

**24<sup>th</sup>**



**International Chemistry Olympiad**

**9 theoretical problems  
1 practical problem**

# THE TWENTY-FOURTH INTERNATIONAL CHEMISTRY OLYMPIAD 11–22 July 1992, PITTSBURGH, UNITED STATES OF AMERICA

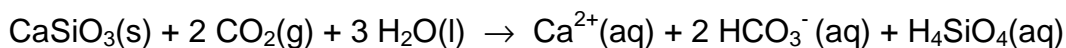
## THEORETICAL PROBLEMS

### PROBLEM 1

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



- 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 ( $\text{C}_6\text{H}_{12}\text{O}_6$ ), calculate the volume of  $\text{CO}_2$  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  $0.23 \text{ cm}^3$  of dissolved  $\text{CO}_2$  per one litre sea water (at 24 °C and 101 kPa).
- 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?
  - 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  $1.37 \times 10^{18} \text{ m}^3$ .
- 1.3** Three percent of the mass of a  $9.1 \times 10^4 \text{ kg}$  adult whale is nitrogen. When a  $9.1 \times 10^4 \text{ kg}$  blue whale dies, what is the maximum mass of  $\text{NH}_4^+$  that can become available for other marine organisms?
- 1.4** Eighteen percent of a  $9.1 \times 10^4 \text{ kg}$  whale's mass is carbon. Carbon can be returned to the atmosphere as  $\text{CO}_2$  and then removed from the atmosphere by weathering of rocks containing calcium silicate.



What are the maximum number of grams of  $\text{CaSiO}_3$  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  $5 \times 365 \times 75 \times 10 = 1.4 \times 10^6$  kg krill which themselves need  $1.4 \times 10^7$  kg of carbohydrates coming from diatoms.

For 180 g  $\text{C}_6\text{H}_{12}\text{O}_6$ ,  $6 \times 44$  g  $\text{CO}_2$  are necessary, and thus

for  $1.4 \times 10^7$  kg carbohydrates  $1.4 \times 10^7 \times (264/180) = 2.00 \times 10^7$  kg of  $\text{CO}_2$  are needed,

i. e.  $1.0 \times 10^{10}$  dm<sup>3</sup>  $\text{CO}_2$

**1.2** i) The amount of water is  $4 \times 10^{13}$  dm<sup>3</sup>.

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

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

$$n(\text{N}) = n(\text{NH}_4^+) = \frac{2.7 \times 10^6 \text{ g}}{14 \text{ g mol}^{-1}} = 1.9 \times 10^5 \text{ mol}$$

$$m(\text{NH}_4^+) = 1.9 \times 10^5 \text{ mol} \times 18 \text{ g mol}^{-1} = 3 \times 10^6 \text{ g NH}_4^+ = 3 \times 10^3 \text{ kg NH}_4^+$$

**1.4** One whale contains  $1.6 \times 10^4$  kg of carbon. It corresponds to  $1.3 \times 10^6$  mol of  $\text{CO}_2$ .

From the equation:  $n(\text{CaSiO}_3) = 6.5 \times 10^5$  mol

$$m(\text{CaSiO}_3) = 6.5 \times 10^5 \text{ mol} \times 116 \text{ g mol}^{-1} = 7.5 \times 10^7 \text{ g CaSiO}_3$$

1000 whales therefore produce  $7.5 \times 10^{10}$  g  $\text{CaSiO}_3$ .

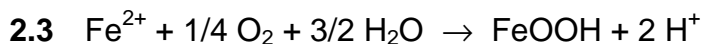
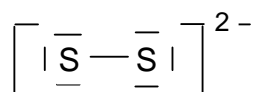
**PROBLEM 2**

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,  $\text{FeS}_2$ , in which the oxidation state of iron is +2. As the iron-rich streams mix with other waters, the dissolved iron precipitates as goethite,  $\text{FeO(OH)}$ , which coats the stream bottom while the water remains acidic.

- 2.1 Draw the electron dot structure that illustrates the bonding in the ion  $\text{S}_2^{2-}$ , showing all valence electrons.
- 2.2 Write a balanced chemical equation to show how hydrogen ions ( $\text{H}^+$ ) 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,  $\text{FeO(OH)}$ .
- 2.4 Calculate how many moles of pyrite would be required to bring  $1.0 \text{ dm}^3$  of pure water to a pH of 3.0 if the pyrite was completely converted into  $\text{FeO(OH)}$  and  $\text{H}^+$  ions. Neglect the formation of  $\text{HSO}_4^-$ .
- 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  $\text{Fe(OH)}_3$  which on aging becomes  $\text{Fe}_2\text{O}_3$ . What mass of  $\text{Fe}_2\text{O}_3$  will be deposited on the bottom of the pond in two years?

**SOLUTION**

2.1



2.4  $[\text{H}^+] = 1 \times 10^{-3}$

$n[\text{H}^+] = 1 \times 10^{-3} \text{ mol}$

From both equations:  $n(\text{FeS}_2) = 2.5 \times 10^{-4} \text{ mol}$

**2.5** Total flow into pond in 2 years =

$$2 \text{ yr} \times 365 \text{ days yr}^{-1} \times 24 \text{ h day}^{-1} \times 60 \text{ min h}^{-1} \times 20.0 \text{ dm}^3 \text{ min}^{-1} = \\ = 2.10 \times 10^7 \text{ dm}^3 \text{ of water}$$

$$n(\text{Fe}^{2+}) \text{ into pond} = 2.10 \times 10^7 \text{ dm}^3 \times 8.35 \times 10^{-3} \text{ mol dm}^{-3} = 1.76 \times 10^5 \text{ mol}$$

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

mass of deposited  $\text{Fe}_2\text{O}_3$ :

$$m(\text{Fe}_2\text{O}_3) = 0.5 \times 1.32 \times 10^5 \text{ mol} \times 159.7 \text{ g mol}^{-1} = 1.05 \times 10^7 \text{ g}$$

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**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  $NaOH$ .

