Note: There are two sources of chromate ions in solution.

Therefore, some of the lead chromate will precipitate from solution.

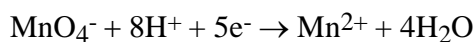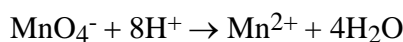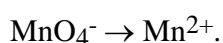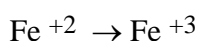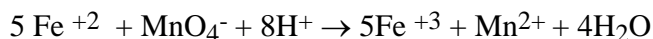c) $\quad S_{PbCrO_4} = CrO_4{}^{2-} = \dfrac{k_{spPbCrO_4}}{3.00 \times 10^{-7} + [CrO_4{}^{2-}]} = \dfrac{1.77 \times 10^{-14}}{3.00 \times 10^{-7} + [CrO_4{}^{2-}]}$

$\quad\quad\quad\quad\quad\quad\quad\quad = 0.505 \times 10^{-7}$ mol/L

SOLUTION 42

Balance the reaction:

$Fe^{+2} \rightarrow Fe^{+3}$ $\quad\quad\quad\quad\quad\quad\quad\quad\quad$ $MnO_4{}^- \rightarrow Mn^{2+}.$

$Fe^{+2} \rightarrow Fe^{+3} + 1e^-$ $\quad\quad\quad\quad\quad\quad$ $MnO_4{}^- \rightarrow Mn^{2+} + 4H_2O$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ $MnO_4{}^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ $MnO_4{}^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$5 (Fe^{+2} \rightarrow Fe^{+3} + 1e^-)$

$1 (MnO_4{}^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O)$

Overall

$5 Fe^{+2} + MnO_4{}^- + 8H^+ \rightarrow 5Fe^{+3} + Mn^{2+} + 4H_2O$
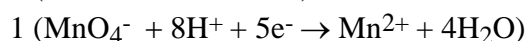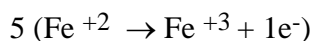
Calculate moles of Fe from the titration:

moles of Fe in sample 1:

$\quad\quad\quad$ = (0.00749 L KMnO$_4$) (0.0592 M KMnO$_4$) (5 mol Fe / 1 mol KMnO$_4$)

$\quad\quad\quad$ = 2.217 x 10^{-3} mol Fe

Calculate weight percent Fe_2O_3 contained in the ore:

wt Fe_2O_3 sample 1 = (2.217 x 10^{-3} mol Fe) (1 mol Fe$_2$O$_3$ / 2 mol Fe) (2(55.847))

$\quad\quad\quad\quad\quad\quad$ + 3(15.9994) g Fe$_2$O$_3$ / mol Fe$_2$O$_3$) = 0.1770 g Fe$_2$O$_3$

wt % Fe_2O_3 sample 1 = 100 (0.1770 g Fe$_2$O$_3$ / 0.500 g ore) = 35.4 % Fe$_2$O$_3$

SOLUTION 43

Calculate grams of cleaner titrated:

(10.000 g / (10.000 g +90.012 g)) (5.000 g) = 0.4999 grams solution

Calculate moles of NH_3 from titration:

moles HCl used = moles NH_3 present = (0.04211 L) (0.05042 M) = 2.123 x 10^{-3} mol

Determine grams of NH_3 from molecular weight:

(2.123 x 10^{-3} mol NH_3) (14.0067 + 3 (1.00797) g /mol) = 3.616 x 10^{-2} g NH_3

Determine percent NH_3 in titrated sample:

wt % NH_3 = 100 (3.616 x 10^{-2} g NH_3 / 0.4999 g solution) = 7.233 %

SOME SPECIFIC COMMENTS ON THE EXPERIMENTAL PROBLEMS

PROBLEM 45 - EXPERIMENTAL
Determination of Lead Ions by Back Titration with EDTA

1) The pH 10 buffer must be an ammonium buffer.
2) Sufficient buffer must be added to ensure that the pH does not fall during the titration.

Sample Calculations:

i) 10.00 mL Mg^{2+} standard solution required 17.00 mL EDTA solution:

$$\frac{1.00 \text{ mg Mg}^{2+}}{1.00 \text{ mL Mg}^{2+}} \text{ x } \frac{10.00 \text{ mL Mg}^{2+}}{17.00 \text{ mL EDTA}} \text{ x } \frac{1000 \text{ mL EDTA}}{1 \text{ L EDTA}} \text{ x } \frac{1 \text{ mole Mg}^{2+}}{24.31 \text{ x } 10^3 \text{ mg Mg}^{2+}} \text{ x } \frac{1 \text{ mole EDTA}}{1 \text{ mole Mg}^{2+}}$$

$$= 2.42 \text{ x } 10^{-2} \text{ M EDTA}$$

ii) 10.00 mL Pb^{2+} solution and 25.00 mL EDTA solution required 11.00 mL Mg^{2+} standard solution:

moles EDTA = moles Mg^{2+} + moles Pb^{2+}

$$25.00 \text{ mL EDTA x } \frac{2.42 \text{ x } 10^{-2} \text{ mol EDTA}}{1000 \text{ mL}} = 6.05 \text{ x } 10^{-4} \text{ mol EDTA}$$

$$11.00 \text{ mL Mg}^{2+} \text{ x } \frac{1.00 \text{ mg Mg}^{2+}}{1.00 \text{ mL Mg}^{2+}} \text{ x } \frac{\text{mol Mg}^{2+}}{24.31 \text{ x } 10^3 \text{ mg Mg}^{2+}} = 4.52 \text{ x } 10^{-4} \text{ mol Mg}^{2+}$$

moles Pb^{2+} = moles EDTA - moles Mg^{2+} = 1.53 x 10^{-4} mol Pb^{2+}

$$\frac{1.53 \text{ x } 10^{-4} \text{ mol Pb}^{2+}}{0.010 \text{ L Pb}^{2+} \text{ sol'n}} = 1.53 \text{ x } 10^{-2} \text{ M Pb}^{2+}$$

PROBLEM 47 - EXPERIMENTAL
Determination of the K_{sp} of $CaSO_4$

Note that each Ca^{2+} displaces two H^+ from the column:

$$K_{sp} \ (CaSO_4) \ = \ [Ca^{2+}] \ [\ SO_4^{2-}]$$

$$[Ca^{2+}] \ = \frac{moles \ Ca^{2+}}{0.0010 \ L \ solution}$$

$$moles \ Ca^{2+} \ = \ 0.5 \ moles \ H^+ \ from \ titration$$

PROBLEM 48 - EXPERIMENTAL
Ritter Reaction

The product is N-tert-butyl benzamide. See *Journal of Chemical Education*, Vol 71, 1994, pages A200-202.

PROBLEM 50 - EXPERIMENTAL
Synthesis and Identification of an Organic Compound

Compound **A**: 2,5-furandione (maleic anhydride)
Compound **B**: butanedioic acid (succinic acid)

Data Sheet/Fiche de données

	Symbol Symbole	Value Quantité numérique	
Atomic mass unit	amu	1.66054×10^{-27} kg	Unité de masse atomique
Avogadro's number	N	6.02214×10^{23} mol^{-1}	Nombre d'Avogadro
Bohr radius	a_0	5.292×10^{-11} m	Rayon de Bohr
Boltzmann constant	k	1.38066×10^{-23} J K^{-1}	Constante de Boltzmann
Charge of an electron	e	1.60218×10^{-19} C	Charge d'un électron
Dissociation constant (H_2O)	K_w	10^{-14} (25 °C)	Constante de dissociation de l'eau (H_2O)
Faraday's constant	F	96,485 C mol^{-1}	Constante de Faraday
Gas constant	R	8.31451 J K^{-1} mol^{-1} 0.08206 L atm K^{-1} mol^{-1}	Constante des gaz
Mass of an electron	m_e	9.10939×10^{-31} kg 5.48580×10^{-4} amu	Masse d'un électron
Mass of a neutron	m_n	1.67493×10^{-27} kg 1.00866 amu	Masse d'un neutron
Mass of a proton	m_p	1.67262×10^{-27} kg 1.00728 amu	Masse d'un proton
Planck's constant	h	6.62608×10^{-34} J s	Constante de Planck
Speed of light	c	2.997925×10^8 m s^{-1}	Vitesse de la lumière

1 Å	=	1×10^{-8} cm
1 eV	=	1.60219×10^{-19} J
1 cal	=	4.184 J
1 atm	=	101.325 kPa
1 bar	=	1×10^5 Pa

This set of preparatory problems was prepared using a Macintosh Centris 610 with Word (version 5.1a from Microsoft) and ChemIntosh (version 3.4.4 from SoftShell International). The fonts used are Times and Symbol (both from Adobe).

An electronic version of these preparatory problems is available by sending a disk to the address below. The file will be provided as a self-extracting StuffIt archive in a Macintosh format. The compressed file is approximately 400 K. The expanded file is approximately 1.8 Meg. Electronic mail transfer of the file is also possible. If this route is chosen, it is strongly recommended that the recipient use Eudora or another mail programme which is capable of receiving and decoding attached files which have been Binhexed.

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NOTES

SOLUTION 1

a)   Bragg law, $n\lambda = 2\,a\sin\theta$, allows one to determine the lattice constant of Au according to the following:

$$a = \frac{n\lambda}{2\sin\theta} = \frac{1 \times 154.05 \times 10^{-12}}{2\sin(10.89^\circ)}$$

$$a = 4.077 \times 10^{-10}\,\text{m} = 4.077 \times 10^{-8}\,\text{cm}$$

The volume of the crystallographic unit (unit cell) of Au equals:
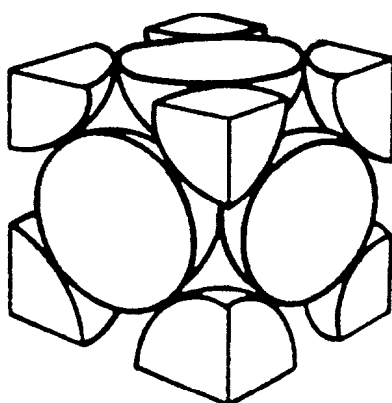
$$V_u = a^3 = \left(4.077 \times 10^{-10}\right)^3 = 6.777 \times 10^{-29}\,\text{m}^3 = 6.777 \times 10^{-23}\,\text{cm}^3$$

The number of crystallographic units of Au within $1.000\,\text{cm}^3$ equals:

$$N = \frac{1.000}{6.777 \times 10^{-23}} = 1.476 \times 10^{22}$$

Each crystallographic cell has four atoms, $n_u = 4$. The corner atoms belong to eight unit cells, thus $1/8$ of each corner atom belongs to the cell; the face atoms belong to two unit cells, thus $1/2$ of each face atom belongs to the cell.

$$n_u = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

Face-centered cubic crystal structure

The number of Au atoms in the $1.000\,cm^3$ cube equals:

$$N_{Au} = N \times n_u = 1.476 \times 10^{22} \times 4 = 5.904 \times 10^{22}$$

b)   The weight of one Au atom (m_{Au}) equals:

$$m_{Au} = \frac{M_{Au}}{N_A} = \frac{196.97}{6.002214 \times 10^{23}} = 3.271 \times 10^{-22}\,g$$

The mass of the unit cell equals:

$$M_u = n_u\,m_{Au} = 4 \times 3.271 \times 10^{-22} = 1.308 \times 10^{-21}\,g$$

c)   The density of Au, thus the weight of the $1.000\,cm^3$ cube, equals the number of unit cells within $1.000\,cm^3$ times the mass of the cell:

$$d_{Au} = N\,M_u = 1.476 \times 10^{22} \times 1.308 \times 10^{-21} = 19.31\,g\,cm^{-3}$$

SOLUTION 2

i)   Determination of the number of Au atoms within the $1.000\,cm$ long square having the (100) surface structure.

The area of the Au(100) surface unit equals:

$$A_u = a_{Au}^2 = \left(4.077 \times 10^{-8}\,cm\right)^2 = 1.662 \times 10^{-15}\,cm^2$$

There are two Au atoms per surface unit cell; the atoms in the corners belong to four unit cells, thus $1/4$ of each corner atom belongs to the (100) surface unit cell, and the atom in the middle of the cell belongs to the cell.

$$n_u = 4 \times \frac{1}{4} + 1 = 2$$

The number of Au atoms (the surface atom concentration) within $1.000\,\text{cm}^2$ of the Au(100) surface equals:

$$\sigma_{Au(100)} = \frac{n_u}{A_u} = \frac{2}{1.662 \times 10^{-15}} = 1.203 \times 10^{15}\ \text{cm}^{-2}$$

ii) Determination of the number of Cu atoms in the epitaxial layer.

In the case of the epitaxial deposition (growth), the Au(100) substrate acts as a template and the Cu layer has the same structure as the substrate. Thus the number of Cu atoms within one monolayer equals 1.203×10^{15} and the number of Cu atoms within the Cu epitaxial deposit (layer) equals:

$$N_{Cu} = 100 \times 1.203 \times 10^{15} = 1.203 \times 10^{17}$$

The number of moles of Cu within the epitaxial layer equals:

$$n_{Cu} = \frac{N_{Cu}}{N_A} = \frac{1.203 \times 10^{17}}{6.02214 \times 10^{23}} = 1.999 \times 10^{-7}\ \text{mol}$$

iii) Determination of the number of moles of $CuSO_4$ in the electrolyte after deposition of the epitaxial layer.

The number of moles of $CuSO_4$ in the electrolyte after the deposition equals the initial number of moles of $CuSO_4$ minus the number of moles of Cu deposited on the Au(100) substrate.

$$n_{Cu} = 1.000 \times 10^{-4} \times 10.000 \times 10^{-3} - 1.999 \times 10^{-7} = 8.001 \times 10^{-7}\ \text{mol}$$

iv) Determination of the concentration of $CuSO_4$ in the electrolyte after deposition of the Cu epitaxial layer

$$c_{CuSO_4} = \frac{8.001 \times 10^{-7}}{10.000 \times 10^{-3}} = 0.0800\ \text{mM}$$

SOLUTION 3

a)   Determination of the spontaneous direction of the reaction.

Oxidation process (process 1): $Zn \rightarrow Zn^{2+} + 2e$

Reduction process (process 2): $2 H^+ + \dfrac{1}{2} O_2 + 2 e \rightarrow H_2O$

The reduction potentials for the two above processes are: $E_1^o = -0.762 \text{ V}$ and $E_2^o = 1.229 \text{ V}$. The standard potential of the overall process (the concentrations of Zn^{2+} and H^+ equal unity) is:

$$E^o = E_2^o - E_1^o = 1.991 \text{ V}.$$

The Gibbs free energy, ΔG^o, of the process equals:

$$\Delta G^o = -n F E^o = -3.842 \times 10^5 \text{ J mol}^{-1}$$

Because ΔG^o is negative, Zn undergoes spontaneous dissolution.

b)   During the dissolution of Zn the concentration of Zn^{2+} increases and that of H^+ decreases. The process ceases when the concentrations of Zn^{2+} and H^+ reach such values that the newly established potential of the process, E, as established through the Nernst equation, equals zero.

$$E = E^o - \dfrac{R\,T}{n\,F} \ln \dfrac{c_{Zn^{2+}}}{c_{H^+}^2}$$

$E = 0.000 \text{ V}$ when $\dfrac{R\,T}{n\,F} \ln \dfrac{c_{Zn^{2+}}}{c_{H^+}^2} = 1.991$ or when $\ln \dfrac{c_{Zn^{2+}}}{c_{H^+}^2} = 155.0$. The latter relation gives after rearrangement the following ratio: $\dfrac{c_{Zn^{2+}}}{c_{H^+}^2} = 2.068 \times 10^{67}$.

Based upon the above ratio, one may evaluate the concentrations of Zn^{2+} and H^+ when the process ceases. The concentration of H^+ decreases twice as fast as the concentration of Zn^{2+} increases. Thus the new concentration of Zn^{2+} and H^+ can be described through the following equations:

$$c_{Zn^{2+}} = 1.000 + \Delta c_{Zn^{2+}}$$

$$c_{H^+} = 1.000 - \Delta c_{H^+}$$

where $\Delta c_{Zn^{2+}}$ is the increase of the concentration of Zn^{2+} caused by Zn dissolution and Δc_{H^+} is the decrease of the concentration of H^+. Bearing in mind that $\Delta c_{Zn^{2+}} = 2\Delta c_{H^+}$, one may rewrite the above equations as follows:

$$c_{Zn^{2+}} = 1.000 + \Delta c_{Zn^{2+}}$$

$$c_{H^+} = 1.000 - 2\,\Delta c_{Zn^{2+}}$$

Substituting these two formulae into $\dfrac{c_{Zn^{2+}}}{c_{H^+}^2} = 2.068 \times 10^{67}$, one gets the following relation:

$$\frac{1 + \Delta c_{Zn^{2+}}}{\left(1 - 2\,\Delta c_{Zn^{2+}}\right)^2} = 2.068 \times 10^{67}$$

which leads to the following quadratic equation (for simplicity we introduce the following coefficient $a = 2.068 \times 10^{67}$):

$$1 + \Delta c_{Zn^{2+}} = a\left(1 - 4\,\Delta c_{Zn^{2+}} + 4\,\Delta c_{Zn^{2+}}^2\right)$$

or

$$4\,a\,\Delta c_{Zn^{2+}}^2 - \left(4\,a + 1\right)\Delta c_{Zn^{2+}} + a - 1 = 0$$

Bearing in mind the very large value of a ($a = 2.068 \times 10^{67}$), thus remembering that $4\,a + 1 \cong 4\,a$ and that $a - 1 \cong a$, one may rewrite the above equation as follows:

$$4\,a\,\Delta c_{Zn^{2+}}^2 - 4\,a\,\Delta c_{Zn^{2+}} + a = 0$$

A solution of this quadratic equation leads to the following value of the increase of concentration of Zn^{2+}: $\Delta c_{Zn^{2+}} = 0.500\,M$. The respective concentrations of Zn^{2+} and H^+ when the dissolution of Zn ceases are $c_{Zn^{2+}} = 1.500\,M$ and $c_{H^+} = 0.000\,M$. Thus the dissolution of Zn ceases when all HCl is consumed in the process.

SOLUTION 4

The respective half-reactions and corresponding reduction potentials are:

$$Ni^{2+} + 2\,e \;\to\; Ni \qquad\qquad E^{o}_{Ni^{2+}/Ni} = -\,0.257\ V$$

$$Cu^{2+} + 2\,e \;\to\; Cu \qquad\qquad E^{o}_{Cu^{2+}/Cu} = 0.342\ V$$

Thus the above cell may be represented by the following scheme:

$$Ni\,|\,Ni^{2+}\,(c_{Ni^{2+}})\,||\,(c_{Cu^{2+}})\,Cu^{2+}\,|\,Cu \quad \text{where } || \text{ represents the salt bridge.}$$
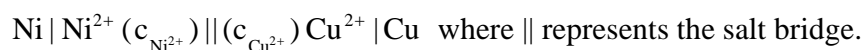
The standard potential of the cells is $E^{o} = 0.599\ V$.

