THE PREPARATORY PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS

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PREPARATORY PROBLEMS

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27 theoretical problems
8 practical problems

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International Chemistry Olympiad
International Information Centre
IUVENTA
Karloveská 64
84258 Bratislava 1, Slovakia
Phone: +421–907–473367
E–mail: anton.sirota@stuba.sk
Web: www.icho.sk

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PREPARATORY PROBLEMS

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PREPARATORY THEORETICAL PROBLEMS

THEORETICAL PROBLEM 1

Separation and Identification of Ions

A student studied the chemical reactions between cations, A^{2+}, B^{2+}, C^{2+}, D^{2+}, E^{2+} in nitrate aqueous solutions and anions X^-, Y^-, Z^-, Cl^-, OH^- in sodium aqueous solutions as well as an organic ligand L. Some precipitation (ppt) products and colored complexes were found as shown in Table 1:

Table 1

	X^-	Y^-	Z^-	Cl^-	OH^-	L
A^{2+}	***	***	***	***	White ppt	***
B^{2+}	Yellow ppt	White ppt	***	***	***	BL_n^{2+} Complex
C^{2+}	White ppt	Brown ppt	Brown ppt	White ppt	Black ppt	CL^{2+}, CL_2^{2+} Complexes
D^{2+}	***	Red ppt	***	***	***	***
E^{2+}	***	Red ppt	White ppt	***	***	***

*** = No reaction,

1.1 Design a flow chart for the separation of A^{2+}, B^{2+}, C^{2+}, D^{2+}, E^{2+} in a nitrate aqueous solution by using various aqueous solutions containing anions X^-, Y^-, Z^-, Cl^-, OH^-, respectively, as testing reagents. Write down the product of the chemical reaction for each step in the flow chart.

1.2 Design a flow chart for the separation of anions X^-, Y^-, Z^-, Cl^-, OH^- in a sodium aqueous solution by using various aqueous solutions containing cations A^{2+}, B^{2+}, C^{2+}, D^{2+}, E^{2+}, respectively, as testing reagents. Write down the product of the chemical reaction for each step in the flow chart.

1.3 The white ppt BY_2 and brown ppt CY_2 have low solubilities in water with solubility products K_{sp} at 25 °C of 3.20×10^{-8} and 2.56×10^{-13}, respectively.

a) Calculate the solubility of BY_2.

b) Calculate the solubility of CY_2.

1.4 A series of solutions containing B^{2+} and L were prepared in 50 cm^3 volumetric flasks by adding 2 cm^3 of solution of B^{2+} (8.2×10^{-3} mol dm^{-3}) to each flask. Varying amounts of a solution of the ligand L ($c = 1.0\times10^{-2}$ mol dm^{-3}) are added to each flask. The solution in each volumetric flask was diluted with water to the mark (50 cm_3). The absorbance (A) of complex BL_n was measured at 540 nm for each solution in a 1.0 cm cell. The data are summarized in Table 2. (Both B^{2+} and ligand L show no absorption (A = 0) at 540 nm.) [Mole Ratio Method]

a) Calculate the value of n (coordination number) in the complex BL_n^{2+}.

b) Calculate the formation constant (K_f) of complex BL_n^{2+}.

Table 2

Added L V_L (cm^3)	Absorbance (A)	Added L V_L (cm^3)	Absorbance (A)
1.00	0.14	2.00	0.26
3.00	0.40	4.00	0.48
5.00	0.55	6.00	0.60
7.00	0.64	8.00	0.66
9.00	0.66	10.00	0.66

1.5 Solid NaY (soluble) was added very slowly to an aqueous solution with a concentration of B^{2+} and C^{2+} equal to 0.10 mol dm^{-3} and 0.05 mol dm^{-3}, respectively, prepared from their respective nitrate aqueous salts.

a) Which cation (B^{2+} or C^{2+}) precipitates first? What is the [Y^-] when this happens? ($K_{sp} = 3.20\times10^{-8}$ for BY_2 and $K_{sp} = 2.56\times10^{-13}$ for CY_2, at 25 ^oC.) [Separation by Precipitation]

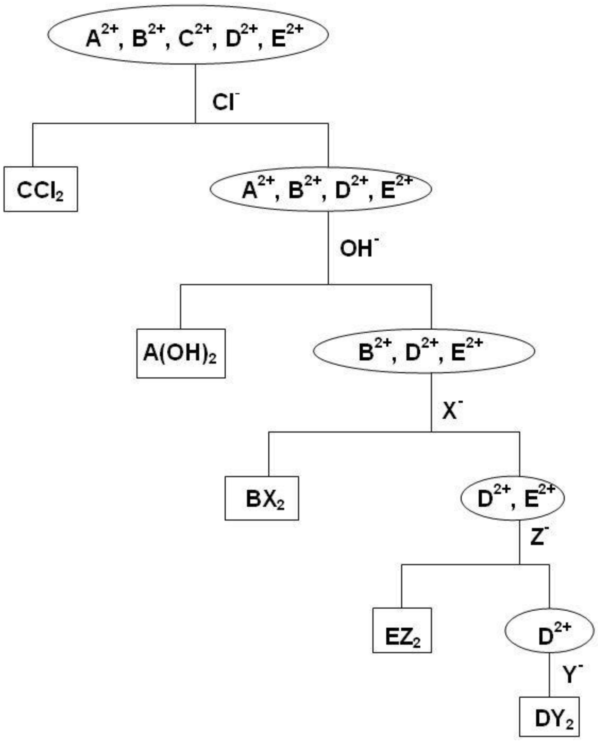
b) What are the concentrations of Y^- and the remaining cation when complete precipitation of the first precipitating cation has occurred (assume that the concentration of the first cation in solution after complete precipitation is ≤ 10^{-6}

mol dm^{-3})? Is it possible to separate B^{2+} and C^{2+} by the precipitation method with Y^- ion as a precipitating agent?

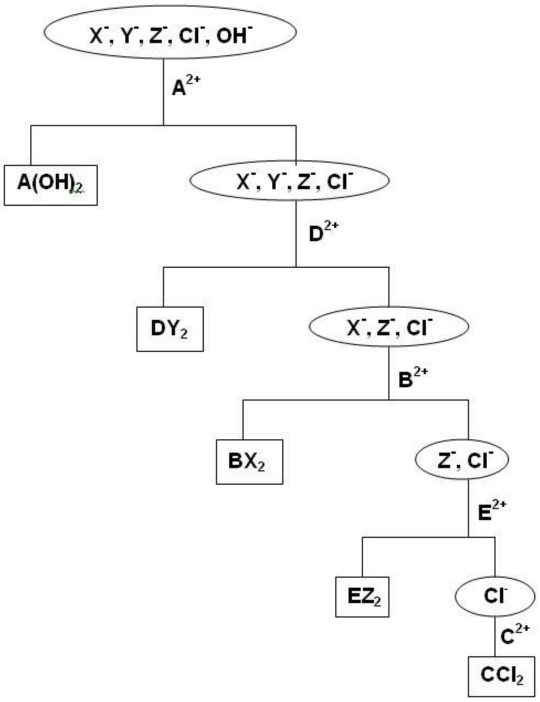
SOLUTION OF PREPARATORY PROBLEM 1

Separation and Identification of Ions

1.1 For example



1.2 For example



1.3 **a)** $BY_2 = B^{2+} + 2\ Y^{-}$ $K_{sp} = (S_1)(2\ S_1)^2 = 3.20\times10^{-8}$

S_1 $2\ S$

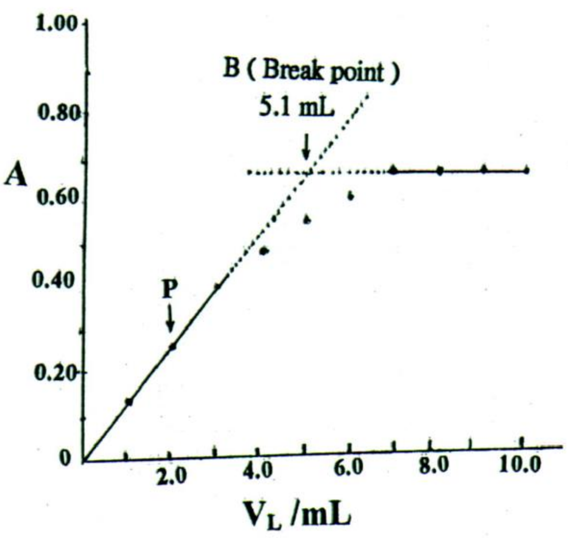
$4\ S_1^{\ 3} = 3.20\times10^{-8}$, S_1(solubility of BY_2) = 2.0×10^{-3} mol dm^{-3}

b) $CY_2 = C^{2+} + 2\ Y^{-}$ $K_{sp} = (S_2)(2S_2)^2 = 2.56\times10^{-13}$

S_2 $2\ S_2$

$4\ S_2^{\ 3} = 2.56\times10^{-13}$, S_2(solubility of CY_2) = 4.0×10^{-5} mol dm^{-3}

1.4 a**)** Plot of absorbance (*A*) vs volume (V_L) of L added as follows:



From the volume of L at break point B (all B^{2+} ions form complex with L) in the plot, n can be calculated:

n/1 = *n*(L) / *n*(B^{2+})

= (0.0051 dm^3 × 1.0×10^{-2} mol dm^{-3}) / (0.0020 dm^3 × 8.2×10^{-3} mol dm^{-3}) ≅ 3

It means that B^{2+} forms $BL_3^{\ 2+}$ complex with L.

b) (1) Calculation of molar absorption coefficient *ε*.

At break point, $A = 0.66 = \varepsilon \times 1 \times c(BL_3^{\ 2+})$

And $\varepsilon = 0.66 / (2.0\ \text{cm}^3 \times 8.2\times10^{-3} / 50\ \text{cm}^3) = 2.01\times10^{3}$

(2) Choose a point in the curve of the plot, for example:

At point P (2.0 cm^3 of L added): *A* = 0.26

$A = 0.26 = \varepsilon \times 1 \times c(BL_3^{\ 2+})$

$c(BL_3^{\ 2+}) = 0.26 / \varepsilon = 0.26 / (2.01\times10^{3}) = 1.29\times10^{-4}$ mol dm^{-3}

$c(B^{2+}) = (2.0\ cm^3 \times 8.2\times10^{-3} - 50\ cm^3 \times 1.29\times10^{-4}\ mol\ dm^{-3}) / 50\ cm^3$

$c(B^{2+}) = 1.99\times10^{-4}\ mol\ dm^{-3}$

$c(L) = (2.0\ cm^3 \times 1.0\times10^{-2} - 3 \times 50\ cm^3 \times 1.29 \times10^{-4}\ mol\ dm^{-3}) / 50\ cm^3$

$c(L) = 1.3 \times 10^{-5}\ mol\ dm^{-3}$

[Calculation of formation constant]

So $K_f = [BL_3^{2+}] / ([B^{2+}][L]^3) = (1.29\times10^{-4}) / ((1.99\times10^{-4})(1.3\times10^{-5})^3)$

$K_f = 2.95\times10^{14}$

1.5 **a)** For CY_2: $K_{sp} = [C^{2+}] [Y^-]^2 = 2.56\times10^{-13}$

$[Y^-] = ((2.56\times10^{-13}) / 0.05)^{1/2} = 7.16\times10^{-6}$ when CY_2 begins to form

For BY_2: $K_{sp} = [B^{2+}] [Y^-]^2 = 3.20\times10^{-8}$

$[Y^-] = ((3.20\times10^{-8}) / 0.05)^{1/2} = 5.66\times10^{-4}$ when BY_2 begins to form

CY_2 forms first

b) The precipitation of C^{2+} as CY_2 considered to be completed at $[C^{2+}] = 1\times10^{-6}$

Thus $K_{sp} = [C^{2+}] [Y^-]^2 = 2.56 \times 10^{-13}$

and $[Y^-] = ((2.56 \times 10^{-13}) / 10^{-6})^{1/2} = 5.06\times10^{-4}$

It means that $[Y^-] = 5.06\times10^{-4}$ when CY_2 precipitates completely.

When $[Y^-] = 5.06\times10^{-4}$ for BY_2 :

$[B^{2+}] [Y^-]^2 = (0.1) (5.06\times10^{-4})^2 = 2.56\times10^{-8} < K_{sp}$ of BY_2 (3.20×10^{-8})

BY_2 (ppt) can not be formed at $[Y^-] = 5.06\times10^{-4}$ and $[B^{2+}] = 0.1$ when CY_2 precipitates completely.

It means that it is possible to separate B^{2+} and C^{2+} ions by precipitation method with Y^- as a precipitating agent.

THEORETICAL PROBLEM 2

Preparation and Applications of Radioisotopes

Radioisotopes can be used in medical diagnosis and therapy as well as industrial analysis. Many radioisotopes, e.g. ^{32}P (Mass number = 32) and ^{60}Co can be generated by the irradiation of neutrons in a nuclear reactor. However, some radioisotopes in nature, e.g. ^{14}C and ^{3}T (tritium), can be produced by the bombardment of nitrogen ^{14}N atoms in the atmosphere by neutrons in the cosmic ray. (Atomic numbers of T & H, C, N, P, Co and neutron are 1, 6, 7, 15, 27 and 0, respectively. ^{32}P can be denoted as $^{32}_{15}P$).

2.1 Write down the equations for the nuclear reactions for the production of ^{14}C and ^{3}T by the bombardment of nitrogen ^{14}N atoms in the atmosphere with neutrons in the cosmic ray.

Radioisotope ^{14}C can be used as a reagent in ^{14}C dating. The activity (A) in terms of counts per minute (cpm) of the radioisotope ^{14}C is proportional to the number (N) of ^{14}C atoms as follows : [^{14}C Dating]

$$A = \boldsymbol{\varepsilon}\,\boldsymbol{\lambda}\,N \qquad (1)$$

where ε is the detection coefficient of a detector for ^{14}C and λ is the decay constant of ^{14}C. An initial amount (N_o) of ^{14}C can be reduced to the amount (N) of ^{14}C by decay after a given time (t) as follows:

$$N = N_o\, e^{-\lambda t} \qquad (2)$$

The half life ($t_{1/2}$) of ^{14}C is 5730 years which is defined as the time required for 50 % of the number of the radioisotope ^{14}C atoms in a sample to undergo decay, that is $N = 1/2\ N_o$. It is well known that activity (A_o) of ^{14}C in a living animal or plant is kept to be around 16.5 cpm/g of carbon. After the death of the animal or plant, the activity (cpm/g of carbon) of ^{14}C in the body of the living animal or plant is decreased by the time passed.

2.2 Give the equation showing the relation between the original activity (A_o) and final activity (A) as function of time for a living animal or plant.

2.3 The activity of ^{14}C in an ancient wood boat is found to be 10.2 cpm/g of carbon. Calculate the age of the ancient boat.

The radioisotope ^{32}P is a very important leveling reagent for biological research and can be produced by the bombardment of ^{31}P by a neutron in a nuclear reactor. The production rate (R_p) of ^{32}P can be estimated as :

$$R_p = N\,\Phi\,\delta \qquad (3)$$

where N and δ are the number of atoms and neutron capture cross section ($\approx 0.9\times10^{-24}$ cm^2/atom) of ^{31}P, respectively, and Φ is the neutron flux (neutron / (cm^2 sec)) of the nuclear reactor. If the detection efficient (ε) of the detector for ^{32}P is 1.0, the decay rate (R_d) and the activity (A) of ^{32}P in the nuclear reactor can be approximately estimated as a function of the number (N*) of ^{32}P atoms as follows:

$$R_d = N\Phi\,\delta\,(\,e^{-\lambda t}\,) \qquad (4)$$

and

$$A = \boldsymbol{\lambda}\ N^* = R_p - R_d \qquad (5)$$

Where λ is the decay constant of ^{32}P, t is the neutron irradiation time in the nuclear reactor and the half life ($t_{1/2}$) of ^{32}P is 14.3 days.

2.4 A 10 mg sample of pure H_3PO_4 is irradiated by neutrons with a neutron flux of 1.00×10^{13} n cm^{-2}sec^{-1} for one hour in a nuclear reactor. Calculate the activity of the sample in cps (counts / second) and Ci. (Ci = Curie, 1 Ci $\approx 3.7\times10^{10}$ cps, atomic weight: H = 1, P = 31, O = 16)

2.5 The radioisotope ^{32}P can be used to measure the volume of water in a pool or the blood volume of an animal. A 2.0 cm^3 solution of 1.0 Ci/ cm^3 ^{32}P was injected into a pool. After mixing well, the activity of 1.0 cm^3 of water in the pool was found to be 12.4 cps (counts / second). Calculate the volume of water (L) in the pool. (Ci = Curie, 1 Ci $\approx 3.7\times10^{10}$ cps)

SOLUTION OF PREPARATORY PROBLEM 2

2.1 $^{14}_{7}N + ^{1}_{0}n \rightarrow ^{14}_{6}C + ^{1}_{1}H$

$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{12}_{6}C + ^{3}_{1}T$

2.2 $A = \varepsilon\, \lambda\, N$, $A_o = \varepsilon\, \lambda\, N_o$ and $N = N_o\, e^{-\lambda t}$

$A / A_o = N / N_o = e^{-\lambda t}$

and $A = A_o\, e^{-\lambda t}$

2.3 $N = N_o\, e^{-\lambda t}$

If $N = 1/2\ N_o$, $t = \lambda\ t_{1/2}$

then $1/2\ N_o = N_o\, e^{-\lambda t_{1/2}}$

$\lambda = 2.303 \log 0.5 / t_{1/2} = 0.693 / t_{1/2}$

For C-14, $\lambda = 0.693 / 5730 = 1.2\times10^{-4}$

Also $A = A_o\, e^{-\lambda t}$

$10.2 = 16.5\, e^{-1.2 \times 10^{-4} t}$

and t = 4008 years

2.4 $A = R_p - R_d = N\, \Phi\, \delta - N\, \Phi\, \delta\, (e^{-\lambda t}) = N\, \Phi\, \delta\, (1 - e^{-\lambda t})$

and $\lambda = 0.693 / (14.3 \times 24 \times 60 \times 60) = 5.61\times10^{-7}$

$N = [(10\times10^{-3}) / 98] \times 6\times10^{23} = 6.12\times10^{19}$

$A = N\, \Phi\, \delta\, (1 - e^{-\lambda t}) = (6.12\times10^{19})(1.00\times10^{13})(0.9\times10^{-24})(1 - e^{-5.61\times10^{-7}\times 60 \times 60})$

and $A = 1.11\times10^{6}$ cps $= 1.11\times10^{6} / (3.7\times10^{10})$ Ci $= 3\times10^{-5}$ Ci = 0.03 mCi

2.5 Total amount of ^{32}P is constant after and before the injection,

so, $V_o\, A_o = V_x\, A_x$ (V = volume, A = Activity, x for pool water)

$2.0 \times 1.0 = V_x\, (12.4 / (3.7\times10^{10})$

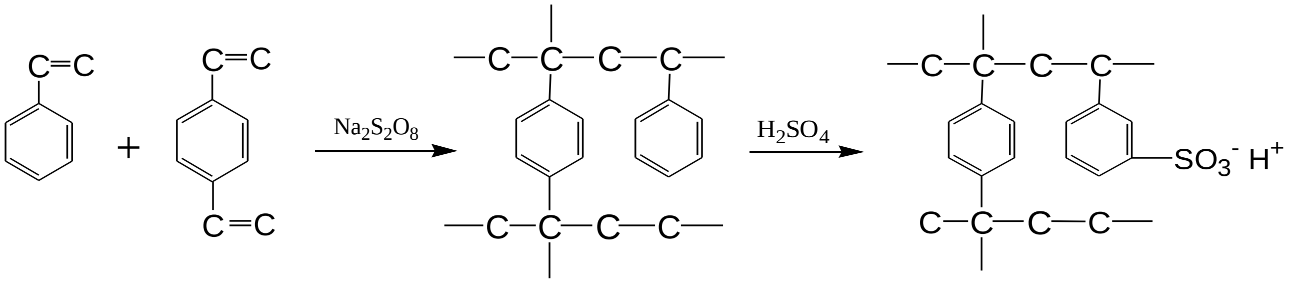
and V_x(pool water) $= 5.97\times10^{9}\ cm^3 = 5.97\times10^{6}\ dm^3$

THEORETICAL PROBLEM 3

Ion Exchangers

Ion exchangers can be employed to adsorb and separate cations and anions. They can be prepared from organic or inorganic materials. An organic, cationic ion exchanger can be synthesized by the polymerization of styrene / divinyl benzene followed by sulfonation with H_2SO_4, as shown in Scheme 1:

Scheme 1



[polymer]

[cationic exchanger]

R^-H^+

Cationic ion exchanger (denoted as R^-H^+) can be employed to adsorb the cations, M^+, the chemical reaction and the equilibrium constant K_c as well as the distribution coefficient K_d can be expressed as follows:

$R^-H^+ + M^+ = RM + H^+$, $K_c = [RM][H^+] / ([M^+][RH])$ (1)

$K_d = [RM] / [M^+]$ (2)

The cationic ion exchanger R^-H^+ can be transformed into the ion exchanger R^-M^+ or R^-M^{z+} by the reaction of R^-H^+ with a metal hydroxide ($M(OH)_z$). The approximate equations are:

$R^-H^+ + MOH = R^-M^+ + H_2O$ (3)

and $z\,R^-H^+ + M(OH)_z = (R^-)_zM^+ + z\,H_2O$ (4)

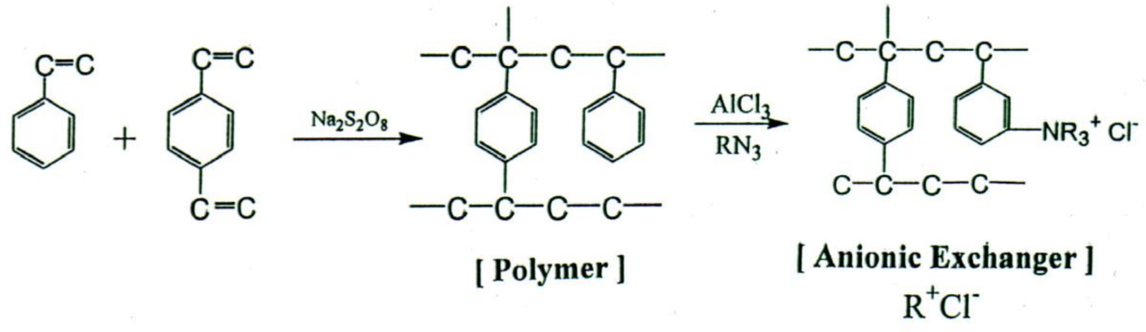
3.1 A cationic ion exchanger R^-Na^+ was employed to remove $CaCl_2$ in tap water, Give the chemical equation for the adsorption of Ca^{2+} by the cationic ion exchanger R^-Na^+.