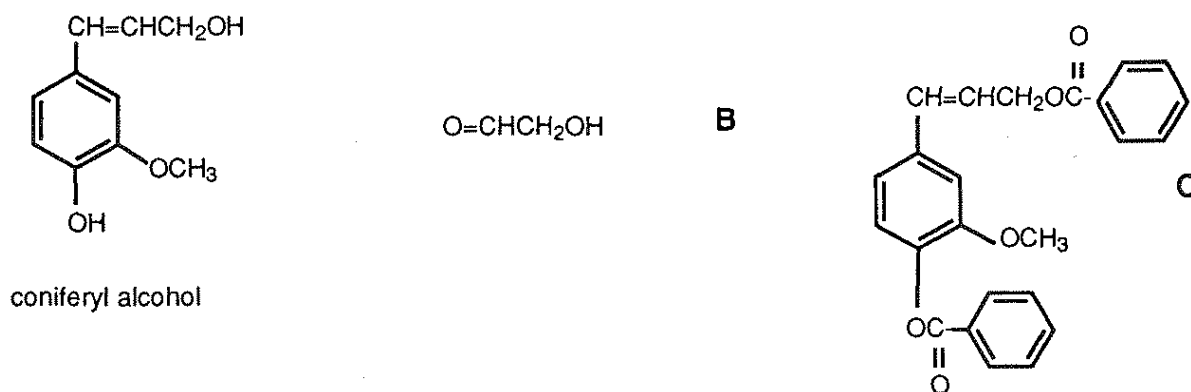
Coniferyl alcohol reacts with cold  $HBr$  to form **D** ( $C_{10}H_{11}O_2Br$ ). Hot  $HI$  converts  $ArOR$  to  $ArOH$  and  $RI$ . Coniferyl alcohol reacts with excess hot  $HI$  to give **E** ( $C_9H_9O_2I$ ) and  $CH_3I$ .  $CH_3I$  in aqueous base reacts with coniferyl alcohol to form **F** (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

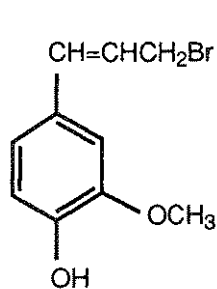
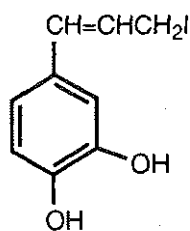
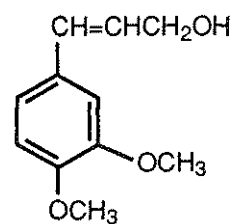
**3.1** Draw the structures of coniferyl alcohol and compounds **A - F**.

**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.

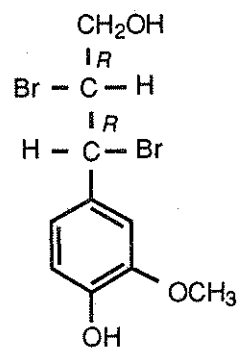
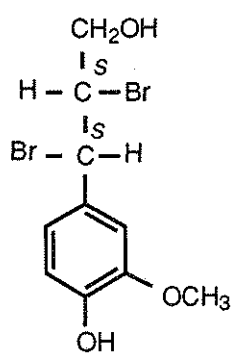
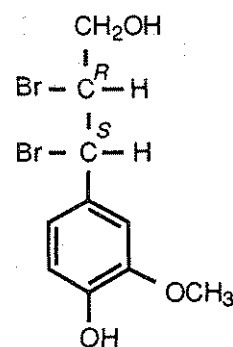
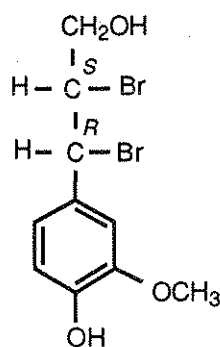
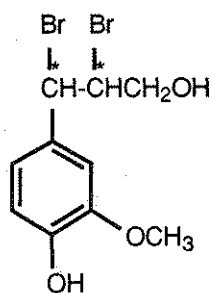
**SOLUTION**

**3.1**




**D**

**E**

**F**
**I**

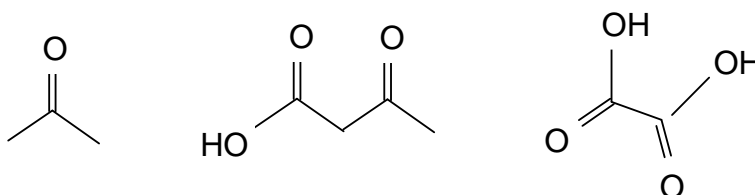
3.2 There are no geometric isomers of compound **A**, but there are 4 diastereomers (2 pairs of enantiomers).



**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  $C_{10}H_{17}Br$ .

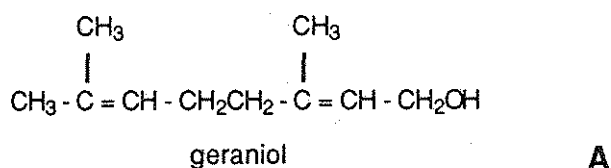
When geraniol is vigorously oxidized, three products are obtained:



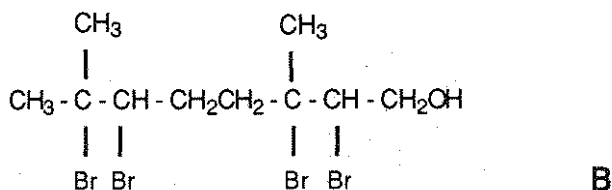
- 4.1 Give the structure of geraniol **A**.
- 4.2 Give the structure of compound **B**.
- 4.3 Give the structures of the two bromides of formula  $C_{10}H_{17}Br$ .
- 4.4 Indicate which of the two bromides is formed in greater proportions.

