M. Sc. (Third Semester) Examination, 2013

CHEMISTRY (Analytical chemistry Special paper)

CHT-303 (A): Principles of Analytical Chemistry

Section-A

Attempt all ten questions. All questions carry equal marks. 10x2 = 20

1. **(i)** Lewis theory of acid-base: An acid is a substance that can accept an electron and a base is a substance that can donate an electron. Example is give below:

H^+ (acid) + $:NH_3$ (base) $\rightarrow H:NH_3$; $AlCl_3 + :OR_2 \rightarrow Cl_3Al:OR_2$

(ii) pH of $1.2x10^{-3}$ M solution of acetic acid

$H^+ = \sqrt{Ka \times C}$,

$[H^+] = \sqrt{1.75x10^{-5}x1.2x10^{-3}}$

$[H^+] = 1.4x10^{-4}$

$pH = -\log (1.4x10^{-4})$

$= 4 - \log 1.4 = 4 - 0.15$; pH = 3.85

(iii) Polyprotic acid: Polyprotic acid is also known as polybasic acid, are able to donate more than one proton. e.g. H_2SO_4 can donate two protons and H_3PO_4 can donate three protons.

$H_2SO_4+H_2O \rightarrow H_3O^+ + HSO4^-$; $HSO4^- + H_2O \rightarrow H_3O^+ + SO4^{2-}$

$H_3PO_4+H_2O \rightarrow H_3O^+ + H_2PO_4^-$; $H_2PO_4^- + H_2O \rightarrow H_3O^+ + HPO_4^{2-}$;

$HPO_4^{2-} + H_2O \rightarrow H_3O^+ + PO_4^{3-}$

(iv)They are important part of many industrial processes e.g. electroplating, leather, photographic material and dying. In bacteriological research, it is very essential to maintain the pH required for the growth of certain bacteria. Human blood is buffered to pH of 7.3-7.4 by means of HCO_3^-, PO_4^{3-} and other nitrogenous bases.

(v) In all multicellular organisms, the fluid within the cell and the fluids surrounding the cells have a characteristic and nearly constant pH. This pH is maintained in a number of ways, and one of the most important is through buffer systems. Two important biological buffer systems are the dihydrogen phosphate system and the carbonic acid system.

The phosphate buffer system operates in the internal fluid of all cells. This buffer system consists of dihydrogen phosphate ions ($H_2PO_4^-$) as hydrogen-ion donor (acid) and hydrogen phosphate ions (HPO_4^{2-}) as hydrogen-ion acceptor (base). These two ions are in equilibrium with each other as indicated by the chemical equation below.

$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$

If additional hydrogen ions enter the cellular fluid, they are consumed in the reaction with HPO_4^{2-}, and the equilibrium shifts to the left. If additional hydroxide ions enter the cellular fluid, they react with $H_2PO_4^-$, producing HPO_4^{2-}, and shifting the equilibrium to the right. The equilibrium-constant expression for this equilibrium is

$$K_a = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-}$$

Another biological fluid in which a buffer plays an important role in maintaining pH is blood plasma. In blood plasma, the carbonic acid and hydrogen carbonate ion equilibrium buffers the pH. In this buffer,

carbonic acid (H_2CO_3) is the hydrogen-ion donor (acid) and hydrogen carbonate ion (HCO_3^-) is the hydrogen-ion acceptor (base).