The cell potential, E, prior to addition of $CuCl_2$ is expressed by the Nernst equation:

$$E = E^{o} - \frac{R\,T}{2\,F}\,\ln\frac{c_{Ni^{2+}}}{c_{Cu^{2+}}}$$

After the $CuCl_2$ addition, the new potential of the cell, E', is expressed by the following formula:

$$E^{'} = E^{o} - \frac{R\,T}{2\,F}\,\ln\frac{c_{Ni^{2+}}}{c^{'}_{Cu^{2+}}}$$

where $c^{'}_{Cu^{2+}}$ is the new concentration of Cu^{2+}. The potential increase, $\Delta E = E' - E$, associated with the $CuCl_2$ addition may be determined on the basis of the above relations:

$$\Delta E = E' - E = \frac{R\,T}{2\,F}\,\ln\frac{c^{'}_{Cu^{2+}}}{c_{Cu^{2+}}}$$

Thus, it is not necessary to know the Ni^{2+} concentration in order to relate the change of the cell potential with the addition of $CuCl_2$.

The above relation allows one to determine the new concentration of Cu^{2+}:

$$c'_{Cu^{2+}} = c_{Cu^{2+}} \exp\left(\frac{2 \, \Delta E \, F}{R \, T}\right) = 0.020 \, M$$

The concentration change upon addition of $CuCl_2$ equals $\Delta c_{Cu^{2+}} = 0.010 \, M$ and the respective number of moles of $CuCl_2$ added to the solution is $1.00 \times 10^{-3} \, mol$.

Finally, one may evaluate the mass of $CuCl_2$ added which is:

$$m_{CuCl_2} = n_{CuCl_2} \times M_{CuCl_2} = 1.344 \, g \, .$$

SOLUTION 5

a) The respective half-reactions and corresponding reduction potentials are:

$$Zn^{2+} + 2\,e \;\rightarrow\; Zn \qquad\qquad E^o_{Zn^{2+}/Zn} = -\,0.762 \, V$$
$$Cu^{2+} + 2\,e \;\rightarrow\; Cu \qquad\qquad E^o_{Cu^{2+}/Cu} = 0.342 \, V$$

Cu has a higher value of the reduction potential than Zn, thus Zn is the anode whereas Cu is the cathode. The above cell may be represented by the following scheme:

$$Zn \,|\, Zn^{2+} \, (c_{Zn^{2+}}) \,||\, (c_{Cu^{2+}}) \; Cu^{2+} \,|\, Cu \text{ where } || \text{ represents the salt bridge.}$$

The standard potential of the cell is $E^o = 1.104 \, V$.

The cell potential, E, prior to the galvanostatic discharge is expressed by the Nernst equation:

$$E = E^o - \frac{R \, T}{2 \, F} \ln \frac{c_{Zn^{2+}}}{c_{Cu^{2+}}}$$

Because the concentrations of the cations are the same in both compartments, the cell potential equals the standard one, thus $E = 1.104 \, V$.

Galvanostatic discharge of the cell results in cathodic deposition of Cu and in anodic dissolution of Zn causing the concentrations of the cations in the respective

compartments to change. The total charge of the galvanostatic discharge of the cell equals:

$$Q = I \times t = 1.00 \times 10^{-2} \times 10^{5} = 1000 \ C$$

The amount of the deposited Cu and that of the dissolved Zn are determined on the basis of the Faraday law or on the basis of the reasoning presented below. The number of moles of the deposited Cu, n_{Cu}, and of the dissolved Zn, n_{Zn}, equals:

$$n_{Cu} = n_{Zn} = \frac{Q}{2 \ e \ N_A} = \frac{1000}{2 \ e \ N_A} = 5.18 \times 10^{-3} \ mol$$

The numbers of moles of Cu^{2+} and Zn^{2+} in the respective compartments after the galvanostatic discharge are:

$$n'_{Cu^{2+}} = 1.00 \times 10^{-2} - 5.18 \times 10^{-3} = 4.82 \times 10^{-3} \ mol$$

$$n'_{Zn^{2+}} = 1.00 \times 10^{-2} + 5.18 \times 10^{-3} = 1.518 \times 10^{-2} \ mol$$

The molar concentrations of Cu^{2+} and Zn^{2+} in the respective compartments of the cell after the discharge are:

$$c'_{Cu^{2+}} = 4.82 \times 10^{-2} \ M$$

$$c'_{Zn^{2+}} = 1.518 \times 10^{-1} \ M$$

b) The cell potential, E', after the galvanostatic discharge is expressed by the formula:

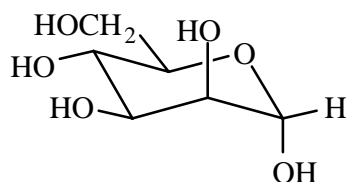$$E' = E^{\circ} - \frac{R \ T}{2 \ F} \ln \frac{c'_{Zn^{2+}}}{c'_{Cu^{2+}}} = 1.104 - \frac{R \times 298.15}{2 \ F} \ln \frac{0.1518}{0.0482} = 1.089 \ V$$

Finally, the potential change cased by the discharge of the cell equals:

$$\Delta E = E' - E = -0.015 \ V$$

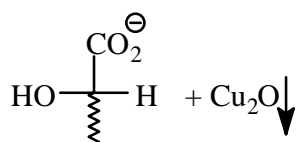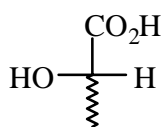**SOLUTION 6**

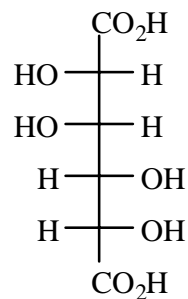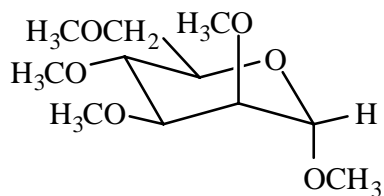The structure of α-D-(+)-mannopyranose is:

The reaction products are:

a)

b)

c)

d)

e)

f)

g)

h)

i)

j)

k)

SOLUTION 7

The only D-aldotetrose which will give an inactive product when oxidized with nitric acid is:

A

A gives **B** and **C** when treated with HCN followed by aqueous $Ba(OH)_2$
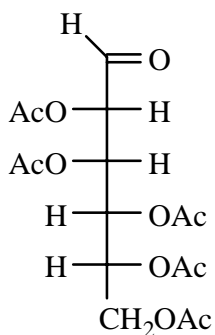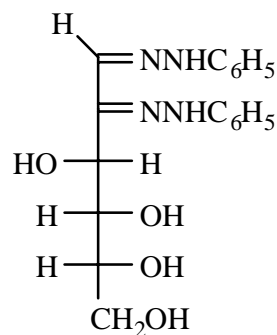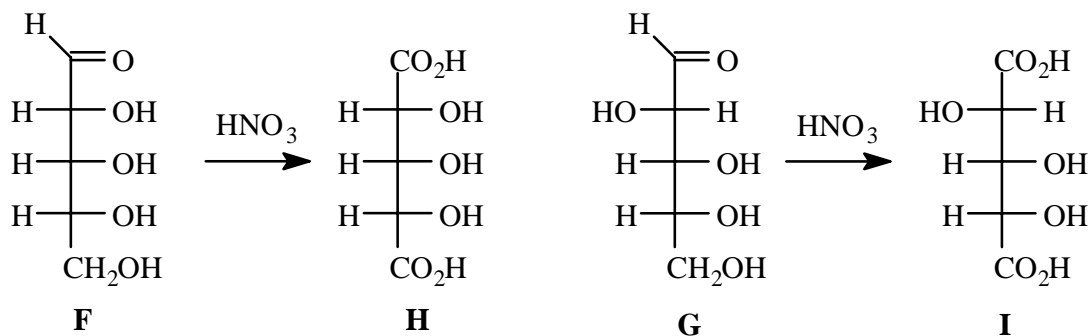

Their respective γ-aldonolactones **D** and **E** are:
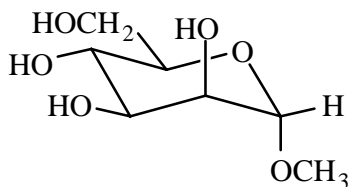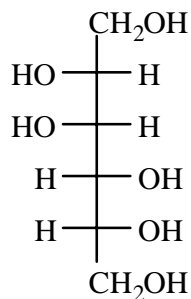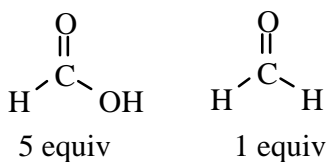
The equilibrium mixture above when treated with Na-Hg and water at pH = 3-5 produces **F** and **G** which when oxidized by nitric acid gives an inactive aldaric acid **H** and an optically active aldaric acid **I**:

$$
\begin{array}{cc}
\underset{\textbf{F}}{
\begin{array}{c}
H\!-\!\!=\!\!O \\
H\!-\!OH \\
H\!-\!OH \\
H\!-\!OH \\
CH_2OH
\end{array}}
&
\xrightarrow{HNO_3}
\underset{\textbf{H}}{
\begin{array}{c}
CO_2H \\
H\!-\!OH \\
H\!-\!OH \\
H\!-\!OH \\
CO_2H
\end{array}}
\qquad
\underset{\textbf{G}}{
\begin{array}{c}
H\!-\!\!=\!\!O \\
HO\!-\!H \\
H\!-\!OH \\
H\!-\!OH \\
CH_2OH
\end{array}}
\xrightarrow{HNO_3}
\underset{\textbf{I}}{
\begin{array}{c}
CO_2H \\
HO\!-\!H \\
H\!-\!OH \\
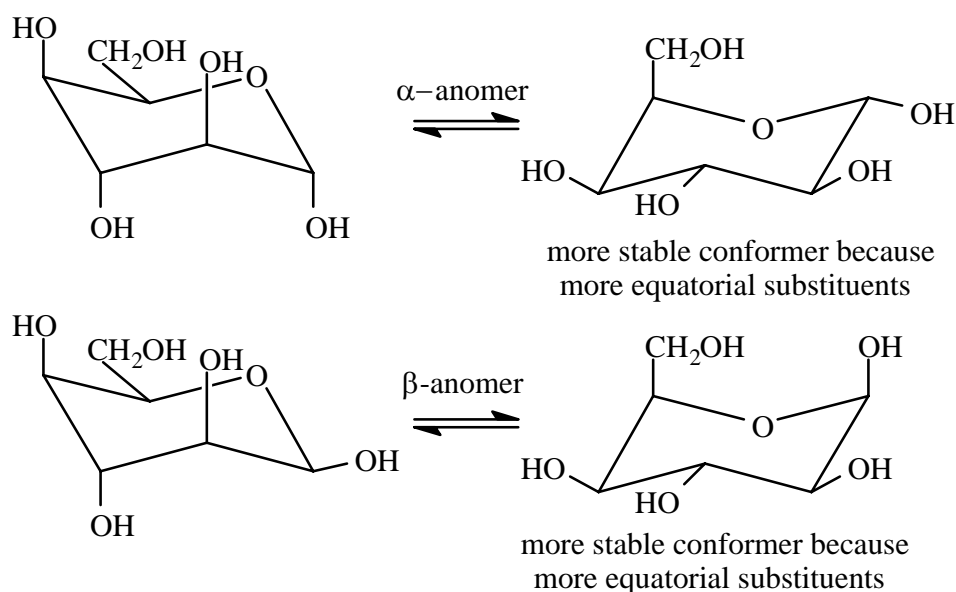H\!-\!OH \\
CO_2H
\end{array}}
\end{array}
$$

SOLUTION 8

Compound **A** is a non-reducing sugar with an α-linkage at the anomeric carbon. Since **A** gives only 2,3,4,6 methylated glucoses on hydrolysis the only possible structure for **A** is to have the two glucose molecules dimerize via their respective anomeric carbons:
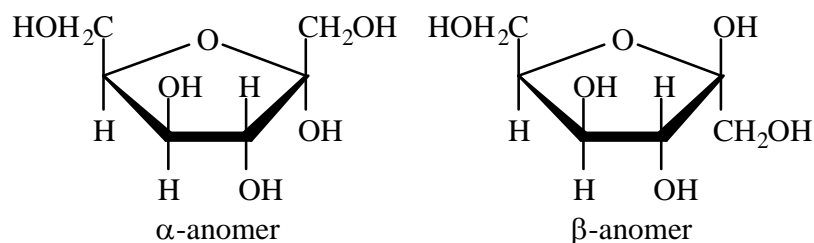

A
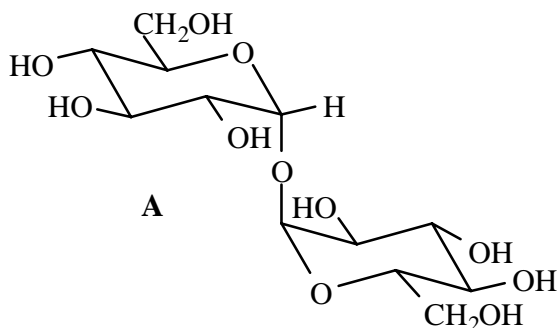
10 moles of HI are needed for the complete cleavage of **A** giving 10 moles of methanoic (formic) acid and 2 moles of methanal (formaldehyde).
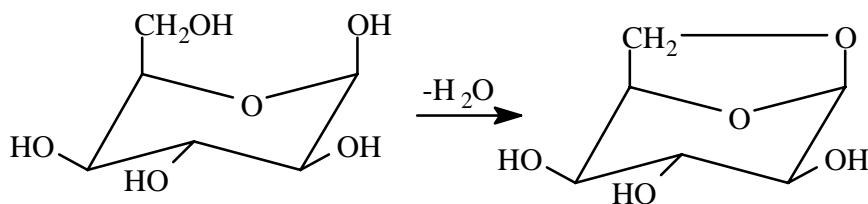
SOLUTION 9

a) Below are the two chair conformations for the two anomers of D-idose:

α−anomer

more stable conformer because
more equatorial substituents

β-anomer

more stable conformer because
more equatorial substituents

b) The two furanose forms of D-sorbose are shown below.
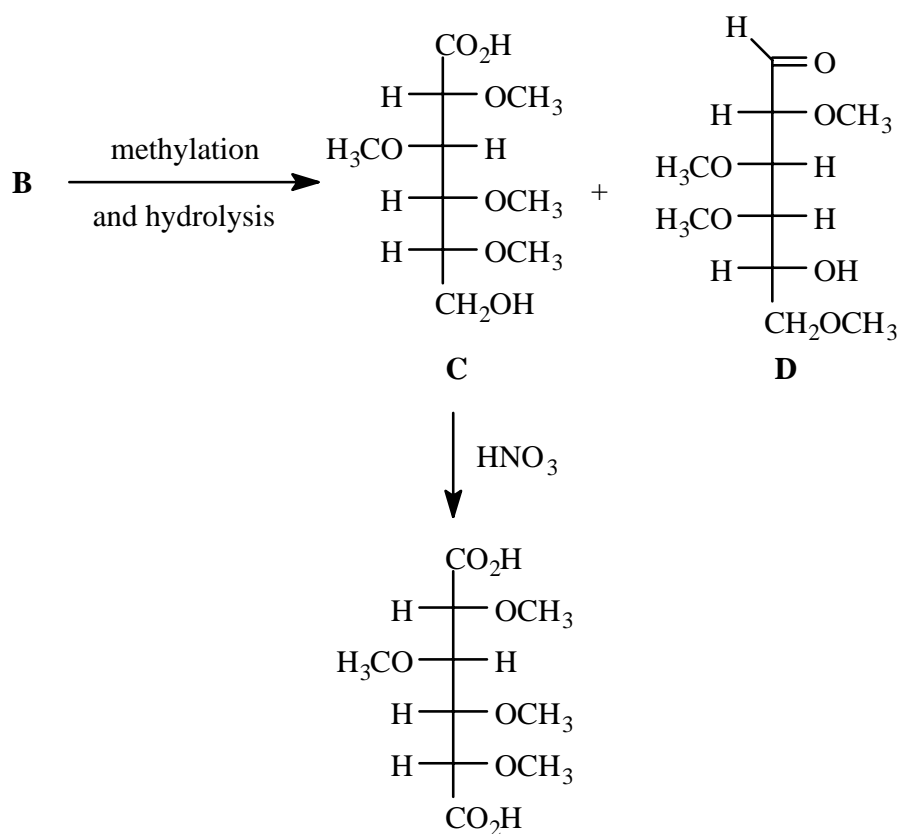

α-anomer β-anomer

c) The indicated conformer of the β-anomer can cyclize internally to form the anhydro-derivative. Glucose cannot undergo this reaction because it requires the C-6 substituent to be axial, and this conformation is too unstable for the glucose molecule.


