

Problem 1: Proton – antiproton atom

We can use the expression for hydrogen-like atoms to calculate the energy levels.

$$E_n = -\frac{2\pi Z^2 e^4 \mu}{(4\pi\epsilon_0)^2 h^2 n^2}$$

where Z is the total number of charges in the nucleus ($= 1$), e is

the electron charge ($= 1.6022 \times 10^{-19}$ C), μ is the reduced mass of the system with $\mu = (m_1^{-1} + m_2^{-1})^{-1}$ and $m_1 = m_2 = m_p = 1.6726 \times 10^{-27}$ kg, thus $\mu = \frac{1}{2} m_p$, ϵ_0 is the permittivity of vacuum ($= 8.8542 \times 10^{-12}$ C² J⁻¹ m⁻¹) [note: $(4\pi\epsilon_0)^{-1}$ is Coulomb's constant], h is the Planck constant ($= 6.626076 \times 10^{-34}$ J s) and n is the principal quantum number of the system taking values 1, 2, ...

For $n = 1$, $E_1 = -m_p \left(\frac{e^2}{4h\epsilon_0} \right)^2 = -2.00129 \times 10^{-15}$ J and for $n = 2$, $E_2 = \frac{E_1}{4}$, hence

$$\Delta E \equiv E_2 - E_1 = \frac{3}{4} E_1 = 1.50097 \times 10^{-15} \text{ J}$$

$$\Delta E = h\nu, \text{ hence } \nu = \frac{\Delta E}{h} = \frac{1.50097 \times 10^{-15} \text{ J}}{6.626076 \times 10^{-34} \text{ J s}} = 2.2652 \text{ s}^{-1}.$$

$$c = \lambda\nu, \text{ hence } \lambda = c/\nu = \lambda = \frac{c}{\nu} = \frac{2.997925 \times 10^8 \text{ m s}^{-1}}{2.2652 \text{ s}^{-1}} = 1.3234 \times 10^{-10} \text{ m} = 1.3234 \text{ \AA}.$$

The Bohr radius is given by

$$\alpha = \frac{h^2(4\pi\epsilon_0)}{4\pi^2\mu e^2} = \frac{2h^2\epsilon_0}{\pi m_p e^2} = 5.76397 \times 10^{-14} \text{ m}$$

which is 1836/2 times smaller than the

hydrogen radius due to the difference in reduced mass of the "atom".

Problem 2: Annulene

The number of π electrons is 18. Two electrons can occupy each state due to the Pauli exclusion principle. Each state above the lowest is two-fold degenerate. Based on these pieces of information, we can fill this table:

N	max number of e ⁻ per state	total e ⁻ up to this state
0	2	2
1	4	6
2	4	10
3	4	14
4	4	18

States up to $N = 4$ are fully occupied with 18 electrons. The lowest possible transition is from state $N = 4$ to state $N = 5$. The path forming a circular well is $L = 18 \times 1.4 \text{ \AA}$. Hence

$$\Delta E = E_5 - E_4 = (5^2 - 4^2) \frac{(6.6260755 \times 10^{-34} \text{ J s})^2}{2 \times (18 \times 1.4 \text{ \AA})^2 \times 9.109389 \times 10^{-31} \text{ kg}} = 3.415 \times 10^{-19} \text{ J}$$

The transition frequency is $\nu = \Delta E/h = 5.1544 \times 10^{14} \text{ s}^{-1}$ and the corresponding wavelength is $\lambda = c/\nu = 581.6 \text{ nm}$.

Problem 3: Chemical bonding: The molecular ion O₂²⁺

- 171.9 kcal/mol
- No

3. Yes

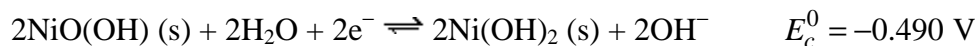
4. 85.6 kcal/mol

5. $(171.9 - 85.6)$ kcal/mol = 86.3 kcal/mol or $(86.3/N_A)$ kcal/molecule = 1.43×10^{-23} kcal/molecule.

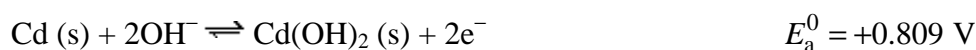
6. $\sim 1.1 \text{ \AA}$

7. $\sim 1.6 \text{ \AA}$

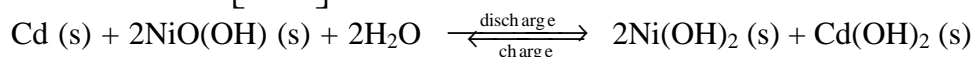
Problem 4: Electrochemistry: Nicad batteries



$$E_c = E_c^0 - \frac{RT}{2F} \ln [\text{OH}^-]^2$$



$$E_a = E_a^0 - \frac{RT}{2F} \ln \frac{1}{[\text{OH}^-]^2}$$



$$E = E_a - E_c = E_a^0 - E_c^0 = 0.809 \text{ V} - (-0.490 \text{ V}) = 1.299 \text{ V}.$$

$$700 \text{ mAh} = 0.700 \text{ A} \times 3600 \text{ s} = 2520.0 \text{ C}$$

$$2520.0 \text{ C} \rightarrow \frac{2520.0}{2 \cdot 96485} \text{ moles of Cd} = 0.013 \text{ moles of Cd} \rightarrow 0.013 \times 112.4 = 1.47 \text{ g of Cd.}$$

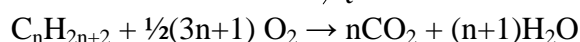
Problem 5: Boiler

$$\text{Tank capacity: } m = V \rho = 4 \text{ m}^3 \times 0.73 \text{ g cm}^{-3} = 2920 \text{ kg}$$

$$\text{Heating power } P = 116 \text{ kW}$$

$$\text{Consumption rate } \frac{m}{t} = \frac{P}{\Delta h / m} = \frac{116 \text{ kJ s}^{-1}}{4.3 \times 10^7 \text{ J kg}^{-1}} = 2.70 \times 10^{-3} \text{ kg s}^{-1} (= 9.73 \text{ kg h}^{-1})$$

$$\text{Operation duration } t = \frac{m}{m/t} = \frac{2920 \text{ kg}}{2.70 \times 10^{-3} \text{ kg s}^{-1}} = 1.08 \times 10^8 \text{ s} = 300 \text{ h} = 12.5 \text{ days}$$



$$\frac{m_{\text{CO}_2}}{m_{\text{C}_n\text{H}_{2n+2}}} = \frac{44n}{14n+2} = \frac{22}{7 + \frac{1}{n}} \quad \text{This ratio does not depend heavily on } n; \text{ for a}$$

representative value of $n = 10$, the ratio takes the value of 3.1.

$$\text{Since } \frac{m_{\text{C}_n\text{H}_{2n+2}}}{t} = 9.73 \text{ kg h}^{-1},$$

$$m_{\text{CO}_2} = \frac{m_{\text{C}_n\text{H}_{2n+2}}}{t} \frac{m_{\text{CO}_2}}{m_{\text{C}_n\text{H}_{2n+2}}} = 9.73 \text{ kg h}^{-1} \times 3.1 = 30.2 \text{ kg h}^{-1}$$

Problem 6: Ammonium nitrate

Mixing is endothermic and the process is adiabatic, thus heat has to be provided by the solution itself. Since water is at its freezing point, it will tend to freeze, but the solution created will experience a depression of freezing point due to the presence of

dissolved ions. The large amount of heat required for solvation will necessitate some freezing of water.

A Hess cycle of 3 steps will be considered.

A. mixing at 0 °C with $\Delta H_1 > 0$

B. lowering of the temperature of the mixture to its final temperature with $\Delta H_2 < 0$

C. freezing of some water m_s with $\Delta H_3 < 0$

The final temperature is given by $\theta_2 = -K_f 2 \frac{n}{m - m_s}$ where K_f is the cryoscopy

constant, 2 is the number of particles per formula weight for NH_4NO_3 , n the number

of moles of NH_4NO_3 $n = \frac{80 \text{ g}}{80 \text{ g mol}^{-1}} = 1 \text{ mol}$, $m = 1000 \text{ g}$.

$$\Delta H_1 = \Delta h_s n = -25.69 \text{ kJ mol}^{-1} \times 1 \text{ mol} = -25.69 \text{ kJ}$$

$\Delta H_2 = c_p \frac{m}{M} \theta_2$ where c_p is the molar heat capacity of water and M its molecular mass (18 g mol^{-1}).

$\Delta H_3 = -\Delta h_f \frac{m_s}{M}$ where Δh_f is the molar enthalpy of fusion.

$\Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H_{\text{total}} = 0$ because no heat is allowed to be exchanged between the system and its surroundings.

Substituting for θ_2 and solving for m_s yields the following expression

$$m_s = \frac{m}{2} + \frac{\Delta h_s}{\Delta h_f} \frac{nM}{2} \pm \sqrt{\left(\frac{m}{2} - \frac{\Delta h_s}{\Delta h_f} \frac{nM}{2} \right)^2 + \frac{2nK_f c_p m}{\Delta h_f}}$$

We discount the solution derived from the + sign as unphysical ($m_s > m$) and arrive at the result $m_s = 28.52 \text{ g ice}$.

Hence $\theta_2 = -3.83 \text{ }^\circ\text{C}$.

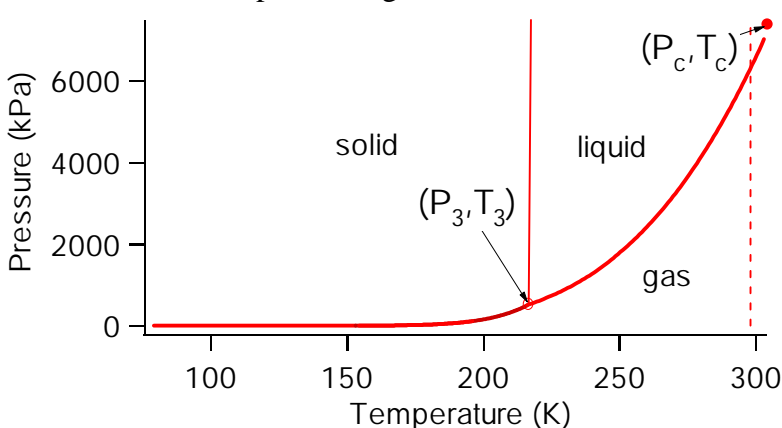
If we made the simplification that we expect $m_s \ll m$, then θ_2 is immediately calculated as $-3.72 \text{ }^\circ\text{C}$, which yields a value for $m_s = 29.9 \text{ g}$. If this result is used to improve the θ_2 value using the exact expression, we get $\theta_2 = -3.83 \text{ }^\circ\text{C}$. Then, m_s can be further improved to 28.5 g .

The process is spontaneous, irreversible, one where separation of components is possible, adiabatic, isobaric, isenthalpic, nearly isoenergetic.

The equation $\Delta G = \Delta H - T \Delta S$ can be used here because T varies less than 2%. $\Delta G < 0$ because the process is spontaneous and $\Delta H = 0$, hence $\Delta S > 0$. This is also to be expected from stability criteria under the constraint $\Delta H = 0$.

Problem 7: Carbon dioxide

A rather accurate phase diagram for CO_2 is shown here using data from Landolt-



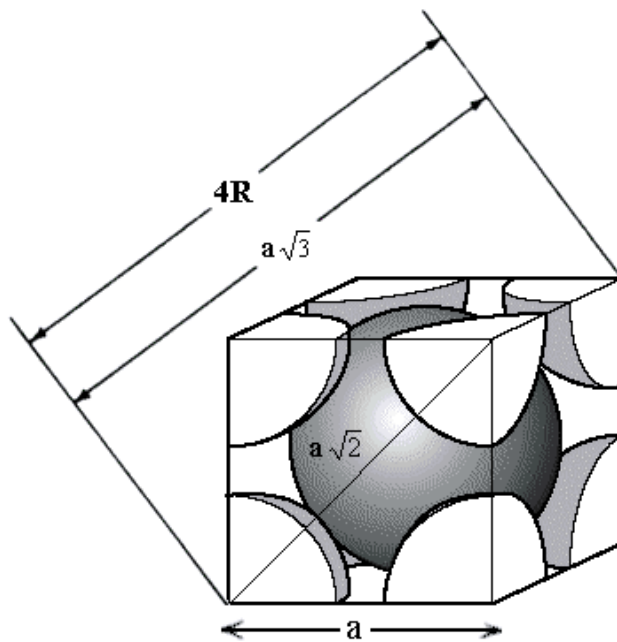
Börnstein New Series IV/20B, p. 22 which has been based on Dykyi, J. Repas, M.: Saturated Vapor Pressure of Organic Compounds, Bratislava, Czech.: Slovakian Academy of Science, 1979.

