24th

ICHO

International Chemistry Olympiad

9 theoretical problems
1 practical problem

THE TWENTY-FOURTH
INTERNATIONAL CHEMISTRY OLYMPIAD
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THEORETICAL PROBLEMS

PROBLEM 1

Diatoms, microscopic organisms, are an abundant food source in the oceans producing carbohydrates from carbon dioxide and water by photosynthesis:

$6\ CO_2 + 6\ H_2O$ + solar energy $\rightarrow$ $C_6H_{12}O_6 + 6\ O_2$

1.1 During the first five years of life blue whales gain 75 kg of mass per day by feeding on krill. The whale must consume ten times this mass of krill each day. The krill must consume 10.0 kg of diatoms to produce 1.0 kg of krill. Assuming that the mass gain in the first years of a whale's life is due to the consumption of carbohydrates ($C_6H_{12}O_6$), calculate the volume of CO_2 at STP (0 °C, 101 kPa) that must be used by the diatoms to produce the carbohydrates consumed by a blue whale in its first five years of life.

1.2 There is 0.23 cm^3 of dissolved CO_2 per one litre sea water (at 24 °C and 101 kPa).

i) If diatoms can completely remove carbon dioxide from the water they process, what volume of water would they process to produce the carbohydrates required by a blue whale during the first five years of life?

ii) What fraction of the total volume of the oceans will be needed to supply the carbon dioxide for the first five years of growth of 1000 blue whales? The volume of the oceans is 1.37×10^{18} m^3.

1.3 Three percent of the mass of a 9.1×10^4 kg adult whale is nitrogen. When a 9.1×10^4 kg blue whale dies, what is the maximum mass of NH_4^+ that can become available for other marine organisms?

1.4 Eighteen percent of a 9.1×10^4 kg whale's mass is carbon. Carbon can be returned to the atmosphere as CO_2 and then removed from the atmosphere by weathering of rocks containing calcium silicate.

$CaSiO_3(s) + 2\ CO_2(g) + 3\ H_2O(l) \rightarrow Ca^{2+}(aq) + 2\ HCO_3^-(aq) + H_4SiO_4(aq)$

What are the maximum number of grams of $CaSiO_3$ that can be weathered by the carbon dioxide produced from the decomposition of 1000 blue whales, the number estimated to die annually?

SOLUTION

1.1 In five years a whale eats carbohydrates coming from $5 \times 365 \times 75 \times 10 = 1.4\times10^6$ kg krill which themselves need 1.4×10^7 kg of carbohydrates coming from diatoms.

For 180 g $C_6H_{12}O_6$, 6×44 g CO_2 are necessary, and thus

for 1.4×10^7 kg carbohydrates $1.4\times10^7 \times (264/180) = 2.00\times10^7$ kg of CO_2 are needed, i. e. 1.0×10^{10} dm^3 CO_2

1.2 i) The amount of water is 4×10^{13} dm^3.

ii) 3×10^{-5} of the total ocean volume (0.03 ‰).

1.3 The mass of nitrogen from a whale is $0.03 \times 9.1\times10^4$ kg = 2.7×10^6 g.

$$n(N) = n(NH_4^+) = \frac{2.7\times10^6\ g}{14\ g\,mol^{-1}} = 1.9\times10^5\ mol$$

$$m(NH_4^+) = 1.9\times10^5\ mol \times 18\ g\ mol^{-1} = 3\times10^6\ g\ NH_4^+ = 3\times10^3\ kg\ NH_4^+$$

1.4 One whale contains 1.6×10^4 kg of carbon. It corresponds to 1.3×10^6 mol of CO_2.

From the equation: $n(CaSiO_3) = 6.5\times10^5$ mol

$$m(CaSiO_3) = 6.5\times10^5\ mol \times 116\ g\ mol^{-1} = 7.5\times10^7\ g\ CaSiO_3$$

1000 whales therefore produce 7.5×10^{10} g $CaSiO_3$.

PROBLEM 2

Many streams drain in areas where coal or metallic ores are mined. These streams have become acidic and contain high concentrations of dissolved iron and sulphate, due to sulphur-containing ores being exposed to the atmosphere or to oxygenated waters. The most common sulphur-containing mineral is pyrite, FeS_2, in which the oxidation state of iron is +2. As the iron-rich streams mix with other waters, the dissolved iron precipitates as goethite, FeO(OH), which coats the stream bottom while the water remains acidic.

2.1 Draw the electron dot structure that illustrates the bonding in the ion S_2^{2-}, showing all valence electrons.

2.2 Write a balanced chemical equation to show how hydrogen ions (H^+) are generated during the oxidation of pyrite to form a solution of iron(II) and sulphate ions.

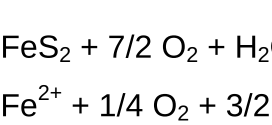
2.3 Write a balanced equation to show how many additional moles of hydrogen are generated when iron(II) ions are oxidized to form the mineral goethite, FeO(OH).

2.4 Calculate how many moles of pyrite would be required to bring 1.0 dm^3 of pure water to a pH of 3.0 if the pyrite was completely converted into FeO(OH) and H^+ ions. Neglect the formation of HSO_4^-.

2.5 The concentration of iron as Fe(II) in a stream is 0.00835 M. At a very narrow point in the stream it empties into a large pond, with a flow rate of 20.0 l each minute. The water in this stream is sufficiently aerated that 75 % of the Fe(II) is oxidized to Fe(III). The pH of the pond is high enough (> 7) that the iron(III) precipitates immediately as $Fe(OH)_3$ which on aging becomes Fe_2O_3. What mass of Fe_2O_3 will be deposited on the bottom of the pond in two years?

SOLUTION

2.1



2.2 $FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$

2.3 $Fe^{2+} + 1/4\ O_2 + 3/2\ H_2O \rightarrow FeOOH + 2\ H^+$

2.4 $[H^+] = 1\times10^{-3}$

$n[H^+] = 1\times10^{-3}$ mol

From both equations: $n(FeS_2) = 2.5\times10^{-4}$ mol

2.5 Total flow into pond in 2 years =

2 yr $\times$ 365 days yr^{-1} $\times$ 24 h day^{-1} $\times$ 60 min h^{-1} $\times$ 20.0 dm^3 min^{-1} =

= 2.10×10^7 dm^3 of water

$n(Fe^{2+})$ into pond = 2.10×10^7 dm^3 $\times$ $8{,}35\times10^{-3}$ mol dm^{-3} = 1.76×10^5 mol

$n(Fe^{3+})$ produced = $0.75 \times 1.76\times10^5$ mol = 1.32×10^5 mol

mass of deposited Fe_2O_3:

$m(Fe_2O_3) = 0.5 \times 1.32\times10^5$ mol $\times$ 159.7 g mol^{-1} = 1.05×10^7 g

PROBLEM 3

Coniferyl alcohol has the molecular formula $C_{10}H_{12}O_3$. It is isolated from pine trees. Coniferyl alcohol is not soluble in water or aqueous $NaHCO_3$. A solution of Br_2 in CCl_4 is decolorized when added to coniferyl alcohol forming **A** ($C_{10}H_{12}O_3Br_2$). Upon reductive ozonolysis coniferyl alcohol produces vanillin (4-hydroxy-3-methoxybenzaldehyd) and **B** ($C_2H_4O_2$). Coniferyl alcohol reacts with benzoyl chloride (C_6H_5COCl) in the presence of a base to form **C** ($C_{24}H_{20}O_5$). This product rapidly decolorizes $KMnO_4$ (aq) and is insoluble in dilute NaOH.