$-H_2O$
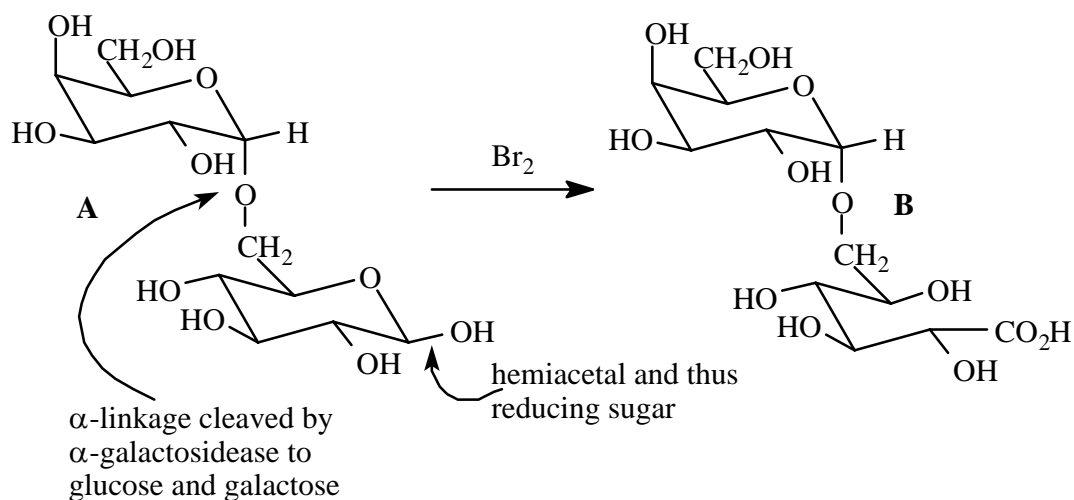
SOLUTION 10

Melibiose **A** is 6-O- α-D-galactopyranosyl-D-glucopyranose

SOLUTION 11

Both reactions involve converting the carboxylic acid into the more nucleophilic carboxylate salt which then reacts in an S_N2 displacement reaction to form the ester. In the former case, iodide anion is the leaving group and in the latter example the carboxylate (formed by initial proton transfer to diazomethane) displaces N_2.
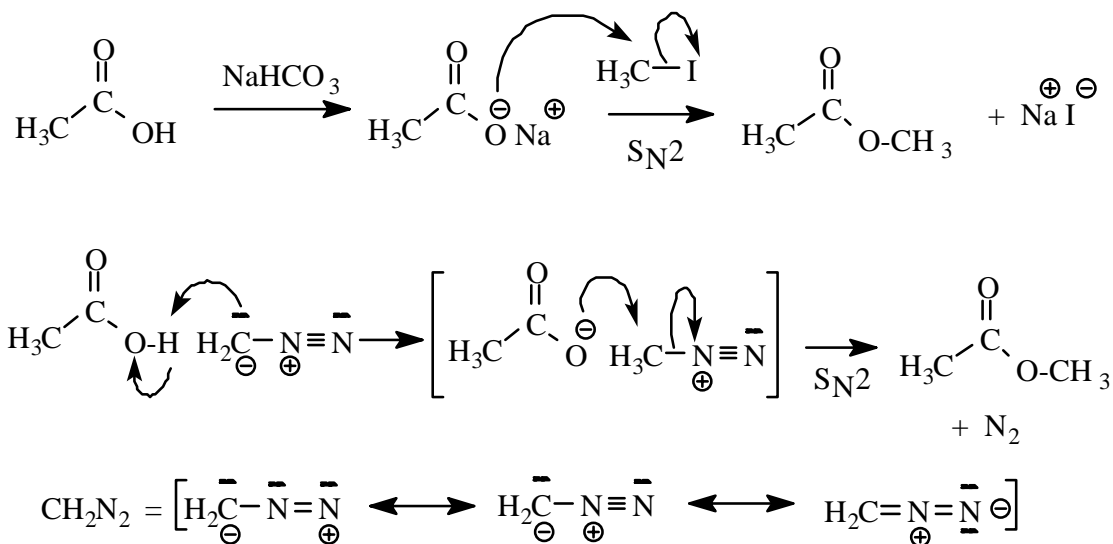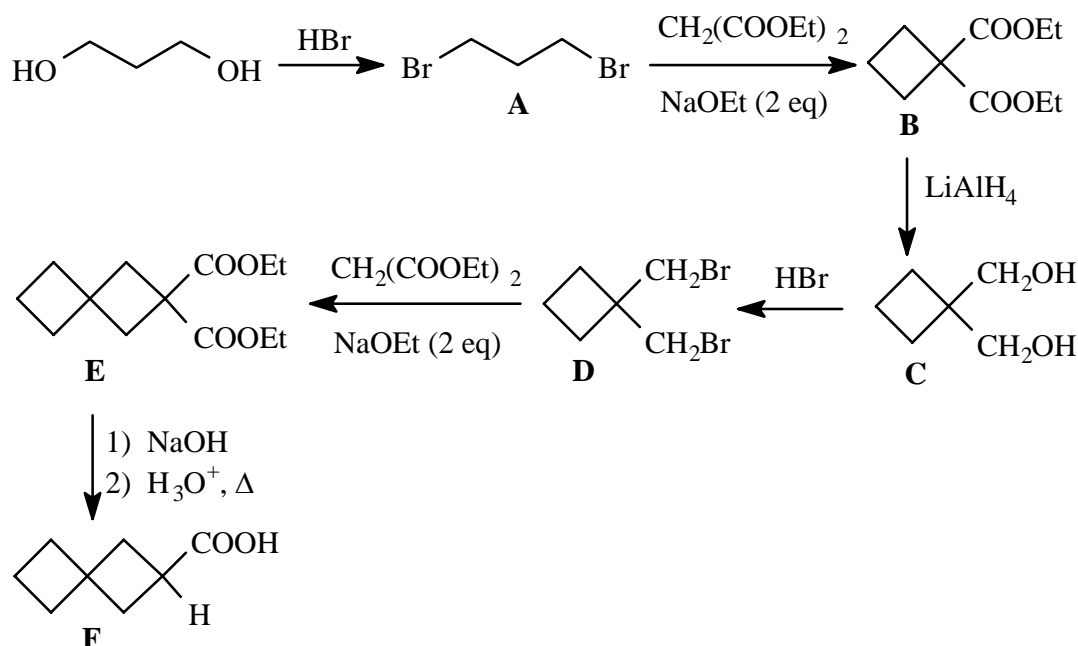
SOLUTION 12

The carbonyl group of cyclohexanone is more reactive (electrophilic) than the one of furfural since the latter is stabilized by conjugation with the aromatic ring. Therefore, if the reaction is quenched after a short period of time, the major product obtained is the one formed the most rapidly, i.e. the kinetic controlled product **D**. However, the reaction is in equilibrium and after enough time, the major compound formed is the most thermodynamically stable product, the semicarbazone **E**. The situation is illustrated by the following energy diagram.
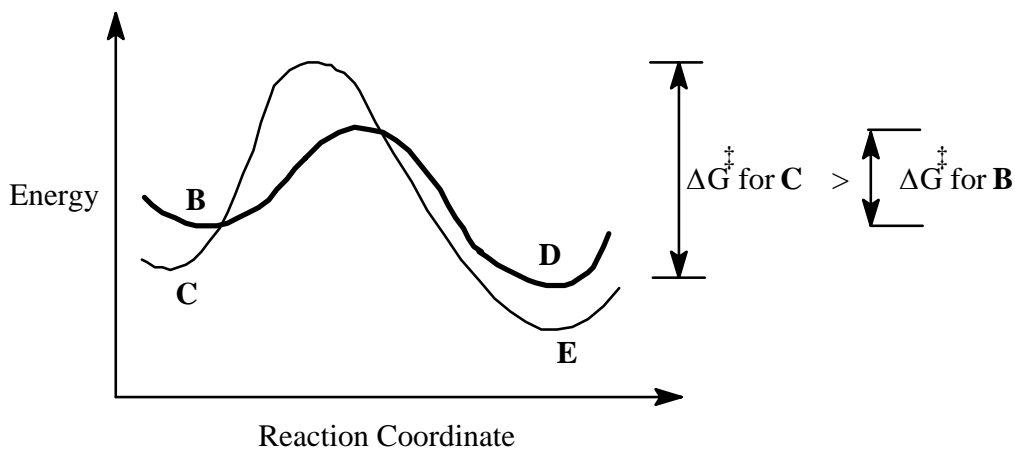
SOLUTION 13

SOLUTION 14

a)   From the formula, the number of unsaturations can be determined: For a saturated hydrocarbon there should be (10 x 2) + 2 = 22 hydrogens. Therefore (22-16)/2 H per unsaturation implies that 3 unsaturations are present.

b)   The hydrogenation product still contains one site of unsaturation and thus there must have been two double bonds present which underwent reduction.

c)   The hydrogenation product still contains one site of unsaturation and thus there must be one ring present which did not undergo reduction.

d)

α-terpinene   6-methylheptane-2,5-dione   glyoxal
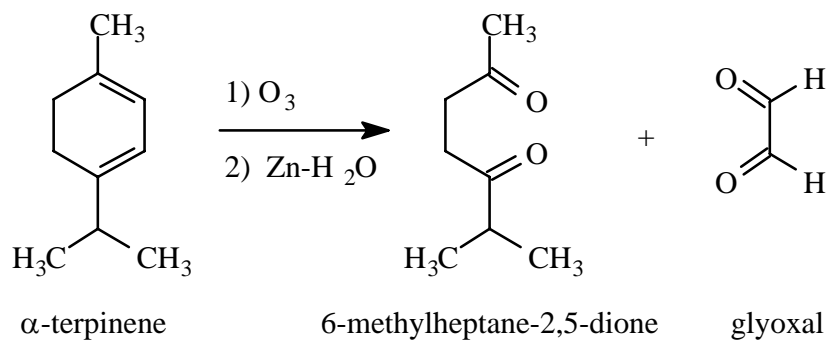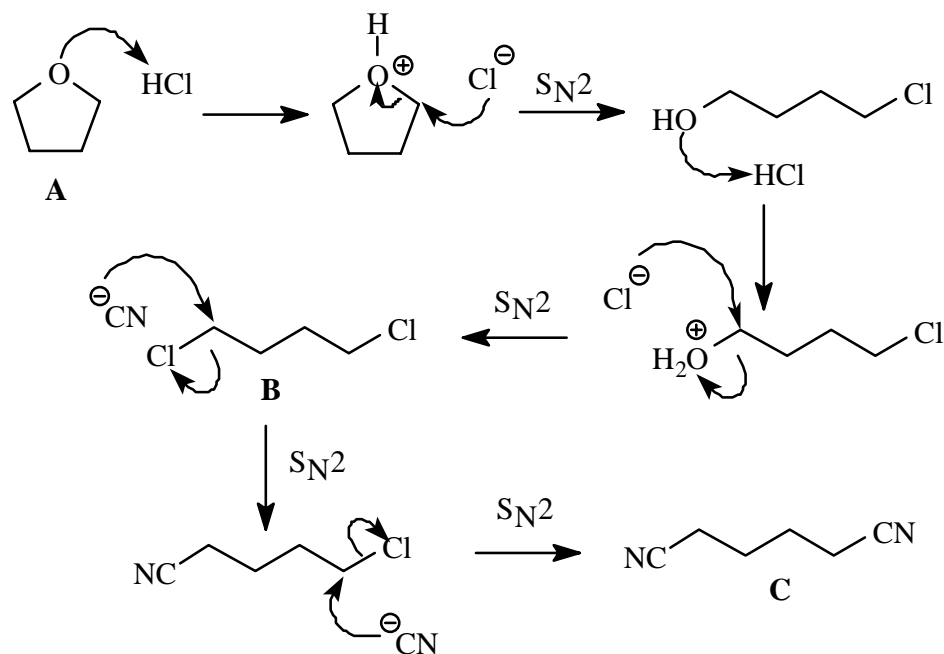
SOLUTION 15

Nitrile reduction converts nitrile groups into amino groups:

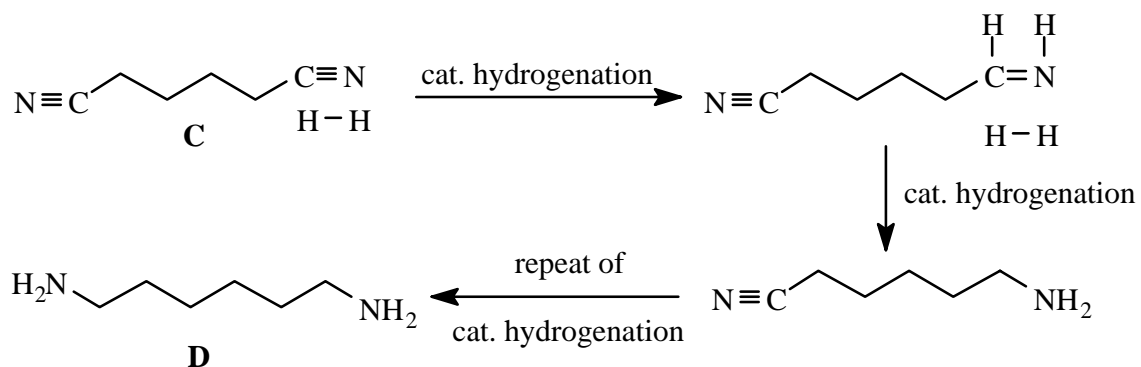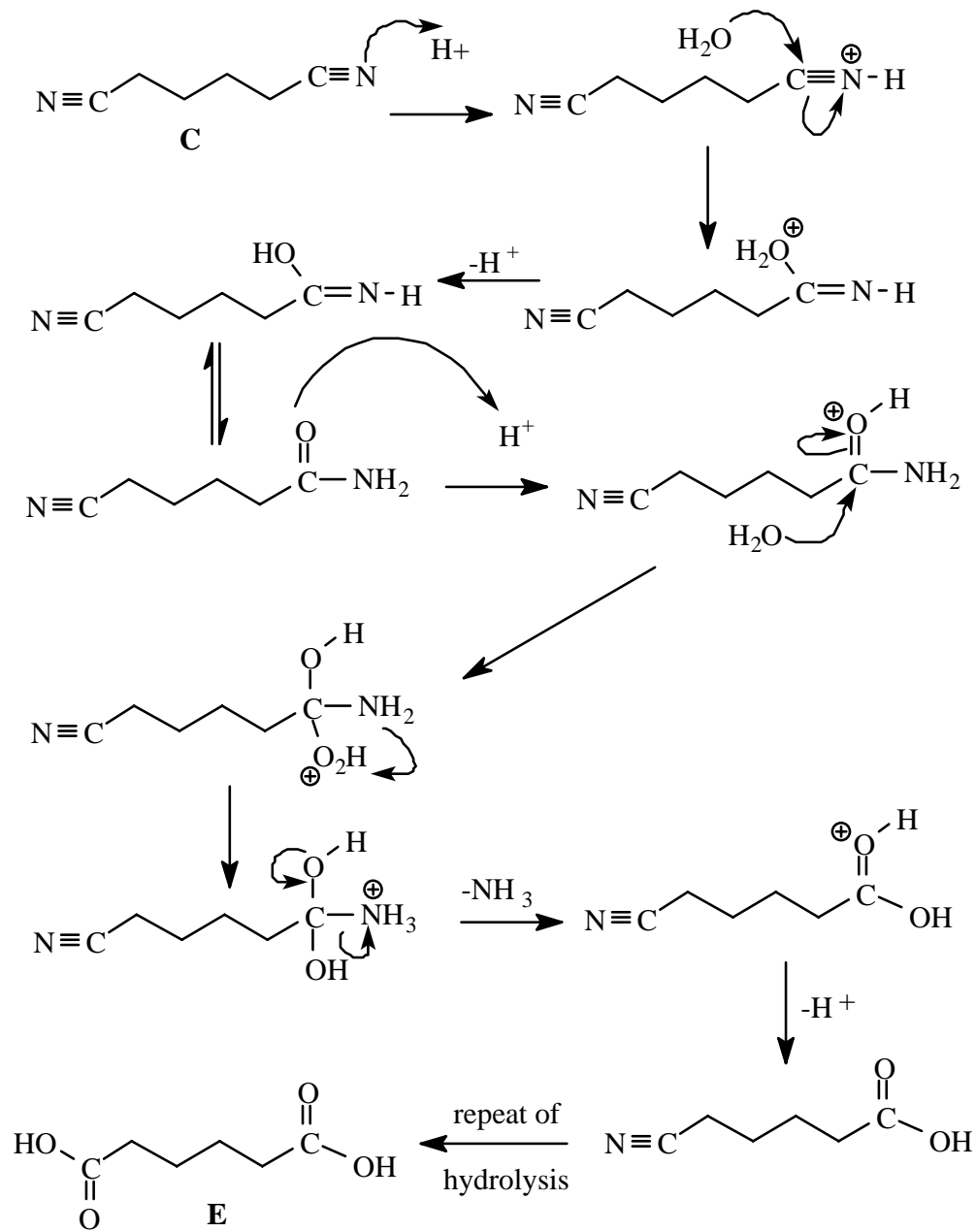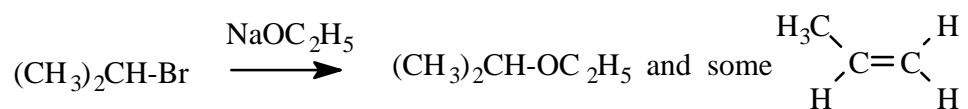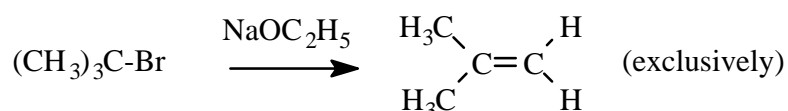Nitrile hydrolysis converts nitrile groups into carboxylic acid groups:

SOLUTION 16

The reaction of chlorohydrocarbons with an aqueous solution of $AgNO_3$ leads to the corresponding alcohols by means of an S_N1 mechanism. Since the rate limiting step in S_N1 reactions is the formation of the carbocation, the compound that generates the most stable cation will react more rapidly. Compound **A** is the least reactive since the carbocation cannot be planar due to its bridge nature. Also the carbocation cannot be stabilized by resonance because delocalization introduces too much strain into the system.
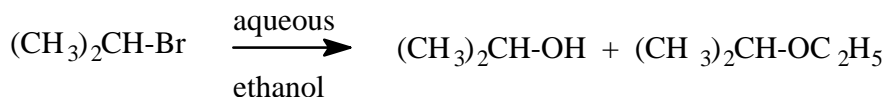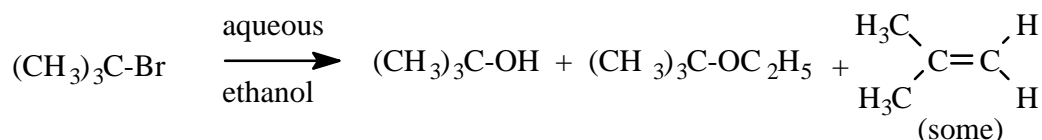
Compound **C** is the most reactive. Its carbocation is tertiary, can adopt a planar structure, and is stabilized by resonance involving the three aromatic substituents. Compound **B** has a reactivity intermediate between those of **A** and **C**.

SOLUTION 17

Sodium ethoxide: 2-methyl-2-bromopropane yields more alkene

$$(CH_3)_3C\text{-Br} \xrightarrow{NaOC_2H_5} \quad \begin{matrix} H_3C \\ H_3C \end{matrix} C{=}C \begin{matrix} H \\ H \end{matrix} \quad \text{(exclusively)}$$

$$(CH_3)_2CH\text{-Br} \xrightarrow{NaOC_2H_5} (CH_3)_2CH\text{-OC}_2H_5 \text{ and some } \begin{matrix} H_3C \\ H \end{matrix} C{=}C \begin{matrix} H \\ H \end{matrix}$$

Aqueous 60% ethanol: 2-methyl-2-bromopropane still yields more alkene

$$(CH_3)_3C\text{-Br} \xrightarrow[\text{ethanol}]{\text{aqueous}} (CH_3)_3C\text{-OH} + (CH_3)_3C\text{-OC}_2H_5 + \begin{matrix} H_3C \\ H_3C \end{matrix} C{=}C \begin{matrix} H \\ H \end{matrix}$$
$$\text{(some)}$$

$$(CH_3)_2CH\text{-Br} \xrightarrow[\text{ethanol}]{\text{aqueous}} (CH_3)_2CH\text{-OH} + (CH_3)_2CH\text{-OC}_2H_5$$

The stronger the base, the higher the percentage of elimination and thus more elimination occurs in sodium ethoxide. Elimination is also favoured over substitution on tertiary halides since the double bond formed is more stable and the substitution site is more sterically hindered than in secondary halides. In the case of aqueous ethanol, a mixture of alcohol and ether are obtained since both water and ethanol can compete as nucleophiles.