A qualitative one can be drawn based on the triple and the critical points. Since the room temperature is well above the triple point, there is no way there can be any solid CO₂ in the fire extinguisher. At 298 K, the CO₂ vapor pressure is 63.1 bar. This value can be estimated by drawing a straight line between the triple and the critical points. It can be calculated also based on the empirical Antoine equation, viz.,

$$\log \frac{P}{\text{kPa}} = A - \frac{B}{C + T/\text{K}} \text{ with } A = 6.46212, B = 748.28 \text{ and } C = -16.9.$$

Problem 8: Iron crystal

(a) Let **R** be the atomic radius of iron and **a** = 2.87 Å the length of the unit cell edge.



Then, as atoms touch each other along the body diagonal and from a Pythagorean theorem in the cube:

$$a\sqrt{3} = 4R \Rightarrow R = (a\sqrt{3})/4 \Rightarrow R = 1.24 \text{ \AA}$$

The Avogadro number (**N_A**) can be calculated from the density (**ρ**) formula. The latter is obtained by finding the number of atoms per unit cell, multiplying this number by the mass of each atom ($\frac{\text{mole of atoms (g/mol)}}{N_A \text{ (atoms/mol)}}$) and,

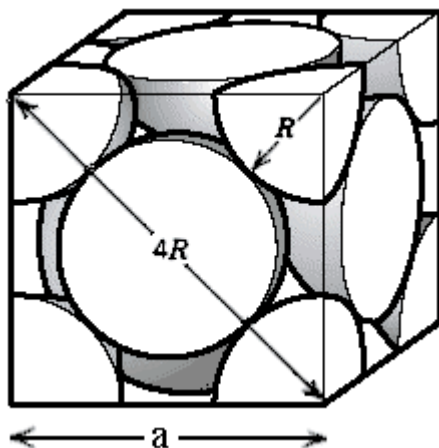
eventually, dividing the result by the volume of the unit cell (**a³**). Note that each bcc unit

cell contains two whole spheres, that is 2 Fe atoms.

$$\rho(\text{g/cm}^3) = \frac{2 \times (55.847 / N_A) \text{ g}}{a^3 (\text{cm}^3)} \Rightarrow$$

$$N_A = \frac{2 \times 55.847 \text{ g}}{7.86 \times (2.87 \times 10^{-8})^3 \frac{\text{g}}{\text{cm}^3} \text{ cm}^3} \Rightarrow N_A \approx 6.01 \times 10^{23}$$

(b) By applying the Pythagorean theorem in the cube, one finds:



$$a^2 + a^2 = (4R)^2 \Rightarrow a = 2R\sqrt{2} \Rightarrow R = \frac{a\sqrt{2}}{4} \Rightarrow R = 1.27 \text{ \AA} \text{ (slightly different from the}$$

value found above for bcc structure, because of the different packing, having an influence on the atomic radius or at least its estimation).

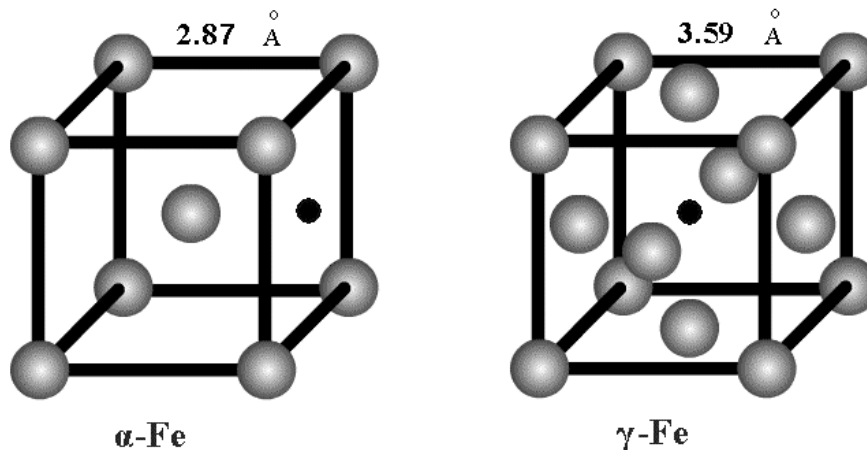
As for the density, recalling that each fcc unit cell contains four whole spheres, that is 4 Fe atoms, once again one has:

$$\rho(\text{g/cm}^3) = \frac{4 \times (55.847 / N_A) \text{ g}}{a^3 (\text{cm}^3)} =$$

$$\frac{4 \times 55.847 \text{ g}}{6.023 \times 10^{23} \times (3.59 \times 10^{-8})^3 \text{ cm}^3} = 8.02 \text{ g/cm}^3$$

The higher value of γ -Fe density, as compared with α -Fe, points at the fact that the fcc structure is denser than bcc. fcc represents the, so called, *cubic close packed* structure which, together with the *hexagonal close packed*, are the most efficient ways of packing together equal sized spheres in three dimensions.

(c) and (d) The unit cells below are illustrated by using reduced size spheres. Note that, in hard spheres packing model the represented atoms must be in contact one to each other.



According to the left figure, a perfectly fitted interstitial atom centered at $(\frac{1}{2}, 0, \frac{1}{2})$ in an α -Fe cell, would have a radius of:

$$R_{\text{interstitial}} = \frac{1}{2} a - R_{\text{Fe}}, \text{ where } a = 2.87 \text{ \AA} \text{ and } R_{\text{Fe}} = 1.24 \text{ \AA} \quad [(\text{see question (a)})].$$

Therefore: $R_{\text{interstitial}} (\alpha\text{-Fe}) \approx 0.20 \text{ \AA}$

Similarly, according to the figure in right, a perfectly fitted interstitial atom centered at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ in an γ -Fe cell, would have a radius of:

$$R_{\text{interstitial}} = \frac{1}{2} a - R_{\text{Fe}}, \text{ where } a = 3.59 \text{ \AA} \text{ and } R_{\text{Fe}} = 1.27 \text{ \AA} \quad [(\text{see question (b)})].$$

Therefore: $R_{\text{interstitial}} (\gamma\text{-Fe}) \approx 0.53 \text{ \AA}$

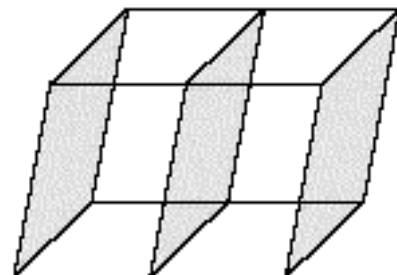
(e) $1 \text{ nm} = 10 \text{ \AA}$. Thus:

$$\text{For } \alpha\text{-Fe: } \frac{R_{\text{carbon}}}{R_{\text{interstitial}}} = \frac{0.77 \text{ \AA}}{0.20 \text{ \AA}} = 3.85$$

$$\text{For } \gamma\text{-Fe: } \frac{R_{\text{carbon}}}{R_{\text{interstitial}}} = \frac{0.77 \text{ \AA}}{0.53 \text{ \AA}} = 1.45$$

Therefore, the carbon atom is roughly four times too large to fit next to the nearest iron atoms in α -Fe without strain, while it is only 1.5 times oversized to fit in the γ -Fe structure. The above estimations explain well the low solubility of carbon in α -Fe ($< 0.1 \%$).

(f) The wavelength (λ) of the X-rays will be calculated from Bragg's law, assuming first order diffraction: $2d \sin\theta = \lambda$, where θ is the angle of diffraction equal to 32.6° and d is the interplanar spacing of the (200) set of parallel lattice planes, that is, the perpendicular distance between any pair of adjacent planes in the set. The (200) planes are shown



shaded in the figure.

Let a be the length of the cubic unit cell edge. Then, from previous data for α -Fe: $a = 2.87 \text{ \AA}$, so the distance between adjacent (200) planes is: $d = \frac{a}{2} = 1.44 \text{ \AA}$ Therefore,

from Bragg's law: $\lambda = 2d \sin\theta = 2 \times 1.44 \times \sin(32.6^\circ) \Rightarrow \lambda \approx 1.55 \text{ \AA}$

This value corresponds to the $K_{\alpha 1}$ transition of iron.

Problem 9: Cyclodextrine

a) $V = a \times c \cdot b = a b c \sin(\beta) = 7474 \text{ \AA}^3$, $V_m = 7474 \text{ \AA}^3 / 4 = 1868 \text{ \AA}^3$

b) $FW = 1535.4 \text{ g mol}^{-1}$, $\rho = FW / (V N_A)$, hence $\rho = 1.3646 \text{ g cm}^{-3}$

Problem 10: Infrared spectroscopy

1. The number of vibrational modes is given by $3N-6$ for non-linear and $3N-5$ for linear molecules, where N is the number of atoms in the molecule. Hence

CO: 1, H_2O : 3, C_6H_6 : 30, C_{60} : 174

2. The fact that the molecules have a vibrational infra red absorption implies that the molecules have a permanent dipole moment, hence these diatomic molecules must be heteronuclear.

For a simple harmonic oscillator-type diatomic molecule, the eigen frequency is given

by the equation $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$, where k is the force constant and μ the reduced mass of

the molecule. In the absence of any further information, nothing can be said about the reduce masses or the force constants (though bond strength is not related to k , but more likely to bond dissociation energy). The eigen frequency is equal to the frequency of the absorbed photons because the vibrational energy is given by $E_v = (v+1/2) h \nu$ and the energy for the resonance transition is $\Delta E = E_{v=1} - E_{v=0} = h \nu$.

Problem 11: Radioactivity and chemical reactivity

1. γ -rays are a form of high energy electromagnetic radiation.
2. There are no stable (non-radioactive) isotopes beyond Bi.
3. There are numerous light isotopes that are radioactive.
4. Xe compounds such as XeF_2 are commercially available.
5. Cs is the element with the lowest ionization potential (3.89 eV).

Problem 12: Carbon dating

a) Let N_0 be the $^{14}C/^{12}C$ ratio in living systems and N the same ratio found in a sample coming from a system that died t years ago. Then, the following relation between them is true: $N = N_0 e^{-\lambda t}$, where $\lambda (= \ln 2 / t_{1/2})$ the disintegration constant for ^{14}C . The above equation becomes

$$t = \frac{-\ln \frac{N}{N_0}}{\lambda} = -\frac{t_{1/2}}{\ln 2} \ln \frac{N}{N_0} = -5700y \frac{\ln 0.25}{\ln 2} = 11400y$$

b) The β decay scheme is based on the nuclear reaction $n \rightarrow p + \beta + \bar{\nu}_e$, where p is a proton and $\bar{\nu}_e$ an electron antineutrino. In the case of ^{14}C we have



hence C becomes a (common) ^{14}N atom.

c) If an organic molecule contains ^{14}C , the consequence of its disintegration can be grave for the structure of the molecule, causing great damage to the molecule in

the vicinity of the ^{14}C atom. At least the chemical bond is ruptured since ^{14}N is a chemically different atom than ^{14}C . Free radicals may also be created.