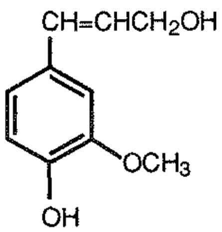
Coniferyl alcohol reacts with cold HBr to form **D** ($C_{10}H_{11}O_2Br$). Hot HI converts ArOR to ArOH and RI. Coniferyl alcohol reacts with excess hot HI to give **E** ($C_9H_9O_2I$) and CH_3I. CH_3I in aqueous base reacts with coniferyl alcohol to form **F** ($C_{11}H_{14}O_3$), which is not soluble in a strong base, but decolorizes Br_2/CCl_4-solution.

3.1 Draw the structures of coniferyl alcohol and compounds **A** - **F**.

3.2 There are a number of stereoisomers of compound **A**. Draw structure of compound **A**. Label each chiral centre in compound **A** with an asterisk (*). For all stereoisomers draw Fischer projections and label each chiral center with the proper *R* or *S* designation giving the absolute configuration about the chiral centre.

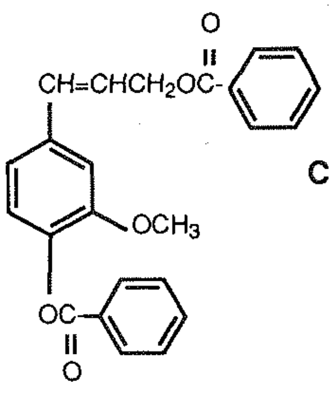
SOLUTION

3.1

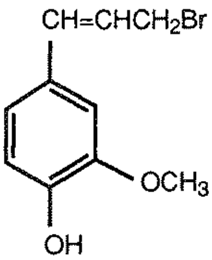


coniferyl alcohol

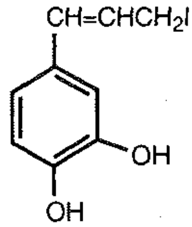
$O=CHCH_2OH$ **B**



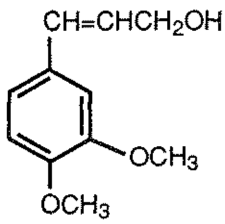
C



D

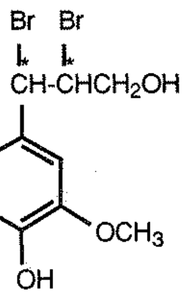


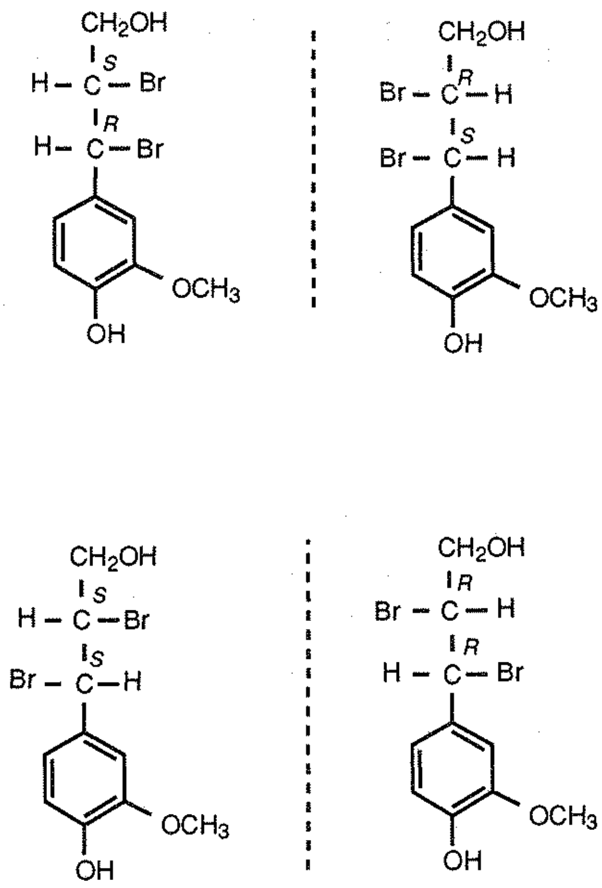
E



F

3.2 There are no geometric isomers of compound **A**, but there are 4 diastereomers (2 pairs of enantiomers).

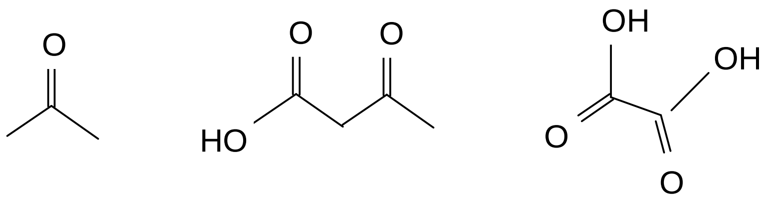




PROBLEM 4

Rose oil is an essential oil obtained from the steam distillation of plant material from roses. It contains a number of terpenes, one of which is geraniol, $C_{10}H_{18}O$ (**A**). Upon oxidation, geraniol can either give a ten-carbon aldehyde or a ten-carbon carboxylic acid. Reaction with two moles of bromine gives a tetrabromide ($C_{10}H_{18}OBr_4$) (**B**). Geraniol reacts with HBr to give two bromides of formula $C_{10}H_{17}Br$.

