

B.Sc. (Honours) Examination, 2018

Semester-I

Chemistry (Honours)

Course: BCHC-13

(Physical Chemistry)

Time: Three Hours

Full Marks: 30

Questions are of value as indicated in the margin.

Answer *any three* questions.

1. a) What is the Boyle temperature? Derive its expression from Dieterici equation. 1.5
b) Arrange the Boyle temperature, the boiling temperature and the critical temperature in the increasing order. 1
c) Derive the reduced equation of state from the van der Waals equation. 1.5
d) Discuss how the second virial co-efficient can be determined experimentally. 1.5
e) Comment on the possibility of defining Boyle temperature of a gas if 2
(i) $a = 0$ and $b = 0$, (ii) $a = 0$ and $b \neq 0$, (iii) $a \neq 0$ and $b = 0$, (iv) $a \neq 0$ and $b \neq 0$
f) Critical temperature, pressure and volume of N_2 are 125.97 K, 33.49 atm. 90.03 cm^3 , respectively. For H_2 critical temperature and pressure are 33.2 K and 12.8 atm., respectively. Calculate the ratio $\sigma_{N_2} : \sigma_{H_2}$. 2.5
2. a) CO_2 gas shows same type of PV vs. P plot as that of H_2 gas – justify or criticize the statement with reason. 1.5
b) Two separate bulbs are filled with an ideal gas A and a non ideal gas B, respectively in such a way that PV remains the same. B is at below its Boyle temperature. Which gas has greater temperature? Give reason. 2
c) State the law of corresponding states. 1
d) Express van der Waals equation of state in the form of Virial equation. 1.5
e) Calculate the reduced pressure, volume and temperature of one mole of van der Waals gas kept in a volume of 5 liters and pressure 5 atm. (given, $V_c = 0.0988 \text{ dm}^3 \text{ mol}^{-1}$, $P_c = 54.6 \text{ atm.}$, and $T_c = 190.2 \text{ K}$). 2.5
f) Find the units and dimension of van der Waals constant 'a' and 'b'. 1.5
3. a) State the first law of thermodynamics for a cyclic process. Show that it defined a state variable. Is this definition depends on the nature of the constituents of a thermodynamic system? Based on your answer could you comment about the place of the words like atom, molecule and ion etc. in the dictionary for the thermodynamics? 0.5+1+1+0.5
b) The change in internal energy of a thermodynamic system can be expressed as
$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$
 - i) Under what circumstances this equation is applicable? 1
 - ii) What is the physical meaning of this equation? 1
c) Prove that $Q_p = Q_v + \Delta nRT$ for an ideal gas reaction mixture. Symbols have usual meaning. Explain why Q_p is different from Q_v . For any other reactive systems which may have condense phase, the above relation can be expressed as $Q_p \approx Q_v + \Delta nRT$, where Δn is the difference between sum of stoichiometric coefficients for gaseous product(s) and reactant(s), respectively. How? What is the reason for this definition of Δn ? 2+1.5+1.5
4. a) Based on both mathematics and P-V diagram compare the maximum work produced in isotherman expansion of a gas for single stage and two stages, respectively. Explain the observation. Based on your answer could you comment whether work is a path or state variable? 3.5+1.5+1

P.T.O.

(2)

- b) One mole of an ideal gas $\bar{C}_V = 20.8 \text{ J/K.mole}$, is transformed at constant volume from 0°C to 75°C . Calculate Q , W , ΔU and ΔH . Comment on the results. Given that $R=8.314 \text{ J/K.mole}$. 3+1
5. a) Change in enthalpy due to chemical reaction at constant temperature and pressure is independent on the enthalpy of the elements, which are involved in the chemical reaction. Criticize or justify the statement with a suitable example. 2.5
- b) Prove that the conventional molar enthalpy of a compound is equal to the enthalpy of formation of the compound at the standard condition. 1
- c) Define heat of neutralization. What is its value for the reaction between a strong acid and a strong alkali? The heat of neutralization of HCN(aq) is 3000 cal at 25°C by a strong alkali. What is the heat of dissociation of HCN , $\text{HCN(aq)} = \text{H}^+(\text{aq}) + \text{CN}^-(\text{aq})$? 0.5+0.5+1
- d) Heat of solution of gas and solid is negative. Justify or criticize the statement with reason. 2.5
- e) If 3.0539 g of liquid ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$, is burned completely at 25°C in a bomb calorimeter, the heat evolved is 90.44KJ.
- i) Calculate the molar ΔH^0 of combustion for ethyl alcohol at 25°C . 1
- ii) If the ΔH_f^0 of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are $-393.51 \text{ kJ/(mol. reac.)}$ and $-285.83 \text{ kJ/(mol. reac.)}$, calculate the ΔH_f^0 of ethyl alcohol. 1
-