SOLUTION 18

a) In the first step, the tert-butyl alcohol is converted to the corresponding carbocation. The latter can lose a proton to yield 2-methylpropene or can abstract a hydride ion from the isopropyl group of the starting material. This reaction is feasible because the new carbocation generated is more stable that the tert-butylcarbocation since it is also tertiary and furthermore is stabilized by resonance with the aromatic ring. The new carbocation can react with the electron-rich 2-methylpropene to yield yet another carbocationic intermediate which can perform an intramolecular electrophilic substitution on the aromatic ring to give the final product.
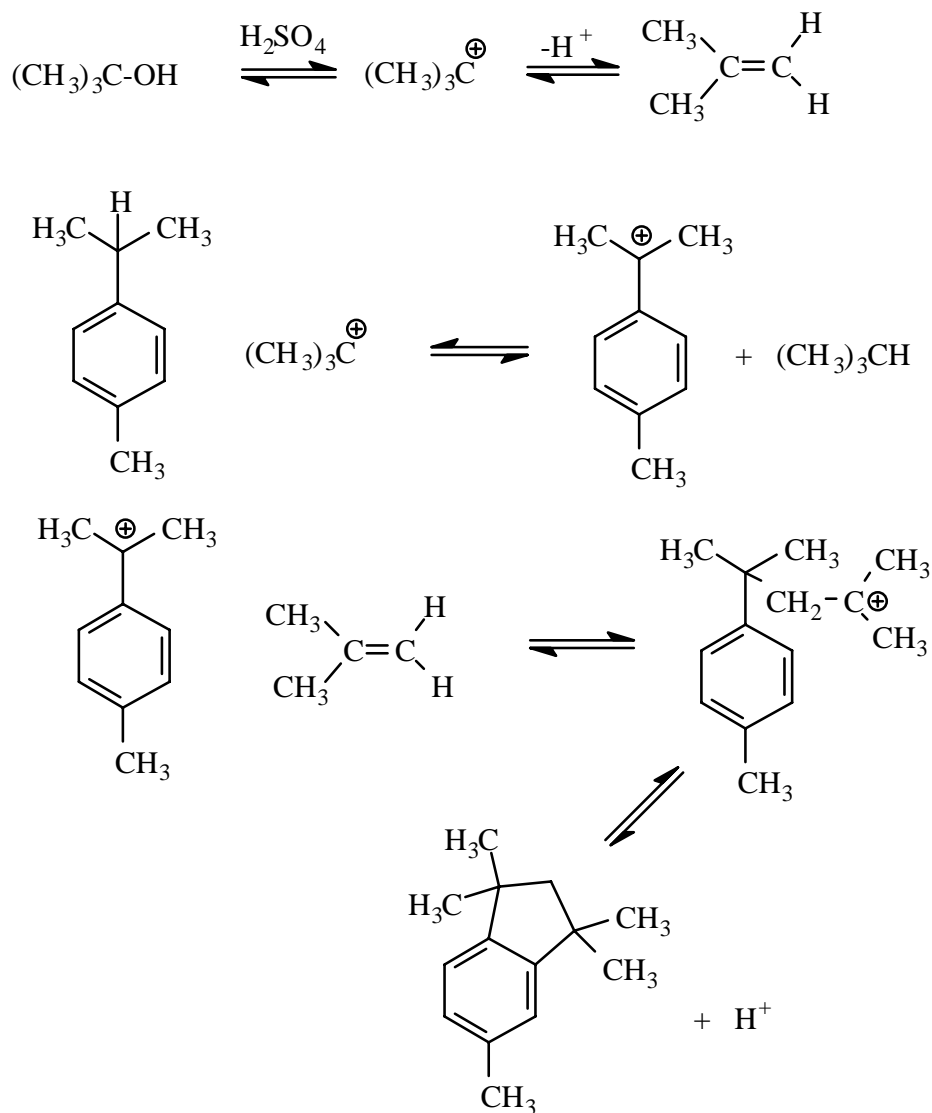
b)   With 1,4-dimethylbenzene, only the 2,5-dimethyl-tert-butylbenzene would be obtained via a normal electrophilic substitution since the abstraction of a hydride ion from a methyl group is unfavourable.
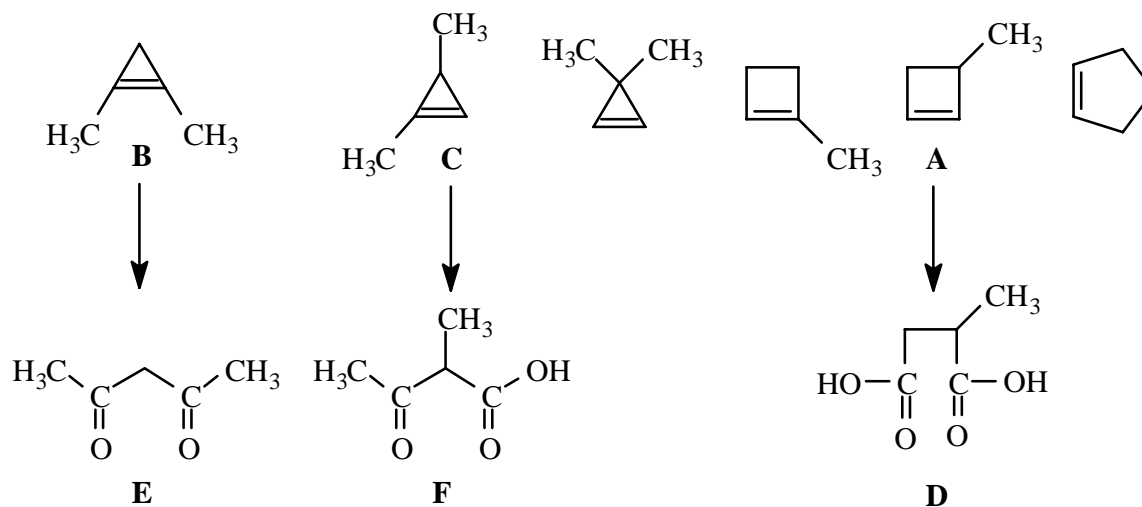
SOLUTION 19

1	2	3	4	5
D	**B**	**E**	**A**	**C**
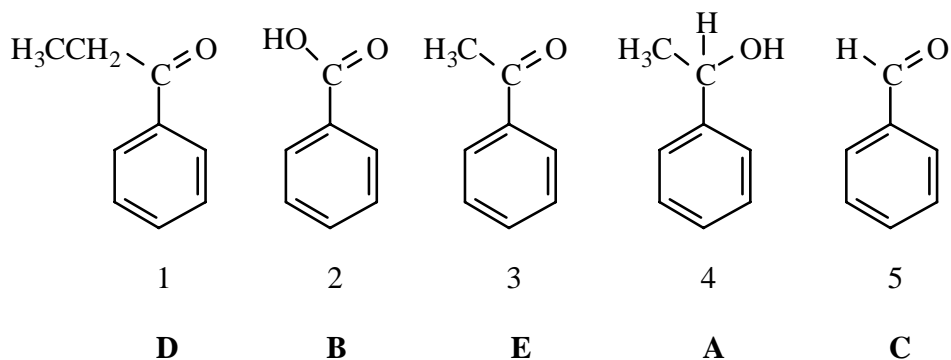
i)   Chromate oxidation will identify readily oxidizable groups such as alcohols and aldehydes and thus 4 and 5 must be **A** and **C** (although which is which cannot be determined yet).

ii)   Permanganate oxidation will also identify readily oxidizable groups such as alcohols and aldehydes in addition to alkenes (absent in this case). This test merely confirms the tentative assignment of part (i).

iii)   Solubility in base and a positive litmus test implies an acidic group. The only acidic system is the carboxylic acid 2 and thus this must be **B**.

iv)   The iodoform test will be positive for methyl ketones and for secondary methyl alcohols (which are oxidized to methyl ketones by the reagent) and thus 3 and 4 must be **A** and **E**. Since from (i) and (ii) above we know that 4 and 5 must be **A** and **C**, it follows that 5 is **C**, 4 is **A** and thus 3 must be **E**. At this point only 1 is unassigned and thus must be **D**.

v)   The 2,4-dinitrophenylhydrazine is a test for aldehydes and ketones. Only 1, 3 and 5 will react which serves to confirm the above carbonyl group assignments.

SOLUTION 20

SOLUTION 21

a)   Both reactions are S_N2 displacements at primary carbon atoms. The S_N2 reaction is primarily controlled by steric interactions. 1-Bromo-2-methylbutane is branched at the β-position which hinders the attack of the thiolate nucleophile, whereas the 1-bromobutane is relatively open to the displacement and thus reacts more rapidly.

b)   The first reaction involves deprotonation/protonation and effects only the O-H bond and not the configuration of the chiral centre. Thus there is no loss of optical activity. The second reaction involves the C-O bond of the chiral centre and proceeds via the formation of a carbocation which is a planar species. Addition of water to the carbocation may occur equally from either side leading to formation of racemic recovered alcohol and thus loss of optical activity.
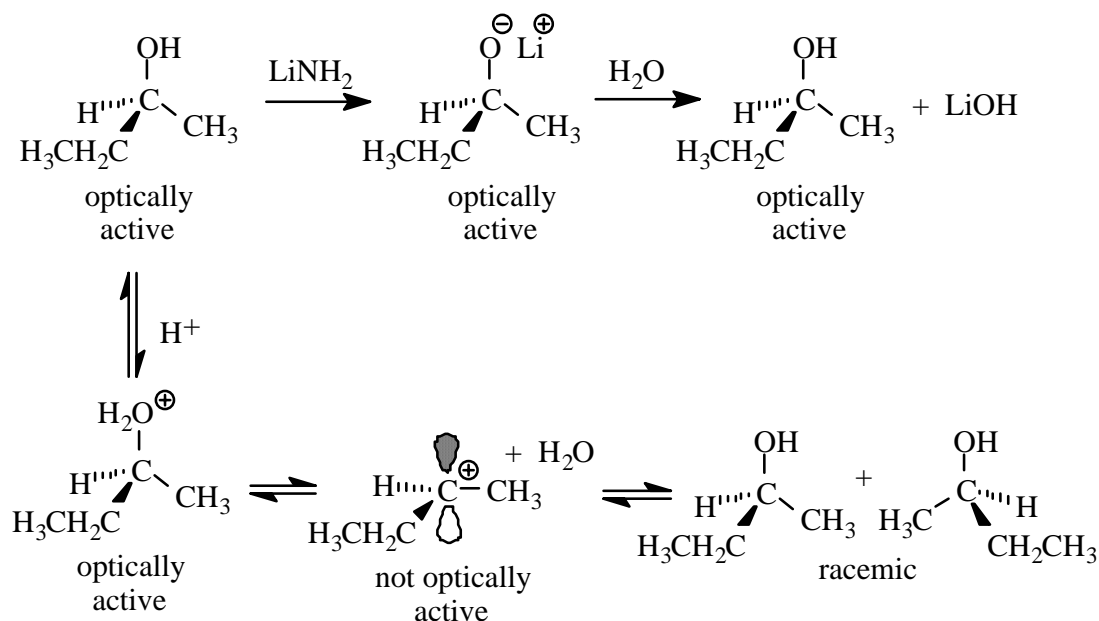
c)   Bromine addition follows an anti process to lead to a trans product. The initial bromonium ion can be formed equally on the top or bottom face of the cyclobutene to form the identical species. Opening of this intermediate at either end of the former double bond by the bromide ion leads an equal mixture of the (R,R)- and (S,S)- products, i.e. a racemate, which is optically inactive. Hydrogen addition (involving any of the isotopes) follows a syn process to lead to a cis product. The addition may again take place with equal ease from the top or the bottom face of the cyclobutene but this time both products are the identical meso compound. The product is also optically inactive.
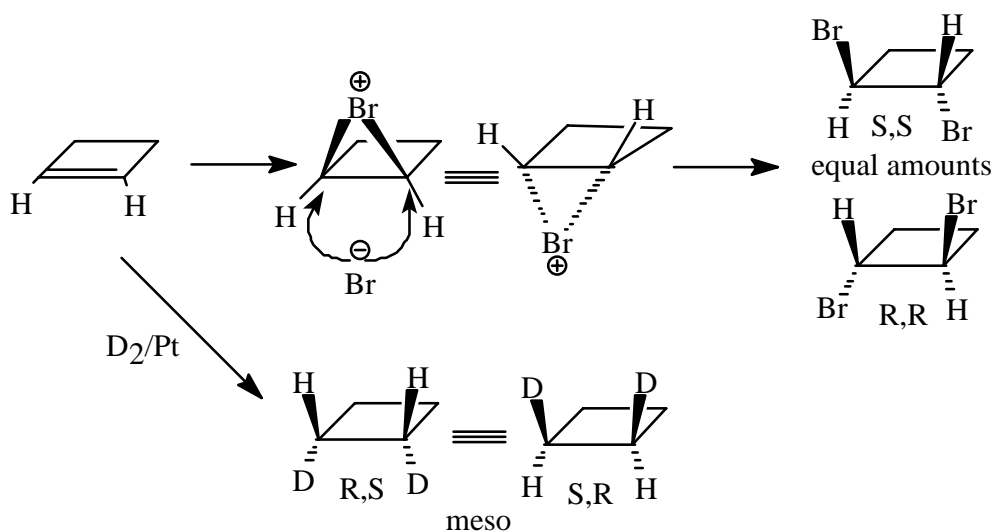
d)   High concentration of the nucleophile (HO⁻) favours the S_N2 reaction which proceeds with 100% inversion of configuration at the displaced centre.

e)   Low concentration of the nucleophile (HO⁻) favours the S_N1 process which proceeds via a carbocation. This planar intermediate can be trapped by the solvent or the nucleophile from either side leading to racemization. Under a given set of conditions, the rate of an S_N1 reaction is directly dependent only on th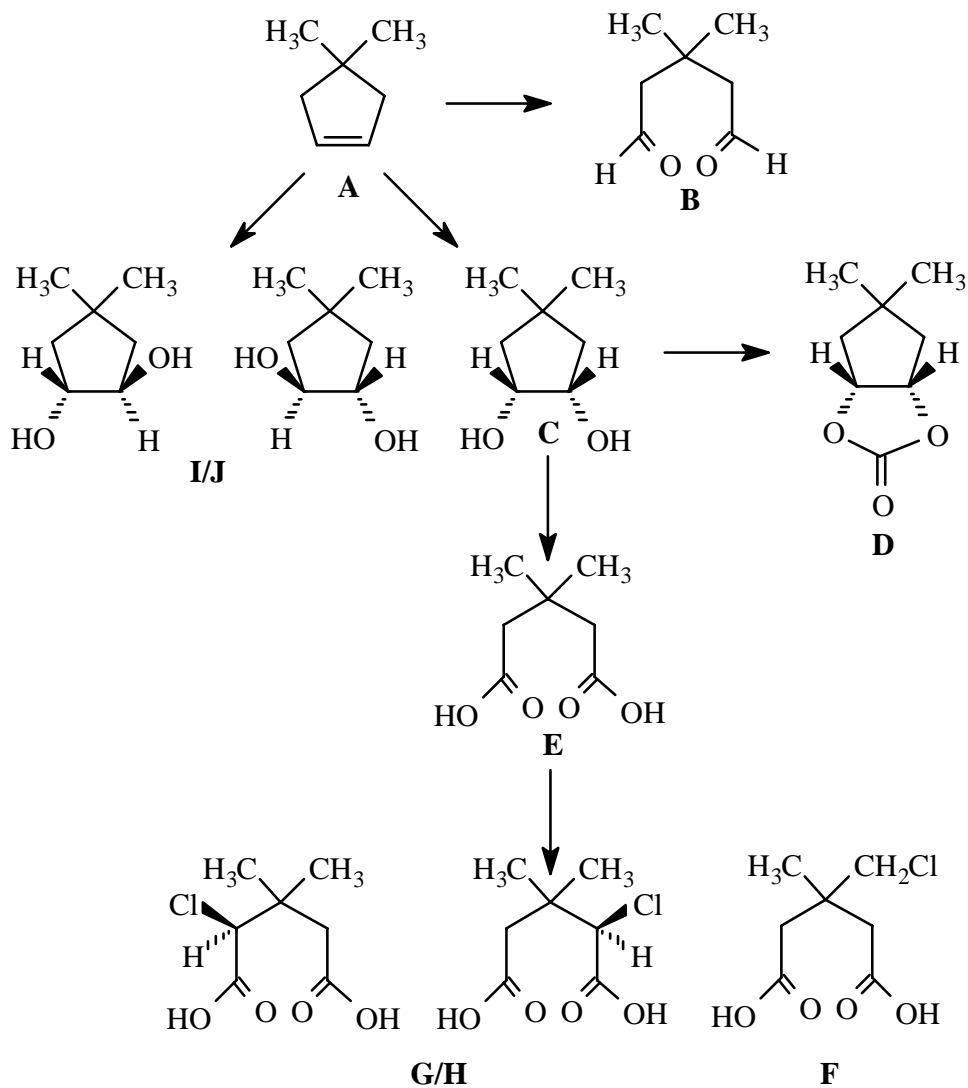e concentration of the alkyl halide. Thus doubling the alkyl halide concentration will double the rate of formation of the alcohol. Doubling the concentration of the nucleophile (HO⁻) will have no effect on the rate of the reaction.

f)   Reaction [1] is an S_N2 reaction in which the nucleophile (CH_3O^-) displaces the bromide anion with inversion of configuration. Elimination is not possible because the bromine and the lone hydrogen on the adjacent carbon atom cannot assume the necessary anti-periplanar conformation; i.e. both cannot be axial.
Reaction [2] is an E_2 elimination process which occurs readily because a "ring flip" of the conformer shown will produce the anti-periplanar arrangement of the hydrogen and the bromine.