When geraniol is vigorously oxidized, three products are obtained:



4.1 Give the structure of geraniol **A.**

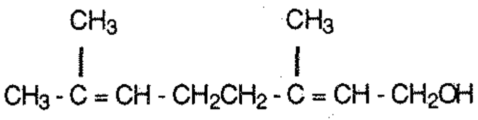
4.2 Give the structure of compound **B.**

4.3 Give the structures of the two bromides of formula $C_{10}H_{17}Br$.

4.4 Indicate which of the two bromides is formed in greater proportions.

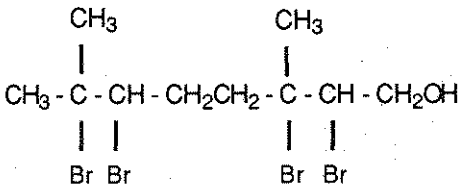
SOLUTION

4.1



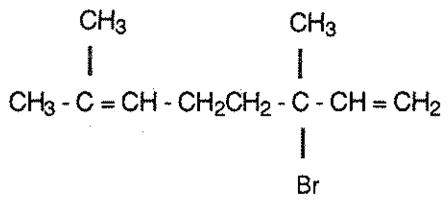
geraniol **A**

4.2

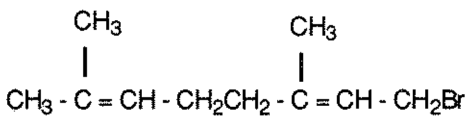


B

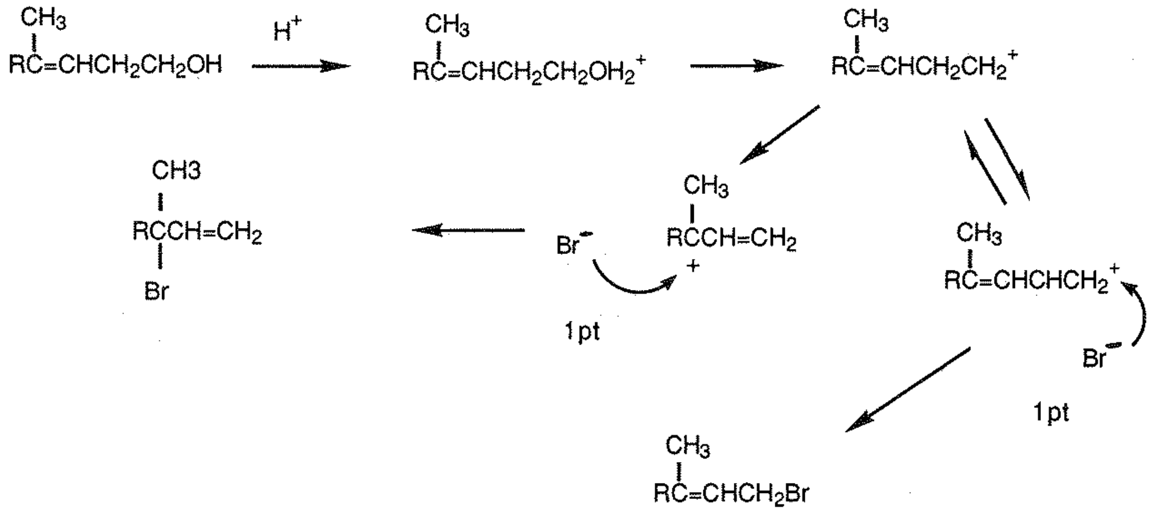
4.3


CH3
CH3
CH3 - C = CH - CH2CH2 - C - CH = CH2
Br

or


CH3
CH3
CH3 - C = CH - CH2CH2 - C = CH - CH2Br

4.4


CH3
RC=CHCH2CH2OH
H+
CH3
RC=CHCH2CH2OH2+
CH3
RC=CHCH2CH2+
CH3
RCCH=CH2
+
Br-
1 pt
CH3
RC=CHCHCH2+
Br-
1 pt
CH3
RCCH=CH2
Br
CH3
RC=CHCH2Br

PROBLEM 5

Nitrogen dioxide NO_2 is one of a number of oxides of nitrogen found in our atmosphere. It can dimerize to give N_2O_4 (g):

$$2\ NO_2(g) \rightleftharpoons N_2O_4(g)$$

5.1 With a diagram, show the bonds present in NO_2(g) using the concept of resonance if necessary. Nitrogen dioxide, NO_2, is paramagnetic.

5.2 Show, with bonding diagrams, how two molecules of NO_2(g) combine to give a molecule of N_2O_4 (g) which is not paramagnetic.

5.3 At 298 K, the ΔG^o of formation for N_2O_4(g) is 98.28 kJ, whereas for NO_2(g) is 51.84 kJ. Starting with one mole of N_2O_4(g) at 1.0 atm and 298 K, calculate what fraction will be decomposed if the total pressure is kept constant at 1.0 atm and the temperature is maintained at 298 K.

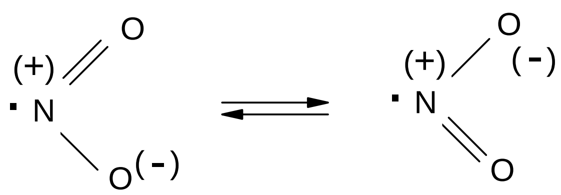
5.4 If ΔH^o for the reaction $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$ is 58.03 kJ, at what temperature would the fraction of N_2O_4 decomposed be double that calculated in part 5.3?

5.5 The dissociation of N_2O_4(g) to give NO_2(g) is a first order process with a specific rate constant of 5.3×10^4 s^{-1} at 298 K. Starting with an initial concentration of 0.10 M, how many seconds would it take for 20 % of the original N_2O_4 to decompose?

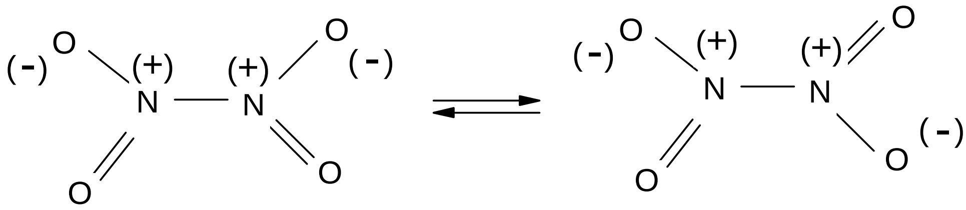
5.6 The association of NO_2(g) to give N_2O_4(g) is a second-order process with a specific rate constant of 9.8×10^6 $dm^3mol^{-1}s^{-1}$ at 298 K. Calculate the concentration equilibrium constant, K_c, at 298 K for the reaction $2\ NO_2(g) \rightleftharpoons N_2O_4(g)$

SOLUTION

5.1 The structure of NO_2:



5.2 The structure of N_2O_4:



(At very low temperatures there is another structure of N_2O_4 possible: O=N—ONO_2 , nitrosyl nitrate)

5.3 $N_2(g) + 2\ O_2(g) \rightarrow N_2O_4(g)$ $\qquad \Delta G^o = 98.28$ kJ

$N_2(g) + 2\ O_2(g) \rightarrow 2\ NO_2(g)$ $\qquad \Delta G^o = 2 \times (51.84) = 103.68$ kJ

$N_2O_4\ (g) \rightarrow 2\ NO_2\ (g)$ $\qquad \Delta G^o = 5.4$ kJ

If x denotes the fraction of decomposed N_2O_4 and P_T the partial pressure and X the mole fraction of the corresponding species, we obtain:

