



**WEST BENGAL STATE UNIVERSITY**

B.Sc. Honours PART-I Examinations, 2018

**CHEMISTRY-HONOURS**

**PAPER-CEMA-I**

Time Allotted: 4 Hours

Full Marks: 100

*The figures in the margin indicate full marks.  
Candidates should answer in their own words and adhere to the word limit as practicable.  
All symbols are of usual significance.*

**Use separate answer scripts for Group-A [CEMAT-11-IA & CEMAT-11-IB and Group-B [CEMAT-11-OA & CEMAT-11-OB]**

**Group-A**

**CEMAT-11-IA**

**Answer any two questions taking one from each unit**

**Unit – I**

1. (a) Show diagrammatically the variation of radial electron density distribution function with  $r$  for the orbitals 3s and 3p in hydrogenic systems. Interpret the diagrams. 3
- (b) Pauli's exclusion principle gives the measure of maximum capacity of an orbital to accommodate the electrons. Justify. 2
- (c) Work out the ground state term symbol for  $\text{Fe}^{2+}$  and  $\text{V}^{3+}$  ions. 2
- (d) The slow neutrons are better projectiles compared to the fast neutrons in the nuclear fission of  $^{235}\text{U}$ . Explain. 2
- (e) The  $^{14}\text{C}$  to  $^{12}\text{C}$  ratio in a piece of old wood is 20% to that in a live sample. Calculate the age of the old wood. ( $t_{1/2}$  of  $^{14}\text{C}$  = 5730 years) 2
- (f) Which one of the following is more unstable nuclei? 2  
(i)  $^{16}\text{C}$                       (ii)  $^{16}\text{N}$   
State the possible mode of decay of both the nuclei.
2. (a) State the limitations of auf bau principle with necessary illustrations. 3
- (b) Calculate the shortest wavelength in the absorption spectrum of hydrogen (Rydberg's constant =  $109737\text{ cm}^{-1}$ ) 2
- (c) What will be the number of orbitals in different sub levels for  $n = 5$ ? Hence work out the total number of orbitals in the level. 2
- (d) What are magic numbers in the context of nuclear stability? Explain with illustrative examples. 3

- (e) The 'Q' value for the  ${}^3\text{He}(n, p)$  reaction is 0.76 MeV. Calculate the nucleonic mass of  ${}^3\text{He}$ . (Given :  $m_n = 1.00867\text{u}$ ,  $m_p = 1.00783\text{u}$  and  $m$  of  ${}^3\text{H} = 3.01605\text{u}$ ).

### Unit – II

3. (a) Calculate the  $Z^*$  for a  $3d$  electron in  $\text{Cu}^+$  ion. 3
- (b) Account for the higher electron affinity of Au (2.3 eV) than that of either Ag (1.2 eV) or Cu (1.22 eV). 2
- (c) The valence shell electronic configuration of both Ca and Zn is  $4s^2$  but first ionisation energy of Ca is lower than Zn. Explain. 2
- (d) Calculate the electronegativity of As in  $\text{AsF}_3$  and  $\text{AsF}_5$ . Given  $E_{\text{As-As}} = 146\text{ kJ/mol}$ ;  $E_{\text{F-F}} = 155\text{ kJ/mol}$ ;  $E_{\text{As-F}} = 484\text{ kJ/mol}$ ;  $E_{\text{As-F}}(\text{AsF}_3) = 406\text{ kJ/mol}$ ;  $\chi_p(\text{F}) = 4.0$ . 3
- (e) Using Pauling's method, calculate the radii of  $\text{K}^+$  and  $\text{Cl}^-$  ions. The observed  $\text{K}^+ - \text{Cl}^-$  distance in KCl crystal is 314 pm. 2
4. (a) Rationalise the trends in specified atomic properties in the following cases: 4
- | Properties                   | Li   | Be    | B    |
|------------------------------|------|-------|------|
| First ionization energy (eV) | 5.39 | 9.32  | 8.30 |
|                              | C    | N     | O    |
| First electron affinity (eV) | 1.27 | -0.07 | 1.46 |
- (b) Assuming Allred-Rochow electronegativity of gold is 2.54, calculate  $Z^*$  of gold. Covalent radius of gold is 140 pm. 3
- (c)  $\text{SnCl}_4$  is relatively more stable than  $\text{SnCl}_2$  but the reverse is true for the corresponding lead compounds. Justify. 3
- (d) Atomic radii of Zr and Hf are almost identical – Explain. 2

