefore, we get

9 10 11 12 13 14

Met- Glu - Thr - Ser - Ilu - Leu .....(4)

Position 5 in the polypeptide can now be firmly assigned to Ilu .....(5)

Positions 15 and 16 in the polypeptide will be beyond residue 8 in the trypsin cleaved peptide (not shown here). We now attempt to construct the remaining trypsin or CNBr fragments.

Table 1 (a) shows Arg in position 1. This will be preceded by a Met. Matching of the unassigned residues in position 2 in Table 1(a) with those in position 1 in Table 1(b) and for subsequent positions by the procedure demonstrated earlier that will give.

Met - Arg - Tyr - Pro - His - Asn - Trp - Phe - Lys - Gly - Cys .....(6)

(The last two residues are the unassigned residues in position 1 and 2 in Table 1b) Considering (2), (5) and (6) together it is now possible to firmly assign position 7 on the polypeptide to Gly .....(7)

a. The amino acid sequence common to the first fragments (N-terminal) obtained by CNBr and trypsin treatments is

1 2 3 4 5

Asp - Pro - Tyr - Val - Ile

b. The sequence of the first fragment generated by CNBr treatment is

1 2 3 4 5 6 7 8

Asp- Pro - Tyr- Val- Ile -Arg -Gly -Tyr

To complete the sequence of the polypeptide we need to construct the sequence of another trypsin fragment. Starting from position 4-(Arg) in Table 1(a) we get the sequence,

Arg-Phe-His-Thr-Ala ..... (8)

At this stage, we again examine the unassigned residues. The Arg in (8) will have to be serially preceded by Asn, Gln, Gly and Met (these are the unassigned residues in respective positions in Table 1(a). We then get the sequence,

Met-Gly-Gln-Asn-Arg-Phe-His-Thr-Ala .....(9)

And following the Ala in (9)

Leu-Ser-Cys-Glu … ..(10)

From (9) and (10), we get the sequence

Met-Gly-Gln-Asn-Arg-Phe-His-Thr-Ala-Leu-Ser-Cys-Glu …..(11)

Since the smallest fragment is a dipeptide (Table 1b) and (6) shows that it follows Lys, it follows that this will be at the C-terminal end. Therefore, the partial sequence shown in (6) will follow the partial sequence shown in (11).Thus, we get

Met-Gly-Gln-Asn-Arg-Phe-His-Thr-Ala-Leu-Ser-Cys-Glu-Met-Arg-Tyr-Pro-His-Asn-Trp-Phe-Lys-Gly-Cys …..(12)

There is already a Met in position 9 of the polypeptide. The next Met can only come earliest at position 17 since CNBr fragment have at least 8 amino acids. Therefore, the starting residues of (12) can be assigned position 17.

This leaves positions 15 and 16 which will be filled by the unassigned residues Val and Ala in the CNBr fragment at positions 6 and 7 (Table 1a).

c. The final sequence, therefore, will be

						Trypsin							**CNBr**									
1	2	3	4	5	6	↓	7	8	9	↓	10	11										
Asp	-	Pro	-	Tyr	-	Val	-	Ile	-	Arg	-	Gly	-	Tyr	-	Met	-	Glu	-	Thr		
										CNBr										**Trypsin**		
12	13	14	15	16	17	↓	18	19	20	21	↓	22										
Ser	-	Ile	-	Leu	-	Val	-	Ala	-	Met	-	Gly	-	Gln	-	Asn	-	Arg	-	Phe		
													CNBr	**Trypsin**								
23	24	25	26	27	28	29	30	↓	31	↓	32	33										
His	-	Thr	-	Ala	-	Leu	-	Ser	-	Cys	-	Glu	-	Met	-	Arg	-	Tyr	-	Pro		
									Trypsin													
34	35	36	37	38	↓	39	40															
His	-	Asn	-	Trp	-	Phe	-	Lys	-	Gly	-	Cys										

Arrows (↓) indicate the CNBr and trypsin-labile sites.

d. There are 6 basic amino acid residues in the polypeptide. 6/40 = 15%

e. An α helix has 3.6 amino acid residues per turn of 5.4Å.

Thus, the length of the polypeptide in α helical conformation will be :

$40/3.6 \times 5.4 = 59.4$ Å.

e. The polypeptide has 40 amino acids. Since each amino acid is coded for by a triplet of nucleotides, the total number of nucleotide pairs in the double stranded DNA of the exon will be

40 x 3 = 120 base pairs.

The molecular weight of the DNA making the exon

= 330 x 2 x 120

= 79200 Da

g. If the exon contains 120 base pairs and A and C are in equal numbers, there will be 60 A-T pairs and 60 G-C pairs. Each A-T pair is held by two H-bonds and each G-C pair is held by three H-bonds. Hence the total number of H-bonds holding this double helix is :

(60 x 2) + (60 x 3) = 300