3.2 Tell how the removal of H^+ from a solution of HCl can be achieved with an anionic ion exchanger if another ion exchanger R^-H^+ is employed instead of R^-Na^+. Give the chemical equation for the process.

(a) Give the chemical equation for the adsorption of Ca^{2+} by the ion exchanger $R^{-}H^{+}$.

(b) Tell which ion exchanger, $R^{-}H^{+}$ or $R^{-}Na^{+}$, is suitable for drinking purpose and give the reason.

An organic, anionic ion exchanger (denoted as $R^{+}Cl^{-}$) can also be synthesized by the polymerization of styrene / divinyl benzene followed by the reaction of the resulting polymer, poly (styrene / divinyl benzene), with the Lewis acid $AlCl_3$ and tertiary amine NR'_3, as shown in Scheme 2:



[Scheme 2]

The anionic ion exchanger $R^{+}OH^{-}$ can be obtained from the chemical reaction of the ion exchanger $R^{+}Cl^{-}$ with a solution of NaOH (c = 3.0 mol dm^{-3}) by the equation:

$$R^{+}Cl^{-} + NaOH \rightarrow R^{+}OH^{-} + NaCl \qquad (5)$$

3.3 Tell how the removal of H^{+} from a solution of HCl can be achieved with an anionic ion exchanger and give the chemical equation for the process.

3.4 Tell how the amount of SO_4^{2-} in tap water can be estimated by using an anionic ion exchanger $R^{+}OH^{-}$. Give all of the chemical equations involved in the process.

The capacity (S) of the cationic ion exchanger $R^{-}H^{+}$ for an adsorbed ion can be expressed in moles of the adsorbed ion per gram of the ion exchanger in 1.0 cm^3 of aqueous solution and can be calculated by using the following equation:

$$S = ([RM] + [RH]) \times 10^{-3} \qquad (6)$$

The capacity (S) of the cationic ion exchanger R^-H^+ for M^+ ions in an aqueous solution can be estimated from the equilibrium constant K_c, the distribution coefficient K_d and the concentrations of M^+ and H^+ ions in the aqueous solution.

3.5 Show that the relationship between K_d, S, K_c, $[M^+]$ and $[H^+]$ as shown by the equation:

1 / Kd = [M+] / (S(103)) + [H+] / (S Kc(103)) (7)

3.6 Ion exchangers can be employed as stationary phase materials in liquid chromatography to adsorb and separate various ions. For example, the anionic ion exchanger R^+OH^- can be used to separate X^- and Y^- ions with the eluent NaOH. The chromatogram for separation of X^- and Y^- ions using a 30 cm of anionic ion exchange column is shown in Figure 1, where t_1, t_2 and t_o are the retention times (t_R) for X^- , Y^- and the pure eluent (NaOH) to traverse the column, respectively. ω_1 and ω_2 are the peak–widths for X^- and Y^-. The number of theoretical plates N and the plate height H (height equivalent of the theoretical plates) of the column can be estimated as shown below:

$$N = 16\,(t_R / \omega)^2 \qquad (8)$$

and

$$H = L / N \qquad (9)$$

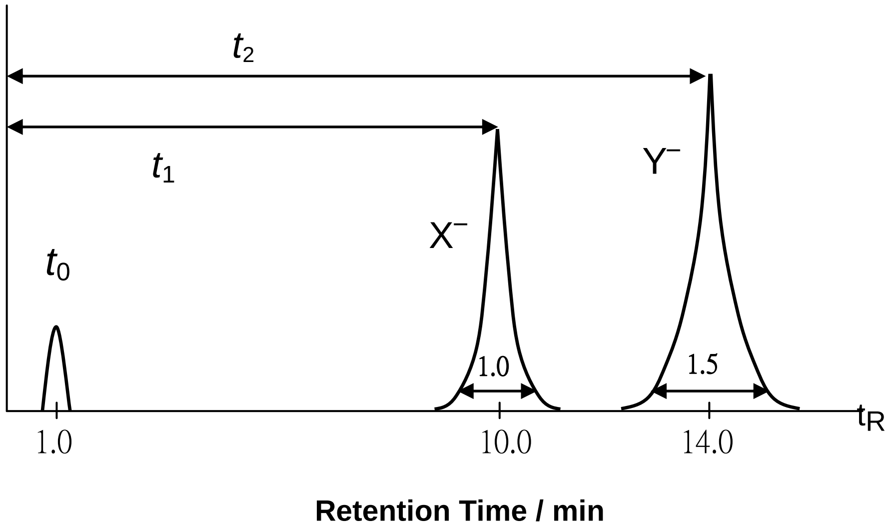


Figure 1. Liquid Chromatogram for X^- and Y^- ions

where L is the length of the column. The resolution (R) of the column and the separation factor (α) for X^- and Y^- also can be estimated using the following equations:

$$R = 2\,(t_2 - t_1) / (\omega_1 + \omega_2) \qquad (10)$$

and

$$\alpha = (t_2 - t_0) / (t_1 - t_0) \qquad (11)$$

3.7 Calculate the average number of theoretical plates N of the column.

3.8 Calculate the plate height H of the column.

3.9 Calculate the resolution (R) of the column for X^- and Y^- ions.

3.10 Calculate the separation factor (α) for X^- and Y^- ions.

Some ion exchangers are derived from inorganic matters. Zeolites $[(M^{z+})(Al_2O_3)_m / (SiO_2)_n]$ (M^{z+} = Na^+, K^+ or Ca^{2+}, Mg^{2+}) are the best known examples of inorganic ion exchangers. Some examples of Zeolites are shown in Figure 2.

A Na^+–Zeolite (denoted as Z–Na^+) with a pore size of 13 Å is an important ion exchanger for the removal of Ca^{2+} or Mg^{2+} ion from tap water. Zeolites with definite pore sizes also behave as highly selective adsorbents for various molecules, e.g. H_2O and iso–butane. Thus, the zeolite can be used as a molecular sieve. The zeolite can also be used as a catalyst by adsorption of a petroleum component, e.g. iso–butane, in petroleum resulting in the enhancement of rate of the cracking of the adsorbed component.

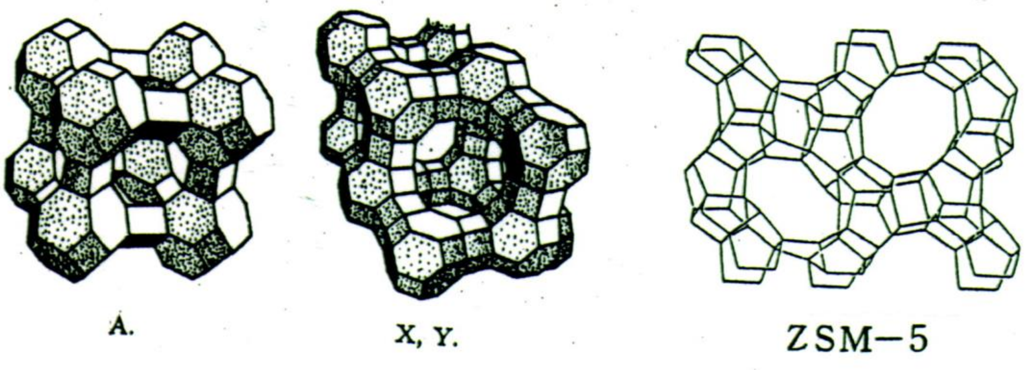


Figure 2. Various types of Zeolites

3.11 Give the chemical equation for the removal of Ca^{2+} ions from tap water with Z–Na^+ zeolite ion exchange column.

3.12 Give the chemical equation for the adsorption of K^+ with Z–Na^+ zeolite**.**

SOLUTION OF PREPARATORY PROBLEM 3

3.1 $2\ R^-Na^+ + Ca^{2+} = 2\ R^-Ca^{2+} + 2\ Na^+$

or $2\ R^-Na^+ + CaCl_2 = (R^-)_2Ca^{2+} + 2\ NaCl$

3.2 **a)** The tap water contains trace HCl after the adsorption of Ca^{2+} by the ion exchanger R^-H^+ and the chemical equation of the adsorption is:

$$2\ R^-H^+ + Ca^{2+} \rightarrow (R^-)_2Ca^{2+} + 2\ H^+$$

or $2\ R^-H^+ + CaCl_2 \rightarrow (R^-)_2Ca^{2+} + 2\ HCl$

b) R^-Na^+ is suitable for drinking purpose because the product of the adsorption of Ca^{2+} by R^-Na^+ is Na^+ or NaCl while the product is H^+ or HCl after the adsorption of Ca^{2+} by R^-H^+.

3.3 The removal of H^+ can be achieved by using the anionic ion exchanger R^+OH^- with the equation:

$$R^+OH^- + HCl \rightarrow R^+Cl^- + H_2O$$

3.4 Firstly, the anionic ion exchanger R^+OH^- is used to adsorb the SO_4^{2-} ion with the equation :

$$2\ R^+OH^- + SO_4^{2-} \rightarrow (R^+)_2SO_4^{2-} + 2\ OH^-$$

Secondly, a standard solution of HCl can be used for the titration of the OH^- in the solution after adsorption of SO_4^{2-} by the anionic ion exchanger R^+OH^-.

$H^+ + OH^- \rightarrow H_2O$ (acid–base titration)

3.5 Firstly, the anionic ion exchanger R^+OH^- is used to adsorb the SO_4^{2-} ion with the equation :

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$H^+ + OH^- \rightarrow H_2O$ (acid–base titration)

3.6 $R^-H^+ + M^+ \rightarrow RM + H^+$, $K_c = [RM][H^+] / ([M^+][RH])$ (3.1)

$K_d = [RM] / [M^+]$ (3.2)

$S = ([RM] + [RH]) \times 10^{-3}$ (3.3)

We substitute Equations (3.1) and (3.2) into Equation (3.3) and obtain:

$S = (K_d\ [M^+] + [RM][H^+] / K_c [M^+]) \times 10^{-3}$

$= (K_d\ [M^+] + K_d\ [M^+] [H^+] / K_c [M^+]) \times 10^{-3}$

$= (K_d [M^+] + K_d\ [H^+] / \mathrm{Kc}) \times 10^{-3}$

$S\ K_c\ 10^3 = K_d\ K_c\ [M^+] + K_d\ [H^+]$

$1 / K_d = [M^+] / (S(10^3)) + [H^+] / (S\ K_c\ (10^3))$ (3.4)

3.7 $N_1 = 16\ (t_1 / \omega_1)^2 = 16\ (10 / 1.0)^2 = 1600$

$N_2 = 16\ (t_2 / \omega_2)^2 = 16\ (14 / 1.5)^2 = 1394$

$N = (N_1 + N_2) / 2 = (1600 + 1394) / 2 = 1497$

3.8 $H = L / N = 30 / 1497 = 0.021$ cm

3.9 $R = 2\ (t_2 - t_1) / (\omega_1 + \omega_2) = 2\ (14 - 10) / (1.0 + 1.5) = 3.2$

3.10 $\alpha = (t_2 - t_0) / (t_1 - t_0) = (14 - 1) / (10 - 1) = 1.44$

3.11 $Z–Na^+ + Ca^{2+} = Z–Ca^{2+} + Na^+$

3.12 $Z–Na^+ + K^+ = Z–K^+ + Na^+$

THEORETICAL PROBLEM 4

Determination of Calcium Ion by Precipitation Followed by Redox Titration

The calcium content of an aqueous sample can be determined by the following procedure:

Step 1 A few drops of methyl red are added to the acidified aqueous sample, followed by thorough mixing with $Na_2C_2O_4$ solution.

Step 2 Urea ($(NH_2)_2CO$) is added and the solution gently boil until the indicator turns yellow (this typically takes 15 min). CaC_2O_4 precipitates out.

Step 3 The hot solution is filtered and the solid CaC_2O_4 is washed with ice-cold water to remove excess $C_2O_4^{2-}$ ions.

Step 4 The insoluble CaC_2O_4 is dissolved in hot H_2SO_4 (c = 0.1 mol dm^{-3}) to give Ca^{2+} ions and $H_2C_2O_4$. The dissolved $H_2C_2O_4$ is titrated with standardized $KMnO_4$ solution until the purple end point is observed.

Relevant reactions and equilibrium constants:

$CaC_2O_4(s) \leftrightarrows Ca^{2+}(aq) + C_2O_4^{2-}(aq)$ $K_{sp} = 1.30\times10^{-8}$

$Ca(OH)_2(s) \leftrightarrows Ca^{2+}(aq) + 2\ OH^{-}(aq)$ $K_{sp} = 6.50\times10^{-6}$

$H_2C_2O_4(aq) \leftrightarrows HC_2O_4^{-}(aq) + H^{+}(aq)$ $K_{a1} = 5.60\times10^{-2}$

$HC_2O_4^{-}(aq) \leftrightarrows C_2O_4^{2-}(aq) + H^{+}(aq)$ $K_{a2} = 5.42\times10^{-5}$

$H_2O \leftrightarrows H^{+}(aq) + OH^{-}(aq)$ $K_w = 1.00\times10^{-14}$

4.1 Write a balanced equation for the reaction that takes place upon the addition of urea (Step 2).

4.2 The calcium content of a 25.00 cm^3 aqueous sample was determined using the above procedure and found to require 27.41 cm^3 of a $KMnO_4$ solution ($c = 2.50\times10^{-3}$ mol dm^{-3} in the final step. Find the concentration of Ca^{2+} ions in the sample.

4.3 Calculate the solubility of CaC_2O_4 in an aqueous solution buffered at pH 4.0. (Neglect activity coefficients.)

In the above analysis a possible source of error was neglected. The precipitation of CaC_2O_4 in Step 1 will be incomplete if an excess of $C_2O_4^{2-}$ ions is added, due to the following reactions:

$$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightarrow CaC_2O_4(s) \qquad K_{f1} = 1.0\times10^{3}$$

$$CaC_2O_{4(aq)} + C_2O_4^{2-}{}_{(aq)} \rightarrow Ca(C_2O_4)_2^{2-}{}_{(aq)} \qquad K_{f2} = 10$$

4.4 Calculate the equilibrium concentrations of Ca^{2+} and $C_2O_4^{2-}$ ions in solution after optimal precipitation of CaC_2O_4 is reached.

4.5 Calculate the concentrations of H^+ and Ca^{2+} in a saturated solution of CaC_2O_4. (Neglect activity coefficients. Any assumptions made during calculation must be clearly stated.)

SOLUTION OF PREPARATORY PROBLEM 4

4.1 $(NH_2)_2CO + H_2O \xrightarrow{\Delta} CO_2 + 2\ NH_3$

4.2 Titration reaction: $5\ H_2C_2O_4 + 2\ MnO_4^- + 6\ H^+ \rightarrow 10\ CO_2 + 2\ Mn^{2+} + 8\ H_2O$

$c(Ca^{2+}) = 2.5\times10^{-3}$ mol dm^{-3} × (0.02741 dm^3 × $\frac{5}{2}$ / 0.025 dm^3) = 6.85×10^{-3} mol dm^{-3}

4.3 Mass–balance:

$[Ca^{2+}] = [C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4] = [C_2O_4^{2-}]\ (1 + [H^+] / K_2 + [H^+]^2 / K_1K_2)$

$[C_2O_4^{2-}] = [Ca^{2+}] / (1 + [H^+] / K_2 + [H^+]^2 / K_1K_2)$ (1)

Substituting (1) into $[Ca^{2+}]\ [C_2O_4^{2-}] = K_{sp}$

$[Ca^{2+}] = 1.92\times10^{-4}$

4.4 $c_{Ca} = [Ca^{2+}] + [CaC_2O_{4(aq)}] + [Ca(C_2O_4)_2^{2-}]$

$$= K_{sp}\left(\frac{1}{[C_2O_4^{2-}]} + K_{f1} + K_{f1}K_{f2}[C_2O_4^{2-}]\right)$$

$$\frac{d\,C_{Ca}}{d[C_2O_4^{2-}]} = 0 = -K_{sp}\frac{1}{[C_2O_4^{2-}]^2} + K_{sp}K_{f1}K_{f2}$$

$[C_2O_4^{2-}] = 1.0\times10^{-2}$

$[Ca^{2+}] = K_{sp} / [C_2O_4^{2-}] = 1.3\times10^{-6}$

4.5 Charge balance: $2\ [Ca^{2+}] + [H^+] = 2\ [C_2O_4^{2-}] + [HC_2O_4^-] + [OH^-]$ (1)

Mass balance: $[Ca^{2+}] = [C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4]$ (2)

Because K_{b2} is too small, $[H_2C_2O_4]$ can be neglected.

Comparing (1), (2), $[HC_2O_4^-] = K_w / [H^+] - [H^+]$ (3)

$[C_2O_4^{2-}] = (K_2 K_w) / [H^+]^2 - K_2$ (4)

$[Ca^{2+}] = K_{sp} / [C_2O_4^{2-}] = K_{sp}[H^+]^2 / (K_2K_w - K_2[H^+]^2)$ (5)

Substituting (3), (4), (5) into (2)

$$K_2[H^+]^5 + (K_2^2 - K_{sp})[H^+]^4 - 2K_2K_w[H^+]^3 - 2K_2^2K_w[H^+]^2 + K_2K_w^2[H^+] + K_2^2K_w^2 = 0$$

Solving $[H^+]$, $[H^+] = 5.5\times10^{-8}$ (or pH = 7.26)

Substituting $[H^+]$ into (5), $[Ca^{2+}] = 1.04\times10^{-4}$

THEORETICAL PROBLEM 5

Nitrogen in Wastewater

In natural water and waste water, the forms of nitrogen of greatest interest are nitrate, nitrite, ammonia, and organic nitrogen. All these forms of nitrogen, as well as nitrogen gas, are biochemically interconvertible and are components of the nitrogen cycle. The macro Kjeldahl method, in combination with a titration method, is often used in the determination of organic nitrogen in wastewater. In the first step, H_2SO_4, K_2SO_4, and $HgSO_4$ are added to the sample solution. After digestion, the solution is neutralized by the addition of concentrated NaOH. The gas liberated by the treatment is then distilled into a solution of excess boric acid and the latter subsequently titrated with 0.01 M-H_2SO_4.

5.1 Identify the product formed in the digestion step.

5.2 Identify the gas liberated upon the addition of NaOH.

5.3 Write a balanced equation for the reaction between the liberated gas and boric acid.

5.4 Write a balanced equation for the final titration step.

5.5 Which of the following indicators is most suitable to be used in the final titration step:
Methyl orange (transition range pH 3.1 – 4.4), phenolphthalein (transition range pH 8.0 – 9.6) is chosen as the indicator. Explain your choice.

Nitrite is known to cause the illness methemoglobinemia in infants. In the laboratory, nitrite can be determined by a colorimetric method. The method requires the preparation of a series of standard nitrite solutions. However, nitrite is readily oxidized in the presence of moisture and hence standardization of the stock nitrite solution is required in order to achieve high accuracy in the subsequent analysis. The standardization is carried out by adding a known excess of standard $KMnO_4$ solution and H_2SO_4 solution are added into the nitrite stock solution. The purple color of the solution due to the presence of excess permanganate was subsequently discharged by the addition of a known quantity of $Na_2C_2O_4$ and the mixture back titrated with standard permanganate solution.

5.6 Write a balanced equation for the reaction of the nitrite solution with $KMnO_4$.

5.7 Write a balanced equation for the back titration.

5.8 Write a mathematical equation for calculation of nitrogen concentration if:

A: mg of N in cm^3 of $NaNO_2$ stock solution

B: total volume (cm^3) of standard $KMnO_4$ solution used

C: concentration of $KMnO_4$ in the standard solution in mol dm^{-3}

D: total volume (cm^3) of standard $Na_2C_2O_4$ solution

E: concentration of $Na_2C_2O_4$ in the standard solution in mol dm^{-3}

F: volume of the stock $NaNO_2$ solution taken for titration

SOLUTION OF PREPARATORY PROBLEM 5

5.1 NH_4^+

5.2 NH_3

5.3 $H_3BO_3 + NH_3 \rightarrow NH_4^+ + H_2BO_3^-$

5.4 $H_2BO_3^- + H_3O^+ \rightarrow H_3BO_3 + H_2O$

5.5 Methyl orange. At the equivalence point, the solution contains boric acid and ammonium ion, therefore, an indicator with an acidic transition interval is required.

5.6 $2\ MnO_4^- + 5\ HNO_2 + H^+ \rightarrow 2\ Mn^{2+} + 5\ NO_3^- + 3\ H_2O$

5.7 $2\ MnO_4^- + 5\ H_2C_2O_4 + 6\ H^+ \rightarrow 2\ Mn^{2+} + 10\ CO_2 + 8\ H_2O$

5.8 $A = [\ 5\ (\ B \times C) - 2\ (\ D \times E\ )\ ] \times 7\ /\ F$

THEORETICAL PROBLEM 6

Use of Isotopes in Mass Spectrometry

Many elements in the periodic table have more than one isotope. The atomic mass of an element is calculated based on the relative abundance of the isotopes. As an example, the atomic mass of chlorine is about 35.5 because the abundance of ^{35}Cl is about three times the abundance of ^{37}Cl. In mass spectrometry, instead of average atomic mass, the isotope peaks are observed. (^{35}Cl 75.77%, ^{37}Cl 24.23%, ^{12}C 98.9%, ^{13}C 1.1%, ^{79}Br 50.7%, ^{81}Br 49.3%)

Isotopes are quite useful in quantitative mass spectrometry.

6.1 In addition to the retention time (migration time), the ratio of M and M^{2+} ions was used as the qualitative criteria in the analysis of 2,3,7,8, tetra chlorinated dioxin (2,3,7,8–TCDD) by gas chromatography / mass spectrometry. Calculate the theoretical ratio of the two ions. The intensities of the isotopic species can be found by applying the following formula: $(a+b)^n$, where a is the relative abundance of the light isotope, b is the relative abundance of the heavy isotope, and n is the number of chlorine atoms present.

6.2 Molecular ion is often selected in quantitative analysis. The intensity of the molecular ion needs to be corrected if the signal is interfered by other compounds. In the analysis of a non-halogenated compound with a molecular mass of 136, the molecular ion was selected for quantitative analysis. Propose a mathematical equation for calculation the corrected signal, if the analyte co-elutes (same migration time) with the compound n–butyl bromide.

