STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86
(For candidates admitted during the academic year 2019 – 20 and thereafter)
SUBJECT CODE: 19CH/MC/PC54
B.Sc. DEGREE EXAMINATION, NOVEMBER 2021
BRANCH IV- CHEMISTRY
FIFTH SEMESTER

COURSE: MAJOR CORE
PAPER: PHYSICAL CHEMISTRY-II
TIME: 3 HOURS **MAX.MARKS: 100**

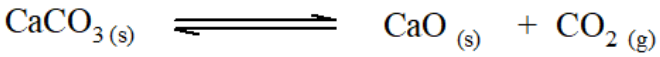
SECTION – A

Answer all the questions **(15x2= 30 marks)**
I Choose the correct answer

1. A certain reaction is exothermic by 220kJ and does 10kJ of work. What is the change in internal energy of the system?

a) 230kJ b) -230kJ c) +210kJ d) -210kJ

2. The decomposition of $CaCO_3$ in a closed vessel is represented by the equation given below, the number of phases and components in below system are _____respectively.



a) 2 and 3 b) 3 and 2 c) 2 and 2 d) 3 and 3

3. A system with lower CST is

a) Phenol- Water b) Triethylamine- Water

c) Nicotine- Water d) Phenol-NaCl

4. One mole of Ammonia (γ=1.33) gas at 27^{o}C is expanded under adiabatic condition to make volume 8 times. Final temperature is_____

a) 150K b) 200K c) 250K d) 100K

5. The 1% solution of substances given below that will have the highest boiling point is_____.

a) NH_2-CO-NH_2 b) $C_{12}H_{22}O_{11}$ c) NaCl d)Na_2SO_4

II. Fill in the blanks:

6. Volt-Coulomb is the unit of electrical energy and its mechanical equivalent of heat is _____.

7. The expression relating the degree of dissociation of a substance and the Van't Hoff factor *i is* _____

8. The variation of μ with P of a constituent *'i'* of a system at constant *T* and composition is given by _____

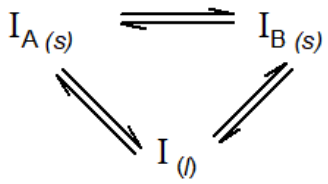
9. For the combustion of one mole of $CH_3\ COOH_{(l)}$ at 25°C, Δn is _____

10. The enthalpy of fusion for benzene (C_6H_6, 78.0 g/mol) is 127.40 kJ/kg, and its melting point is 5.5°C. Its entropy change when 2 mole of benzene melts at 5.5°C is _____

III- Answer the following: (5x2 = 10)

11. What is efflorescence? Name two substances showing efflorescence.

12. Draw a phase diagram for the given system:



13. Give the of Clausius Inequality equation.

14. Calculate the maximum efficiency of a steam engine operating between 100° and 25°C?

15. Write expressions for *Kp* for the following reactions.

i. $4KO_2(s) + 2H_2O(g) \rightleftharpoons 4KOH(s) + 3O_2(g)$ ii. $2Fe(s) + \frac{3}{2}O_2(g) \rightleftharpoons Fe_2O_3(s)$

Section B

IV. Answer any five questions (5 x 8 =40)

16. a. If $G = f(T, P, n_1, n_2, n_3,.)$, Derive a mathematical expression for variation of μ with *P* for an ideal gaseous system. **(5)**

b. The equilibrium constant *Kp* for the dissociation reaction $2H_2S \leftrightarrow 2H_{2(g)} + S_{2(g)}$ is 1.18×10^{-2} at 1338K and the enthalpy change ΔH = 177.4kJ. Calculate the equilibrium constant at 1573K. **(3)**