- d) The total carbon inside a human body of 75 Kg is $75 \text{ kg} \times 0.185 = 13.9 \text{ kg}$. The total radioactivity (R) is $R = 0.277 \text{ Bq} / \text{g} \times 13.9 \text{ kg} = 3850 \text{ Bq}$

The amount of ^{14}C present is estimated from the total radioactivity as follow:

$$R \equiv -\frac{dN}{dt} = \lambda N$$

Then

$$N = \frac{A}{\lambda} = A \frac{t_{1/2}}{\ln 2} = 3850 \text{ s}^{-1} \frac{5700 \text{ y}}{0.693} \frac{60 \times 60 \times 24 \times 365.25 \text{ s}}{\text{y}} = 1.00 \times 10^{15} \text{ atoms} = 1.66 \text{ nmol}$$

Problem 13: Uranium

- a) alpha decay: $X(A,Z) \rightarrow X(A-4, Z-2) + {}^4\text{He}^{2+}(2p+2n)$ ($\Delta A = -4, \Delta Z = -2$)

beta decay: $X(A,Z) \rightarrow X(A, Z+1) + \beta + \bar{\nu}_e$ ($\Delta A = 0, \Delta Z = +1$)

Since changes in the mass number (ΔA) are due to the emission of alpha particles only, in each series we have:

$$\text{total alpha particles emitted} = \Delta A_{\text{total}}/4$$

Alpha emission also changes the atomic number (Z) ($\Delta Z = -2$), so the total decrease in Z due to the total alpha particles emitted would be twice their total number. But Z of the final (stable) element of the radioactive series is higher than the expected Z based on alpha emission. This difference in Z is due to the number of beta particle emitted. Thus

$${}^{238}\text{U} \rightarrow {}^{206}\text{Pb}, \alpha = \Delta A/4 = (238-206)/4 = 32/4 = 8, \beta = 2\alpha - \Delta Z = 18 - (92-82) = 6$$

$${}^{235}\text{U} \rightarrow {}^{207}\text{Pb}, \alpha = \Delta A/4 = (235-207)/4 = 28/4 = 7, \beta = 2\alpha - \Delta Z = 14 - (92-82) = 4$$

- b) This occurs when an alpha decay ($\Delta Z = -2$) is followed by two successive beta decays ($\Delta Z = +2$).

- c) For each radioisotope of uranium we can write

$${}^{235}\text{N} = {}^{235}\text{N}_0 \exp(-\lambda_{235} t) \text{ and } {}^{238}\text{N} = {}^{238}\text{N}_0 \exp(-\lambda_{238} t)$$

where N the number of nuclei at time t , N_0 at time $t = 0$ and $\lambda = \ln 2 / t_{1/2} = 0.693 / t_{1/2}$ the disintegration constant.

At $t = 0$, ${}^{235}\text{N}_0 = {}^{238}\text{N}_0$, then

$$\frac{\exp(-\lambda_{238} t)}{\exp(-\lambda_{235} t)} = \frac{{}^{238}\text{N}}{{}^{235}\text{N}} = \frac{99.3}{0.7} = 142$$

Thus

$$\lambda_{235} t - \lambda_{238} t = \ln 142 = 4.95$$

$$\lambda_{238} = 0.693/t_{1/2} = 0.693/4.5 \times 10^9 = 1.54 \times 10^{-10} \text{ y}^{-1}$$

$$\lambda_{235} = 0.693/t_{1/2} = 0.693/7.1 \times 10^8 = 9.76 \times 10^{-10} \text{ y}^{-1}$$

$$t = \frac{4.95}{(9.76 - 1.54) \times 10^{-10} \text{ y}^{-1}} = \frac{4.95 \times 10^{10} \text{ y}}{8.22} = 6.0 \times 10^9 \text{ y}$$

- d) The energy released by the complete fission of $1 \text{ g } {}^{235}\text{U}$ is

$$E = (1/235) \times 6.022 \times 10^{23} \times 200 \text{ MeV} = 5.13 \times 10^{23} \text{ MeV}$$

and the energy released upon combustion of 1 g C is

$$E = (1/12) \times 6.022 \times 10^{23} \times 4.1 \text{ eV} = 2.06 \times 10^{23} \text{ eV} = 2.06 \times 10^{17} \text{ MeV}$$

Hence the amount of carbon that would release the same amount of energy as the fission of $1 \text{ g } {}^{235}\text{U}$ is

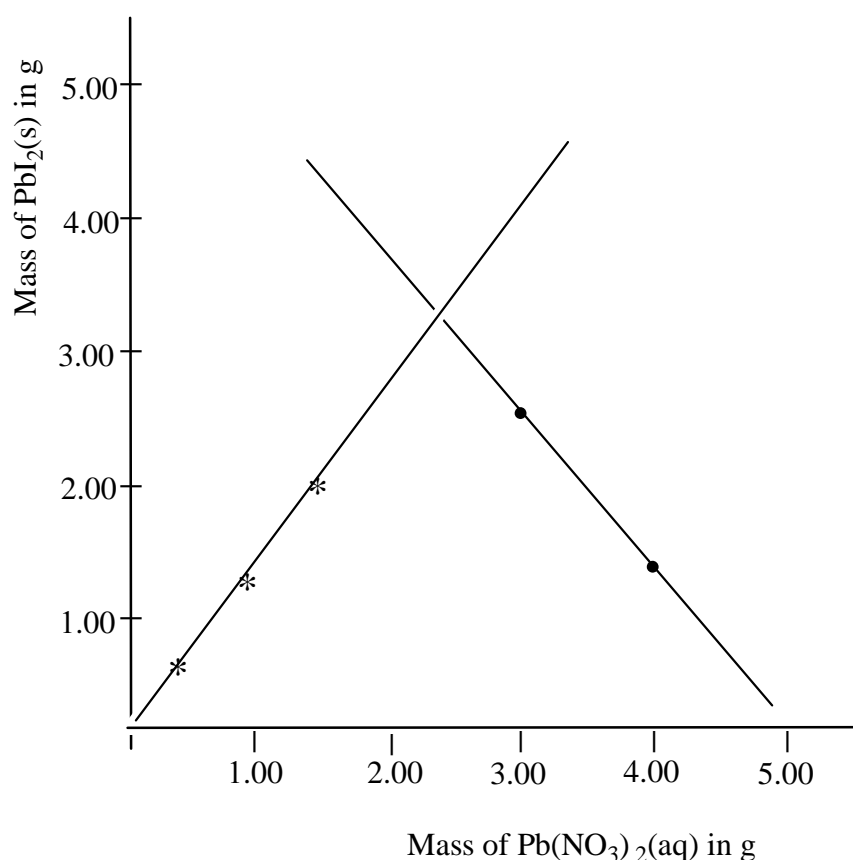
$$m = (5.13 \times 10^{23}) / (2.06 \times 10^{17}) = 2.49 \times 10^3 \text{ kg C}$$

Problem 14: Lead iodide

1. The graph obtained is one of two straight lines, meeting at a peak of about 2.50 g $\text{Pb}(\text{NO}_3)_2$.

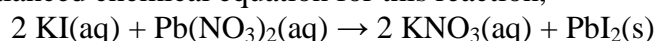
Data according to the reaction
 $2 \text{KI}(\text{aq}) + \text{Pb}(\text{NO}_3)_2(\text{aq}) \rightarrow 2 \text{KNO}_3(\text{aq}) + \text{PbI}_2(\text{s})$

Mass of $\text{Pb}(\text{NO}_3)_2$ (g)	Mass of PbI_2 (g)
0.500	0,696
1.000	1.392
1.500	2.088
4.000 (1.000 g KI)	1.389
3.000 (2.000 g KI)	2,778



2. The total quantity of reactant is limited to 5.000 g. If either reactant is in excess, the amount in excess will be “wasted”, because it cannot be used to form product. Thus, we obtain the maximum amount of product when neither reactant is in excess; there is a stoichiometric amount of each.

The balanced chemical equation for this reaction,



shows that stoichiometric quantities are two moles of KI (166.00 g/mol) for each mole of $\text{Pb}(\text{NO}_3)_2$ (331.21 g/mol). If we have 5.000 g total, we can let the mass of KI equal x g, so that the mass of $\text{Pb}(\text{NO}_3)_2 = (5.000 - x)$ g. Then we have

$$\text{amount KI} = x \text{ g KI} \times \frac{1 \text{ mol KI}}{166.00 \text{ g KI}} = \frac{x}{166.00}$$

$$\text{amount Pb}(\text{NO}_3)_2 = (5.000 - x) \text{ g Pb}(\text{NO}_3)_2 \times \frac{1 \text{ mol Pb}(\text{NO}_3)_2}{331.21 \text{ g Pb}(\text{NO}_3)_2} = \frac{5.000 - x}{331.21}$$

At the point of stoichiometric balance, amount KI = $2 \times$ amount $\text{Pb}(\text{NO}_3)_2$

$$\frac{x}{166.00} = 2 \times \frac{5.000 - x}{331.21} \quad \text{or} \quad 331.21x = 10.00 \times 166.00 - 332.00x$$

$$x = \frac{1660.0}{331.21 + 332.00} = 2,503 \text{ g KI} \times \frac{1 \text{ mol KI}}{166.00 \text{ g KI}} = 0.01508 \text{ mol KI}$$

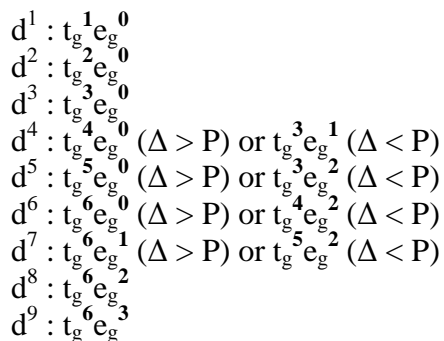
$$5.000 - x = 2.497 \text{ g Pb}(\text{NO}_3)_2 \times \frac{1 \text{ mol Pb}(\text{NO}_3)_2}{331.21 \text{ g Pb}(\text{NO}_3)_2} = 0.007539 \text{ mol Pb}(\text{NO}_3)_2$$

To determine the proportions precisely, we use the balanced chemical equation.

$$\text{maximum PbI}_2 \text{ mass} = 2.503 \text{ g KI} \times \frac{1 \text{ mol KI}}{166.00 \text{ g KI}} \times \frac{1 \text{ mol PbI}_2}{2 \text{ mol KI}} \times \frac{461.0 \text{ g PbI}_2}{1 \text{ mol PbI}_2} =$$

3.476 g PbI₂

Problem 15: Octahedral complexes

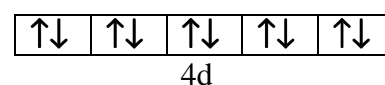
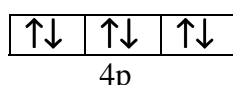
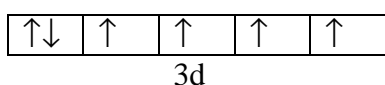
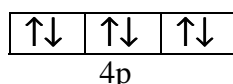
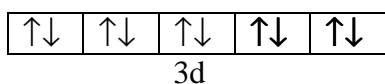


Problem 16: Isomerism in Inorganic Chemistry

1. ${}_{27}\text{Co} [1s^2 2s^2 2p^6 3s^2 3p^6] 3d^7 4s^2$

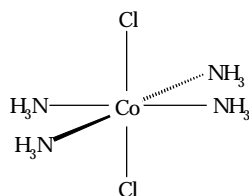


2. dative covalent by the ligand into an empty metal orbital. $d^2 sp^3$ hybridization

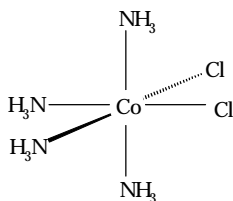


outer sphere paramagnetic complex

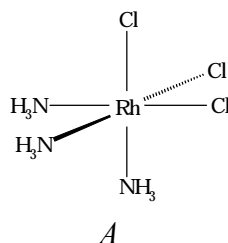
3. *trans*



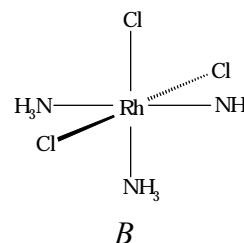
cis



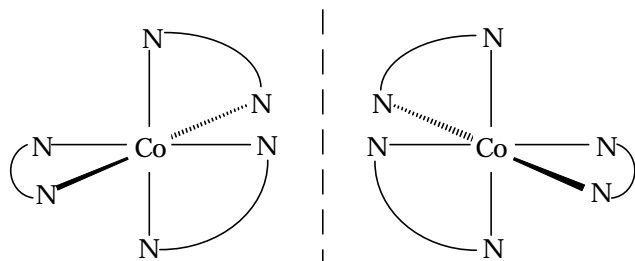
4. *fac*



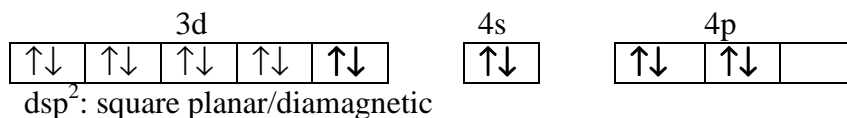
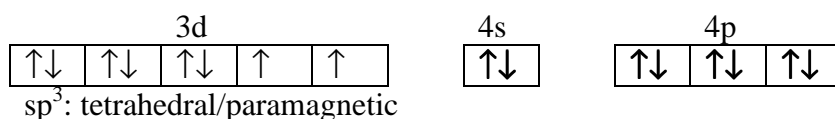
mer



5. 2 enantiomers $\pm \text{Co}(\text{en})_3^{3+}$



Problem 17: Tetrahedral and square complexes



Problem 18: Copper enzyme

- Cu: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$, Cu(I): $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$,
 a. Cu(II): $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$
- Oxidised PC
- $A = \epsilon \cdot c \cdot l \Rightarrow c = 0.700 / (4500 \times 1) = 1.56 \times 10^{-4} \text{ mol dm}^{-3}$. 5 cm^3 of the solution contain $1.56 \times 10^{-4} \times 5 \times 10^{-3} \times 10500 \times 1000 = 8.2 \text{ mg PC}$. #Cu atoms = $1.56 \times 10^{-4} \times 5 \times 10^{-3} \times 6.0221 \times 10^{23} = 4.7 \times 10^{17}$
- Electronic configurations :
 Zn(II): $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$, Cd(II): $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10}$,
 Co(II): $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$, Ni(II): $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$. Redox inactive are the Zn(II) and Cd(II) reconstituted Blue Copper Proteins.

