This question paper contains **16+4** printed pages]

H.P.A.S. (Main)—2011

CHEMISTRY

Paper I

Time : 3 *Hours* *Maximum Marks :* 150

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

1. (*a*) Write the Hamiltonian for H_2^+ and H_2 molecular species.

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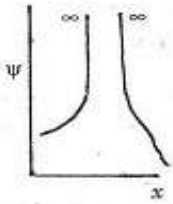
(b) Which of the diagrams given below satisfies the condition for the acceptability of a wave function ψ :

(i)



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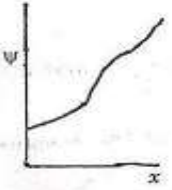

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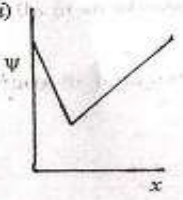

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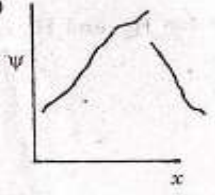


(c) In an electrolysis experiment of an aqueous solution of Na_2SO_4 the substance formed at anode is :

(i) Na

(ii) SO_2

(iii) O_2

(iv) H_2.

(d) Complete the following equations and name the elements x, y and z :

(i) $^{242}_{94}Pu + ^{22}_{10}Ne \rightarrow ^{260}_{104}X + ...$

(ii) $^{249}_{98}C_f + ^{15}_{7}N \rightarrow ^{260}_{105}Y + ...$

(iii) $^{249}_{98}C_f + ^{18}_{8}O \rightarrow ^{263}_{106}Z + ...$

(e) Write Gibbs adsorption isotherm equation for adsorption from solution.

(*f*) State third law of thermodynamics.

(*g*) State zeroth law of thermodynamics.

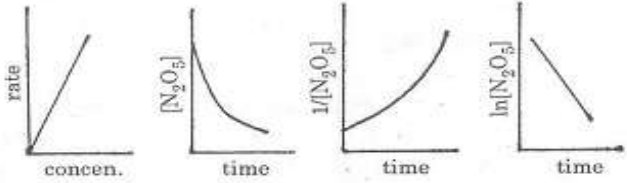
(*h*) Give electrode reactions in a lead storage cell or battery (a source of electrical energy for automobiles). Why we do not require a porous partition in this cell ?

(*i*) Work out the number of unpaired electron in the following ionic species :

La^{+3}, Ce^{+4}, Lu^{+3}, Yb^{+2}, Eu^{+2}, Tb^{+4} and Gd^{+3}.

(*j*) For the hypothetical reaction, $A + B \rightarrow C + D$ the activation energy is 32 kJ/mol. For the reverse reaction, $C + D \rightarrow A + B$, the activation energy is 58 kJ/mol. Is the reaction exothermic or endothermic ? Give schematic diagram to show the above reactions. 10×3=30

2. (a) The decomposition of N_2O_5 in the gas phase has been thoroughly studied. Some data for the concentration of N_2O_5 have been plotted below. Infer with reasons the order of a reaction and deduce rate law and hence $t_{½}$ of the reaction :



(b) Give chain mechanism for the formation of HCl in the photochemical reaction of hydrogen and chlorine. Derive rate law expression for the formation of HCl in the above photochemical reaction using steady state approximation.

(c) If the rate constant for a reaction triples in value when the temperature rises from 300 K to 310 K. What is the activation energy of the reaction ? [log 2 = 0.3010 and log 3 = 0.4771].

(d) The NO and O_2 gaseous reaction may occur as follows :

Mechanism I :

$NO + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} OONO(g)$ fast reaction

$NO + OONO \xrightarrow{k_2} 2NO_2(g)$ slow reaction

Overall reaction : $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

Mechanism II :

$NO(g) + NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g)$ fast reaction

$N_2O_2 + O_2(g) \xrightarrow{k_2} 2NO_2(g)$ slow reaction

Overall reaction : $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

Show that both reaction mechanisms lead to the same observed rate law.

(e) The dehydration of ethane to ethene follows the chain mechanism given below :

(i) $CH_2CH_3 \xrightarrow{k_1} 2\dot{C}H_3$

(ii) $\dot{C}H_3 + CH_3CH_3 \xrightarrow{k_2} CH_4 + \dot{C}H_2CH_3$

(iii) $\dot{C}H_2CH_3 \xrightarrow{k_3} CH_2 = CH_2 + \dot{H}$

(iv) $\dot{H} + CH_3CH_3 \xrightarrow{k_4} H_2 + \dot{C}H_2CH_3$

(v) $\dot{H} + \dot{C}H_2CH_3 \xrightarrow{k_5} CH_3CH_3$.

Write the rate expressions for the formation of C_2H_4, $\dot{C}H_3$, $\dot{H}$ and $CH_3\dot{C}H_2$ and hence show that $\left[\dot{C}H_3\right] = \frac{2k_1}{k_2}$. 5×6=30

3. (a) Distinguish between :

(i) physisorption and chemisorption

(ii) adsorption isobar and adsorption isotere.