S_N2 [1]

E_2 [2]

CH_3OH

SOLUTION 22

A

CH_3SO_2Cl

Et_3N

a mesylate

$Br^{\ominus}$

S_N2

B

C
trans

D
cis

F

E
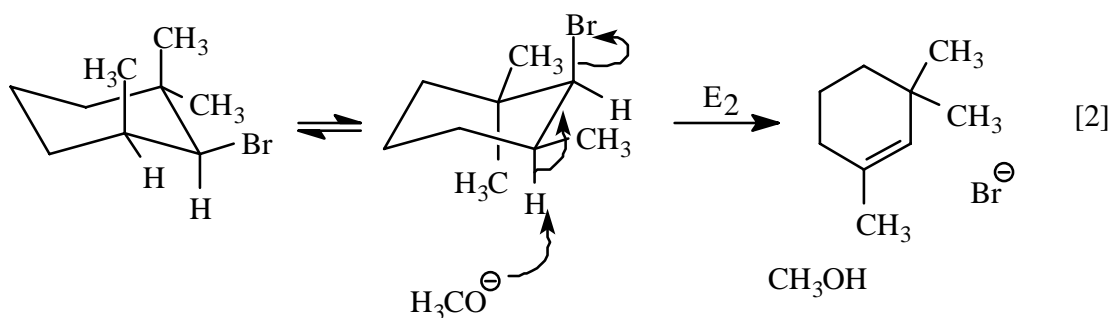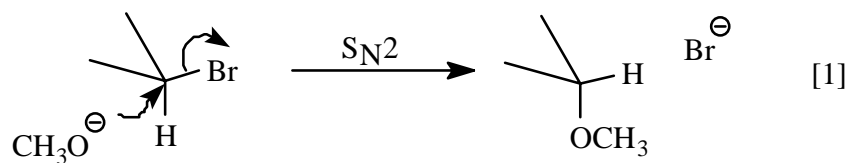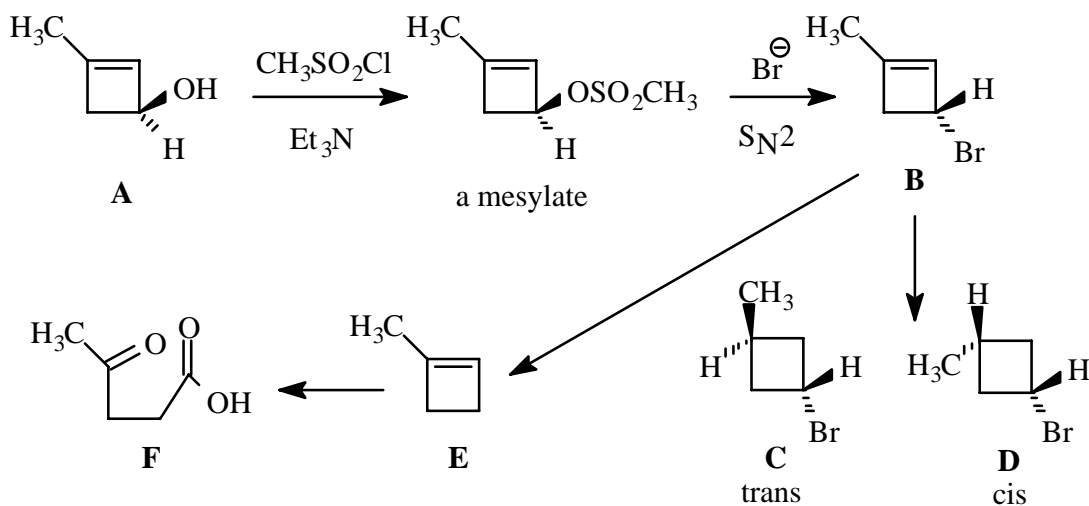
SOLUTION 23

SOLUTION 24

a)

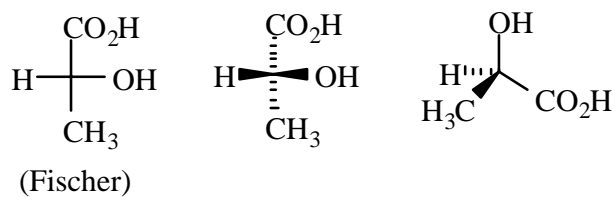$$Ca_5(PO_4)_3OH \ (s) \xrightleftharpoons{\ H_2O \ (l)\ } 5Ca^{2+} \ (aq) \ + \ 3PO_4^{3-} \ (aq) \ + \ HO^- \ (aq)$$
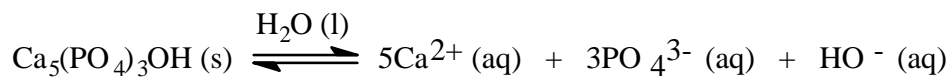
b) other variations also possible

(Fischer)

IUPAC name: (2*R*)-(-)-2-hydroxypropanoic acid
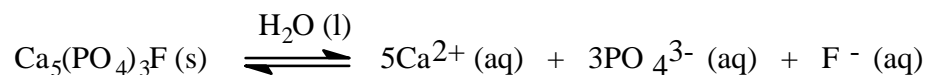
other variations include: (2*R*)-(*l*)-2-hydroxypropanoic acid

(*R*)-(-)-2-hydroxypropanoic acid

(*R*)-(*l*)-2-hydroxypropanoic acid

(2*R*)-(-)-lactic acid

(2*R*)-(*l*)-lactic acid

(*R*)-(-)-lactic acid

(*R*)-(*l*)-lactic acid

c)   Tooth decalcification is related to the reaction of demineralization of hydroxyapatite, or to the shift of its equilibrium through the formation of the ions in solution. So, the influence of an acidic medium should shift the equilibrium to the right. Since the quantity of solid hydroxyapatite has no effects, one has to look at the species that can react with acids. In an acidic medium, the H^+ ions can strongly react with two of the three ions produced during demineralization of hydroxyapatite, namely OH^- and PO_4^{3-} ions. The latter are strong bases which will react with H^+ ions to form their respective conjugate acid as shown by the following equations:

$$HO^- \text{ (aq) } + \text{ } H^+ \text{ (aq) } \rightleftharpoons \text{ } H_2O \text{ (l)} \qquad\qquad K_w^{-1}$$

$$PO_4^{3-} \text{ (aq) } + \text{ } H^+ \rightleftharpoons \text{ } HPO_4^{2-} \text{ (aq)} \qquad\qquad K_{a3}^{-1}$$

d)

$$Ca_5(PO_4)_3F \text{ (s) } \xrightarrow{\text{ } H_2O \text{ (l)} \text{ }} 5Ca^{2+} \text{ (aq) } + \text{ } 3PO_4^{3-} \text{ (aq) } + \text{ } F^- \text{ (aq)}$$

The dissolution of x mol of $Ca_5(PO_4)_3F$ in 1 L of water will produce 5x mol/L of Ca^{2+}, 3x mol/L of PO_4^{3-} and x mol/L of F^-.

The solubility product, K_{sp}, of fluoroapatite is expressed as:

$$K_{sp} = [Ca^{2+}]^5 \text{ } [PO_4^{3-}]^3 \text{ } [F^-] = 1.0 \text{ x } 10^{-60}$$

$$1.0 \text{ x } 10^{-60} = (5x)^5 \text{ } (3x)^3 \text{ } (x) = (3125x^5) \text{ } (27x^3) \text{ } (x) = 84375x^9$$

$$x = [(1.0 \text{ x } 10^{-60})/84375]^{1/9} = 6.1 \text{ x } 10^{-8} \text{ mol/L}$$

The solubility of fluoroapatite in water is 6.1 x 10^{-8} mol/L.

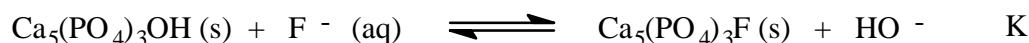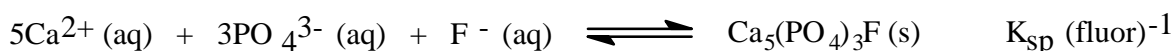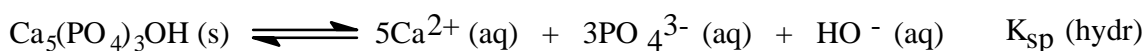Similarly, and according to the equation of part a), one can calculate the solubility of hydroxyapatite in water.

$$K_{sp} = [Ca^{2+}]^5 \, [PO_4^{3-}]^3 \, [OH^-] = 6.8 \times 10^{-37}$$

$$6.8 \times 10^{-37} = (5x)^5 \, (3x)^3 \, (x) = (3125x^5) \, (27x^3) \, (x) = 84375x^9$$

$$x = [(6.8 \times 10^{-37})/84375]^{1/9} = 2.7 \times 10^{-5} \text{ mol/L}$$

The solubility of hydroxyapatite in water is 2.7×10^{-5} mol/L

e)   In order to show how the remineralization process is preferred in presence of F^- ions, one must evaluate the equilibrium constant of the reaction of hydroxyapatite with F^-. This reaction can be described as the sum of the following reactions:

$$Ca_5(PO_4)_3OH \text{ (s)} \;\rightleftharpoons\; 5Ca^{2+} \text{ (aq)} \; + \; 3PO_4^{3-} \text{ (aq)} \; + \; HO^- \text{ (aq)} \qquad K_{sp} \text{ (hydr)}$$

$$5Ca^{2+} \text{ (aq)} \; + \; 3PO_4^{3-} \text{ (aq)} \; + \; F^- \text{ (aq)} \;\rightleftharpoons\; Ca_5(PO_4)_3F \text{ (s)} \qquad K_{sp} \text{ (fluor)}^{-1}$$

$$Ca_5(PO_4)_3OH \text{ (s)} \; + \; F^- \text{ (aq)} \;\rightleftharpoons\; Ca_5(PO_4)_3F \text{ (s)} \; + \; HO^- \qquad K$$

$$\text{where } K = K_{sp}(\text{hydr.}) / K_{sp}(\text{fluor.})$$

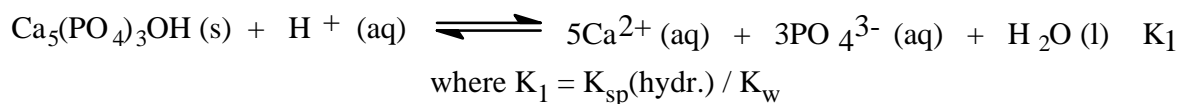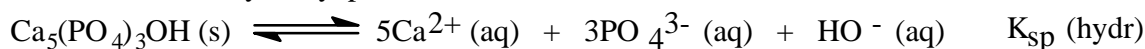$$K = (6.8 \times 10^{-37}) / (1.0 \times 10^{-60})$$

$$K = 6.8 \times 10^{23}$$

Since the value of K is very large, this reaction will always be complete, so that the remineralization process is preferred when hydroxyapatite is in the presence of F^- ions.

f)   Here again, we have to calculate the equilibrium constants of the reactions of hydroxyapatite (or fluoroapatite) with the H^+ ions of the acidic medium.
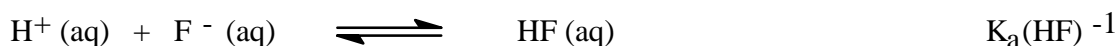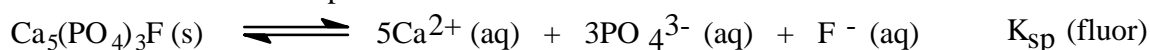
Reaction with hydroxyapatite:

$$Ca_5(PO_4)_3OH \text{ (s)} \rightleftharpoons 5Ca^{2+} \text{ (aq)} + 3PO_4^{3-} \text{ (aq)} + HO^- \text{ (aq)} \qquad K_{sp} \text{ (hydr)}$$

$$H^+ \text{ (aq)} + HO^- \text{ (aq)} \rightleftharpoons H_2O \text{ (l)} \qquad K_w^{-1}$$

$$Ca_5(PO_4)_3OH \text{ (s)} + H^+ \text{ (aq)} \rightleftharpoons 5Ca^{2+} \text{ (aq)} + 3PO_4^{3-} \text{ (aq)} + H_2O \text{ (l)} \quad K_1$$

$$\text{where } K_1 = K_{sp}(\text{hydr.}) / K_w$$

$$K_1 = (6.8 \times 10^{-37}) / (1.0 \times 10^{-14})$$

$$K_1 = 6.8 \times 10^{-23}$$

Reaction with fluoroapatite:

$$Ca_5(PO_4)_3F \text{ (s)} \rightleftharpoons 5Ca^{2+} \text{ (aq)} + 3PO_4^{3-} \text{ (aq)} + F^- \text{ (aq)} \qquad K_{sp} \text{ (fluor)}$$

$$H^+ \text{ (aq)} + F^- \text{ (aq)} \rightleftharpoons HF \text{ (aq)} \qquad K_a(HF)^{-1}$$

$$Ca_5(PO_4)_3F \text{ (s)} + H^+ \text{ (aq)} \rightleftharpoons 5Ca^{2+} \text{ (aq)} + 3PO_4^{3-} \text{ (aq)} + HF \text{ (aq)} \quad K_2$$

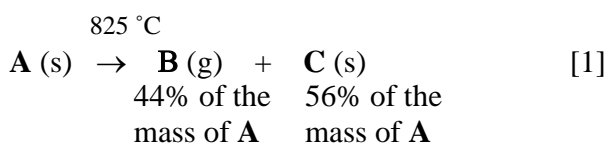$$\text{where } K_2 = K_{sp}(\text{fluor.}) / K_a(HF)$$
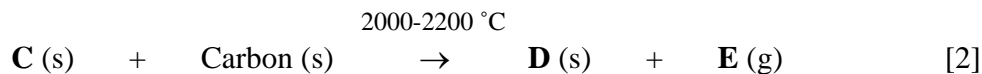
$$K_2 = (1.0 \times 10^{-60}) / (7.2 \times 10^{-4})$$

$$K_2 = 1.4 \times 10^{-57}$$

Since the equilibrium constant K_2 is smaller, the reaction of hydroxyapatite with H^+ ions is preferred relative to the reaction of fluoroapatite with H^+ ions.

SOLUTION 25

The best way to start this problem is to write the chemical equations including the unknowns in order to represent the different steps with their details.
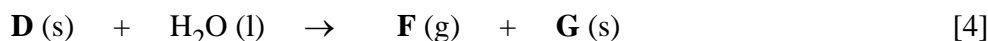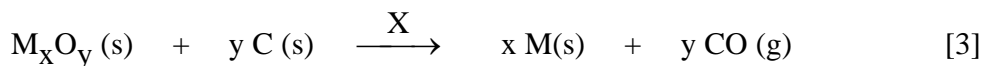
$$\overset{825\ °C}{A \text{ (s)} \rightarrow \underset{\substack{44\% \text{ of the} \\ \text{mass of } A}}{B \text{ (g)}} + \underset{\substack{56\% \text{ of the} \\ \text{mass of } A}}{C \text{ (s)}}} \qquad [1]$$

$$\text{C (s)} \quad + \quad \text{Carbon (s)} \quad \xrightarrow{\text{2000-2200 °C}} \quad \textbf{D} \text{ (s)} \quad + \quad \textbf{E} \text{ (g)} \qquad [2]$$

Gas **E** contains the same elements as gas **B**, but in different proportions. Some possibilities are: NO, NO_2, N_2O, NO_3, CO, CO_2, SO_2, and SO_3. It can not be a pure gaseous element since gases **B** and **E** contains the same elements. Hydrogen halides (HX) must also be excluded since no other gases with H and X can be formed with other proportions. Large evolutions of nitrogen- or sulfur-based gases are rarely observed during the pyrolysis of minerals. Moreover, the temperature of reaction [1] can correspond to that of a calcification with CO_2 gas evolution (**B**).

The original purpose of reaction [2] was to isolate the metal in **C** according to reaction [3] below (where **C** would be a metallic oxide), but products **D** and **E** were obtained instead. Gas **E** could be carbon monoxide, CO. In reaction [2], the metal must be in **D** since **E** is a gas.

$$M_xO_y \text{ (s)} \quad + \quad y \text{ C (s)} \quad \xrightarrow{\text{X}} \quad x \text{ M(s)} \quad + \quad y \text{ CO (g)} \qquad [3]$$

$$\textbf{D} \text{ (s)} \quad + \quad H_2O \text{ (l)} \quad \rightarrow \quad \textbf{F} \text{ (g)} \quad + \quad \textbf{G} \text{ (s)} \qquad [4]$$
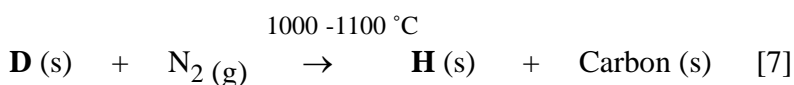
The hydrolysis reaction can be the addition of a water molecule to **D**, an oxidation of **D**, or an acid-base reaction. Since **F** is a gas and **D** contains a metal, then the insoluble compound **G** must contain this metal. A large volume of gas **F** was produced and the latter burns with a brilliant, sooty flame. The major constituents of **F** form a large proportion of **D** and it must contain carbon. If **F** reacts with water to form an aldehyde **L**, it does not initially contain an oxygen atom. Its reactivity with water indicates that **F** can be ethene (C_2H_4), ethyne (C_2H_2), propene (C_3H_6) or propyne (C_3H_4). The heavier alkenes or alkynes are not gases. Nevertheless, ethyne and propyne are more probable since the formation of aldehyde **L** would be difficult with only one unsaturation in the molecule. Reaction [4] would then be an acid-base reaction. The anionic part of **D** acts as a base and removes the H^+ ions from H_2O, and the OH^- ions are associated with the metal cation. Before hydrolysis, the anion of **D** could be C_2^{2-}, HC_2^-, $C_3H_2^{2-}$ (less probable!) or $C_3H_3^-$. The poorly soluble solid **G** must contain at least one OH^- ion.

$$\textbf{G} \text{ (s)} \quad \xrightarrow{\Delta} \quad \textbf{C} \text{ (s)} \quad + \quad H_2O \text{ (l)} \qquad [5]$$

Pyrolysis of **G** produces water and compound **C**. There must be another source of H in **G**. If other OH⁻ ions are present in **G**, then compound **C** is an oxide. This reinforces the hypothesis stated from the results of reaction [2].

$$\textbf{G (s)} \quad + \quad \textbf{B (g)} \quad \rightarrow \quad H_2O \text{ (l)} \quad + \quad \textbf{A' (s)} \qquad\qquad [6]$$
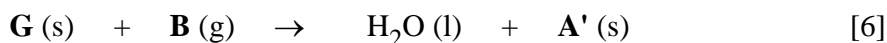
The composition of **A'** is exactly the same as that of the mineral substance **A**. If **B** is CO_2 then **A** (or **A'**) must be a carbonate, which is possible for a mineral substance. Compound **A'** could be calcium carbonate which is the most common natural carbonate. Compound **G**, containing at least one OH⁻ ion, can be calcium hydroxide, which has a relatively low solubility.

$$\overset{1000 \text{ -} 1100 \text{ °C}}{\textbf{D (s)} \quad + \quad N_{2\text{ (g)}} \quad \rightarrow} \quad \textbf{H (s)} \quad + \quad \text{Carbon (s)} \quad [7]$$

Compound **H** is ionic and very reactive. It contains 15%C and 35%N, the remaining material being the metal. So, the anionic part is made of carbon and nitrogen.

Assume 100 g of compound **H**: (15 g C) / (12.011 g/mol) = 1.2<u>5</u> mol C
(35 g N) / (14.007 g/mol) = 2.5<u>0</u> mol N

Empirical formula of the anion: $(CN_2)_n{}^{x-}$

If the formula of the anion is CN_2 and that of compound **H** is MCN_2, then 50 g of the metal is equivalent to 1.25 mol of this metal. The molar mass of the latter would then be 40 g and it would be calcium. This is highly probable taking into account the information deduced already.
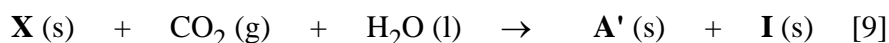
If the formula of the anion is $(CN_2)_2$ or C_2N_4 and that of compound **H** is MC_2N_4, then 50 g of the metal is equivalent to 0.625 mol of this metal. The molar mass would be 80 g but there is no metal having such a molar mass.

If the formula of the anion is $(CN_2)_3$ or C_3N_6 and that of compound **H** is MC_6N_6 then 50 g of the metal is equivalent to 0.417 mol of this metal. The molar mass of the latter would be of 120 g which could be a heavy metal like tin or lead. However, these metals are not present as carbonates in nature.

In reaction [1], we noticed a weight loss of 44% between **A** and **C**. So the mass ratio of **C/A** is 56%. Assuming that **B** is CO_2, **A** would be calcium carbonate and **C** would be calcium oxide. The mass ratio of $CaO/CaCO_3$ is 56%. Gas **E** would be CO, which is frequently observed during the reactions of metallic oxides with carbon. So we are dealing with calcium compounds.

$$\textbf{H} \text{ (s)} \quad + \quad H_2O \text{ (l)} \quad \rightarrow \quad \textbf{G} \text{ (s)} \quad + \quad \textbf{X} \text{ (s)} \qquad \text{[8]}$$
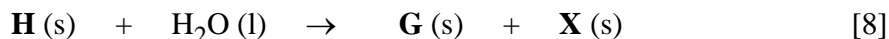
Since **H**, **G**, and **X** are ionic, and they are formed from the same metal, the anionic part containing C and N is in compound **X**. As in reaction [4], it is a hydrolysis where an acid reacts with a base. The base is the cyanamide ion, CN_2^{2-}, that is partially hydrogenated into HCN_2^- which is an intermediate species in the formation of dihydrogen cyanamide, H_2CN_2.

$$\textbf{X} \text{ (s)} \quad + \quad CO_2 \text{ (g)} \quad + \quad H_2O \text{ (l)} \quad \rightarrow \quad \textbf{A'} \text{ (s)} \quad + \quad \textbf{I} \text{ (s)} \quad \text{[9]}$$
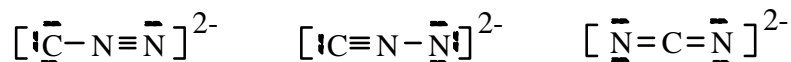
Under these conditions, **X** must be $Ca(HCN_2)_2$ and both protons from the carbonic acid produced by reaction of CO_2 and H_2O allow the formation of dihydrogen cyanamide, H_2CN_2, i.e. compound **I**.

$$\textbf{I} \text{ (s)} \quad + \quad H_2O \text{ (l)} \quad \rightarrow \quad \textbf{J} \text{ (s)} \qquad \text{[10]}$$
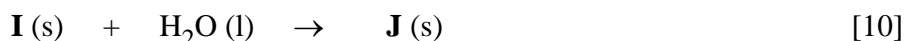
Since only one compound was formed in reaction [10], the hydrolysis must now be an addition of water to **I**. To deduce the structure of compound **J**, one must know that of compound **I**. To deduce the latter, one can refer to that of the cyanamide ion, CN_2^{2-}.