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

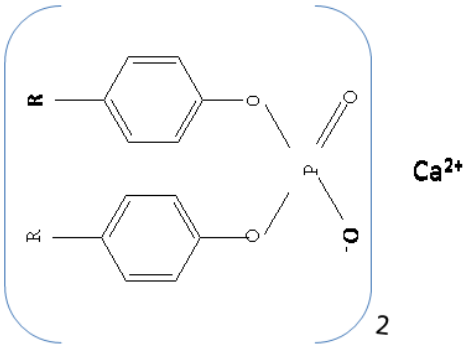
(vi) A photometric titration is based on Lamberts- beers' law according to which (with some restrictions) the absorbance observed is proportional to the concentration of absorbing species. Consequently, if in a photometric titrations, a graph is plotted between absorbance and volume of titrant.
A= Ecl

(vii) Photometric titration does not involve the use of indicators. Multiple species determination can be done through selecting appropriate wavelength simultaneously. It is more sensitive and accurate results are obtained.
While in conventional titrations, indicators are generally used. Simultaneously, multispecies cannot be determined. Chance of error is more because of manual handling.

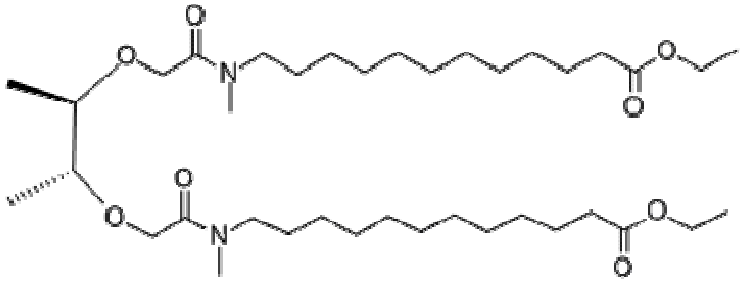
(viii) A chemical sensor is a self-contained analytical device that can provide information about the chemical composition of its environment, that is, a liquid or a gas phase.[1] The information is provided in the form of a measurable physical signal that is correlated with the concentration of a certain chemical species (termed as analyte). Two main steps are involved in the functioning of a chemical sensor, namely, recognition and transduction. In the recognition step, analyte molecules interact selectively with receptor molecules or sites include in the structure of the recognition element of the sensor. Consequently, a characteristic physical parameter varies and this variation is reported by means of an integrated transducer that that generates the output signal.
In biomedicine and biotechnology, sensors which detect analytes thanks to a biological component, such as cells, protein, nucleic acid or biomimetic polymers, are called biosensors.

(ix) Two ionophores used:

(1) BBTP: cationic ionophores:



(2)ETH-1001: neutral ionophore



(x) The sensor is an inexpensive, portable, foolproof device that responds with perfect and instantaneous selectivity to a particular target chemical substance (analyte) present in any desired medium in order to produce a measurable signal output at any required analyte concentration.

Section-B

2. Hammett acidity function:

Hammett acidity function (H_0) was introduced by physical organic chemist Louis Plack Hammett which is used to extend the measure of Bronsted-Lowry acidity beyond the dilute aqueous solutions (pH scale is used). This is used for the strong acid including super acids. Henderson-Hasselbalch equation cannot be useful for highly concentrated acid due to the variations of the activity coefficients. H_0 is used in acid-catalyzed reaction where a very high concentrated acid is used. Thus, H_0, can substitute the pH equation, which is analogous to the Henderson-Hasselbalch equation:

$H_0=pK_{BH+}+\log [B]/[BH^+]$

pK_{BH+} is $-\log(K)$ for the dissociation of BH^+, which is the conjugate acid of a very weak base B, with a very negative pK_{BH+}.

The values of H_0 for some of the strong concentrated acids are given below:

(i) H_2SO_4: −12, (ii) Pyrosulfuric acid: −15, (iii) Fluoroantimonic acid: −31.3, (iv) Magic acid: −19.2, (iv) Triflic acid −14.1, (v) Fluorosulfuric acid: −15.1

Equation for calculating the pH for polyprotic acid:

Many acids or bases are polyfunctional that is having more than one ionizable protons or hydroxide. These substances ionize stepwise and equilibrium constant can be written as below. Consider the ionization of phosphoric acid:

$H_3PO_4 \rightarrow H^+ + H_2PO_4^-$ $\quad K_{a1}=\frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$

