

2019

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. Answer the following as directed : 1×7=7

(a) A system in which exchange of both matter and energy with the surroundings is possible is called

(i) homogeneous system

(ii) closed system

(iii) open system

(iv) isolated system

(Choose the correct option)

(2)

- (b) State the first law of thermodynamics.
- (c) For an ideal gas, calculate the difference between molar heat capacity at constant pressure and molar heat capacity at constant volume.
- (d) State the entropy statement of second law of thermodynamics.
- (e) Calculate the entropy change for fusion of 1 mole of a solid which melts at 300 K. The latent heat of fusion of the solid is 2930 J mol^{-1} .
- (f) Give the SI unit of rate constant of a zeroth-order reaction.
- (g) Give the statement of steady-state approximation.

2. Answer the following : $2 \times 4 = 8$

- (a) Give the molecular interpretations of heat and work.
- (b) Calculate the work done during isothermal expansion of 2 moles of an ideal gas from 50 bar pressure to 5 bar pressure at 300 K.

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(Continued)

(3)

- (c) Define chemical potential. Give its physical significance.
- (d) Define half-life time of a reaction. Show that half-life time of a first-order reaction is independent of initial molar concentrations of the reactants.

3. Answer any *three* of the following : $5 \times 3 = 15$

- (a) State and explain the Hess's law of constant heat summation. Given bond enthalpies of H—H and O=O bonds respectively are 436 kJ mol^{-1} and 498 kJ mol^{-1} and enthalpy of formation of $\text{H}_2\text{O}(\text{g})$ is $-242.0 \text{ kJ mol}^{-1}$. Calculate the bond enthalpy of O—H bond. $2+3=5$
- (b) Define heat capacity at constant pressure and heat capacity at constant volume. Show that

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P \quad 2+3=5$$

- (c) What is Joule-Thomson effect? Show that the process in Joule-Thomson experiment takes place at constant enthalpy. Define Joule-Thomson coefficient. $1+3+1=5$

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(Turn Over)

(4)

(d) Define Helmholtz function and Gibbs' function. Show that decrease in Helmholtz function in any process at constant temperature gives the maximum work that can be obtained from the system during any change.

1+1+3=5

(e) Derive integrated rate equation for a first-order reaction. For a first-order reaction, $t_{0.5}$ is 100 s. Calculate the time required for the reaction to be completed by 75%.

3+2=5

4. Answer either (a) and (b) or (c) and (d) :

(a) For an adiabatic process, show that

$$TV^{\gamma-1} = \text{a constant}$$

$$\text{where, } \gamma = \bar{C}_P / \bar{C}_V$$

Hence for an ideal gas show that $PV^{\gamma} = \text{constant}$.

4+2=6

(b) One mole of an ideal gas at STP is compressed adiabatically and reversibly to occupy a volume of 2.24 L. Calculate the amount of work done during the process.

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(5)

(c) Using the relation $\Delta G = \Delta H - T\Delta S$, give the conditions when ΔG can be positive or negative. Obtain the relation between Gibbs' free energy change and equilibrium constant of an equilibrium reaction.

2+4=6

(d) Of the following pairs, which has higher chemical potential?

(i) $\text{H}_2\text{O}(\text{l})$ at 298 K, 1 atm and $\text{H}_2\text{O}(\text{g})$ at 298 K, 1 atm

(ii) $\text{H}_2\text{O}(\text{s})$ at 273 K, 1 atm and $\text{H}_2\text{O}(\text{l})$ at 273 K, 1 atm

(iii) $\text{H}_2\text{O}(\text{s})$ at 268 K, 1 atm and supercooled $\text{H}_2\text{O}(\text{l})$ at 268 K, 1 atm

(iv) Glucose(s) at 298 K, 1 atm and glucose (aq) at 298 K, 1 atm

Give brief reason in each case.

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5. Answer either (a) and (b) or (c) and (d) from the following :

(a) What are Maxwell's relations? By using Maxwell relation, show that

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

2+4=6

(6)

(b) 4.0 g of helium gas is allowed to expand reversibly and isothermally at 300 K from a pressure of 1 atm to a pressure of 0.1 atm. If helium gas behaves ideally, calculate the change in Gibbs' free energy. Also predict whether the expansion is spontaneous or not. 4

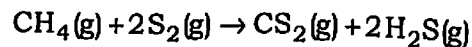
(c) Deduce the Gibbs-Helmholtz equation. Give the physical significance of this equation. 4+2=6

(d) What are partial molar quantities? Show that

$$\left(\frac{\partial G}{\partial P}\right)_{T, \text{composition}} = V \quad 4$$

6. Answer either (a) and (b) or (c) and (d) from the following :

(a) Define activation energy of a reaction. The gas-phase reaction between methane and diatomic sulphur is given by the equation



For this reaction, the rate constant at 300 K is $1.1 \text{ dm}^3 \text{ mol}^{-1} \text{ s}$ and at 400 °C

the rate constant is $6.4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}$.

Calculate activation energy of the reaction. 1+4=5

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(Continued)

(7)

(b) What are competing reactions? Give one suitable example of competing reaction showing the different steps involved in it. How can a desired product be obtained as major product in the competing reactions? 1+3+1=5

(c) What are homogeneous catalyses? Give a suitable example of homogeneous catalysis. Explain how a homogeneous catalyst changes the rate of a reaction. 1+1+3=5

(d) Distinguish between order and molecularity of a reaction. Give one example of reaction in which order and molecularity are the same. The rate of reaction $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$ becomes doubled when the concentration of Cl_2 is doubled. But when the concentrations of both the reactants are doubled, the rate becomes eight times. Determine order of the reaction. 2+1+2=5

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3 (Sem-1) CHM M 1 (O)