2017

CHEMISTRY

(Major)

Paper : 1.1

(Physical Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. *(a)* How is it possible to find the value of Δu and not the value of u? 1

(b) Which of the following is correct expression for the first law of thermodynamics under adiabatic condition? 1

(i) $\Delta u = q + W$

(ii) $\Delta u = q - W$

(iii) $q = -W$

(iv) $\Delta u = W$

(c) Given the following thermochemical equations :

(i) $S(\text{rhombic}) + O_2(g) \rightarrow SO_2(g)$
$\Delta H = -297 \cdot 5 \text{ kJ mol}^{-1}$

(ii) $S(\text{monoclinic}) + O_2(g) \rightarrow SO_2(g)$
$\Delta H = -300 \cdot 0 \text{ kJ mol}^{-1}$

Calculate ΔH for the transformation of one gram atom of rhombic sulphur into monoclinic sulphur. 2

2. (a) Give a statement which includes the main ideas of the first law and second law of thermodynamics. 1

(b) Why, for predicting the spontaneity of a reaction, free energy criteria is better than the entropy criteria? 1

(c) Calculate residual entropy for CO crystal at 0 K. 2

3. (a) Reactions of higher molecularity are less observed. Explain. 1

(b) The half-life for a given reaction was doubled when the initial concentration was doubled. Evaluate the order of the reaction. 1

(c) On the basis of Arrhenius equation, answer the following : 2

(i) What is the limiting value of rate constant k as temperature of reaction becomes infinitely large?

(ii) Which reaction will have the greater temperature dependence for the rate constant—one with a small value of E_a or one with a large value of E_a?

4. Answer any *two* of the following : 3×2=6

(a) Define the following with example :

(i) An isolated system

(ii) State functions

(iii) Reversible process

(b) If a specified set of reactants can be converted to a specified set of products through more than one path, the enthalpy change in each case remains the same. Discuss the significance with an example.

(c) What is bond enthalpy? Determine the enthalpy change for the given reaction :

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

Bond energies are given as follows :

C—H = 412 kJ mol^{-1}

C—Cl = 338 kJ mol^{-1}

Cl—Cl = 242 kJ mol^{-1}

H—Cl = 431 kJ mol^{-1}

5. Answer any *two* of the following : 3×2=6

(a) Define Gibbs' energy. Enthalpy and entropy changes of a reaction are 40·63 kJ mol^{-1} and 108·8 JK^{-1} mol^{-1} respectively. Predict the feasibility of the reaction at 27 °C.

(b) Discuss variation of free energy change with temperature and pressure.

(c) Show that for a mixture of two components, A and B at constant temperature and pressure

$$^{n}A^{d\mu}A + {}^{n}B^{d\mu}B = 0$$

6. Answer any *two* of the following : 3×2=6

(a) For a reaction of nth order, show that

$$t_{½} = \frac{2^{n-1} - 1}{a^{n-1}k(n-1)}$$

where a, k and $t_{½}$ are the initial concentration of the reactant, rate constant and half-life period of the reaction.

(b) For the reaction

$$2\,N_2O_5 \rightarrow 4NO_2 + O_2$$

the proposed mechanism is

$$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{k_2} NO + NO_2 + O_2$$

$$NO_3 + NO \xrightarrow{k_3} 2NO_2$$

Applying steady state approximation, derive the rate law.

(c) Half-life of a first-order reaction is 69 hours at 300 K. Also, the rate of this reaction is doubled as temperature is increased from 300 K to 310 K. Determine activation energy and pre-exponential factor for this reaction.

7. Answer any *two* of the following : 5×2=10

(a) What is an adiabatic process? Obtain the P, V, T relation for adiabatic expansion of an ideal gas. How does it differ from that of an isothermal expansion? 1+3+1=5

(b) One mole of an ideal gas (monatomic) at 27 °C expands adiabatically against a constant external pressure of 1 atm

from a volume of 10 dm^3 to a volume of 20 dm^3. Calculate *(i)* q, *(ii)* w, *(iii)* Δu and *(iv)* ΔH for this process. Also calculate the final temperature of the gas. Assume that $C_v = \frac{3}{2}R$. 5

(c) *(i)* How do you relate reaction enthalpy to internal energy change? 3

(ii) The enthalpy of combustion of glucose $C_6H_{12}O_6$ (s) is -2816 kJ mol^{-1} at 25 °C. Calculate ΔH_f° ($C_6H_{12}O_6$). The ΔH_f° values for CO_2 (g) and H_2O (l) are $-393{\cdot}5$ kJ mol^{-1} and $-285{\cdot}9$ kJ mol^{-1} respectively. 2

8. Answer any *two* of the following : 5×2=10

(a) Using the combined form of the first law and second law of thermodynamics and appropriate Maxwell relations, derive the two thermodynamic equations of state.

(b) Starting from Clausius inequality, arrive at a condition of spontaneity for isothermal process involving Helmholtz free energy.

(c) Give the physical interpretation of entropy. State the third law of thermodynamics and its usefulness in obtaining absolute entropies.

9. Answer any *two* of the following : 5×2=10

(a) For the zero-order reaction

$$\nu A \rightarrow \text{Products}$$

obtain the integrated rate law

$$[A] = [A]_0 - kt$$

Draw a graph to show the variation of concentration of the reactant with time. Determine the time required for the completion of the reaction. Under what conditions, a reaction is zero order?

(b) What are chain reactions? Discuss the kinetics of branching chain reactions.

(c) Give the mechanism of acid catalyzed reactions and obtain an expression for the rate of the reaction. Under what conditions are such reactions said to be subjected to general acid catalysis and specific hydrogen ion catalysis?

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