$H_2PO_4^- \rightarrow H^+ + HPO_4^{2-}$ $\quad K_{a2}=\frac{[H^+][H_2PO_4^{2-}]}{[H_2PO_4^-]}$

$HPO_4^{2-} \rightarrow H^+ + PO_4^{3-}$ $\quad K_{a3}=\frac{[H^+][H_2PO_4^{3-}]}{[H_2PO_4^{2-}]}$

The values of ionization constants k_{a1}, k_{a2} and k_{a1} are 1.1×10^{-2}, 7.5×10^{-8} and 4.8×10^{-13}, respectively and the overall ionization constants $K_a= 4.0\times10^{-22}$

The overall ionization is the some of these individual steps and the overall ionization constant product of the individual ionization constants:

$H_3PO_4 \rightarrow 3H^+ + PO_4^{3-}$ $\quad K_a=\frac{[H^+][PO_4^{3-}]}{[H_3PO_4]}$

Taking –log both sides of the above equation

-log Ka =-log $[H^+]$-log $\frac{[PO_4^{3-}]}{[H_3PO_4]}$

pH= pKa+ log $\frac{[H_3PO_4]}{[PO_4^{3-}]}$ = pH = pKa+ log $\frac{[Proton\ acceptor]}{[Proton\ donor]}$

3. (a) Ionization of HCl and H_2O

$HCl \rightarrow H^+ + Cl^-$; $H_2O \rightarrow H^+ + OH^-$

$[H^+][OH^-]=1.0x10^{-14}$; $[H^+]_{H2O\ diss} = [OH^-]_{H2O\ diss} = x$

Since the hydrogen ions contributed from the ionization of water are not negligible compared to HCl

$[H^+] = C_{HCl} + [H^+]_{H2O}$ diss

$([H^+]_{HCl} + x)(x) = 1.0x10^{-14}$; $(1.0x10^{-7}+x)(x) = 1.0x10^{-14}$

$x^2+1.0x10^{-7}x1.0-1.0x10^{-14} = 0$

Using the quadratic equation, $\frac{-b\pm\sqrt{b^2-4ac}}{2a}$

$x=-1.0x10^{-7}\pm\sqrt{1.0x10^{-14}+4(1.0x10^{-14})}/2 = 0.62x10^{-7}$

Therefore the total H^+ concentration $=1.0x10^{-7}+0.62x10^{-7}=1.62\ x10^{-7}$

pH = $-\log 1.62\ x10^{-7} = 7.0-0.21 = 6.79$; pH = **6.79**

pOH=14.00−6.79=**7.21**

(b).

Let x be the concentration after the ionization of HOAC and OH^- and $C_{OAC^-}-x$ is the concentration at equilibrium for OAC^-. $C_{OAC^-} = 0.10$ M

$NaOAC \rightarrow Na^+ + OAC^-$

$OAC^- + H_2O \leftrightarrow HOAC + OH^-$

$(C_{OAC^-} - x)$ x x

$K_b = \frac{[HOAC][OH-]}{OAC-} = \frac{Kw}{Ka} = 1.0x10^{-14}/1.75x10^{-5} = 5.7x10^{-10}$

$Kb = \frac{[OH-][OH-]}{COAC-x} = [OH^-] = \sqrt{5.7x10^{-10}x0.10} = 7.6x10^{-6}$

$[OH^-] = 7.6x10^{-6}$ M

$[H^+] = 1.0x10^{-14}/7.6\ x\ 10^{-6} = 1.3x10^{-9}$ M

pH = $-\log (1.33x10^{-9}) = 9.0-\log 1.3 = 9.0-0.11$; pH = **8.89**

8.89+pOH = 14.0; pOH = **5.11**

4. A **buffer** is an aqueous solution consisting of a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid. ItspH changes very little when a small amount of strong acid or base is added to it and thus it is used to prevent changes in the pH of a solution. Buffer solutions are used as a means of keeping pH at a nearly constant value in a wide variety of chemical applications.

