[This question paper contains 16 printed pages]

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 quesions 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, Al_2O_3 are important industrial abrasives. Comment on the structures for these compounds to explain why they have such hardness.

(*e*) Has the peroxide ion O_2^{2-}, a longer or shorter bond length than O_2 ? 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 ΔH 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 :

(i) $H_{2(g)} + I_{2(g)} \overset{500°C}{\rightleftharpoons} 2HI_{(g)}$

(ii) $2HI_{(g)} \overset{500°C}{\rightleftharpoons} H_{2(g)} + I_{2(g)}$

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

(i) NH_3

(ii) $HClO$

(iii) $HClO_2$

(iv) $HClO_3$. 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 0.529×10^{-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 $r = a_0$.

(*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, ΔU, ΔH and ΔS 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 :

$$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(S) \ ?$$

(*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 ? 5×6=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_{i_2} than in F_2. 5×6=30

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

(*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 ? 5×6=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 $Pd(NH_3)_2Cl_2$ 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*) dichlorotetraamminerhodium (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. 5×6=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 $(CH_3)_2X$ (where X = O, S, Se or Te), the stability of complexes decreases as X progresses from O to Te. Explain this trend in the order of stability of complexes.

(*d*) How is benzene bound to Cr in the compound $Cr(CO)_3(C_6H_6)$? Explain.

(e) When an individual is being treated for exposure to carbon monoxide, oxygen is administered ? Explain the basis for this treatment. 5×6=30