

2011

CHEMISTRY

(Major)

Paper : 1.1

Full Marks : 60

Time : 2½ hours

The figures in the margin indicate full marks for the questions

1. Choose the correct option/Answer the following : 9-33
1×7=7

(a) What is the difference between standard enthalpy of ionization ($\Delta_{\text{ion}}H^\circ$) and ionization energy (E_i) for sodium?

(b) If we plot internal energy against temperature at constant volume, then the slope of the curve at any temperature gives

(i) C_p of the system

(ii) ΔU of the system

(iii) C_V of the system

(iv) μ_{JT} of the system

- (c) How do you define the criterion for the spontaneity of any process in terms of entropy (S)?
- (d) What is the order of a decay process of a radioactive isotope?
- (e) State the first law of thermodynamics.
- (f) The rate of reaction $A + B \rightarrow P$ is given by the equation $r = k[A][B]$. If B is taken in large excess, the order of the reaction will be
- 2
 - 1
 - 0
 - 3
- (g) When 1 mol of H_2O is added to a huge volume of pure ethanol at $25^\circ C$, the volume increases by $14 \text{ cm}^3 \text{ mol}^{-1}$. The quantity $14 \text{ cm}^3 \text{ mol}^{-1}$ is called
- specific volume of water
 - molar volume of water
 - partial molar volume of water in ethanol
 - partial molar volume of ethanol in water

12A—1500/125

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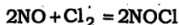
2. Answer the following :
- Write two limitations of thermodynamics.
 - Give the mathematical statement of Clausius inequality and its significance.
 - Give two examples of reactions catalyzed by enzymes.
 - Obtain an expression for the change in entropy in a reversible isothermal expansion of an ideal gas.
3. Answer any three of the following :
- What do you mean by a closed system? Give the definition of molar enthalpy of combustion. The molar enthalpy of combustion of $C(s, \text{graphite}) \rightarrow CO_2(g)$ is $-393.51 \text{ kJ mol}^{-1}$ and the molar enthalpy of combustion of $C(s, \text{diamond}) \rightarrow CO_2(g)$ is $-393.412 \text{ kJ mol}^{-1}$. Calculate the molar enthalpy of the transition $C(s, \text{graphite}) \rightarrow C(s, \text{diamond})$.
 - Starting from the definition of Gibbs free energy (G), deduce the relation between G and A to show the variation of G with T and P for a closed system. Based on these relations, draw the necessary graphs to show the variation of G with T and P for a closed system in its gaseous phases of a pure substance.

12A—1500/125

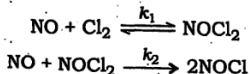
- (c) For the reaction $A \rightarrow P$, the rate law is given by

$$\frac{-d[A]}{dt} = k[A]^{1/2}$$

- (i) Integrate the rate law.
 (ii) On the basis of this integrated rate law, draw a plot of $[A]^{1/2}$ against t .
 (iii) Derive an expression for half-life period in terms of k and $[A]_0$. 2+1+2
- (d) Deduce the fundamental equations of thermodynamics for a closed system. From these fundamental equations, obtain Maxwell relations. Using Maxwell relation, deduce thermodynamic equation of state. 1+2+2
- (e) Explain the principle of steady-state approximation. For the reaction



the following mechanism has been proposed :



Assuming $k_2[\text{NO}] \ll [\text{Cl}_2]$, derive the rate law. 2+3

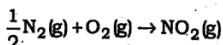
12A—1500/125

(Continued)

4. (a) (i) Explain why C_p is greater than C_v .
 (ii) Show that entropy is a state function.
 (iii) What is an A.T.G. reaction? can you obtain an example?
 Or
 (i) How much work can be obtained from 1.00 mol of CH_4 at 298 K condition at 298 K? [Given $\Delta S^\circ = 1.36 \text{ J/K}$, $\Delta H^\circ = -890 \text{ kJ}$]
 (ii) Show how the thermodynamic stability of a substance starting from 1 mol of the substance.
 (iii) Discuss one of the methods for the determination of the rate constant of a reaction.
- (b) (i) Show that for a first order reaction the time required for the completion of the reaction is independent of the initial concentration of the reactant required for 90% completion.

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- (ii) Deduce Kirchoff's equation to show the variation of enthalpy of a reaction with temperature.
- (iii) Calculate $\Delta_r H^\circ$ at 373 K for the reaction



Enthalpy of the reaction at 298 K is $-33.18 \text{ kJ mol}^{-1}$. Molar heat capacity of $\text{NO}_2(\text{g})$, $\text{O}_2(\text{g})$ and $\text{N}_2(\text{g})$ are $37.20 \text{ JK}^{-1} \text{ mol}^{-1}$, $29.36 \text{ JK}^{-1} \text{ mol}^{-1}$ and $29.13 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively. Assume that heat capacities are independent of temperature. 3+3+4

Or

- (i) What is an adiabatic process? For the reversible adiabatic expansion of an ideal gas, show that

$$PV^\gamma = \text{constant}$$

$$\text{where } \gamma = \frac{C_{p,m}}{C_{v,m}}$$

12A—1500/125

(Continued)

- (ii) Derive the rate decomposition of CH_3CHO in absence of a catalyst.



considering the proposed mechanism.

- (iii) Calculate K_p for the reaction



if $\Delta G^\circ = -34.8 \text{ kJ mol}^{-1}$

- (c) (i) Define Joule-Thomson inversion temperature and calculate it for CO_2 . Deduce from it the inversion temperature of CO_2 .

- (ii) Deduce the relationship between equilibrium constant K_x and K_p . Show that K_x is independent of pressure.

Or

- (i) Derive Michaelis-Menten equation and show that v is equal to the maximum rate of formation of product at half maximum substrate concentration.

12A—1500/125

- (ii) One mole of an ideal monoatomic gas expands reversibly from a temperature of 25 °C and pressure of 1 atm to a temperature of 0 °C and pressure of 500 mm of Hg. Calculate ΔS for the process. Assume $C_V = \frac{3}{2}R$. Given that $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$.

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