SOLUTION OF PREPARATORY PROBLEM 6

6.1 0.77

6.2 Corrected signal = (m/z 136 signal) – 1.03 (m/z 138 signal)

TEORETICAL PROBLEM 7

Atomic Orbitals

One way to describe the shape of atomic orbitals of H–atom is in terms of the nodal surfaces, or nodes, where the electron has zero probability. According to wave mechanics, the number of nodes increases as n increases. For given set of orbitals nlm, there are "n – l – 1" spherical nodes, "l" angular nodes.

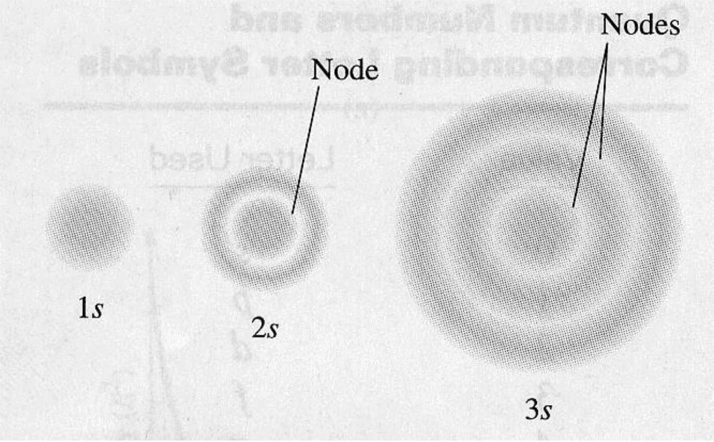
7.1 Describe the electron probability distribution for the 1s, 2s and 3s orbitals. How many nodes does each orbital have, respectively?

7.2 Describe the electron probability distribution for the $2p_z$ and $3p_z$ orbitals. How many nodes does each orbital have, respectively?

7.3 Imagine that you are travelling along the z axis, beginning your journey at a distance far from the nucleus on the z axis, passing through the nucleus to a distant point on the –z axis. How many nodal surfaces would you pass through for each of the following orbitals: 1s, 2s, 3s, $2p_z$ and $3p_z$.

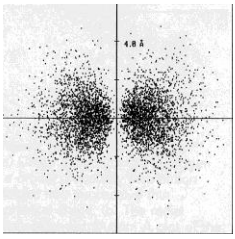
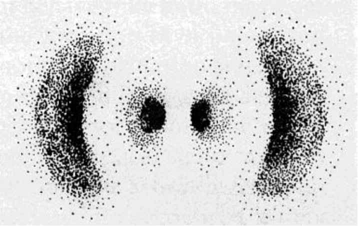
SOLUTION OF PREPARATORY PROBLEM 7

7.1



1s: 0, 2s: 1 and 3s: 2.

7.2

$2p_z$  , $3p_z$ 

There is one angular node for $2p_z$; one angular node and one spherical node for $3p_z$.

7.3 (0, 2, 4, 1, 3)

THEORETICAL PROBLEM 8

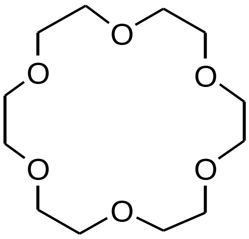
Intermolecular Forces

***I**ntermolecular* forces occur between, rather than within, molecules. Ion – dipole interaction and dipole – dipole interaction are two common types of intermolecular forces.

Part 1: Ion–Dipole Interactions

The bonding of an ion, such as Na^+, with a polar molecule, such as water, is an example of an ion–dipole interaction. Shown below are a sodium ion, a water molecule, and a crown ether compound.

Na^+ H_2O



8.1 Draw the geometrical structure of the product resulting from the interaction between the sodium ion and water molecules.

8.2 Draw a diagram showing the interaction between the sodium ion and the crown ether molecule.

Part 2: Dipole–Dipole Interactions

A hydrogen bond may be regarded as a particular kind of dipole–dipole interaction. Strong hydrogen bonding forces are seen among molecules in which hydrogen is bound to a highly electronegative atom, such as nitrogen, oxygen, or fluorine.

$$^{\delta-}O–H^{\delta+}\cdots N^{\delta-}$$

Compared to other intermolecular forces, hydrogen bonds are relatively strong; their energies are of the order of 15 to 40 kJ mol^{-1}. Hydrogen bonding is so strong that, in some cases, it survives even in a vapor.

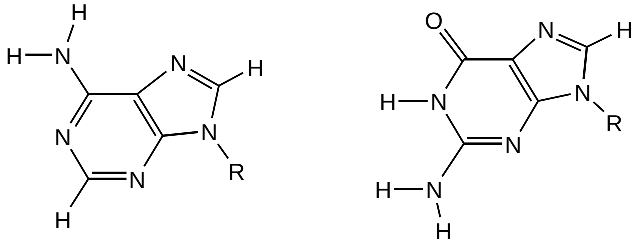
8.3 In gaseous hydrogen fluoride, many of the HF molecules are associated into $(HF)_6$. Draw the structure of this hexamer.

8.4 Draw a diagram showing the hydrogen–bonding interactions between two acetic acid (CH_3CO_2H) molecules.

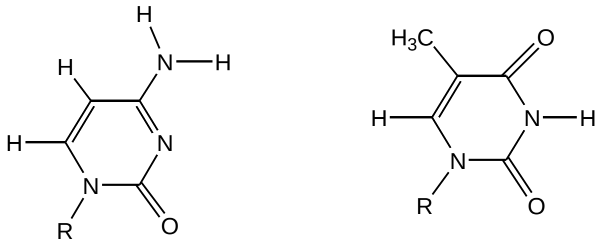
Part 3: Hydrogen–bonding in Living Matter

Some chemical reactions in living matter involve complex structures such as proteins and DNA, and in these reactions certain bonds must be easily broken and reformed. Hydrogen bonding is the only type of bonding with energies of just the right magnitude to allow this.

The key to DNA's functioning is its double–helical structure with complementary bases on the two strands. The bases form hydrogen bonds to each other.



Adenine (A) Guanine (G)



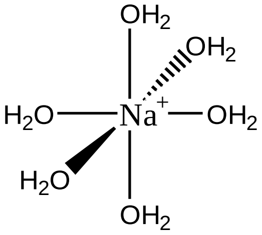
Cytosine (C) Thymine (T)

The organic bases found in DNA

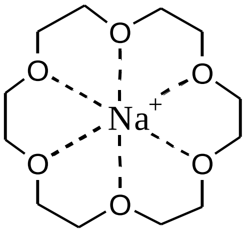
8.5 There are two kinds of hydrogen–bonded base pairs, T–A and G–C, in DNA. Draw these two base pairs, showing the hydrogen–bonding interactions.

SOLUTION OF PREPARATORY PROBLEM 8

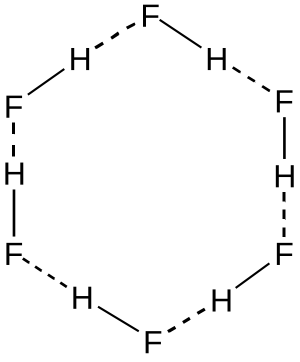
8.1



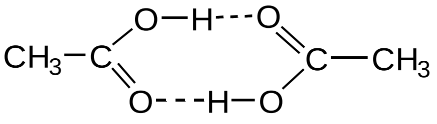
8.2



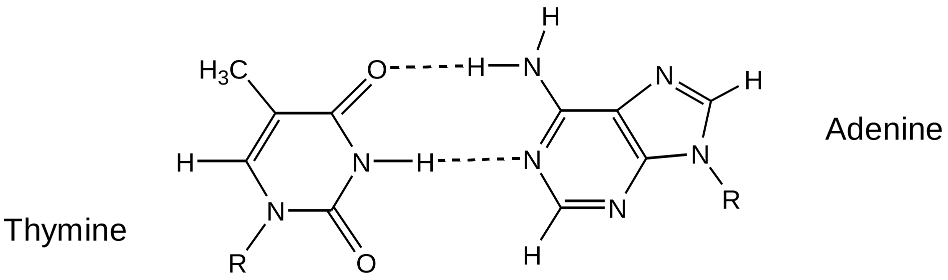
8.3

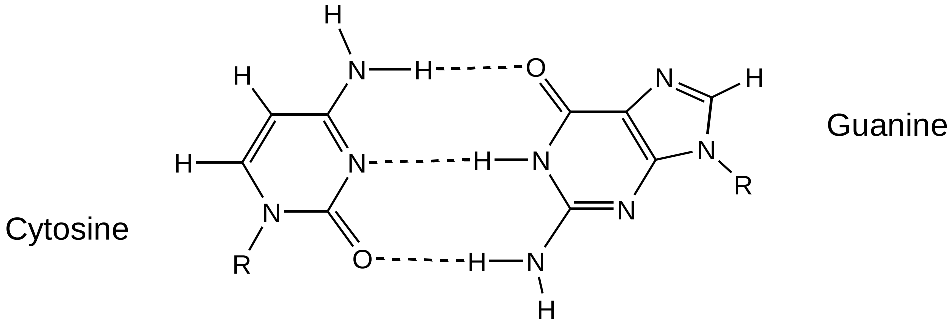


8.4



8.5

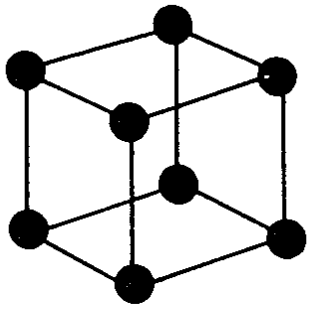



Cytosine
Guanine
H
N
O
R

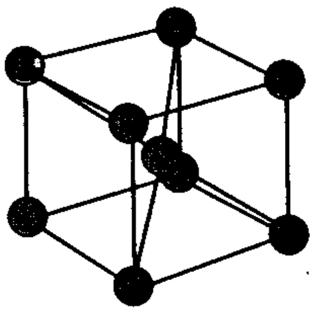
THEORETICAL PROBLEM 9

Crystal Packing

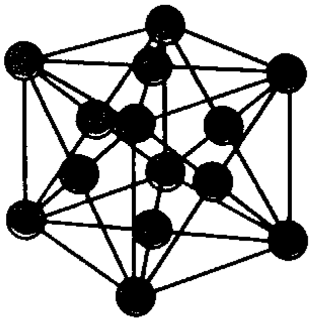
There are three cubic unit cells for the atomic solids, namely, simple cubic, body–centered cubic and face–centered cubic. They are illustrated in the following figures:



Simple cubic



Body-centered cubic



Face-centered cubic

9.1 How many nearest neighbour atoms are in each packing, respectively?

9.2 In each packing, the packing efficiency is defined by

$$f_{\mathrm{v}} = \frac{\text{volume occupied by spheres in the unit cell}}{\text{volume of the unit cell}}$$

What is the value of f_{v} in each type of packing, respectively?

9.3 Silver crystallizes in a cubic closest packed structure, i.e. face–centered cubic. The radius of a silver atom is 144 pm. Calculate the density of silver.

9.4 X–ray diffraction is commonly used for the determination of crystal structures. In one such determination, the emitted X rays were diffracted by a LiF crystal (d = 201 pm), and the first–order diffraction was detected at an angle of 34.68°. Calculate the wavelength of the X–ray emitted by the metal.

SOLUTION OF PREPARATORY PROBLEM 9

9.1 Simple cubic: 6, body–centred cubic: 8 and face–centred cubic: 12

9.2 For simple cubic, $a = 2\,r$, $f_\text{v} = \dfrac{\frac{4}{3}\pi\, r^3}{a^3} = 52.4\,\%$

For body–centred cubic, $\sqrt{3}\,a = 4\,r$, $f_\text{v} = \dfrac{2\times\frac{4}{3}\pi\, r^3}{a^3} = 68\,\%$

For face–centred cubic, $\sqrt{2}\,a = 4\,r$, $f_\text{v} = \dfrac{4\times\frac{4}{3}\pi\, r^3}{a^3} = 74\,\%$

9.3 $\sqrt{2}\,a = 4\,r$, $a = 2\sqrt{2}\,r = 407\,\text{pm}$

$$d = \frac{4\times\dfrac{107.9}{6.02\times10^{23}}}{(407\,\text{pm})^3} = 10.6\ \text{g cm}^{-3}$$

9.4

$2d\ \sin\theta = \lambda$

$\lambda = 2\times 201\times \sin 17.34^\text{o} = 229\,\text{pm}$

THEORETICAL PROBLEM 10

Applications of Transition Metals

The transition metal elements are widely distributed in the Earth's crust. Many of these elements find uses in everyday objects: iron pipes, copper wiring, chromium auto parts, etc.

Part 1: Properties of Chromium

Chromium is a silvery–white, lustrous metal, whose name (from the Greek chroma, meaning color) alludes to its many colorful compounds. The bright colors of chromium (VI) compounds lead to their use in pigments for artists paints and ceramic glazes.

10.1 In an acidic solution, the yellow chromate ion (CrO_4^{2-}) changes into the orange dichromate ion ($Cr_2O_7^{2-}$). Write the equation for the reaction.

10.2 What is the oxidation state of each metal center in the chromate ion and the dichromate ion?

10.3 Is this a redox reaction? Explain.

10.4 What is the main factor that controls the equilibrium position?

10.5 Draw the three–dimensional structures of CrO_4^{2-} and $Cr_2O_7^{2-}$.

Part 2: Uses of Chromium

An antique automobile bumper is to be chrome plated. The bumper is dipped into an acidic $Cr_2O_7^{2-}$ solution where it serves as the cathode of an electrolytic cell. (The relative atomic mass of Cr is 51.996; 1 F = 96485 C.)

10.6 Given that oxidation of H_2O occurs at the anode, write equation for the two half–reactions and the overall cell reaction.

10.7 How many moles of oxygen gas will be evolved for every 52.0 g of chromium deposited?

10.8 If the current is 10.0 amperes, how long will it take to deposit 52.0 g of chromium onto the bumper?

10.9 What is the chemical reason that chromium is so useful for decorative plating on metals?

SOLUTION OF PREPARATORY PROBLEM 10

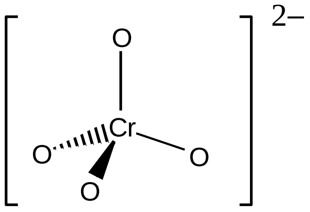
10.1 $2\ CrO_4^{2-}(aq) + 2\ H^+(aq) \rightleftarrows Cr_2O_7^{2-}(aq) + H_2O(l)$

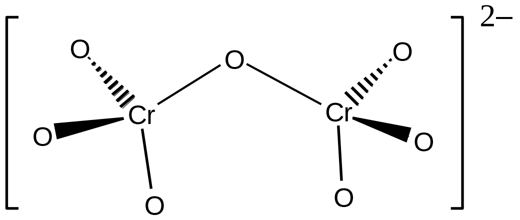
10.2 CrO_4^{2-}: VI, $Cr_2O_7^{2-}$: VI.

10.3 This is not a redox reaction because the oxidation state in each metal centre does not change.

10.4 Hydrogen ion concentration is the main factor to control the equilibrium position.

10.5





10.6 Cathode: $Cr_2O_7^{2-} + 14\ H^+ + 12\ e^- \rightarrow 2\ Cr + 7\ H_2O$

Anode: $2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$

Overall: $Cr_2O_7^{2-}(aq) + 2\ H^+(aq) \rightarrow 2\ Cr(s) + H_2O(l) + 3\ O_2\ (g)$

10.7 $52\ \text{g Cr} \times \dfrac{1\ \text{mol}}{52\ \text{g}} \times \dfrac{3\ \text{mol}\ O_2}{2\ \text{mol Cr}} = 1.5\ \text{mol}\ O_2$

1.5 mol of oxygen gas will evolve.

10.8 $52\ \text{Cr} \times \dfrac{1\ \text{mol Cr}}{52\ \text{g}} \times \dfrac{6\ \text{F}}{\text{mol Cr}} \times \dfrac{96485\ \text{C}}{1\ \text{F}} \times \dfrac{1\ \text{sec}}{10\ \text{C}} \times \dfrac{1\ \text{min}}{60\ \text{sec}} \times \dfrac{1\ \text{h}}{60\ \text{min}} = 16\ \text{h}$

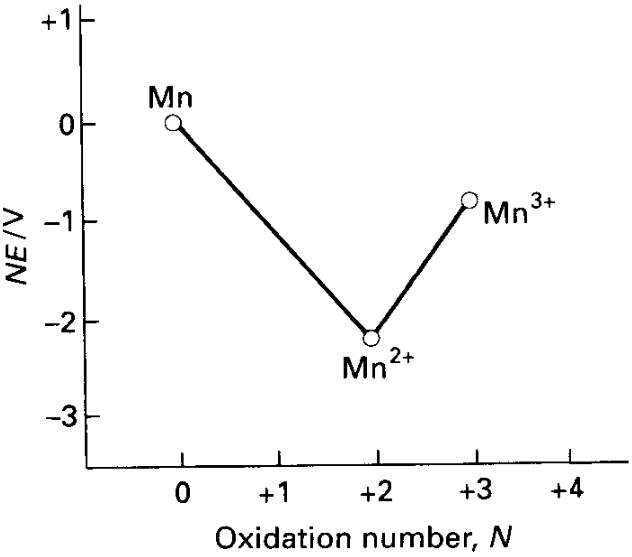
10.9 Chromium readily forms a thin, adherent, transparent coating of Cr_2O_3 in air, making the metal extremely useful as an attractive protective coating on easily corroded metals.

THEORETICAL PROBLEM 11

Electrochemistry of Inorganic Compounds

Some inorganic compounds exhibit a variety of oxidation states, for example, many Mn compounds are known with oxidation states ranging from 0 to VII. The standard reduction potential of a half reaction is measured against the hydrogen electrode. In this problem, the reduction $Mn^{2+} + 2\ e^{-} \rightarrow Mn$, $E° = –1.18$ V is expressed as Mn^{2+} (–1.18) Mn. For Mn in acidic solution the reduction series: $Mn^{3+} \rightarrow Mn^{2+} \rightarrow Mn$ can be represented as follows: Mn^{3+} (1.5) Mn^{2+} (–1.18) Mn

A redox reaction takes place spontaneously if the redox potential is positive. A Frost diagram, a plot of n$E°$ (n is the number of electron transferred in the half reaction) of the reduction couple X(N) / X(0) against the oxidation number, N, of the element, is used to indicate the most stable species of the compounds in different oxidation states. The Frost diagram of Mn^{3+} / Mn^{2+} / Mn is shown below.



11.1 The reduction potential depends on the concentration of the species in solution. The K_{sp} of $MnCO_3$ is 1.8×10^{-11}. Use the Nernst equation to determine the potential at 25°C for the voltaic cell consisting of Mn(*s*) | Mn^{2+}(*aq*) (1 M) || Mn^{2+}(*aq*) / $MnCO_3$ | Mn(*s*), if the concentration of Mn^{2+} in the right hand side of the cell is 1.0×10^{-8} mol dm^{-3}.

11.2 For oxygen, the standard reduction potential in acidic solution can be represented as: O_2 (0.70) H_2O_2 (1.76) H_2O. Construct the Frost diagram for oxygen, and use the information contained in the diagram to calculate the reduction potential of the half reaction for reduction of O_2 to H_2O. Could H_2O_2 undergo disproportionation spontaneously?

Xenon difluoride can be made by placing a vigorously dried flask containing xenon gas and fluorine gas in the sunlight. The half–reaction for the reduction of XeF_2 is shown below:

$XeF_2(aq) + 2\ H^+(aq) + 2e^- \rightarrow Xe(g) + 2\ HF(aq) \quad E° = 2.32\ V$

11.3 Use the VSEPR model to predict the number of electron–pairs and molecular geometry of XeF_2. Show that XeF_2 decomposes in aqueous solution, producing O_2, and calculate the E^o for the reaction. Would you expect this decomposition to be favoured in an acidic or a basic solution? Explain.

$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^- \quad E^o = -1.23\ V$

SOLUTION OF PREPARATORY PROBLEM 11

11.1 For the concentration cell: Mn(s) | Mn^{2+}(aq) (1M) || Mn^{2+}(aq) / $MnCO_3$ | Mn(s), (M = mol dm^{-3})

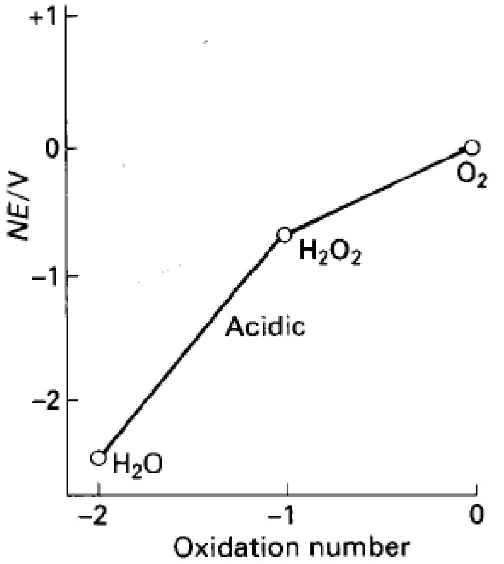
$E_{cell} = E^o - (0.0592 / 2) \log ([Mn^{2+}]_{right} / [Mn^{2+}]_{left})$

$K_{sp} = 1.8\times10^{-11} = [Mn^{2+}][CO_3^{2-}]$

$[Mn^{2+}]_{right} = 1.0\times10^{-8}$ and $[Mn^{2+}]_{left} = 1.0$ with $E^o = 0.0$ V (both are Mn)

$E_{cell} = 0.0 - (0.0592 / 2) \log (1.0\times10^{-8} / 1.0) = 0.237$ V

11.2



Reduction of O_2 to H_2O is obtained as (0.70 V + 1.76 V) / 2 = 1.23 V,

for $O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O$ $E^o = 1.23$ V

The E^o value could be obtained directly from the diagram by dividing the differences (2.46) of O_2 and H_2O by the differences of the oxidation number (2).

For $H_2O_2 \rightarrow O_2 + H_2O$ $E^o = 1.06 > 0.0$

The disproportionation reaction is spontaneous.

11.3 The number of electron pair should be 5 (trigonal bipyramidal) with three electron pairs in the equatorial plane, thus the molecular geometry of XeF_2 is linear.

