## 2021

## CHEMISTRY - HONOURS

## Third Paper

(Group - B)

## Full Marks: 50

The figures in the margin indicate full marks.
Candidates are required to give their answers in their own words as far as practicable.

## CHT-23a

## Unit - I

Answer any three questions.

1. (a) Derive the Gibbs-Duhem equation.
(b) Chemical potential is a measure of escaping tendency- Justify or criticize.
2. (a) Derive the differential form of van't Hoff equation for temperature dependence of equilibrium constant.
(b) For the equilibrium $\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$

The vapour pressure of liquid water at 373 K is 1 bar . Find its value at 323 K . Given $\Delta_{\text {vap }} \mathrm{H}^{\mathrm{o}}=44.01 \mathrm{~kJ} \mathrm{~mol}^{-1}$.
3. (a) Show that $\mu_{i}=\left(\frac{\partial U}{\partial n_{i}}\right)_{S, V, n_{j(\neq i)}}=\left(\frac{\partial G}{\partial n_{i}}\right)_{P, T, n_{j(\neq i)}}$.
(b) Chemical potential $\mu$ and standard chemical potential $\mu^{\circ}$ of a real gas is related as $\mu=\mu^{\circ}+\mathrm{RT} \ln f$, where ' $f$ ' is the fugacity. Comment on the pressure and temperature dependence of $\mu$ and $\mu^{\circ}$.
4. (a) For the dissociation $\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}_{2}(\mathrm{~g})$, check whether $K_{p}=K_{x}$ and $\xi_{e}=\left(\frac{K_{p}}{K_{p}+4 P}\right)^{1 / 2}$. [ $\xi_{e}=$ degree of advancement of the reaction at equilibrium]
(b) The solubility of AgCl increases when $\mathrm{NaNO}_{3}$ is added to it. Justify or criticize.
5. (a) Consider a salt of concentration C mol. $\mathrm{lit}^{-1}$ which hydrolyses to weak acid and strong base. Show that $\mathrm{pH}=\frac{1}{2} \mathrm{pK}_{\omega}+\frac{1}{2} \mathrm{Pk}_{\mathrm{a}}+\frac{1}{2} \log \mathrm{C}$.
(b) What is buffer solution? Give an example of alkaline buffer solution.

## Unit - II

Answer any two questions.
6. (a) Establish that surface tension and surface energy of a liquid at a particular temperature are numerically equal.
(b) Find the change in surface energy when two identical liquid drops of diameter 1.5 nm merge isothermally to form one drop.
(Given surface tension of the liquid at that temperature is 490 dynes $/ \mathrm{cm}$ ).
7. (a) How does the surface tension of a liquid change with temperature? Explain graphically.
(b) Deduce the mathematical expression for measuring the surface tension of a liquid by capillary rise method explaining the terms involved.
8. (a) A spherical solid steel ball of density $10.0 \mathrm{~g} / \mathrm{cc}$ having a diameter of 4 mm is dropped into a column of liquid. It takes 5 seconds to fall through a distance of 10 cm . Calculate the viscosity of the liquid. [Given density of liquid $=3.8 \mathrm{~g} / \mathrm{cc}$ ].
(b) Define coefficient of viscosity $(\eta)$ of a liquid and find its dimension.

## CHT-23b

Unit - I
Answer any three questions.
9. (a) A football weighing 200 g is moving with a particular velocity. If its position is located with an uncertainty of 500 nm , what will be the uncertainty with respect to its velocity? Comment on the result. [Planck's constant, $h=6 \cdot 627 \times 10^{-34} \mathrm{Js}$ ].
(b) Write down the physical meaning of $|\psi|^{2}$ and $\int|\psi|^{2} d \tau$.
10. (a) Show that non-degenerate eigenfunctions of Hermitian operator are orthogonal.
(b) Given operator $\hat{\mathrm{A}}=x \frac{d}{d x}$. Find the expression of $\hat{\mathrm{A}}^{2}$.
11. (a) The work function for platinum metal is $8 \times 10^{-19} \mathrm{~J}$. Will a radiation of wavelength 200 nm be able to cause photoelectric effect in it?
(b) For a free particle the two solutions of the Schrödinger's wave equation are given by $\psi_{1}(x)=A_{1} e^{+i k x}$ and $\psi_{2}(x)=A_{2} e^{-i k x}$. E, the energy, being positive and $k=\sqrt{\frac{2 m E}{\hbar}}$. Show that the momentum of the particle has a definite value and the total energy is not quantized. ( $\mathrm{A}_{1}$ and $\mathrm{A}_{2}$ are real constants)
12. (a) Calculate the degeneracy of a particle of mass ' $m$ ' confined in a cubical box of edge length ' $l$ ' having an energy of (i) $\frac{9 h^{2}}{8 m l^{2}}$ and (ii) $\frac{12 h^{2}}{8 m l^{2}}$.
(b) Show that the function $\psi(x)=\left(x^{2}-a^{2}\right) /(x-a)$ is not acceptable for describing the state of a particle in a one-dimensional box ranging from $x=-2 a$ to $x=2 a$.
13. Of the three functions $\psi, \psi_{2}$ and $\psi_{3}$ given below, choose the acceptable wave function citing proper reason. Normalize the acceptable wave function ( $A_{1}, A_{2}$ and $A_{3}$ are real constants).

$$
\begin{align*}
& \psi_{1}=A_{1} \sin x[0 \leq x \leq 2 \pi] \\
& \psi_{2}=A_{2} \sin ^{-1} y[-1 \leq y \leq 1]  \tag{5}\\
& \psi_{3}=A_{3} \exp (z)[-\infty \leq z \leq+\infty]
\end{align*}
$$

## Unit - II

Answer any two questions.
14. (a) Define conductance, specific conductance and equivalent conductance of an electrolyte solution. What are their units?
(b) Draw the equivalent conductance versus concentration plot for weak electrolyte. Justify whether it is possible to determine the equivalent conductance of a weak electrolyte at infinite dilution from the above plot.
15. (a) Derive the Nernst's equation to determine emf of the cell reaction.
(b) Arrange the ionic conductances of following ions in ascending order, with explanation :
$\mathrm{Li}^{(+)}, \mathrm{Na}^{(+)}, \mathrm{K}^{(+)}$.
16. (a) Construct an electrochemical cell, where the following chemical reaction takes place
$\mathrm{HgO}(\mathrm{s})+\mathrm{H}_{2}(\mathrm{~g})=\mathrm{Hg}(\mathrm{l})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
(b) Given $\mathrm{Fe}^{3+}+\mathrm{e} \rightarrow \mathrm{Fe}^{2+} \quad \mathrm{E}_{298}^{\mathrm{o}}=0.77 \mathrm{~V}$

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\mathrm{Fe}^{2+}+2 \mathrm{e} \rightarrow \mathrm{Fe} \quad \mathrm{E}_{298}^{\circ}=0.44 \mathrm{~V} \text { at } 25^{\circ} \mathrm{C}
$$

Calculate $\mathrm{E}^{\circ}$ and $\Delta \mathrm{G}^{\circ}$ for the reaction $\mathrm{Fe}^{3+}+3 \mathrm{e} \rightarrow \mathrm{Fe}$ and hence indicate standard chemical potential $\mu^{\circ}$ of $\mathrm{Fe}^{3+}$ at $25^{\circ} \mathrm{C}$.