$\Delta G^0 = -RT \ln K$; $\qquad K = e^{(-\ 5.4\ \text{kJ}/\ 8.314 \times 10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1})}$

$$K_p = 0.113 = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{(P_T X_{NO_2})^2}{P_T X_{N_2O_4}} = \frac{\left(\dfrac{2x}{1+x}\right)^2}{\left(\dfrac{1-x}{1+x}\right)} = \frac{4\ x^2}{1-x^2}$$

wherefrom <u>x = 0.166</u>

5.4 If $2 \times 0.166 = 0.332$ mol N_2O_4 decomposes, 0.664 mol NO_2 are formed, thus

$$K_p = \frac{\left(\dfrac{0.664}{1.332}\right)^2}{\dfrac{1-0.332}{1.332}} = 0.496$$

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{0.496}{0.113}\right) = -\frac{58.03\ \text{Jmol}^{-1}}{8.314\ \text{Jmol}^{-1}\text{K}^{-1}}\left(\frac{1}{T_2} - \frac{1}{298\ \text{K}}\right)$$

$T_2 = 318$ K

5.5 $\ln\dfrac{[N_2O_4]_t}{[N_2O_4]_0} = -k\,t$

$$\ln 0.80 = -\,(5.3\times10^{4}\ s^{-1})\ t$$

$$t\ =\ 4.2 \times 10^{-6}\ \text{s}$$

5.6 $$K = \frac{k_{\text{forward}}}{k_{\text{reverse}}} = \frac{9.8\times10^{6}}{5.3\times10^{4}} = 1.8\times10^{2}$$

PROBLEM 6

The concentration of carbon dioxide in the atmosphere has increased substantially during this century and is predicted to continue to increase. The [CO_2] is expected to be about 440 ppm (440×10^{-6} atm) in the year 2020.

6.1 Calculate the concentration (in mol dm^{-3}) of CO_2 dissolved in distilled water equilibrated with the atmosphere in the year 2020.

6.2 Calculate the *pH*-value of the solution in 6.1.

6.3 Calculate the enthalpy of reaction between CO_2 (aq) and H_2O.

6.4 If the temperature of an equilibrated solution of CO_2 is increased and the concentration of dissolved carbon dioxide is maintained constant, the *pH* of the solution may change. Predict whether the *pH* will increase or decrease.

Data:

Henry's Law constant for CO_2 at 298 K: 0.0343 $dm^3\ mol^{-1}\ atm^{-1}$

Thermodynamic values, in kJ/mol at 298 K are:

	$\Delta_f G^0$	$\Delta_f H^0$
CO_2 (aq)	–386.2	–412.9
H_2O (l)	–237.2	–285.8
HCO_3^- (aq)	–587.1	–691.2
H^+ (aq)	0.00	0.00

SOLUTION

6.1 $[CO_2\,(aq)] = K_H\, p_{CO2} = 0.0343 \text{ M atm}^{-1} \times 440\times10^{-6} \text{ atm} = \underline{1.51\times10^{-5} \text{ M}}$

6.2 $CO_2(aq) + H_2O(l) \rightarrow H^+(aq) + HCO_3^-(aq) \qquad \Delta G^o = 36.3 \text{ kJ mol}^{-1}$

$K = e^{-\Delta G / RT} = 4.37\times10^{-7}$

Since $x = [H^+] = [HCO_3^-]$,

$$K = \frac{[H^+][HCO_3^-]}{[CO_2]} = \frac{x^2}{[CO_2]}$$

Solving for x yields $[H^+] = 2.57\times10^{-6}$; $\underline{pH = 5.59}$

6.3 $\Delta H^o = \Delta H^o_f(HCO_3^-) - \Delta H^o_f(CO_2) - \Delta H^o_f(H_2O) =$

$= -691.2 - (-412.9) - (-285.8) = \underline{7.5 \text{ kJ mol}^{-1}}$

6.4 Since the reaction is endothermic, the equilibrium constant will increase with temperature. Therefore, $[H^+]$ will also increase and the *pH* will decrease.

PROBLEM 7

When the fresh-water rivers that run into the Chesapeake Bay flood after heavy rains in the spring, the increase in fresh water in the Bay causes a decrease in the salinity in the areas where oysters grow. The minimum concentration of chloride ions needed in oyster beds for normal growth is 8 ppm (8 mg dm^{-3}).

After one week of heavy rain, the following analysis is done on water from the bay. To a 50.00 cm^3 sample of bay water a few drops of a K_2CrO_4 solution are added. The sample is then titrated with 16.16 cm^3 of a 0.00164 M $AgNO_3$ solution. After $AgNO_3$ solution has been added to the sample a bright red-orange precipitate forms.

7.1 What is the molar concentration of chloride in the sample?

7.2 Does the water contain sufficient chloride for the normal growth of oysters? Show your calculation.

7.3 Write a balanced equation for the reaction of the analyte with the titrant.

7.4 Write a balanced net-ionic equation that describes the reaction responsible for the colour change at the endpoint of the titration. Which compound produces the brick-red colour?

7.5 The concentration of chromate at the endpoint is 0.020 M. Calculate the concentration of chloride ions in the solution when the red precipitate forms.

7.6 For this titration to work most effectively, the solution being titrated must be neutral or slightly basic. Write a balanced equation for the competing reaction that would occur in acidic medium that would influence the observed endpoint of this titration.

Typically, a buffer is added to the solution being titrated to control the pH if the initial sample is acidic. Suppose the *pH* of the sample of bay water was 5.10, thus too acidic to perform the analysis accurately.

7.7 Select a buffer from the list that would enable you to establish and maintain a *pH* of 7.20 in aqueous medium. Show the calculations which lead to your choice.

	Buffer systems	K_a of weak acid
1.	0.10 M lactic acid / 0.10 M sodium lactate	1.4×10^{-4}
2.	0.10 M acetic acid / 0.10 M sodium acetate	1.8×10^{-5}

3.	0.10 M sodium dihydrogen phosphate / / 0.10 M sodium hydrogen phosphate	6.2×10^{-8}
4.	0.10 M ammonium chloride / 0.10 M ammonia	5.6×10^{-10}

7.8 Using the selected buffer system, calculate the mass (in g) of weak acid and of conjugated base you would need to dissolve in distilled water to prepare 500 cm^3 of a stock solution buffered at a pH of 7.2.

7.9 The chloride concentration in another 50.00 cm^3 sample of bay water was determined by the Volhard method. In this method an excess of $AgNO_3$ is added to the sample. The excess Ag^+ is titrated with standardized KSCN, forming a precipitate of AgSCN. The endpoint is signalled by the formation of the reddish-brown $FeSCN^{2+}$ complex that forms when Ag^+ is depleted. If the excess Ag^+ from the addition of 50.00 cm^3 of 0.00129 M $AgNO_3$ to the water sample required 27.46 cm^3 of 1.41 10^{-3} M KSCN for titration, calculate the concentration of chloride in the bay water sample.