Following are the three possible structures for cyanamide ion of compound **H**:

$$\left[\,\overline{\underline{C}} - N \equiv \overline{N} \, \right]^{2-} \qquad \left[\,C \equiv N - \overline{\underline{N}}\, \right]^{2-} \qquad \left[\, \overline{\underline{N}} = C = \overline{\underline{N}} \, \right]^{2-}$$

The first two must be excluded because of the heavy negative charge (2-) on their respective carbon and nitrogen atoms. In the third structure, the two negative charges are evenly distributed on the two terminal nitrogen atoms. Adding two protons to this structure, one obtains a possible structure of compound **I** which is a symmetrical molecule.
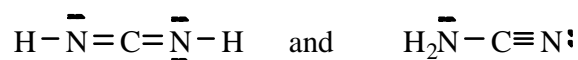
$$H - \underline{N} = C = \underline{N} - H$$
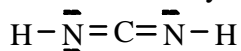
The addition of a water molecule to such a compound produces urea which is frequently used in fertilizers. So compound **J** is urea, $H_2N(CO)NH_2$.

$$\textbf{J} \text{ (s)} \quad + \quad H_2O \text{ (l)} \quad \rightarrow \quad \textbf{B} \text{ (g)} \quad + \quad \textbf{K} \text{ (g)} \qquad \text{[11]}$$
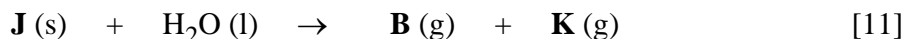
Hydrolysis of **J** causes the complete oxidation of carbon into CO_2 (gas **B**) and into NH_3 (gas **K**). The latter has a strong, characteristic odour.

a)   **A or A':** $CaCO_3$ (s)   Calcium carbonate (or calcareous rocks)

   B: CO_2 (g)   Carbon dioxide

   C: CaO (s)   Calcium oxide

   D: CaC_2 (s)   Calcium carbide

   E: CO (g)   Carbon monoxide

   F: C_2H_2 (g)   Ethyne

   G: $Ca(OH)_2$ (s)   Calcium hydroxide

   H: $CaCN_2$ (s)   Calcium cyanamide

   I: H_2CN_2 (s)   Dihydrogen cyanamide

   J: $H_2N(CO)NH_2$ Urea

   K: NH_3 Ammonia

   L: CH_3CHO Ethanal

   M: CH_3CO_2H Ethanoic acid

   X: $Ca(HCN_2)_2$ Calcium hydrogen cyanamide

b)   The two possible structures of dihydrogen cyanamide are:

$$H-\overset{\bullet\bullet}{\underset{\bullet\bullet}{N}}=C=\overset{\bullet\bullet}{\underset{\bullet\bullet}{N}}-H \quad \text{and} \quad H_2\overset{\bullet\bullet}{N}-C\equiv N\colon$$

The second structure does not possess any center of symmetry and its $-C \equiv N$ function can absorb between 2260 and 2220 cm^{-1} in its infrared spectrum. It is thus the major structure.

c)   The Lewis structure of urea is:

$$\overset{\displaystyle \colon \!\! O \!\! \colon}{\underset{\displaystyle H_2N \diagup \overset{C}{} \diagdown NH_2}{\|}}$$
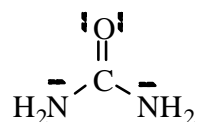
d)   The crystal structure of CaC_2 is shown below. Each unit cell contains 4 Ca^{2+} ions and 4 C_2^{2-} ions. The distance between two Ca^{2+} cations on the edge of the cell is equal to the thickness "d" of this cell. This distance is the cubic root of volume "V" of the cell. From the density of CaC_2 one can calculate the volume of its unit cell.

● Ca^{2+}　　○—○ C_2^{2-}
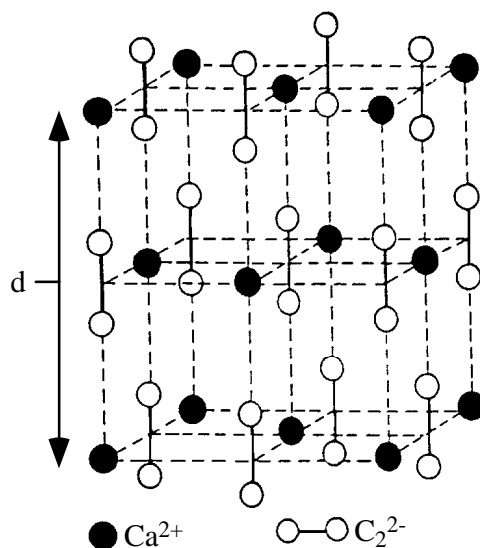
$d = (V)^{1/3}$;　　$\rho = 2.22$ g/cm^3;　　$M = 80.105$ g/mol

volume of 1 mol = M/ρ = (80.105 g/mol) / (2.22 g/cm^3) = 36.1 cm^3

$V = [(36.1$ cm$^3) / (6.022$ x 10^{23} CaCN$_2$/mol)] x (4 CaCN$_2$/unit cell)

$V = 2.40$ x 10^{-22} cm^3

$d = (2.40$ x 10^{-22} cm$^3)^{1/3}$

$d = 6.21$ x 10^{-8} cm

e)

$$\overset{825\,°C}{CaCO_3\,(s) \quad \rightarrow \quad CO_2\,(g) \;+\; CaO\,(s)} \qquad [1]$$

$$\overset{2000\text{-}2200\,°C}{CaO\,(s) \;+\; 3\,C\,(s) \quad \rightarrow \quad CaC_2\,(s) \;+\; CO\,(g)} \qquad [2]$$

$$CaC_2\,(s) \;+\; 2\,H_2O\,(l) \quad \rightarrow \quad C_2H_2\,(g) \;+\; Ca(OH)_2\,(s) \qquad [4]$$

$$\overset{HgSO_4}{C_2H_2 \;+\; H_2O\,(l) \quad \rightarrow \quad CH_3CHO} \qquad [4']$$

[O], Mn cat.

$CH_3CHO \quad \rightarrow \quad CH_3CO_2H$ [4"]

$$Ca(OH)_2 \text{ (s)} \quad \xrightarrow{\Delta} \quad CaO \text{ (s)} \quad + \quad H_2O \text{ (l)} \qquad\qquad [5]$$

$$Ca(OH)_2 \text{ (s)} \quad + \quad CO_2 \text{ (g)} \quad \rightarrow \quad H_2O \text{ (l)} \quad + \quad CaCO_3 \text{ (s)} \qquad\qquad [6]$$

$$CaC_2 \text{ (s)} \quad + \quad N_2 \text{ (g)} \quad \xrightarrow{1000\text{-}1100\ ^\circ C} \quad CaCN_2 \text{ (s)} \quad + \quad C \text{ (s)} \qquad\qquad [7]$$

$$2\ CaCN_2 \text{ (s)} \quad + \quad 2\ H_2O \text{ (l)} \quad \rightarrow \quad Ca(OH)_2 \text{ (s)} \quad + \quad Ca(HCN_2)_2 \text{ (s)} \qquad\qquad [8]$$

$$Ca(HCN_2)_2 \text{ (s)} + CO_2 \text{ (g)} + H_2O \text{ (l)} \rightarrow CaCO_3 \text{ (s)} + 2\ H_2CN_2 \text{ (s)} \qquad [9]$$

$$H_2CN_2 \text{ (s)} \quad + \quad H_2O \text{ (l)} \quad \rightarrow \quad H_2N(CO)NH_2 \text{ (s)} \qquad\qquad [10]$$

$$H_2N(CO)NH_2 \text{ (s)} \quad + \quad H_2O \text{ (l)} \quad \rightarrow \quad CO_2 \text{ (g)} \quad + \quad 2\ NH_3 \text{ (g)} \qquad\qquad [11]$$
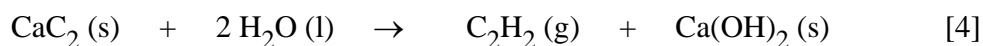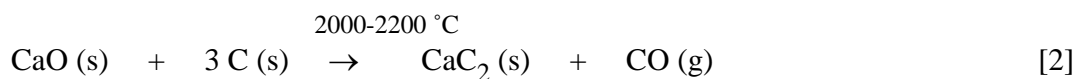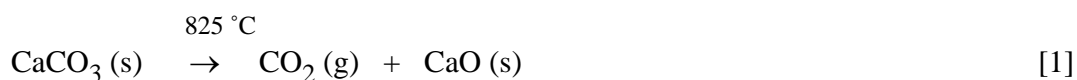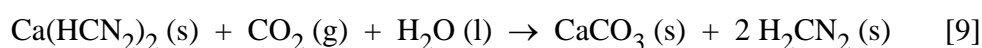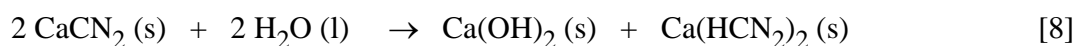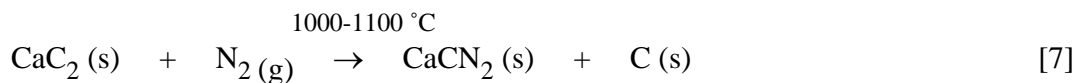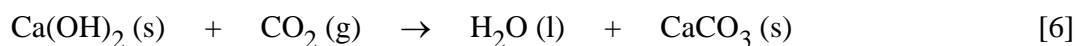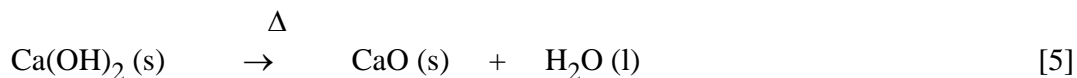
SOLUTION 26

a) Acheson Process:

$$SiO_2 + 3C \quad \xrightarrow{\Delta} \quad SiC + 2CO$$
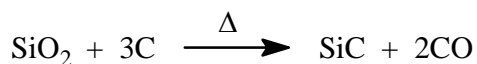
Theoretical ceramic yield = $M[SiC] / (M[SiO_2] + 3\ M[C])$

Yield = $(40.097 \text{ g mol}^{-1}) / [(60.086 \text{ g mol}^{-1}) + 3 \times (12.011 \text{ g mol}^{-1})]$

Theoretical ceramic yield = 41.7%

Since all other processes refer to thermal treatment of polymers, one can take only the mass of their monomers to do the calculations.
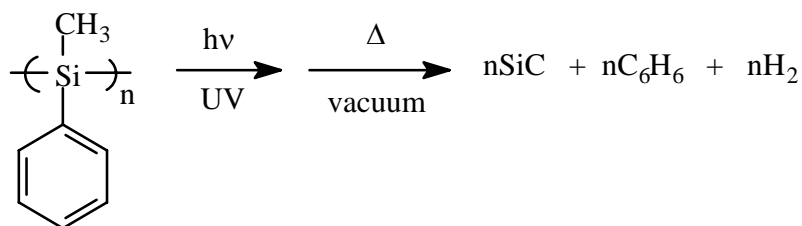
Yajima Process:
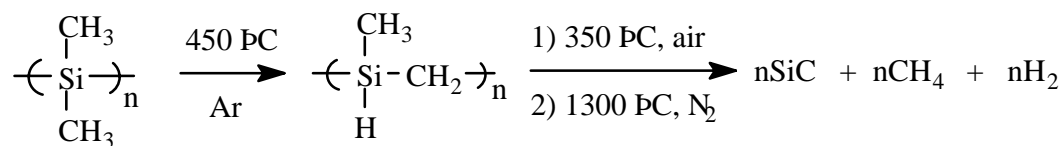
Theoretical ceramic yield = $M[SiC] / M[(CH_3)_2Si]$

Yield = (40.097 g mol^{-1}) / (58.156 g mol^{-1})]

Theoretical ceramic yield = 68.9%

West Process:

$$hv / UV \quad \xrightarrow{\Delta, \text{ vacuum}} \quad nSiC + nC_6H_6 + nH_2$$

Theoretical ceramic yield = $M[SiC] / M[(CH_3)(C_6H_5)Si]$

Yield = $(40.097 \text{ g mol}^{-1}) / (120.227 \text{ g mol}^{-1})]$
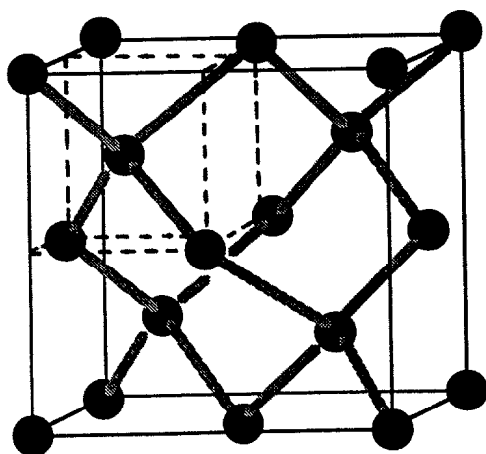
Theoretical ceramic yield = 33.4%

Harrod Process:

$$\xrightarrow{\Delta} \quad nSiC + nH_2$$
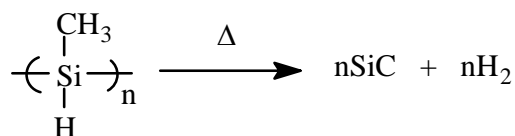
Theoretical ceramic yield = $M[SiC] / M[(CH_3)(H)Si]$
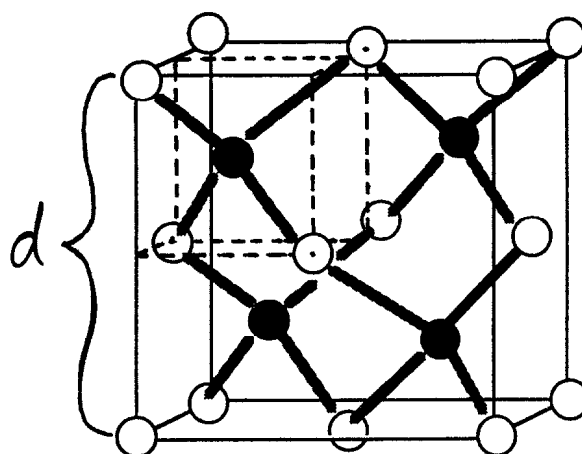
Yield = $(40.097 \text{ g mol}^{-1}) / (44.129 \text{ g mol}^{-1})]$

Theoretical ceramic yield = 90.9%

b)   The cubic structures of diamond and silicon carbide are shown below. That of SiC corresponds to the structure of zinc blende (ZnS).

Diamond   SiC

According to these structures, each unit cell of diamond contains 8 carbon atoms, and each unit cell of silicon carbide contains 4 carbon atoms and 4 silicon atoms.

In diamond, each carbon atom bonds to 4 other carbon atoms forming a tetrahedron. The unit cell of diamond contains 4 of these tetrahedrons, and each one occupies the volume of a small cube having half the edge length of the unit cell.

In silicon carbide, we have a lattice of silicon atoms having a face-centered cubic structure, and 4 carbon atoms that occupy half of the tetrahedral holes available in the cell. The edge of the small cube containing each tetrahedron corresponds to half the edge "d" of the SiC unit cell. From the density of SiC, one can evaluate the volume "V" of the unit cell, the value of "d", then that of the edge of the small cube. Simple trigonometry allows us to calculate the Si-C distance (d_{Si-C}) then, knowing the atomic radius of carbon, one can calculate the atomic radius of silicon by difference.

$$\text{Volume of 1 mole of SiC} = M[SiC] / \rho(SiC) = (40.097 \text{ g mol}^{-1}) / (3.21 \text{ g cm}^{-3})$$

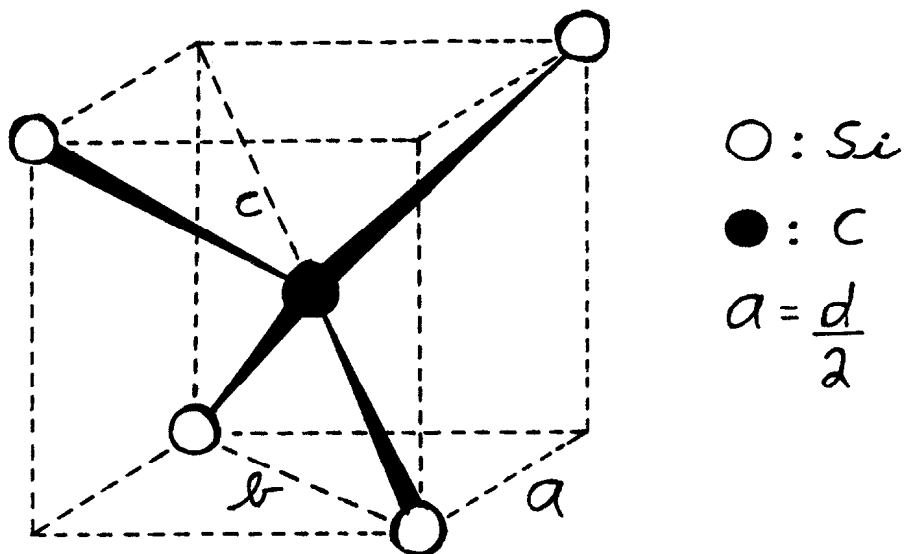$$\text{Volume of 1 mole of SiC} = 12.5 \text{ cm}^3$$

$$V = [(12.5 \text{ cm}^3) / (6.022 \times 10^{23} \text{ SiC/mol})] \times 4 \text{ SiC/unit cell}$$

$$V = 8.30 \times 10^{-23} \text{ cm}^3 = d^3$$

$$d = (V)^{1/3} = (8.30 \times 10^{-23} \text{ cm}^3)^{1/3}$$

$$d = 4.36 \times 10^{-8} \text{ cm}$$

Each carbon atom is in the center of a small cube in which is the silicon atoms tetrahedron. The length of the edge of the small cube is d/2. The Si-C distance, d_{Si-C}, is half the length of the diagonal passing through the center of the small cube (c/2).