### CEMAT-11-IB

Answer any *two* questions taking one from each unit

#### Unit – I

5. (a)  $\text{NH}_4\text{F}$  crystallises as wurtzite structure (Madelung constant 1.641 and Born exponent 8). The closest distance between  $\text{NH}_4^+$  and  $\text{F}^-$  ions in the crystal is 2.63 Å. Calculate the lattice energy of  $\text{NH}_4\text{F}$ . 3
- [Given  $\epsilon_0 = 8.854 \times 10^{-12}\text{ C}^2/\text{Nm}^2$ ]
- (b) Solubility of  $\text{HgX}_2$  in water decreases from X = chloride to iodide. Explain. 2
- (c) Explain the trend of H-M-H bond angles:  $\text{NH}_3 > \text{NF}_3$  but  $\text{PH}_3 < \text{PF}_3$ . 3
- (d) Predict the hybridisation of the central atom and structure of the following molecules: 3
- $\text{H}_5\text{IO}_6$ ,  $\text{SO}_2\text{Cl}_2$  and  $\text{HClO}_4$

- (e) State two limitations of VSEPR theory. 2
6. (a) Why does KCl adopt NaCl structure in spite of radius ratio greater than 0.732? Given  $r_{K^+}$  in coordination number 6 = 1.38 Å and coordination number 8 = 1.51 Å.  $r_{Cl^-}$  = 1.81 Å. Madelung constants for NaCl and CsCl structure are 1.748 and 1.763 respectively. 3
- (b) What are the various kinds of stoichiometric defects found in ionic crystals? Explain with examples. How do such defects affect the density of the crystals? 3
- (c) Using VSEPR theory predict the shapes of the following: 3  
 $IO_2F_2^+$ ,  $SbF_6^-$ ,  $XeOF_4$
- (d) Why is the melting point of CuCl (422°C) much lower than that of KCl (776°C)? 2
- (e) Between  $CH_3$  and  $CF_3$ , one is pyramidal and other is planar. Explain the structures. 2

### Unit-II

7. (a) Arrange the given ions in order of increasing acidity in aqueous medium with justification:  $[Ni(H_2O)_6]^{2+}$ ,  $[Fe(H_2O)_6]^{3+}$ ,  $[Al(H_2O)_6]^{3+}$ ,  $[Mn(H_2O)_6]^{2+}$  3
- (b) Which of the following reactions have  $K_{eq} > 1$ ? 2  
 (i)  $R_3P-BBr_3 + R_3N-BF_3 \longrightarrow R_3P-BF_3 + R_3N-BBr_3$   
 (ii)  $AgCl_2^- + 2CN^- \longrightarrow [Ag(CN)_2]^- + 2Cl^-$
- (c) The  $pK_a$  values of  $NH_4^+$ , HF and  $HCO_3^-$  are 9.2, 3.2 and 10.2 respectively. Calculate pH of the 0.01 (M) solutions of the corresponding conjugate weak bases. 3
- (d) 100 ml of a buffer solution of pH = 9 is to be prepared by mixing 0.1N HCl and 0.1N  $NH_4OH$ . Calculate the volume of each solution required to prepare the buffer. [Given  $K_b = 2 \times 10^{-5}$ ] 2
- (e)  $SnCl_2$  can act both as Lewis acid and Lewis base. Explain. 2
8. (a) Identify the structural difference of  $H_3PO_3$  and  $H_3AsO_3$  using Pauling's rules for prediction of the strengths of oxo acids. 3  
 $[pK_a (H_3PO_3) \sim 2.0; pK_a (H_3AsO_3) \sim 9.0]$
- (b) Arrange according to increasing Lewis acid character: 3  
 $BF_3$ ,  $BCl_3$ ,  $BBr_3$ ,  $BI_3$   
 Explain your point of view.
- (c) Calculate the pH of the following solutions: 4  
 (i) 50 ml of 0.1 N HCl is mixed with 50 ml of 0.2 N aqueous  $NH_3$   
 (ii) 50 ml of 0.2 N HCl is mixed with 50 ml of 0.1 N aqueous  $NH_3$   
 $[pK_b \text{ of aqueous } NH_3 = 4.7]$
- (d) Formaldehyde can enhance the acid strength of  $NH_4^+$  significantly. Explain. 2