$2 H_2O \rightarrow O_2 + 4 H^+ + 4 e^-$ $E^o = -1.23$ V

$XeF_2(aq) + 2 H^+(aq) + 2 e^- \rightarrow Xe(g) + 2 HF(aq)$ $E° = 2.32$ V

$2 XeF_2(aq) + 2 H^+(aq) + 2 H_2O \rightarrow 2 Xe(g) + O_2 + 4 HF(aq)$ $E° = 1.09$ V

The decomposition of XeF_2 in aqueous solution is favoured in acidic solution.

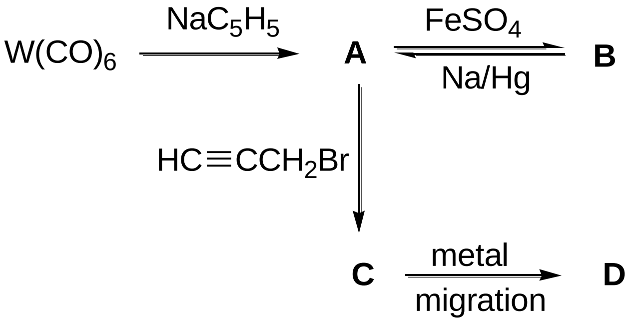
THEORETICAL PROBLEM 12

Metal Carbonyl Compounds

Carbon monoxide, as a two electron donor ligand, coordinates to transition metals to form metal carbonyl compounds. For example, iron forms the pentacarbonyl metal complex, $Fe(CO)_5$. Nickel tetracarbonyl, $Ni(CO)_4$, has been used for the purification of Ni metal in the Mond process. Electron counts of these metal carbonyl complexes show that they obey the 18-electron rule. Cobalt and manganese react with CO to form dinuclear complexes $Co_2(CO)_8$ and $Mn_2(CO)_{10}$, respectively. (Electronic configuration of Mn is $[Ar](3d)^5(4s)^2$) A metal–metal bond between the metal centres is considered essential in order for the compounds to obey the 18 electron rule. The cyclopentadienyl anion $C_5H_5^-$ has also been widely used as a η^5–ligand. For example, ferrocene $(C_5H_5)_2Fe$, a classical compound, obeys the 18 electron rule.

The reaction of $W(CO)_6$ with sodium cyclopentadienide NaC_5H_5 yields an air sensitive compound **A**. Oxidation of **A** with $FeSO_4$ yields compound **B**. Compound **A** can also be prepared from the reaction of **B** with Na/Hg, a strong reducing agent. In the 1600 – 2300 cm^{-1} region of the IR spectrum, **A** shows absorption bands at 1744 and 1894 cm^{-1} and **B** absorption bands at 1904, and 2010 cm^{-1}. Compound **A** is a strong nucleophile and a good starting material for the synthesis of organometallic compounds containing metal–carbon bonds. The reaction of **A** with propargyl bromide ($HC\equiv CCH_2Br$) gives compound **C** containing a metal–carbon σ–bond. At room temperature compound **C** undergoes a transformation to yield compound **D**. The same chemical composition was found for compounds **C** and **D**. The chemical shifts (δ) of the CH_2 and CH resonances and coupling constants $J_{H–H}$ of propargyl bromide, **C** and **D** in the respective ^1H NMR spectra are listed in the following table.

^1H NMR	$HC\equiv CCH_2Br$	**C**	**D**
δ (CH_2)	3.86	1.90	4.16
δ (CH)	2.51	1.99	5.49
JH–H (Hz)	2.7	2.8	6.7



12.1 Explain the differences in the IR spectra of **A** and **B**.

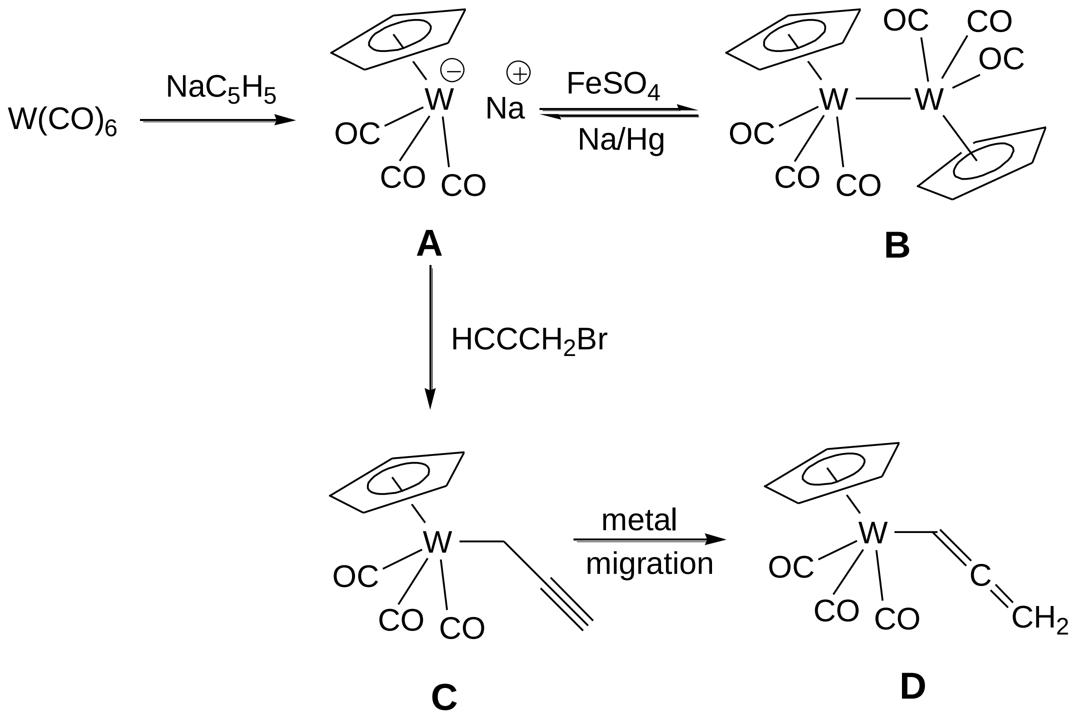
12.2 Draw chemical structures for **A**, **B**, **C** and **D**.

12.3 The transformation of **C** to **D** involves a migration of the metal on the propargyl ligand. If $DC{\equiv}CCH_2Br$ is used for the synthesis of **C**, draw the structures of **C** and **D**.

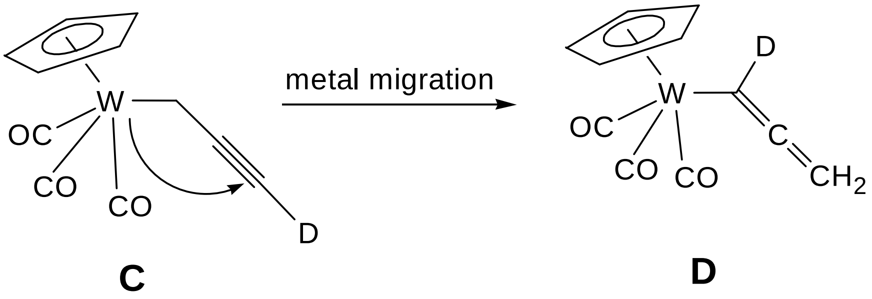
SOLUTION OF PREPARATORY PROBLEM 12

12.1 Compound A is anionic, the absorption bands attributed to CO stretching appear at lower frequency because of stronger back donation of the anionic charge to the anti bonding orbital of CO thus weakening the CO bond. For the neutral species **B**, absorption bands appear at the higher frequency.

12.2



12.3

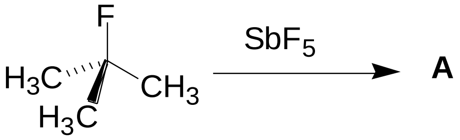


THEORETICAL PROBLEM 13

Carbocations and Aromaticity

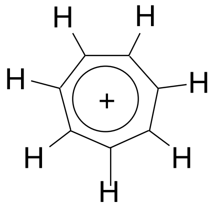
Carbocations are reactive intermediates having a charge of +1 on the central carbon atom, with three groups attached. The carbocation center is electron deficient and lies in the same plane of the three attached atoms. Proton NMR is one of the primary instrumental methods applied to determine the structure and properties of carbocations. In a superacid media, such as SbF_5, stable carbocations can be generated and directly observed by NMR. SbF_5 is a strong Lewis acid that complexes with a weak base such as F^- to form SbF_6^-.

13.1 What is the product A in the following reaction?



13.2 Two proton NMR spectra of $(CH_3)_3CF$ were obtained using neat $(CH_3)_3CF$ and $(CH_3)_3CF$ in SbF_5, respectively. One spectrum, denoted as spectrum I, showed a singlet at δ 4.35, and the other, spectrum II, revealed a doublet at δ 1.30 with a coupling constant J = 20 Hz. Which spectrum was obtained from $(CH_3)_3CF$ in SbF_5?

13.3 Tropylium ion **B** is one of the most stable carbocations. How many π electrons are there in the tropylium ion?



B

13.4 Is tropylium ion **B** an aromatic structure? Explain.

13.5 The chemical shift of benzene in the 1H NMR spectrum is δ = 7.27. What does the proton NMR spectrum of **B** look like?

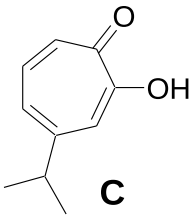
(a) A singlet at δ 9.17.

(b) A singlet at δ 5.37

(c) A triplet at δ 9.17.

(d) A Triplet at δ 5.37.

13.6 4–Isopropyltropolone **C** was the first example of a non–benzenoid aromatic compound. It was isolated from cypress trees in Taiwan by Professor T. Nozoe at the National Taiwan University in 1938. Draw resonance structure(s) to illustrate the aromaticity of C.



C

13.7 The proton of the OH group in tropolone is acidic. Three moles of tropolone **C** can react with one mole of tris(2,4–pentanedionato)iron(III) (Fe(acac)$_3$) to form a red complex **D**. What is the structure of **D**?

SOLUTION OF PREPARATORY PROBLEM 13

13.1 $(CH_3)_3C+ SbF_6^-$

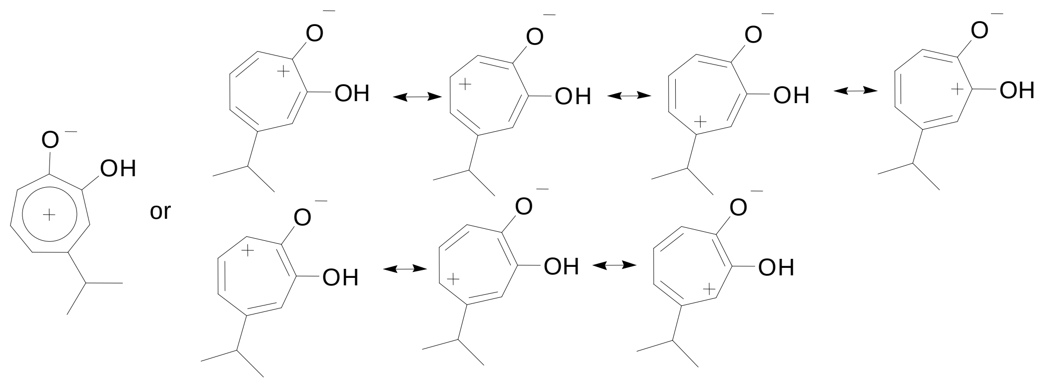
13.2 Spectrum I: $(CH_3)_3CF$ in SbF_5

13.3 6 π electrons

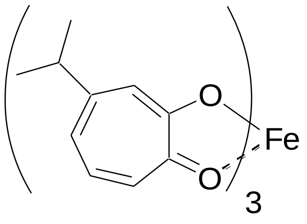
13.4 yes

13.5 (a) A singlet at δ 9.17

13.6



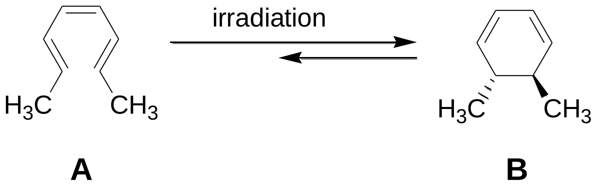
13.7 D



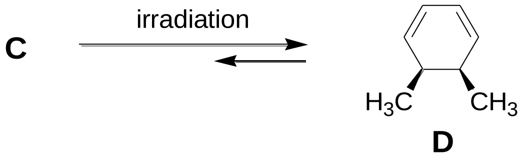
THEORETICAL PROBLEM 14

Photochemical Ring Closure and Opening

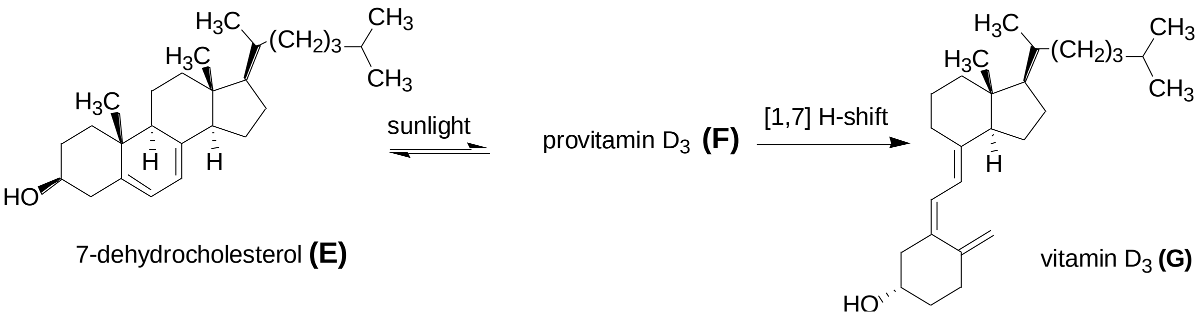
1,3,5–Hexatriene is known to undergo light–induced cyclization to give 1,3–cyclohexadiene. The photochemical reaction is reversible and stereospecific. Thus, irradiation of (2E,4Z,6E)-octatriene (A) with UV-light gives cyclohexadiene (**B**). The choice of the wavelength of light depends on the absorption maximum of the compound to be irradiated, and the absorption maximum is related to the number of conjugated double bonds in a chain.



14.1 What is the chemical name of the starting triene (**C**) for the related reaction shown below?



A similar reaction mechanism is involved in the synthesis of biologically active molecules. For example, in the presence of sunlight, 7–dehydrocholesterol (**E**) undergoes an electrocyclic ring opening reaction to give provitamin D3 (**F**), which can be further transformed through a [1,7]–hydrogen shift to yield vitamin D3 (**G**).

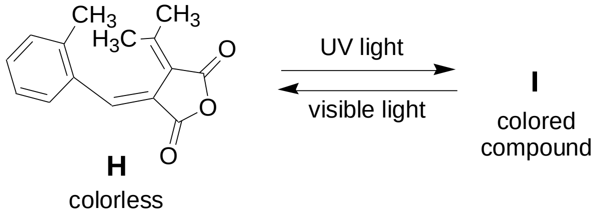


14.2 Of the two compounds 7–dehydrocholesterol (E) and vitamin D3 (**G**), which would you expect to absorb light with the higher energy? (**E** or **G**)

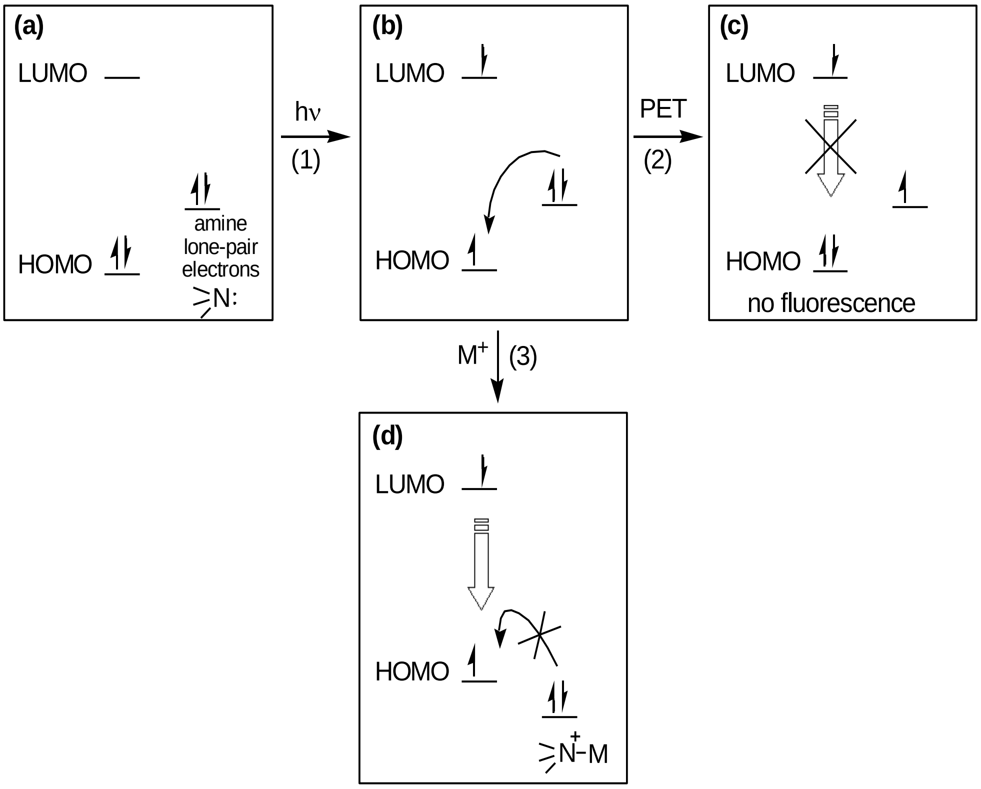
14.3 What is the chemical structure of **F**?

This principle has been elaborated to develop photochromic materials. For example, irradiation of colorless compound **H** with UV light gives colored compound **I**. The color change is reversed upon exposure to visible light.

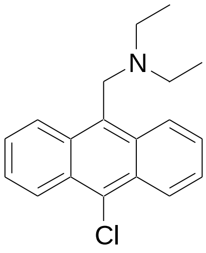
14.4 Give the structure of colored compound **I**.



Aromatic hydrocarbons are usually highly fluorescent. However, a neighbouring amino substituent may quench the fluorescence. This quenching mechanism is due to Photoinduced Electron Transfer (PET), which can be clearly illustrated by the molecular orbital diagrams shown below. Upon irradiation with a light of suitable wavelength (step 1), the initial aromatic chromophore (state a) will pump an electron from the highest occupied molecular orbital (HOMO) up to the lowest unoccupied molecular orbital (LUMO) (state b). In the presence of a neighbouring amino group, one of the lone–pair electrons at the nitrogen atom moves to the HOMO of the excited chromophore (step 2), and thus blocks the normal fluorescent pathway (state c). Coordination of the amine lone–pair electrons to proton or metal ions efficiently inhibits the PET process, and retrieves the fluorescence of the aromatic chromophore (step 3).



Many interesting and sensitive proton or metal ions fluorescent sensors have been developed based on the manipulation of the PET process. For example, compound **J** is used as a pH–sensor.



J

14.5 Do you expect that compound **J** is fluorescent in an alkaline solution (pH = 10.0)?

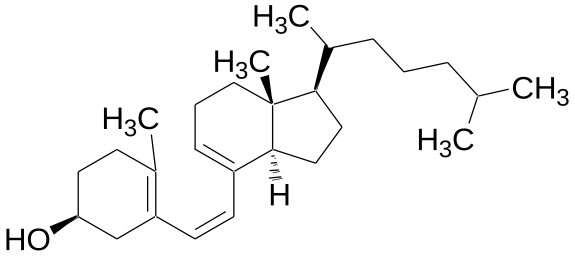
____

SOLUTION OF PREPARATORY PROBLEM 14

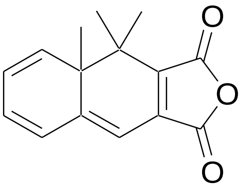
14.1 (2*E*,4*Z*,6*Z*)–octatriene

14.2 **E**

14.3 **F**



14.4 **I**

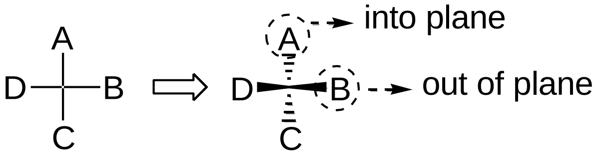


14.5 No.

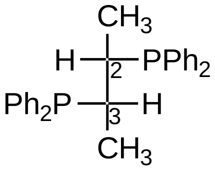
THEORETICAL PROBLEM 15

Stereochemistry

A simple two–dimensional representation for showing the three–dimensional arrangement of groups bonded to a carbon centre is called a "Fischer projection". In this molecular representation, the intersection point of two perpendicular lines represents an sp3 center. The horizontal lines connecting B and D to the central carbon atom represent the bonds that are out of plane relative to the observer. The vertical lines connecting A and C to the central carbon atom represent the bonds that are directed away from the observer into the plane of the page.

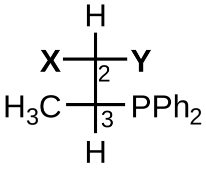


15.1 ChiraPhos was developed by Prof. Kagan and has found useful applications in asymmetric synthesis. Using the Fischer projection shown below, assign the absolute configuration of the chiral centers of ChiraPhos in terms of the R/S notation according to the Cahn–Ingold–Prelog sequence rule.



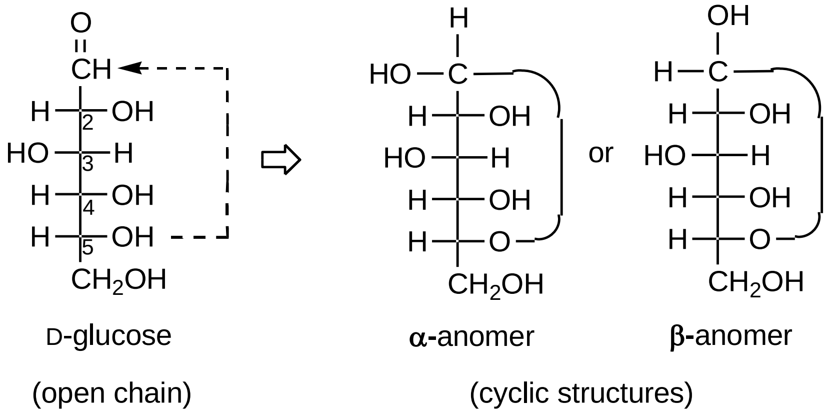
ChiraPhos

15.2 One of the stereoisomers of ChiraPhos is a meso compound. What are the identities of X and Y in the Fischer projection shown below?



meso-ChiraPhos

It is very useful and common to use Fischer projections for the stereo representation of carbohydrates. For example, the following Fischer projection represents the structure of D–glucose. It is interesting to note that the open–chain glucose can be interconverted with cyclic structures through the hemiacetal formation between the C_5–OH and the C_1–aldehyde group.