Problem 19: Palladium nanoclusters

$$1. N = \frac{N_o \cdot \rho \cdot V}{AtomicWeight} = 307 \text{ Pd(0) atoms per nanocluster}$$

$$V = \text{the volume of a nanocluster} = \frac{4}{3} \pi \left(\frac{D}{2} \right)^3$$

According to the equation $y=10n^2+2$, the number of Pd(0) atoms in a 4 full-shells nanocluster is $N = 1+12+42+92+162 = 309$, hence it is a full shell cluster.

2. From Fig. 4 the H_2 uptake is $\Delta P_{H_2} = 4.15 - 2.05 = 2.10 \text{ atm}$ in 184 min.

$$\Delta P_{H_2} V = \Delta n_{H_2} RT, \text{ hence } \Delta n_{H_2} = 0.029 \text{ mol where } V = 400-55=345 \text{ cm}^3$$

$$\text{Initially } n_{C_6H_{12}} = \frac{V \rho}{M} = \frac{5 \text{ cm}^3 \times 0.81 \text{ g cm}^{-3}}{(6 \times 12.0107 + 12 \times 1.00794) \text{ g mol}^{-1}} = 0.048 \text{ mol}$$

$$(i) \text{ Conversion} = \frac{\text{reacted moles}}{\text{initial moles}} = \frac{0.029}{0.048} = 0.60 = 60\%$$

$$(ii) \text{ The catalytically active Pd(0) atoms are } \frac{162}{309} = 0.524 = 52.4\% \text{ of the total Pd(0)}$$

$$\text{amount. So: } TON = \frac{n_{H_2}}{n_{Pd}} = \frac{0.029 \text{ mol}}{0.524 \times 50 \times 10^{-6} \text{ mol}} = 1106 \text{ and}$$

$$TOF = \frac{TON}{t} = \frac{1106}{184 \text{ min}} = 6.0 \text{ min}^{-1}$$

3. The spectral regions (δ / ppm) and the respective relative integrals in the 1H -NMR spectrum of hex-1-ene (Fig. 5a and Table) are assigned as follows:

1	2	3	4	5	
CH ₃ (CH ₂) ₂ CH ₂ CH=CH ₂					
	1	2	3	4	5
	0.88-0.96	1.15-1.32	1.99-2.08	5.65-5.79	4.85-4.98
	(3)	(4)	(2)	(1)	(2)

The integral ratios of the second $^1\text{H-NMR}$ spectrum (Fig. 5b and Table) suggest that both hex-1-ene and hexane are present. The differences in the integral values of the spectral regions 0.88-0.96 ppm and 1.12-1.37 ppm must be due to the presence of hexane. The relative integrals of second spectrum are converted as shown in the table below:

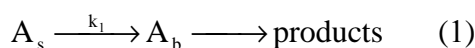
	δ / ppm	relative integral
Solution of the reaction (Fig. 5b)	0.88-0.96	3+6
	1.12-1.37	4+8
	1.99-2.08	2
	4.85-4.98	2
	5.65-5.79	1

So, the spectral regions (δ / ppm) and the respective relative integrals in the $^1\text{H-NMR}$ spectrum corresponding to hexane are assigned as follows:

1' 2' 1'	1'	2'
$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	0.88-0.96 (6)	1.15-1.32 (8)

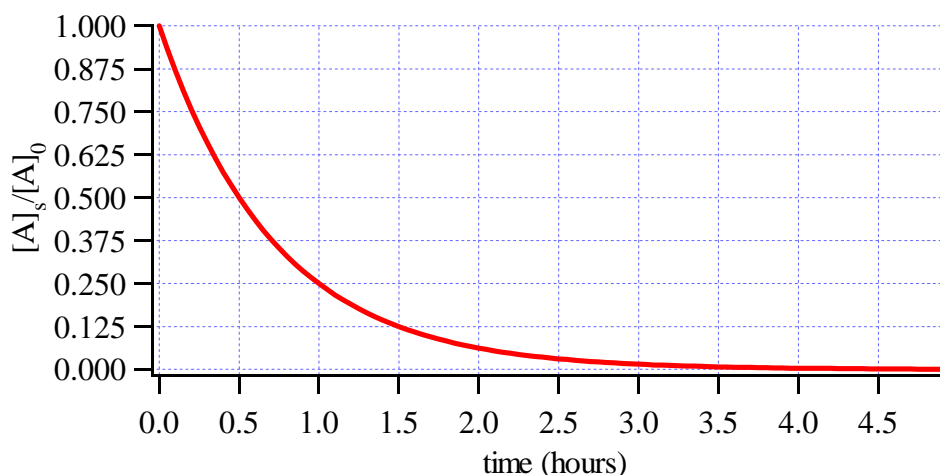
Finally, comparing the integral values per proton for the hex-1-ene and hexane the % conversion of hex-1-ene to hexane, after 30 min is 50%

Problem 20: Drug kinetics



$$-\frac{d[A]_s}{dt} = k_1[A]_s \quad (2)$$

Integration of Eq. 2 gives $[A]_s = [A]_0 \exp(-k_1 t)$, where $[A]_0$ the concentration of the drug in the stomach at zero time.



$\frac{[A]_0 - [A]_s}{[A]_0} = 0.75 \Rightarrow \frac{[A]_s}{[A]_0} = 0.25 = \left(\frac{1}{2}\right)^2$ Since $\frac{1}{4}$ of the initial amount remains after one hour, $(\frac{1}{4})^2 = 1/16 = 0.0625$ will remain after 2 hours, which corresponds to 4 half lives. That is 6.25% of $[A]_s$ is left.

Problem 21: Br₂ + CH₄ reaction mechanism

1 The rate of formation of CH₃Br is given by the equation:

$$v = + \frac{d[\text{CH}_3\text{Br}]}{dt} = k_3[\text{CH}_3][\text{Br}_2] \quad (1)$$

The “steady state” approximations for CH₃ and Br are given by the equations:

$$\frac{d[\text{CH}_3]}{dt} = k_2[\text{Br}][\text{CH}_4] - [\text{CH}_3](k_3[\text{Br}_2] + k_4[\text{HBr}]) = 0 \quad (2)$$

$$\frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2][\text{M}] - k_2[\text{Br}][\text{CH}_4] + [\text{CH}_3](k_3[\text{Br}_2] + k_4[\text{HBr}]) - 2k_5[\text{Br}]^2[\text{M}] = 0 \quad (3)$$

From equation (2):

$$[\text{CH}_3]_{\text{st}} = \frac{k_2[\text{Br}][\text{CH}_4]}{k_3[\text{Br}_2] + k_4[\text{HBr}]} \quad (4)$$

From equations (3) and (4):

$$[\text{Br}]_{\text{st}} = \left(\frac{k_1}{k_5} [\text{Br}_2] \right)^{\frac{1}{2}} \quad (5)$$

By combining equations (1), (4) and (5) the expression for the rate of formation of CH₃Br as a function of the concentrations of the stable species that are involved in the reaction is given by equation (6):

$$v = \left(\frac{k_1}{k_5} \right)^{\frac{1}{2}} k_2 \cdot \frac{[\text{Br}_2]^{\frac{1}{2}} [\text{CH}_4]}{\frac{k_4[\text{HBr}]}{k_3[\text{Br}_2]} + 1} \quad (6)$$

2

Start of the reaction	II
Steady state condition	I
Near to the end of the reaction	III

3

Start of the reaction	[Br ₂] >> [HBr] and since k ₃ ≈ k ₄ : k ₃ [Br ₂] >> k ₄ [HBr], so k ₄ [HBr] / k ₃ [Br ₂] << 1
Steady state condition	-
Near to the end of the reaction	[Br ₂] << [HBr] and since k ₃ ≈ k ₄ : k ₃ [Br ₂] << k ₄ [HBr], so k ₄ [HBr] / k ₃ [Br ₂] >> 1

Problem 22: Buffer solutions

1. The equilibrium, which governs the concentration of H^+ within the solution is $HCOOH \rightleftharpoons HCOO^- + H^+$

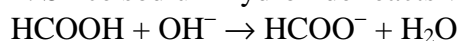
$$\text{Hence } K_a = \frac{[H^+][HCOO^-]}{[HCOOH]} = 2.1 \times 10^{-4}$$

and since $[HCOOH] \approx 0.200 \text{ M}$ and $[HCOO^-] \approx 0.150 \text{ M}$

$$[H^+] = 2.1 \times 10^{-4} \times \frac{0.200}{0.150} = 2.8 \times 10^{-4} \text{ M}$$

and **pH = 3.55**.

2. Since sodium hydroxide reacts with formic acid:



the concentration of formic acid in the solution is reduced to

$$[HCOOH] = 0.200 \text{ M} - 0.0100 \text{ M} = 0.190 \text{ M}$$

and the concentration of formate is increased to

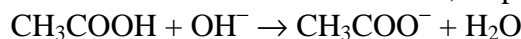
$$[HCOO^-] = 0.150 \text{ M} + 0.0100 \text{ M} = 0.160 \text{ M}$$

$$\text{Therefore: } [H^+] = 2.1 \times 10^{-4} \times \frac{0.190}{0.160} = 2.5 \times 10^{-4} \text{ M}$$

and **pH = 3.60**

Note that the addition of sodium hydroxide, which is a strong base, causes a very small increase of the pH of the solution.

3. Let V the volume of the solution of sodium hydroxide. Therefore, the final volume of the solution will be $(100.0 + V)$ mL and the number of mmol of CH_3COOH and OH^- which are mixed are $100.0 \text{ mL} \times 0.150 \text{ mmol/mL} = 15.00 \text{ mmol}$ and $V \text{ mL} \times 0.200 \text{ mmol/mL} = 0.200 \times V \text{ mmol}$, respectively. From the reaction:



it is obvious that the amount of acetate produced is $0.200 \times V$ mmol and the amount of acetic acid which remains unreacted is $(15.00 - 0.200 \times V)$ mmol. Hence, the concentration of each constituent in the buffer solution is:

$$[CH_3COOH] = \frac{(15.00 - 0.200 \times V)}{100.0 + V} \text{ M}$$

$$\text{and } [CH_3COO^-] = \frac{0.200 \times V}{100.0 + V} \text{ M}$$

From the acid dissociation constant expression of acetic acid

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

$$\text{it can be derived } \frac{[CH_3COO^-]}{[CH_3COOH]} = \frac{K_a}{[H^+]}$$

$$\text{and } \frac{\frac{0.200 \times V}{100.0 + V} \text{ M}}{\frac{(15.00 - 0.200 \times V)}{100.0 + V} \text{ M}} = \frac{1.8 \times 10^{-5}}{1.0 \times 10^{-5}}$$

from which **$V = 48.21 \text{ cm}^3$** .