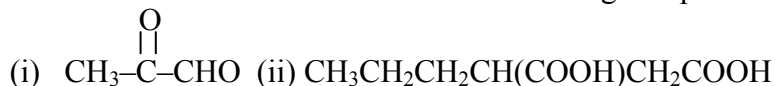
## Group-B

## CEMAT-11-OA

Answer any *two* questions taking one from each unit

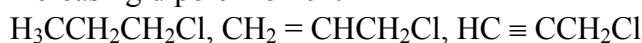
## Unit-I

9. (a) Write down the IUPAC names of the following compounds: 2

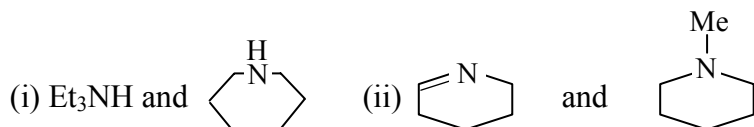


- (b) Draw the
- $\Pi$
- M.O.'s of 1, 3, 5-hexatriene and indicate HOMO in the ground state. 4

- (c) Arrange with explanations the following compounds in their order of increasing dipole moment 3



- (d) Predict with proper reasoning which member in each of the following pair behaves as a better base towards
- $\text{BH}_3$
- : 3



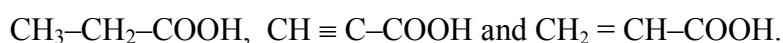
- (e) Calculate the double bond equivalent (DBE) of the molecule with molecular formula
- $\text{C}_8\text{H}_{11}\text{ON}$
- . 1

- 10.(a) Draw the canonicals of 'acyl cation' and indicate which is more stable with reason. 2

- (b) Using Frost- diagram, label bonding and antibonding
- $\Pi$
- molecular orbitals of benzene and hence explain why it is aromatic in nature. 2+1

- (c) Compared to 4-nitrophenol, 2-nitrophenol is more soluble in benzene and less soluble in water. Explain. 2

- (d) Arrange the following compounds in their increasing order of stability with proper explanation: 2



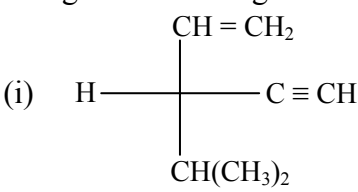
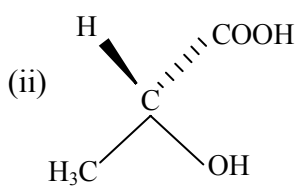
- (e) Arrange the following compounds in order of their increasing heat of hydrogenation value with explanation. 3



