## $27^{\text {th }}$



International Chemistry Olympiad

6 theoretical problems
3 practical problems

## THE TWENTY-SEVENTH <br> INTERNATIONAL CHEMISTRY OLYMPIAD 13-20 JULY 1995, BEIJING, CHINA

## THEORETICAL PROBLEMS

## PROBLEM 1

1.1 Excavated Chinese ancient bronze musical instrument, carillon, was covered entirely by rust. Chemical analysis showed that the rust contains $\mathrm{CuCl}, \mathrm{Cu}_{2} \mathrm{O}$ and $\mathrm{Cu}_{2}(\mathrm{OH})_{3} \mathrm{Cl}$. Simulation experiments showed that CuCl was formed first under the action of both air and Cl containing aqueous solution and then $\mathrm{Cu}_{2}(\mathrm{OH})_{3} \mathrm{Cl}$ produced through the following two different ways:


Using the molar standard formation Gibbs free energies of the species concerned answer the following questions:

| Species | $\mathrm{Cu}_{2} \mathrm{O}(\mathrm{s})$ | $\mathrm{CuO}(\mathrm{s})$ | $\mathrm{CuCl}(\mathrm{s})$ | $\mathrm{Cu}_{2}(\mathbf{O H})_{3} \mathrm{Cl}(\mathrm{s})$ | $\mathrm{Cl}(\mathrm{aq})$ | $\mathrm{OH}(\mathrm{aq})$ | $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\Delta_{\mathrm{f}} \mathrm{G}^{0}(298 \mathrm{~K})$ <br> $\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$ | -146 | -130 | -120 | -1338 | -131 | -157 | -237 |

i) Write balanced equations for reactions (a), (b) and (c).
ii) Calculate the molar standard Gibbs free energy $\Delta_{\mathrm{f}} G^{0}(298 \mathrm{~K})$ for reactions (a), (b) and (c).
iii) Decide the spontaneous direction of reaction (a) in air through calculation, when $T=298 \mathrm{~K}, c(\mathrm{HCl})=1.0 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}$.
1.2 Rate constants $k_{\mathrm{c}}$ for reaction (c) were measured at various temperatures in a simulation experiment in order to obtain its kinetic parameters. On the basis of the data given below answer the following questions:

$$
\begin{array}{ccc}
t{ }^{\circ} \mathrm{C} & 25 & 40 \\
k_{\mathrm{c}} / \mathrm{mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1} & 1.29 \times 10^{-4} & 2.50 \times 10^{-4}
\end{array}
$$

i) Write the equation for calculating the activation energy of reaction (c) and fínd the value.
ii) Assign the overall reaction order of reaction (c).
iii) Knowing that the rate determining step of reaction (c) is the monolayer adsorption of $\mathrm{O}_{2}(\mathrm{~g})$ on solid CuCl , write the overall rate equation of this heterogeneous reaction (c). Under what condition might the reaction order be the same as that you have given in ii)? Assume only $\mathrm{O}_{2}$ can be adsorbed.
1.3 A copper plate was divided into two parts, $\mathrm{Cu}(1)$ and $\mathrm{Cu}(2) . \mathrm{Cu}(1)$ was then hammered so that $\mathrm{Cu}(1)$ and $\mathrm{Cu}(2)$ are different in certain thermodynamic properties.
i) An galvanic cell with $\mathrm{Cu}(1)$ and $\mathrm{Cu}(2)$ was designed as $\mathrm{Cu}(1) \mathrm{ICuSO}_{4}(\mathrm{aq}) \mathrm{ICu}(2)$ and the electromotive force $E$ of the above cell was expressed as $E=\Phi_{R}-\Phi_{L}$, where $\Phi_{\mathrm{R}}$ and $\Phi_{\mathrm{L}}$ being the right and left electrode potentials (i. e. half-cell potentials), respectively. Please choose the correct $E$ value from the following and give the thermodynamic reason for your choice.
(A) $E<0$
(B) $E=0$
(C ) $E>0$
(D) It cannot be decided
ii) Write the net cell reaction for the cell.
1.4 In a Cu-Zn alloy the molar fractions of Cu and Zn are 0.750 and 0.250 , respectively. The structure type of the alloy is the same as that of pure copper, except Zn atoms substitute some Cu atoms randomly and statistically, i. e. at every atomic position, the probability of the occupation of Cu and Zn is proportional to the composition of the alloy. In this sense the alloy can be considered as composed of statistical atoms $\mathrm{Cu}_{\mathrm{x}} \mathrm{Zn}_{1-\mathrm{x}}$. X-ray analysis shows that the arrangement of atoms in the alloy is of the cubic face-centred close packing type. Density of the alloy $d=8.51 \mathrm{~g} \mathrm{~cm}^{-3}$. Calculate the radius of the statistical atoms in the alloy.
Given: $\quad A_{r}(\mathrm{Cu})=63.5, \quad A_{r}(\mathrm{Zn})=65.4$.