4. a

5. (i) c, (ii) b

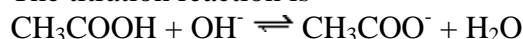
6. (i) b, (ii) d

7. (i) c, (ii) c

8. (i) b, (ii) c

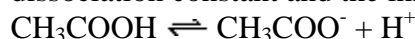
Problem 23: Titrations of weak acids

The titration reaction is



a) Initial pH

The pH of the solution before the titration begins, is calculated by the acid dissociation constant and the initial concentration of CH_3COOH :



From the acid dissociation constant expression:

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$

the concentration of H^+ can be calculated:

$$[\text{H}^+] = \sqrt{1.8 \times 10^{-5} \times 0.1000} = 1.34 \times 10^{-3} \text{ M} \text{ and } \text{pH} = 2.87$$

b) pH after the addition of 10.00 cm^3 of titrant

The solution contains acetic acid and sodium acetate. Therefore it is a buffer solution.

The concentration of each constituent is calculated:

$$[\text{CH}_3\text{COOH}] = \frac{(50.00 \text{ cm}^3 \times 0.1000 \text{ M}) - (10.00 \text{ cm}^3 \times 0.1000 \text{ M})}{60.00 \text{ cm}^3} = 0.0667 \text{ M}$$

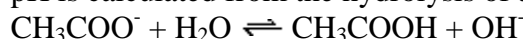
$$[\text{CH}_3\text{COO}^-] = \frac{10.00 \text{ cm}^3 \times 0.1000 \text{ M}}{60.00 \text{ cm}^3} = 0.01667 \text{ M}$$

These concentrations are then substituted into the dissociation constant expression of acetic acid for calculating the concentration of $[\text{H}^+]$:

$$[\text{H}^+] = 1.8 \times 10^{-5} \times \frac{0.0667}{0.01667} = 7.20 \times 10^{-5} \text{ M} \text{ and } \text{pH} = 4.14$$

c) pH at the equivalence point

At the equivalence point, all acetic acid has been converted to sodium acetate and the pH is calculated from the hydrolysis of acetate ions:



The volume of titrant required for the equivalence point (V_{ep}) is calculated:

$$V_{\text{ep}} = \frac{50.00 \text{ cm}^3 \times 0.1000 \text{ M}}{0.1000 \text{ M}} = 50.00 \text{ cm}^3$$

and the total volume of solution is 100.0 cm^3 . Therefore, at this point of the titration

$[\text{CH}_3\text{COOH}] = [\text{OH}^-]$ and

$$[\text{CH}_3\text{COO}^-] = \frac{50.00 \text{ cm}^3 \times 0.1000 \text{ M}}{100.0 \text{ cm}^3} - [\text{OH}^-] \approx 0.0500 \text{ M}$$

$$\frac{[\text{OH}^-]^2}{0.0500 \text{ M}} = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

$$[\text{OH}^-] = \sqrt{0.0500 \times 5.56 \times 10^{-10}} = 5.27 \times 10^{-6} \text{ M}$$

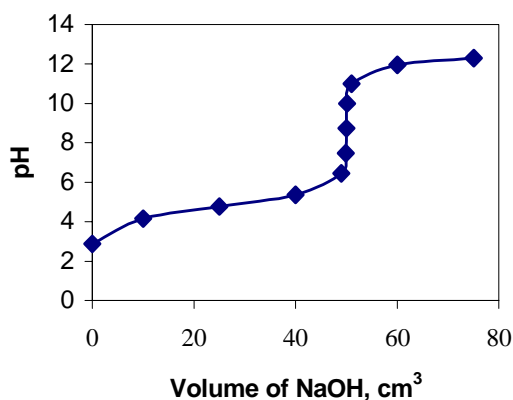
$\text{pOH} = 5.28$ and thus $\text{pH} = 14 - 5.28 = 8.72$

d) pH after the addition of 50.10 cm^3 of titrant

At this stage, all acetic acid has been converted to sodium acetate and the pH of the solution is calculated by the excess of sodium hydroxide, which has been added:

$$[\text{OH}^-] = \frac{(50.10 \text{ cm}^3 \times 0.1000 \text{ M}) - (50.00 \text{ cm}^3 \times 0.1000 \text{ M})}{100.1 \text{ cm}^3} = 1.0 \times 10^{-4} \text{ M}$$

Therefore $\text{pOH} = 4.00$ and $\text{pH} = 10.00$



Titration curve of 0.1000 M acetic acid with 0.1000 M NaOH

e) Selection of indicator

Since the pH at the equivalence point is 8.72, the appropriate acid base indicator is phenolphthalein.

2. (i) b, (ii) c, (iii) a, (iv) b, (v) c, (vi) d

Problem 24: Separation by extraction

1 Starting with an amount W_0 of S in phase 1, after the extraction this amount is distributed between the two phases as follows:

$$W_0 = (C_S)_1 V_1 + (C_S)_2 V_2$$

Since $D = (C_S)_2 / (C_S)_1$, we have

$$W_0 = (C_S)_1 V_1 + D(C_S)_1 V_2 = (DV_2 + V_1)(C_S)_1$$

Therefore, after removing phase 2, the remaining amount of S in phase 1 is:

$$W_1 = (C_S)_1 V_1 = W_0 \frac{V_1}{DV_2 + V_1}$$

By repeating extraction with a fresh portion of volume V_2 of phase 2, the amount W_1 of S is similarly distributed. After removing phase 2, the remaining amount of S in phase 1 is:

$$W_2 = (C_S)_1 V_1 = W_1 \frac{V_1}{DV_2 + V_1} = W_0 \left(\frac{V_1}{DV_2 + V_1} \right)^2$$

and so on. Therefore after n extractions with a fresh portion of volume V_2 of phase 2, the remaining amount of S in phase 1 will be:

$$W_n = W_0 \left(\frac{V_1}{DV_2 + V_1} \right)^n$$

2. (a) The remaining fraction of S after 1 extraction with 100 mL of chloroform is calculated using Equation 1.4:

$$f_1 = \frac{W_1}{W_0} = \left(\frac{50}{3.2 \times 100 + 50} \right)^1 = 0.135,$$

therefore the percentage of S extracted is $100 - 13.5 = \mathbf{86.5\%}$

(b) The remaining fraction of S after 4 extractions with 25 mL of chloroform each time is similarly calculated:

$$f_4 = \frac{W_4}{W_0} = \left(\frac{50}{3.2 \times 25 + 50} \right)^4 = 0.022,$$

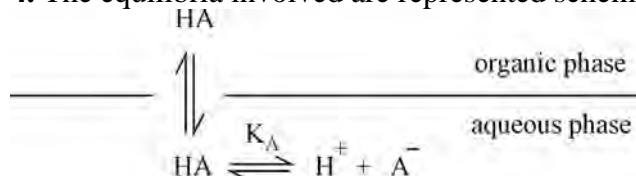
therefore the percentage of S extracted is $100 - 2.2 = 97.8\%$. The result is indicative of the fact that successive extractions with smaller individual volumes of extractant are more efficient than a single extraction with all the volume of the extractant.

3. Using Equation 1-4 we have:

$$0.01 = \left(\frac{100.0}{9.5 \times 25.0 + 100.0} \right)^n \quad \text{or} \quad 0.01 = 0.2963^n \quad \text{hence } n = \log(0.01)/\log(0.2963) =$$

3.78, therefore at least **4** extractions are required.

4. The equilibria involved are represented schematically as follows:



We have (subscripts w and o denote concentrations in aqueous and organic phase, respectively)

$$D = \frac{(C_{\text{HA}})_o}{(C_{\text{HA}})_w} = \frac{[\text{HA}]_o}{[\text{HA}]_w + [\text{A}^-]_w}$$

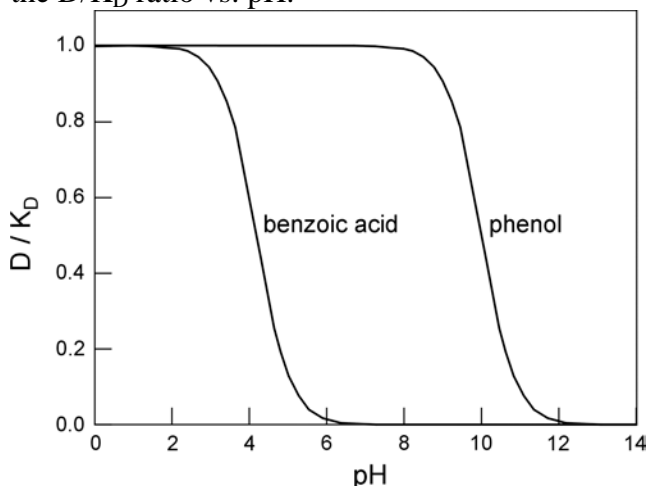
$$K_D = [\text{HA}]_o / [\text{HA}]_w \quad \text{and} \quad K_a = [\text{H}^+]_w [\text{A}^-]_w / [\text{HA}]_w$$

Combining all three equations we finally obtain:

$$D = \frac{K_D [\text{H}^+]_w}{[\text{H}^+]_w + K_a} \quad (1.5)$$

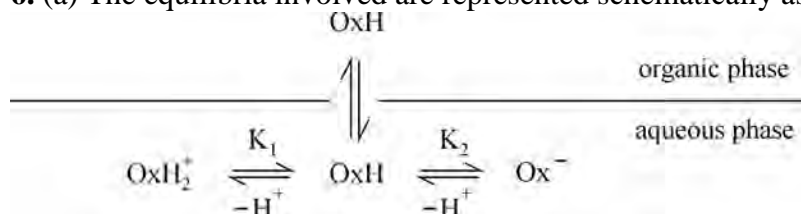
Last equation predicts that if $[\text{H}^+]_w \gg K_a$ (strongly acidic aqueous phase), then $D \approx K_D$ (i.e. D acquires the maximum possible value) and the acid is extracted (or prefers to stay) in the organic phase. On the other hand, if $[\text{H}^+]_w \ll K_a$ (strongly alkaline aqueous phase), we have $D \approx K_D [\text{H}^+]_w / K_a$, and because of the small value of D the acid is then extracted (or prefers to stay) in the aqueous phase. In this way, by regulating the pH of the aqueous phase, the course of extraction is shifted towards the desired direction.

5. (a) By using the previously derived Equation 1.5, we obtain the following plots of the D/K_D ratio vs. pH.



(b) From these plots it is clear that at the pH region 7-8 the distribution ratio for benzoic acid will be practically 0, whereas that of phenol will acquire the maximum possible value. Therefore, phenol can be efficiently separated from an aqueous solution of both compounds by extraction with diethylether, provided that the pH of this solution has been adjusted in the range 7 to 8 (e.g. by the presence of excess of NaHCO_3).

