**INDIAN INSTITUTE OF TECHNOLOGY, KHARAGPUR**
**CHEMISTRY DEPARTMENT**

**Date of Examination:** .... **Time:** 3 Hrs. **Full Marks:** 60 **No. of Students:** 17
**Semester:** Autumn 2010-11 **Department:** Chemistry **Subject No.** CY20101
**2nd Year Int. MSc.** **Subject Name:** Physical Chemistry I

{$k = 1.38 \times 10^{-23}$ J $K^{-1}$; $R = 8.314$ J $K^{-1}$ $mol^{-1}$; 1 bar = $1 \times 10^5$ Pa; $g = 9.81$ $ms^{-2}$}

**Q1. Fill in the blanks** **...(2 x 6 = 12)**

**(i)** The total heat of solution when 0.1 mole of sulfuric acid is mixed into 2.0 moles of water, is equal to _____; when the partial molar heat of solutions for sulfuric acid and water are given to be –16 k cal and – 45 cal respectively?

**(ii)** The maxima of an isoenthalpic curve for a gas correspond to the inversion point..... of the gas, for which the $\mu_{JT}$ value is.....

**(iii)** Complete the expression for n moles of an ideal gas: $\left(\frac{\partial S}{\partial V}\right)_T$ = _____

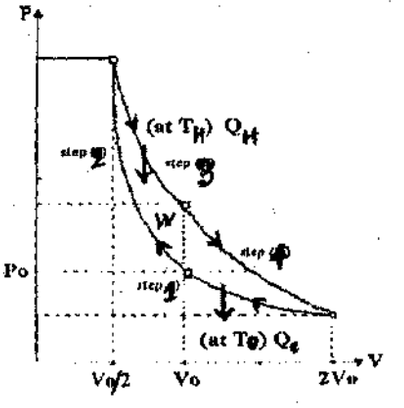
**(iv)** Conditions for reversibility for a closed system, with no non p-V (additional) work are: _____

**(v)** The expression for Gibbs-Helmholtz relation for a chemical reaction is :_____

**(vi)** If a gas undergoes cooling through adiabatic expansion process then the term, $\left[\frac{\partial(PV)}{\partial P}\right]_T$, for the process would always be _____

**viii).** What will be net work obtained/done and the heat absorbed/ rejected for the four step cyclic process shown in the P-V diagram

_____




**Q2.** State whether the following statements are **TRUE** or, **FALSE** and justify your answer analytically and with appropriate reasoning. **...(2 x 8 = 16)**

**(i)** During the compression stroke of an engine, the Helmholtz free energy is known to decrease as the temperature of the process increases.

**(ii)** In the transformation of melting of ice at 0°C and at normal atmospherics pressure, the value of **ΔA** will be greater than of **ΔG** for the transformation.

(iii) The volume of a mixture ($V_{mix}$) of one mole of pure water and one mole of pure ethanol at 4 °C will be more than the sum of molar volumes of the pure water ($V_m°_{,water}$) and pure ethanol ($V_m°_{,ethanol}$).

(iv) Water, unlike most other liquids, has a lower value of standard entropy of vaporization at its normal boiling.

(v) All isothermal processes are isoenergetic and isoenthalpic for an ideal gas.

(vi) Internal pressure for an ideal gas at a given temperature is greater that zero while for a real gas it is zero.

(vii) State of equilibrium for an isolated system is achieved when its entropy is minimized.

(viii) The change in internal energy for a constant pressure process will always differs from the internal change for a constant volume process for the same change in temperature.

**Q3.** An ideal gas is heated at constant pressure until its final temperature is 100 degrees higher than its initial temperature. After this, the gas is cooled 100 degrees at constant volume. The final and initial temperatures of the gas are thus the same. **(a)** How much heat is transferred to the gas? **(b)** How much work is done on the gas? **(c)** Does the entropy and enthalpy of the gas increase, decrease, or stay the same in this process? **...(4)**

**Q4.** What would be the rise in temperature when 1 cc of water at 10 °C is reversibly and adiabatically compressed from 0 to 1000 atm.? [Given: coefficient of expansion = $5 \times 10^{-5}$ $cc^{-1}$ and $C_{p,\ water}$ = 1.005 cal $gm^{-1}$ $K^{-1}$]. **...(6)**

**Q5.** What contributions towards $(C_p - C_v)$ for liquids and solids. Deduce the condition and justify. **...(6)**

**Q6.** A carnot engine converts $1/6^{th}$ of the heat supplied into work. If the temperature of the sink be reduced by 62 °C, the efficiency of the engine is doubled. Find the temperature of the source and the sink. **...(4)**

**Q7.** What would be the change in entropy when 10 gm of tin is heated from 293 K to 573 K.[Given: melting point of tin = 505 K; latent heat of fusion of tin = 14 cal/gm; specific heat of solid and liquid tin are 0.055 and 0.064 cal $gm^{-1}$ $K^{-1}$] **...(6)**

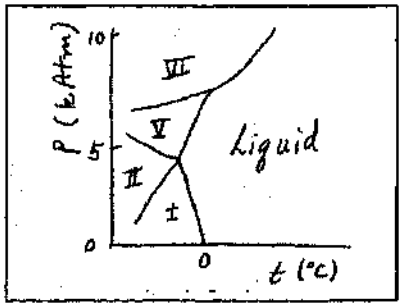
**Q8.** The vapor pressures of solid and liquid HCN are given as a function of temperature by:

(a) $\log_{10} P\ (\text{solid}) = 9.339 - \dfrac{1864 \cdot 8}{T}$ (from 243.7 °C to 258 °C)

(b) $\log_{10} P\ (\text{liquid}) = 7.7446 - \dfrac{1453 \cdot 06}{T}$ (from 265.0 °C to 300.4°C)

Calculate **(i)** the Heat of sublimation, **(ii)** the Heat of vaporization, **(iii)** the Heat of fusion, **(iv)** triple point temperature **(v)** normal boiling point **(vi)** vapor pressure of solid HCN at triple point **(vii)** vapor pressure of liquid HCN at triple point **...(6)**

**Q9.** Before ice III was discovered, phase diagram of water looked like what is shown in the given figure.
**(a)** What, in principle, is wrong with this phase diagram?
**(b)** What principle does this phase diagram violate? **...(4)**

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*Signature of the paper setter*

AMITA (PATHAK) MAHANTY
*Name in Capital Letters*