## SOLUTION

1.1 i)
a) $2 \mathrm{CuCl}(\mathrm{s})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow \mathrm{Cu}_{2} \mathrm{O}(\mathrm{s})+2 \mathrm{H}^{+}(\mathrm{aq})+2 \mathrm{Cl}^{-}(\mathrm{aq})$
b) $\mathrm{Cu}_{2} \mathrm{O}(\mathrm{s})+1 / 2 \mathrm{O}_{2}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I})+\mathrm{H}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq}) \rightarrow \mathrm{Cu}_{2}(\mathrm{OH})_{3} \mathrm{Cl}(\mathrm{s})$
c) $2 \mathrm{CuCl}(\mathrm{s})+1 / 2 \mathrm{O}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{Cu}_{2}(\mathrm{OH})_{3} \mathrm{Cl}(\mathrm{s})+\mathrm{H}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq})$
ii) a) $\Delta G^{0}=69 \mathrm{~kJ} \mathrm{~mol}^{-1}$
b) $\Delta G^{0}=-824 \mathrm{~kJ} \mathrm{~mol}^{-1}$
c) $\Delta G^{0}=-755 \mathrm{~kJ} \mathrm{~mol}^{-1}$
iii) Calculation (dilute HCl solution can be considered as an ideal solution)
$\Delta_{r} G=\Delta_{r} G^{0}+2 R T \ln \left[\mathrm{H}^{+}\right]\left[\mathrm{Cl}^{-}\right]=-22.3 \mathrm{~kJ} \mathrm{~mol}^{-1}<0$
Spontaneous: to the right
1.2 i) Formula: $\ln \frac{k_{c}\left(T_{2}\right)}{k_{c}\left(T_{1}\right)}=\frac{E_{a}}{R}\left(\frac{1}{T_{1}}-\frac{1}{T_{2}}\right)$

$$
E_{a}=34.2 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

ii) overall reaction order $=0$
when $\mathrm{b} p\left(\mathrm{O}_{2}\right) \gg 1$
$r=k_{c} \theta=\frac{k_{c} b p\left(O_{2}\right)}{1+b p\left(O_{2}\right)} ; r=k_{c} \quad z e r o$ order
1.3 i) (C) $E>0$
ii) Net cell reaction: $\mathrm{Cu}(1)=\mathrm{Cu}(2)$

Thermodynamic reason for choosing $3(C)$ is $\Delta_{r} G<0, \Delta_{r} G=-n F E$ and $E>0$
$1.4 r=1.30 \times 10^{-10}$
formula: $a=2 \sqrt{2 r}$
$d=\frac{4(63.5 \times 0.75+65.4 \times 0.25) \times 10^{-3}}{a^{3} N_{A}}=8.51 \times 10^{-3} \mathrm{~kg} \mathrm{~m}^{-3}$
$r^{3}=2.209 \times 10^{-30} \mathrm{~m}^{3}$
$r=1.30 \times 10^{-10} \mathrm{~m}$

## PROBLEM 2

To control the quality of milk serum, a dairy by-product, the concentration of $\mathrm{NO}_{3}^{-}$ion in serum is monitored by means of an ion selective electrode. Generally there is about 15 $\mathrm{mg} \mathrm{NO}_{3}^{-}$ion per litre in serum, measured on the basis of nitrogen mass.
2.1 For a nitrate ion selective electrode a calibration curve as shown below was obtained using a series of standard nitrate solutions containing $0.5 \mathrm{~mol} \mathrm{dm}{ }^{-3} \mathrm{~K}_{2} \mathrm{SO}_{4}$, $1.0 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{H}_{2} \mathrm{SO}_{4}$ and $2.6 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{Cl}^{-}$ion as the background. Decide whether it is feasible to measure concentration $\mathrm{NO}_{3}^{-}$in serum under the above conditions.

