CHUKA UNIVERSITY

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE IN

CHEM 322: PHYSICAL CHEMISTRY III

STREAMS: **TIME: 2 HOURS**

DAY/DATE: TUESDAY 23/03/2021 **11.30 A.M – 1.30 P.M**

INSTRUCTIONS:

Answer question one and any other two questions

USEFUL DATA

C = 3.0 x 10^{8} m/s

R = 8.31447 J K^{-1} mol^{-1}

= 8.31447 x 10^{-2} L bar K^{+1} mol^{-1}

== 8.20574 x 10^{-2} L atm K^{+1} mol^{-1}

= 6.23637 x 10^{-2} L Torr K^{+1} mol^{-1}

$\theta / ℃$ **= T/K -273.15**

1 cal = 4.184J

1 atm = 101.325 k pa

= 760 Torr

1 L atm = 101.325 J

QUESTION ONE (20 MARKS)

1. (a) Comment on the following statements:

(i) Below 0℃ super cooled water changes spontaneously into ice. [2 marks]

(ii) If the same change of state from state A to state B is effected in a system in different ways, the free energy change in each case will be same provided the process is reversible. [1 mark]

(iii) An adiabatic process is always isoentropic. [2 marks]

(iv) If a closed system at rest in the absence of external field undergoes an adiabatic process that has w = 0, then the temperature of the system must remain constant. (W = work) [4 marks]

(b) One mole of an ideal gas with CV = 3 cal deg^{-1} initially at S.T.P is subject through the following reversible cycle:

- State 1 to state 2 heated at constant volume to twice the initial temperature.

- State 2 to state 3 expanded a adiabatically until it is back to initial temperature.

- State 3 to 1 compressed isothermally back to state 1

(i) Depict the cycle in a V – T diagram. [½ marks]

(ii) Calculate the heat (Q) work done (W) and change in internal energy for

(I) Isochoric process [2½ marks]

(II) Adiabatic reversible change [2½ marks]

(III) Isothermal compression (Y = 1.66) [2½ marks]

C(i) A compressor designed to compress air is used instead to compress helium. It is found that the compressor over heats. Explain this effect, assuming that the compression is approximately adiabatic and starting pressure is the same for both gases. [2 marks]

(ii) 104 gm of He were kept in a cylinder covered by a piston at 127° and 25 atm pressure. The pressure is suddenly released to 1 atm adiabatically.

(I) Calculate the final temperature and work done [3½ marks]

(II) What would be the final temperature and work done if the change was carried out reversibly and adiabatically? [4 marks]

(III) What would be the work done if the change was carried out reversibly and isothermal? [1 mark]

(IV) Calculate change in internal energy (Δu¿ and enthalpy change (ΔH¿ { Assume ideal monotomic gas . [½ mark]

(d) A steam engine operates between 14℃ and 30℃. Calculate the minimum a mount of heat that must be withdrawn to obtain 100J of work. [1 mark]

QUESTION TWO (20 MARKS)

2(a) (i) Explain the difference between isothermal and adiabatic processes. [4 marks]

(ii) Draw carnot cycle diagrammatically in V vs P,T vs S, S vs T, P vs T and V vs T with reference to P vs V diagram. Indicate each step.

Reference plot

Where V- volume, P = pressure, T = temperature, S = entropy [4½ marks]

(ii) Explain the following statement given " though entropy is a fundamental state function and free energy is a derived one, the latter can be used more conveniently. [3½ marks]

(b) (i) In what proportions should n- hexane and n-heptane be mixed to achieve the greatest ΔS_{mix} (change of entropy of mixing) assuming ideal mixing. [2 marks]

(ii) For copper β = 0.8 x $10^{-6} atm^{-1.}$

(I) What is the change in Gibbs free energy when 63.546 gm of copper is subjected to an extra pressure of 1000 atm? [5½ marks]

(II) What would be change in Gibbs free energy (ΔG¿ if β is a assumed to be zero? {The density of copper is 8.93 gm/cm^3, β = co-efficient of thermal compressibility} [½ mark]

QUESTION THREE (20 MARKS)

3(a) (i) 5 mole of an ideal gas initially at 50 atm and 300k is expanded irreversibly where the pressure suddenly drops to 10 atm. The work involved is 4000J. Show that the final temperature is greater than a reversible adiabatic expansion to the same pressure. If cv = 1.5 R, Calculate the entropy change during the irreversible expansion. [3 marks]

(ii) Briefly explain short notes on heat engines. [5 marks]

(iii) Two heat engines working between three temperatures T_1, T_2 and T_3 and shown in the figure

Find the relations between the temperatures T_2, T_3 and T_3

If

(I) Two engines have the same efficiency. [1½ marks]

(II) Two engines do the same a mount of work. [½ mark]

(b) A heat engine operating between $800^0 C$ and 25℃ produces work (absorbing heat Q at 800℃) that is entirely used to run a refrigerator operating between 0℃ and 25℃ . Calculate the ratio of the heat absorbed by the pump at 0℃ (Q_2¿ to that absorbed by the engine (Q). Assuming ideal operation for both, calculate Q_1, Q_2, W(work done) and the heat rejected by the heat pump at 25 ℃, if Q_2 heat absorbed at 0℃ leads to conversion of 100gm of water to ice, cp =325g/gm. How much heat is rejected by the engine at 25℃. [5 marks]

(c) A polytropic process is one that obeys the relation $PV^n = C$, where n and c are constants. Derive a general expression for work done (W) heat (Q) to change in internal energy (ΔU ¿ for such a change from state 1 state 2 carried out reversibly. Show that they provide familiar relation when n = 0, 1 ∞, Y.

QUESTION FOUR (20 MARKS)

4.(a) Explain the following laws of thermodynamics.

(i) Zeroth law of thermodynamics. [1 mark]

(ii) Third law of thermodynamics [4 marks]

(b) (i) State any five applications of clapeyron clausius equation. [2½ marks]

(ii) The pressure of triple point of water is 4.56 mmHg. 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 Lf = 80 cal/gm. {R = 8.314 NM $k^{-1} mol^{-1}$ =0.0821 L atm $k^{-1} mol^{-1}$ = 1.987 $cal\, k^{-1} mol^{-1}$} [3 marks]

(c)(i) It is found that $\Delta H = -2810\, KJ\, mol^{-1}$ and ΔS = 182.4Jk^{-1} when glucose is oxidized at 300k according to the reaction. $C_6H_2O_6(S) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2Q(L)$

(I) How much of the above energy can be extracted as heat? [½ mark]

(II) How much of it can be extracted as work {$\Delta H = enthalpy$ change, Δs entropy change} [2½ marks]

(ii) One mole of water vapor is compressed reversibly to liquid water at 373 K°. Calculate W, $\Delta H, \Delta S, \Delta G \wedge \Delta A$

ΔH_{vap} at 373k = 2258J gm^{-1} where W= work done

Q= Heat

ΔA = change Helmholtz free energy or the work function

ΔH = Enthalpy change

ΔS =Entropy change

$\Delta G =$ ¿Change in Gibbs free energy [3½ marks]

(d) What are the difference between Joule Thomson (J-J) cooling and adiabatic cooling.
[3 marks]
