H.P.A.S. (Main)—2013

CHEMISTRY

Paper I

Time : 3 Hours   Maximum Marks : 150

Note :— Question No. 1 is compulsory and attempt any four questions out of the remaining six questions i.e. attempt five questions in all. All parts of a question must be attempted in continuation at one place.

1. (a) Predict the magnetic moment for Co^{3+}.

   (b) Explain why the +2 oxidation states of tin and lead are more stable than those of carbon and silicon.

P.T.O.
(c) Explain in words the meaning of a negative value of electron affinity. Does any element have a negative ionization potential?

(d) Carborundum, SiC and corundum, Al₂O₃ are important industrial abrasives. Comment on the structures for these compounds to explain why they have such hardness.

(e) Has the peroxide ion O₂²⁻, a longer or shorter bond length than O₂⁺? Explain.

(f) An astronaut in an orbiting spaceship spilled a few drops of his drink and the liquid floated around the cabin. In which geometrical shape was each drop most likely to be found? Explain.
(g) A system is changed from an initial state to a final by a manner such that \( \Delta H = q \). If the change from the initial state to final state were made by different path, would \( \Delta H \) and \( q \) be the same as that for the first path?

(h) In terms of reaction kinetics, explain why each of the following speeds up a chemical reaction:

(i) Catalyst

(ii) Increase in temperature

(iii) Increase in concentration.
(i) Write an equilibrium constant expression for each of the following reactions. What relationship do the constants have to one another:

\[
\begin{align*}
(i) & \quad \text{H}_2(g) + \text{I}_2(g) \xrightleftharpoons{500^\circ\text{C}} 2\text{HI}(g) \\
(ii) & \quad 2\text{HI}(g) \xrightleftharpoons{500^\circ\text{C}} \text{H}_2(g) + \text{I}_2(g).
\end{align*}
\]

(j) Which is the strongest acid of the following? Explain:

(i) \(\text{NH}_3\)

(ii) \(\text{HClO}\)

(iii) \(\text{HClO}_2\)

(iv) \(\text{HClO}_3\)

10×3=30
2. (a) The solution to the Schrödinger equation for an electron in the ground state of the hydrogen atom is:

\[ \psi_{1s} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \]

where \( r \) is the distance from nucleus and \( a_0 \) is \( 0.529 \times 10^{-8} \) cm. The probability of finding an electron at any point in space is proportional to \( |\psi|^2 \). Using calculus, show that the maximum probability of finding the electron in the 1s orbital of hydrogen occurs at \( r = a_0 \).

P.T.O.
(b) For a given number of moles of gas, show that the van der Waals equation predicts greater deviation from ideal behavior:

(i) at high pressure rather than low pressure at a given temperature

(ii) at low temperature rather than high temperature at a given pressure.

(c) Compute the packing factor for spheres occupying:

(i) a body-centered cubic and

(ii) a simple cubic structure,

where closest neighbours in both cases are in contact.
(d) Because \( U \) is a state function therefore:

\[
\left( \frac{\partial}{\partial V} \left( \frac{\partial U}{\partial T} \right)_V \right)_T = \left( \frac{\partial}{\partial T} \left( \frac{\partial U}{\partial V} \right)_T \right)_V.
\]

Using this relation show that:

\[
\left( \frac{\partial C_V}{\partial V} \right)_T = 0
\]

for an ideal gas.

(e) One mole of an ideal gas with

\[
C_V = \frac{3}{2} R
\]

undergoes the transformation from an initial state described by \( T = 300 \) K and \( P = 1.00 \) bar to 450 K at constant pressure of 1.00 bar. Calculate \( q, w, \Delta U, \Delta H \) and \( \Delta S \) for each process. 5×6=30
3. (a) Why are the triple point temperature and the normal freezing point very close in temperature for most substances? Do all triple points correspond to a gas-liquid-solid equilibrium?

(b) Which of the experimental results for the photoelectric effect suggest that light can display particle-like behaviour?

(c) How is it possible to deposit Cu on a Au electrode at a potential lower than that corresponding to the reaction:

\[ \text{Cu}^{2+}(aq) + 2e \rightleftharpoons \text{Cu(S)} \]
(d) What is the difference in the chemical potential and the electrochemical potential for an ion and for a neutral species in solution? Under what conditions is the electrochemical potential equal to the chemical potential for an ion?

(e) Why is the magnitude of the boiling point elevation less than that of the freezing point depression?  

5x6=30

4. (a) Assume that a particle is confined to a box of length $a$, and that the system wave function:

$$\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$$
(i) Is this state an eigen function of the position operator?

(ii) Calculate the average value of the position \( x \) that would be obtained for a large number of measurement. Explain your result.

(b) (i) Why is it not possible to normalize the free particle wave functions over the whole range of motion of the particle?

(ii) What is the difference between probability and probability density?

(c) Calculate the maxima in the radial probability distribution for the \( 2s \) orbital. What is the most probable distance from the nucleus for an electron in this orbital? Are there subsidiary maxima?
(d) Why is atomic absorption spectroscopy more sensitive in many applications than atomic emission spectroscopy?

(e) Explain why S-P mixing is more important in $L_{\text{i}_2}$ than in $F_2$.

5. (a) Determine the total energy of an ensemble consisting of $N$ particles that have only two energy levels separated by energy $\epsilon_r$. 

(b) What is the relationship between ensemble energy and the thermodynamic concept of internal energy?
(c) (i) What is the difference between a strong and weak electrolyte?

(ii) According to Kohlrausch's law, how will the molar conductivity for a strong electrolyte change with concentration?

(d) What is a half-life? Is the half-life for a first order reaction dependent on concentration?

(e) What is the difference between a homogeneous and a heterogeneous catalyst?

5x6=30

6. (a) (i) What desirable and undesirable features are characteristic of a lead storage battery?

(ii) Explain why a porous plate or a salt bridge is not required in a lead storage cell.
(b) Explain how the freezing of water in the crevices of rocks causes mechanical degradation.

(c) A freshly prepared aqueous solution of \(\text{Pd(NH}_3\text{)}_2\text{Cl}_2\) does not conduct electricity. Is this compound to be regarded as a strong or weak electrolyte? Explain in terms of its structure.

(d) Write the formula for:

(i) dichlorotetraamminerrhodium (III) ion

(ii) tetrahdroxodiaquoaluminate (III) ion

(iii) tetrachlorozincate (II) ion
(iv) aluminum nitrate

(v) hexaammine cobalt (III) tetrachlorodiammine chromate (III)

(vi) Hexacarbonylchromium (0).

(e) Would Jahn-Teller distortion be as significant for tetrahedral complexes as it is for octahedral complexes? For which of the electron configuration would Jahn-Teller distortion occur. 

5\times6=30

7. (a) Explain why water is a better medium than liquid ammonia for a reaction that requires an acidic medium whereas the opposite is not true for a reaction that requires a basic medium.
(b) On the basis of their properties, explain why separation of the lanthanides is possible but difficult.

(c) When aluminum alkyls form complexes with \((\text{CH}_3)_2X\) (where \(X = \text{O}, \text{S}, \text{Se} \text{ or Te}\)), the stability of complexes decreases as \(X\) progresses from \(\text{O}\) to \(\text{Te}\). Explain this trend in the order of stability of complexes.

(d) How is benzene bound to Cr in the compound \(\text{Cr(CO)}_3(\text{C}_6\text{H}_6)\)? Explain.

P.T.O.
(e) When an individual is being treated for exposure to carbon monoxide, oxygen is administered? Explain the basis for this treatment.