The resistance to change in pH on the addition of an acid or alkali is called as buffer capacity (β).

$$\beta = \frac{db}{d\ (pH)}$$

Where db=amount of base added, dpH= change in pH

<u>Expression of buffer capacity for acidic buffer:</u>

Let, For acidic buffer contains amount of acid=a, amount of salt=s

$$pH_1 = pKa + \log\left(\frac{s}{a}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

To this buffer, a little amount of base Δb is added,Since the addition of base converts weak acid into equivalent amount of salt, we will have

$$pH_2 = pKa + \log\left(\frac{s+\Delta b}{a-\Delta b}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(2)$$

The change in pH is given by

$$\Delta pH = pH_2 - pH_1 = \log\left(\frac{s+\Delta b}{a-\Delta b}\right) - \log\left(\frac{s}{a}\right)$$
$$= \log\left(\frac{s+\Delta b}{a-\Delta b} \cdot \frac{s}{a}\right)$$
$$= \log\left(\frac{1+\Delta b/s}{1-\Delta b/a}\right)$$

Since, $\Delta b/s << 1$ & $\Delta b/a << 1$, we get,

$$\Delta pH = \frac{1}{2.303}\left(\frac{\Delta b}{s} + \frac{\Delta b}{a}\right) = \frac{\Delta b}{2.303}\left[\frac{a+s}{as}\right]$$

For infinitesimal value of Δb, we can write

$$\frac{db}{d(pH)} = \beta = 2.303\left(\frac{as}{a+s}\right)$$

5. A basic **buffer** is an aqueous solution consisting of a mixture of a weak base and its conjugate acid. For example: $NH_4OH + NH_4Cl$

Let, $NaHCO3 \rightarrow NaHA \rightarrow Na^+ + HA^-$

$$HA^- + H_2O \underset{K2}{\overset{Kb2}{\leftrightarrow}} H_2A + OH^-$$

$$HA^- + H_2O \leftrightarrow A^{--} + H_3O^+$$
$$\underset{K1}{}$$

$$H_2A + H_2O \leftrightarrow HA^- + H_3O^+$$

CB : $[Na^+] + [H_3O^+] = [OH^-] + 2[A^{--}] + [HA^-]$

MB: $NaHA = [HA^-] + [H_2A] + [A^{--}]$

After subtraction of CB and MB

$$[H_3O^+] = [OH^-] - [H_2A] + [A^{--}]$$
$$= \frac{kw}{[H3O+]} + \frac{k2\,[HA-]}{[H3O+]} - \frac{kw\,[HA-]}{k1[OH-]}$$
$$= \frac{kw}{[H3O+]} + \frac{k2\,[HA-]}{[H3O+]} - \frac{kw\,[HA-][H3O+]}{k1[OH-]kw}$$

Multiplied by $[H3O+]$-

$$[H_3O^+]^2 = k1kw + k1k2\,[HA^-] - \frac{[HA-][H3O+]2}{k1}$$

$$K1\,[H_3O^+]^2 \left\{1 + \frac{[HA-]}{k1}\right\} = kw + k2\,[HA^-]$$

$$[H_3O^+] = \sqrt{\frac{k1kw + k1\,k2\,[HA-]}{k1 + [HA-]}}$$

K1k2 = neg since k1k2 <<<< k1k2[HA^-]