2.2 Given are selective coefficients of $\mathrm{Cl}^{-}, \mathrm{SO}_{4}^{2-}$ and $\mathrm{ClO}_{4}^{-}$versus $\mathrm{NO}_{3}^{-}$as follow
$K_{\mathrm{NO}_{3}^{-}, \mathrm{Cr}}=\frac{C_{\mathrm{NO}_{3}}}{C_{\mathrm{Cr}}}=4.9 \times 10^{-2} \quad K_{\mathrm{NO}_{3}^{-}, \mathrm{SO}_{4}^{2}}=\frac{c_{\mathrm{NO}_{3}}}{C_{\mathrm{SO}_{4}^{1 / 2}}}=4.1 \times 10^{-3}$
$K_{\mathrm{NO}_{3}, \mathrm{ClO}_{4}^{-}}=\frac{C_{\mathrm{NO}_{3}^{-}}}{C_{\mathrm{ClO}_{4}^{-}}}=1.0 \times 10^{-3}$
where the units of the concentrations are in $\mathrm{mol} \mathrm{dm}^{-3}$ which is the best to reduce the interference of $\mathrm{Cl}^{-}$to $\mathrm{NO}_{3}^{-}$determination, so as to control the error in the $\mathrm{NO}_{3}^{-}$ concentration within $1 \%$, when there are $1.40 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NO}_{3}^{-}$and $1.60 \times 10^{-2} \mathrm{~mol}$ $\mathrm{dm}^{-3} \mathrm{Cl}^{-}$in serum:
(a) $\mathrm{AgNO}_{3}$
(b) $\mathrm{Ag}_{2} \mathrm{SO}_{4}$
(c) $\mathrm{AgClO}_{4}$

Calculate the amount of the salt that should be added to $1 \mathrm{dm}^{3}$ of the sample solution to be measured.
2.3 The $\mathrm{NO}_{3}^{-}$ion concentration was determined by this method at 298 K . For $25.00 \mathrm{~cm}^{3}$ sample solution the electronic potential, $E$, is measured to be -160 mV . After adding $1.00 \mathrm{~cm}^{3} 1.00 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NO}_{3}^{-}$standard solution to the above solution, $\boldsymbol{E}$ changes to -130 mV . Find the $\mathrm{pNO}_{3}$ of the serum.
2.4 The selective coefficient of $\mathrm{CH}_{3} \mathrm{COO}^{-}$versus $\mathrm{NO}_{3}^{-} K\left(\mathrm{NO}_{3}^{-} / \mathrm{CH}_{3} \mathrm{COO}^{-}\right)=2.7 \times 10^{-3}$. If $\mathrm{AgCH}_{3} \mathrm{COO}$ instead of $\mathrm{Ag}_{2} \mathrm{SO}_{4}$ is added to the sample solution of question 2.2, find the upper limit of the pH value below which the same requirement in question 2.2 can be met.
$K_{\text {sp }}(\mathrm{AgCl})=3.2 \times 10^{-10} K_{\text {sp }}\left(\mathrm{Ag}_{2} \mathrm{SO}_{4}\right)=8.0 \times 10^{-5}$
$K_{\text {sp }}\left(\mathrm{AgCH}_{3} \mathrm{COO}\right)=8.0 \times 10^{-3} \quad K_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=2.2 \times 10^{-5}$
$A_{r}(\mathrm{~N})=14.00$

## SOLUTION

### 2.1 Yes

2.2 B
$\left(1.4 \times 10^{-3} \times 0.01\right) /[\mathrm{Cl}]=4.9 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}$
$\left[\mathrm{Cl}^{-}\right]=2.9 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}$
Excess $[\mathrm{CI}]=1.6 \times 10^{-2}-2.9 \times 10^{-3} \cong 1.6 \times 10^{-2} \mathrm{~mol} \mathrm{dm}^{-3}$
To reduce the interference of $\mathrm{Cl}^{-}$at least $1.6 \times 10^{-2} \mathrm{~mol} \mathrm{Ag}$ ion or $8.0 \times 10^{-3} \mathrm{~mol}$ $\mathrm{Ag}_{2} \mathrm{SO}_{4}$ has to be added to $1 \mathrm{dm}^{3}$ sample solution.
$2.3 \Delta E=E_{2}-E_{1}=0.059 \log \left\{\left(c_{x} V_{x}+c_{S} V_{S}\right)\left(c_{x}\left[V_{x}+V_{s}\right]\right)\right\}$
$0.03=0.059 \log \left[\left(25.00 V_{x}+0.10\right) /\left(26.00 \times c_{x}\right)\right]$
$c_{x}=1.7 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3}$
$p \mathrm{NO}_{3}=2.77$
$2.4 \mathrm{pH}=4.4$
$\left(1.4 \times 10^{-3} \times x\right) \div 1.6 \times 10^{-2}=2.7 \times 10^{-3}$
$x=3.1 \%>1 \%$
$\left(1.4 \times 10^{-3} \times 0.01\right) \div\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]=2.7 \times 10^{-3}$
$\left[\mathrm{CH}_{3} \mathrm{COO}\right]=5.2 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3}$
$1.6 \times 10^{-2}-5.2 \times 10^{-3}=1.08 \times 10^{-2} \mathrm{~mol} \mathrm{dm}^{-3}$
$\left\{\left[\mathrm{H}^{+}\right] \times 5.2 \times 10^{-3}\right\} \div\left(1.08 \times 10^{-2}\right)=2.2 \times 10^{-5}$
$\left[\mathrm{H}^{+}\right]=4.3 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}$
$p H=4.4$