**SOLUTION**

4.1

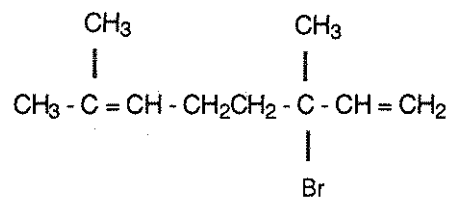


4.2

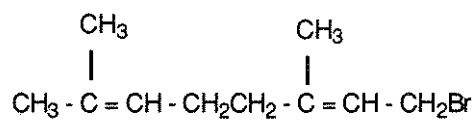




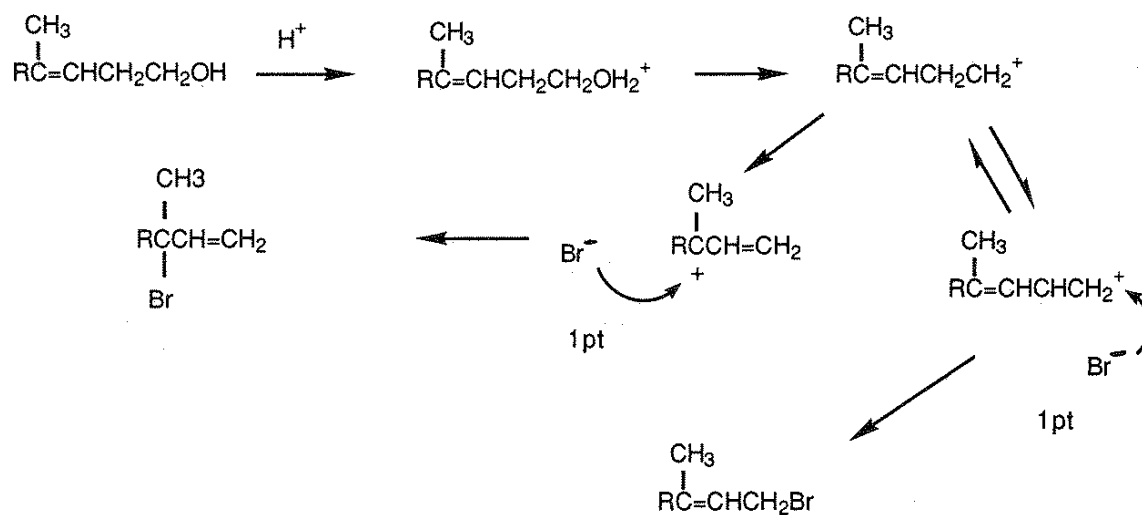
4.3



or

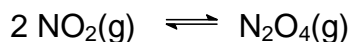


4.4



**PROBLEM 5**

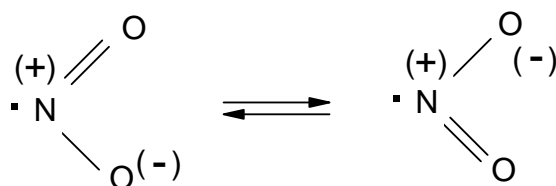
Nitrogen dioxide  $\text{NO}_2$  is one of a number of oxides of nitrogen found in our atmosphere. It can dimerize to give  $\text{N}_2\text{O}_4$  (g):



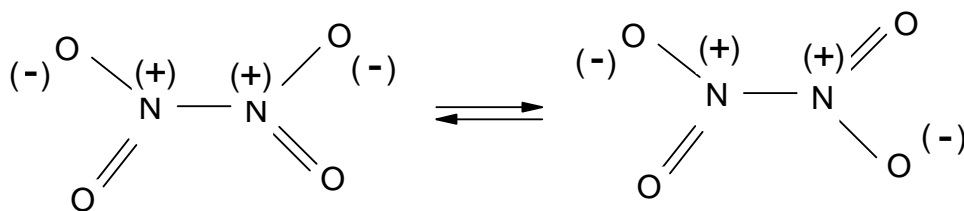
- 5.1** With a diagram, show the bonds present in  $\text{NO}_2(\text{g})$  using the concept of resonance if necessary. Nitrogen dioxide,  $\text{NO}_2$ , is paramagnetic.
- 5.2** Show, with bonding diagrams, how two molecules of  $\text{NO}_2(\text{g})$  combine to give a molecule of  $\text{N}_2\text{O}_4$  (g) which is not paramagnetic.
- 5.3** At 298 K, the  $\Delta G^\circ$  of formation for  $\text{N}_2\text{O}_4(\text{g})$  is 98.28 kJ, whereas for  $\text{NO}_2(\text{g})$  is 51.84 kJ. Starting with one mole of  $\text{N}_2\text{O}_4(\text{g})$  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  $\Delta H^\circ$  for the reaction  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$  is 58.03 kJ, at what temperature would the fraction of  $\text{N}_2\text{O}_4$  decomposed be double that calculated in part 5.3?
- 5.5** The dissociation of  $\text{N}_2\text{O}_4(\text{g})$  to give  $\text{NO}_2(\text{g})$  is a first order process with a specific rate constant of  $5.3 \times 10^4 \text{ s}^{-1}$  at 298 K. Starting with an initial concentration of 0.10 M, how many seconds would it take for 20 % of the original  $\text{N}_2\text{O}_4$  to decompose?
- 5.6** The association of  $\text{NO}_2(\text{g})$  to give  $\text{N}_2\text{O}_4(\text{g})$  is a second-order process with a specific rate constant of  $9.8 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 298 K. Calculate the concentration equilibrium constant,  $K_c$ , at 298 K for the reaction  $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$

**SOLUTION**

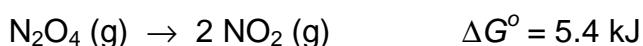
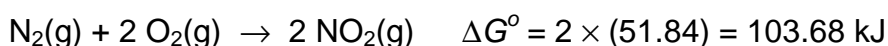
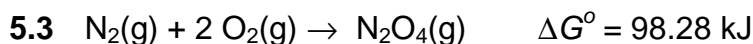
- 5.1** The structure of  $\text{NO}_2$ :



- 5.2** The structure of  $\text{N}_2\text{O}_4$ :



(At very low temperatures there is another structure of  $\text{N}_2\text{O}_4$  possible:  $\text{O}=\text{N}-\text{ONO}_2$ , nitrosyl nitrate)