In natural waters with much higher concentration of Cl^-, the Cl^- can be determined gravimetrically by precipitating the Cl^- as AgCl. A complicating feature of this method is the fact that AgCl is susceptible to photodecomposition as shown by the reaction:

$$AgCl(s) \rightarrow Ag(s) + ½ Cl_2(g).$$

Furthermore, if this photodecomposition occurs in the presence of excess Ag^+, the following additional reaction occurs:

$$3 Cl_2 (g) + 3 H_2O + 5 Ag^+ \rightarrow 5 AgCl + ClO_3^- + 6 H^+$$

If 0.010 g of a 3.000 g sample of AgCl contaminated with excess Ag^+ undergoes photodecomposition by the above equations

j) Will the apparent weight of AgCl be too high or too low? Explain your answer showing by how many grams the two values will differ.

Data: $K_{sp}(AgCl) = 1.78 \times 10^{-10}$

$K_{sp}(Ag_2CrO_4) = 1.00 \times 10^{-12}$

SOLUTION

7.1 $n(Ag^+) = n(Cl^-)$

$c(Cl^-) = \dfrac{0.01616\ dm^3 \times 0.00164\ mol\ dm^{-3}}{0.050\ dm^3} = 5.30\times10^{-4}\ mol\ dm^{-3}$

7.2 Concentration in mg dm^{-3} = 5.30×10^{-4} mol dm^{-3} × 35.5 g mol^{-1} = 0.0188 g dm^{-3} =
= 18.8 mg dm^{-3}

Thus the chloride concentration is sufficiently high for normal oyster growth.

7.3 $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl \downarrow(s)$

7.4 $2\ Ag^+(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2CrO_4 \downarrow(s)$ (brick-red colour)

7.5 $K_{sp}(Ag_2CrO_4) = [Ag^+]^2[CrO_4^{2-}] = 4\ x^3$ if $x = [Ag^+]$ $\Rightarrow$

$[Ag^+] = 7.07 \times 10^{-6}$; $[CrO_4^{2-}] = 2 \times10^{-2}$

$[Cl^-] = \dfrac{K_{sp}(AgCl)}{[Ag^+]} = \dfrac{178 \times 10^{-10}}{7.07 \times 10^{-6}} = 2.5 \times 10^{-5}$

7.6 $2\ CrO_4^{2-} + 2\ H^+ \rightarrow Cr_2O_7^{2-} + H_2O$

either/or

$CrO_4^{2-} + H^+ \rightarrow HCrO_4^- + H_2O$

7.7 A buffer system has its maximum buffer capacity when $pH = pK_a$. So, the system 3 would be best since $pK_a = 7.2$

7.8 $m(NaH_2PO_4) = 0.10\ mol\ dm^{-3} \times 0.500\ dm^3 \times 119.98\ g\ mol^{-1} = 6.0\ g$

$m(Na_2HPO_4) = 0.10\ mol\ dm^{-3} \times 0.500\ dm^3 \times 141.96\ g\ mol^{-1} = 7.1\ g$

7.9 mol Ag^+ added: $n(Ag^+)_{ad} = 0.05\ dm^3 \times 0.00129\ mol\ dm^{-3} = 6.45\times10^{-5}$ mol

mol Ag^+ left over: $n(Ag^+)_{left} = 0.02746\ dm^3 \times 0.0141\ mol\ dm^{-3} = 3.87\times10^{-5}$ mol

mol Cl^- in sample:

$n(Cl^-) = n(Ag^+)_{ad} - n(Ag^+)_{left} = (6.45\times10^{-5}\ mol) - (3.87\times10^{-5}\ mol) = 2.58\times10^{-5}$ mol

$\Rightarrow \quad [Cl^-] = \dfrac{2.58\times10^{-5}}{0.050} = 5.16\times10^{-4}\ mol\ dm^{-3}$

j) *n*(AgCl) lost: $\frac{0.010 \text{ g AgCl}}{143.35 \text{ gmol-1}}$ = 6.98 × 10^{-5} mol

n(Cl_2) produced: ½ (6.98×10^{-5} mol) = 3.49×10^{-5} mol

n(AgCl) new prod.: 5/3 (3.49×10^{-5} mol) = 5.82×10^{-5} mol ≡ 8.34 mg

The amount of Ag formed is equal to the amount of AgCl lost, thus

$[Ag]_{formed}$ = 6.98×10^{-5} mol × 107.9 g mol^{-1} = 7.53×10^{-3} g

The mass of the sample is equal to 3.0 g – 0.010 g + 0.00834 g + 0.00753 g =

= 3.006 g. Therefore the total mass of the solid (AgCl + Ag) will be too high and the difference is 6 mg.

PROBLEM 8

The Pourbaix diagrams for water, nitrogen and manganese are depicted in Fig. 1.

8.1 Write the formula of the species of nitrogen that is predominant

i) in O_2-rich lakes of pH ≈ 6,

ii) in highly O_2-depleted lakes that are strongly contaminated with acid rain (pH ≈ 3),

8.2 Which species of manganese is predominant

i) in O_2-rich lakes of pH ≈ 6,

ii) in highly O_2-depleted lakes that are strongly contaminated with bases (pH ≈ 12)?

8.3 People often find that clear, slightly acidic (pH ≈ 5) water drawn from wells deposits a black manganese-containing solid on standing in toilet bowls.

i) Write the chemical formula of the black solid?

ii) Write the formula for the species of manganese found in well water while it is still underground ?

8.4 According to Pourbaix diagrams two species of nitrogen should oxidize Mn(s) to Mn^{2+}(aq).

i) Write the formulas of these two nitrogen species.

ii) Which of the two species of nitrogen does not oxidize Mn(s) (in practice) at room temperature ?

8.5 According to the Poubaix diagrams, some of the chemical forms of manganese should oxidize NH_3(aq) or NH_4^+(aq) to N_2(g).

Choose in the following list the forms of Mn that should do it:

Mn, $Mn(OH)_2$, Mn^{2+}, Mn_3O_4, Mn_2O_3, MnO_2, MnO_4^{2-} , MnO_4^-

8.6 Ammonium permanganate, NH_4MnO_4, is a well-known salt, but ammonium manganate, $(NH_4)_2MnO_4$, is a rarely known salt.

i) Is NH_4MnO_4 expected to be thermodynamically stable? (YES or NO)

ii) Is $(NH_4)_2MnO_4$ expected to be thermodynamically stable? (YES or NO)

iii) Write and balance an equation for the decomposition of NH_4MnO_4 to give MnO_2 a N_2.

iv) Write and balance an equation for the decomposition of $(NH_4)_2MnO_4$ to give Mn a N_2.

