STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86
(For candidates admitted during the academic year 2008 – 09)

SUBJECT CODE: CH/PC/TP14

M.Sc. DEGREE EXAMINATION, NOVEMBER 2008
BRANCH IV- CHEMISTRY
FIRST SEMESTER

REG.NO ……...

COURSE: MAJOR CORE
PAPER : THERMODYNAMICS AND PHASE RULE
TIME : 30 MINUTES **MAX.MARKS : 20**

SECTION – A (20x1=20)

To be answered on the question paper itself.

Answer all the questions

I Choose the correct answer

1. If water is kept in an insulated vessel at -10^{o}C and is frozen suddenly the entropy change of the system
   a) increases b) decreases c) is zero d) is equal to that of surroundings

2. If one mole of an ideal gas expands isothermally and reversibly at 300K from 10 to 100 litres then the change in free energy is
   a) -13728 Cal b) -2764 Cal c) -691 Cal d) Zero

3. The heat of formation is zero for
   a) carbon (graphite) b) carbon (diamond) c) CO_2 (liquid) d) CO_2 (solid)

4. For a reversible reaction the quantity which is not zero is
   a) ΔG b) ΔS c) Kp d) ΔH

5. Partial molal volume is an example of
   a) a colligative property b) extensive property
   c) intensive property d) nonadditive property

6. The root mean square velocity of nitrogen at 298K is equal to the root mean square velocity of helivin at
   a) 4.26K b) 0.426K c) 426K d) 42.6K

7. Which amongst the following is not a colligative property.
   a) osmotic pressure b) elevation in boiling point
   c) entropy d) relative lowering of vapour pressure

8. Gibbs Duhem equation can be represented as
   a) $\sum \mu_i n_i = 0$ b) $\sum n_i d\mu_i = 0$ c) $\sum \mu_i dn_i = 0$ d) $\sum d\mu_i . dn_i = 0$

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9. The phase rule for a ternary system is
   a) $F = 3 - P$ b) $F = 4 - P$ c) $F = 5 - P$ d) $F = 5 + P$

10. Particles with half integral spin are known as
    a) Bosons b) Fermions c) Nuons d) Mesons

II Fill in the blanks

11. For an ideal gas $\left(\frac{\partial H}{\partial P}\right)_T$ =_____.

12. The Vant Hoff reaction isotherm is given by the expression _____.

13. A mixture of water and sulphwic acid which cannot be separated completely by fractional distillation is known as _____ mixture.

14. For the equilibrium $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ a ten fold increase in pressure results in _____ in Kp.

15. According to III law of thermodynamics the absolute entropy of any substance is _____ at 0K.

III Answer the following in one or two sentences

16. What is degree of advancement of a reaction

17. State Nernst heat theorem.

18. What are state functions ?

19. State LeChatelier principle

20. Calculate the number of vibrational and rotational degrees of freedom for NO_2 molecule.

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COURSE: MAJOR CORE
PAPER : THERMODYNAMICS AND PHASE RULE
TIME : 2½ HOURS **MAX.MARKS : 80**

SECTION – B

ANSWER ANY FIVE QUESTIONS **(5X8=40)**

1. a) Derive Gibbs Helmholtz equation.
   b) Three moles of oxygen gas and one mole of nitrogen gas are mixed at 25^{o}C & at one atmosphere pressure. The final pressure is also one atmosphere. Calculate the molar entropy of mixing. (5+3)

2. What is chemical potential? Derive an expression for its variation with temperature and pressure. (8)

3. a) What is residual entropy?
   b) Discuss the criteria for spontaneity and equilibrium in terms of free energy and entropy. (4+4)

4. Write notes on the different types of ensembles. (8)

5. a) Derive the thermodynamic relation $\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$

   b) Prove the Maxwell's relations $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

   $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ (4+4)

6. Discuss the application of phase rule to the system Ag-Cu. (8)

7. Derive an expression for the Maxwell's distribution of molecular velocities. (8)

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SECTION – C

ANSWER ANY TWO QUESTIONS **(2 X 20 = 40)**

8. a) Derive an expression for the Joule Thomson coefficient for a Vander waals gas. What is the significance of inversion temperature?
   b) How is the absolute entropy of a substance determined using third law of thermodynamics? (10+10)

9. a) Derive the Clausius-Clapeyron equation.
   b) Discuss the application of phase rule to the system $CH_3COOH - CHCl_3 - H_2O$ with the help of a phase diagram.
   c) The vapour pressure of pure water at 100^oC is 760mm. What will be the vapour pressure at 95^oC. Molar heat of vapourisation of water $\Delta H_v = 41.27\, KJ\, mol^{-1}$. (8+8+4)

10. a) Compare the Fermi Dirac and Bose Einstein statistics with respect to their salient features.
    b) Derive the onsagaer relationships from the principle of microscopic reversibility. (10+10)

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