## PROBLEM 3

1,3-Dihydroxyacetone can be converted to glyceraldehyde. On standing this glyceraldehyde changes spontaneously into a six member cyclic dimer $\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}$. The infrared spectrum of the dimer shows no absorption peak between $1600-1800 \mathrm{~cm}^{-1}$ and the dipole moment of the dimer is determined to be zero.
3.1 Write the Fischer projection structural formula(e) for the resulting glyceraldehyde and indicate configuration using $\mathrm{D}(+)$ and/or $\mathrm{L}(-)$.
3.2 Write the structural formula for the reaction intermediate of the conversion of 1,3dihydroxyacetone to glyceraldehyde.
3.3 Write the structural formula for the dimer.
3.4 Using Haworth projection formula represent the possible stereoisomers which fit the dipole moment data.
3.5 Denote each chiral carbon atom in the above formulae with $R$ or $S$.

## SOLUTION

## 3.1



$\mathrm{D}(+)$
$\mathrm{L}(-)$

## 3.2


3.3

3.4



## 3.5




## PROBLEM 4

Poly[(R)-3-hydroxyalkanoic acids], PHAs, are synthesized by a variety of bacteria and function as intracellular carbon and energy storage materials. These polymers are also biodegradable in environments, such as soil, anaerobic sewage and sea water. The inherent biologically mediated environmental degradability, useful physical properties, slow hydrolytic degradation and other favourable properties make bacterial polyesters exciting materials for both disposable biodegradable plastics (good for a clean environment) and special medical products.
4.1 PHB, Poly(3-hydroxybutanoic acid), produced by bacteria contains only (R)-HB repeating units, while that synthesized by polymer chemists may contain only (R)-HB or only (S)-HB or both (R)-and (S)-HB in an alternating manner or both but in random distributions. Sketch chain structures of the atactic PHB, syndiotactic PHB and isotactic PHBs and denote each chiral carbon with $(R)$ or $(S)$. Five monomeric units are enough for each chain.
\{Note: In "PHB", P means "poly" or "polymer of, HB represents the monomeric units contained in poly(3-hydroxybutanoic acid) molecules.)
4.2 Suggest two types of monomers that could be used for polymer chemists to synthesize a PHB, regardless of the stereochemistry of the products.
4.3 Poly[(R)-3-hydroxybutanoic acid] can be synthesized by feeding the bacteria (such as Alcaligenes Eutrophus) with sodium acetate in a nitrogen-free media. It is believed that the key steps for the conversion of acetate to PHB are the activation of acetate molecules by coenzyme $A$ and the subsequent formation of the coenzyme $A$ activated acetoacetate, which is then reduced by a reductase to form coenzyme A activated monomer 3-hydroxybutyrate. Polymerization of the monomer is achieved by a polymerase which would build the polymer molecules with unique stereospecificity. Sketch these steps with structural formulae. For coenzyme A the conventional abbreviation, $-\mathrm{S}-\mathrm{CoA}$ (-CoA is as good), should be used in the sketch.
4.4 If sodium propanoate is used (as the sole carbon source) in the feeding media instead of sodium acetate, the principal product will be a copolymer of 3hydroxybutanoic acid and 3-hydroxypentanoic acid with the following generalized structure:


Rationalize the result.
(Note: Two different monomers are needed for the formation of the copolymer. The letters m and n in the structural formula are numbers of the units and have nothing to do with the answer, in other words, you may leave them out in your answer.)

## SOLUTION

## 4.1


(S)
(S)
(R)
(S)
(R)

Other arrangements with $(R)$ and $(S)$ randomly distributed along the chain are correct, e.g. RSRRS, SRSSR, RRSRS, etc.

Syndiotactic PHB: This polymer has $(R)$ and $(S)$ units positioned along the chain in an alternating manner: RSRSR (or SRSRS).