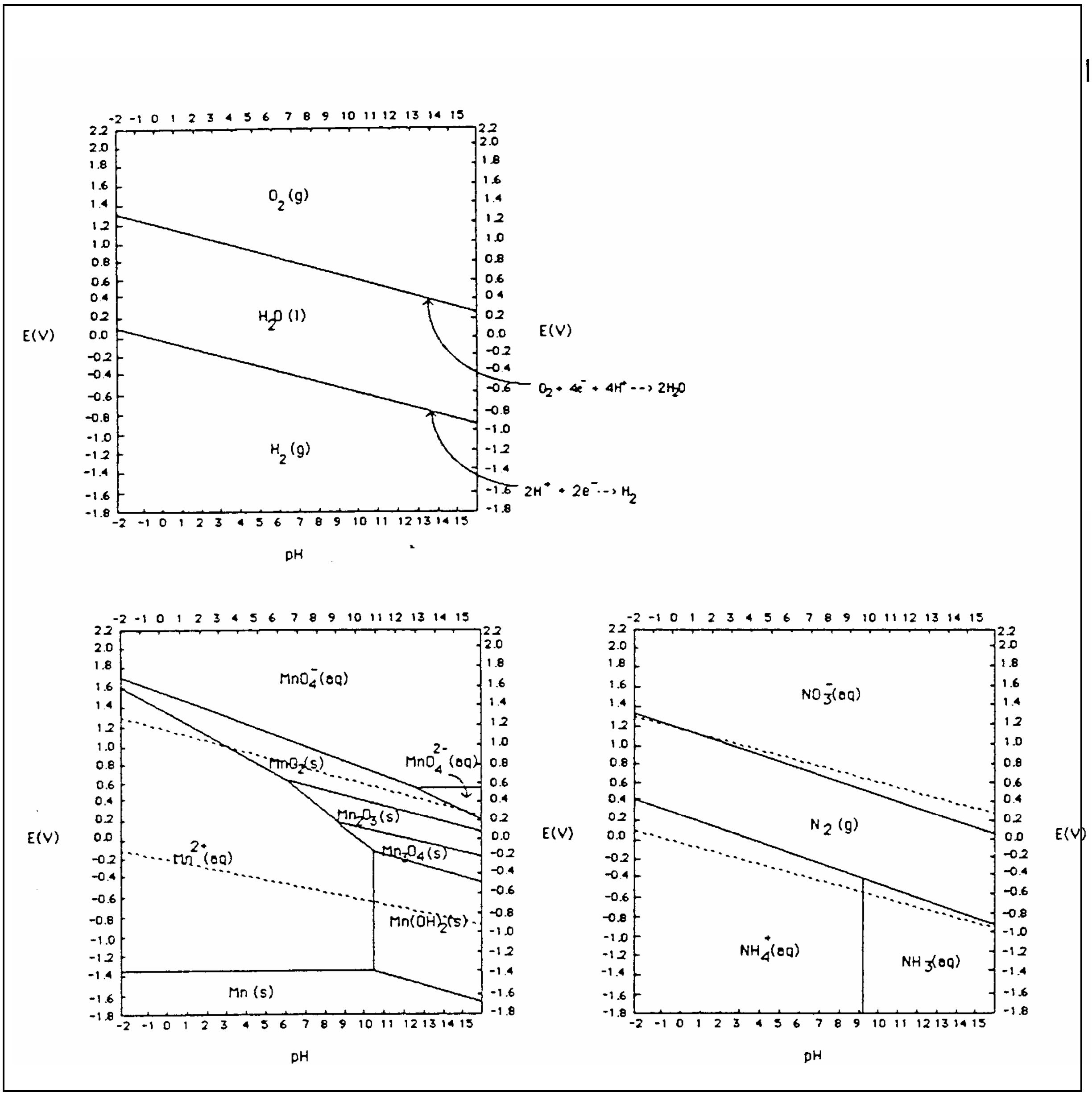
8.7 According to the Pourbaix diagrams, is it dangerous to grind together in a mortar and pestle

i potassium nitrate and manganese metal,

ii) potassium nitrate and manganese dioxide?

8.8 The standard reduction potential, E^0, for the reduction of MnO_4^- to MnO_2 is 1.692 V. Applying the Nernst equation calculate the reduction potential, E, for the reduction of 0.00100 M MnO_4^- solution at a pH = 4.0.

Figure 1



SOLUTION

8.1 i) N_2 ii) NO_3^-

8.2 i) MnO_2 ii) $Mn(OH)_2$

8.3 i) MnO_2, ii) Mn^{2+}

8.4 NO_3^- and N_2. In practice only NO_3^- would oxidize Mn, since the activation energy for N_2 in order to break the triple bonds is very high.

8.5 Mn_3O_4, Mn_2O_3, MnO_2, MnO_4^{2-}, MnO_4^-

8.6 i) NH_4MnO_4: YES

ii) $(NH_4)_2MnO_4$: NO

iii) $2\ NH_4MnO_4 \rightarrow 4\ H_2O + 2\ MnO_2 + N_2$

iv) $(NH_4)_2MnO_4 \rightarrow 4\ H_2O + Mn + N_2$

8.7 According to the diagrams, KNO_3 is easily reduced by Mn whereas the potential of MnO_2 is more positive than the potential of NO_3^-. So a mixture of KNO_3 and Mn could be explosive.

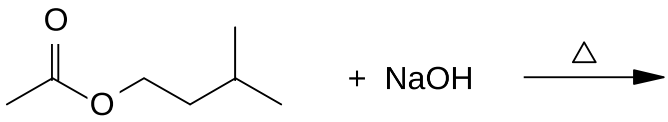
8.8 $E = E^o + \frac{0.0591}{3}\log[MnO_4^-] + \frac{0.0591}{3}\log[H^+]^4) =$

$= 1.692 + 0.0197 \log 0.001 - 0.0788\ pH = 1.633 - 0.0788\ pH = \underline{1.34\ V}$

PROBLEM 9

Pheromones are chemicals or mixtures of certain chemicals secreted by insects and some animals for communication. They bring about certain responses in another individual of the same species. In the problem below you will find a number of pheromones undergoing reactions which were used in determining their structures. In each case give the structure or structures of the products produced. Show geometric (cis/trans) isomers where appropriate (in part (9.5). You may ignore other forms of stereoisomerism.