(b) Give essential features of Langmuir's theory of adsorption and hence derive an expression for Langmuir's adsorption isotherm. Show that at normal pressure Langmuir's adsorption isotherm becomes identical with Freundlich adsorption isotherm.

(c) A solution of palmitic acid (molecular weight 256) in benzene contains 4.24 g of acid per dm^3. Where this solution is dropped on a water surface the benzene evaporates and the palmitic acid forms a monolayer (molecular) film of the solid type. If we wish cover an area 500 cm^2 with a monolayer, what volume of the solution should be used. [The area covered by one palmitic acid molecule may be taken as 0.21 nm^2]

(d) What do you understand by heterogeneous and homogeneous catalysis ? Give *one* suitable example in each case. Discuss the mechanism and kinetics of acid-base catalysis in which a proton is transferred from an acid $\overset{+}{A}H$ to the substrate S, the acid form of the substrate reacts with a base A to the form the product P

$$\left[S + \overset{+}{A}H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S\overset{+}{H} + A;\ S\overset{+}{H} + A \xrightarrow{k_2} \overset{+}{A}H + P\right]$$

(e) Normalise the wave function :

$$\psi = A \sin \frac{n\pi}{a} x,$$

for a particle in one-dimensional box. 5×6=30

4. (a) Write the time independent Schröndinger equation of a particle in three-dimensional cubical box with edges of length 'a'. Give the final result of the solution of this equation.

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Explain the meaning of degeneracy of states by taking an example of an energy level which six fold degenerate. What is the total energy of the particle in this energy level ?

(b) Define heat of combustion. The heat of combustion data is obtained by using Bomb calorimeter.

Why the mathematical statement, $\Delta H = \Delta E + P\Delta V$, made by an experimentalist working on Bomb calorimeter is wrong ?

Calculate heat of transition of yellow phosphorus to red phosphorus from the following data :

'One gram atom of yellow phosphorus on oxidation to phosphoric acid gives 2386 cal. of heat. Red phosphorus on similar treatment gives 2115 cal. of heat.'

(c) Using Euler criterion or the reciprocity relationship [i.e., if x is a single valued function of the variables y and z, then $dx = Mdy + Ndz$ where M and N are also functions of y and z. $\left(\frac{\partial M}{\partial z}\right)_y = \left(\frac{\partial N}{\partial y}\right)_z$]. Obtain Maxwell relations from E, H, A and G equations, symbols have their usual meanings.

Using one of the above Maxwell relations and third law of thermodynamics show that :

$$\lim_{T \to 0} \left(\frac{\partial V}{\partial T}\right)_P = 0.$$

(d) Distinguish between open and closed. What do you understand by partial molar property ? Explain the concept of chemical potential and its significance.

(e) Using the following thermodynamic data, justify the feasibility of the reaction :

$NH_4NO_3(s) + 3H_2(g) \rightarrow 3H_2O(g) + N_2H_4(g)$

	ΔH°_f kJ mol^{-1}	ΔS° J/mol K
NH_4NO_3	–365.0	150.00
$H_2(g)$	0.00	130.00
$H_2O(g)$	–242.0	189.00
N_2H_4	50.0	120.00

5×6=30

5. (a) Name *three* indicator electrodes which are used to measure hydrogen ion concentration in a given solution. Out of these three electrodes describe the construction of an electrode which can also be used as standard electrode. Give the limitation of these electrodes.

(b) Define a fuel cell. Give a schematic diagram of methane-oxygen fuel cell. Give electrode reactions and a cell reaction. What is the efficiency of such a fuel cell ?

(c) Explain what do you understand by corrosion. Explain mechanism of rusting of iron. Why the process of rusting is speeded up by the formation of rust ?

(d) A zinc rod is placed in 0.1 M solution of zinc sulphate at 25°C. Assuming the electrolyte to be 40% dissociated at this temperature. Calculate the potential of this electrode. If this electrode is now coupled with a standard hydrogen electrode which is acting as cathode and forms a electrochemical cell. Find whether this cell will function or not. $\left(E^0_{Zn^{+2}/Zn} = -0.76\ V\right)$

(e) Give Debye Hückel limiting law equation. Explain its experimental validity. Calculate the mean activity coefficient $r_{\pm}$ of sodium chloride at a molality of 0.01 at 25°C. 5×6=30

6. (a) Complete the following chemical equations of acid-base reaction in non-aqueous solvents and explain each reaction :

(i) $NH_4NO_3 + KNH_2 \xrightarrow[\text{liquid } NH_3]{\text{in}}$

(ii) $CH_3COONa + HCl \xrightarrow[\text{glacial acetic acid}]{\text{in}}$

(iii) $SOCl_2 + Cs_2SO_3 \xrightarrow[\text{liquid } SO_2]{\text{in}}$

(b) Explain complex formation in the following reaction with chemical equation :

(i) $FeCl_3$ and triethyl ammonium cyanide in liquid HCN.

