(b) (i) The fraction of surface (θ) covered by an absorbate at a pressure (P) is given by

$\theta = \frac{m_1 P}{1+m_2 P}$, where m_1 and m_2 are constants.

Suggest two plots that are liner. Comment on the slopes and intercepts of such plots.

(ii) A gas obeys the equation of state P(V–b) = RT. Show that the gas does not have Boyle temperature.

(iii) Established the Maxwell's relation

$\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta S}{\delta V}\right)_V$ and hence show that

$$TdS = C_v dT + T\left(\frac{\delta P}{\delta T}\right)_V dV = C_P dT - T\left(\frac{\delta V}{\delta T}\right)_P dP$$

(2+1)+2+(2+3)

B.Sc. 1st Semester (Honours) Examination-2022-23

CHEMISTRY

Course ID : 11412 Course Code : SH/CHEM/102/C-2

Course Title : Physical Chemistry-I (New)

Time : 1 Hour 15 Minutes *Full Marks :* 25

The figures in the right hand margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

1. Answer any *five* questions : 1×5=5

(a) As no heat enters into a system under adiabatic conditions, its energy is conserved during expansion.—Justify or criticize.

(b) For every system, $\oint dH = 0$, why?

(c) State Hess's law.

(d) Correct the statement : A gas can be liquefied at $T = T_C$ and $P = P_c$.

(e) Express Van der Waals constant 'b' in terms of molecular diameter σ.

(f) What is the unit of 'A' in the Arrhenius rate equation?

(g) Cite one example of pseudo-unimolecular reaction.

(h) Draw the potential energy diagram of an enzyme catalyzed reaction.

2. Answer any *two* questions : 5×2=10

(a) (i) Derive the expression of rate constant for a zero order reaction and hence calculate the time required for its completion.

(ii) If a first order reaction is 20% completed in 20 minutes, how long will it take to complete 85%? 2+1+2

(b) (i) Starting from Maxwell velocity distribution construct the energy distribution equation in three dimension.

(ii) Show that if Z = PV, then Z is a state function. 3+2

(d) (i) Evaluate $\left(\frac{\partial V}{\partial T}\right)_P$ for one mole of a Van dar Walls gas.

(ii) According to collision theory, how does the frequency factor depend on temperature? 3+2

3. Answer any *one* question : 10×1=10

(a) (i) Half life of a reaction is doubled when the initial concentration of the reactant is doubled. What is the order of the reaction with respect to the reactant?

(ii) For the reaction, NH_3 (g) = $\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g), \Delta H^0$ at 25^0C = 11,040 cal. Find the value of ΔE^0 of the reaction at 25^0C.

(iii) Write the virial equation of state of a gas. Obtain the expression of second virial coefficient of a van der Waals gas and hence find the Boyle temperature of gas. 3+2+5

2. Answer any *two* questions : 5×2=10

(a) (i) Derive the expression of rate constant for a zero order reaction and hence calculate the time required for its completion.

(ii) If a first order reaction is 20% completed in 20 minutes, how long will it take to complete 85%?

2+1+2

(b) (i) Starting from Maxwell velocity distribution construct the energy distribution equation in three dimension.

(ii) Show that if Z = PV, then Z is a state function.

3+2

(c) (i) Establish the relation PV^{γ} = constant for an adiabatic process.

(ii) 10 mole or an ideal gas at 300 K expands isothermally and reversibly and reversibly from a pressure of 10 atm 1 atm. Calculate w and q.

3+2

(c) (i) Establish the relation PV^{γ} = constant for an adiabatic process.

(ii) 10 mole of an ideal gas at 300 K expands isothermally and reversibly from a pressure of 10 atm 1 atm. Calculate w and q.

3+2

(d) (i) Evaluate $\left(\frac{\partial V}{\partial T}\right)_P$ for one mole of a van dar Walls gas.

(ii) According to collision theory, how does the frequency factor depend on temperature?

3+2

3. Answer any *one* question : 10×1=10

(a) (i) Half life of a reaction is doubled when the initial concentration of the reactant is doubled. What is the order of the reaction with respect to the reactant?

(ii) Heat of neutralization of HCN by NaOH is - 12.13 kJ/mol. Calculate the molar heat of ionization of HCN.

(iii) Write the virial equation of state of a gas. Obtain the expression of second virial coefficient of a van der Waals gas and hence find the Boyle temperature of the gas. 3+2+5

(b) (i) The fraction of surface (θ) covered by an adsorbate at a pressure (P) is given by

$\theta = \frac{m_1 P}{1+m_2 P}$, where m_1 and m_2 are constants.

Suggest two plots that are liner. Comment on the slopes and intercepts of such plots.

(ii) A gas obeys the equation of state P(V–b) = RT. Show that the gas does not have Boyle temperature.

(iii) What is the reduced equation of state? Write down its utility.

(iv) For the reaction, $NH_3(g)=(1/2)\ N_2(g)+(3/2)\ H_2(g)$, ΔH^0 at 25°C=11,040 cal. Find the value of ΔE^0 of the reaction at 25°C (2+1)2+3+2

Course Title : Physical Chemistry-I (Old)

1. Answer any *five* questions : 1×5 =5

(a) As no heat enters into a system under adiabatic conditions, its energy is conserved during expansion.—Justify or criticize.

(b) For every system, $\oint dH = 0$, why?

(c) H_2 at room temperature gets warmed up when subjected to Joule Thomson expansion. Why?

(d) Correct the statement : A gas can be liquefied at $T = T_C$ and $P < P_c$.

(e) Express van der Waals constant 'b' in terms of molecular diameter σ.

(f) Find out the unit of $\frac{d\ln k}{dt}$ for a n-th order reaction.

(g) Cite one example of pseudo-unimolecular reaction.

(h) Draw the potential energy diagram of an enzyme catalyzed reaction.