

CHUKA



UNIVERSITY

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE

CHEM 322: PHYSICAL CHEMISTRY III

STREAMS: BSC

TIME: 2 HOURS

DAY/DATE: TUESDAY 02/02/2021

2.30 P.M. – 4.30 P.M.

**INSTRUCTIONS: Answer ALL questions**

**QUESTION ONE (30 MARKS)**

1. a. Distinguish between

- (i) Isothermal and adiabatic process (2 marks)
- (ii) State function and path function (2 marks)
- (iii) Reversible and irreversible process (2 marks)
- (iv) Gibbs and Helmholtz free energy (2 marks)

b (i). State Kirchoff's law and derive it with the help of first law of thermodynamics (4 marks)

(ii) With the help of first law of thermodynamics, show that:

- (I) Heat absorbed by a system at constant volume is equal to increase in internal energy of the system (2 marks)
- (II) Heat absorbed by a system at constant pressure is equal to the increase in the enthalpy (2 marks)

c (i) Derive an expression in each of the following cases:

- (I) Isobaric reversible process (2 marks)
- (II) Isothermal reversible expansion when pressure are known and when volume are known for the initial and final states (2 marks)

(d) An ideal gas undergoes a single stage expansion against a constant external pressure (P) from  $P_1, T, V_1$  to  $P_2, T, V_2$

- (i) What is the magnitude of work done by the system? (2 marks)

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- (ii) What is the largest mass,  $M$  which can be raised through a height,  $h$ , in this expansion (2 marks)
- (iii) The system is now restored to its initial state by a single stage compression. What is the magnitude of work done on the system? (2 marks)
- (iv). What is the smallest mass  $M'$  which must fall through the height,  $h$  to restore the system (2 marks)
- (v). What is the net work done on the system in the cyclic transformation (2 marks)

### QUESTION TWO (20 MARKS)

- 2a (i). Describe Carnot's cycle for establishing the maximum convertibility of heat into work. How does it lead to the definition of second law of thermodynamics (5 marks)
- (ii) One mole of an ideal gas, originally at a volume of 5 liters at 500K is allowed to expand adiabatically until the final volume is 15 liters. For the gas  $C_v = 3/2R$ . Calculate final temperature and  $\Delta S$ , when
- (I) The expansion takes place reversibly (3 marks)
- (II) The expansion takes place against a constant pressure of 3 atm. (3 marks)
- (III) The change in volume is due to a free expansion (3 marks)
- (b). Comment on the following:
- (i) Entropy of the universe is increasing (2 marks)
- (ii) Death is natural and life abnormality (2 marks)
- (iii) Entropy change at equilibrium is zero (1 mark)
- (iv) 0 K cannot be reached experimentally (1 mark)

### QUESTION THREE (20 MARKS)

- 3 a) For a certain reaction,  $\Delta G$  (cal/mole) =  $13580 + 16.1T \log_{10}T - 72.59T$ . Find  $\Delta S$  and  $\Delta H$  of the reaction at 27°C (8 marks)
- b) 5 moles 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  $C_v = 1.5R$ . Calculate the entropy change during the irreversible expansion. (8 marks)
- c). Though entropy is a fundamental state function and free energy is a derived one, the latter can be used more conveniently. Explain (4 marks)
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