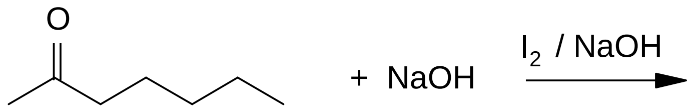
9.1



isoamyl acetate,
bee alarm pheromene

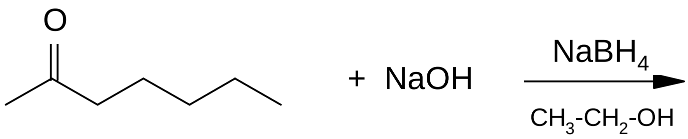
9.2

i)

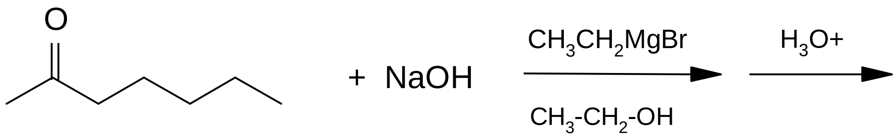


2-heptanone
ant alarm pheromone

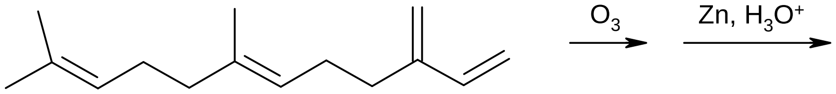
ii)



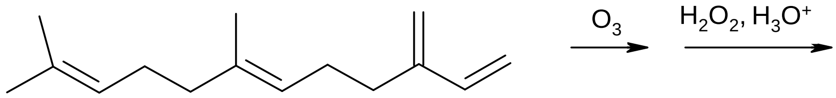
iii)



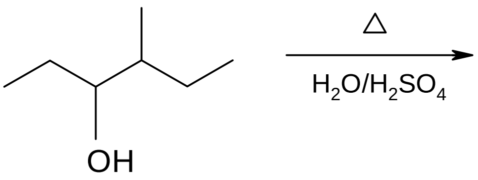
9.3

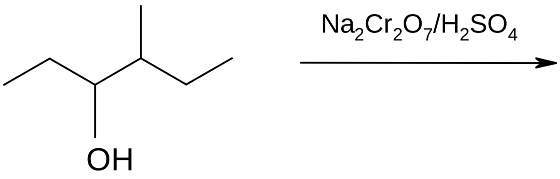
i) 

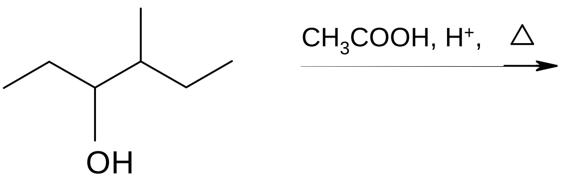
green peach -
aphid pheromone

ii) 

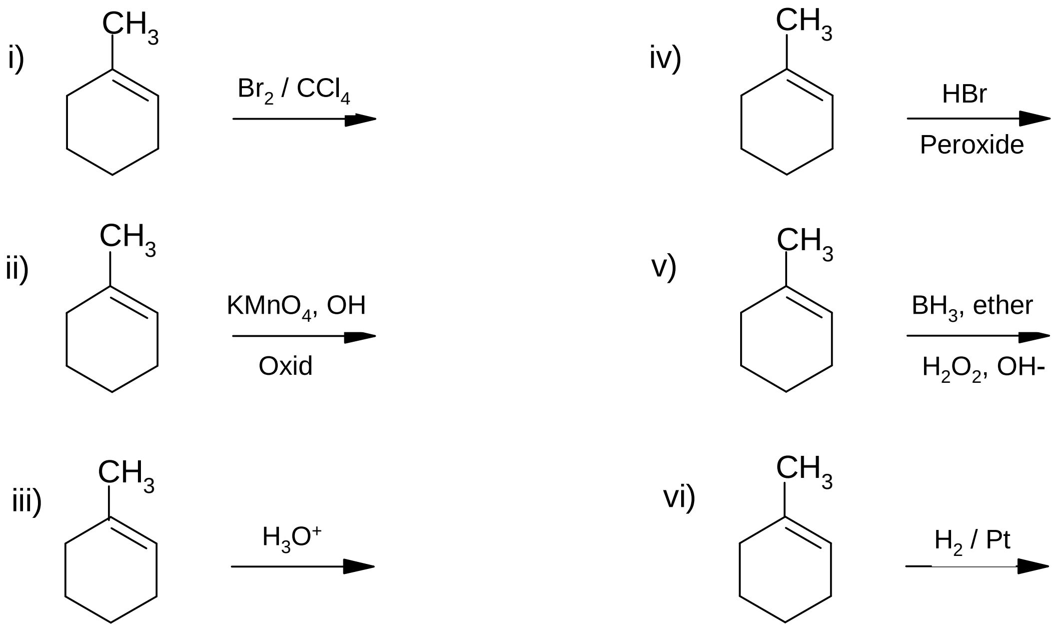
9.4

(i) 

(ii) 

(iii) 

9.5



SOLUTION

9.1

$CH_3\text{-}C(=O)\text{-}O^{(-)}\ Na^{(+)}$ and $HOCH_2CH_2CH(CH_3)_2$

9.2 i)

CHI_3 and $CH_3\text{-}(CH_2)_4\text{-}C(=O)\text{-}O^{(-)}\ Na^{(+)}$

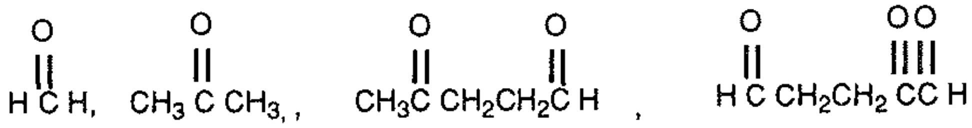
ii)

$CH_3\text{-}(CH_2)_4\text{-}CH(OH)\text{-}CH_3$

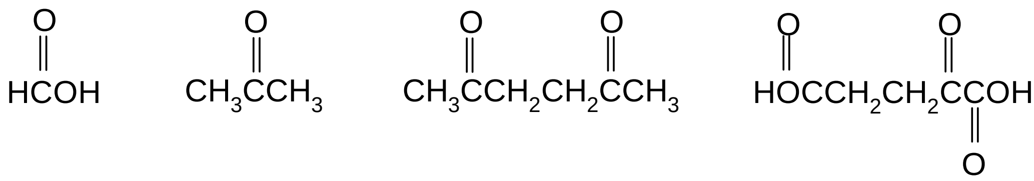
iii)

$CH_3\text{-}(CH_2)_4\text{-}C(OH)(CH_2\text{-}CH_3)\text{-}CH_3$

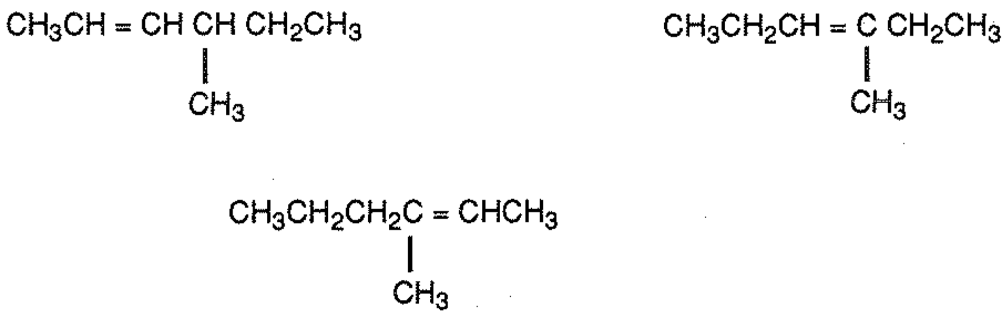
9.3 i)

