# M. Sc. CHEMISTRY <br> FIRST SEMESTER <br> Analytical Chemistry <br> MSC - 101 

Duration: 3 Hrs.
Marks: 70

> Part : A (Objective) $=20$
> Part : B (Descriptive) $=50$
[ PART-B: Descriptive]
Duration: 2 Hrs. 40 Mins.
Marks: 50

## [Answer question no. One (1) \& any four (4) from the rest]


#### Abstract

1. i. How will you identify the presence of a carbonyl functional group in a sample? Write the reaction.


ii. What is meant by accuracy and precision? Explain with examples.
iii. Calculate the number of oxygen atoms in 0.2 mole of $\mathrm{Na}_{2} \mathrm{CO}_{3} \cdot 10 \mathrm{H}_{2} \mathrm{O}$
iv. According to Le-Chateliers' principle, write the favourable condition for the forward reaction of the following reaction

$$
\begin{equation*}
\mathrm{H}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2} \rightleftharpoons \quad \mathrm{H}_{2} \mathrm{O}(\mathrm{l}), \quad \Delta \mathrm{H}=-285.9 \mathrm{KJ} \tag{3}
\end{equation*}
$$

2. i. What are the classical quantitative analytical methods?

ii. What are the conditions to be met in order for a chemical reaction to
be used as a basis for a volumetric analysis?
iii. Give the examples of different types of reactions generally considered in volumetric analysis.
iv. 300 mg of a $\mathrm{Na}_{2} \mathrm{C}_{2} \mathrm{O}_{4}(\mathrm{mw}=134) 95 \%(\mathrm{w} / \mathrm{w})$ pure reagent was transferred to a titration conical flask. After adding acid solution and a suitable indicator, $\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}$ was titrated with $\mathrm{KMnO}_{4}$ unknown solution according to the following titration reaction equation:

$$
2 \mathrm{MnO}_{4}^{-}+5 \mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}+16 \mathrm{H}^{+} \rightarrow 2 \mathrm{Mn}^{2+}+10 \mathrm{CO}_{2}+8 \mathrm{H}_{2} \mathrm{O}
$$

If the volume of $\mathrm{KMnO}_{4}$ solution at the equivalent point was 34 mL , calculate the molarity of $\mathrm{KMnO}_{4}$ solution?
v. What is the result of the following calculations reported to the correct number of significant figures?
a. $135.621+96.35+21.2256$
b. $3.39 \times 0.4896 \times 21.1257 \times 2.245$
c. $\quad 43.56 \times 0.321$

$$
15.501
$$

3. i. A mixture of mercurous chloride (FW 472.09) and mercurous bromide (FW 560.99) weighs 2.00 g . The mixture is quantitatively reducedto mercury metal (Atomic weight 200.59) which weighs 1.50 g . Calculate the \% mercurous chlorideand mercurous bromide in the originalmixture.
ii. Define common ion effect with an example. How can you predict precipitation in a reaction from solubility product
4. i. Find out the number of significant zeros in the following measurements
a. 0.005015990
b. 0.110035408
ii. What are the main sources of errors? Explain with examples.
iii. A student has grown 6 crystals from a sample solution and measured the length of each crystal in millimeters. The measurements are given below:

$$
9.25,9.18,9.30,9.26,9.17,9.22
$$

Calculate the mean, standard deviation, co-efficient of variation and variance of the lengths of the crystals.
5. i. What is meant by Linear least square method?
ii. A refrigerator thermometer is read ten times and registers degrees Celsius as: $39.1,39.4,39.1,39.2,39.1,39.2,39.1,39.1,39.4$, and 39.1. However, the real temperature inside the refrigerator is $37{ }^{\circ} \mathrm{C}$. Find out the accuracy and precision of the thermometer readings.
iii. Explain any two effective methods for minimization of determinate error.
iv. A solution of hydrogen peroxide $15.2 \%$ by mass. What is the molarity of the solution? The solution has a density $1.01 \mathrm{~g} / \mathrm{mL}$
6. i. Integrate the rate expression for $2^{\text {nd }}$ order reaction of type
$\mathrm{A}+\mathrm{B} \rightarrow \mathrm{P}$
ii. The following data were obtained for the reaction
$2 \mathrm{~A}+2 \mathrm{~B} \rightarrow \mathrm{C}+3 \mathrm{D}$

| $[\mathrm{A}]$ | $[\mathrm{B}]$ | Rate, r |
| :---: | :---: | :---: |
| $\left(\mathrm{mol} \mathrm{L}^{-1}\right)$ | $\left(\mathrm{mol} \mathrm{L}^{-1}\right)$ | $\mathrm{mol} \mathrm{L}^{-1} \mathrm{sec}^{-1}$ |
| $3 \times 10^{-3}$ | $1 \times 10^{-3}$ | 0.012 |
| $3 \times 10^{-3}$ | $2 \times 10^{-3}$ | 0.024 |
| $6 \times 10^{-3}$ | $1 \times 10^{-3}$ | 0.192 |

Determine order of the reaction with respect to A and B. Also write the rate law expression.
7. i. If the equilibrium constant for the reaction $A_{2}+B_{2} \Longrightarrow 2 A B$ is $K_{1}$ and that for $A B \Longrightarrow 1 / 2 A_{2}+1 / 2 B_{2}$ is $K_{2}$, then prove that $K_{1} K_{2}{ }^{2}$ $=1$
ii. The half-life of the homogeneous gaseous reaction
$\mathrm{SO}_{2} \mathrm{Cl}_{2} \rightarrow \mathrm{SO}_{2}+\mathrm{Cl}_{2}$, which obeys first order kinetics is 8.0 minute. How long will it take for the concentration of $\mathrm{SO}_{2} \mathrm{Cl}_{2}$ to be reduced to $1 \%$ of the initial value?
8. Write briefly about the basic principle, instrumentation and application of Atomic Absorption Spectroscopy.