(ii) Zinc nitrate and potash amide in liquid NH_3.

(c) Explain ammonolytic reaction between Hg_2Cl_2 and NH_3. What will be the pH of the following solutions in liquid ammonia :

(i) 1 M $\left[NH_4^+\right]$ = 1 M

(ii) Neutral solution

(iii) $\left[NH_2^-\right]$ = 1 M.

(d) Explain autoionisation of the non-aqueous solvents :

(i) Liquid $SeOCl_2$

(ii) Liquid HCN

(iii) Liquid HF.

(e) Complete the following chemical equations of redox reactions in non-aqueous solvents and explain each reaction :

(i) $Sn(NH_2)_6^{-4} + I_2 \rightarrow$

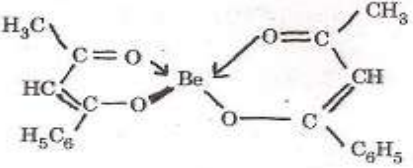
(*ii*) $N_2O + 2K + NH_3 \rightarrow$

(*iii*) $6KMnO_4 + 6KNH_2 \rightarrow$

(*iv*) $K_2MnO_4 + 4K + 3NH_3 \rightarrow$ 5×6=30

7. (*a*) What kind of isomerism is seen in the following metal complexes ? Explain :

(*i*) (A)



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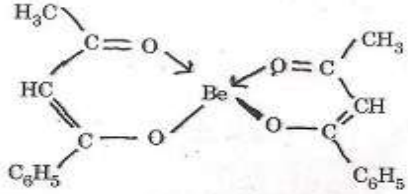
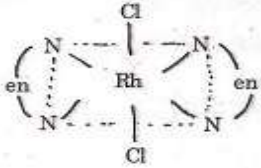


bis-(benzoylacetonato) Be(II) complex.

(*ii*) (A)



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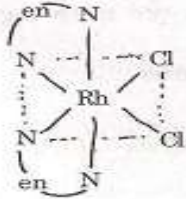
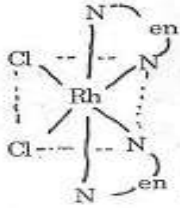


(C)



dichloro bis(ethylene diamine) rhodium (III).

(*iii*) Two distinct compounds $Co(NH_3)_5\ BrSO_4$ are known one of them gives a white precipitate with $BaCl_2$ while other gives a white precipitate with $AgNO_3$. Write the formula of the two compounds and name each of them.

P.T.O.

(b) Explain the following with the help of crystal field theory :

(i) Hydrated Cu(II) salts are blue in colour whereas anhydrous Cu(I) salts are colourless.

(ii) Co(III) is stabilised in the presence of strong field ligands while Co(II) is stabilised in the presence of weak field ligands.

(iii) Low spin tetrahedral complexes are not known.

(c) Which of the following complexes in the pair given below have high Δ_0 and why :

(i) $Fe(C_2O_4)_3^{-4}$ and $Fe(C_2O_4)_3^{-3}$

(ii) $Co(NH_3)_6^{+3}$ and $Rh(NH_3)_6^{+3}$

(iii) $[Cr(en)_3]^{+3}$ and $Cr(C_2O_4)_3^{-3}$.

(*d*) Give salient features of organometallic compounds of transition elements taking the example of bis (pentahaptocyclopentadienyl) iron and discuss bonding in these complexes briefly.

(*e*) Give salient features of complexes of π-acceptor ligands. Discuss bonding in metal carbonyls (linear M-C-O group). 5×6=30

8. (*a*) Complete the following chemical equations :

(*i*) $ThO_2 + CCl_4 \xrightarrow{600°C}$

(*ii*) $UCl_4 + K_2C_8H_8 \xrightarrow{THF}$

(*iii*) $EuCl_2 + K_2C_8H_8 \xrightarrow{liq.\ NH_3}$

(*iv*) $AmO_2 + 2CCl_4 \xrightarrow{800°C}$

(*v*) $PuO_3 + H_2 + 6HF \xrightarrow{500°C}$

(*vi*) $(NH_4)_2U_2O_7 \xrightarrow{250°C}$

(b) The magnetic moment as calculated by spin only formula agrees well with experimental value for gadolinium but not for other lanthanides. Some lanthanides are diamagnetic while others are paramagnetic. Explain this magnetic behaviour in lanthanides.

(c) Discuss +2 oxidation states in lanthanides and actinides.

(d) Why lanthanides are rare earths. Are these rare elements ? Describe ion exchange procedures in separation of lanthanides in their preparation.

(e) (i) Discuss electronic configuration of lanthanides and hence oxidation states very briefly.

(ii) Explain actinides have greater tendency to form complexes than lanthanides. 5×6=30