Isotactic PHB: All the chiral centres have the same configuration. There are 2 types of the isotactic PHBs: SSSSS and RRRRR.
4.2 Monomer 1 :


3-hydroxybutanoic acid

Monomer 2:


## 4.3




## 4.4



(Coenzyme A activated monomer 3-hydroxypentanoic acid)

This monomer may also be written in the following way:


Polymerization of these two monomers will result in the desired copolymer:



## PROBLEM 5

The action of nitric oxide upon human body is dual. The nitric oxide generated in nerve cells will damage the cells, while the nitric oxide generated in endothelial cells of blood vessels can relax the vessels and control blood pressure.
5.1 Indicate the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of NO molecule using one of symbols $\pi, \sigma, \pi^{*}$ or $\sigma^{*}$, and indicate the electron(s) residing in the corresponding orbital using symbols $\uparrow$ and/or $\downarrow$.
5.2 The relaxation of blood vessels is caused by a series of changes which are mediated by the coordination of NO molecule to iron ion, the latter being a component of an enzyme containing heme. It was known that the coordinated NO behaves as CO molecule (isoelectronic), which one of the following species really exists in the iron complex?
a) NO
b) $\mathrm{NO}^{+}$
c) $\mathrm{NO}^{-}$
5.3 The cell damage is caused by free radical OH , which is one of the product of reaction between $\mathrm{O}_{2}^{-}$and NO :
$\mathrm{O}_{2}^{-}+\mathrm{NO}+\mathrm{H}^{+} \rightarrow \mathrm{HOONO} \rightarrow \bullet \mathrm{NO}_{2}+\bullet \mathrm{OH}$
in which an intermediate with composition of HOONO is evolved. HOONO is a weak acid. Choose the structural formula with correct bond angles for the intermediate.

5.4 For preservation of meat, sodium nitrite is usually added and as a result NO is, then, formed. Consequently, NO reacts with the sulphur and iron atoms from decomposition of proteins, forming $\left[\mathrm{Fe}_{4} \mathrm{~S}_{3}(\mathrm{NO})_{7}\right]^{-}$. The complex anion is bacteriostatic and antiseptic. X-ray crystallography shows that the complex anion has a structure as shown below:

i) Blacken all the circles corresponding to iron atoms and add symbols $\mathrm{Fe}(\mathrm{A})$, $\mathrm{Fe}(\mathrm{B}), \mathrm{Fe}(\mathrm{C})$ and $\mathrm{Fe}(\mathrm{D})$ beside the circles in the sequence of top $\rightarrow$ left $\rightarrow$ right.
ii) The configuration of 3d electron shell of the iron atoms has been studied with modern structural analysis. Knowing that the mean oxidation number of the four iron atoms is -0.5 , give their configurations of 3 d shell, respectively. Assume that each iron atom adopt sp hybridization.
$5.5\left[\mathrm{Fe}_{4} \mathrm{~S}_{3}(\mathrm{NO})_{7}\right]^{-}$anion can be reduced and a new complex $\left[\mathrm{Fe}_{2} \mathrm{~S}_{2}(\mathrm{NO})_{4}\right]^{2-}$ is formed which contains a cyclic structure unit of $\mathrm{Fe}_{2} \mathrm{~S}_{2}$.
i) Write the structural formula for the anion $\left[\mathrm{Fe}_{2} \mathrm{~S}_{2}(\mathrm{NO})_{4}\right]^{2-}$.
ii) Give the oxidation state of each iron atom with Arabic numerals.
iii) $\left[\mathrm{Fe}_{2} \mathrm{~S}_{2}(\mathrm{NO})_{4}\right]^{2-}$ can be converted into $\left[\mathrm{Fe}_{2}\left(\mathrm{SCH}_{3}\right)_{2}(\mathrm{NO})_{4}\right]^{n}$, a carcinogen. Which of the following three species is added to $\left[\mathrm{Fe}_{2} \mathrm{~S}_{2}(\mathrm{NO})_{4}\right]^{2-}: \mathrm{CH}_{3}{ }^{+}$, $-\mathrm{CH}_{3}$ or $\mathrm{CH}_{3}^{-}$? Assign the value of n .

## SOLUTION

1. The HOMO of NO molecule is $\pi^{*}$, its electron arrangement $\uparrow$; The LUMO of NO molecule is $\pi^{*}$.
2. (b)
3. B
4. 


$\mathrm{Fe}(\mathrm{A})$ has $3 \mathrm{~d}^{7}$ configuration;
$\mathrm{Fe}(\mathrm{B}), \mathrm{Fe}(\mathrm{C})$, and $\mathrm{F}(\mathrm{D})$ have $3 d^{9}$ configuration.
5. i)

ii) $\mathrm{Fe}(-1) \quad \mathrm{Fe}(-1)$
iii) The species added to S atom is $\mathrm{CH}_{3}^{+} ; \mathrm{n}=0$.

## PROBLEM 6

A surfactant molecule can generally be modelled as Fig. 1 where a circle presents the polar head (PH), i.e. the hydrophilic part of the molecule, and a rectangle represents the non-polar tail (NT), i. e. the hydrophobic part of the molecule.