6. (a) The equilibria involved are represented schematically as follows:



We have the expressions

$$D = \frac{(C_{\text{OxH}})_o}{(C_{\text{OxH}})_w} = \frac{[\text{OxH}]_o}{[\text{OxH}_2^+]_w + [\text{OxH}]_w + [\text{Ox}^-]_w}$$

$$K_D = [\text{OxH}]_o / [\text{OxH}]_w = 720$$

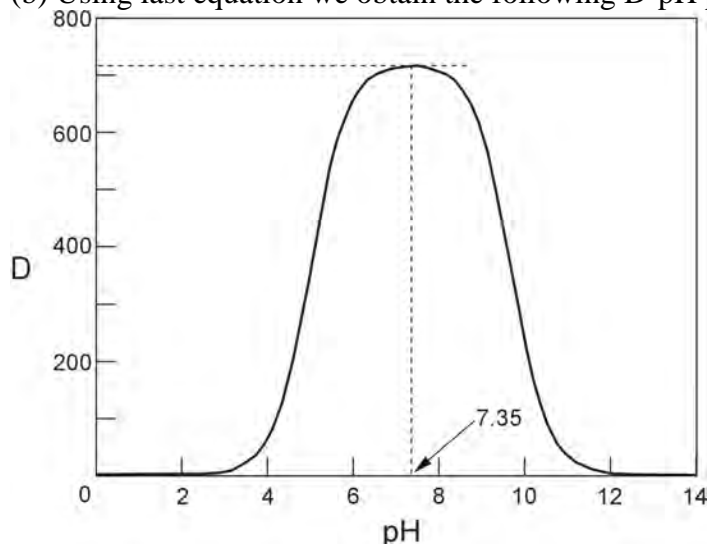
$$K_1 = \frac{[\text{OxH}]_w [\text{H}^+]_w}{[\text{OxH}_2^+]_w} = 1 \times 10^{-5}$$

$$K_2 = \frac{[\text{Ox}^-]_w [\text{H}^+]_w}{[\text{OxH}]_w} = 2 \times 10^{-10}$$

Combining all four equations, we have the sought-for expression

$$\begin{aligned}
 D &= \frac{[\text{OxH}]_o}{\frac{[\text{OxH}_2^+]_w [\text{H}^+]_w}{K_1} + [\text{OxH}]_w + \frac{K_2 [\text{OxH}]_w}{[\text{H}^+]_w}} \\
 &= \frac{[\text{OxH}]_o}{[\text{OxH}]_w} \cdot \frac{1}{\frac{[\text{H}^+]_w}{K_1} + 1 + \frac{K_2}{[\text{H}^+]_w}} = \frac{K_D}{\frac{[\text{H}^+]_w}{K_1} + 1 + \frac{K_2}{[\text{H}^+]_w}}
 \end{aligned}$$

(b) Using last equation we obtain the following D-pH plot:



(c) We calculate the 1st and 2nd derivative of the denominator, i.e.,

$$F([\text{H}^+]_w) = \frac{[\text{H}^+]_w}{K_1} + 1 + \frac{K_2}{[\text{H}^+]_w}$$

$$\text{whereupon we have the 1st derivative } F'([\text{H}^+]_w) = \frac{1}{K_1} - \frac{K_2}{[\text{H}^+]_w^2}$$

$$\text{and for the 2nd derivative } F''([\text{H}^+]_w) = \frac{2K_2}{[\text{H}^+]_w^3}$$

Since always $F''([H^+]_w) > 0$, then when $F'([H^+]_w) = 0$, $F([H^+]_w)$ is minimum under these conditions. Consequently, the distribution ratio is maximum when

$$\frac{1}{K_1} - \frac{K_2}{[H^+]^2} = 0 \text{ or } [H^+]_w = \sqrt{K_1 K_2} = \sqrt{(1 \times 10^{-5})(2 \times 10^{-10})} = 4.5 \times 10^{-8} \text{ M}$$

or pH = 7.35

Problem 25: Mass spectroscopy

1 The ionic fragment SiCl_2^+ will be represented by the following peaks:

M = 98	$^{28}\text{Si}^{35}\text{Cl}_2^+$
M+1 = 99	$^{29}\text{Si}^{35}\text{Cl}_2^+$
M+2 = 100	$^{28}\text{Si}^{35}\text{Cl}^{37}\text{Cl}^+ + ^{30}\text{Si}^{35}\text{Cl}_2^+$
M+3 = 101	$^{29}\text{Si}^{35}\text{Cl}^{37}\text{Cl}^+$
M+4 = 102	$^{30}\text{Si}^{35}\text{Cl}_2^+ + ^{28}\text{Si}^{35}\text{Cl}^{37}\text{Cl}^+$
M+5 = 103	$^{29}\text{Si}^{37}\text{Cl}_2^+$
M+6 = 104	$^{30}\text{Si}^{37}\text{Cl}_2^+$

Therefore, the correct answer is 7.

2 The expected peaks and the corresponding probabilities are:

m/z = 45	$^{10}\text{B}^{35}\text{Cl}$	$0.199 \times 0.7577 = 0.151$
m/z = 46	$^{11}\text{B}^{35}\text{Cl}$	$0.801 \times 0.7577 = 0.607$
m/z = 47	$^{10}\text{B}^{37}\text{Cl}$	$0.199 \times 0.2423 = 0.048$
m/z = 48	$^{11}\text{B}^{37}\text{Cl}$	$0.801 \times 0.2423 = 0.194$

Hence, the base peak has nominal mass M = 46 and the relative intensities are:

M-1 = 45	$(0.151/0.607) \times 100 = 24.9\%$
M = 46	$= 100\%$
M+1 = 47	$(0.048/0.607) \times 100 = 7.9\%$
M+2 = 48	$(0.194/0.607) \times 100 = 32.0\%$

Therefore, the correct answer is C.

3 For the ion N_2^+ we have:

$$\begin{aligned} \text{M: } & ^{14}\text{N}^{14}\text{N} = (0.99634)^2 = 0.9927 \\ \text{M+1: } & ^{14}\text{N}^{15}\text{N} + ^{15}\text{N}^{14}\text{N} = 2 \times (0.99634 \times 0.00366) = 0.007293 \end{aligned}$$

hence, $(\text{M+1})/\text{M} = 0.007293/0.9927 = 0.00735$ or 0.735%

For the ion CO^+ we have:

$$\begin{aligned} \text{M: } & ^{12}\text{C}^{16}\text{O} = 0.989 \times 0.99762 = 0.9866 \\ \text{M+1: } & ^{12}\text{C}^{17}\text{O} + ^{13}\text{C}^{16}\text{O} = (0.989 \times 0.00038) + (0.011 \times 0.99762) = 0.01135 \end{aligned}$$

hence, $(\text{M+1})/\text{M} = 0.01135/0.9866 = 0.0115$ or 1.15%

For the ion CH_2N^+ we have:

$$\begin{aligned} \text{M: } & ^{12}\text{C}^1\text{H}_2^{14}\text{N} = 0.989 \times (0.99985)^2 \times 0.99634 = 0.9851 \\ \text{M+1: } & ^{13}\text{C}^1\text{H}_2^{14}\text{N} + ^{12}\text{C}^1\text{H}^2\text{H}^{14}\text{N} + ^{12}\text{C}^2\text{H}^1\text{H}^{14}\text{N} + ^{12}\text{C}^1\text{H}_2^{15}\text{N} = \\ & 0.011 \times (0.99985)^2 \times 0.99634 + 2 \times 0.989 \times 0.99985 \times 0.00015 \times 0.99634 + \\ & + 0.989 \times (0.99985)^2 \times 0.00366 = 0.01487 \end{aligned}$$

hence, $(\text{M+1})/\text{M} = 0.01487/0.9851 = 0.0151$ or 1.51%

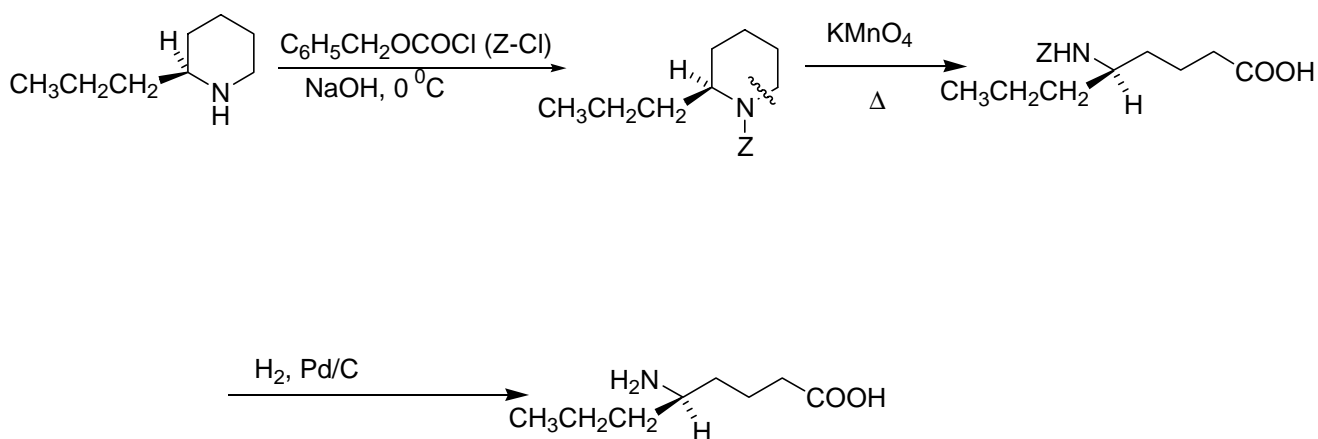
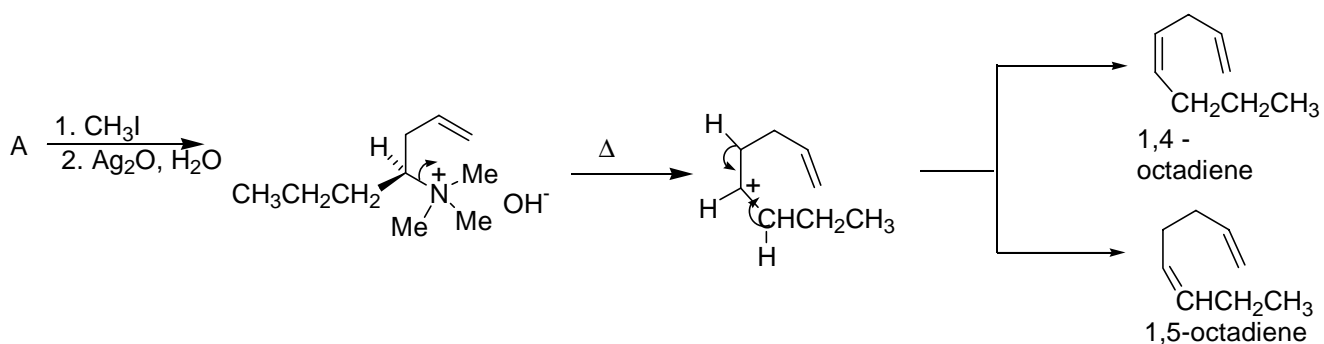
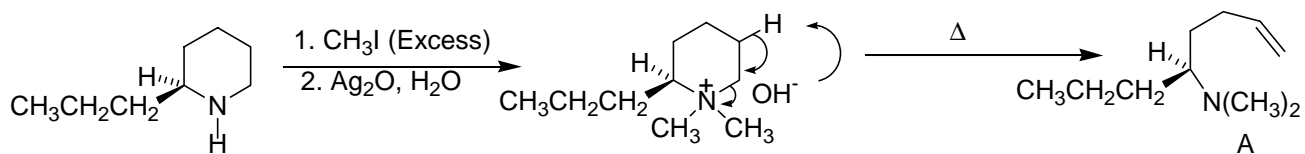
For the ion C_2H_4^+ we have:

$$\begin{aligned} \text{M: } & ^{12}\text{C}_2^1\text{H}_4 = (0.989)^2 \times (0.99985)^4 = 0.9775 \\ \text{M+1: } & ^{13}\text{C}^{12}\text{C}^1\text{H}_4 + ^{12}\text{C}^{13}\text{C}^1\text{H}_4 + ^{12}\text{C}_2^2\text{H}^1\text{H}_3 + ^{12}\text{C}_2^1\text{H}^2\text{H}^1\text{H}_2 + \\ & + ^{12}\text{C}_2^1\text{H}_2^2\text{H}^1\text{H} + ^{12}\text{C}_2^1\text{H}_3^2\text{H} = 2 \times 0.011 \times 0.989 \times (0.99985)^4 + \\ & + 4 \times 0.989 \times 0.00015 \times (0.99985)^3 = 0.02234 \end{aligned}$$

hence, $(\text{M+1})/\text{M} = 0.02234/0.9775 = 0.0229$ or 2.29%

Therefore the correct answer is (b) CO^+

Problem 26 Chemical Structure and Absolute Stereochemistry of Coniine

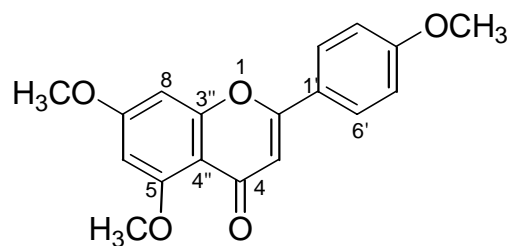


(S)- 5-amino-octanoic acid

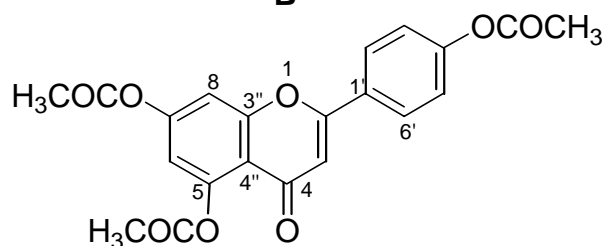
The KMnO_4 oxidation reaction step is based on A. M. Castano, J.M. Cuerva, A. M. Echavarren, *Tetrahedron Letters*, 35, 7435-7438 (1994)

Problem 27: The chemistry and identification of flavonoids

1.