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Choose the correct answer from the following: $\mathbf{1 \times 2 0}=\mathbf{2 0}$

1. In $5 \%$ ethyl acetate-hexane eluent, compound ' $A$ ', ' $B$ ' \& ' $C$ ' have $R_{f}=0.4,0.1, \& 0.8$ respectively for a $\mathrm{SiO}_{2}$ coated glass plate. While doing column chromatographic separation of a mixture of A \& B using silica gel as stationary phase and solvent $5 \%$ ethyl acetate in hexane as eluent, the compound expected to come out first from the column is
a. compound ' $A$ '
b. compound ' B '
c. compound ' $C$ '
d. all will come together
2. The correct statement among the following is
a. Gravimetric and volumetric analysis both are related to equivalence point
b. Gravimetric and volumetric analysis both are related to precipitation
c. Gravimetric \& volumetric analysis are related to equivalence point \& precipitation respectively
d. Gravimetric \& volumetric analysis are related to precipitation \& equivalence point respectively
3. Which one of the following is an explosive precursor?
a. Oxides
b. Azides
c. Halides
d. Sulfides
4. For a chemical reaction, you need to take a 25 mL of liquid reagent. Which one of the following glass apparatus you will use for the measurement?
a. 50 mL measuring cylinder
b. 100 mL beaker
c. 100 mL conical flask
d. 50 mL burette
5. Which of the following error is caused by poor calibration of instrument?
a. Random error
b. Gross error
c. Determinate error
d. Precision error
6. The significant figures in the number 0.032040 is
a. 3
b. 5
c. 4
d. 6
7. For an instrument the degree of repeatability or reproducibility in measurements is an alternative way of expressing its
a. Precision
b. Accuracy
c. Linearity
d. Sensitivity
8. Random errors in a measurement system are due to
a. Environmental changes
b. Use of uncalibrated instrument
c. Poor cabling practices
d. Unpredictable effects
9. The error between mean of finite data set and mean of infinite data set is known as
a. True error of the mean
b. Standard error of the mean
c. Finite error
d. Infinite error
10. Zero digit between two significant figures is
a. Significant
b. Non-significant
c. May not be significant
d. May be significant
11. Choose the correct order of ppb scale
a. 10-6
b. $10^{-8}$
c. $10^{-9}$
d. $10^{-12}$
12. Phosphoric acid is
a. Monoprotic
b. Diprotic
c. Triprotic
d. Both $\mathbf{a}$ and $\mathbf{b}$
13. Identify the zero order reaction from the following expression
a. $\mathrm{K}=5.6 \times 10^{-4} \mathrm{sec}^{-1}$
b. $\mathrm{K}=4.5 \times 10^{-3} \mathrm{~L} \mathrm{~mol}^{-1} \mathrm{sec}^{-1}$
c. $\mathrm{K}=3.2 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{sec}^{-1}$
d. $K=2.6 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{sec}$
14. The half life for a $2^{\text {nd }}$ order reaction with initial concentration ' $a$ ' is a. $0.693 / \mathrm{K}$
b. $1 / \mathrm{Ka}$
c. a/2K
d. $0.693 \mathrm{a} / \mathrm{K}$
15. At low temperature and low entropy, $\Delta \mathrm{G}$ for an endothermic reaction is
a. Negative
b. Positive
c. Zero
d. Unity
16. At temperature $T$ and $\Delta n=-1$, the relationship between $K_{p}$ and $K_{c}$ is
a. $K_{p}=K_{c}$
b. $K_{p}=K_{c} R T$
c. $K_{p}=K_{c} / R T$
d. $K_{c}=K_{p} / R T$
17. Addition of NaOH to a solution of $\mathrm{NH}_{4} \mathrm{OH}$, pushes the equilibrium towards
a. Right
b. Left
c. Equilibrium remain same
d. None of the above
18. If $f^{\circ}$ is the fugacity of a substance in its pure state and $f$ is that of another state of same substance, then activity is
a. $a=f / f o$
b. $a=f o / f$
c. $\ln f / f^{o}$
d. $\ln f \circ / f$
19. Air-acetylene flames have a temperature range of
a. $1800^{\circ} \mathrm{C}-2150{ }^{\circ} \mathrm{C}$
b. $1700{ }^{\circ} \mathrm{C}-2000^{\circ} \mathrm{C}$
c. $2150{ }^{\circ} \mathrm{C}-2300^{\circ} \mathrm{C}$
d. $2300{ }^{\circ} \mathrm{C}-2500^{\circ} \mathrm{C}$
20. Full form of SEM is
a. Scanning Emission Microscope
b. Scanning Engine Machine
c. Scanning Electron Microscope
d. Scanning Electron Machine