Fig. 1
6.1 AOT is a surfactant. Its systematic name (IUPAC name) is sulfobutanedioic acid 1,4-bis-(2-ethylhexyl) ester sodium salt (formula $\mathrm{C}_{20} \mathrm{H}_{37} \mathrm{NaO}_{7} \mathrm{~S}$ ).
i) Write the structural formula for AOT and fill its PH and NT in the circle and rectangle on your answer sheet.
ii) Choose the type of surfactant AOT among the following.
a) Non-ionic;
b) Anionic;
c) Cationic;
d) Others.
6.2 Mixing an aqueous solution of 50 mmol AOT with isooctane (volume ratio $1: 1$ ), a micellar extraction system will be formed in the isooctane phase (organic phase).
i) Using the model as shown in Fig. 1, draw a micelle with 10 AOT molecules under the given condition.
ii) What species are in the inner cavity of this micelle? Write their chemical formulas.
6.3 There is an aqueous solution containing the proteins as listed below:

| Protein | Molecular mass $\left(M_{r}\right) \times 10^{4}$ | Isoelectronic point (PI) |
| :---: | :---: | :---: |
| A | 1.45 | 11.1 |
| B | 1.37 | 7.8 |
| C | 6.45 | 4.9 |
| D | 6.80 | 4.9 |
| E | 2.40 | 4.7 |
| F | 2.38 | 0.5 |

The separation of proteins can be performed by mixing the AOT micellar extraction system with the solution. Adjusting the pH value of the solution to 4.5 , only three of the above listed six proteins can be extracted into the micelles. Which proteins will be extracted?
6.4 The three proteins entered into the micelles will be separated from each other by the following procedure shown as in Fig. 2. Each extracted protein can be sequentially transported into a respective water phase.


Fig. 2
Note: (w) represents water phase; (o) represents organic phase

Fill the three extracted proteins in the left boxes first and then separate them by the procedure given, and give the separation conditions above each arrow as well.

## SOLUTION

6.1 i)

ii) (b)

## 6.2 i)



### 6.3 A, B, and E.

## 6.4



## PRACTICAL PROBLEMS

## PROBLEM 1 (Practical)

## Identification of Unknown Solutions

You are supplied with five different solutions contained in five test tubes labelled as $A, B, C, D$ and $E$, respectively. The solution in each test tube contains one of the following compounds:
$\begin{array}{lllllll}\mathrm{NH}_{4} \mathrm{Cl} & \left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4} & \mathrm{NaNO}_{3} & \mathrm{MgCl}_{2} & \mathrm{Na}_{2} \mathrm{SO}_{4}\end{array}$
Identify these solutions.

## Reagents

| $\mathrm{H}_{2} \mathrm{SO}_{4}$ (conc.) | $\mathrm{H}_{2} \mathrm{SO}_{4}\left(6 \mathrm{~mol} \mathrm{dm}{ }^{-3}\right)$ |
| :---: | :---: |
| $\mathrm{HNO}_{3}$ (conc.) | $\mathrm{HNO}_{3}\left(6 \mathrm{~mol} \mathrm{dm}{ }^{-3}\right)$ |
| HCl (conc.) | $\mathrm{HCl}\left(6 \mathrm{~mol} \mathrm{dm}{ }^{-3}\right)$ |
| $\mathrm{Ba}(\mathrm{OH})_{2}$ (satd.) | $\mathrm{NaOH}\left(6 \mathrm{~mol} \mathrm{dm}{ }^{-3}\right)$ |
| $\mathrm{BaCl}_{2}\left(0.5 \mathrm{~mol} \mathrm{dm}{ }^{-3}\right)$ | $\mathrm{Ba}\left(\mathrm{NO}_{3}\right)_{2}\left(0.5 \mathrm{~mol} \mathrm{dm}{ }^{-3}\right)$ |

## NOTES:

(1) You can only select the provided reagents and use a procedure as simple as possible to complete your task. You are getting a mark not only according to the correct identification, but also to the number of steps you have taken.
(2) You have to carry out the whole analysis by using the provided amount of these unknown solutions. Supplement of them will be available, but it will reduce the mark you obtain.

## PROBLEM 2 (Practical)

## Preparation of cis-Copper-bis-Glycinate Hydrate [Cu(gly) $\mathbf{2}^{2} \times \mathrm{XH}_{2} \mathrm{O}$ ]

Copper(II) amino acidate coordination compounds are monometric units for synthesizing important biopolymers such as metalloenzymes like ceruloplasmin, on which every living organism depends. In laboratory cis-copper-bis-glycinate hydrate can be produced by the reaction of cupric hydroxide with glycine at a temperature of ca. $70{ }^{\circ} \mathrm{C}$.

