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UNIVERSITY OF PETROLEUM & ENERGY STUDIES
DEHRADUN
End Semester Examination - December, 2017

Program/Course: M. Tech. Chemical Engineering (PD) **Semester–I**
Subject: Advanced Thermodynamics **Maximum Marks : 100**
Code: CHPD-7003 **Durations : 3 Hrs.**
No. of Pages: 2(Two)

Section-A (2x30 = 60 marks)

Answer all **Two** Questions

1. **a)** *i)* One mole of Ideal Gas undergoes irreversible isothermal expansion from the initial volume, V_1, to the final volume, V_2 in two steps. (5)

$$gas(p_1, V_1, T) \Longrightarrow gas(p_3, V_3, T) \Longrightarrow gas(p_2, V_2, T) \qquad p_1 > p_3 > p_2$$

Find the total work done by the gas.

ii) One mole of Ideal Gas undergoes reversible isothermal expansion from the initial volume, V_1, to the final volume, V_2. (5)

$$gas(p_1, V_1, T) \Longrightarrow gas(p_2, V_2, T)$$

Find the expression for the work done by the gas. Show that in the above cases (two steps irreversible and the reversible expansion), the magnitude of the **reversible** expansion work is greater than that of the **irreversible** work.

iii) State **Hess's law**. Write a short note on the **Heat of Reaction**, explaining it with an arbitrary example. What is the criterion that a reaction would be exothermic? (5)

iv) Describe Joule's Experiment on expansion of gas into a vacuum. Write the expression for Joule's coefficient, η_J, in terms of thermodynamic variables.. (5)

b) Write a short note on the Triple Point of a pure substance. Provide a rough sketch of Phase Diagram of carbon dioxide. Mark the Triple Point on the graph indicating the numerical values of pressure and temperature at triple point. Also mark the Critical Point furnishing the numerical values of critical temperature, T_c and critical pressure, P_c respectively. (10)

2. **a)** Describe the Carnot Cycle. Define the Efficiency of a Carnot Heat Engine. Find out the expression for its Efficiency. (15)

Hint: $\text{Efficiency}(\varepsilon) = \dfrac{\text{Work Output to Surroundings}}{\text{Heat input}}$

b) Find the expression for Efficiency of the Carnot Heat Engine for the Ideal Gas. Explain the Third Law of thermodynamics from the Efficiency relation. Is the efficiency of irreversible Carnot Engine is equal to its reversible counter part? If not, explain. (15)

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Section-B (1x40 = 40 marks)

Answer any **one** Question

3. a) For the phase equilibrium or phase transition of one or multiple components system

- What is the driving potential for phase transition or phase equilibrium? If the driving potential (μ_l), in the liquid phase is less than that (μ_s) of the solid phase, which phase is physically **stable**? (5)
- Calculate the number of degrees of freedom, required to describe the state of a single component (pure system) and two-phase system. How many degrees of freedom are required to represent the Triple Point, where three phases coexist in equilibrium? (5)
- Derive the Clapeyron Equation that represents the effect of Temperature (T) on Pressure (P) in phase equilibrium, from the fundamental equation [$dG = -SdT + VdP$] of thermodynamics. (10)
- Derive the Clapeyron Equation for vapor-liquid equilibrium, when the vapor behaves as an ideal gas. **Hint:** $G = H - TS$. (10)

b) The Clausius-Clapeyron Equation for vapor liquid equilibrium is given by

$$\frac{dP}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2} P$$

where ΔH_{vap} is the molar latent heat of vaporization. If ΔH_{vap} of water is 10,000 cal/mole at its normal ($P = 1$ bar) boiling point, T_b (=373°K), then show that (10)

$$\ln P = 13.4 - \frac{5000}{T}$$

What is the major assumption that has been used to derive the above equation? Does this assumption play a major role for the above equation to be different from the Antoine equation ($\ln P = A - \frac{B}{C+T}$)?

4. a) • Write a short note on Le-Chatelier Principle. (7)

• Over a small temperature range, when $\triangle C_p(T_2 - T_1)$ can be assumed small and the heat of reaction, $\triangle \boldsymbol{H}^{\mathbf{0}}_{\mathbf{rxn}}$, independent of temperature, then for a chemical reaction

$$\nu_A \mathsf{A} + \nu_B \mathsf{B} \leftrightarrows \nu_C \mathsf{C} + \nu_D \mathsf{D}$$

of the ideal gas, the temperature (T) dependence of equilibrium constant, $K(T)$, is given by

$$\ln \frac{K(T_2)}{K(T_1)} = \frac{\triangle \boldsymbol{H}^{\mathbf{0}}_{\mathbf{rxn}}}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

✓ Which way the equilibrium would shift, for an Exothermic Reaction, if the temperature of the reaction is increased. (4)

✓ For an Endothermic Reaction, how the equilibrium would respond with the increase in temperature? (4)

b) Show that for the reaction of an ideal gas, the temperature dependence of the equilibrium constant, $K(T)$, is governed by (10)

$$\frac{d \ln K(T)}{dT} = \frac{\triangle \boldsymbol{H}^{\mathbf{0}}_{\mathbf{rxn}}}{RT^2}$$

State all the assumptions to be made to derive the equation.

Hint: $\ln K(T) = -\dfrac{\triangle \boldsymbol{G}^{\mathbf{0}}_{\mathbf{rxn}}}{RT}$; $\left(\dfrac{\partial \triangle G^0_{\text{rxn}}}{RT} \right)_p = -\triangle S^0_{\text{rxn}}(T)$

c) Calculate the change in entropy of 10 kg. of water heated from 20^{o}C to 60^{o}C. The heat capacity of water is assumed to be constant (4.2kJ/kg-K) in this temperature interval. (5)

d) One mole of ideal gas undergoes Joule expansion ($P_{op.} = 0$) from the volume V, to the final volume, $2V$. Calculate the change in entropy for the expansion. (10)