G 3722 (Pages : 2) Reg. No.....

Name.....

M.Sc. DEGREE (CSS) EXAMINATION, MARCH 2013

First Semester

Faculty of Science

Branch—Chemistry

AN 1C 04/AP 1C 04/ CH 1C 04/PH 1C 04/ POH 1C 04—CLASSICAL AND STATISTICAL THERMODYNAMICS

(Common to All Branches of Chemistry)

(2012 Admissions)

Time : Three Hours Maximum Weight : 30

Section A

Answer any **ten** *questions.*
Each question carries a weight of 1.

1. What is meant by activity of a substance ? How is it related to pressure and fugacity ?
2. Explain the term chemical potential. Derive the Gibb-Duhem equation.
3. State and explain the third law of thermodynamics.
4. Explain the exergonic nature of ATP hydrolysis.
5. Depict a phase diagram for three pain of partially miscible liquids and explain.
6. Derive an expression for the excess entropy of a binary mixture.
7. Explain the principle of microscopic reversibility.
8. Explain the terms (a) phase space ; (b) micro states ; (c) macrostates.
9. Write the Stirling approximation. Calculate the values of 101 and 501 and their logarithm to the base 10 using Stirling's approximations.
10. Derive the relation between thermodynamic probability and entropy.
11. Briefly explain Bose-Einstein condensation.
12. What are the limitations of Debye theory of solids ?
13. Derive the equation for the relation partition function and internal energy.

(10 × 1 = 10)

Turn over

Section B

Answer any **five** *questions by attempting not more than* three *questions from each bunch.*
Each question carries a weight of 2.

BUNCH 1 (Short essay type)

14. What do you understand by partial molar quantities. Write the general expression for partial molar quantity of a component *i* in a mixture.
15. Derive Gibbs Duhem Margules equation and give its applications.
16. Prove that complete partition function for a system is the product of translational, rotational, vibrational and electronic partition function.
17. Derive the value of 13 used in statistical mechanics.

BUNCH 2 (Problem type)

18. Calculate the entropy change when $10m^3$ of an ideal gas ($C_{p,m}$ = 2.5 R) at 27°C and 1.01×10^5 Nm^{-2} pressure are heated at constant pressure to 127°C.
19. Calculate the free energy change accompanying the compression of 1 mole of a gas at 57°C from 25 to 200 atmospheres. The fugacities of the gas at 57°C may be taken as 23 and 91 atmospheres, respectively, at pressure of 25 and 200 atmospheres.
20. Calculate the rotational partition function for hydrogen molecules at 300K. Moment of inertia of hydrogen molecule is 4.59×10^{-47} kgm^2 symmetry number $\sigma = 2$.
21. Calculate the number of ways of distributing distinguishable molecules a, b, c between three energy levels so as to obtain the following set of occupation number. $N_0 = 1, N_1 = 1, N_2 = 1$. Also write the different configurations.

$(5 \times 2 = 10)$

Section C

Answer any two *questions.*
Each question carries a weight of 5.

22. (a) Explain the variation of free energy change with temperature and pressure.
    (b) What are Maxwell's relationships ? Explain.
23. What is Nernst heat theorem ? Explain the determination of absolute entropies using third law.
24. Derive equation for translational partition function and explain its significance.
25. Derive Debye theory of heat capacity of solids. How does it differ from Einstein theory ?

$(2 \times 5 = 10)$