$a = d/2;$ $\qquad b^2 = 2a^2;$ $\qquad c^2 = a^2 + b^2 = 3a^2$

$$c = (3a^2)^{1/2} = [3(d/2)^2]^{1/2}$$

$$c = [3 \times ((4.36 \times 10^{-8} \text{ cm})/2)^2]^{1/2}$$

$$c = 3.78 \times 10^{-8} \text{ cm}$$

$$d_{Si-C} = c/2 = (3.78 \times 10^{-8} \text{ cm})/2$$

$$d_{Si-C} = 1.89 \times 10^{-8} \text{ cm}$$

Atomic radius of Si $= d_{Si-C}$ - Atomic radius of C

where atomic radius of C $= (1.54 \times 10^{-8} \text{ cm})/2 = 0.77 \times 10^{-8} \text{ cm}$

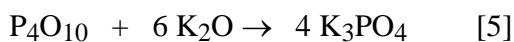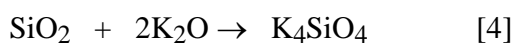Atomic radius of Si $= (1.89 \times 10^{-8} \text{ cm})$ - $(0.77 \times 10^{-8} \text{ cm})$

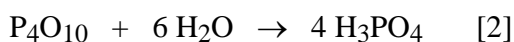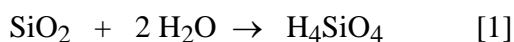Atomic radius of Si $= 1.12 \times 10^{-8} \text{ cm}$

(literature value $= 1.17 \times 10^{-8}$ cm; Butler & Harrod, 1988, p. 48)

SOLUTION 27

a)   Silica, SiO_2, is a covalent lattice compound in which each Si is surrounded by a tetrahedron of O and each O bridges between two Si atoms. To melt this lattice requires rupture of very strong chemical bonds and hence the compound has a very high melting point. Phosphorus pentoxide is actually P_4O_{10} in the solid state. The P is surrounded by a tetrahedron of O, three of which are bonding to other P's and the fourth, a P=O is terminal. The solid consists of a lattice of these molecules, with relatively weak secondary bonding forces holding the lattice together. Hence the relatively low melting point compared to SiO_2. Sulfur trioxide is also a simple molecular compound and in the solid the intermolecular forces are weak. It is monomeric and of substantially lower molecular weight than P_4O_{10}, hence its lower melting point.

b)

$$SiO_2 \; + \; 2\,H_2O \; \rightarrow \; H_4SiO_4 \qquad [1]$$

$$P_4O_{10} \; + \; 6\,H_2O \; \rightarrow \; 4\,H_3PO_4 \qquad [2]$$

$$SO_3 \; + \; H_2O \; \rightarrow \; H_2SO_4 \qquad [3]$$

$$SiO_2 \; + \; 2\,K_2O \rightarrow \; K_4SiO_4 \qquad [4]$$

$$P_4O_{10} \; + \; 6\,K_2O \rightarrow \; 4\,K_3PO_4 \qquad [5]$$

$$SO_3 \; + \; K_2O \rightarrow \; K_2SO_4 \qquad [6]$$

Energetics:

[1] is an endothermic reaction. A large amount of energy is required to break strong Si-O-Si bonds; the resulting acid is weak due to the low electronegativity of Si and hence not much H^+ solvation energy is available to compensate (the hydration of a proton in water liberates a large amount of energy). The higher electronegativities of P(V) and S(VI) result in strong acids in [2] and [3]; the ionization of H^+ is essentially complete, liberating a huge amount of hydration energy. In [4], [5] and [6], the oxide ion is a powerful base, which has no difficulty in attacking the electron deficient Si, P or S to produce additional strong X-O- bonds. The formation of highly charged ions in these reactions also gives rise to very large, favourable electrostatic attraction energies, known as lattice energies in the solid compounds.

c)   The Si-O-Si bond is not appropriate as an energy storage bond because its hydrolysis is not exothermic under physiological conditions. In addition it reacts only very slowly with mild reagents (witness the geological time-scale for the erosion of silicate rocks!). The S-O-S bond (pyrosulfate) hydrolyses exothermically, but the hydrolysis occurs too easily (rapidly) for pyrosulfate to be used as a storage device. The pyrophosphate link hydrolyses exothermically, but only does it very slowly under physiological conditions. Thus the bond energy can be stored and only released in the presence of a suitable catalyst. Living systems are rich in natural catalysts (enzymes) with the special function of catalyzing the reaction of pyrophosphate linkages to take advantage of the stored energy.

SOLUTION 28

a) $2\,Y_2O_3 \;+\; 8\,BaCO_3 \;+\; 12\,CuO \;+\; O_2 \rightarrow \; 4YBa_2Cu_3O_7 \;+\; 8CO_2$

b) $YBa_2Cu_3O_7$ has 14 negative charges from the 7 O^{2-}.

The positive charges from the metal ions sum to:
$$Y(3^+) + Ba(2 \times 2^+) + Cu(3 \times n^+) = 14.$$

Therefore, the average $n = \dfrac{7}{3}$ is the oxidation state of Cu in this material.

c)   Molecular weight of $YBa_2Cu_3O_7$ is 666 g mol^{-1}.
Observed weight loss is 9.88/10.00 = 1.2 per cent. 1.2 per cent of 666 g = 7.99 g.
If this is all O, then we have lost 0.5 g atom. Therefore, the new composition is $YBa_2Cu_3O_{6.5}$. There are now only 13 negative charges, which requires 6 positive charges from the Cu so the average oxidation state of the Cu is now 2.

d)   The common oxidation states of Cu are I, II and (rarely) III. For three Cu ions to have an average oxidation state of $\dfrac{7}{3}$, there are 2 x Cu(II) and a single Cu(III). In the deoxygenated material all three Cu's are Cu(II).

SOLUTION 29

a)   The valence electron counts of the relevant atoms are : H(1), C(4), N(5), O(6).

O_2^-: (2 x 6) electrons from O + one for the charge   = 13 *

NO: 5 electrons from N + 6 electrons from O   = 11*

$[ONO_2]^-$: 5 electrons from N + (3 x 6) electrons from O + one for the charge   = 24

CO_2: 4 electrons from C + (2 x 6) electrons from O   = 16

$[HCO_3]^-$: 1 electron from H + 4 electrons from C + (3 x 6) electrons from O

+ one for the charge   = 24

$[ONO_2CO_2]^-$: 4 electrons from C + 5 electrons from N + (5 x 6) electrons

from O + one for the charge   = 40

The unpaired electron on the superoxide will pair with the unpaired electron on the N to form a covalent bond. This is a radical combination reaction. Because the N in the product has a lone pair, the molecule will be bent, thus:

$$\overline{\underline{O}}=\overline{N} \diagdown$$
$$|\underline{O}-\overline{\underline{O}}|^{\ominus}$$
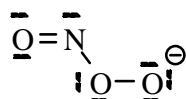
$[ONO_2]^-$

CO_2 is a weak Lewis acid and the peroxonitrite is a weak Lewis base. We will get an acid/base reaction. It is hard to predict whether the peroxonitrite will bond through the lone pair on the N or through the O. Two structures are possible:
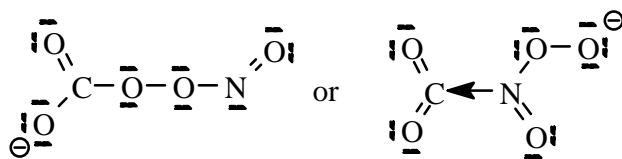
$[ONO_2CO_2]^-$

b)   Radical combination and acid/base reactions. See discussion in part (a).

c) $Cu^+ + NO_2^- + 2 H^+ \rightarrow Cu^{2+} + NO + H_2O$

d)   Compression of NO to 100 atm at 50 ˚C leads to a disproportionation according to the equation:

$$3 NO \rightarrow N_2O + NO_2$$

Because the number of molecules drops to 2/3 of the initial amount, the pressure at constant volume will drop to 2/3 its original value. Because NO_2 can dimerize (it is an odd electron count molecule with an unpaired electron on the N), the pressure will drop even more, i.e. to less than 2/3 the original value.

SOLUTION 30

a) The Cr^{3+} and Co^{3+} belong to a class of ions we now call "substitution inert". Unlike most transition ions in aqueous solution, the equilibration between the ligands initially attached to the metal and the large excess of water solvent is very slow with these particular ions. This allows their synthesis, isolation, recrystallization etc. without loss of ligands by water substitution, or without rapid equilibration of isomers.

b)

   i) $[(NH_3)_4Cl_2Cr]Cl$. This compound has a unipositive complex cation in which a Cr^{3+} is surrounded by two Cl's and four NH_3 molecules at the corners of an octahedron. There are two distinct ways of placing the Cl ligands, either on adjacent corners, or on diagonally opposite corners. These are known as the cis and trans isomers respectively and this is a case of geometric isomerism.

   The compounds are: *trans*-tetraamminedichlorochromium(III) chloride
   *cis*-tetraamminedichlorochromium(III) chloride

   trans $[(NH_3)_4Cl_2Cr]Cl$ cis
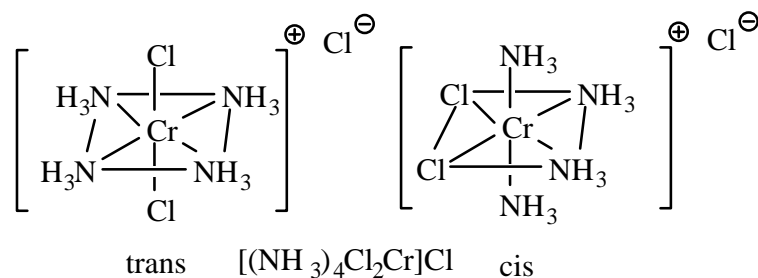
   ii) $[py_3Cl_3Co]$. This neutral Co^{3+} complex is also octahedral. There are two different ways of arranging the triads of like ligands. The facial isomer is obtained when they are all on the corners of a common triangular face of the octahedron (placing three like ligands on a common face forces the other three to occupy the diagonally opposite triangular face of the octahedron). The meridional isomer results from placing three like ligands at three corners of an equatorial square of the octahedron (the other three are then forced to occupy

three corners of another equatorial square perpendicular to the first). This type of isomerism is also geometric.

The compounds are: *fac*-trichlorotris(pyridine)cobalt(III)

mer-trichlorotris(pyridine)cobalt(III)

$[py_3Cl_3Co]$

facial   meridional
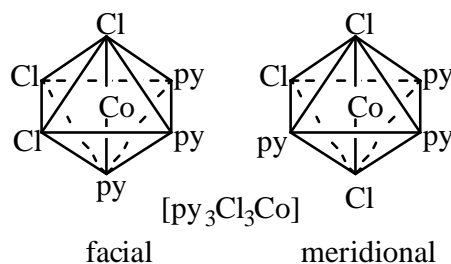
iii) $[(H_2O)_5(CNS)Co]Cl$: There is only one geometric arrangement of the five water and one CNS ligands. However, the CNS may be attached either by the C atom, or by the S atom.


$[(H_2O)_5(CNS)Co]Cl$
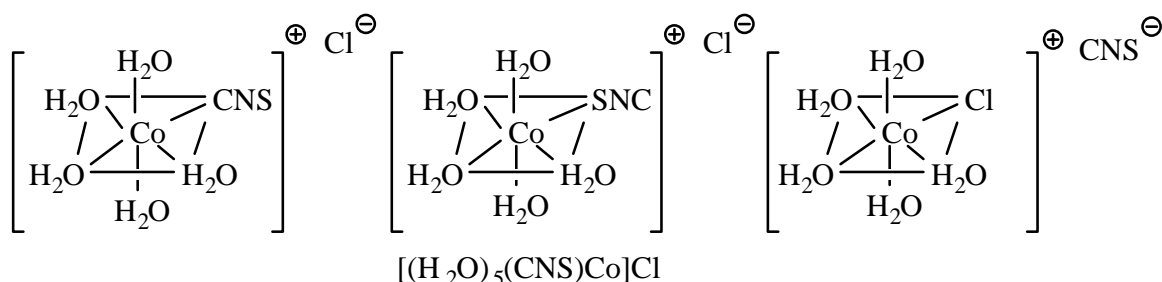
The resulting isomers are known as linkage isomers. Another possible isomer of this compound would result from interchange of the coordinated CNS with the free Cl. This is known as ionization isomerism.

The compounds are: pentaaquathiocyanato-C-cobalt(II) chloride.

pentaaquathiocyanato-S-cobalt(II) chloride

pentaaquachlorocobalt(II) thiocyanate

iv) $[(Me_3P)_3ClPt]Br$: The complex ion consists of a Pt^{2+} coordinated to three neutral phosphines and a uninegative Cl at the corners of a square. There is

only one possible geometric arrangement, but interchange of the Cl and the Br gives rise to ionization isomers.

The compounds are: chlorotris(trimethylphosphine)platinum(II) bromide

bromotris(trimethylphosphine)platinum(II) chloride

$[((CH_3)_3P)_3ClPt]Br$
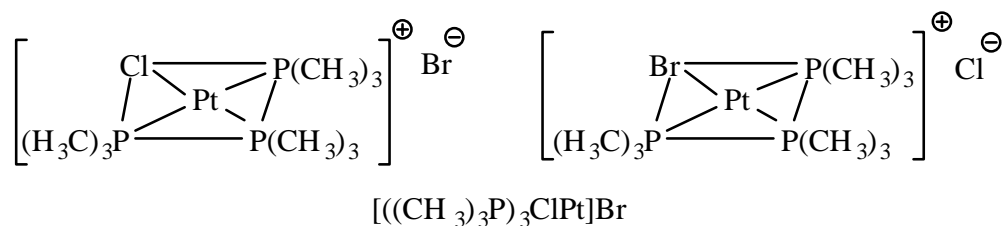
c)   The relevant concept was the recognition that compounds possessing the property of not being superimposable on their mirror image (we now call this property chirality) cause a rotation in the plane of polarization of plane-polarized light. Werner therefore set out to prepare a coordination compound with this property. On the assumption that Co^{3+} complexes have octahedral geometry, he deduced that $[en_2Cl_2Co]Cl$ should have two non-superimposable structures that differ only in that they are mirror images of each other. This was indeed found to be the case, establishing that the geometry of the complex is rigid and octahedral.

cis   enantiomers   cis   trans
            optically active   not optically active
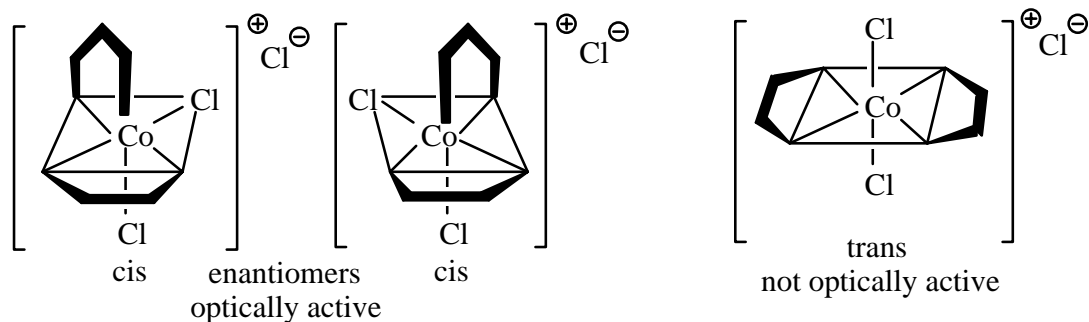
d)   The new theory was the theory of ionic conductivity. The new theory allowed the determination of the number of ions in an ionic compound from conductivity measurements. The series of compounds $[(NH_3)_xCl_3Cr]$ (x=3 to 6) are : $[(NH_3)_3Cl_3Cr]$ (neutral); $[(NH_3)_4Cl_2Cr]Cl$ (2 ions); $[(NH_3)_5ClCr]Cl_2$ (3 ions); $[(NH_3)_6Cr]Cl_3$ (4 ions). From the numbers of ions, it is possible to conclude that the number of ligands coordinated to Cr^{3+} remains at 6 throughout the series.

SOLUTION 31

a) $\Delta E = q + w$ (conservation of energy)

b) $\Delta S = \int \dfrac{dq_{rev}}{T}$ and can <u>only</u> be calculated for a reversible process

c) Since $E = \dfrac{3}{2}(nRT)$, it is thus independent of volume.

Thus $\Delta E = 0$ in this process which is isothermal.

Since $\Delta E = 0$, thus $q = -w$ and therefore $dq = -dw$.
The only work performed is PV work and since $dw_{rev} = -P_{ext}dV$, thus
$dq = -dw = +P_{ext}dV$

From b) $\Delta S = \int \dfrac{dq_{rev}}{T}$ and thus $dS = \dfrac{dq_{rev}}{T}$; substituting $dw_{rev} = -P_{ext}dV$ we obtain

$$dS = \frac{-dw_{rev}}{T} = \frac{P_{ext}dV}{T}$$

Since $PV = nRT$ we can again substitute to obtain

$$dS = \frac{-dw_{rev}}{T} = \frac{P_{ext}dV}{T} = \frac{nRTdV}{VT} = nR\frac{dV}{V}$$

Integrating gives:
$$\Delta S = \int dS = \int_{V}^{2V} nR\frac{dV}{V}$$
$$= nR\ln 2V - nR\ln V$$
$$= nR\ln\frac{2V}{V} = nR\ln 2$$

Thus $\Delta S = nR\ln 2$ (which is > 0)

Since $G = H - TS$ it follows that $G = (U + PV) - TS$ and that $\Delta G = \Delta U + \Delta(PV) - T\Delta S$
But $\Delta E = 0$ and $PV = nRT$ which is a constant and thus $\Delta(PV) = 0$.
Therefore $\Delta G = -T\Delta S$ and from above $\Delta S = nR\ln 2$ which upon substitution gives
$\Delta G = -nRT\ln 2$ (which is < 0)

d)   Each of E, S and G are state functions and are thus independent of the pathway.
      Therefore:

$\Delta E_{rev} = \Delta E_{irrev} = 0$

$\Delta S_{rev} = \Delta S_{irrev} = nRln2$

$\Delta G_{rev} = \Delta G_{irrev} = -nRTln2$

e)   For spontaneity and irreversibility: $\Delta S > 0$ and $\Delta G < 0$.

f)   From the Second Law of Thermodynamics, $\Delta S_{total} = 0$ or $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = 0$

$$\Delta S_{sys} = \int \frac{dq_{rev}}{T} = nR\ln 2$$

$$\Delta S_{surr} = -\int \frac{dq_{rev}}{T} = -nR\ln 2$$

g)   Note that if each particle has two possible states, then with N_o particles there are 2^{N_o}
      possible arrangements.

