
ANSWER ANY FIVE QUESTIONS ALL QUESTIONS CARRY EQUAL MARKS

1. (a) Name the following systems with proper explanation.
- A container having water and ice exchanging heat with surrounding.
 - A system consisting of sugar in water.
 - A system consisting of air in a closed container having perfectly insulated walls.
- (b) Bring out the differences among the following.
- Thermodynamic system
 - Thermodynamic process
 - Thermodynamic cycle.
2. (a) For an adiabatic process prove $pV = \text{constant}$.
- (b) Explain the usefulness of Kirchoff's equation in thermodynamics.
- (c) Calculate the percentage error in the determination of heat of reaction of pure solid Na_2O with HCl gas at 1 atmosphere pressure to form solid and NaCl water at 250. The standard heats of formation in Kcal.Mol^{-1} are.
- $\text{NaCl(s)} : -98.6 \pm 0.2$
 $\text{Na}_2\text{O(s)} : -100.7 \pm 1.2$
 $\text{HCl(g)} : -22.0 \pm 0.1$
 $\text{H}_2\text{O(l)} : -68.32 \pm 0.01$
3. (a) Discuss the second law of thermodynamics using classical viewpoint. How is entropy defined in this approach? Can the entropy of a system decrease? Explain.
- (b) Calculate standard entropy of a metal at 6500C if its entropy at 270C = 5 Cal/gm/mole and $C_p = 5.4 + 1.2 \times 10^{-3}T$ Cal/gm/mole. [
4. (a) Explain the applications of Boltzmann equation.
- (b) Explain the differences between classical thermodynamics and statistical thermodynamics.
5. (a) Define Helmholtz energy function and explain its significance.
- (b) Derive the relationship between the standard free energy change and the equilibrium constant of a reaction.
6. (a) Explain the deductions of third law of thermodynamics.
- (b) Explain various methods of calculation of ΔS_0 for a chemical reaction.

7. (a) Derive Clausius-Clapeyron equation starting from fundamentals. State the conditions under which approximation is valid.

(b) Prove that violation of the Kelvin-Planck statement leads to violation of the Clausius statement of the second law of thermodynamics.

8. (a) Suppose that the absolute rate of a certain process cannot be measured but the ratio of the rates r_2/r_1 , at the two temperatures T_2 and T_1 can be measured. Find the activation energy of this process in terms of T_2 , T_1 and r_2/r_1 .

(b) Distinguish between the molecularity and order of a reaction

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