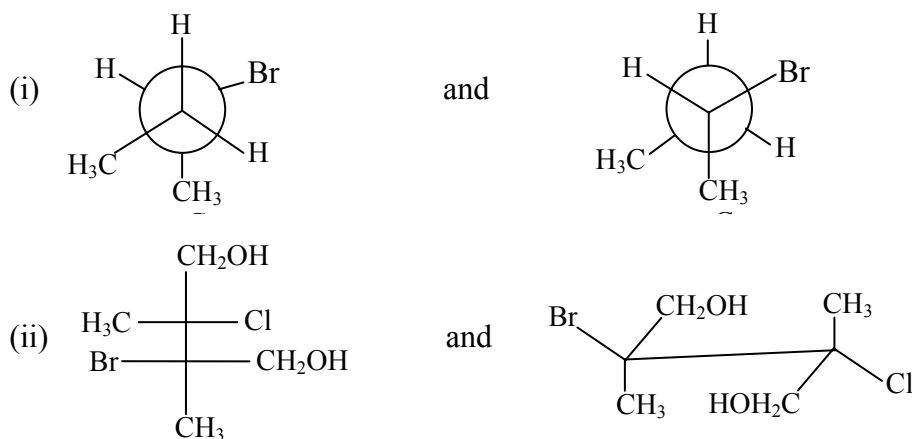
- (f) Draw the structure of 12-C-4. 1

## Unit-II

- 11.(a) Represent
- meso*
- tartaric acid in Fischer projection formula. What type of conformation does it represent? Represent
- meso*
- tartaric acid in its most stable conformation in sawhorse perspective formula and Newman projection formula. 1+1+2

- (b) Define the following terms with suitable example: 3  
 (i) Centre of Symmetry and (ii) Stereogenic Centre.
- (c) Designate the configuration of the following compounds by R/S notation. 2
- (i)  (ii) 
- (d) How can primary kinetic isotope effect be used to establish the r.d.s. in the nitration of benzene by mixed acid? – Explain. 3

- 12.(a) Draw the conformational energy diagram for 1, 2-difluoroethane (Angle of torsion vs. Potential energy). Explain the maxima and minima qualitatively. 3
- (b) Write down the possible stereoisomers of 1-bromo-1, 2-diphenylpropane with R/S and threo/erythro designations. 3
- (c) Label the following pairs of structures as homomer, enantiomer or diastereoisomer. 3



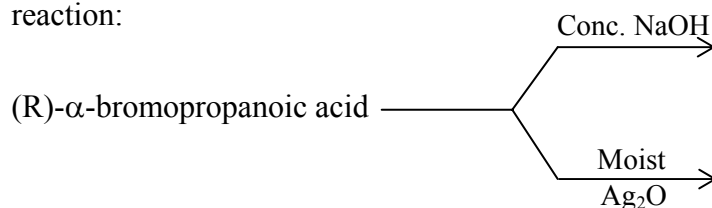
- (d) Draw the energy profiles of one step endothermic and exothermic reactions. What does Hammond postulate predict about the transition states of these reactions? 3

### CEMAT-11-OB

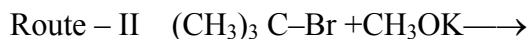
Answer any *two* questions taking one from each unit

#### Unit – I

- 13.(a) Acetylene is less reactive towards bromine than ethylene – Explain. 2
- (b) Give the products with the configurational descriptors (R/S) in the following reaction: 3

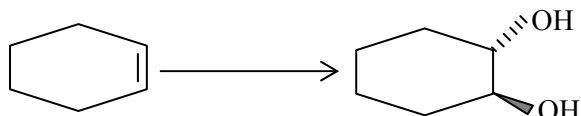


- (c) For the synthesis of Me-O-CMe<sub>3</sub> two plausible reaction routes are given below. Find out the favourable reaction route with explanation. 2

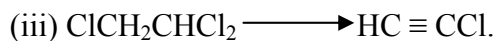
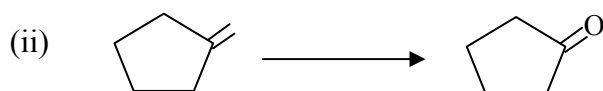
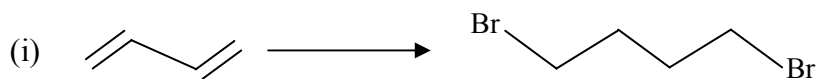