The hemiacetal formation generates two stereoisomers, which are called "anomers". The pure α–anomer of D–glucose has a specific rotation of +112.2°, whereas the pure β–anomer has a specific rotation of +18.7°. In water, either one of the two anomers gives an equilibrium mixture with a specific rotation of +52.6°.

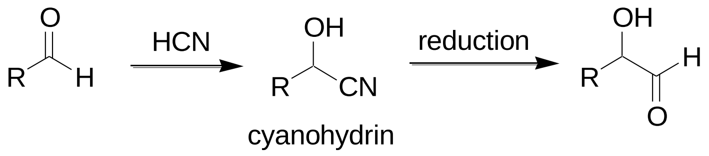
15.3 Calculate percentage of α–anomer in the equilibrium mixture of D–glucose in water.

15.4 Which is the more stable anomer in water? (α or β)

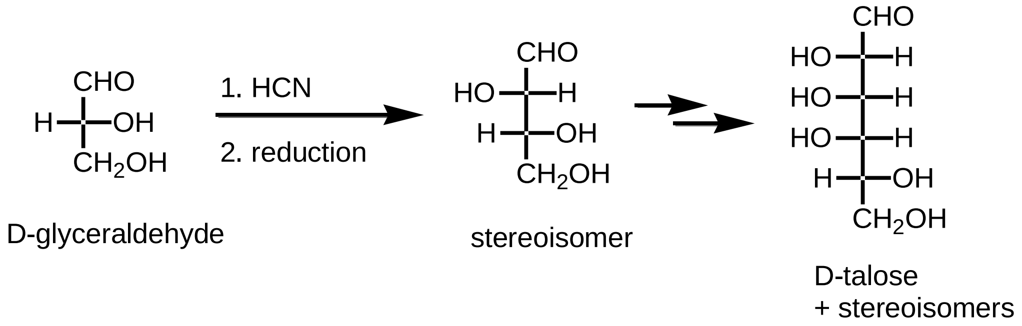
15.5 Draw the chair conformation of the β–anomer.

15.6 What is the common intermediate for the interconvertion between the α– and β–anomers?

The addition reaction of HCN to an aldehyde generates a cyanohydrin, which can be further reduced to form an α–hydroxyaldehyde.



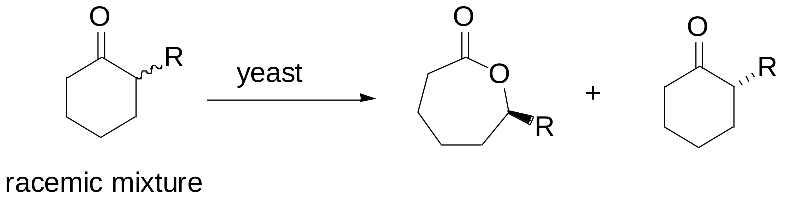
High homologs of carbohydrates, such as D–talose, can be synthesized from D–glyceraldehyde by repeating the same reaction conditions three times as shown below.

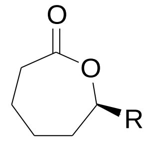
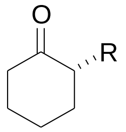


15.7 How many pairs of enantiomers will appear in the final product mixture?

Enzymes are remarkable biological catalysts that control the pattern of chemical transformations in living organisms. Because of their striking catalytic power and specificity, applying enzymes in organic synthesis has become one of the fastest growing areas for the development of new synthetic methodology. Following are the data for the yeast–mediated kinetic resolution of racemic 2–substituted cyclohexanone via Baeyer Villiger reactions (Table 1).

Table 1. Yeast–mediated kinetic resolution of racemic 2–substituted cyclohexanone via Baeyer Villiger reactions



		 O O R		 O R	
Entry	R	Yield (%)	ee%	Yield (%)	ee%
1	Et	79	95	69	98
2	n–Pr	54	97	66	92
3	Allyl	59	98	58	98

ee: enantiomeric excess

15.8 What is the ratio of (R)/(S) isomers of 6–allylcaprolactone in entry 3?

15.9 MCPBA (meta–chloroperbenzoic acid) is a common oxidizing agent for Baeyer Villiger reactions. Using MCPBA as an oxidizing agent, instead of yeast, for the above reaction, what will be the ee% of the caprolactone product?

SOLUTION OF PREPARATORY PROBLEM 15

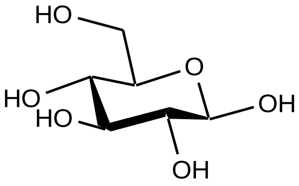
15,1 (2*S*,3*S*)

15,2 X= CH_3, Y = PPh_2

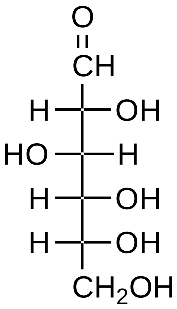
15,3 36%

15,4 β

15,5



15.6



15.7 none

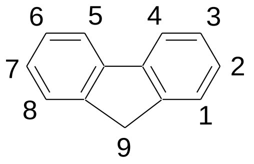
15.8 99:1

15.9 0

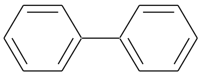
THEORETICAL PROBLEM 16

Organic Synthesis

One of the primary demands for the development of organic light emitting diodes (OLEDs) is the search for highly efficient luminescent materials which can be either small molecules or polymers. For example, fluorene, a methylene–bridged biphenyl, exhibits a higher quantum yield of fluorescence than biphenyl.

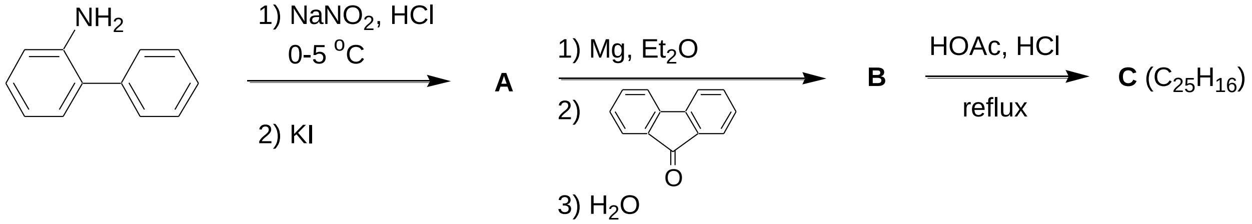


Fluorene



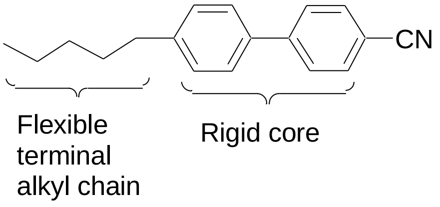
Biphenyl

Many fluorene derivatives have been developed that have subsequently found promising applications in flat–panel–display technology. In order to avoid intermolecular interactions, bulky substituents have been introduced at the C_9 position of fluorene. One example of this is compound **C**, an interesting and useful building block in the development of a highly efficient blue light emitting material, the synthesis of which is shown in the following scheme.

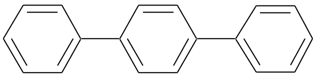


16.1 Draw the structures of **A**, **B**, and **C**.

Liquid crystals have become a part of our daily life, from wristwatches, pocket calculators, to full color flat–panel displays. Liquid crystal molecules usually contain a rigid core with a flexible terminal alkyl chain as shown in the example below.

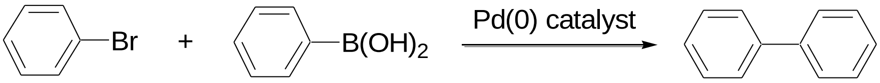


Biphenyl and terphenyl are common basic skeletons for the rigid core of liquid crystals. This kind of structure can be effectively synthesized through palladium catalyzed coupling of an aryl bromide or iodide with arylboronic acid, known as the Suzuki coupling reaction.

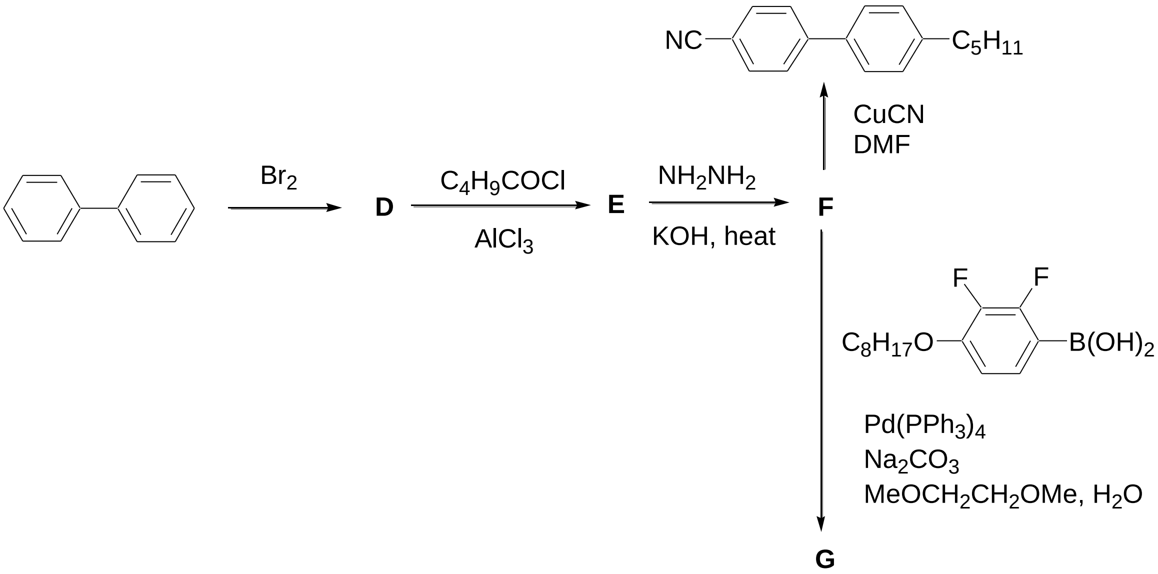


Terphenyl

A typical example of a Suzuki coupling reaction is shown below. Bromobenzene reacts with phenylboronic acid in the presence of a palladium catalyst to give biphenyl.



The following is a synthetic scheme for the preparation of two liquid crystal molecules, 4–cyano–4’–pentylbiphenyl and **G**.

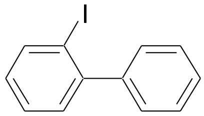


16.2 What are the structures of **D**, **E**, **F**, and **G**?

SOLUTION OF PREPARATORY PROBLEM 16

16.1

A =



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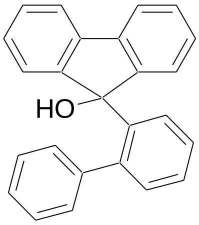
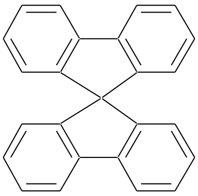
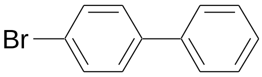


C =

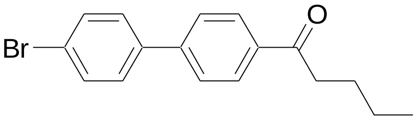


16.2

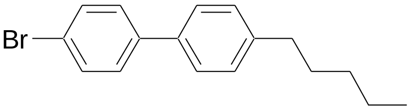
D =



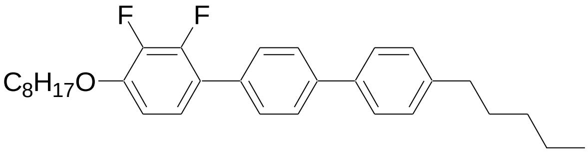
E =



F =



G =



THEORETICAL PROBLEM 17

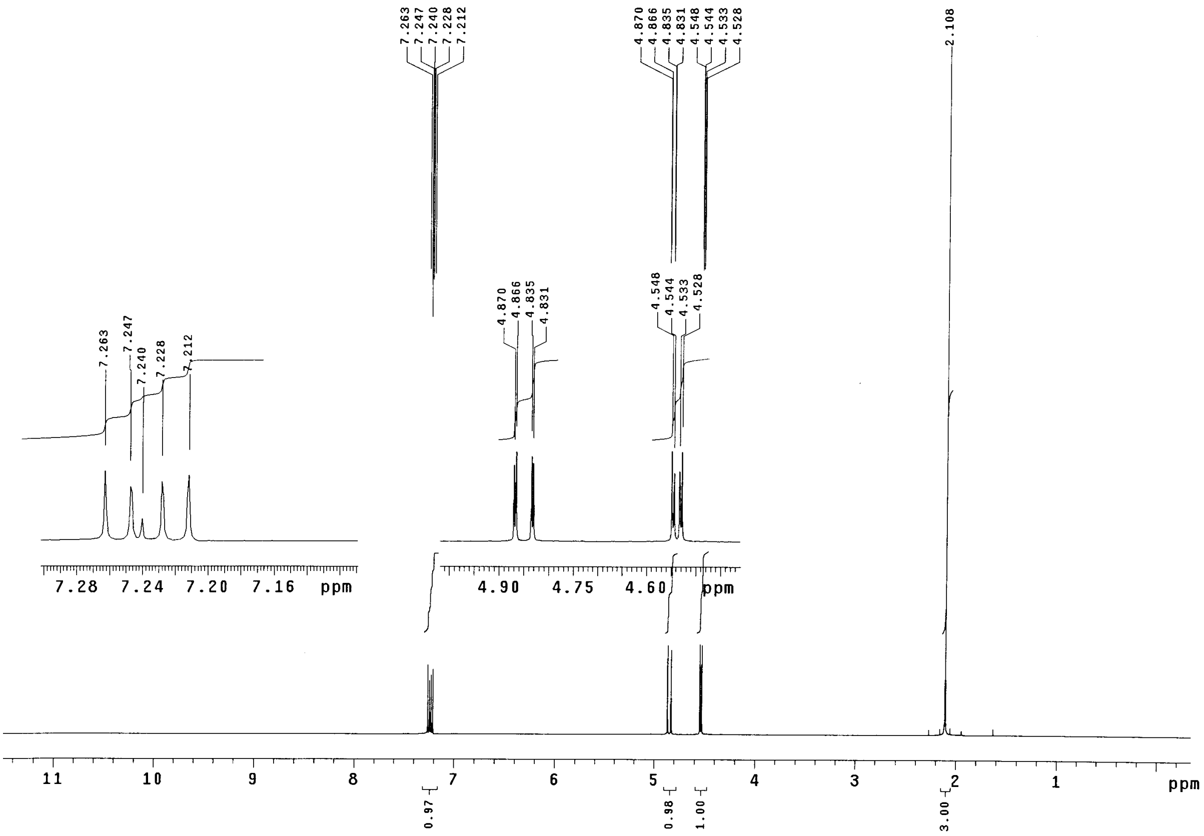
Spectroscopy and Polymer Chemistry

Organic polymers have had a great impact on our daily lives. Millions of tons of different kinds of polymers are produced every year. Synthetic organic polymers have a variety of uses, from textiles to computer chips, and to the life saving artificial heart valve. They are widely used as plastics, adhesives, engineering materials, biodegradable plastics, and paints. Poly(vinyl alcohol) (PVA) is an important example of a water–soluble polymer. One synthetic route to PVA is summarized in Scheme 1.

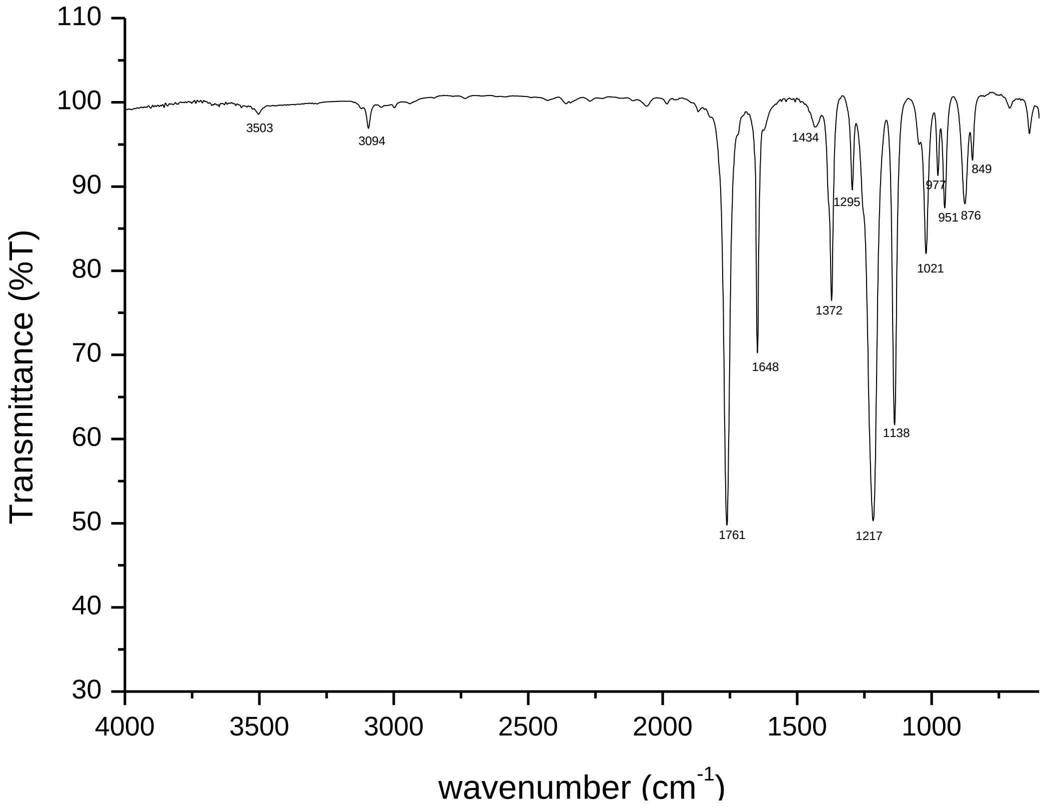
Scheme 1

$$\textbf{Monomer A} \xrightarrow{\text{polymerization}} \textbf{Polymer B} \longrightarrow \textbf{Poly(vinyl alcohol) PVA}$$

Polymer **B** shown above is also a major component in chewing gum. Elemental analysis of **A** suggests a ratio of C : H : O = 56 : 7 : 37. In addition, elemental analysis of **B** gives an almost identical composition of C, H, and O. The following IR and ^{1}H NMR spectra were recorded for monomer **A**.



^{1}H NMR spectrum of Monomer A



IR Spectrum of Monomer A

17.1 What is the molecular formula of **A**?

17.2 Which functional group would give an IR absorption band at 1761 cm^{-1}?

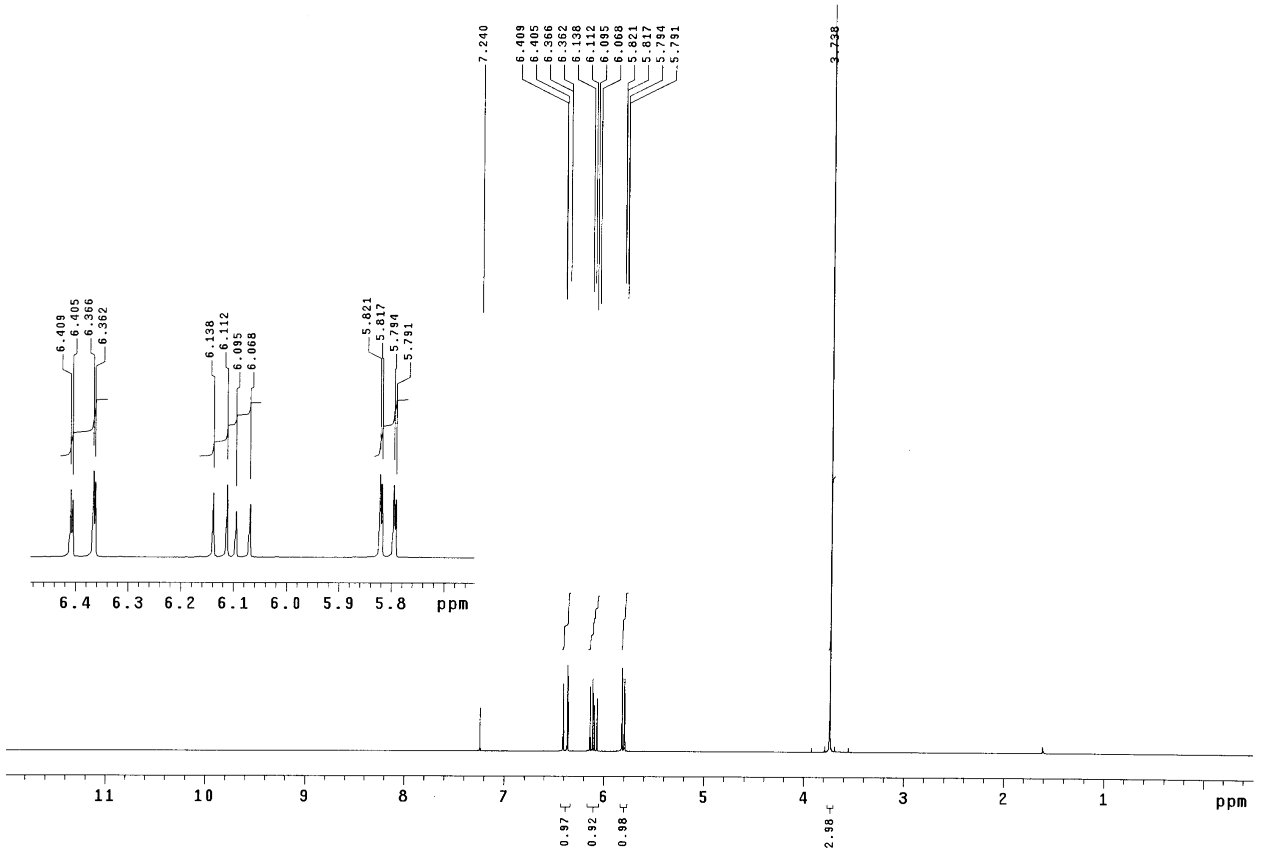
17.3 What is the chemical structure of **A**?