If  $x$  denotes the fraction of decomposed  $\text{N}_2\text{O}_4$  and  $P_T$  the partial pressure and  $X$  the mole fraction of the corresponding species, we obtain:

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

$$K_p = 0.113 = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = \frac{(P_T X_{\text{NO}_2})^2}{P_T X_{\text{N}_2\text{O}_4}} = \frac{\left(\frac{2x}{1+x}\right)^2}{\left(\frac{1-x}{1+x}\right)} = \frac{4x^2}{1-x^2}$$

wherefrom  $x = 0.166$

**5.4** If  $2 \times 0.166 = 0.332 \text{ mol}$   $\text{N}_2\text{O}_4$  decomposes,  $0.664 \text{ mol}$   $\text{NO}_2$  are formed, thus

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

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

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

$$T_2 = 318 \text{ K}$$

**5.5**  $\ln \frac{[\text{N}_2\text{O}_4]_t}{[\text{N}_2\text{O}_4]_0} = -kt$

$$\ln 0.80 = -(5.3 \times 10^4 \text{ s}^{-1}) t$$

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

**5.6**  $K = \frac{k_{\text{forward}}}{k_{\text{reverse}}} = \frac{9.8 \times 10^6}{5.3 \times 10^4} = 1.8 \times 10^2$

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**PROBLEM 6**

The concentration of carbon dioxide in the atmosphere has increased substantially during this century and is predicted to continue to increase. The  $[\text{CO}_2]$  is expected to be about 440 ppm ( $440 \times 10^{-6}$  atm) in the year 2020.

- 6.1** Calculate the concentration (in  $\text{mol dm}^{-3}$ ) of  $\text{CO}_2$  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  $\text{CO}_2$  (aq) and  $\text{H}_2\text{O}$ .
- 6.4** If the temperature of an equilibrated solution of  $\text{CO}_2$  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:

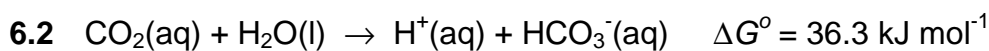
Henry's Law constant for  $\text{CO}_2$  at 298 K:  $0.0343 \text{ dm}^3 \text{ mol}^{-1} \text{ atm}^{-1}$

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

	$\Delta_f G^0$	$\Delta_f H^0$
$\text{CO}_2$ (aq)	-386.2	-412.9
$\text{H}_2\text{O}$ (l)	-237.2	-285.8
$\text{HCO}_3^-$ (aq)	-587.1	-691.2
$\text{H}^+$ (aq)	0.00	0.00

**SOLUTION**

6.1  $[\text{CO}_2(\text{aq})] = K_{\text{H}} p_{\text{CO}_2} = 0.0343 \text{ M atm}^{-1} \times 440 \times 10^{-6} \text{ atm} = \underline{1.51 \times 10^{-5} \text{ M}}$



$$K = e^{-\Delta G^\circ / RT} = 4.37 \times 10^{-7}$$

Since  $x = [\text{H}^+] = [\text{HCO}_3^-]$ ,

$$K = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = \frac{x^2}{[\text{CO}_2]}$$

Solving for  $x$  yields  $[\text{H}^+] = 2.57 \times 10^{-6}$ ; pH = 5.59

6.3  $\Delta H^\circ = \Delta H_f^\circ(\text{HCO}_3^-) - \Delta H_f^\circ(\text{CO}_2) - \Delta H_f^\circ(\text{H}_2\text{O}) =$   
 $= -691.2 - (-412.9) - (-285.8) = \underline{7.5 \text{ kJ mol}^{-1}}$

6.4 Since the reaction is endothermic, the equilibrium constant will increase with temperature. Therefore,  $[\text{H}^+]$  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 ( $8 \text{ mg dm}^{-3}$ ).

After one week of heavy rain, the following analysis is done on water from the bay. To a  $50.00 \text{ cm}^3$  sample of bay water a few drops of a  $\text{K}_2\text{CrO}_4$  solution are added. The sample is then titrated with  $16.16 \text{ cm}^3$  of a  $0.00164 \text{ M AgNO}_3$  solution. After  $\text{AgNO}_3$  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  $0.020 \text{ M}$ . 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.

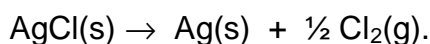
	Buffer systems	$K_a$ of weak acid
1.	0.10 M lactic acid / 0.10 M sodium lactate	$1.4 \times 10^{-4}$
2.	0.10 M acetic acid / 0.10 M sodium acetate	$1.8 \times 10^{-5}$

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

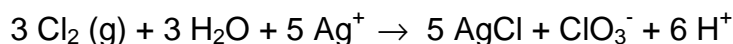
**7.8** Using the selected buffer system, calculate the mass (in g) of weak acid and of conjugated base you would need to dissolve in distilled water to prepare 500 cm<sup>3</sup> of a stock solution buffered at a pH of 7.2.

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

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



Furthermore, if this photodecomposition occurs in the presence of excess Ag<sup>+</sup>, the following additional reaction occurs:



If 0.010 g of a 3.000 g sample of AgCl contaminated with excess Ag<sup>+</sup> undergoes photodecomposition by the above equations

**7.10** 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:  $K_{sp}(\text{AgCl}) = 1.78 \times 10^{-10}$   
 $K_{sp}(\text{Ag}_2\text{CrO}_4) = 1.00 \times 10^{-12}$



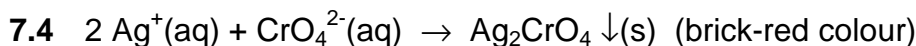
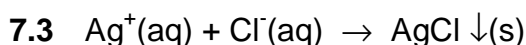
**SOLUTION**

$$7.1 \quad n(\text{Ag}^+) = n(\text{Cl}^-)$$

$$c(\text{Cl}^-) = \frac{0.01616 \text{ dm}^3 \times 0.00164 \text{ mol dm}^{-3}}{0.050 \text{ dm}^3} = 5.30 \times 10^{-4} \text{ mol dm}^{-3}$$

$$7.2 \quad \text{Concentration in mg dm}^{-3} = 5.30 \times 10^{-4} \text{ mol dm}^{-3} \times 35.5 \text{ g mol}^{-1} = 0.0188 \text{ g dm}^{-3} = 18.8 \text{ mg dm}^{-3}$$

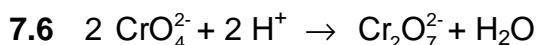
Thus the chloride concentration is sufficiently high for normal oyster growth.