- (d) Reactions of both 1-butene and 2-butene with HCl give the same product but with different rates. Explain the observation with the help of energy profiles and hence indicate the faster reaction between them. Comment on the regio- and stereoselectivity of the reactions. 4

- (e) Carry out the following conversion showing plausible mechanism. 2



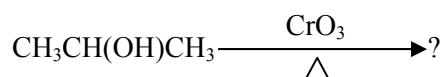
- 14.(a) Carry out the following conversions showing mechanisms. 2×3 = 6



- (b) Dehydration with conc. H<sub>2</sub>SO<sub>4</sub> of either (R) or (S) PhCH(OH)CH<sub>2</sub>CH<sub>3</sub> lead to the same product. Write the product and explain with mechanism. 2

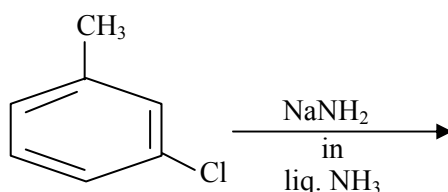
- (c) Polar aprotic solvent is suitable for conducting S<sub>N</sub>2 reaction. Explain. Give an example of such a solvent. 2+1

- (d) Write the product with the mechanism involved. 2

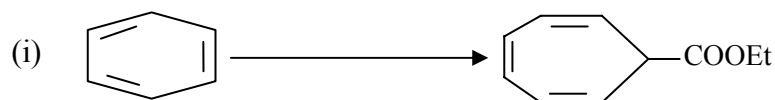


### Unit – II

- 15.(a) Write down the possible products formed in the following reaction. Which would be the major product? Explain with mechanism. 3



- (b) Carry out the following conversions. Show the plausible mechanism for the first conversion.  $2.5 \times 2 = 5$



- (c) What happens when 2, 4-dinitrofluorobenzene is treated with primary alkylamine? Explain the formation of the product. 2
- (d) What is ylide? Give one example of it. 2
- 16.(a) What are  $\sigma$ - and  $\Pi$ -complexes in connection with aromatic electrophilic substitution reaction? Explain with a suitable reaction. 3
- (b) What is nitrene? Give one suitable process to generate it. Mention one of its uses in organic synthesis. 3
- (c) Explain the following observations. 2+2
- (i) Nitrobenzene undergoes chlorination with deactivation and shows meta orientation.
- (ii) Chlorobenzene undergoes nitration with deactivation and shows *O/p*-orientation.
- (d) What is a zwitterion? Write down with a suitable example. 2

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## WEST BENGAL STATE UNIVERSITY

B.Sc. Honours PART-I Examinations, 2018

### CHEMISTRY-HONOURS

#### PAPER-CEMA-II

Time Allotted: 2 Hours

Full Marks: 50

*The figures in the margin indicate full marks.  
Candidates should answer in their own words and adhere to the word limit as practicable.  
All symbols are of usual significance.*