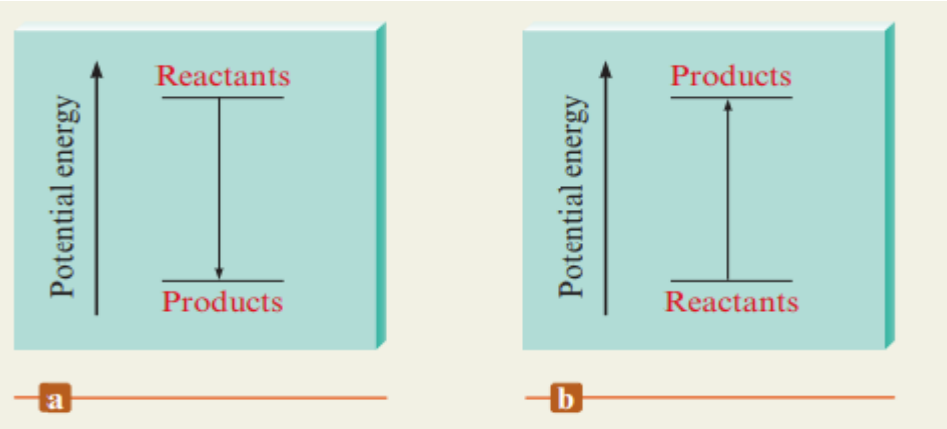
17. a. A solution containing 1.5g of barium nitrate in 0.1 kg of water freezes at 272.72K. Calculate the apparent degree of dissociation of the salt. Molecular weight of $Ba(NO_3)_2$ is 261g/mol and K_f of water is 1.86 K.Kg /mole. **(4)**

b. Prove that $\left(\frac{\partial A}{\partial T}\right)_V = -S$ and $\left(\frac{\partial A}{\partial V}\right)_T = -P$. Hence prove $\left(\frac{\partial S}{\partial T}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$. **(4)**

18. a. Identify whether the given mixtures are ideal or non- ideal solutions. Explain characteristics of each of them.

(i) CCl_4- $SiCl_4$ (ii) MeOH- H_2O **(5)**

b. Consider the following potential energy diagrams for two different reactions.



Which plot represents an exothermic reaction?

In plot a, do the reactants on average have stronger or weaker bonds than the products?

In plot b, reactants must gain potential energy to convert to products.

How does this occur? **(3)**

19. a. Derive the thermodynamic phase rule. **(5)**

b. For the following reactions at constant pressure, predict if $\Delta H > \Delta U$, $\Delta H < \Delta U$ or $\Delta H = \Delta U$

a. $2HF(g) \longrightarrow H_2(g) + F_2(g)$

b. $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

c. $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$ **(3)**

20. a. Prove $PV^{\gamma} = constant$, for a reversible adiabatic process. From this deduce a relation in terms of P and T. **(5)**

b. Consider the reaction

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

carried out at 25°C and 1 atm. Calculate $\Delta H°$, $\Delta S°$, and $\Delta G°$ using the following data:

Substance	H_f° (kJ/mol)	$S°$ (J/K · mol)
$SO_2(g)$	−297	248
$SO_3(g)$	−396	257
$O_2(g)$	0	205

(3)

21. a. Illustrate steam distillation process for the purification of aniline. **(5)**

b. Calculate the mole fraction of HCl in a solution of HCl in H_2O, containing 36% HCl by weight. **(3)**

22.a. Starting from Vander Waal's equation of state, derive an expression for Joule Thomson coefficient for real gases. **(5)**

b. At 1100 K, K_p = 0.25 for the reaction, $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$. What is the value of K_C at this temperature? (3)

Section C

V. Answer <u>any two</u> questions (2 x 15 = 30)

23. a. Draw the phase diagram of Na_2SO_4 - H_2O system and explain the following - (i) Solubility curves (ii) Transition point curve (iii) Metastable curves **(10)**

b. Prove that the efficiency of Carnot's heat engine is always less than one. A machine absorbs 390J of heat from a hot reservoir and converts 30% of it into work. Calculate the amount of heat rejected by the machine. **(5)**

24. a. Derive a relation for the elevation in boiling point and its dependence on molality of the solution using the expression below **(8)**

$$\Delta\overline{S_v}.dT = \left(\frac{\partial\mu_1^l}{\partial\mu_1}\right)_{T,P}.dx_1$$

b. Explain the various features of phase diagram of Nitrobenzene -hexane system. **(4)**

c. What would happen to the position of equilibrium (which direction will it shift- right or left) when the following changes are made to the reaction below? **(3)**

$2SO_{3\,(g)} \rightleftharpoons 2SO_{2\,(g)} + O_{2\,(g)}$

(i) Sulfur dioxide is added to the system _____

(ii) Sulfur trioxide is removed from the system _____

(iii) Oxygen is added to the system _____

25. a. Starting from Vander Waal's equation of state, derive an expression for joule Thomson coefficient of real gases. Subsequently deduce a relation for inversion temperature **(10)**

b. Explain the transformation of Nernst distribution law equation when the solute under study associates. **(5)**

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