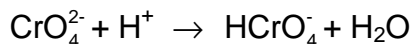
$$7.5 \quad K_{sp}(\text{Ag}_2\text{CrO}_4) = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = 4x^3 \text{ if } x = [\text{Ag}^+] \Rightarrow$$

$$[\text{Ag}^+] = 7.07 \times 10^{-6}; \quad [\text{CrO}_4^{2-}] = 2 \times 10^{-2}$$

$$[\text{Cl}^-] = \frac{K_{sp}(\text{AgCl})}{[\text{Ag}^+]} = \frac{1.78 \times 10^{-10}}{7.07 \times 10^{-6}} = 2.5 \times 10^{-5}$$



either/or



7.7 A buffer system has its maximum buffer capacity when  $\text{pH} = \text{pK}_a$ . So, the system 3 would be best since  $\text{pK}_a = 7.2$

$$7.8 \quad m(\text{NaH}_2\text{PO}_4) = 0.10 \text{ mol dm}^{-3} \times 0.500 \text{ dm}^3 \times 119.98 \text{ g mol}^{-1} = 6.0 \text{ g}$$

$$m(\text{Na}_2\text{HPO}_4) = 0.10 \text{ mol dm}^{-3} \times 0.500 \text{ dm}^3 \times 141.96 \text{ g mol}^{-1} = 7.1 \text{ g}$$

$$7.9 \quad \text{mol Ag}^+ \text{ added: } n(\text{Ag}^+)_{\text{ad}} = 0.05 \text{ dm}^3 \times 0.00129 \text{ mol dm}^{-3} = 6.45 \times 10^{-5} \text{ mol}$$

$$\text{mol Ag}^+ \text{ left over: } n(\text{Ag}^+)_{\text{left}} = 0.02746 \text{ dm}^3 \times 0.0141 \text{ mol dm}^{-3} = 3.87 \times 10^{-5} \text{ mol}$$

mol  $\text{Cl}^-$  in sample:

$$n(\text{Cl}^-) = n(\text{Ag}^+)_{\text{ad}} - n(\text{Ag}^+)_{\text{left}} = (6.45 \times 10^{-5} \text{ mol}) - (3.87 \times 10^{-5} \text{ mol}) = 2.58 \times 10^{-5} \text{ mol}$$

$$\Rightarrow [\text{Cl}^-] = \frac{2.58 \times 10^{-5}}{0.050} = 5.16 \times 10^{-4} \text{ mol dm}^{-3}$$

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

$n(\text{Cl}_2)$  produced:  $\frac{1}{2} (6.98 \times 10^{-5} \text{ mol}) = 3.49 \times 10^{-5} \text{ mol}$

$n(\text{AgCl})$  new prod.:  $\frac{5}{3} (3.49 \times 10^{-5} \text{ mol}) = 5.82 \times 10^{-5} \text{ mol} \equiv 8.34 \text{ mg}$

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

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

The mass of the sample is equal to  $3.0 \text{ g} - 0.010 \text{ g} + 0.00834 \text{ g} + 0.00753 \text{ g} = 3.006 \text{ g}$ . Therefore the total mass of the solid (AgCl + Ag) will be too high and the difference is 6 mg.

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**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<sub>2</sub>-rich lakes of pH ≈ 6,
- ii) in highly O<sub>2</sub>-depleted lakes that are strongly contaminated with acid rain (pH ≈ 3),

**8.2** Which species of manganese is predominant

- i) in O<sub>2</sub>-rich lakes of pH ≈ 6,
- ii) in highly O<sub>2</sub>-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<sup>2+</sup>(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 Pourbaix diagrams, some of the chemical forms of manganese should oxidize NH<sub>3</sub>(aq) or NH<sub>4</sub><sup>+</sup>(aq) to N<sub>2</sub>(g).

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

Mn, Mn(OH)<sub>2</sub>, Mn<sup>2+</sup>, Mn<sub>3</sub>O<sub>4</sub>, Mn<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, MnO<sub>4</sub><sup>2-</sup>, MnO<sub>4</sub><sup>-</sup>

**8.6** Ammonium permanganate, NH<sub>4</sub>MnO<sub>4</sub>, is a well-known salt, but ammonium manganate, (NH<sub>4</sub>)<sub>2</sub>MnO<sub>4</sub>, is a rarely known salt.

