CBCS SCHEME



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18BT45

# Fourth Semester B.E. Degree Examination, July/August 2021
## Biochemical Thermodynamics

Time: 3 hrs. Max. Marks: 100

**Note:** *1. Answer any FIVE full questions.*
*2. Draw Figures wherever necessary.*



1 a. Develop an equation for flow process. **(10 Marks)**

b. The PVT behavior of nitrogen is represented by the ideal gas equation PV = nRT, where 'n' is the number of moles of the gas and R, the ideal gas constant (R = 8.314 kJ/Kmol-K). The heat capacities of the gas are $C_V = 20.8$ and $C_P = 29.1$ kJ/K mol K. The gas initially at 10 bar and 280K is undergoing a change of state to the final condition of 1 bar and 340K. Determine the change in internal energy and the change in enthalpy. **(10 Marks)**

2 a. With neat figures explain Kelvin-Planck and Clausius statements. **(10 Marks)**

b. Using ideal gas as Carnot engine working substance, show that the ideal gas temperature and the absolute thermodynamic temperature are identical. **(10 Marks)**

3 a. Show that the work done in an adiabatic process involving ideal gas is given by

$$W = \frac{P_1V_1}{\gamma - 1}\left[1 - \left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma}\right]$$ **(10 Marks)**

b. An ideal gas is undergoing a series of three operations: The gas is heated at constant volume from 300K and 1 bar to a pressure of 2 bar. It is expanded in a reversible adiabatic process to a pressure of 1 bar. It is cooled at constant pressure of 1 bar to 300K. Determine the heat and work effects for each step. Assume $C_p$ as 29.3kJ/K mol-K. **(10 Marks)**

4 a. For the following reaction, the standard heat of reaction at 298K is -164.987 kJ.

$$CO_2(g) + 4H_2(g) \rightarrow 2H_2O(g) + CH_4(g)$$

The constants in the heat capacity (J/mol K) equations. $C_p = \alpha + \beta T + \gamma T^2$ are given below:

| | $\alpha$ | $\beta$ | $\gamma$ |
|---|---|---|---|
| $CO_2$ | 26.75 | $42.26 \times 10^{-3}$ | $-14.25 \times 10^{-6}$ |
| $H_2$ | 26.88 | $4.35 \times 10^{-3}$ | $-0.33 \times 10^{-6}$ |
| $H_2O$ | 29.16 | $14.49 \times 10^{-3}$ | $-2.02 \times 10^{-6}$ |
| $CH_4$ | 13.41 | $77.03 \times 10^{-3}$ | $-18.74 \times 10^{-6}$ |

Calculate the standard heat of reaction at 773K. **(08 Marks)**

b. Discuss Vander Waals equation and the correction factors introduced to explain the PVT behavior of real gases. **(08 Marks)**

c. Calculate the standard heat of reaction at 298K for the following reaction:

$$4HC\ell_{(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} + 2C\ell_{2(g)}$$

The standard heats of formation are -92.307 kJ/mol for HC*l* (g) and -241.818 kJ/mol for $H_2O(g)$. **(04 Marks)**

5 a. Define Helmholtz free energy and prove that at constant temperature the decrease in work function measures the maximum work available from a given change of state. **(08 Marks)**

b. Derive Maxwell's equations for all four energy properties. What is their importance in establishing relationships between thermodynamic properties? **(12 Marks)**

6 a. Obtain the relationship between $C_P$, $C_V$, coefficient of volume expansion ($\beta$) and coefficient of compressibility (K). **(08 Marks)**

b. What is fugacity? Explain the effect of temperature and pressure on fugacity. **(08 Marks)**

c. Derive an expression for fugacity coefficient of a gas obeying the equation of state $z = a + bp + cP^2$, where P is in bar. Determine fugacity of oxygen at 293K and 100 bar, given that $a = 1.0$ ; $b = -0.753 \times 10^{-3}$ and $c = 0.15 \times 10^{-5}$. **(04 Marks)**

7 a. Discuss Gibbs – Duhem equation and its various forms. Mention the applications of Gibbs-Duhem equation. **(10 Marks)**

b. Define chemical potential. Obtain equations for the effect of temperature and pressure on chemical potential. **(10 Marks)**

8 a. State the criterion of equilibrium in terms of entropy work function and Gibbs free energy. **(10 Marks)**

b. n-Heptane and toluene form ideal solution. At 373K, their vapour pressures are 106 and 74kPa respectively. Determine the composition of the liquid and vapour in equilibrium at 373K and 101.3kPa. **(04 Marks)**

c. What are azeotropes? With proper phase diagrams, distinguish between minimum and maximum boiling azeotropes. What is the effect of pressure on the azeotropic composition? **(06 Marks)**

9 a. The following reaction occurs in a mixture consisting of 2 mol methane, 1 mol water, 1 mol carbon monoxide and 4 mol hydrogen initially $CH_4 + H_2O \rightarrow CO + 3H_2$ Deduce expression relating the mole fractions of various species to the extent of reaction. **(06 Marks)**

b. Define equilibrium constant 'K' of a chemical reaction. How is it related to $k_f$ and $k_p$? **(08 Marks)**

c. Derive Van't Hoff's equation to predict the effect of temperature on the equilibrium constant. **(06 Marks)**

10 a. n-Butane is isomerised to i-butane by the action of catalyst at moderate temperatures. It is found that the equilibrium is attained at the following compositions:

| Temperature (K) | Mole %, n-butane |
|---|---|
| 317 | 31.00 |
| 391 | 43.00 |

Assuming that activities are equal to the mole fractions, calculate the standard free energy of the reaction at 317K and 391K and average value of heat of reaction over this temperature range. **(08 Marks)**

b. Show that $\Delta G° = -RT\ln K$. **(08 Marks)**

c. Calculate the equilibrium constant at 298K of the reaction $N_2O_4(g) \rightarrow 2NO_2(g)$ given that the standard free energies of formation at 298K are 97,540 J/mol for $N_2O_4$ and 51,310 J/mol for $NO_2$. **(04 Marks)**

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