17.4 Draw a portion of polymer **B**. Show at least three repeat units.

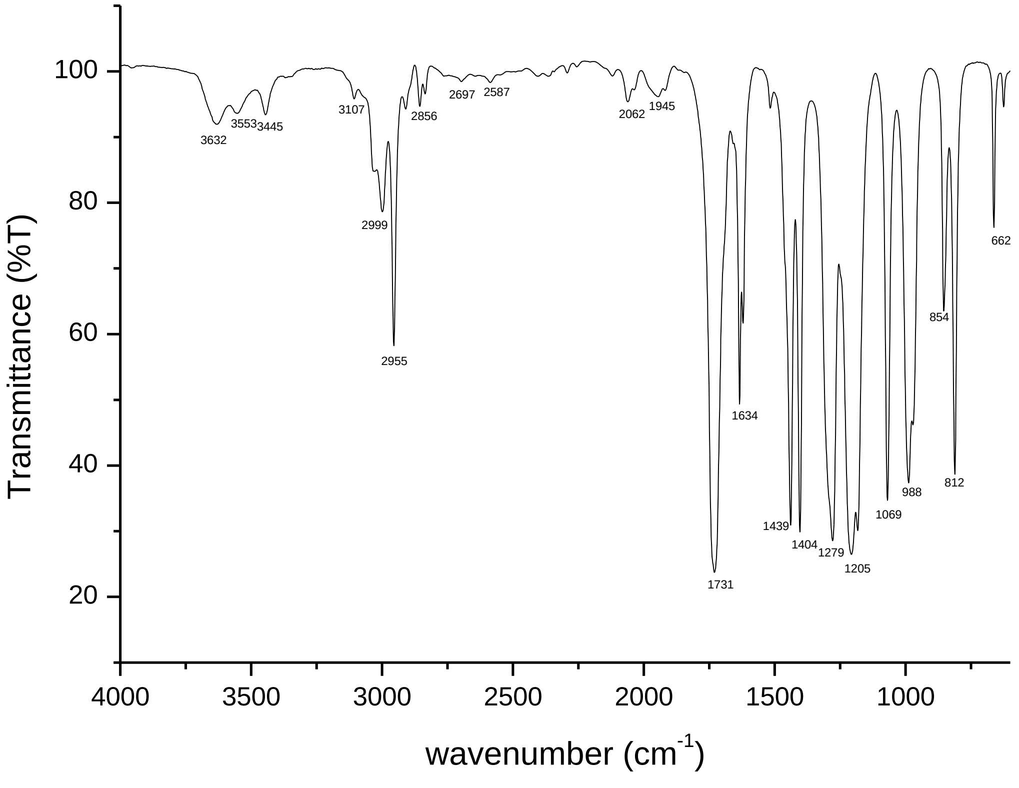
17.5 Provide a method for the transformation of **B** to PVA.

17.6 How many pairs of enantiomers would be obtained from polymer **B** with a molecular mass of 8600, assuming that the polymer is terminated by hydrogen abstraction and the mass of the terminal groups can be ignored?

17.7 Compound **C**, an isomer of **A**, is also an important monomer for the synthesis of polymers. On the basis of its ^{1}H NMR and IR spectra provided below, deduce the chemical structure of **C**.

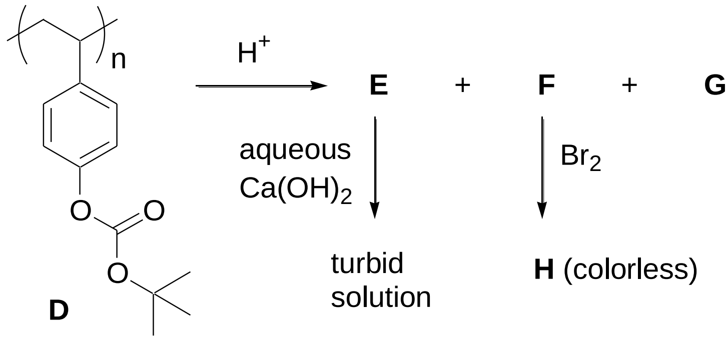


^{1}H NMR spectrum of monomer C



IR Spectrum of monomer **C**

Polymer **D** is an acid sensitive macromolecule. On treatment of **D** with a protic acid, gases **E** and **F** are released, and a new polymer **G** is formed. Gas **E** turns an aqueous solution of $Ca(OH)_2$ into a turbid solution while gas **F** reacts with bromine to give a colorless solution of **H**.



17.8 Draw the chemical structures of **E**, **F**, **G** and **H**?

Polymer **D** has been used to formulate a photo–imaging material by mixing it with a photo acid–generator (PAG). After being coated onto a substrate and exposed to light, protons are generated from the PAG, catalyzing a chemical reaction within the polymer matrix. Sometimes baking after exposure is necessary to accelerate the acid catalyzed reaction. If light is applied through a mask (Figure 1), a latent image of the mask is formed in the polymer matrix. After baking and using an aqueous basic developer to wash away the acidic materials, a patterned substrate **I** is obtained.

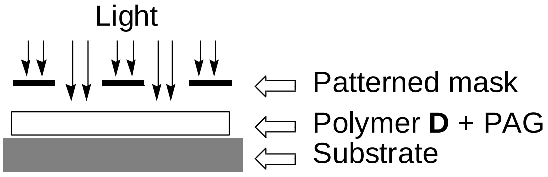


Figure 1

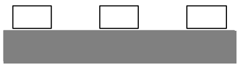
17.9 Which of the following diagrams best illustrates the patterned structure of substrate I?

(a)

(b)

(c)

(d)



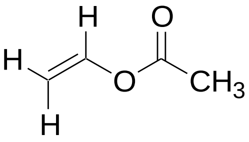
The dark areas represent a polymeric coating that is structurally different from the original one.

SOLUTION OF PREPARATORY PROBLEM 17

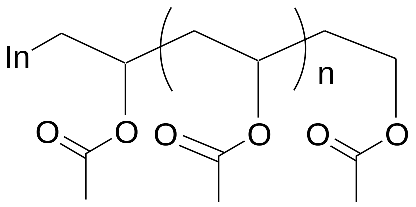
17.1 $C_4H_6O_2$

17.2 C=O group

17.3 **A**



17.4 **B**

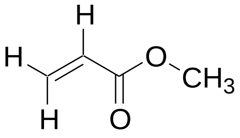


In: initiator

17.5 Organic reactions that could transform acetate to alcohol such as acid or base hydrolysis, alcoholysis, or $LiAlH_4$ reduction.

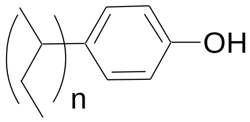
17.6 There are 100 units/molecule. However, the last one does not contain chiral center, therefore, there are 99 chiral centers and each of which would have *R* or *S* configuration. Totally there will be 299 stereoisomers, including enantiomers and diastereomers. Therefore, the number of pairs of enantiomers is 299/2 = 298.

17.7 **C**



17.8 **E**: CO_2 **F**: $(CH_3)_2C=CH_2$

G: **H**: $(CH_3)_2CBr–CH_2Br$



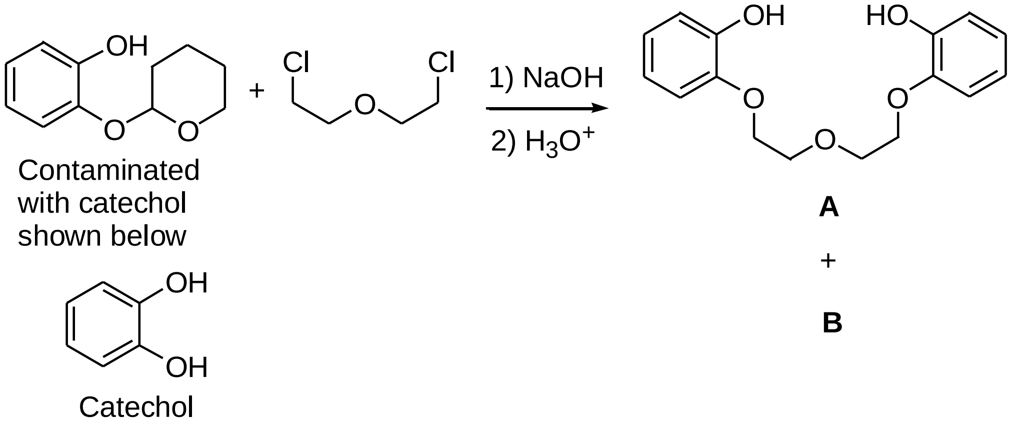
17.9 **I**: (d)

THEORETICAL PROBLEM 18

Crown Ether and Molecular Recognition

The discovery of crown ethers was made by Charles Pederson in 1967. He was rewarded with a share of the 1987 Nobel Prize for chemistry with Jean–Marie Lehn and Donald Cram for their contributions to supramolecular chemistry.

The following schematic diagram shows a synthetic route to the linear diol A. However, because of the presence of catechol in the starting material, the resulting product was a mixture of **A** and the minor product **B**.



The molecular weight of B was found to be 360.1 and it had an elemental composition of C : H : O = 66.5 : 6.7 : 26.6. The ^{1}H NMR spectrum of B showed four sets of proton signals. Two of which were observed at δ 7.0 – 7.5 and the other two at δ 3.7 – 4.2. The integration ratio of the four sets of signals was 1 : 1 : 2 : 2. Compound B strongly binds with the potassium ion. A striking example is the use of B to assist the dissolution of $KMnO_4$ in benzene to give a purple coloration.

18.1 What is the chemical structure of **B**?

18.2 What is the major function of H_3O^+ in the above reaction?

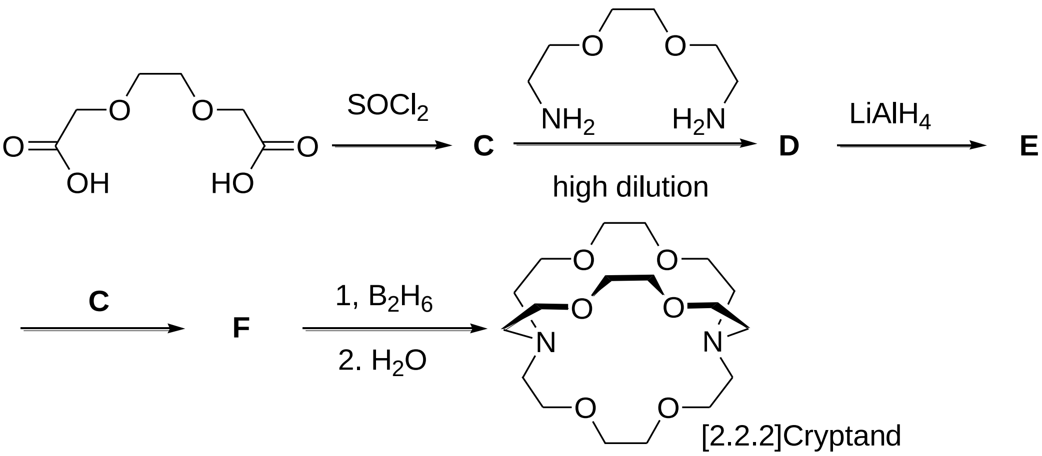
(a) To activate $ClCH_2CH_2OCH_2CH_2Cl$.

(b) To neutralize NaOH.

(c) To remove the tetrahydropyran group.

(d) To act as a buffer to control the pH of the solution.

The following is the synthetic route to [2.2.2]cryptand:



18.3 Draw the structures of **C** – **F**.

18.4 Why are high dilution conditions required in the synthesis of **D** from **C**?

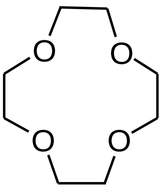
(a) Since the reaction between **C** and the diamine is highly exothermic, a high dilution condition is used to dissipate the heat released from the reaction.

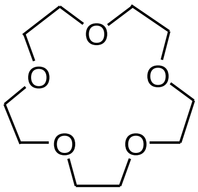
(b) A high dilution condition is employed in order to inhibit oligomer or polymer formation.

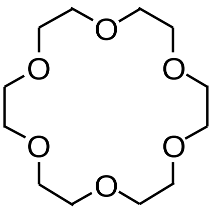
(c) Thermal equilibrium is favored to give **D** in higher yield under high dilution conditions.

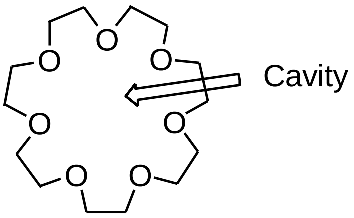
(d) The solubility of the starting material is low.

The affinity of a metal cation is controlled by several factors such as size matching between the host cavity of the crown ether and the guest cation, and the number of donor atoms of the host. Table 1 shows the radii of different alkali metal cations and the diameters of the cavities of several crown ethers.


12-C-4


15-C-5


18-C-6



21-C-7

Table 1. Radii of different alkali metal cations and diameters of the cavities of crown ethers.

Cation (radius, pm)	Cavity of the crown ether (diameter, pm)
Li^+ (68)	12–C–4 (120 – 150)
Na^+ (98)	15–C–5 (170 – 220)
K^+ (133)	18–C–6 (260 – 320)
Cs^+ (165)	21–C–7 (340 – 430)

18.5 On the basis of the above data, match the experimental curves **I–III** in Figure 1 with appropriate cyclohexyl crown ethers **G – I** .

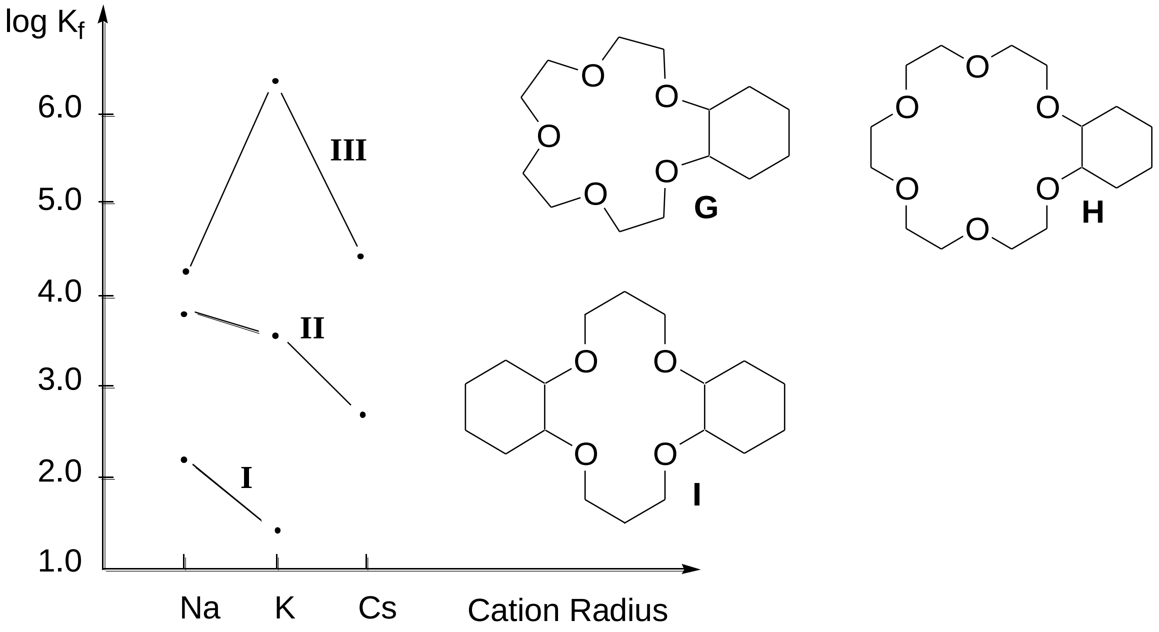


Figure 1. Complexation of Crown Ethers with Cations in Methanol

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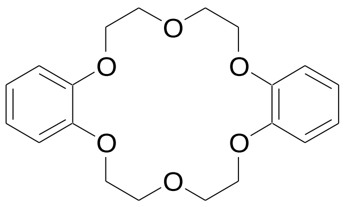
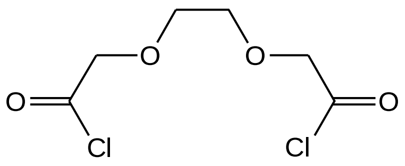
SOLUTION OF PREPARATORY PROBLEM 18

18.1 **B**

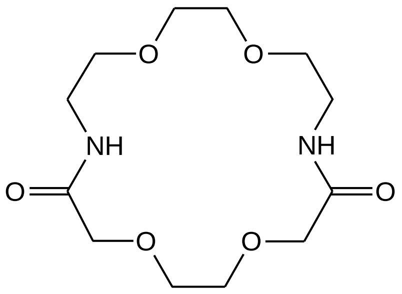


18.2 (c) To remove the tetrahydropyran group

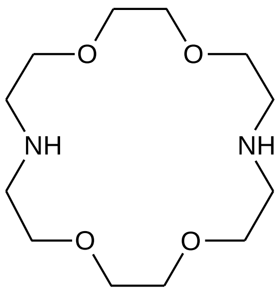
18.3 **C**



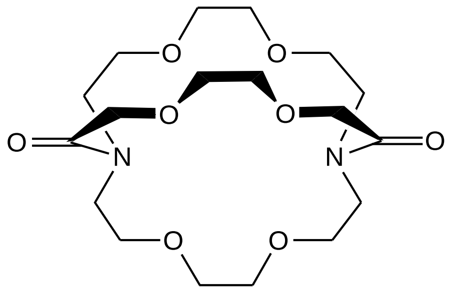
D



E



F



18.4 (b) A high dilution condition is employed in order to inhibit polymer formation.

18.5 Curve **I** to I; Curve **II** to G; Curve **III** to H

THEORETICAL PROBLEM 19

Enzyme Catalysis

In biological systems, oxidases catalyze the following reaction

$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$

The reaction is the key to respiration in living systems. The electrons come from Cytchrome c, which contains an iron center. The half reaction is

$Fe^{II}cyt\ c \rightarrow Fe^{III}cyt\ c + e^-$

The extinction coefficients of Fe^{II}cyt c and Fe^{III}cyt c at 550 nm are 27.7 and 9.2 mM cm^{-1} (M = mol dm^{-3}), respectively.

The absorbance of cyt c at 550 nm was observed to decrease at a rate of 0.1 A sec^{-1} in a 5 cm^3 solution containing 2.7×10^{-9} M oxidase, and sufficient cyt c and oxygen.

19.1 How many moles of cyt c were oxidized each second?

19.2 How many moles of oxygen were consumed each second?

19.3 What is the turnover number for oxidase? (Turnover number: the number of product produced by one catalyst per second)

SOLUTION OF PREPARATORY PROBLEM 19

19.1 $A = \varepsilon\ b\ C$; $\Delta C = \Delta A\ /\ \Delta\varepsilon\ b$; $\Delta\text{mol} = \Delta C \times V$ (volume)

$[0.1 / ((27.7 - 9.2) \times 103)] \times 5\times10^{-3} = 2.7\times10^{-8}$ mol sec^{-1}

19.2 Four electrons are needed to reduce one molecule of oxygen, therefore, the oxygen consuming rate is $2.7\times10^{-8} / 4 = 6.75\times10^{-9}$ mol sec^{-1}

19.3 By definition, the turnover number equals 6.75×10^{-9} (mol sec^{-1}) / (2.7×10^{-9} M × 5×10^{-3} dm^3). Therefore, oxidase has a turnover number of 500.

THEORETICAL PROBLEM 20

Work in Thermodynamics

An ideal gas at 0 °C and 10 atm has the volume of 10 dm^3. Calculate the final volume and work done under the following three sets of conditions if the final pressure is 1 atm.

20.1 Isothermal reversible expansion.

20.2 Adiabatic reversible expansion.

20.3 Irreversible adiabatic expansion is carried out as follows: Assume that the pressure is suddenly decreased to 1 atm and the gas expands adiabatically at a constant pressure.

[Note that the molar heat capacity at constant volume is given by the relation: $\bar{C}_v = \frac{3}{2}R$, where R is the gas constant.]

SOLUTION OF PREPARATORY PROBLEM 20

20.1 Isothermal reversible expansion

We have 100 / 22.41 = 4.461 moles, and the final volume is

$$V_2 = \frac{p_1 V_1}{p_2} = \frac{10 \times 10}{1} = 100\ \text{dm}^3 \qquad (1)$$

The work done by gas is

$$-w = q = n\,R\,T\ \ln\frac{V_2}{V_1} = 4.461 \times 8.314 \times 273.2\ \ln 10 = 23335\ \text{J} \qquad (2)$$

20.2 Adiabatic reversible expansion

Notice that

$$\gamma = \frac{C_\text{p}}{C_\text{v}} = \frac{\frac{3}{2}R + R}{R} = \frac{5}{3} \qquad (3)$$

Thus

$$V_2 = \left(\frac{p_1}{p_2}\right)^{\frac{1}{\gamma}} V_1 = (10)^{\frac{3}{5}} \times 10 = 39.8 \qquad (4)$$

and the final temperature is obtained from

$$T_2 = \frac{p_2\,V_2}{n\,R} = \frac{1 \times 39.81}{4.461 \times 0.08205} = 108.8\ \text{K} \qquad (5)$$

For adiabatic processes,

$q = 0$ and $\Delta E = q + w = w$

i. e.

$$w = \Delta E = n\,\overline{C_v}\ \Delta T = -\,9141\ \text{J} \qquad (6)$$

20.3 Irreversible adiabatic expansion

Since $q = 0$, we have

$$\Delta E = w = n\,\overline{C_v}\ (T_2 - T_1) \qquad (7)$$

$$w = -\,p_2(V_2 - V_1) \qquad (8)$$

and

$$-\frac{3}{2}\,n\,R\,(T_2 - 273.2\,) = \left(\frac{n\,R\,T_2}{1} - \frac{n\,R \times 273.2}{10}\right) \qquad (9)$$

It follows that

$$T_2 = 174.8\ \text{K} \tag{10}$$

and

$$\Delta E = w = \frac{3}{2}\, n\, R\ (174.8 - 273.2\ ) = -\,5474\ \text{J} \tag{11}$$

THEORETICAL PROBLEM 21

Kinetics — Atmospheric Chemistry

The following second–order reaction is important in air pollution.

$2\ NO_2 \rightarrow 2\ NO + O_2$

21.1 Derive an integrated relationship between the total pressures in the reaction vessel, originally containing pure NO_2, at the time *t*.

21.2 It was found that when a 2 liter vessel is filled with NO_2 at a pressure of 600 mm of Hg and a temperature of 600 °C, the reaction is 50% complete after 3 min. Calculate the rate constant.