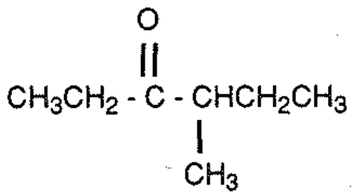


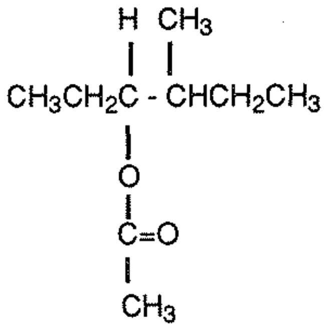
ii)



9.4 i)

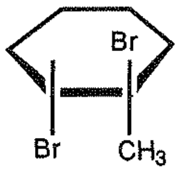


(ii) 

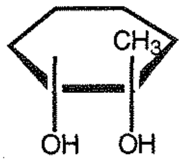
(iii) 

9.5

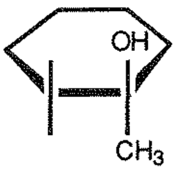
(i)



(ii)



(iii)



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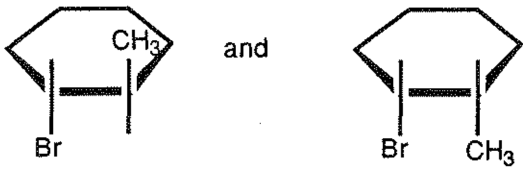
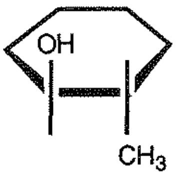


(v)



(vi)

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Effects of CO_2 on Solubility

Calcium carbonate is a partially soluble material commonly known as limestone, marble, chalk, or calcite. In the presence of CO_2-rich groundwater, calcium carbonate dissolves to form cavities and caves in limestone formations.

In this experiment you will determine the solubility of calcium carbonate in an aqueuos solution saturated with carbon dioxide and in solution free of carbon dioxide. The $[Ca^{2+}]$ will be determined by complexometric titration with EDTA (ethylenediamine-tetraacetic acid).

a) Procedure for the determination of $[Ca^{2+}]$

1. Calibrate your *pH* meter.
2. Measure and record the *pH* of the sample equilibrated with solid $CaCO_3$ and CO_2 gas.
3. Filter all your sample into a second 250 cm^3 plastic bottle to remove any suspended $CaCO_3$. Quickly cap the bottle when the filtering is complete.
4. Uncap the bottle long enough to measure and record the pH of the filtered solution and recap the bottle until you are ready for the next step.
5. As rapidly as possible, transfer three 25 cm^3 aliquots of this sample to three Erlenmeyer flasks. Recap the sample bottle after removing each 25 cm^3 aliquot.
6. Add 15 drops of 6 M HCl to each of the three flasks with stirring. Any $CaCO_3$ that may have formed should dissolve. Before proceeding with the next step, make sure there is no solid $CaCO_3$ in the Erlenmeyer flasks. If a flask has some solid present, then more stirring is necessary.
7. To one, and only one flask, add 5 cm^3 of a pH 10 NH_3 buffer. Proceed immediately with steps 8 - 10.
8. Add 20 drops of 0.001 M $Mg^{2+}/EDTA^{4-}$ solution to the flask in order for the indicator to function properly.
9. Add 5 drops of Calmagite indicator to the sample.

10. Titrate the sample with an approximately 0.01 M EDTA solution provided (to be standardized as directed below) to a colour change from red to blue. You may wish to make a reference for colour with water, buffer, two drops EDTA and indicator.
11. Quickly repeat steps 7 - 10 for each remaining flask, one at a time.
12. After steps 1 - 11 have been completed to your satisfaction, transfer the remaining filtered, saturated solution from step 3 to a suitable beaker. Heat this solution to 96 – 99 ^{o}C and allow it to remain at that temperature, with magnetic stirring, for 5 minutes. A stirrer setting on 6 is adequate, and an initial high setting of heat will be required. You should see CO_2 being evolved and some $CaCO_3$ may precipitate.
13. At the end of the five minutes heating period, use the beaker tongs to remove the beaker from the hot plate and place it in an ice bath. Allow the solution to cool to room temperature.
14. Measure and record the *pH* of the cooled solution.
15. Filter the solution to remove any suspended $CaCO_3$.
16. Transfer three 25 cm^3 aliquots of this filtered solution to three Erlenmeyer flasks. Add about 25 cm^3 of deionized water to each flask, followed by 15 drops of 6 M HCl.
17. Titrate each sample according to steps 7 - 11.

b) <u>Procedure for standardization of EDTA</u>

1. Weigh approximately 0.35 g of dried primary standard $CaCO_3$, (molar mass 100.09 g mol^{-1}) which will be found in the weighing bottle in the desiccator. Note: $CaCO_3$ is hygroscopic.
2. Add 25 cm^3 of deionized water to the $CaCO_3$, then carefully add 5 cm^3 of 6 M HCl. Quickly cover with a watch glass.
3. When the $CaCO_3$ has dissolved, quantitatively transfer the solution to a 250 cm^3 volumetric flask and dilute to the mark.
4. Transfer three 25 cm^3 aliquots of the standard Ca^{2+} solution to three Erlenmeyer flasks.
5. Proceed to titrate each sample according to steps 7 - 11, following each step in sequence.

Tasks:

1.1 Calculate the solubility of calcium carbonate (expressed in mol dm^{-3}) in a solution saturated with both $CaCO_3$ and CO_2 and in solution free of CO_2.

1.2 List all the ionic species that increase in concentration as a result of the dissolving of $CaCO_3$ in water.

1.3 Given below are brief descriptions of two solutions. Circle the one in which the concentration of CO_3^{2-} would be highest:

a) a solution produced by dissolving $CaCO_3$(s) in CO_2 -saturated water

b) a solution produced by dissolving $CaCO_3$(s) in CO_2 -free water

1.4 Will the solubility of $CaCO_3$ increase or decrease in a solution from which the CO_2 has been removed?

SOLUTION

1.1 The results of the titration (volumes of titrants, mass of $CaCO_3$) and calculation of the concentration of the standardized EDTA solution were required to be written on the Answer Sheet.

Moreover, it was necessary to measure and record *pH* values of the sample at steps 2, 4, and 14.

It was expected to show the calculation of the solubility of $CaCO_3$ in its saturated solutions containing CO_2 and in those without CO_2.

The other tasks to be solved:

1.2 The ionic species mentioned above are as follows: Ca^{2+}, HCO_3^-, OH^-.

1.3 Correct answer: (b) A solution produced by dissolving $CaCO_3$(s) in CO_2-free water.

1.4 The solubility of $CaCO_3$ will decrease.