STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI 600 086
(For candidates admitted during the academic year 2004-05 & thereafter)

SUBJECT CODE: CH/MC/PC44

B.Sc. DEGREE EXAMINATION, APRIL 2008
BRANCH IV - CHEMISTRY
FOURTH SEMESTER

Reg. No ……..

COURSE : MAJOR – CORE
PAPER : PHYSICAL CHEMISTRY-I
TIME : 30 MINUTES **MAX. MARKS : 30**

SECTION – A

TO BE ANSWERED ON THE QUESTION PAPER ITSELF.

ANSWER ALL THE QUESTIONS. **(30x1=30)**

I. Choose the correct answer:

1. The adiabatic process is
   a) Isochoric b) Isobaric c) isoenthalpic d) Isoentropic

2. The intensive property among the following is
   a) ΔH b) ΔU c) ΔG d) C_p

3. The ΔH for a reaction is independent of
   a) temperature b) the path followed c) the initial and final states d) ΔV

4. The maximum efficiency of an engine operating between 110^oC and 25^oC is
   a) 22.2% b) 2.22% c) 0.222% d) 0.022%

5. If heat is measured in Joules, the units of entropy are
   a) Joules b) Joules per degree c) Joules-degree per mol d) degree/Joules

II. Fill in the blanks:

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

7. Exact differential can be _____ between appropriate _____, where as inexact differentials cannot be done so.

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8. The increase in internal energy of one mole of a gas per degree rise of temperature would otherwise be called as _____.

9. The temperature above which a gas cannot be cooled on expansion is known as the _____.

10. The vapourization of a liquid is accompanied by _____ in entropy.

III. Match the following:

11.	Hess' law	-	probability
12.	Zeroth law	-	enthalpy
13.	Entropy	-	Thermometer
14.	Kirchoff's	-	Helmholtz
15.	Work function	-	heat capacity
		-	free energy

IV. State whether the following statements are TRUE or FLASE :

16. The total entropy change for a reversible isothermal cycle is zero.

17. All naturally occurring processes always tend to change spontaneously in a direction which will lead to equilibrium and are uni directional.

18. The ratio of fugacities in the given state to those in the standard state is called the activity coefficient.

19. Absolute entropy of a solid is always zero

20. The mixing of two ideal gases at a given temperature leads to increase in disorder and entropy.

21. Bond enthalpies of diatomic molecules is equal to bond enthalpies of dissociation.

22. ΔH is always greater than ΔE for reactions.

23. The most common substance for the standardisation of calorimeter is benzoic acid.

24. The enthalpy of neutralization of HCl by $NaOH$ is less than the enthalpy of neutralization of CH_3COOH by $NaOH$.

25. The decrease in Helmholtz free energy is equal to the amount of reversible work done.

V Substantiate the following statements in one or two sentences: 5x1=5

26. Molar heat capacity of a gas at constant pressure is greater than that at constant volume.

27. Entropy of a system and surroundings taken together remains constant in a reversible process, while the same increases in an irreversible process.

28. The heat absorbed in the endothermic reaction does not lead to rise in temperature. On the other hand fall in temperature is observed.

29. Assuming the additive property of bond energy, the theoretical dissociation energy calculated has been found to be 534.1 KJ/mole, where as the experimental value is 5535.1 KJ/mol.

30. The second law of thermodynamics further establishes the first law.

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TIME : 2 ½ HOURS **MAX. MARKS : 70**

SECTION – B

ANSWER ANY FIVE QUESTIONS: **(5x6=30)**

1. a) Calculate the enthalpy of combustion of methane at 25°C and at 1 atm. Given that $\Delta Hf^0(CO_2) = -393.5\,KJ/mol$; $\Delta Hf^0(H_2O) = -285.9\,KJ/mol$; $\Delta Hf^0(CH_4) = -74.8\ KJ/mol$. (3 marks)
   b) Establish that $C_p - C_v = R$. (3 marks)

2. State and explain the Zeroth law of thermodynamics. What is the significance of this law?

3. Derive Clapeyron-Clausius equation for Liquid $\rightleftharpoons$ Vapour equilibrium.

4. What is chemical potential? Derive Gibbs-Duhem equation. How does chemical potential vary with temperature and pressure?

5. Explain the Nernst heat theorem. How does it lead to the enunciation of the third law of thermodynamics?

6. A sample of hydrogen is confined to a cylinder fitted with a piston of $5cm^2$ cross-section. It occupies $500cm^3$ and at room temperature it exerts a pressure of $2\ atm$. What is the change of entropy of the gas when the piston is drawn through $100cm$? [Given $R = .082\ dm^3\ atm\ k^{-1}mol^{-1}$]

7. Derive mathematical relationship between different thermodynamic quantities using Maxwell relations.

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SECTION – C

ANSWER ANY TWO QUESTIONS: (2x20=40)

8. a) What do you understand by the term fugacity? Explain the determination of fugacity by graphical method. (10)
   b) Obtain thermodynamically an expression for the equilibrium constant. (10)

9. a) Derive Kirchoff's equation depicting the variation of enthalpy of reaction with temperature. Write down the integrated form of the equation. (10)
   b) What is cyclic process? Describe in detail the Carnot reversible cycle for establishing the maximum convertibility of heat into work. (10)

10. a) What is Joule-Thomson effect? Obtain an expression for Joule-Thomson coefficient and inversion temperature. (10)
    b) Derive expressions for the work done in reversible isothermal expansion and reversible isothermal compression of an ideal gas. What is meant by maximum work? (10)

11. a) Define the terms Gibbs free energy and Helmholtz free energy. How is each of these terms related to maximum work done by a system during a given change. Discuss the variation of ΔG with variation in (i) Temperature & Pressure (ii) Pressure and volume. (10)
    b) Derive an expression for the entropy of a mixture of ideal gases. Deduce from it an expression for the entropy of mixing of ideal gases. (10)

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