B. Sc. CHEMISTRY
SECOND SEMESTER
PHYSICAL CHEMISTRY II
BSC – 202 OLD COURSE [REPEAT]
[USE OMR FOR OBJECTIVE PART]

Duration: 3 hrs. **Full Marks: 70**

Objective

Time: 30 min. **Marks: 20**

Choose the correct answer from the following: ***1X20=20***

1. Entropy remain constant in
   a. Adiabatic process b. Isolated system
   c. Isochoric process d. Isothermal process
2. The set of condition which makes a process spontaneous is
   a. $\Delta H > 0; \Delta S < 0$ b. $\Delta H < 0; \Delta S > 0$
   c. $\Delta H = 0; \Delta S > 0$ d. $\Delta H < 0; \Delta S < 0$
3. The correct relation is
   a. $(\delta A/\delta T)_V = +S$ b. $(\delta A/\delta T)_V = -P$
   c. $(\delta A/\delta T)_V = -S$ d. $(\delta A/\delta T)_V = +P$
4. The efficiency of a heat engine operating between 127^0C and 27^0C is
   a. 80% b. 75% c. 50% d. 25%
5. In a simple irreversible cycle if Q_2 is the heat taken at a temperature T_2 and Q_1 is the heat rejected at temperature T_1then
   a. $Q_1/T_1 > Q_2/T_2$ b. $Q_1/T_1 < Q_2/T_2$
   c. $Q_1/T_1 = Q_2/T_2$ d. $Q_1/T_2 > Q_2/T_1$
6. Which one of the following is correct pair?
   a. Boiling point elevation; Ebullioscopic constant b. Freezing point depression; Cryscopic constant
   c. Both a & b d. None of them
7. Excess value of which of the following is not equal to experimentally observed value?
   a. Entropy b. Enthalpy
   c. Volume d. All of them
8. Concept of vapour pressure is used in which of the following theory of semepermeability.
   a. Sieve theory b. Solubility theory
   c. Adsorption theory d. Capillary theory

9. Rate of flow of salt through membrane is (choose the correct one)
   a. Inversely proportional to concentration difference
   b. Directly proportional to thickness of membrane
   c. Inversely proportional to membrane area
   d. Directly proportional to membrane permeability coefficient.
10. Which one is correct
   a. Rault's law is special case of Henry's law
   b. Henry's law is special case of Rault's law
   c. Rault's law & henry's law are unrelated
   d. None of them
11. If the pressure P (system) is greater than P (Surroundings), then
   a. Work is done on the system by the surroundings
   b. Work is done on the surroundings by the system
   c. Work done on the system by the surroundings is equal to the Work done on the surroundings by the system.
   d. Internal Energy of the system increases.
12. The enthalpies of elements in their standard states are taken as zero. The enthalpy of formation of a compound
   a. is always negative
   b. is always positive
   c. may be positive or negative
   d. is never negative
13. The value of $\Delta U - \Delta H$ for the reaction

$$Fe_2O_3\,(S) + 3C\,(S) \rightarrow 2Fe\,(S) + 3CO_2\,(g)$$

   a. – 3RT b. +3RT c. RT d. – RT
14. First Law of thermodynamics is related to
   a. Energy
   b. Entropy
   c. Temperature
   d. Numerical Value of entropy
15. Which is not a state function
   a. Internal energy
   b. Enthalpy
   c. Temperature
   d. Work
16. If Kp and Kc are equilibrium constants in terms of partial pressure and concentration then
   a. $Kp = Kc/RT$
   b. $Kp = KcRT$
   c. $Kp = Kc/(RT)^{\Delta n}$
   d. $Kp = Kc(RT)^{\Delta n}$
17. van't Hoff equation is
   a. $d\ln Kp = -\Delta H°/RT^2dT$
   b. $d\ln Kp = \Delta H°/RT^2dT$
   c. $d\ln Kp = -\Delta H°/RTdT$
   d. $d\ln Kp = \Delta H°/RTdT$

18. What will be the affect of increase in pressure on the following equilibrium?
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

a. Shift the equilibrium towards right
b. Shift the equilibrium towards right
c. No change
d. Cannot predict

