Indian Association for the Cultivation of Science
(Deemed to be University under *de novo* Category)
Integrated Bachelor's-Master's Program
End-Semester Examination-2019 (Semester- I)

Subject: Energetics and Bonding ***Subject Code(s): CHS 1101***
Full Marks: 50 ***Time Allotted: 3 h***

Section –A

(There are SEVEN questions in this section. Answer any FIVE. Each question carries 4 marks)

1) Show that for liquid and solid $\left(\frac{\partial H}{\partial P}\right)_T = V$ whereas for ideal gas $\left(\frac{\partial H}{\partial P}\right)_T = 0$, to a good degree of approximation.

2) If one mole of an ideal gas undergoes a reversible polytropic expansion the relation $PV^n = c$ holds; $n > 1$ and $c =$ constant.
   (a) Calculate work w for expansion from v_1 to v_2, if $T_1 = 300$ K and $T_2 = 200$ K and $n = 2$.
   (b) If $C_v = \frac{5}{2}R$, calculate heat q and internal energy change ΔE.

3) Answer the following questions:
   (a) Use cyclic rule for P, V and T to show $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\kappa}$, where α and κ are coefficient of thermal expansion and the coefficient of compressibility, respectively.
   (b) Show that for a reversible transformation at constant T and P, decrease in Gibbs free energy in a system is equal to the non-mechanical work.

4) A cylinder with adiabatic walls is closed at both ends and is divided into two volumes by a frictionless piston that is thermally insulating. Initial pressure, volume and temperature on both sides are P_0, V_0 and T_0, respectively. A heating coil in right-hand compartment is used to heat slowly the gas in that side until its pressure reaches $P_1 = \frac{64}{27}P_0$. If $\frac{C_P}{C_V} = 1.5$ then find out:
   (a) Entropy change of the gas on the left-hand compartment.

(b) The final volume of left-hand compartment in terms of V_0.

(c) The final temperature of the left-hand compartment in terms of T_0.

5) Answer the following questions:
   (a) Calculate the entropy of mixing of n_1 and n_2 moles of two substances. Show that this does not depend on the nature of the substance.
   (b) Show that the entropy of mixing per mole of this binary mixture must lie between 0 and 5.76 Joule/K.

6) Explain quantitatively how does the equilibrium constant of a chemical reaction vary with temperature.

7) A capillary tube of internal diameter 0.2 mm is dipped into a liquid when the liquid rises 15 cm. Assuming the angle of contact nearly equal to zero calculate the surface tension of the liquid. density of liquid = 2 gm/cc

Section-B

(There are SEVEN questions in this section. Answer any SIX.]

8. (a) For NSF_3 molecule: (i) Draw the Lewis structure, (ii) explain the geometry using the VSEPR model, and (iii) find the point group. [3]

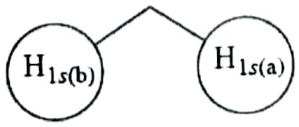
   (b) How the bond angle changes in HFO and F_2O compared to that in H_2O. Explain. [2]

9. (a) Molecules of the type AX_5 with no lone pair of electron on A are not stereochemically very stable. Explain the statement. How such molecules may be made stereochemically stable? [3]

   (b) Explain why BF_3 possesses an S_3 axis, but NF_3 does not? [2]

10. (a) What are the different symmetry elements present in B_2H_6. [2.5]

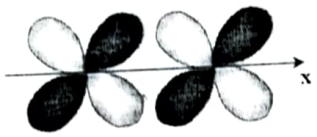
    (b) In the following geometry of two hydrogens, shown the transformation of $H_{1s(a)}$ for different operations under C_{2v} symmetry. [2.5]



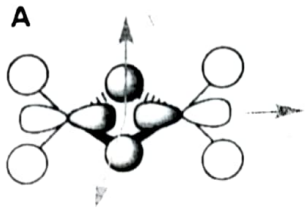
11. The H_3^+ ion is the most prevalent molecular ion in interstellar space. It is also one of the most important molecules in existence. It may hold secrets of the formation of the first stars after the Big Bang. From the MO of this molecule, predict its geometry and stability. [5]

12. (a) Explain with a sketch why bonding (or anti-bonding) molecular orbitals cannot be constructed from overlap of the 2s orbital on C and the $2p_y$ orbital on O. [1.5]

(b) What is the symmetry of the orbital formed from the side-on overlap of two d orbitals as shown below (σ,π, or δ; bonding or anti-bonding; g or u). The lobes of both orbitals lie in the plane of the paper. The x-axis is the internuclear axis. [1.5]



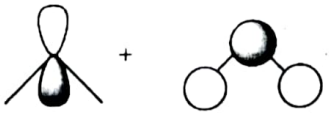
(c) In the diagram of a MO **A** given below, identify all the interactions that are important in evaluating the overall bonding or antibonding character of this MO? [2]



13. Prepare a molecular orbital diagram for SH^-, including sketches of the orbital shapes and the number of electrons in each of the orbitals. The S orbital energies are –22.7 eV (3*s*) and –11.6 eV (3*p*); the 1*s* of H has an energy of –13.6 eV. [5]

14. (a) Rank with explanation the following in order of ionization energy, from lowest to highest: He, HeH^+, H^-, He^+, H. [2]

(b) Show how the new bonding and antibonding pair would look like upon mixing the following MOs. Will the new antibonding MO be stabilized or destabilized when the L-M-L angle becomes 180°? [3]



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