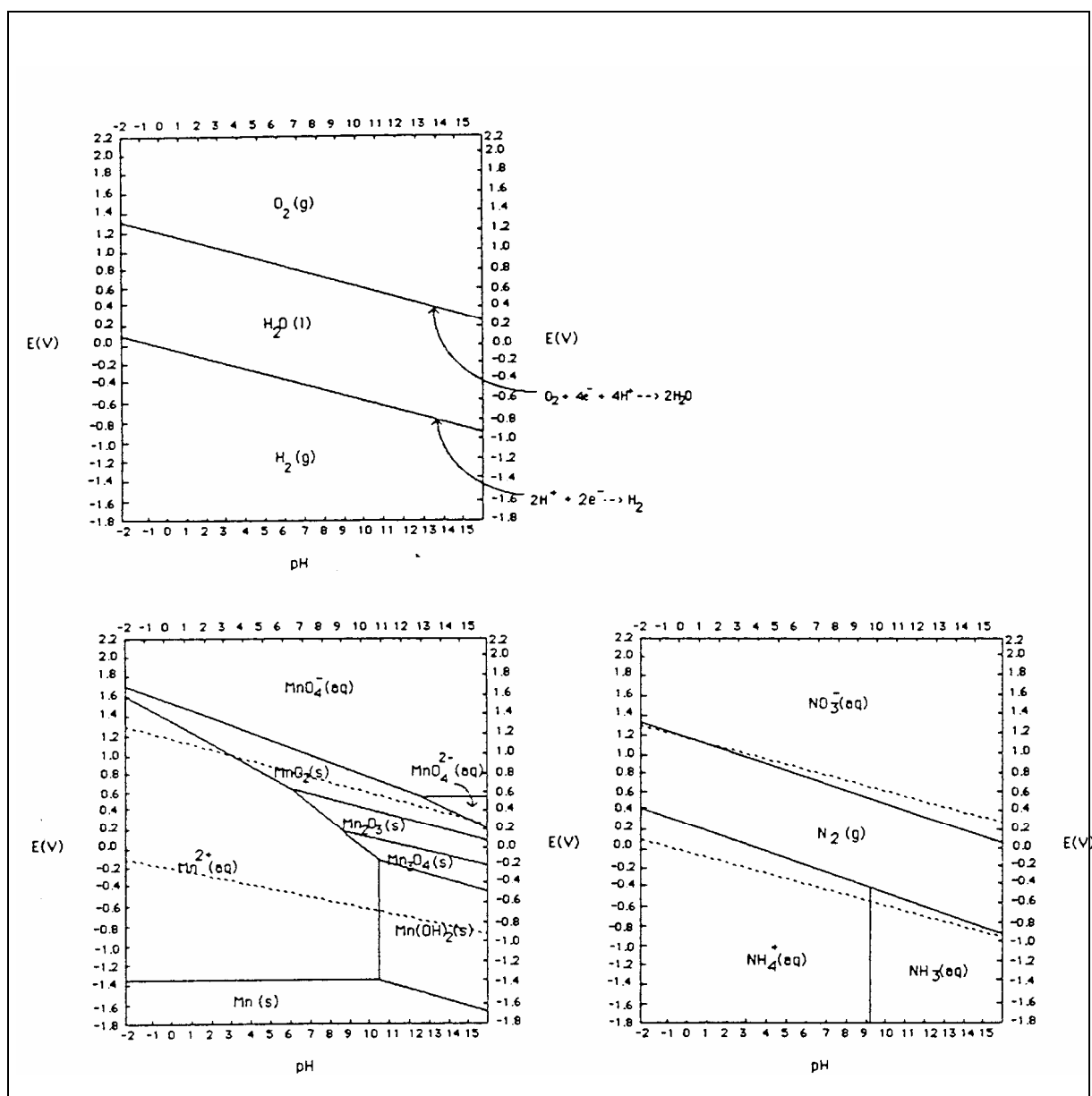
- i) Is NH<sub>4</sub>MnO<sub>4</sub> expected to be thermodynamically stable? (YES or NO)
- ii) Is (NH<sub>4</sub>)<sub>2</sub>MnO<sub>4</sub> expected to be thermodynamically stable? (YES or NO)
- iii) Write and balance an equation for the decomposition of NH<sub>4</sub>MnO<sub>4</sub> to give MnO<sub>2</sub> and N<sub>2</sub>.
- iv) Write and balance an equation for the decomposition of (NH<sub>4</sub>)<sub>2</sub>MnO<sub>4</sub> to give Mn and N<sub>2</sub>.

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  $\text{MnO}_4^-$  to  $\text{MnO}_2$  is 1.692 V. Applying the Nernst equation calculate the reduction potential,  $E$ , for the reduction of 0.00100 M  $\text{MnO}_4^-$  solution at a  $\text{pH} = 4.0$ .

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.

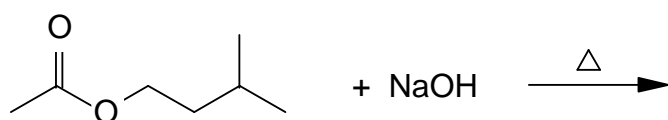
$$8.8 \quad E = E^\circ + \frac{0.0591}{3} \log[MnO_4^-] + \frac{0.0591}{3} \log[H^+]^4 =$$

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

**PROBLEM 9**

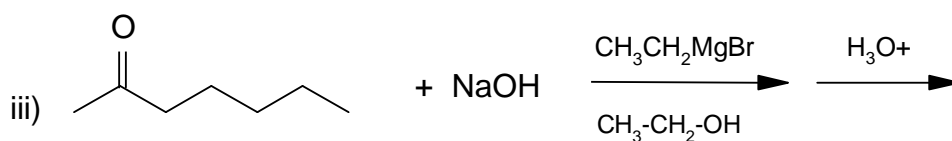
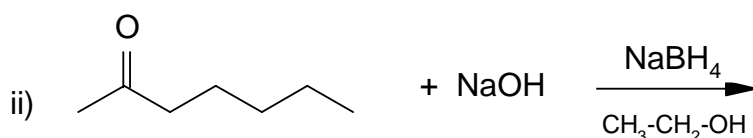
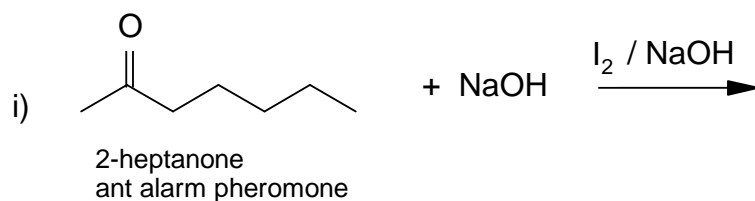
Pheromones are chemicals or mixtures of certain chemicals secreted by insects and some animals for communication. They bring about certain responses in another individual of the same species. In the problem below you will find a number of pheromones undergoing reactions which were used in determining 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