19. The relation between Kp and Kc for the following reaction is
$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

a. $Kp = Kc$
b. $Kp = Kc(RT)$
c. $Kp = Kc/(RT)$
d. $Kc = Kp(RT)$

20. Van't Hoff reaction isotherm is

a. $\Delta G^\circ = -RT\ln Kp$
b. $\Delta H^\circ = -RT\ln Kp$
c. $\Delta G^\circ = RT\ln Kp$
d. $\Delta H^\circ = RT\ln Kp$

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(Descriptive)

Time : 2 hrs. 30 min. **Marks : 50**

[Answer question no.1 & any four (4) from the rest]

1. a. Write the statement of Zeroth law and first law of thermodynamics. Write the mathematical expression of the first law of thermodynamics. Explain. **3+3+4 =10**

   b. Derive Gibb's-Duhem equation.

   c. Derive the relation between Gibbs free energy of reaction and equilibrium constant, Kp.

2. a. Write the concept of entropy with its SI unit. Calculate the change of entropy in a reversible cycle. **5+5=10**

   b. Write the Planck statement of 2nd law of thermodynamics. Discuss how Boltzmann Proposed the entropy of a system. Explain residual entropy

3. a. Define Gibb's free energy function and Helmholtz work function. Deduce the equation $[\delta(\Delta G/t)/\delta(1/t)] = \Delta H$ Where ΔG is the change of free energy and ΔH is the change of enthalpy. **5+5=10**

b. Deduce the following two relations

i) $(\delta S/\delta V)_T = (\delta P/\delta T)_V$

ii) $(\delta V/\delta T)_P = -(\delta S/\delta P)_T$

4. **a.** A solution of A and B with 30 mole percent of A is in equilibrium with its vapour which contains 60 mole percent of A. Assuming ideality of the solution and the vapour calculate the ratio of the vapour pressure of pure A to that of pure B. **3+4+3 =10**

b. 0.50 g of a nonvolatile organic substance was dissolved in 100 ml of carbon tetrachloride at 30^0C. The vapour pressure of the solution was found to be 141.9 torr. Calculate the molar mass of the substance. Vapour pressure of carbon tetrachloride at 30^0C is 143.0 torr and its density is 1.58 g ml^{-1}.

c. Derive the relation between the equilibrium constants Kp and Kx.

5. **a.** Discuss three effects of osmosis and semipermeability. **3+4+3 =10**

b. What are isotonic solutions. A solution containing 8.6 g per dm^3 of urea (molar mass = 60 g/mol) was found to be isotonic with a 5 percent solution of an organic nonvolatile solute. Calculate the molar mass of the later.

c. A certain solution of benzoic acid in benzene boils at 82.6^0C and freezes at 3.1^0C. What information about the number of particles and the structure of benzoic acid at the two temperatures can be deduced from the above data? The boiling point and freezing point of pure benzene are 80.1^0C and 5.5^0C respectively. $K_f = 5.12$ K kg mol^{-1} ; $K_b = 2.57$ K kg mol^{-1}.

6. **a.** What is Extensive and Intensive property? Give examples. **2+3+2+ 3=10**

b. Derive the expression for work done for a reversible isothermal compression for gas molecules.

c. Derive the relation $C_P - C_V = R$

d. The heat capacity of 10 mol of an ideal gas at a certain temperature is 300 J/K at constant pressure. Find the heat capacity at constant volume of the same gas at the same temperature.

7. **a.** What is enthalpy of formation and enthalpy of combustion? Explain. **2+3+2+ 3=10**

b. Derive the Kirchhoff's equation. Write down the integrated from of the Kirchhoff's equation.

c. Explain the Hess's law and its applications.

d. The value of Kp for the following water gas reaction is 1.06×10^5 at 25°C. Calculate $\Delta G°$ for this reaction.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

8. a. Derive integrated van't Hoff equation. The equilibrium constant Kp for the reaction **5+5=10**

$$H_2(g) + S(g) \rightleftharpoons H_2S(g)$$

is 20.2 atm^{-1} at 945°C and 9.1 atm^{-1} at 1065°C. Calculate $\Delta H°$.

b. State Le Chateliers principle. With the help of this principle, explain the effect of change in temperature and pressure on the following reaction

$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$; $\Delta H° = +59.0$ kJ

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