#### CEMAT-12-PA

**Answer any two questions taking one from each Unit**

##### Unit-I

1. (a) The number of gas molecules of mass  $m$  having speed in the range  $c$  and  $c + dc$  is given as  $dN = Ac^2 e^{-\frac{mc^2}{2k_B T}} dc$ . 3  
Obtain an expression for 'A'. What is the unit of 'A'?  
Given:  $\int_0^{\infty} x^2 e^{-ax^2} dx = \frac{1}{4} \left( \frac{\pi}{a^3} \right)^{1/2}$ .
- (b) The mass of each molecule of a Maxwellian gas is  $5.18 \times 10^{-23}$  g. Find the average momentum of the gas molecules at  $27^\circ\text{C}$ . 2
- (c) Calculate the frequency of nitrogen-nitrogen collisions in one cubic centimeter of air at 1 bar and  $20^\circ\text{C}$ . Assume that 80% of the molecules are nitrogen molecules. 4  
The collision cross section of nitrogen molecule is  $4.5 \times 10^{-19} \text{ m}^2$ .
- (d) The principle of equipartition of energy predicts the value of heat capacity ratio  $\gamma$  ( $\gamma = C_p/C_v$ ) for  $\text{H}_2(\text{g})$  more accurately at 110 K compared to that at 10 K. The Boyle temperature of  $\text{H}_2(\text{g})$  is 110 K. Comment on the result. 2
- (e) The mean free path of an ideal gas at  $27^\circ\text{C}$  and 1.0 atm is  $10^{-5}$  cm. Suppose the gas is taken to a high altitude where the pressure is only 100 mm of Hg. Calculate the temperature at which the gas will have the same mean free path at the high altitude. 2
2. (a) Write down Maxwell's expression for the distribution of molecular speeds in three dimensions and derive the expression for the number of molecules with translational kinetic energies greater than  $\varepsilon'$ , assuming  $\varepsilon' \gg kT$ . 5

- (b) Find the dimension of  $1/(\sigma^2 n \bar{c})$  where  $\sigma$ ,  $n$  and  $\bar{c}$  are the collision diameter, number of molecules per unit volume and mean speed of molecules respectively. 2
- (c) Show schematically the Maxwellian distribution of speed of gas molecules. Indicate on the plot the following. 4
- (i) most probable, rms and average speed (relative values)
- (ii) fraction of molecules having speed greater than a certain value ( $c$  say)
- How will be the plot be different for  $\text{CO}_2$  and He at the same value of temperature?
- (d) Find an expression for the number of molecules striking the unit area of wall of container per unit time. 2

### Unit-II

3. (a) The Lennard-Jones potential is expressed as  $U(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$ , 3

where  $r$  is the internuclear separation. Find an expression for the minimum value of the internuclear separation ( $r_{\min}$ ) in terms of  $\sigma$  and hence show that the minimum value of the potential energy is  $U(r_{\min}) = -\epsilon$ .

- (b) Calculate the change in surface energy when two identical mercury droplets of diameter 2 mm merge to form one drop (assume the process to be isothermal). Surface tension of mercury =  $490 \text{ dyne cm}^{-1}$ . 3
- (c) For the He gas,  $P_c = 2.24 \text{ atm}$  and  $T_c = 5.2 \text{ K}$ . Calculate the radius of the molecule of helium gas. 3
- (d) The virial equation in terms of  $\bar{V}$  ( $\bar{V}$  is molar volume) is given as: 3

$$Z = 1 + \frac{B_{2V}(T)}{\bar{V}} + \frac{B_{3V}(T)}{\bar{V}^2} + \dots$$

Where,  $Z$  is the compressibility factor. Express the van-der Waals equation for a gas in terms of the virial equation and hence justify that in the limit of every low pressure or very high temperature the behavior of the gas approaches ideality.

4. (a) Draw schematically the  $PV$  vs  $P$  isotherms for  $\text{N}_2$  stating the characteristic features at temperatures below, above and at  $T_B$ . 3
- (b) The second virial coefficient of methane can be approximated by the empirical equation  $B(T) = a + be^{-c/T^2}$ , where  $a = -0.1993 \text{ bar}^{-1}$ ,  $b = 0.2002 \text{ bar}^{-1}$  and  $c = 1131 \text{ K}^2$ . 3
- What is the Boyle temperature for methane?
- (c) Glycerol flows faster at higher temperatures. — Explain. 3
- (d) Find the numerical value of compressibility factor ( $Z$ ) of a gas that obeys the equation of state  $P(V - nb) = nRT$ . The pressure and temperature are such that  $V/n = 10b$ . 3

## CEMAT-12-PB

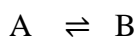
Answer any *two* questions taking one from each Unit

