| Unique Paper Code | $: 32171102$ |
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| Name of the Paper | $:$ Physical Chemistry-I |
| Name of the Course | $:$ B.Sc. (Hons.) Chemistry |
| Semester | $:$ I |
| Duration | $: 3$ hours |
| Maximum Marks | $: 75$ |

## Instructions for Candidates:

i. The candidate must write the following details on the first page of the answer sheet: University roll No, Unique paper code, Course, Semester, and Paper name.
ii. Write page numbers on every page of the answer script.
iii. Attempt any Four questions in all. All questions carry equal marks.
iv. Attempt all parts of a question together.

1. (a) Write the mathematical expression for Maxwell's distribution of molecular speed and derive the expression for the most probable and root mean square velocity of the gas.
(b) Define the surface tension of the liquid. Describe the drop number method for the determination of the surface tension of a liquid.
(c) Explain the following:
(i) The cleansing action of detergents.
(ii) Why the addition of NaCl increases the surface tension of water whereas the addition of acetone reduces the surface tension of water.
(d) Will a precipitate form if $50 \mathrm{~cm}^{3}$ of $0.01 \mathrm{M} \mathrm{AgNO}_{3}$ and $50 \mathrm{~cm}^{3}$ of 0.0004 M NaCl are mixed? Given $\mathrm{K}_{\text {sp }}$ of $\mathrm{AgCl}=1.7 \times 10^{-10} \mathrm{M}^{2}$.
2. (a) Starting from van der Waals equation of state, derive the mathematical expression of Boyle's temperature.
(b) The critical constants for water are $647 \mathrm{~K}, 22.09 \mathrm{MPa}$, and $0.0566 \mathrm{dm}^{3} \mathrm{~mol}^{-1}$. Calculate the values of van der Waals constants $\mathrm{a}, \mathrm{b}$ and R and also explain the abnormal value of R .
(c) (i) What are buffer solutions? Explain clearly how does a buffer act?
(ii) Determine Exact pH of $10^{-8} \mathrm{M} \mathrm{NaOH}$.
(d) With the given viscometer, the times of flow at $20^{\circ} \mathrm{C}$ for water and an unknown liquid ( $\mathrm{d}=1.22 \mathrm{~g} \mathrm{~cm}^{-3}$ ) were found to be 155 sec and 80 sec respectively. Calculate the absolute viscosity of the unknown liquid at $20^{\circ} \mathrm{C}$ if viscosity and density of water are 1.005 centipoise and $1 \mathrm{~g} \mathrm{~cm}^{-3}$ respectively.
$(5,4,5,4.75)$
3. (a) Describe the powder diffraction method to determine crystal structure. Explain how this method can be used to analyze the structure of a cubic system.
(b) X-ray diffraction is not useful for distinguishing between atoms that differ by only the possession of one additional electron. Explain.
(c) Show that the pH of an aqueous solution of salt formed from a strong acid and weak base is given by

$$
\mathrm{pH}=7-\frac{1}{2}\left(\mathrm{pK}_{\mathrm{b}}+\log \mathrm{c}\right)
$$

(d) Silver is known to be crystallized in cubic form. The Bragg angles using copper $\mathrm{K}_{\alpha}$ X-rays with $\lambda=154.1 \mathrm{pm}$, for the first six diffraction lines are as follows:

$$
\begin{array}{llllll}
\theta & 19.08^{\circ} & 22.17^{\circ} & 32.26^{\circ} & 38.74^{\circ} & 40.82^{\circ}
\end{array} 49.00^{\circ}
$$

What is the type of cubic crystal formed by Silver?
(6, 3, 5, 4.75)
4. (a) Explain the terms $\sigma, \lambda, \mathrm{Z}_{1}$ and $\mathrm{Z}_{11}$. Discuss the effect of temperature and pressure on these terms.
(b) Calculate $\lambda, \mathrm{Z}_{1}$, and $\mathrm{Z}_{11}$ for oxygen at 298 K and $10^{-3} \mathrm{mmHg}$. Given $\sigma=3.61 \times 10^{-8}$ cm .
(c) Write a short note on any three of the followings:
(i) Continuity of state
(ii) Law of constancy of interfacial angles.
(iii) Law of rational indices
(iv) Symmetry elements
(d) Determine pH of water at $363 \mathrm{~K}\left(\mathrm{~K}_{\mathrm{w}}\right.$ at $\left.363 \mathrm{~K}=1 \times 10^{-12} \mathrm{M}^{2}\right)$. Will it be neutral at 363 K? Explain.
5. (a) What is an acid-base indicator? How does its color change with the $\mathrm{H}^{+}$ion concentration of the solution? What is the indicator range?
(b) Starting from the postulate of the kinetic theory of gases, derive the kinetic gas equation.
(c) Calculate the temperature at which the average velocity of $\mathrm{SO}_{2}$ equals that of $\mathrm{O}_{2}$ at 20 K.
(d) A solution is $0.1 \mathrm{M} \mathrm{in}^{-1}$ and .001 M in $\mathrm{CrO}_{4}{ }^{2-}$. If solid $\mathrm{AgNO}_{3}$ is gradually added to this solution, which will precipitate first, AgCl or $\mathrm{Ag}_{2} \mathrm{CrO}_{4}$ ? Assume that the addition causes no change in volume. Given: $\mathrm{K}_{\text {sp }}(\mathrm{AgCl})=1.7 \times 10^{-10} \mathrm{M}^{2}$ and $\mathrm{K}_{\text {sp }}\left(\mathrm{Ag}_{2} \mathrm{CrO}_{4}\right)=$ $1.9 \times 10^{-12} \mathrm{M}^{3}$.
$(5,5,3.75,5)$
6. (a) Show that the concentration of $\mathrm{H}_{3} \mathrm{O}^{+}$in an aqueous solution of a diprotic acid $\mathrm{H}_{2} \mathrm{~A}$ is given by
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left\{\frac{\left[\mathrm{H}_{2} \mathrm{~A}\right]_{0} \mathrm{~K}_{1}}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]+\mathrm{K}_{1}+\frac{\mathrm{K}_{1} \mathrm{~K}_{2}}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}}\right\}\left\{1+\frac{2 \mathrm{~K}_{2}}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}\right\}+\frac{\mathrm{Kw}}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}$
Under what conditions can the following expressions be used
(i)

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left\{\frac{\left[\mathrm{H}_{2} \mathrm{~A}\right]_{0} \mathrm{~K}_{1}}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]+\mathrm{K}_{1}+\frac{\mathrm{K}_{1} \mathrm{~K}_{2}}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}}\right\}\left\{1+\frac{2 \mathrm{~K}_{2}}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}\right\}
$$

(ii) $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{\left[\mathrm{H}_{2} \mathrm{~A}\right]_{0} \mathrm{~K}_{1}}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]+\mathrm{K}_{1}}$
(b) Define solubility and solubility product. Determine the solubility of $\mathrm{Mg}(\mathrm{OH})_{2}$ in pure water and a buffer solution having $\mathrm{pH}=12 . \mathrm{K}_{\text {sp }}$ of $\mathrm{Mg}(\mathrm{OH})_{2}=1.2 \times 10^{-11} \mathrm{M}^{3}$.
(c) Explain why the titration of a weak acid and weak base is not carried out using an acid-base indicator.
(d) What is capillary action? Derive: $\gamma= \pm 1 / 2 \mathrm{~h} \rho \mathrm{gr}$, where the symbols have their usual meanings.
(6, 5, 3, 4.75)