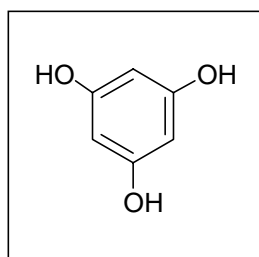
B



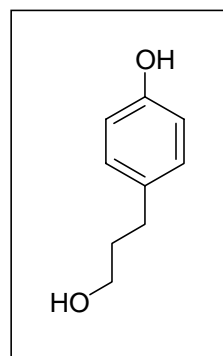
C

2. a) down field. The $^1\text{H-NMR}$ resonance of phenolic proton involvement in hydrogen bonding will be observed at very low magnetic field ($\sim 12\text{ppm}$).

3.

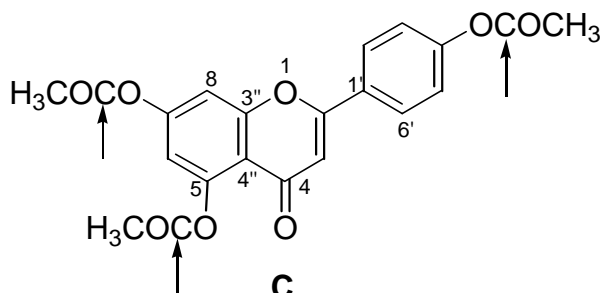


D



E

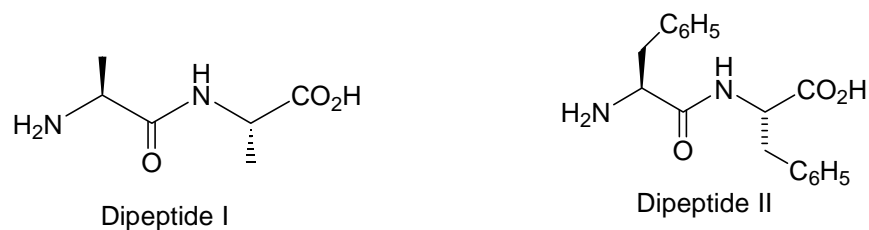
4. $^{13}\text{C-NMR}$ would be expected to show three characteristic peaks of the three different carbonyl groups.



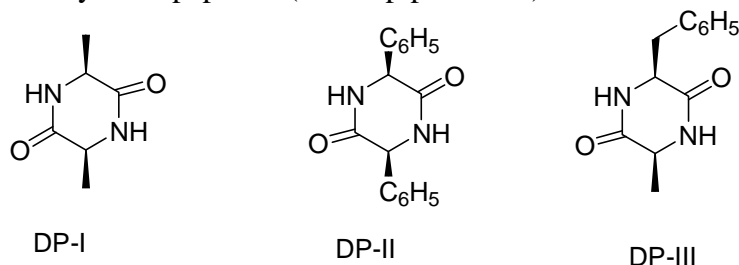
C

Problem 28: Synthesis of peptides

1

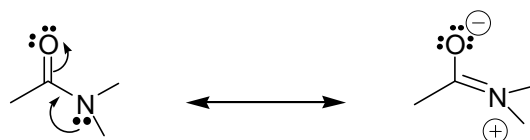


The cyclic dipeptides (diketo piperazines) must also be considered:

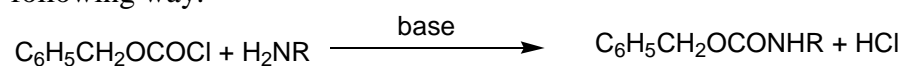


2. Best answers are 5 and 2.

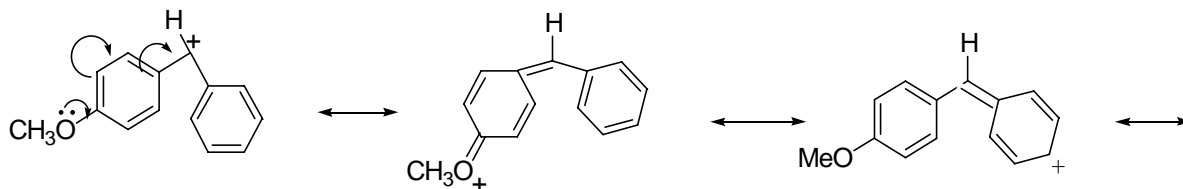
3.



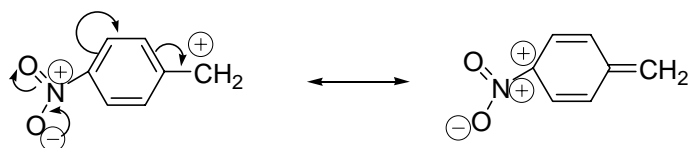
4. Benzyl chloroformate, reagent N^o 4, would react easily with an amine in the following way:



5. If we assume the intermediate formation of a carbonium ion, the ease of formation of such ion would parallel its stability. Electron delocalization is most extensive in case D:



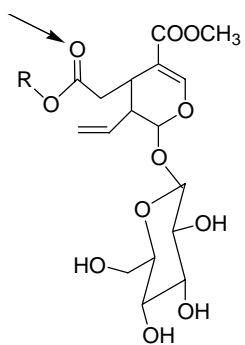
And least effective in case A:



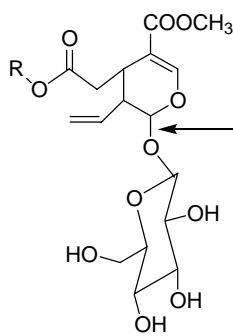
In the same way the cation from B is better stabilized than the cation from C. Therefore, the order of increasing lability is: A < C < B < D.

Problem 29: Oleuropein hydrolysis

1.

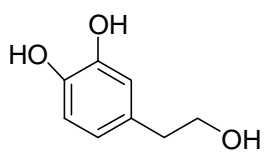


(a)



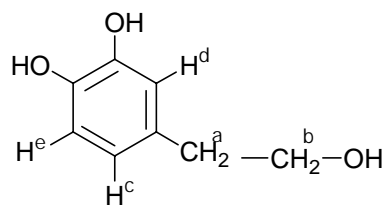
(b)

2.

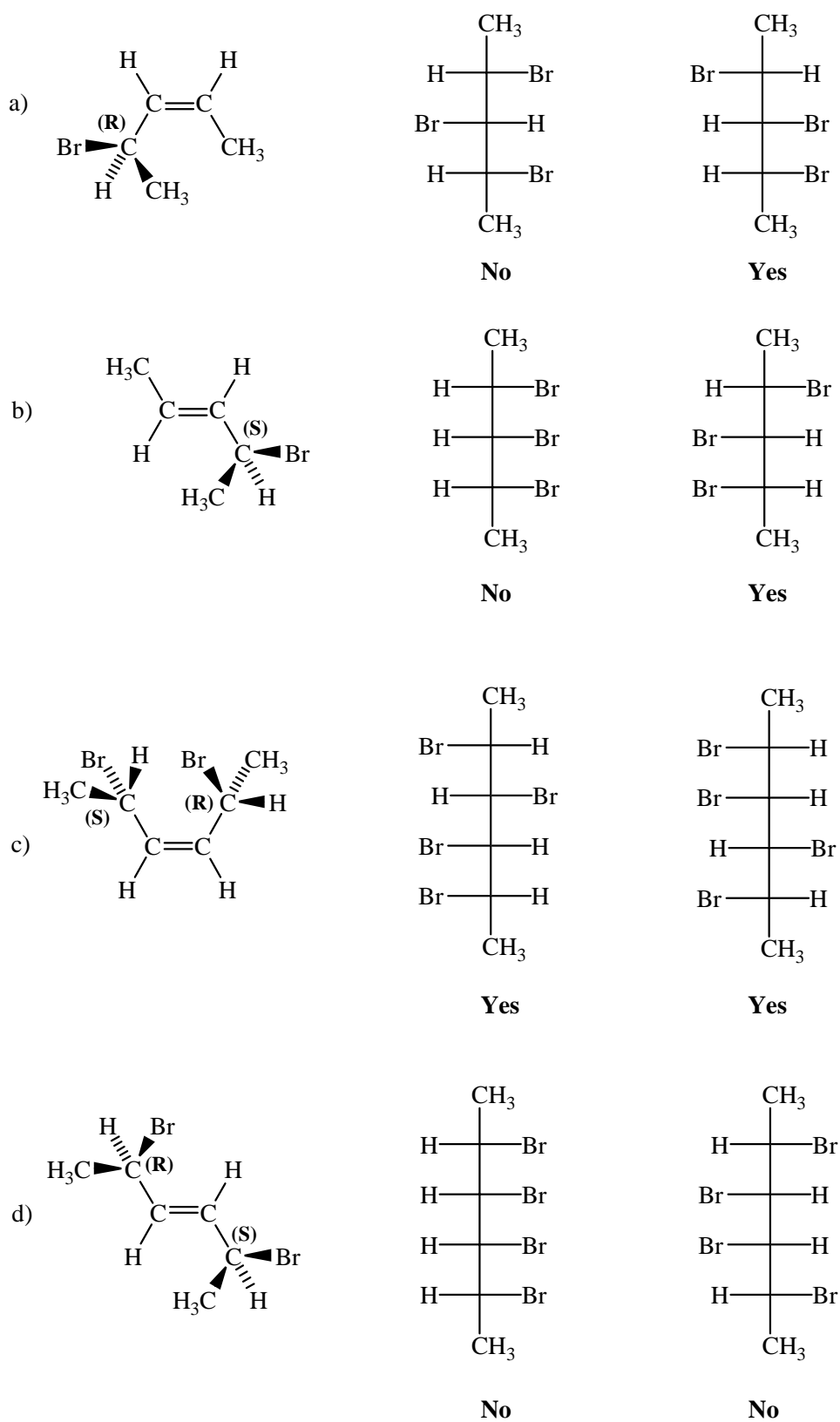


The correct structure is C

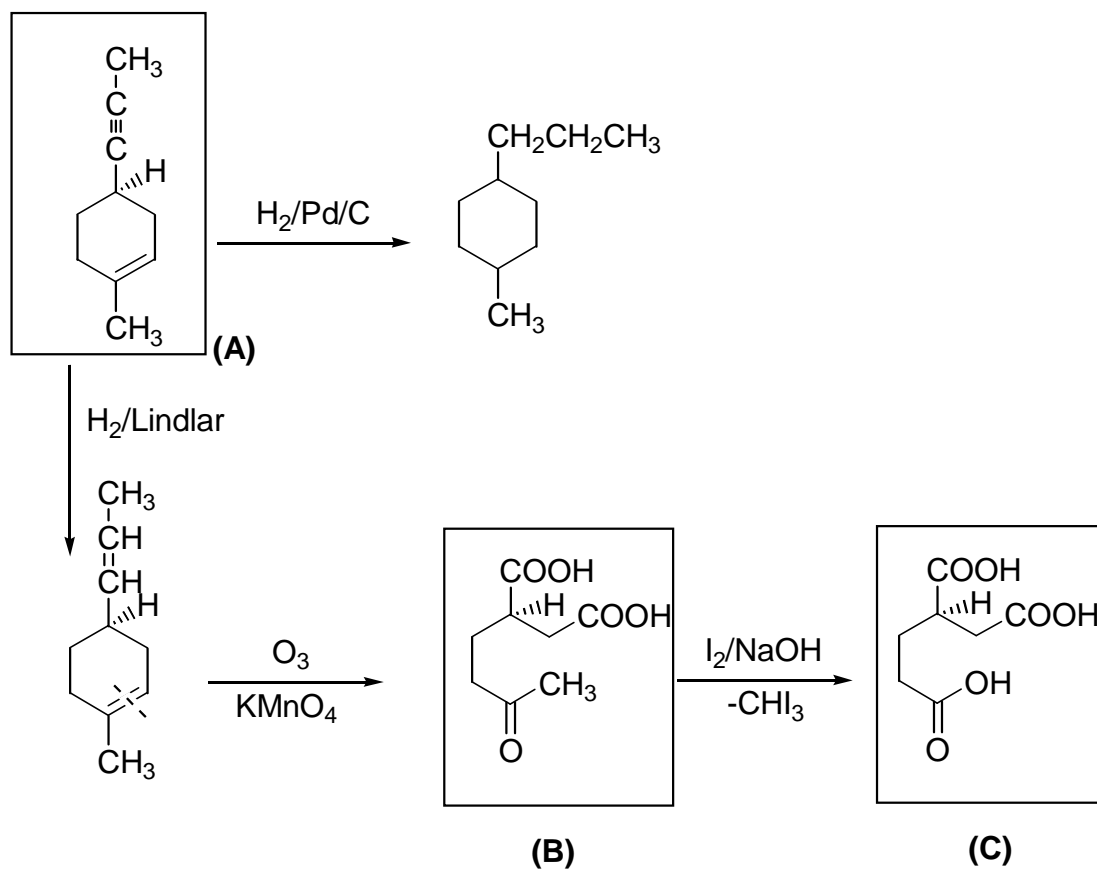
3.



