

This question paper contains 16 printed pages]

**HPAS (M)—2014**

**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) What are the shapes of the Nitrate ion,  $\text{NO}_3^-$ , and Carbonate ion,  $\text{CO}_3^{2-}$  ?

P.T.O.

- (b) Why are transition metals hard and brittle ?
- (c) Cobalt (II) is stable in aqueous solutions but in the presence of complexing reagents it is easily oxidised. Explain.
- (d) Explain the phenomenon of Fluorescence.
- (e) Chemisorption is monolayer whereas physical adsorption is usually multilayer. Explain.
- (f) Reaction of third and higher order are not very common. What are the reasons for this ?
- (g) Derive the relationship  $TV^\gamma - 1 = \text{constant}$  for a reversible adiabatic expansion.

(h) What is the role of salt bridge in electrochemical cells ?

(i) Which is more conducting Li or Cs, and why ?

(j) "While the viscosity of a gas increases with increase in temperature, that of a liquid decreases with increase in temperature." How do you account for this ?

10×3=30

2. (a) The pH of a 0.10 M hydrocyanic acid solution is 5.2. What is the value of  $K_a$  for hydrocyanic acid ?

P.T.O.

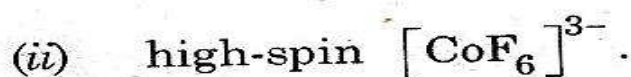


(b) Compare the elements Na, B, Al and C with regard to the following properties :

- (i) Which has the largest atomic radius ?
- (ii) Which has the most negative electron affinity ?
- (iii) Place these elements in order of increasing ionization energy.

(c) Determine the standard free energy change,  $\Delta G^\circ$ , for the formation of 1.00 mol of  $\text{NH}_3(\text{g})$  from nitrogen and hydrogen, and use this value to calculate the equilibrium constant for this reaction at  $25^\circ\text{C}$ .

(d) Give the electron configuration for each of the following complexes. How many unpaired electrons are present in each complex ? Are the complexes paramagnetic or diamagnetic ?



(e) What is a wave ? Explain the following terms associated with waves :

Wavelength, frequency and amplitude.  $5 \times 6 = 30$

3. (a) In general, ionization energy increases from left to right across a given period. Aluminium,

however, has a lower ionization energy than magnesium. Explain.

Arrange the following in order of increasing first ionization energy :

F, K, P, Ca and Ne.

(b) X-rays of wavelength 0.154 nm strike an

Aluminium crystal : the rays are reflected at an angle of  $19.3^\circ$ . Assuming that  $n = 1$ , calculate the spacing between the planes of Aluminium atoms (in pm) that is responsible for this reflection angle. The conversion factor is obtained from

$$1 \text{ nm} = 1000 \text{ pm}.$$

- (c) Describe the hybridization of phosphorus in  $\text{PF}_5$ .
- (d) Distinguish between an unsaturated solution, a saturated solution and a supersaturated solution. From which type of solution out of these mentioned above does crystalization or precipitation occur ? How does a crystal differ from a precipitate ?
- (e) What are the units for the rate constants of zero order, first order, and second order reactions ?
- What is meant by the order of a reaction ?

 $5 \times 6 = 30$ 

P.T.O.



4. (a) What are ion-pairs ? What effect does ion-pair formation have on the colligative properties of a solution ?

(b) Distinguish between homogeneous catalysis and heterogeneous catalysis. A certain reaction is known to proceed slowly at room temperature. Is it possible to make the reaction proceed at a faster rate without changing the temperature ?

(c) A factory that specializes in the refinement of transition metals such as titanium was on fire. The firefighters were advised not to douse the fire with water. Why ?



(d) Predict the relative strengths of the oxoacids in each of the following groups :

(i) HClO, HBrO and HIO

(ii) HNO<sub>3</sub> and HNO<sub>2</sub>.

(e) At the start of a reaction, there are 0.249 mol N<sub>2</sub>,  $3.21 \times 10^{-2}$  mol H<sub>2</sub> and  $6.42 \times 10^{-4}$  mol NH<sub>3</sub> in a 3.50 L reaction vessel at 375°C. If the equilibrium constant ( $K_C$ ) for the reaction :



is 1.2 at this temperature, decide whether the system is at equilibrium. If it is not, predict which way the net reaction will proceed.

5×6=30

P.T.O.

5. (a) Calculate the solubility of silver chloride (in g/L) in a  $6.5 \times 10^{-3}$  M silver nitrate solution.

(b) How does the entropy a system change for each of the following processes ?

(i) A solid melts

(ii) A liquid freezes

(iii) A liquid boils

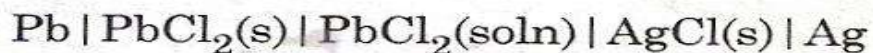
(iv) A vapour condenses to a liquid

(v) A solid sublimates

(vi) Urea dissolves in  $H_2O$ .



(c) For the following cell :



the potential at 298 K is 0.490 V and temperature

coefficient of the emf is  $-1.86 \times 10^{-4} \text{ V K}^{-1}$ .

Calculate the  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  for the reaction.

at 298 K.

(d) Define quantum yield. How is quantum yield determined experimentally ?

(e) Steel hardware, including, nuts and bolts, is often coated with a thin plating of Cadmium.

P.T.O.

Explain the function of the Cadmium layer. What is the difference between a Galvanic cell and electrolytic cell ?

Or

Discuss Jahn-Teller effect.

5×6=30

6. (a) List *two* chemical and *two* physical properties that distinguish a metal from a non-metal. State whether each of the following elements are metals, metalloids, or non-metals :

(i) Cs

(ii) Ge



(iii) I

(iv) Kr

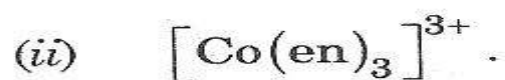
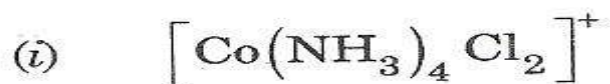
(v) W

(vi) Ga

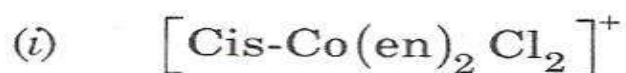
(vii) Te

(viii) Bi.

(b) Draw structures of all the geometric and optical isomers of each of the following cobalt complexes :



(c) Write the IUPAC names for the following ions and compounds :



(d) Compounds containing the  $\text{Sc}^{3+}$  ions are colourless, whereas those containing the  $\text{Ti}^{3+}$  ions are coloured. Explain.

(e) Why is atomic emission more sensitive to flame instability than atomic absorption ?

What is the function of flame in flame photometry ?

5×6=30

7. (a) Set up the Schrödinger equation for a particle in a one-dimensional box and hence derive the expression :

$$E = \frac{n^2 h^2}{8mL^2}.$$

- (b) What are the permitted values of the quantum number  $n$  ? Explain why a zero value of  $n$  is not permitted ?
- (c) What is the importance of Lambert-Beer's law in quantitative analysis ? What are its limitations ?

(d) Actinides have a greater tendency to form complexes than Lanthanides. Explain.

(e) Lanthanoid ions typically display weak but sharp adsorption spectra. Explain.

5×6=30