

CHUKA



UNIVERSITY

UNIVERSITY EXAMINATIONS

**THIRD YEAR EXAMINATION FOR THE AWARD OF DEGREE
OF BACHELOR OF SCIENCE IN CHEMISTRY**

CHEM 322: PHYSICAL CHEMISTRY III

STREAMS: B.Ed (SC) (BS.c)

TIME: 2 HOURS

DAY/DATE: FRIDAY 8/12/2017

8.30 A.M - 10.30 A.M.

INSTRUCTIONS:

- Answer Question ONE and any other TWO Questions

QUESTION ONE

- (a) (i) Differentiate between open, closed and isolated system. [3 Marks]
- (ii) State two important characteristics of a state function. [2 Marks]
- (iii) Comment on the following statements
- (I) When a system expands work is done on the system. [2 Marks]
- (II) A process in which the final temperature is equal to initial temperature must be an isothermal process. [2 Marks]
- (iv) Differentiate between intensive and extensive properties of a system. Give an example in each case. [3 Marks]
- (b) If one mole of ice at 0°C and 4.6 mm Hg pressure is converted to water vapour at the same temperature and pressure by increasing the space above ice sufficiently, calculate the enthalpy and intrinsic energy change. Latent heat of fusion of ice is 80 calories per g and latent heat of vaporization of liquid at 0°C is 596 calories per gram (12 atm = 101.325 J, 1 cal = 4.184 J) [6 Marks]
- (c) (i) Show that the work done by an ideal gas in a reversible adiabatic expansion is given by the equation $W = \frac{P_1V_1 - P_2V_2}{\gamma - 1} = C_v T_1 \left[1 - \left(\frac{P_2}{P_1} \right)^{R/C_p} \right]$

$$= C_v T_1 \left[1 - \left(\frac{V_1}{V_2} \right)^{R/C_v} \right] \quad [6 \text{ Marks}]$$

CHEM 322

(ii) Calculate the work of expansions of 1 mole of an ideal gas initially at 25°C, the pressure being changed from 1 to 5 atmosphere under

(I) Isothermal conditions [1 Mark]

(II) Adiabatic conditions.

$$C_p = 7.0 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

$$C_v = 5.0 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

$$R = 8.313 \times 10^7 \text{ ergs, } 1 \text{ J} = 10^7 \text{ ergs}$$

$$1 \text{ cal} = 4.184 \text{ J} = 4.336 \times 10^{-5} \text{ ev} = 4.184 \times 10^7 \text{ ergs} \quad [1 \text{ Mark}]$$

(d) 2 moles of an ideal monatomic gas ($C_v = 2.09 \text{ J mol}^{-1} \text{ K}^{-1}$) are heated from 300K to 350K. the volume of the gas changes from 0.02 m^3 to 0.2 m^3 . Assuming that the heat capacity remains constant in this temperature range, calculate the entropy change for the system, the surroundings and the universe if the process is carried out;

(i) Reversibly [2 Marks]

(ii) Irreversibly

By placing the system in contact with a reservoir at 500k and allowing the gas to expand against a constant external pressure equal to the final pressure of the gas ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) [2 Marks]

QUESTION TWO

Suppose 0.01 mol of a perfect gas having $C_v = 1.50 R$ independent of temperature undergoes the reversible cyclic process $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1$ show in figure below, where either

CHEM 322

P or V is held constant in each step.

Calculate

- (i) w [4 Marks]
(ii) q [3 Marks]
(iii) Δu [2½ Marks]

For each step and for the complete cycle

$q = \text{Heat}$, $w = \text{work}$, $\Delta u = \text{change in internal energy}$

(b) (i) Two identical metal blocks of constant heat capacities are at the same temperature T_1 . A refrigerator operates between these two blocks until one is cooled to the temperature T_2 . If the blocks remain at constant pressure and do not undergo any phase changes, show that the minimum amount of work needed to do this is given by $W_{min} = C_p \left[\frac{T_1^2}{T_2} + T_2 - 2T_1 \right]$ where C_p is the heat capacity of the metal blocks at constant pressure. [2 Marks]

(ii) A mole of an ideal monoatomic gas at 20 atm and 300K is expanded adiabatically against a constant pressure of 10 atm. Calculate the entropy change of the gas ($C_v = 12.55 \text{ J K}^{-1} \text{ mol}^{-1}$)

$$R = 0.082 \text{ litre atm}$$

$$1 \text{ atm} = 1.01325 \times 10^5 \text{ Nm}^{-2}, 1 \text{ litre} = 10^{-3} \text{ m}^3 \quad [6 \text{ Marks}]$$

(c) Two moles of an ideal gas expand isothermally from one litre to 10 litres at 300K. Calculate the change in free energy of the gas. [2½ Marks]

QUESTION THREE

(a) Show that:

$$\Delta S = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

Where ΔS = entropy change C_p = Heat Capacity at a constant pressure T = Temperature and P = Pressure. [10 Marks]

(b) A certain diatomic gas $C_p = 29.3 \text{ J K}^{-1} \text{ mol}^{-1}$ expands adiabatically from an initial state: $V_1 = 10^{-2} \text{ m}^3$, $P_1 = 100 \text{ atm}$ and $T_1 = 400 \text{ K}$ to the final state until the pressure is 1 atm. Calculate the entropy for the gas if the expansion is

- (i) Reversible
(ii) Irreversible against a constant external pressure of 1 atm. [2 Marks]

Assume ideal behavior for the gas and temperature independence for the heat capacity in the temperature range. [8 Marks]

QUESTION FOUR

(a) (i) Derive clausius –clapeyron equation for a phase change process. [5 Marks]

(ii) State various applications of clausius-clapeyron equation. [5 Marks]

(b) The pressure at triple point of water is 4.56 mm of Hg. Under this condition, the volume of liquid water per gram is 1.0001 cm^3 and that of ice is 1.0906 cm^3 . Find out the temperature of the triple point $L_f = 80 \text{ cal /gm}$. [4 Marks]

(c) The latent heat of evaporation of water is about $2.25 \times 10^6 \text{ J/Kg}$ and the vapor density is 0.0598 kg m^{-3} . Calculate the rate of change of boiling point with altitude near sea level in $^\circ\text{C}$ per km. The air temperature may be assumed to remain constant at 300K.

$\text{mol wt of air} = 29.04$

$h = 10^5 \text{ cm}$. $\text{W} = 10^7 = 10^7 \text{ ergs}$. [4 Marks]

(d) Derive an expression for the standard entropy change of the general reaction $n_A A + n_B B \rightarrow n_C C + n_D D$ as a function of temperature at $P^\circ = 1 \text{ atm}$. [2 Marks]

.....