2016

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)* Calculate the change in the internal energy of a system that releases 2300 J of heat and that does 7043 J of work on the surroundings. 1

(b) The value of ΔH° for the reaction below is –504 kJ :

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

Calculate the heat (in kJ) released to the surroundings when 12 g of CO(g) reacts completely. 1

(c) What do you mean by inversion temperature? 2

2. *(a)* How do you define the criterion for the spontaneity of any process in terms of free energy? 1

(b) Explain what you understand by the term 'standard Gibbs free energy change'. 1

(c) Discuss the physical interpretation of any one of the Maxwell relations. 2

3. (a) Sketch the plot of rate versus concentration of a zero-order reaction. 1

(b) Write down the differential rate law and integrated rate law for a reaction of order $\frac{1}{2}$. 1

(c) Explain the term 'shape selective catalysis' with examples. 2

4. Answer any *two* of the following : $3 \times 2 = 6$

(a) A piece of magnesium of mass 15 g is dropped into a beaker of dilute hydrochloric acid. Calculate the work done by the system as a result of the reaction. The atmospheric pressure is 1·1 atm and the temperature is 23 °C.

(b) What is the physical significance of ΔH? What are the factors that affect the enthalpy of a reaction (ΔH)?

(c) Explain the principle of liquefaction of gases by Joule-Thomson effect.

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

(a) How is the entropy of a substance affected by *(i)* an increase in temperature, *(ii)* a decrease in volume, *(iii)* changing from a liquid to solid and *(iv)* dissociating into individual atoms?

(b) Calculate ΔG_T° value at 100 °C for the following reaction :

$$N_2O_4(g) \rightarrow 2NO_2(g)$$

Given that for—

$N_2O_4(g)$; $\Delta H_f^\circ = +9{\cdot}67$ kJ/mol and $S^\circ = +304$ J/mol K

$NO_2(g)$; $\Delta H_f^\circ = +33{\cdot}8$ kJ/mol and $S^\circ = +240{\cdot}5$ J/mol K

(c) Show how the third law of thermodynamics was arrived at starting from the Nernst theorem.

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

(a) Write the rate equation of a second-order reaction and explain how the half-life of this type of reaction is affected by the initial reactant concentration.

(b) A patient is given a certain amount of iodine-131 as a part of a diagnostic procedure for a thyroid disorder. Given that the half-life of radioactive iodine-131 is 8 days. What fraction of the initial iodine-131 would be present in the patient after 24 h, if none of it was eliminated through natural body processes?

(c) In what way is the rate law for a reaction related to the rate-determining step? Explain with an example.

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

(a) What do you mean by heat capacity and an adiabatic process? For the reversible adiabatic expansion of an ideal gas, show that PV^{γ} = constant, where

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

What is the physical significance of γ?

2+3=5

(b) A sample of 4·50 g of methane occupies 12·7 dm^3 at 310 K.

(i) Calculate the work done when the gas expands isothermally against a constant external pressure of 200 torr until its volume has increased by 3·3 dm^3.

(Continued)

(ii) Calculate the work that would be done if the same expansion occurred reversibly.

(c) Deduce Kirchhoff's equation to show the variation of enthalpy of a reaction with temperature.

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

(a) Derive Gibbs-Duhem equation and show that intensive variables of a system are not independent.

(b) Starting from the definition of Gibbs' free energy (G), deduce the expressions to show the variations of G with T and P. Based on these expressions, draw the necessary graphs to show the variations of G with T and P for solid, liquid and gaseous phases of a substance.

(c) Find an expression for the entropy change in an isothermal reversible expansion of n mol of an ideal gas from a volume V_1 to a volume V_2. Volume of 1 mol of an ideal gas is doubled by a reversible isothermal expansion at 298 K. Calculate ΔS for the gas. What will be the entropy change of the gas, when the same expansion is carried out irreversibly?

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

(a) What is a homogeneous catalyst? How does it function in general terms? What do you understand by the catalytic efficiency of an enzyme? 1+2+2=5

(b) Sulfuryl chloride SO_2Cl_2 is used to manufacture the antiseptic chlorophenol. The following data were collected on the decomposition of SO_2Cl_2 at a certain temperature :

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

Initial concentration of SO_2Cl_2 (mol L^{-1})	Initial rate of formation of SO_2 (mol L^{-1} s^{-1})
0·100	$2{\cdot}2\times10^{-6}$
0·200	$4{\cdot}4\times10^{-6}$
0·300	$6{\cdot}6\times10^{-6}$

What are the rate laws for the reaction? Give the reasons to justify your answer. Calculate the rate constant of the reaction from above data.

(c) Derive the rate law for the thermal decomposition of ethanal (CH_3CHO) in absence of air (shown below) considering the Rice-Herzfeld mechanism :

$$CH_3CHO(g) \rightarrow CH_4(g) + CO(g) + CH_3CH_3(g)$$

★★★