$\Delta S = S_2 - S_1$

$\quad = klnW_2 - klnW_1$

$\quad = kln(2^{N_o}) - kln(1^{N_o})$

$\quad = kln(2^{N_o})$

$\quad = N_o kln2$

$\quad = nRln2$ (since $k = R/N_o$)

SOLUTION 32

a)   The process is adiabatic and thus $q = 0$ and thus

$$\Delta E = -w = n\overline{C}_v \Delta T = 1(\overline{C}_p - R)\Delta T = 1(28.2 - 8.314)(-30) = -597 \text{ J}$$

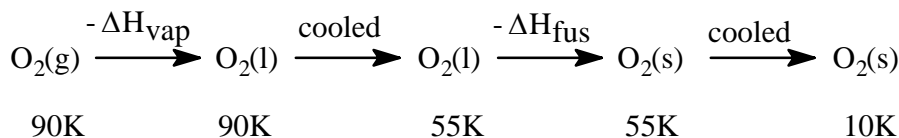(also $\Delta E = \Delta H - \Delta(PV) = \Delta H - nR\Delta T = -846 - 8.314(-30) = -597$ J)
and therefore w = +597 J.

$$\Delta H = n\overline{C}_p \Delta T = 28.2(-30) = -846 \text{ J}$$

$$\Delta S_{sys} = n\overline{C}_p \ln(T_1/T_2) - nR\ln(P_2/P_1) = n\overline{C}_v \ln(T_2/T_1) + nR\ln(V_2/V_1)$$

$$= 28.2\ln(90/120) - 8.314\ln(1/4)$$

$$= -8.11 + 11.53$$

$$= 3.42 \text{ JK}^{-1} \text{ (which is as it must be } \geq 0)$$

$$\Delta S_{surr} = \int -\frac{q_{rev}}{T} = 0 \text{ since the process is adiabatic}$$

b)   The overall process is:

$$O_2(g) \xrightarrow{-\Delta H_{vap}} O_2(l) \xrightarrow{\text{cooled}} O_2(l) \xrightarrow{-\Delta H_{fus}} O_2(s) \xrightarrow{\text{cooled}} O_2(s)$$

$$\quad\ 90K \qquad\qquad 90K \qquad\qquad 55K \qquad\qquad 55K \qquad\qquad 10K$$

The entire process of cooling is at constant pressure and thus $\Delta H = q_p$.

$$\Delta H_{sys} = -\Delta H^o_{vap} + \int_{90}^{55} n\overline{C}_p(l)\,dT - \Delta H^o_{fus} + \int_{55}^{10} n\overline{C}_p(s)\,dT$$

$$\Delta H_{sys} = -6820 + 54(55-90) - 420 + 41(10-55) = -10975 \text{ J} = -10.97 \text{ kJ}$$

$$\Delta S_{sys} = -\frac{\Delta H^o_{vap}}{T_{bp}} + \int_{90}^{55} \frac{n\overline{C}_p(l)\,dT}{T} - \frac{\Delta H^o_{fus}}{T_{mp}} + \int_{55}^{10} \frac{n\overline{C}_p(s)\,dT}{T}$$

$$\Delta S_{sys} = -6820/90 + 54\ln(55/90) - 420/55 + 41\ln(10/55)$$

$$= -75.8 - 26.6 - 7.6 - 69.9$$

$$= -179.9 \text{ JK}^{-1}$$

SOLUTION 33

a) $\Delta H^\circ_{rxn} = \Sigma\Delta H^\circ_f(\text{prod}) - \Sigma\Delta H^\circ_f(\text{reactants})$

$$= \Delta H^\circ_f(NH_3) + \Delta H^\circ_f(CO_2) - \Delta H^\circ_f(\text{urea}) - \Delta H^\circ_f(H_2O)$$

$$= (2(-80.8) + (-412.9)) - ((-317.7 - 285.8))$$

$$= 29.0 \text{ kJ}$$

$$\Delta S°_{rxn} = \Sigma \Delta S°(prod) - \Sigma \Delta S°(reactants)$$
$$= 2(110) + 121 - 176 - 69.9 = 95.1 \text{ JK}^{-1}$$

$$\Delta G°_{rxn} = \Delta H°_{rxn} - T\Delta S°_{rxn}$$
$$= 29000 - 298(95.1)$$
$$= 660 \text{ J}$$

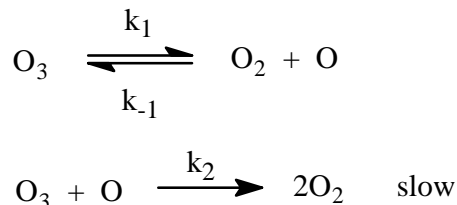Since $\Delta G° = -RT\ln K$, thus $K = e^{\frac{-\Delta G°}{RT}} = e^{-0.266} = 0.766$

b) $\Delta G = \Delta G° + RT\ln Q$ and $Q = \dfrac{(0.1)(0.01)^2}{(1)(55.5)}$

Thus $\Delta G = 660 + 8.314(298)(-15.53) = -37.8 \text{ kJ}$

Since $\Delta G < 0$ the hydrolysis of urea would proceed forward under the given reaction conditions.

SOLUTION 34

a)

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$$

$$O_3 + O \xrightarrow{k_2} 2O_2 \quad \text{slow}$$

$$\frac{-d[O_3]}{dt} = k_1[O_3] - k_{-1}[O_2][O] + k_2[O_3][O]$$

The steady state approximation gives $\dfrac{d[O]}{dt} = 0 = k_1[O_3] - k_{-1}[O_2][O] - k_2[O_3][O]$

Therefore we have $[O] = \dfrac{k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]}$ and substitution of this into the above gives:

$$-\frac{d[O_3]}{dt} = k_1[O_3] - \frac{k_1[O_3]k_{-1}[O_2]}{k_{-1}[O_2] + k_2[O_3]} + \frac{k_1[O_3]k_2[O_3]}{k_{-1}[O_2] + k_2[O_3]} \quad \text{which simplifies to:}$$

$$-\frac{d[O_3]}{dt} = k_1[O_3]\left(\frac{2k_2[O_3]}{k_{-1}[O_2]+k_2[O_3]}\right) = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2]+k_2[O_3]}$$

If $k_{-1}[O_2] \gg k_2[O_3]$ then: $\quad -\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2]} = \frac{2k_1k_2[O_3]^2[O_2]^{-1}}{k_{-1}} = k_{exp}[O_3]^2[O_2]^{-1}$

If $k_{-1}[O_2] \ll k_2[O_3]$ then: $\quad -\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_2[O_3]} = 2k_2[O_3]^2 = k'_{exp}[O_3]^2$

Thus $k_{exp} = \dfrac{2k_1k_2}{k_{-1}}$ and $k'_{exp} = 2k_1$

SOLUTION 35

a) Assuming that the rate law has the form: $\quad \dfrac{d[P]}{dt} = k[X]^x[Y]^y[Z]^z$

Then by inspection $x = 2$, $y = 0$, and $z = 1/2$

Thus $\quad \dfrac{d[P]}{dt} = k[X]^2[Z]^{\frac{1}{2}}$

b) Substituting in data from the first experiment:

$$0.002 \text{ M h}^{-1} = \frac{d[P]}{dt} = k[0.01M]^2[0.01M]^{\frac{1}{2}}$$
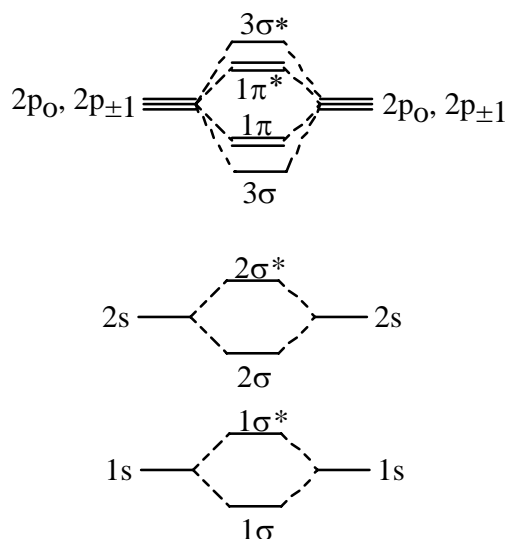
which provides $k = 200 \text{ M}^{\frac{3}{2}}\text{h}^{-1}$

There is a large excess of Y and Z with respect to X and thus the rate equation simplifies and becomes: rate $= k'[X]^2$ where $k' = k[2.00]^{0.5}$

Pseudo second order kinetics now apply and thus:

$$t_{\frac{1}{2}} = \frac{1}{c_0 k'} = \frac{1}{(0.01)(283M^{-1}h^{-1})} = 0.35h \, (21 \text{ min})$$

SOLUTION 36

a)

b)

H_2:	$1\sigma^2$	Bond order 1
H_2^-:	$1\sigma^2 1\sigma^{*1}$	Bond order 0.5
He_2:	$1\sigma^2 1\sigma^{*2}$	Bond order 0
He_2^-:	$1\sigma^2 1\sigma^{*2} 2\sigma^1$	Bond order 0.5

c)   From the bond orders in (b) it is apparent that H_2^- and He_2^- have the same stability.

d) O_2 has 16 electrons and an MO description of: $1\sigma^2 1\sigma^{*2} 2\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 1\pi^{*2}$

The $1\pi^*$ orbital is doubly degenerate and thus from Hund's Rule $1\pi^*_+(\uparrow)\ 1\pi^*_-(\uparrow)$ giving two unpaired electrons and thus a biradical, paramagnetic species.

e)   The electronic configuration of Hg is $[Xe]5d^{10}6s^2$ and therefore Hg^+ will have a configuration of $[Xe]5d^{10}6s^1$. All electrons are paired up except for the valence 6s electron. In the monomeric species there is a single unpaired electron and no bond. On the other hand in the dimeric species the inner electrons can all still be paired and the new σ_{6s} MO ($6s_a + 6s_b$ combination) will gain one electron from each of the Hg^+ ions to provide stability with the net formation of a single bond. Thus the dimer is more stable than the monomer.

SOLUTION 37

a)   Mg has the configuration [Ne]($3s^2$) and does not possess any p orbitals in its valence shell. It thus only has σ electrons available and cannot become involved in the π bonding.

b)   The hexagon of benzene can be regarded as being made up of 6 equilateral triangles and thus the radius of the ring is equal to the length along one edge.

$$r_b = 1.50 \times 10^{-8} \text{ cm}$$

For the chlorophyll core which is being approximated by a dodecagon, the ring can be regarded as being made up of 12 isosceles triangles
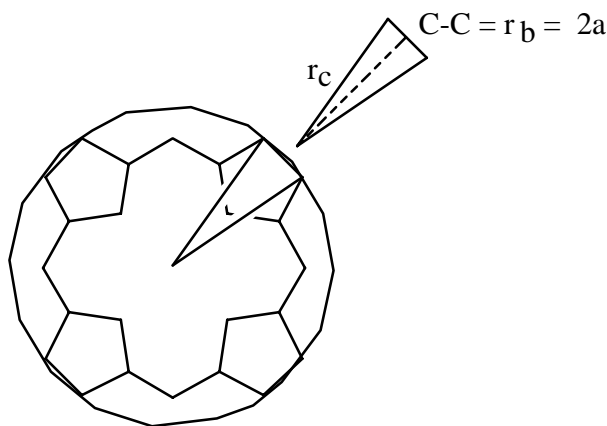

with the internal angle at the centre of each triangle thus being 360 °/12 = 30 ° and a base of one C-C bond length which is equal to $r_b = 1.50 \times 10^{-8}$ cm. Dividing the isosceles triangle in half so that it is made up of two right triangles, we thus have:

$$\sin(30Þ2) = \frac{a}{r_c}$$

$$\therefore r_c = \frac{\frac{1}{2}r_b}{\sin(15Þ)} \approx \frac{\frac{1}{2}r_b}{0.25} = 2r_b = 3.00 \times 10^{-8} \text{ cm}$$

c) Recall that each atomic orbital will be transformed into a molecular orbital. Thus from the six atomic centres donating an electron each to the π system of benzene we will generate six molecular orbitals. From the 18 atomic centres involved in the chlorophyll core we will similarly generate 18 molecular orbitals. To obtain a crude estimate of where the molecular orbitals are with respect to each other, the following scheme works quite well. Inscribe a circle around the atomic framework which involves the π system being sure that a single vertex is at the lowest point of the circle. Each vertex of the system will map onto a molecular orbital, some of which will be at the same level (i.e. will be degenerate). Thus for benzene we obtain 6 orbitals, two sets of which are degenerate. The lower three are the bonding molecular orbitals and the upper three are anti-bonding orbitals. The π-electrons are placed into the orbitals according to Hund's rule to arrive at the ground-state configuration of the molecule. A similar operation with the chlorophyll core will lead to nine bonding (one lowest level and four degenerate pairs) and nine anti-bonding orbitals (four degenerate pairs and one at the highest level).

MO levels
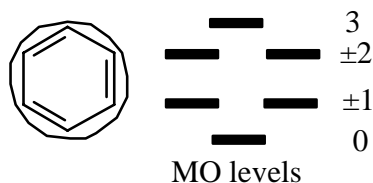
For benzene the 6 electrons will be placed in the lowest three MO's and thus the HOMO will be that involving $l = \pm 1$. For chlorophyll, the 18 electrons will fully fill up to and including the orbital having $l = \pm 4$.

Benzene HOMO $l = \pm 1$: $\qquad E_{\pm 1} = \dfrac{\hbar^2}{2mr_b^2}$

Chlorophyll HOMO $l = \pm 4$: $\quad E_{\pm 4} = \dfrac{\hbar^2 4^2}{2mr_c^2} = \dfrac{16\hbar^2}{2m(2r_b)^2} = \dfrac{16\hbar^2}{8mr_b^2} = \dfrac{2\hbar^2}{mr_b^2}$

d) Benzene LUMO $l = \pm 2$: $\qquad E_{\pm 2} = \dfrac{\hbar^2 2^2}{2mr_b^2} = \dfrac{4\hbar^2}{2mr_b^2}$

Chlorophyll LUMO $l = \pm 5$: $\quad E_{\pm 5} = \dfrac{\hbar^2 5^2}{2mr_c^2} = \dfrac{25\hbar^2}{2m(2r_b)^2} = \dfrac{25\hbar^2}{8mr_b^2}$

e) Benzene: $\Delta E_{abs} = E_2 - E_1 = \dfrac{4\hbar^2}{2mr_b^{\ 2}} - \dfrac{\hbar^2}{2mr_b^{\ 2}} = \dfrac{3\hbar^2}{2mr_b^{\ 2}} = \dfrac{12\hbar^2}{8mr_b^{\ 2}}$

Chlorophyll: $\Delta E_{abs} = E_5 - E_4 = \dfrac{25\hbar^2}{2mr_c^{\ 2}} - \dfrac{16\hbar^2}{2mr_c^{\ 2}} = \dfrac{9\hbar^2}{2mr_c^{\ 2}} = \dfrac{9\hbar^2}{8mr_b^{\ 2}}$

Thus ΔE_{abs} (chlorophyll) is predicted to be less than ΔE_{abs} (benzene) by a factor of 12:9 whereas the observed ratio is 2:1 (or 12:6).

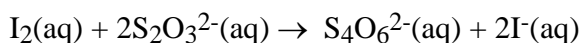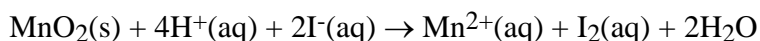In chlorophyll, the C-C-C path is actually longer than the direct C-C distance determined above. The effective distance is actually about $\sqrt{2}$ x r_c. Thus reworking the above relationship gives:

$$\Delta E_{abs} = E_5 - E_4 = \frac{25\hbar^2}{2m(\sqrt{2}r_c)^2} - \frac{16\hbar^2}{2m(\sqrt{2}r_c)^2} = \frac{9\hbar^2}{2m(\sqrt{2}r_c)^2} = \frac{9\hbar^2}{4m(r_c)^2} = \frac{9\hbar^2}{16mr_b^{\ 2}}$$

Thus ΔE_{abs}(chlorophyll) is again predicted to be less than ΔE_{abs}(benzene) but now by a factor of about 12:4.5 which agrees much better with the experimental value of 12:6. (Closer agreement is obtained with a more detailed analysis of the two systems — the assumptions made in this question are very crude.)

f) From Hund's rule the electrons will go into the orbitals in an unpaired manner until required to form pairs. The $l_{\pm4}$ orbital is degenerate but will be completely filled with the last of the 18 electrons. The resulting species will have S = 0 and will be diamagnetic.

SOLUTION 38

a) $2\,Mn^{2+}(aq) + O_2(aq) + 4OH^-(aq) \rightarrow 2\,MnO_2(s) + 2H_2O$

$MnO_2(s) + 4H^+(aq) + 2I^-(aq) \rightarrow Mn^{2+}(aq) + I_2(aq) + 2H_2O$

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

b) $n(S_2O_3^{2-}) = (9.75 \times 10^{-3} \text{ mol/L}) (0.02753 \text{ L})$

$= 2.68 \times 10^{-4} \text{ mol}$

ratio of $O_2 = S_2O_3^{2-}$ is 1:4

moles of $O_2 = \dfrac{2.68 \times 10^{-4}}{4} \text{ mol} = 6.71 \times 10^{-5}$

O_2 g/mol = 2 x 15.999 = 31.998 g/mol

O_2mol/L sample $= \dfrac{6.71 \times 10^{-5}}{0.25 \text{L}} \text{ mol} = 26.84 \times 10^{-4} \text{ mol}$

O_2 g/L = 2.684 x 10^{-5} mol/L x 31.998 g/mol

= 0.008588 g/L

= 8.59 mg/L

= 8.59 ppm

SOLUTION 39

a)   First, correcting for the dilution of the aliquot during the second measurement.

Corrected absorbance $= 0.517 \times \dfrac{26.0}{25.0} = 0.538$

Absorbance due to 0.05 mg of phosphate = 0.538 - 0.428 = 0.110

b)   mg phosphate in the aliquot of specimen $= \dfrac{0.428}{0.110} \times 0.05 = 0.195$ mg

c)   Concentration of phosphate in the patient's urine

$= \dfrac{100}{25.0} \times 0.195 \times \dfrac{1}{5.00} = 0.156$ mg/mL

= 0.156 mg/mL x 1000 mL/L

= 156 mg/L phosphate

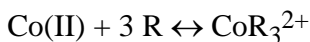d)   No matrix effect; greater accuracy and precision; rapid.

SOLUTION 40

a)   Ligand to cation ratio

From the graph of absorbance versus R concentration obtain a mole ratio of 3.0 and therefore the complex is CoR_3^{2+}

b)   Formation constant
Stoichiometry where lines intersect indicates the following :

$$Co(II) + 3 R \leftrightarrow CoR_3^{2+}$$

formation constant $K_f = \dfrac{[CoR_3^{2+}]}{[Co(II)][R]^3}$
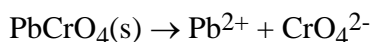
at A_1, $Co(II) = CoR_3^{2+} = 2.5 \times 10^{-5}$ mol/L
$R = 7.5 \times 10^{-5}$ mol/L

therefore $K_f = \dfrac{2.5 \times 10^{-5}}{(2.5 \times 10^{-5})(7.5 \times 10^{-5})^3} = 2.37 \times 10^{-12}$

SOLUTION 41

a)   The solubility product K_{sp} of lead chromate at 18 °C is 1.77×10^{-14}.
The dissolution of lead chromate is represented by the following equation:

$$PbCrO_4(s) \rightarrow Pb^{2+} + CrO_4^{2-}$$

Therefore, in pure water, the solubility of lead chromate is equal to the concentration of either the Pb^{2+} or the CrO_4^{2-} in a saturated salt solution.
Therefore,

$$Pb^{2+} = CrO_4^{2-} = S_{PbCrO_4} = 1.33 \times 10^{-7} \text{ mol/L } (\sqrt{k_{sp}})$$

b)   In such a solution, the solubility of lead chromate is no longer equal to the concentration of chromate ions since a large part of these ions are provided by potassium chromate. However, its solubility is equal to the concentration of lead ions all provided by lead chromate.

Therefore,

$$S_{PbCrO_4} = S_{Pb^{2+}} = \dfrac{k_{spPbCrO_4}}{[CrO_4^{2-}]} = \dfrac{1.77 \times 10^{-14}}{0.1} = 1.77 \times 10^{-13}$$