Problem 30: Stereochemistry of the Addition Reactions to Alkenes

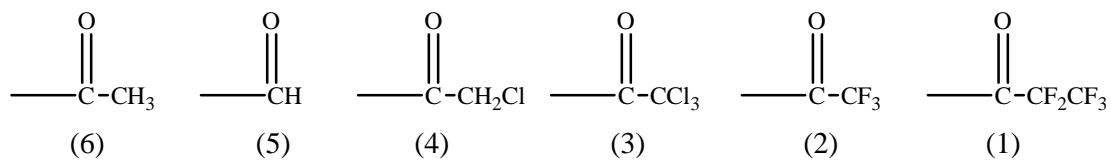


Problem 31: Identification of Organic Compounds

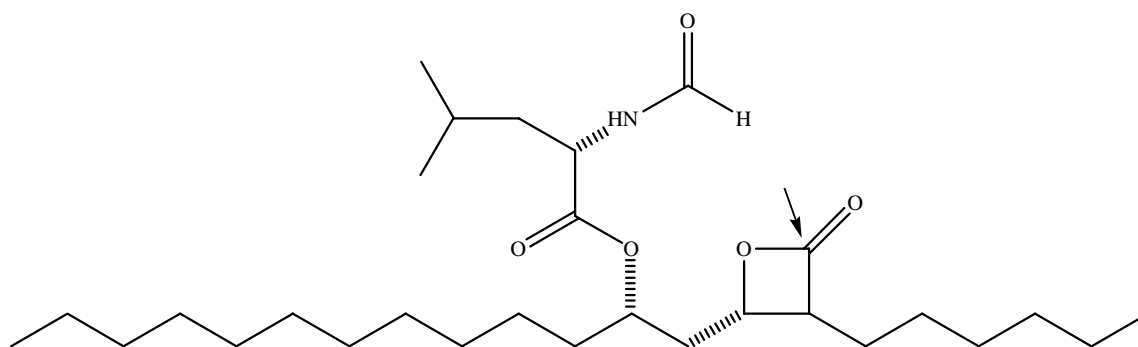


Problem 32: Lipases

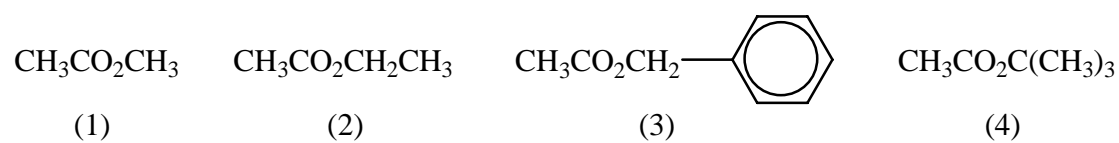
a)



b)



c)

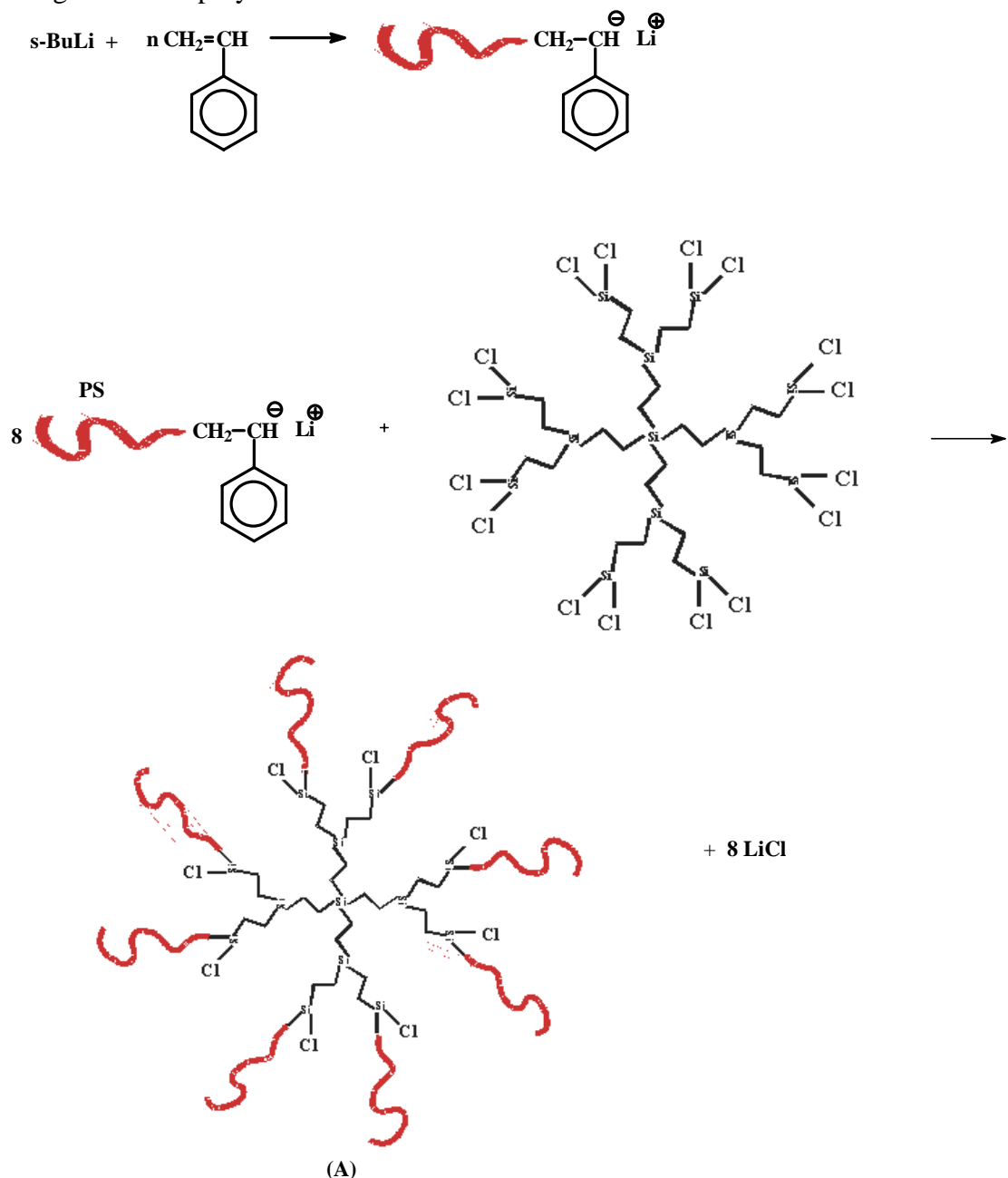


Problem 33: Polymers

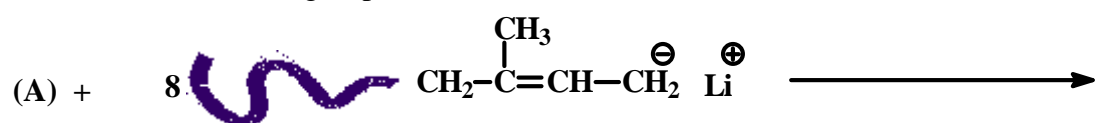
1. The volume of the Larnax is $40.9 \text{ cm} \times 34.1 \text{ cm} \times 17.0 \text{ cm} = 23.7 \text{ dm}^3$.
Consequently, the Larnax will be filled with $m = V d = 23.2 \text{ kg}$

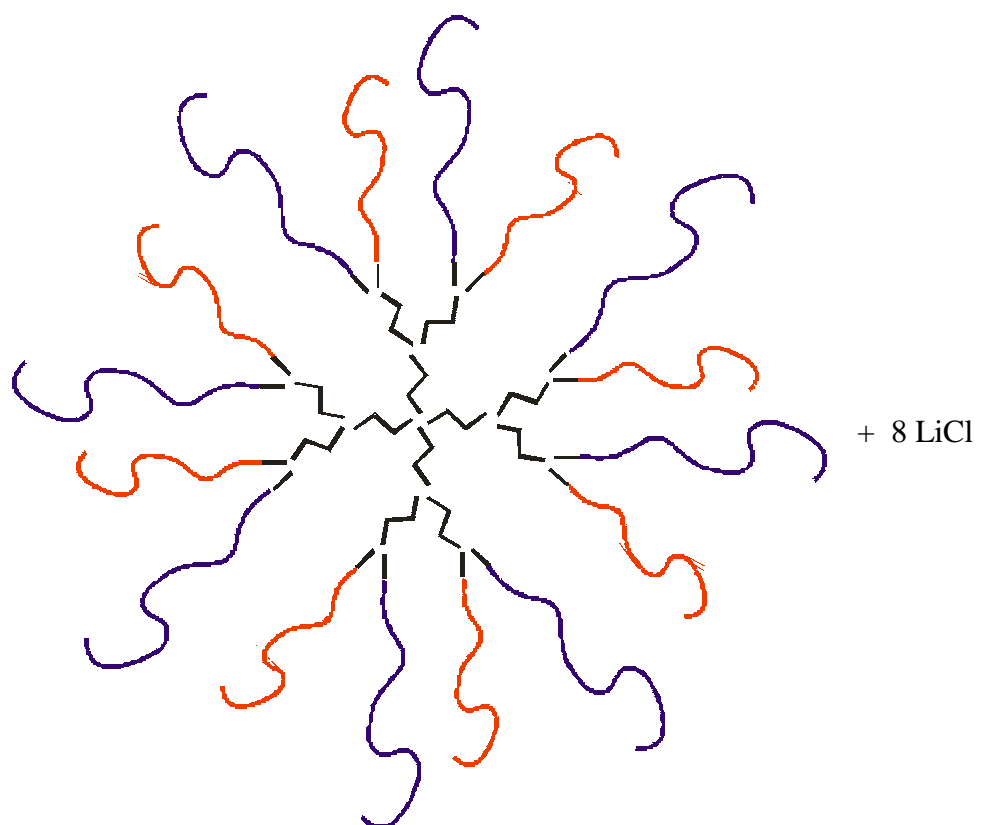
This quantity corresponds to $(23200/10^6) \times N_A$ Vergina Star Copolymers, or $0.0232 \times N_A$ Vergina Star Copolymers, where N_A is the Avogadro number.

2. The following reaction scheme should be followed in order to synthesize the Vergina Star Copolymer:



Due to the steric hindrance of the styryllithium anion, only one polymeric chain can react with each $-\text{SiCl}_2$ group.





Due to the lower steric hindrance of the polyisoprenyllithium living ends, the reaction goes to completion.