

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 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  $\text{Co}^{3+}$ .
- (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,  $\text{Al}_2\text{O}_3$  are important industrial abrasives. Comment on the structures for these compounds to explain why they have such hardness.
- (e) Has the peroxide ion  $\text{O}_2^{2-}$ , a longer or shorter bond length than  $\text{O}_2$  ? 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  $\Delta H$  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 :

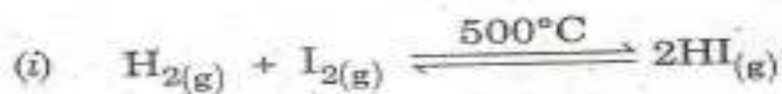
(i) Catalyst

(ii) Increase in temperature

(iii) Increase in concentration.

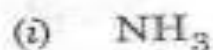
P.T.O.

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



- (j) Which is the strongest acid of the following ?

Explain :



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

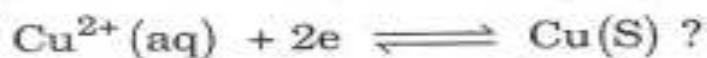
$$C_V = \frac{3}{2}R$$

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.  $5 \times 6 = 30$

P.T.O.



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 :





(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 :

$$\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$$

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- (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  $h\nu$ .

(b) What is the relationship between ensemble energy and the thermodynamic concept of internal energy ?

P.T.O.

- (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  $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$  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) dichlorotetraamminerhodium (III) ion
  - (ii) tetrahydrodiaquoaluminate (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.  $5 \times 6 = 30$

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  $(\text{CH}_3)_2\text{X}$  (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  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)$  ? 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