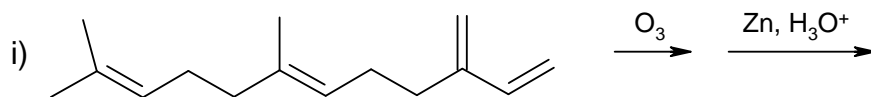


isoamyl acetate,  
bee alarm pheromone

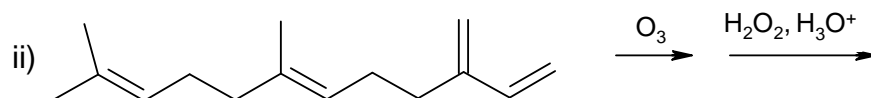
9.2



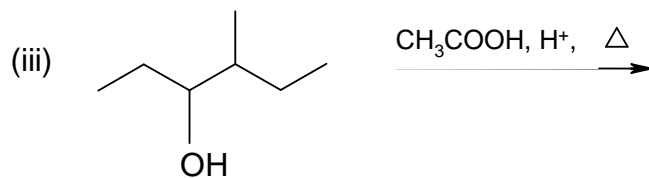
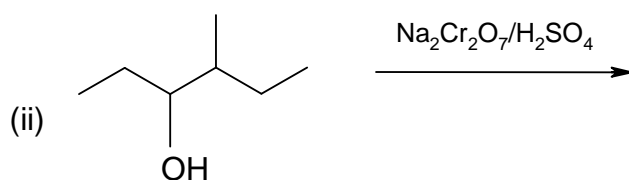
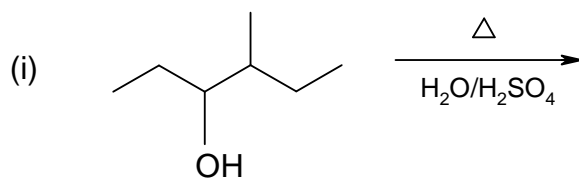
## 9.3



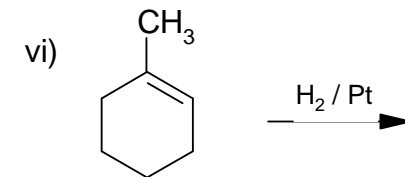
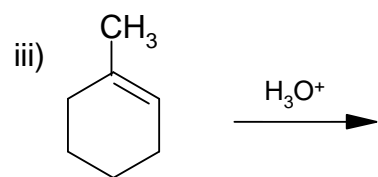
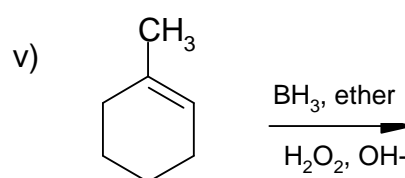
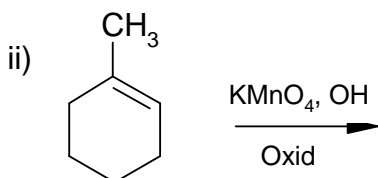
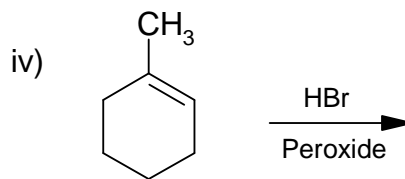
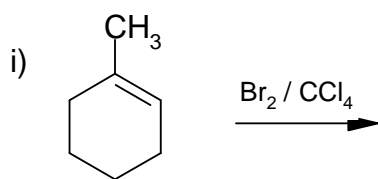
green peach -  
aphid pheromone



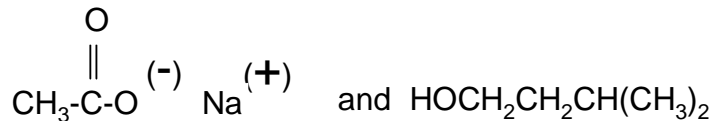
## 9.4



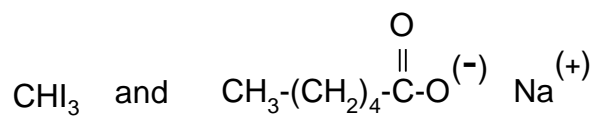
9.5


**SOLUTION**

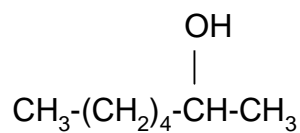
9.1



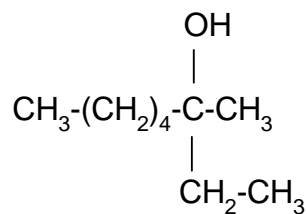
9.2 i)



ii)

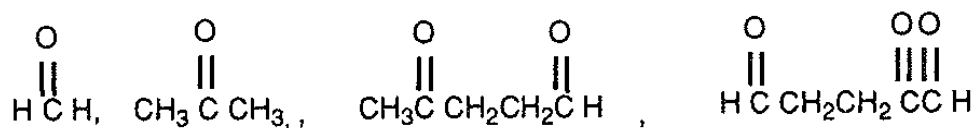


iii)

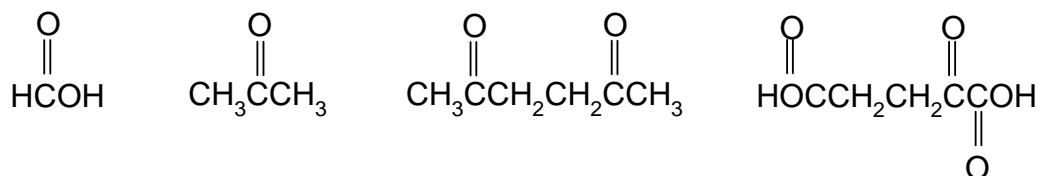




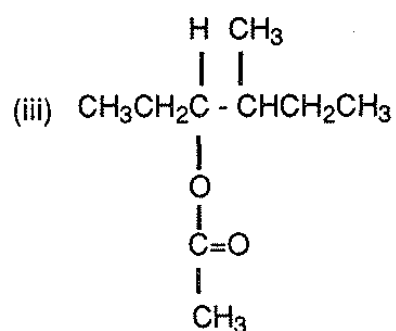
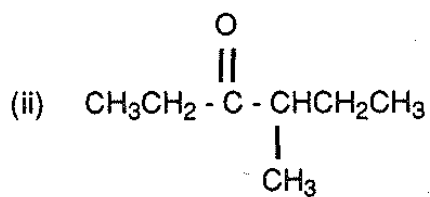
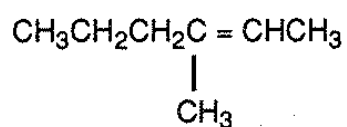
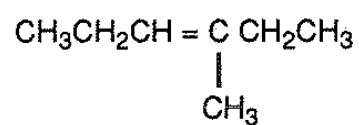
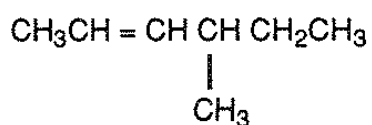
9.3 i)