## Reagents:

$\mathrm{CuSO}_{4} \cdot 5 \mathrm{H}_{2} \mathrm{O}(\mathrm{s})$
$\mathrm{NH}_{3}(\mathrm{aq})\left(3 \mathrm{~mol} \mathrm{dm}^{-3}\right)$
glycine(s)
95\% ethanol,
acetone
$\mathrm{NaOH}\left(2 \mathrm{~mol} \mathrm{dm}^{-3}\right)$
$\mathrm{BaCl}_{2}\left(0.5 \mathrm{~mol} \mathrm{dm}^{-3}\right)$

## 1. Preparation of $\mathrm{Cu}(\mathrm{OH})_{2}$

Procedure:
(1) Dissolve your pre-weighted sample of $\mathrm{CuSO}_{4} \cdot 5 \mathrm{H}_{2} \mathrm{O}(6.0 \mathrm{~g})$ in $40 \mathrm{~cm}^{3}$ of water with a $250 \mathrm{~cm}^{3}$ beaker as a container.
(2) Add slowly $3 \mathrm{~mol} \mathrm{dm}^{-3}$ ammonia solution to the $\mathrm{CuSO}_{4}$ solution, gently stirring, until the precipitate is completely dissolved and the solution is turning blue-violet.
(3) Add $2 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NaOH}$ solution to the above solution until no more precipitate formed.
(4) Filter the precipitate over a Büchner funnel under reduced pressure. Wash the precipitate with water until no $\mathrm{SO}_{4}^{2-}$ ion is detected in the filtrate.
(5) Collect $\mathrm{Cu}(\mathrm{OH})_{2}$ for the preparation of $\mathrm{Cu}(\mathrm{gly})_{2} . \mathrm{x}_{2} \mathrm{O}$.

Write the equations for the main chemical reactions having taken place in the above procedure.

## 2. Preparation of cis-Copper-bis-Glycinate Hydrate

Procedure:
(1) Dissolve a pre-weighted sample of glycine $(3.6 \mathrm{~g})$ in $130 \mathrm{~cm}^{3}$ of water and then warm the solution in a hot water bath $\left(70^{\circ} \mathrm{C}\right)$. Add the $\mathrm{Cu}(\mathrm{OH})_{2}$ to the solution, stir gently until the precipitate is dissolved. Perform a hot filtration and add $10 \mathrm{~cm}^{3}$ of $95 \%$ ethanol.
(2) Cool the solution and when needle-like crystals appear, place it in the ice water bath for 10 min .
(3) Filter the crystals over a Büchner funnel under reduced pressure, wash once with 10 $\mathrm{cm}^{3}$ of ethanol-water mixing solvent and then twice with $10 \mathrm{~cm}^{3}$ acetone, squeeze the crystals as dry as possible on the funnel.
(4) Collect the crystals to a watch glass and dry it (consult your supervisor).
(5) Half an hour later weigh the product. Write the mass of product and the percentage of yield on your student's report. Give the expressions for calculation to show how you calculate.

## SOLUTION

The following values were required to be written on the Answer Sheet :

- Mass of the product.
- The calculated theoretical yield ing.
- The yield obtained as a percentage of the theoretical yield.


## Tasks:

Write down the balanced chemical equations used in the preparation:
Solution of the tasks:

1. $\mathrm{Cu}^{2+}+2 \mathrm{NH}_{3}+2 \mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{Cu}(\mathrm{OH})_{2}+2 \mathrm{NH}_{4}^{+}$

$$
\mathrm{Cu}(\mathrm{OH})_{2}+4 \mathrm{NH}_{3} \rightarrow\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}+2 \mathrm{OH}^{-}
$$

2. $\mathrm{Cu}(\mathrm{OH})_{2}+2 \mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{COOH} \rightarrow \mathrm{Cu}\left(\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{COO}^{-}\right)_{2}+2 \mathrm{H}_{2} \mathrm{O}$

## PROBLEM 3 (Practical)

## Determination of Copper(II) Content in $\mathrm{Cu}(\mathrm{gly})_{2} . \mathrm{x} \mathrm{H}_{2} \mathrm{O}$

The $\mathrm{Cu}(\mathrm{II})$ content in $\mathrm{Cu}(\mathrm{gly})_{2} . x \mathrm{H}_{2} \mathrm{O}$ crystals prepared yourself can be determined by iodometry with starch solution as indicator. Based on the data obtained one can calculate
the moles of hydrate in $\mathrm{Cu}(\mathrm{gly})_{2} . x \mathrm{H}_{2} \mathrm{O}$.

