This question paper contains 7 printed pages]

Roll No. | | | | | | | | | | |

S. No. of Question Paper : **5815**

Unique Paper Code : **2172011203**

Name of the Paper : **Chemical Thermodynamics and its Applications**

Name of the Course : **B.Sc. (H) Chemistry**

Semester : **II**

Duration : **3 Hours** Maximum Marks : **90**

(Write your Roll No. on the top immediately on receipt of this question paper.)

Attempt *six* questions in all.

Question No. 1 is compulsory.

Use of scientific calculators and log tables is allowed.

1. Answer the following questions (any *five*) : 5×3=15

(*a*) The entropy of crystalline ice is not zero at 0 K. Explain.

(*b*) Giving suitable examples, explain the meaning of endergonic and exergonic reactions.

P.T.O.

(*c*) The enthalpy of neutralization of a strong monoprotic acid with a strong monoprotic base is always constant. Explain.

(*d*) With the help of mathematical expressions, explain why ΔA is called "work function".

(*e*) Classify the following as extensive/intensive— Kinetic energy, Pressure, entropy, molar heat capacity, chemical potential, Temperature.

(*f*) To predict the spontaneity of a process both ΔS_{sys} and ΔS_{surr} are considered but ΔG alone is sufficient for the same. Explain.

(*g*) Define integral enthalpy of solution and dilution.

2. (*a*) Derive cyclic rule

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T + 1 = 0$$

Prove it for $PV_m = RT$.

(*b*) With the help of suitable mathematical expression, discuss under what conditions heating and cooling effects are produced in the Joule Thomson experiment involving real gases. Define Inversion temperature and write down its expression for a real gas.

(*c*) Six moles of an ideal gas expands isothermally and reversibly from a pressure of 10 atm to 2 atm at 27°C. Calculate the values of q, w, ΔU and ΔH involved in the process. Will the values of heat and work be the same or different had the process been carried out irreversibly ? Why ? 5,5,5

3. (*a*) Write down the statement of Hess's law of constant heat summation and explain it with the help of an example. Is Hess's law valid for heat exchanged 'q' in a process ? Is it valid for entropy change 'ΔS' ? Give reason for your answer.

(*b*) Using the given data, calculate the enthalpy of formation of acetic acid :

(*i*) Enthalpy of sublimation of graphite = 718.39 kJ mol^{-1}

(*ii*) Enthalpy of dissociation of hydrogen gas = 435.97 kJ mol^{-1}

(*iii*) Enthalpy of dissociation of oxygen gas = 495.04 kJ mol^{-1}

Bond	**Bond enthalpy** (kJ mol^{-1})
C—C	347.69
C—H	413.38
C = O	728.02
C—O	351.46
O—H	462.75

P.T.O.

(*c*) Derive an expression for determination of variation of enthalpy of reaction with temperature. 5,5,5

4. (*a*) Describe Carnot cycle. A Carnot engine operates between 500 K and 250 K. If it absorbs 1000 J of heat from the hot reservoir, calculate the work done and efficiency.

(*b*) Define enthalpy of combustion. Calculate the enthalpy of formation of ethyl alcohol given the enthalpy of combustion of ethyl alcohol is -1381 kJ mol^{-1}, and enthalpy of formation of H_2O (*l*) and CO_2 (*g*) are -287 kJ mol^{-1} and -395 kJ mol^{-1} respectively.

(*c*) Show mathematically that the magnitude of the work involved in a reversible expansion of an ideal gas from volume V_1 and V_2 is larger than the corresponding work involved in an irreversible expansion against a constant pressure of P_2. 5,5,5

5. (*a*) Derive :

(*i*) $$\left(\frac{\partial S}{\partial P}\right)_T = -\frac{1}{\left(\frac{\partial T}{\partial V}\right)_P}$$

(*ii*) $$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P.$$

(*b*) State third law of thermodynamics. Absolute entropy of liquid water at 298 K has to be calculated. Write all the steps involved. Also write the final expression for calculation of entropy.

(*c*) Calculate the $\Delta_{mix}G$, $\Delta_{mix}S$ and $\Delta_{mix}H$ when 20 mol of an ideal gas A is mixed in 20 mol of ideal gas B, at 298 K and 1 atm pressure. 5,5,5

6. (*a*) Calculate $\Delta_r G$ for the following process : H_2O (l, 2 atm, 373 K) $\rightarrow$ H_2O (g, 2 atm, 373 K) where atm stands for atmospheric pressure.

(*b*) Derive the expression for the entropy of mixing for two ideal gases and show how it contributes to the spontaneity of the mixing process.

(*c*) Predict if ΔS_{sys} is positive, negative or zero in each of the following giving reason :

(*i*) NH_4NO_3 (s) + $3H_2$ (g) $\rightarrow$ $3H_2O$ (g) + N_2H_4 (g)

(*ii*) Crystallization of NaCl

(*iii*) Reversible adiabatic expansion of an ideal gas

(*iv*) 2 SO_2 (g) + O_2 (g) $\rightarrow$ 2 SO_3 (g)

(*v*) C (graphite) + $\frac{1}{2}O_2$ (g) $\rightarrow$ CO (g). 5,5,5

P.T.O.

7. (*a*) Show that $\Delta_r H = \Delta_r U + \Delta v_g RT$ for a chemical reaction involving gases. What will be the relation for condensed phases ?

(*b*) Partial molar volume of a component in a solution depends on the nature as well as the amount of the other components. Explain qualitatively.

(*c*) Derive the relations :

(*i*) $$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

(*ii*) $$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_j's} = V_{i,pm}.$$ 5,5,5

8. (*a*) Starting from $H = U + PV$ and first law of thermodynamics, derive the following expression for an ideal gas :

$$\Delta S = nC_{p;m} \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1}.$$

(*b*) Explain the term escaping tendency. Prove that a substance will flow spontaneously from a region of higher chemical potential to a region of lower chemical potential.

(c) Calculate $\Delta_r G°$ for the following reaction at 300 K from the data provided :

$$2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$$

	N_2O_5	NO_2	O_2
$\Delta_f H°$/kJ mol^{-1}	11.3	33.18	0
$S°$/J K^{-1} mol^{-1}	355.7	240.06	205.14

Is the reaction spontaneous ? 5,5,5