## Unit-I

5. (a) For a fixed change in volume, the reversible adiabatic expansion will produce the maximum drop in temperature than the irreversible one. Justify or criticize. 2
- (b) The temperature of an ideal gas, with constant heat capacity, is changed from  $T_1$  to  $T_2$  by a constant pressure process and by a constant volume process, then  $\Delta S_P = \Delta S_V$  ( $\Delta S$  refers of the gas). Justify or criticize. 3
- (c) Prove that:  $C_P - C_V = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P$  and hence find the condition when  $C_P = C_V$ . Give one example of such a system. 4
- (d) Explain whether the heat of an uncatalysed reaction is different from that of a catalysed reaction at a given temperature. When will be the heat of a reaction independent of temperature? 4
6. (a) Justify or criticize any one of the following statements: 2
- (i)  $\Delta H = q$  for a process in which the initial and final pressures are same but the pressure is not constant throughout.
- (ii) Any adiabatic process must be isentropic.
- (b) Show that  $\left( \frac{\delta\alpha}{\delta p} \right)_T + \left( \frac{\delta\beta}{\delta T} \right)_p = 0$ , where  $\alpha$  is the coefficient of thermal expansion and  $\beta$  is the compressibility factor. 2
- (c) Using a suitable thermodynamic equation of state evaluate the quantity  $\left( \frac{\partial U}{\partial V} \right)_T$  for an ideal gas and a van-der Waals gas. Comment on the results. 4
- (d) 1 mole of an ideal gas is subject to undergo a reversible cycle involving the following steps: 5
- Step 1:* Isothermal expansion at temperature  $T_1$  from  $p_1, V_1 \rightarrow p_2, V_2$
- Step 2:* Isochoric change of state from  $p_2, T_1 \rightarrow p_3, T_2$  ( $p_3 < p_2$ )
- Step 3:* Adiabatic compression from  $p_3, V_2, T_2 \rightarrow p_1, V_1, T_1$ .
- (i) Represent the cycle on a properly labeled  $p$ - $V$  diagram.
- (ii) Elucidate the expression for work-done for each step.
- (iii) Show that the efficiency of the cycle is  $\eta = 1 - \frac{T_1 - T_2}{T_1 \ln(T_1/T_2)}$ .

## Unit-II

7. (a) A first order reaction is 20% complete in 15 minutes at 300 K. The same reaction is 39% complete in 10 minutes at 320 K. Calculate the energy of activation ( $E_A$ ). Will the result (the value of  $E_A$ ) differ if the reaction be of second order? 4
- (b) A catalyst increases the rate of the forward reaction by 10%. Calculate the change of rate (increase / decrease) of the backward reaction. 2
- (c) Consider the following process 4



$$t = 0 \quad a \quad 0$$

$$t = t \quad a - x \quad x$$

Find  $x$  as a function of  $t$  and find also the value of  $x$  as  $t \rightarrow 0$  and  $t \rightarrow \infty$ .

- (d) It is customary, in the study of kinetics of a reaction, to “chill” the reaction by adding an aliquot of the reaction mixture in a *large volume of cold water*. Explain why these two conditions are used. 2
8. (a) Write the Arrhenius equation for the variation of rate constant with temperature. Show plots of (i)  $k$  vs  $T$  and (ii)  $\log k$  vs  $1/T$ . 2
- (b) Draw schematically the energy profile for an exothermic reaction and indicate (i) the activation energy for the forward and the backward reactions, (ii)  $\Delta H$  of the reaction, (iii) effects of addition of a positive catalyst. 3
- (c) (i) The rate constant ( $k$ ) of a reaction is given as a function of temperature ( $T$ ) as follows. 2

$$\log k = +2.1 - \frac{2.5}{T} + 0.5 \log T$$

Find the value of the activation energy of the reaction.

- (ii) Find the time for completion for a second order reaction. 2
- (d) Explain the term entropy of activation ( $\Delta S^\ddagger$ ). Comment on the sign of  $\Delta S^\ddagger$ . 3

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