SOLUTION OF PREPARATORY PROBLEM 21

21.1

$$\frac{d\,p_{NO_2}}{d\,t} = -k\,p_{NO_2}^2$$

$$\frac{1}{p_{NO_2}} = \frac{1}{P_{NO_2}^0} + kt$$

where $p_{NO_2}^0$ devotes the initial pressure of NO_2

21.2 At $t = t_{1/2}$, $p_{NO_2} = \frac{1}{2} p_{NO_2}^0$

$$k = \frac{1}{p_{NO_2}^0\, t_{1/2}}$$

or

$$k = \frac{1}{3 \times \frac{600}{760}} = 0.422\ \text{l atm}^{-1}\ \text{min}$$

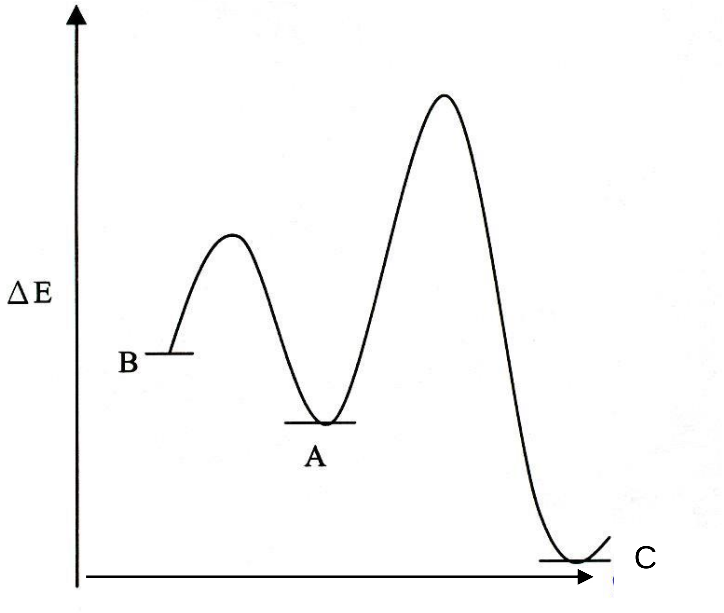
THEORETICAL PROBLEM 22

Kinetics and Thermodynamics

The concept of kinetic versus thermodynamic control of reaction products has frequently been employed in organic synthesis to direct product formation, for example, in sulfonation, Diels–Alder, isomerization and addition reactions. Here the interconversion of two different products can be achieved competitively by controlling the reaction conditions. It is normally represented as a concurrent reaction scheme, as shown below for the case where the reaction of A proceeds competitively toward products B and C.

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{C}$$

The energy profile for the reaction is depicted in the Figure below.



22.1 The rate constants are as follows: $k_1 = 1$, $k_{-1} = 0.01$, $k_2 = 0.1$, and $k_{-2} = 0.0005$ min^{-1}. Estimate the product ratio B/C in the first 4 minutes of the reaction.

22.2 Using the same rate constants, estimate the product ratio B/C when the reaction time exceeds 4 days.

22.3 B is called the kinetic–controlled product, while C is called the thermodynamic–controlled product. Which reaction process is favoured when the temperature of the system increases?

SOLUTION OF PREPARATORY PROBLEM 22

22.1 In the beginning 4 min of the reaction,

$$\frac{d[B]}{dt} = k_1\,[A] \qquad (1)$$

$$\frac{d[C]}{dt} = k_2\,[A] \qquad (2)$$

(1) divided by (2) gives

(1) divided by (2) gives

$$\frac{d[B]}{d[C]} = \frac{k_1}{k_2} \qquad \frac{B}{C} = \frac{k_1}{k_2} = \frac{1}{0.1} = 10$$

22.2 When the reaction is complete, the system reaches thermal equilibrium.

$$\frac{[B]}{[A]} = \frac{k_1}{k_{-1}} \qquad \frac{[C]}{[A]} = \frac{k_2}{k_{-2}}$$

$$\frac{[B]}{[C]} = \frac{k_1/k_{-1}}{k_2\,/\,k_{-2}} = \frac{1/0.01}{0.1/0.0005} = \frac{100}{200} = \frac{1}{2}$$

22.3 A → C thermodynamical controlled reaction process is favoured when temperature increases. The system will reach thermal equilibrium more rapidly.

THEORETICAL PROBLEM 23

Phase Diagram

The phase diagram is a convenient way to indicate the phases of a substance as a function of temperature and pressure. Answer the following questions based on the phase diagram of water given below:

23.1 What phases are present at A, B, and C?

23.2 Why does ice not sink in its own liquid?

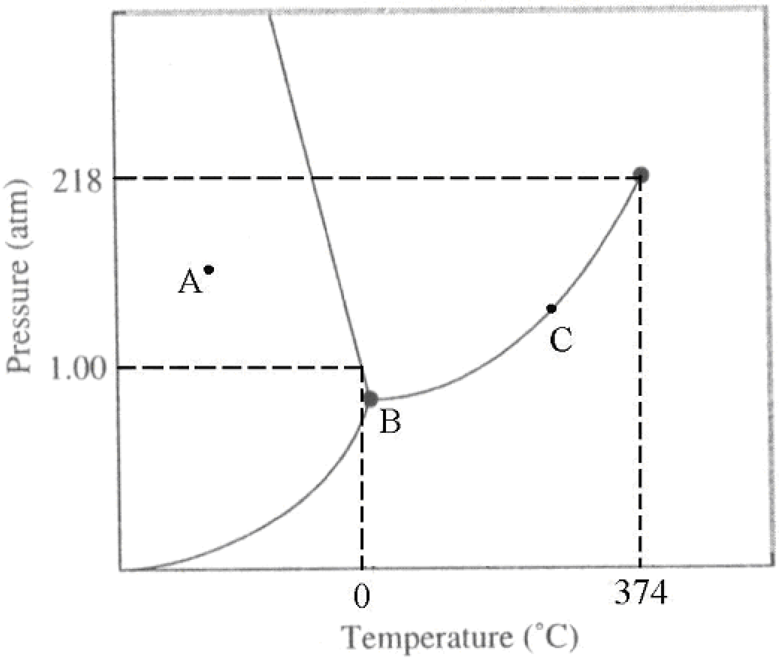
23.3 When water freezes, it expands. Explain this observation using the Clapeyron equation, which may be expressed by

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H}{T\,\Delta V}$$

Here, ΔH and ΔV denote the change of molar enthalpy and molar volume of water, respectively.

23.4 A glass container partially filled with water is connected to a vacuum pump. What changes will be observed when the pump is turned on?

23.5 A man is skating on the surface of a sheet of ice where the air pressure is 1 atm and the temperature is 0 °C. What changes will be observed along the skating track on the surface of the ice, assuming the ice can withstand his weight without cracking?



SOLUTION OF PREPARATORY PROBLEM 23

23.1 A: solid; B: solid, liquid, and gas states coexist; C: liquid and gas states coexist.

23.2 The negative slope of the solid/liquid line indicates the liquid state of water is denser than its solid state. Therefore, ice may not sink in its own liquid.

23.3 Clapeyron equation is expressed as

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H}{T\,\Delta V} \ ,$$

where ΔH is molar enthalpy of water and ΔV is volume change. The phase diagram shows that the slope of d*p*/d*T* for the liquid–solid coexistence region is negative, indicating the volume expands when water freezes.

23.4 As pressure is lowered, liquid phase transforms directly to gas phase at the same temperature. Thus water may vaporize. At the same time, the process of water evaporation is endothermic as to make the surrounding cooled. The left water becomes frozen. The solid state will sublime until none is left, if the pump is left on.

23.5 The ice surface, exerted by a pressure more than one atm, turns to liquid state at 0 °C.

THEORETICAL PROBLEM 24

Standard Deviation in One-Dimensional Quantum Mechanics

Some measurable physical quantity, if measured numerically, may lead to an uncertainty which is expressed by a standard deviation, σ. Such a standard deviation is defined as

$$\sigma = \sqrt{<G^2> - <G>^2}\ ,$$

where G is a measurable physical property; $<G>$ is the average value of G; $<G_2>$ is the average value of G_2. The average values, $<G>$ and $<G_2>$, can be obtained by integrating the corresponding physical quantity multiplied by its probability distribution over all the values of G. This definition may be applied to both classical and quantum mechanical worlds. Two examples related to the estimate of σ, one for the kinetic property of gaseous molecules and the other for the particle motion in one dimension, are given in the following.

24.1 The distribution of speeds of gaseous molecules at a fixed temperature can be described by the following probability density, called the Maxwell–Boltzmann distribution,

$$F(\mathrm{v}) = 4\pi v^2 \left(\frac{M}{2\pi RT}\right)^{3/2} \exp\left(\frac{-Mv^2}{2RT}\right)$$

where v is the speed of molecule, M is the mass of molecule, T is the temperature in Kelvin, and R is the gas constant. Calculate the average speed, $<v>$, and the standard deviation, $\sigma\, v$, of the distribution of speeds of the O_2 molecules at 300 K. ($M(O_2) = 32$ g mol^{-1}, $R = 8.31$ J K^{-1}mol^{-1})

24.2 Suppose a particle moving in the x direction has a normalized wave function,

$$j = [(1/\sqrt{2\pi})\exp(-x^2/2)]^{1/2}\ ; \quad -\infty \le x \le \infty\ ,$$

Calculate the average position, $<x>$, and the standard deviation, σ_x, of the position distribution of the particle after a large number of measurements of x.

24.3 In quantum mechanics, momentum for one dimension can be expressed by an operator, i.e., $p = -\frac{i\,h}{2\pi}\frac{d}{\mathrm{dx}}$, where h is the Planck's constant. Calculate the average momentum, $\langle p \rangle$, and the standard deviation, σp, for the particle with the same wave function described in part 2.

24.4 Calculate the uncertainty product of position and momentum, $\sigma x \sigma p$, for the above quantum mechanical example.

Some useful integrals are given below:

$$\int_0^{\infty} x^{2n} \exp(-ax^2)\,dx = \frac{1 \times 3 \times 5 \ldots.(2n-1)}{2^{n+1}} \left(\frac{\pi}{a^{2n+1}} \right)^{1/2}$$

$$\int_0^{\infty} x^{2n+1} \exp(-ax^2)\,dx = \frac{n!}{2a^{n+1}} \qquad \text{where } n = 0,1,2,3\ldots$$

SOLUTION OF PREPARATORY PROBLEM 24

24.1 Average speed <*v*>:

$$<v>=\int_0^{\infty} v\,F(v)\,\mathrm{dv} = 4\pi\left(\frac{M}{2\,\pi\,R\,T}\right)^{3/2}\int_0^{\infty}\exp\left(\frac{-M\,v^2}{2\,R\,T}\right)v^3\,\mathrm{d}v$$

$$=\sqrt{\frac{8\,R\,T}{\pi\,M}}=\sqrt{\frac{8\times 8.31\times 300}{3.14\times 0.032}}=4.45\times 10^2\ \mathrm{ms^{-1}}$$

Standard deviation σ_V:

$$<\mathrm{v}^2>=\int_0^{\infty} v\,F(v)\,\mathrm{dv} = 4\pi\left(\frac{M}{2\,\pi\,R\,T}\right)^{3/2}\int_0^{\infty}\exp\left(\frac{-M\,v^2}{2\,R\,T}\right)v^4\,\mathrm{d}v$$

$$=\frac{8\,R\,T}{M}=\frac{3\times 8.31\times 300}{0.032}=2.33\times 10^5\ \ \mathrm{m^2\,s^{-2}}$$

$$\sigma\mathrm{v}=\sqrt{<\mathrm{v}^2>-<\mathrm{v}>^2}=\sqrt{2.33\times 10^5-(4.45\times 10^2)^2}=1.87\times 10^2\ \mathrm{ms^{-1}}$$

24.2 Average position <x>:

$$<\mathrm{x}> = \int_{-\infty}^{\infty}\varphi^*\,x^2\,\varphi\,\mathrm{dx}=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}x^2\,exp(-\frac{x^2}{2})dx=1$$

Standard deviation σx:

$$<\mathrm{x}^2> = \int_{-\infty}^{\infty}\varphi^*\,x\,\varphi\,\mathrm{dx}=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}x\,exp(-\frac{x^2}{2})dx=0$$

$$\sigma\mathrm{x} = \sqrt{<x^2>-<x>^2}=1$$

24.3 $$<\mathrm{p}> = \int_{-\infty}^{\infty}\varphi^*\left(-i\,\frac{h\,\partial}{2\,\pi\,\partial x}\right)\varphi\mathrm{dx}=\int_{-\infty}^{\infty}\frac{i\,h\,x\,e^{-x_2/2}}{4\,\pi\,\sqrt{2\pi}}dx=0$$

$$<\mathrm{p}^2> = \int_{-\infty}^{\infty}\varphi^*\left(-i\,\frac{h^2\,\partial^2}{4\,\pi^2\,\partial x^2}\right)\varphi\mathrm{dx}=\frac{h^2}{16\,\pi^2}$$

$$\sigma\mathrm{p}=\ \sqrt{<p^2>-<p>^2}=\frac{h}{4\,\pi}$$

24.4 $$\sigma\mathrm{x}\ \sigma\mathrm{p}=\frac{h}{4\,\pi}$$

THEORETICAL PROBLEM 25

A Particle in a 2–D Box Quantum Mechanics

The π-electrons of the iron–heme of a hemoglobin molecule can be visualized as a system of free electrons moving in a two–dimensional box. According to this model, the energy of the electron is limited to the values

$$E_{n_x,n_y} = \frac{h^2}{8\,m_e\,L^2}\left(n_x^2 + n_y^2\right) \qquad n_x,\; n_y = 1, 2, 3, \ldots.$$

where $h = 6.63\times10^{-34}$ J s is the Planck constant; n_x and n_y are the principal quantum numbers; $m_e = 9.11\times10^{-31}$ kg is the electron mass; L is the length of the box.

25.1 Construct an energy level diagram showing the relative ordering of the lowest 17 orbitals.

25.2 Given the molecule contains 26 electrons, determine the electron population of the highest occupied orbitals in the ground state.

25.3 Assuming Hund's rule can be applied to this system, predict whether or not this system is paramagnetic.

25.4 Light is absorbed only when the condition $h\nu = \Delta E$ is satisfied. If the length L for this 2D box is 1 nm, what is the longest wavelength of light that can lead to excitation? Express your result in nm. [The speed of light, $c = 3.00\times10^{8}$ m s^{-1}.]

SOLUTION OF PREPARATORY PROBLEM 25

25.1 $E_{1,1} = 2\ E_0$

$E_{1,2} = E_{2,1} = 5\ E_0$

$E_{2,2} = 8\ E_0$

$E_{1,3} = E_{3,1} = 10\ E_0$

$E_{2,3} = E_{3,2} = 13\ E_0$

$E_{1,4} = E_{4,1} = 17\ E_0$

$E_{3,3} = 18\ E_0$

$E_{2,4} = E_{4,2} = 20\ E_0$

$E_{3,4} = E_{4,3} = 25\ E_0$

$E_{1,5} = E_{5,1} = 26\ E_0$

where $E_0 = h^2 / 8\ m\ L^2$

25.2 The total number of electrons in the highest occupied energy level is 4.

25.3 Ground state is diamagnetic.

25.4 The longest–wavelength excitation energy is $\Delta E = (25 - 20)\ E_0$, where

$E_0 = (6.63\times10^{-34}\text{ J s})\ 2\ /\ [8 \times 9.11\times10^{-31}\text{ kg} \times (1\times10^{-9}\text{ m})^2] = 6.02\times10^{-20}\text{ J}$ (1)

$\Delta E = (25 - 20)\ E_0 = 3.01\times10^{-19}\text{ J}$ (2)

The wavelength is

$\lambda = h\ c\ /\ \Delta E = [6.63\times10^{-34}\text{ J s} \times 3\times10^8]\ /\ 3.01\times10^{-19} = 660\text{ nm}$ (3)

THEORETICAL PROBLEM 26

Spectral Analyzer

The configuration of the distributed feedback dye laser (DFDL) system is shown in Fig. 1, and consists of an oscillator and a preamplifier.

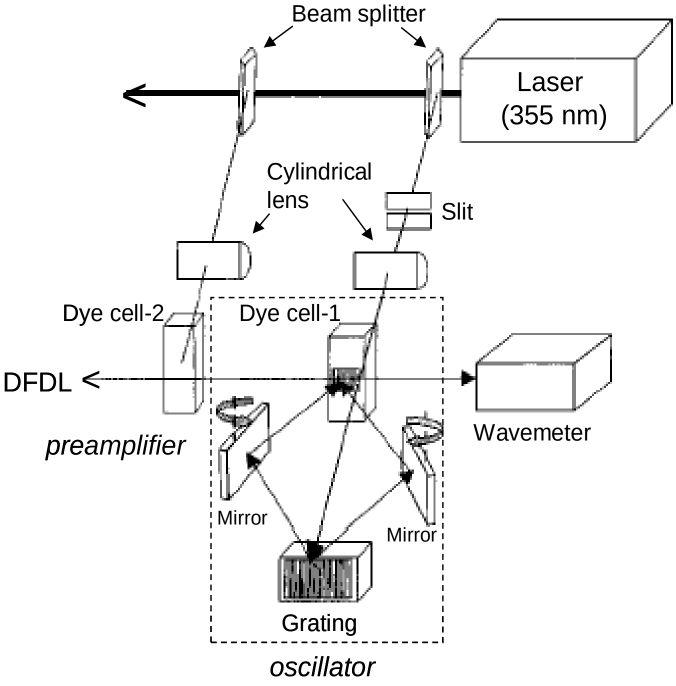


Fig. 1. Block diagram of the distributed–feedback dye laser.

The oscillator is made of a quartz cuvette (dye cell–1) equipped with a dye circulation pump. The detailed construction of the oscillator is shown in Fig. 2.

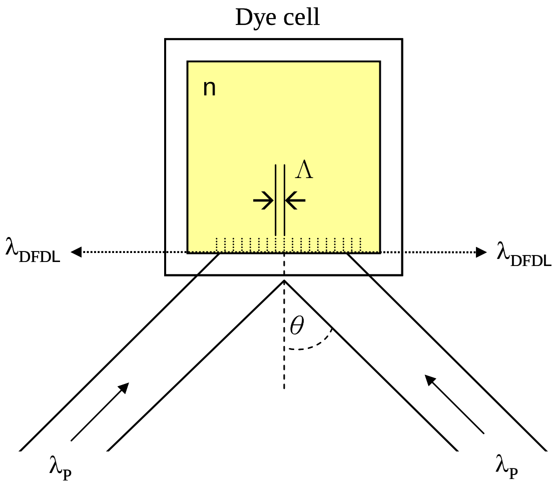


Fig. 2. The detailed construction of a DFDL oscillator

Two laser beams (λ_P = 355.00 nm) are reflected by two rotating dielectric mirrors and subsequently focused onto the dye solution to form an interference pattern, the spacing of which determines the wavelength of the laser emission. The wavelength of the laser emission, λ_{DFDL}, can be calculated using the following equations:

$$\lambda_{DFDL} = 2\, n\, \Lambda$$

$$\Lambda = \lambda_P / 2 \sin \theta$$

where n is the refractive index of the medium; Λ, the fringe spacing; and θ, the angle from the normal surface. The laser wavelength can also be determined from the fringe spacing, which, in turn, can be determined from the angle of incidence of the pump beam. The DFDL beams come from two sides of the cell. The wavelength of the DFDL can be measured by a Wavemeter. The power of the DFDL can also be amplifier by passing it through a preamplifier (the second dye cell; dye cell–2).

26.1 What would be the wavelength of the DFDL when the angle of θ is 60.00° and the refractive index of the medium is 1.40?

(a) 374 nm
(b) 474 nm
(c) 574 nm
(d) 674 nm
(e) 774 nm

SOLUTION OF PREPARATORY PROBLEM 26

26.1 $\Lambda = 355.00 / 2 \sin 60.00° = 204.96$

$\lambda_{DFDL} = 2 \times 1.40 \times 204.96 = 573.89$ nm

THEORETICAL PROBLEM 27

Time–of–Flight Mass Spectrometer

There are numerous ways in which we may separate and select ions in a mass spectrometer. Magnetic and electric fields, as well as radio frequency are often used to separate ions in mass spectrometers. The time–of–flight (TOF) mass spectrometer is the simplest type of common mass analyser and it has a very high sensitivity. With the introduction of matrix–assisted laser desorption / ionization (MALDI) or electrospray ionization (ESI), which is used to introduce and ionize macromolecules such as proteins, DNA, and polymers, the measurement of a large mass range became achievable. It is now possible to desorb and analyze ions with molecular weights upwards of one million atomic mass units (amu; 1 amu = 1.6605×10^{-27} kg). In general, the sample ions are generated in a source zone of the instrument, by whatever ionization method is being employed. A high voltage (HV) potential is applied across the source to extract and accelerate the ions from the source into the field–free “drift” zone of the instrument. The fundamental operating principle of TOF is that ions of the same kinetic energy will move with different velocities depending on their m / z value. This can be seen in the following equation, the classical equation for kinetic energy.

$\mathrm{KE} = ½\, m\, v^2$

This relationship may be rearranged to give velocity in terms of kinetic energy and m / z.

$v = (2 \times \mathrm{KE} / \mathrm{m})^{½}$

If the distance from the point of ion formation to the detector at some fixed point is L (neglecting the extraction time from the source), the time of flight (t) can be calculated by the following equation:

$t = \mathrm{L} / v = \mathrm{L} / (2 \times \mathrm{KE} / \mathrm{m})^{½}$

In most modern TOF mass spectrometer, ions are generally accelerated to kilo–electron volt (keV) energies. At these energies, flight times will be in the range of a few tens to a few hundreds of microseconds (μs) (depending on the flight distance). The kinetic energy of an ion accelerated by a potential is given by:

$\mathrm{KE} = z\, e\, V$

where z is the number of charges on the ion, e is the fundamental unit of charge (1.6022×10^{-19} C) and V is the applied accelerating potential in volts.

27.1 An average protonated cytochrome has a molecular weight of 12,361 amu. What will be the velocity of the (MH^+) ion of the cytochrome when accelerated by a potential of 20,000 volts?