Reagents:
Standard $\mathrm{KIO}_{3}$ (see the label on the bottle to get the accurate concentration)
$\mathrm{H}_{2} \mathrm{SO}_{4}\left(1.0 \mathrm{~mol} \mathrm{dm}^{-3}\right)$ as indicator.
$\mathrm{KI}\left(0.6 \mathrm{~mol} \mathrm{dm}^{-3}\right)$
KSCN ( $2 \mathrm{~mol} \mathrm{dm}^{-3}$ )
Starch (0.5 \%)
$\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ (to be standardized)

## 1. Standardization of $\mathrm{Na}_{2} \underline{S}_{2} \underline{O}_{3} \underline{\text { solution }}$

Procedure
(1) Transfer $25.00 \mathrm{~cm}^{3}$ of standard $\mathrm{KIO}_{3}$ solution to an Erlenmeyer flask.
(2) Add $5 \mathrm{~cm}^{3}$ of water, $10 \mathrm{~cm}^{3}$ of KI solution and $5 \mathrm{~cm}^{3}$ of $\mathrm{H}_{2} \mathrm{SO}_{4}\left(1.0 \mathrm{~mol} \mathrm{dm}{ }^{-3}\right)$ to the flask.
(3) Titrate immediately with $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ solution.
(4) Add $2 \mathrm{~cm}^{3}$ starch solution when the colour of the titrand turns pale yellow.
(5) Continue titrating until the blue colour of the solution disappears.
(6) Proceed with step (1) - (5) twice parallel.
2. Determination of $\mathrm{Cu}(\mathrm{II})$ content in $\mathrm{Cu}(\mathrm{g} / \mathrm{y})_{2} \mathrm{XH}_{2} \mathrm{X}_{2} \mathrm{O}$
(1) Weigh $1.0-1.2 \mathrm{~g}$ (precision of $\pm 0.0002 \mathrm{~g}$ ) of $\mathrm{Cu}(\mathrm{gly})_{2} . x \mathrm{H}_{2} \mathrm{O}$ with a dry $100 \mathrm{~cm}^{3}$ beaker as the container.
(2) Dissolve it with $40 \mathrm{~cm}^{3}$ of water and $8 \mathrm{~cm}^{3}$ of $\mathrm{H}_{2} \mathrm{SO}_{4}\left(1.0 \mathrm{~mol} \mathrm{dm}^{-3}\right)$.
(3) Transfer the above solution quantitatively to a $100 \mathrm{~cm}^{3}$ volumetric flask and dilute to the mark.
(4) Transfer $25.00 \mathrm{~cm}^{3}$ of the $\mathrm{Cu}(\mathrm{II})$ solution to an Erlenmeyer flask, add $50 \mathrm{~cm}^{3}$ of water and $10 \mathrm{~cm}^{3}$ of KI solution to the flask.
(5) Titrate immediately with standardized $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ solution.
(6) Add $2 \mathrm{~cm}^{3}$ of starch solution and $3 \mathrm{~cm}^{3}$ of KSCN solution to the flask when the colour of the titrand turns from brown to pale yellow.
(7) Titrate continuously until the blue colour of the solution disappears.
(8) Proceed with steps (4) - (7) twice parallel.

## SOLUTION

The following values were required to be written on the Answer Sheet :
Part 1

- Volumes of $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ solution
- Calculation of the concentration of $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ solution.


## Part 2

- Mass of the product.
- Volumes of $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ solution
- Mass \% of $\mathrm{Cu}(\mathrm{II})$ in $\mathrm{Cu}\left(\mathrm{gly}^{-}\right)_{2} . \mathrm{x}_{2} \mathrm{O}$. Calculation.
- The value of $x$ in the formula of the product. Calculation.


## Other Tasks:

1. Write two equations for chemical reactions taking place during the standardization of $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ solution.
2. Write the equation for the reaction between $\mathrm{Cu}^{2+}$ and $\mathrm{I}^{-}$.

Solutions of the tasks:

1. $\mathrm{IO}_{3}^{-}+5 \mathrm{I}^{-}+6 \mathrm{H}_{3} \mathrm{O}^{+} \rightarrow \mathrm{I}_{2}+9 \mathrm{H}_{2} \mathrm{O}$
$\mathrm{I}_{2}+2 \mathrm{~S}_{2} \mathrm{O}_{3}^{2-} \rightarrow 2 \mathrm{I}^{-}+\mathrm{S}_{4} \mathrm{O}_{6}^{2-}$
2. $2 \mathrm{Cu}^{2+}+4 \mathrm{I}^{-} \rightarrow 2 \mathrm{CuI}+\mathrm{I}_{2}$