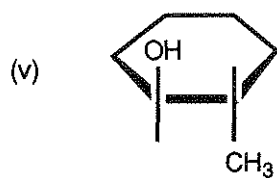
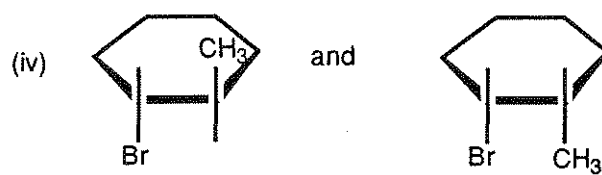
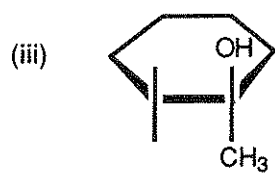
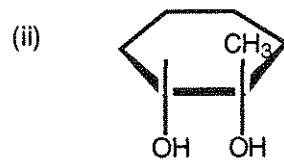
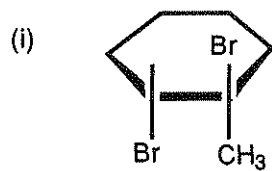
ii)



9.4 i)



## 9.5



**PRACTICAL PROBLEMS****PROBLEM 1 (Practical)**Effects of CO<sub>2</sub> on Solubility

Calcium carbonate is a partially soluble material commonly known as limestone, marble, chalk, or calcite. In the presence of CO<sub>2</sub>-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 aqueous solution saturated with carbon dioxide and in solution free of carbon dioxide. The [Ca<sup>2+</sup>] will be determined by complexometric titration with EDTA (ethylenediamine-tetraacetic acid).

- a) Procedure for the determination of [Ca<sup>2+</sup>]
1. Calibrate your *pH* meter.
  2. Measure and record the *pH* of the sample equilibrated with solid CaCO<sub>3</sub> and CO<sub>2</sub> gas.
  3. Filter all your sample into a second 250 cm<sup>3</sup> plastic bottle to remove any suspended CaCO<sub>3</sub>. 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<sup>3</sup> aliquots of this sample to three Erlenmeyer flasks. Recap the sample bottle after removing each 25 cm<sup>3</sup> aliquot.
  6. Add 15 drops of 6 M HCl to each of the three flasks with stirring. Any CaCO<sub>3</sub> that may have formed should dissolve. Before proceeding with the next step, make sure there is no solid CaCO<sub>3</sub> 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<sup>3</sup> of a *pH* 10 NH<sub>3</sub> buffer. Proceed immediately with steps 8 - 10.
  8. Add 20 drops of 0.001 M Mg<sup>2+</sup>/EDTA<sup>4-</sup> 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 °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<sub>2</sub> being evolved and some CaCO<sub>3</sub> 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<sub>3</sub>.
16. Transfer three 25 cm<sup>3</sup> aliquots of this filtered solution to three Erlenmeyer flasks. Add about 25 cm<sup>3</sup> of deionized water to each flask, followed by 15 drops of 6 M HCl.
17. Titrate each sample according to steps 7 - 11.

b) Procedure for standardization of EDTA

1. Weigh approximately 0.35 g of dried primary standard CaCO<sub>3</sub>, (molar mass 100.09 g mol<sup>-1</sup>) which will be found in the weighing bottle in the desiccator. Note: CaCO<sub>3</sub> is hygroscopic.
2. Add 25 cm<sup>3</sup> of deionized water to the CaCO<sub>3</sub>, then carefully add 5 cm<sup>3</sup> of 6 M HCl. Quickly cover with a watch glass.
3. When the CaCO<sub>3</sub> has dissolved, quantitatively transfer the solution to a 250 cm<sup>3</sup> volumetric flask and dilute to the mark.
4. Transfer three 25 cm<sup>3</sup> aliquots of the standard Ca<sup>2+</sup> 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<sup>-3</sup>) in a solution saturated with both CaCO<sub>3</sub> and CO<sub>2</sub> and in solution free of CO<sub>2</sub>.
- 1.2 List all the ionic species that increase in concentration as a result of the dissolving of CaCO<sub>3</sub> in water.
- 1.3 Given below are brief descriptions of two solutions. Circle the one in which the concentration of CO<sub>3</sub><sup>2-</sup> would be highest:
- a) a solution produced by dissolving CaCO<sub>3</sub>(s) in CO<sub>2</sub>-saturated water
  - b) a solution produced by dissolving CaCO<sub>3</sub>(s) in CO<sub>2</sub>-free water
- 1.4 Will the solubility of CaCO<sub>3</sub> increase or decrease in a solution from which the CO<sub>2</sub> has been removed?
- 

## SOLUTION

- 1.1 The results of the titration (volumes of titrants, mass of CaCO<sub>3</sub>) 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<sub>3</sub> in its saturated solutions containing CO<sub>2</sub> and in those without CO<sub>2</sub>.

The other tasks to be solved:

- 1.2 The ionic species mentioned above are as follows: Ca<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, OH<sup>-</sup>.
- 1.3 Correct answer: (b) A solution produced by dissolving CaCO<sub>3</sub>(s) in CO<sub>2</sub>-free water.
- 1.4 The solubility of CaCO<sub>3</sub> will decrease.
- 
-