(a) 18000 m s^{-1}

(b) 28000 m s^{-1}

(c) 38000 m s^{-1}

(d) 48000 m s^{-1}

(e) 58000 m s^{-1}

27.2 If the detector is positioned 1.00 m from the point of ion formation, the time of flight for the ion will be approximately:

(a) 40 μs

(b) 50 μs

(c) 60 μs

(d) 70 μs

(e) 80 μs

SOLUTION OF PREPARATORY PROBLEM 27

27.1 (a)

$v = [(2 \times 1 \times 1.6022\times10^{-19}\text{ C} \times 20000\text{ V}) / (12362 \times 1.6605\times10^{-27}\text{ kg})]^{½}$

$v = 17669.5\text{ m s}^{-1}$

27.2 (c)

$t = 1.00\text{ m} / 17669.5\text{ m s}^{-1} = 56.59\ \mu\text{s}$

PRACTICAL PREPARATORY PROBLEMS

PREPARATORY PROBLEM 28 (PRACTICAL)

Identification of Unknown Solid Samples

There are 12 unknown solid samples in vials numbered A_{01} to A_{12} on your table. Each vial contains about 100 mg of crystals or powder of one pure compound. The unknown samples are as following:

$NaCl$ $CdSO_4$ $Pb(NO_3)_2$ $Ba(OH)_2$ $Na_2S_2O_3$
$BaCl_2$ $FeSO_4$ KI $NaHCO_3$ NH4SCN

Note:

(1) There are two duplicated unknown samples.
(2) The hydrated H_2O of crystal is omitted in the formulas listed above.

On your table, there are also 14 empty droppers, 12 empty vials, 12 coffee stirrers, and 5 droppers containing the following reagents:

- $AgNO_3$, aqueous solution (c = 0.1 mol dm^{-3}),
- 3 % H_2O_2, aq.
- Na_2S, aqueous sol. (c = 0.1 mol dm^{-3}),
- HCl, aq. (c = 1 mol dm^{-3}),
- 0.01 % phenolphthalein

Procedure:

1. Use the coffee stirrers provided to transfer about 20 mg of each unknown sample into separate empty vial, add about 1 cm^3 of distilled water to each vial to make the unknown solutions and label them appropriately.
2. Use the five reagents provided and mutual reactions between the unknown solutions to identify each unknown sample.

Note:

(1) This practical exercise is a kind of spot test. You can do it on the provided pallet or on a sheet of white paper.

(2) Be sure to confirm your observations before writing your answers in the blanks of the Data Sheet.

Data Sheet 28

Compound	Code	Compound	Code	Compound	Code
KI	_____	$BaCl_2$	_____	$Na_2S_2O_3$	_____
NaCl	_____	$FeSO_4$	_____	NH_4SCN	_____
$Pb(NO_3)_2$	_____	$CdSO_4$	_____	$NaHCO_3$	_____
$Ba(OH)_2$	_____				

PREPARATORY PROBLEM 29 (PRACTICAL)

Identification of Unknown Solutions (I) – Spot Test without Electrolysis

1. This is a practical exercise best performed using spot test.
2. In a plastic bag, there are 12 unknown samples in droppers numbered X01 to X12. Each sample in the 1 cm^3 droppers, contains a aqueous solution of a simple compound (with a concentration of 0.1 mol dm^{-3}). A list of the compounds is given in the Data Sheet. There are also a dropper containing phenolphthalein, two empty droppers, a pallet, two coffee stirrers, a bottle of distilled water, and a small pack of tissue paper for your use.
3. Use the materials provided and mutual reactions of the unknown solution to identify each unknown sample and write your answer (code number) in the blank of the Data Sheet.

Note:

(1) Three samples are duplicated.

(2) The volume of each sample is about 0.6 cm^3. No more solution will be provided.

(3) Each correct answer gets 8 points, and each incorrect answer will be penalized 2 points.

Data Sheet 29

Compound	Number	Compound	Number	Compound	Number
NaCl	____	$AgNO_3$	____	KI	____
HCl	____	$PbNO_3)_2$	____	$BaCl_2$	____
H_2SO_4	____	Na_2CO_3	____	NaOH	____

Questions

29.1 How to find out the unknown sample of H_2SO_4 in this work?

29.2 How to confirm the H_2SO_4 solution in this work?

PREPARATORY PROBLEM 30 (PRACTICAL)

Identification of Unknown Solutions (II) – Spot Test with Electrolysis

Reagents and Equipment

Acid–base indicator	1
Bromothymol Blue	1
Distilled water	1
Simple electrolysis apparatus as shown in Fig 1.	
Coffee stirrer	2
Tissue paper	
Unknown samples, 10 unknown samples are shown in the Data Sheet.	

Identification of Unknown Solutions

Identify 10 unknown samples (code number: X01 ~ X10)

Note: (1) The compounds in the unknown solutions are given in the Data Sheet.
(2) Each unknown sample contains only one compound.
(3) The concentration of each unknown solution is about 0.1 mol dm^{-3}.
(4) Write your answers (code number) in the blanks of your Data Sheet.

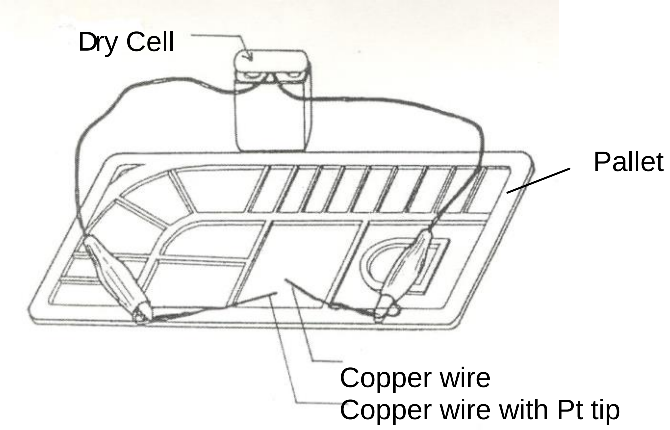


Fig 1. Simple Electrolysis Apparatus

Data Sheet 30

Compound	Number	Compound	Number	Compound	Number
$Cd(NO_3)_2$	____	Na_2S	____	H_2SO_4	____
KI	____	$Pb(NO_3)_2$	____	NaOH	____
$Na_2S_2O_3$	____	HCl	____	$Zn(NO_3)_2$	____
NaCl	____				

PREPARATORY PROBLEM 31 (PRACTICAL)

Quantitative Analysis of Ascorbic Acid in a Vitamin C Tablet

The major ingredient in commercial vitamin C is ascorbic acid ($H_2C_6H_6O_{27}$, M_r = 176.12). It is acidic and a reductant, therefore, both acid–base and redox titrations can be used to measure the amount of ascorbic acid in commercial vitamin C tablets.

This experiment has two parts, the first part involves using an acid–base titration to determine the amount of ascribed acid in a vitamin C tablet. The second part involves using a redox titration to perform a similar determination.

The evaluation is based on accuracy. The acid–base titration accounts for 30 %; the redox titration 60 %; and a comparison of these two methods 10 % of the final score.

CHECK REAGENTS AND APPARATUS BEFORE YOU START

Reagents

NaOH solution, (concentration is shown on the label)
Thiosulfate ($Na_2S_2O_3$) solution, (concentration is shown on the label)
Iodine solution (0.01 mol dm^{-3})
Indicators:
Phenolphthalein solution
Methyl Red solution
Starch solution

Apparatus

Spatula	1
graduated cylinder, 10 cm^3	1
graduated cylinder, 100 cm^3	1
funnel	1
pipette, 20 cm^3	1
safety bulb	1
Pasteur pipettes (dropper)	6
brush	1
beakers, 100 cm^3	2

- beakers, 250 cm^3	2
- Erlenmeyer flasks, 125 cm^3,	4
- Erlenmeyer flasks, 250 cm^3	2
- filter papers	10
- weighing papers	10
- mold and pastel,	1 set
- burettes (1 rack)	2
- burette brush	1
- volumetric flask, 100 cm^3	1

Procedure

Preparation of the ascorbic acid solution

Dissolve the vitamin C tablet in water; filter if necessary. The final volume of the solution should be 100 cm^3.

1. *Acid–Base Titration*

1 a Pipette 10 cm^3 of the above solution into an Erlenmeyer flask. Choose the appropriate indicator to perform titration.

1 b Repeat step 1a a total of 3 times.

Titration	Volume of vitamine C solution, cm^3	Volume of NaOH solution, cm^3
1		
2		
3		

Part 2: *Determination of the concentration of the provided iodine solution using the standardized thiosulfate solution.*

2 a Pipette 20 cm^3 of the iodine solution into an Erlenmeyer flask, and titrate by using standard $Na_2S_2O_3$ solution. Use starch as the indicator.

2 b Repeat step 2a a total of 3 times.

Titration	Volume of iodine solution, cm^3	Volume of $Na_2S_2O_3$ solution, cm^3
1		
2		
3		

Part 3 *Determination of the amount of ascorbic acid*

3 a Pipette 10 cm^3 of the solution from step 1 into an Erlenmeyer flask. Add a few drops of starch as indicator and titrate with the iodine solution.

3 b Repeat step 3a a total of 3 times.

Titration	Volume of ascorbic acid solution, cm^3	Volume of $Na_2S_2O_3$ solution, cm^3
1		
2		
3		

Questions

31.1 Assume that ascorbic acid is a monoprotic acid, use the data from acid–base titration to calculate the amount of ascorbic acid in the whole vitamin C tablet.

31.2 The reaction of I_2 with $Na_2S_2O_3$:

$2\ S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2\ I^-$

Calculate the concentration of the iodine solution.

31.3 The reaction of ascorbic acid with I_2:

$H_2C_6H_6O_6 + I_2 \rightarrow C_6H_6O_6 + 2\ I^- + 2\ H^+$

Calculate the amount of ascorbic acid in the whole vitamin C tablet.

31.4 Compare the advantage and disadvantage of the two titration methods.

PREPARATORY PROBLEM 32 (PRACTICAL)

Determination of an Equilibrium Constant

Equilibrium constant is an important property of a chemical reaction. It indicates the direction of a reaction. The concentration of each reaction species can be calculated from the equilibrium constant. For a reaction of the type

$$a\,A + b\,B \leftrightarrows c\,C + d\,D,$$

the equilibrium constant, K_{eq}, is given by the expression:

$$K_{eq}, = \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

From the equation, K_{eq} can be easily computed if the concentrations of all species at equilibrium are known. Once the K_{eq} is determined, concentrations at equilibrium can be calculated from any given starting condition.

The aim of this experiment is to deduce the K_{eq} for the reaction of $Fe(NO_3)_3$ with KSCN. You are provided with 20 cm^3 of a starter of each of the reactant: $Fe(NO_3)_3$ and KSCN with a concentration of 0.1 mol dm^{-3}. Three test tubes containing the product from the reaction are also provided. Each of these contains the product with a known concentration (in mol dm^{-3}) of: 3.214×10^{-3}, 1.360×10^{-3}, 1.375×10^{-4}×for tubes 1, 2, and 3; respectively. These standard solutions are used as a colorimetric reference.

You have to design an experiment to determine the K_{eq} for the reaction of $Fe(NO_3)_3$ with KSCN using the given reagents. Your data should be listed in a table as shown below:

Starting concentration of the reactants		Equilibrium concentration of the reactants		Concentration of the product	Reaction equilibrium constant
$Fe(NO_3)_3$	KSCN	$Fe(NO_3)_3$	KSCN	?	K_{eq}
?	?	?	?	From colorimetric measurement	?

Carefully design your experiment before you start. More reagents can be obtained from the TAs upon request. However, 5 points will be deducted for each additional reagent. Marks for this experiment will be primarily awarded on the basis of the accuracy of the result.

Besides the reactants, the following equipment has also been provided on your bench:

•	Sheets of paper	3
•	Kimwipe,	1 box
•	Labels	
•	Test tubes	20
•	Test tube rack	1
•	Safety bulb	1
•	Rubber bulbs	4
•	Pipettes	4
•	Glass rods	2
•	Test tube brushes	2 (thin and thick, one each)
•	Wash bottle	1
•	Ruler (15 cm)	1
•	Beakers, 100 cm^3	2
	250 cm^3	2
	500 cm^3	2
1.	Graduated cylinders, 10 cm^3	1
	25 cm^3	1
2.	Volumetric flasks, 25 cm^3,	2
3.	Erlenmeyer flask, 100 cm^3	4
4.	Burets,5 cm^3	2
	1 cm^3	2

Questions

32.1 Write a balanced equation for the reaction.

32.2 What is the expression for the equilibrium constant of this reaction?

K_{eq} =

32.3 What is the calculated value of K_{eq} from your data sheet?

PREPARATORY PROBLEM 33 (PRACTICAL)

Preparation of Acetylsalicylic Acid (Aspirin)

Acetylation of compounds containing the amino or hydroxyl group is usually accomplished by means of acetyl chloride or acetic anhydride. The reaction is catalyzed by a catalyst such as pyridine or sulfuric acid.

Aspirin may be prepared from salicylic acid and acetic anhydride. Sulfuric acid is frequently used as a catalyst in this reaction.

$$HOC_6H_4COOH + (CH_3CO)_2O \xrightarrow{H^+} CH_3COOC_6H_4COOH + CH_3COOH$$

Procedure

In a 125 cm^3 Erlenmeyer flask place 3.5 g of salicylic acid, 3.5 cm^3 of acetic anhydride (density: 1.08 g/cm^3), and 5 drops of concentrated sulfuric acid (some heat may be generated). Heat the flask in a hot water bath and stir for 5 minutes. During this time, the solid dissolve completely.

Remove the flask from the bath and add 15 cm^3 of ice water to it. Cool the flask to crystallize the products. Collect the crystals by suction filtration.

Transfer the crystals to a 125 cm^3 Erlenmeyer flask, add 8 cm^3 of ethanol. Heat the flask in a water bath until the solid has dissolved. Add 20 cm^3 of hot water to the flask and heat it until the solution clears. Remove the flask from the bath, cover it, and allow it to cool at room temperature. Collect the needle–like crystals by suction filtration. Wash the crystals with cold water and allow it to dry thoroughly.

Weight the crystals obtained and calculate the percentage yield of this experiment. Determine the melting points of the products.

Questions

33.1 What is the purpose of adding ice water?

33.2 Why the crystals was needed to wash with water?

33.3 Calculate the percentage yield of this reaction.

33.4 What is the melting point of aspirin you obtained?

PREPARATORY PROBLEM 34 (PRACTICAL)

Analysis of Aspirin Tablets

For many reasons, materials packaged for domestic use are often “diluted” by inert substances, often referred to as fillers. In the case of drugs, one reason for this procedure is to provide the correct dosage in a tablet of acceptable size. For example, aspirin, acetylsalicylic acid, is often mixed with a filler in commercial preparations. The aim of this experiment is to determine the percentage of aspirin in a readily available tablet.

Aspirin or acetylsalicylic acid can be considered to be the product of reaction of acetic acid (CH_3COOH) and salicylic acid (HOC_6H_4COOH). When treated with a solution of sodium hydroxide, aspirin is hydrolyzed and the two acids are simultaneously neutralized.

$$CH_3COOC_6H_4COOH + 2\ NaOH \rightarrow CH_3COONa + HOC_6H_4COONa + H_2O$$

If an excess of NaOH solution is used in this reaction, the amount of excess can be determined by a back titration with H_2SO_4. It is essential, however, that the H_2SO_4 used in this titration does not also react with sodium acetate and sodium salicylate, both of which contain basic anions. This can be avoided by the selection of either phenol red (pH range 6.8 – 8.4) or phenolphthalein (pH range 8.3 – 10.0) as the indicator.

Procedure

Weigh out accurately sufficient aspirin tablets to give a mass of about 1.5 g. Record the number of tablets and the mass.

Transfer the tablets to a 150 cm^3 conical flask. Add a 25 cm^3 aliquot of a carefully prepared NaOH solution together with a similar volume of water. Heat gently for about 10 minutes to hydrolyze the acetylsalicylic acid, according to the equation above. Cool the reaction mixture by holding the flask under running water and carefully transfer the contents, without loss, to a 250 cm^3 volumetric flask. Rinse the reaction vessel several times with water, adding the washings to the volumetric flask. Dilute the solution to the calibration mark and mix well by shaking.

Take a 25 cm^3 aliquot of the diluted reaction mixture and transfer it to a clean conical flask. Titrate the aliquot with H_2SO_4 solution with the concentration of 0.05 mol dm^{-3} using phenol red or phenolphthalein as the indicator. Record the actual concentration of the acid and the titre obtained. Repeat the determination until consistent titres are determined. Calculate the average titre.

Using a pipette and a volumetric flask, dilute a sample of the NaOH solution (c = 1 mol dm^{-3}) to final concentration of 0.1 mol dm^{-3}. Titrate 25 cm^3 aliquots of the dilute solution with the H_2SO_4 solution (c = 0.05 mol dm^{-3}) using the same indicator as before.

Questions

34.1 Why was it essential to cool the reaction mixture?

34.2 Why was it essential to mix thoroughly?

34.3 With what should the pipette first be rinsed?

34.4 With what should the flask have been rinsed?

34.5 Why was it necessary to dilute the NaOH solution?

34.6 Record the titres of acid and determine the concentration (mol dm^{-3}) of the original NaOH solution, showing all steps in your calculation.

34.7 Determine the amount of substance (moles) of NaOH originally added to the aspirin sample and that of NaOH (in moles) used in the hydrolysis step.

34.8 Calculate the amount of substance (in moles) of acetylsalicylic acid present in the determined sample.

34.9 Calculate the mass of acetylsalicylic acid in each tablet and compare this with the specification shown on the package.

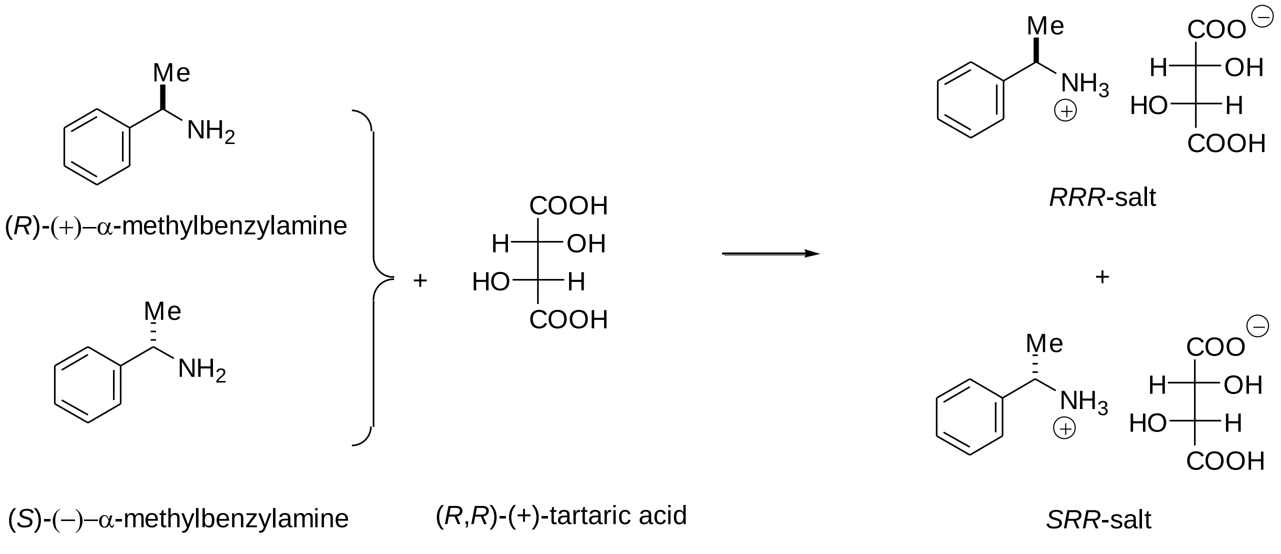
34.10 Analyze your own technique and assumptions in the experiment. List in estimated order of importance various sources of errors which could arise in this analysis.

PREPARATORY PROBLEM 35 (PRACTICAL)

Resolution of (±) – α – Methylbenzylamine and Determination of the Optical Purity

The traditional method for resolving a racemic mixture into its enantiomers is to use an enantiomerically pure natural product that bonds with the compound to be resolved. The enantiomers in the racemic mixture bond with the optically pure resolving agent to form two diastereomers. The diastereomers are separated, and then the resolving agent is cleaved from the separated enantiomers. The optical purity of a compound is defined as the ratio of its optical rotation to the rotation of a pure enantiomer.

A racemic mixture of α–methylbenzylamine is readily resolved by (R,R)–(+)–tartaric acid. The resulting (S)–(–)–α–methylbenzylaminium (R,R)–(+)–tartrate salt, SRR–salt, has a lower solubility than its diastereomeric counter part, (R)–(+)–α–methylbenzylaminium (R,R)–(+)–tartrate salt, RRR–salt. The SRR salt is induced to crystallize, whereas the RRR salt stays in solution. The crystals are removed by filtration and purified, and (S)–(–)–α–methylbenzylamine is regenerated by treatment with a base.



Procedure and Questions:

In an Erlenmeyer flask (250 cm^3) are placed (R,R)–(+)–tartaric acid (7.8 g, 52.0 mmol) and methanol (125 cm^3). The mixture is heated on a hot plate until the solution is nearly boiling. A racemic mixture of α–methylbenzylamine (6.25 g, 51.6 mmol) is added slowly over a period of 5 minutes to the solution. (Caution: at this step, the mixture is very likely to froth and boil over) Stopper the flask and let it stand overnight (18 hours).

Formation of prismatic crystals indicates a complete resolution of enantiomers, whereas impure isomers will appear in needles. Needles should be dissolved by careful heating, and crystallized again on cooling slowly. A seed of prismatic crystal can be added to induce the recrystallization.

The crystals are filtered through a Büchner funnel, and rinsed with a few portions of cold methanol. The crystals are transferred to a pre-weighed Erlenmeyer flask (50 cm^3), and purged with a stream of nitrogen. The dry crystals are weighed, and the yield is calculated. The crystals in the flask are treated with water (25 cm^3), and 50% aqueous sodium hydroxide solution (4 cm^3) is added slowly. The mixture is extracted with 10 cm^3 of methylene chloride for three times using a separatory funnel. The organic layers from each extraction are combined in a stoppered flask, and dried over anhydrous sodium sulfate (1.0 g) for about 10 minutes. The dried solution is decanted into a round–bottom flask (50 cm^3), and methylene chloride is removed by rotary evaporation. The residual α–methylbenzylamine is weighed, and the yield is calculated. Every effort should be taken to avoid prolonged exposure of the amine to air. Transfer the α–methylbenzylamine into a polarimeter tube cell, and measure its optical rotation. The reported specific rotation of (S)–(–)–α–methylbenzylamine is [α]D23 = –40.3° (neat). Calculate the percentage for each of the enantiomers in the resolved sample.