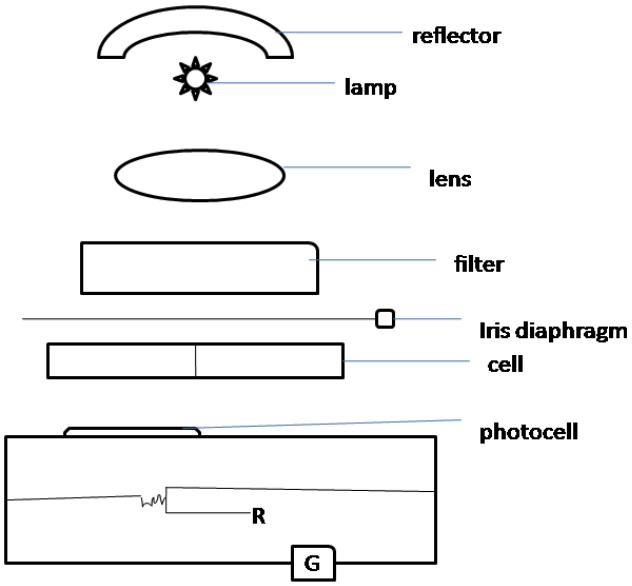
$k1 + [HA-] = [HA^-]$ since k1 <<< [HA^-]

$$[H_3O^+] = \sqrt{k1k2} = \sqrt{10^{-7}} \times 10^{-11} = 10^{-9}$$

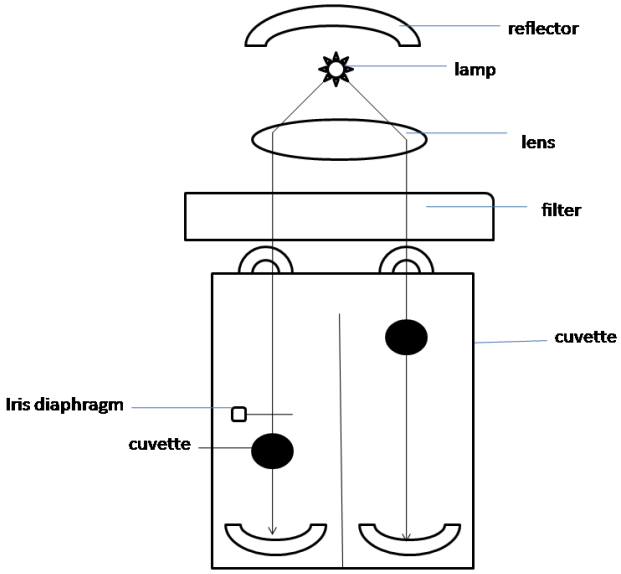
So, pH= 9

6. There are two major classes of devices: single beam and double beam. A single-beam spectrophotometer measures the relative light intensity of the beam before and after a test sample is inserted. Although comparison measurements from double-beam instruments are easier and more stable, single-beam instruments can have a larger dynamic range and are optically simpler and more compact.

Single beam photometer:



Double beam photometer: A double beam spectrophotometer compares the light intensity between two light paths, one path containing a reference sample and the other the test sample.



7. A **glass electrode** is a type of ion-selective electrode made of a doped glass membrane that is sensitive to a specific ion. It is an important part of the instrumentation for chemical analysis and physico-chemical studies. In modern practice, widely used membranous ion-selective electrodes (ISE, including glasses) are part of a galvanic cell. The electric potential of the electrode system in solution is sensitive to changes in the content of a certain type of ions, which is reflected in the dependence of the electromotive force (EMF) of galvanic element concentrations of these ions.

Glass electrodes are commonly used for pH measurements. There are also specialized ion sensitive glass electrodes used for determination of concentration of lithium, sodium, ammonium, and other ions. Glass electrodes have been utilized in a wide range of applications — from pure research, control of industrial processes, to analyze foods, cosmetics and comparison of indicators of the environment and environmental regulations: a microelectrode measurements of membrane electrical potential of a biological cell, analysis of soil acidity, etc.

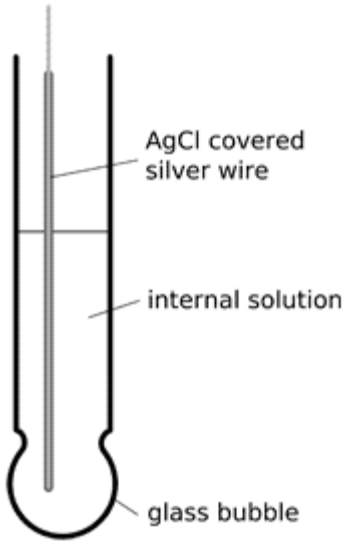
A typical modern pH probe is a combination electrode, which combines both the glass and reference electrodes into one body. The combination electrode consists of the following parts (see the drawing):

1. a sensing part of electrode, a bulb made from a specific glass
2. internal electrode, usually silver chloride electrode or calomel electrode
3. internal solution, usually a pH=7 buffered solution of 0.1 mol/L KCl for pH electrodes
4. when using the silver chloride electrode, a small amount of AgCl can precipitate inside the glass electrode
5. reference electrode, usually the same type as 2
6. reference internal solution, usually 0.1 mol/L KCl
7. junction with studied solution, usually made from ceramics or capillary with asbestos or quartz fiber.
8. body of electrode, made from non-conductive glass or plastics.

The bottom of a pH electrode balloons out into a round thin glass bulb. The pH electrode is best thought of as a tube within a tube. The innermost tube (the inner tube) contains an unchanging 1×10^{-7} mol/L HCl solution. Also inside the inner tube is the cathode terminus of the reference probe. The anodic terminus wraps itself around the outside of the inner tube and ends with the same sort of reference probe as was on the inside of the inner tube. It is filled with a reference solution of 0.1 mol/L KCl and has contact with the solution on the outside of the pH probe by way of a porous plug that serves as a salt bridge.

Glass electrode || Reference Solution || **Test Solution** || Glass electrode

Ag(*s*) | AgCl(*s*) | KCl(*aq*) || 1×10^{-7}M H^+ solution || glass membrane || **Test Solution** || ceramic junction || KCl(*aq*) | AgCl(*s*) | Ag(*s*)



A combined pH/Ref electrode is located inside the barrel of the NH3 probe.
A gas permeable membrane is inserted at the end of the barrel and barrel is filled with an NH4Cl solution. pH/ref electrode monitor the pH of the inner NH4Cl solution. This probe is immersed in the solution producing free NH3. NH3 gas diffuses through gas permeable into the inner NH4Cl solution and pH shifts according to equilibrium

$$NH3 + H2O \leftrightarrow NH4OH + OH-$$

The glass pH sensitive membrane within the probe responds to the pH of NH4Cl according to equilibrium and therefore indirectly to [NH3] of the sample.

$$E=const-59.1\ pH$$

$$E= const - 59.1 \log [NH3]$$

It is ideal for the determination of dissolved NH3 in waste water and natural water. It is also very useful in turbid and colored solution.

8. A **fluoride selective electrode** is a type of ion selective electrode sensitive to the concentration of the fluoride ion. A common example is the lanthanum fluoride electrode.

In the lanthanum fluoride electrode, the sensing element is a crystal of lanthanum fluoride LaF_3, doped with europium fluoride EuF_2 to make the membrane more functional. Such a crystal is an ionic conductor by virtue of the mobility of fluoride ions which jump between lattice vacancies. An electrochemical cell may be constructed using such a crystal as a membrane separating two fluoride solutions. This cell acts as a concentration cell with transference where the fluoride transport number is 1. As transference of charge through the crystal is almost exclusively due to fluoride, the electrode is highly specific to fluoride. The only ion which significantly interferes is hydroxide (OH^-). Generally such "alkaline error" can be avoided by buffering the sample to a pH below 7.

The cell diagram of a typical experimental arrangement is:

Cu' | Ag,AgCl | KCl || solution | LaF_3 | KF,KCl | AgCl,Ag | Cu

The internal electrolyte is at fixed composition and the electrode response is given by the Nernst equation:
$E = E^0 - RT/F \ln a_{F^-}$