

CHUKA



UNIVERSITY

UNIVERSITY EXAMINATIONS

**EXAMINATION FOR THE AWARD OF DEGREE OF
BACHELOR OF EDUCATION SCIENCE, BACHELOR OF SCIENCE**

CHEM 322: PHYSICAL CHEMISTRY III

STREAMS: BED (SCI), BSC

TIME: 2 HOURS

DAY/DATE: TUESDAY 03/12/2019

2.30 PM – 4.30 PM

INSTRUCTIONS:

Answer Question One and any other Two Questions

Useful Data

QUESTION ONE (30 MARKS)

(a) Define with appropriate examples, the following terms

- | | | |
|-------|-----------------------------------|-------------|
| (i) | Closed system | [1 mark] |
| (ii) | Adiabatic process | [1 mark] |
| (iii) | Thermal equilibrium | [1 mark] |
| (iv) | Intensive and extensive variables | [2 ½ marks] |

- (b) (i) The internal energy change when 1.0 mol CaCO_3 in the form of calcite converts to aragonite is +0.21 kJ. Calculate the difference between the enthalpy change and the change in internal energy when the pressure is 1.0 bar given that the densities of the solids are 2.71 g cm^{-3} and 2.93 g cm^{-3} respectively
[2 marks]
- (ii) Determine the difference in the work done when, 500 ml of a gas at pressure of 2 atmospheres is compressed to 100 ml reversibly and
- (I) Isothermally [1 ½ marks]
(II) Adiabatically (γ for this gas is 1.35) [2 ½ marks]
- (iii) If one mole of ice at 4.6 torr pressure is converted to water vapour at the same temperature and pressure by increasing the space above ice sufficiently; calculate the changes in enthalpy and intrinsic energy. Given latent heat of fusion of ice is 334.7 J/g and latent heat of vaporization of liquid water at 101325 Pa is 2494 J/g .
[4 marks]
- (c) (i) Consider a mass of air $m=10 \text{ kg}$ cooled isochorically from $P_1=1 \text{ MPa}$, $T=500 \text{ K}$ to the temperature of the surroundings $T_2=300 \text{ K}$. Determine the entropy change of the air, the surroundings and universe. Comment on yours obtained.
[6 marks]
- (ii) The equilibrium constant K_p for a reaction is 10 . Calculate the enthalpy of the reaction
[1 mark]

QUESTION TWO (20 MARKS)

- (a) (i) Derive the integral Clausius Clapeyron equation in the form for an ideal gas.
[1 ½ marks]
- (ii) At 373.6 K and 372.6 K the vapour pressure of H_2O are 1.018 and 0.982 atm respectively calculate the heat of vapourization of water in Joules
[1 ½ marks]
- (b) (i) Explain the following observations “though entropy is a fundamental state function and free energy is a derived one, the latter can be used more conveniently”.
[2 marks]
- (ii) State the third law of thermodynamics. [½ marks]

- (iii) Discuss the importance of the third law of thermodynamics and its limitation.

[8 ½

marks]

- (c) (i) Calculate the entropy change when one kilogram of water at T_1 is converted to super heated steam at 200 under constant atmospheric pressure. (Specific capacity of liquid water = 4180 J/Kg),
Specific heat capacity of steam = $(1670+0.49T)$ J/kg at T and latent heat of vaporization is

- (ii) 5 moles of an ideal gas, initially at 50 atm and 300K is expanded irreversibly where the pressure suddenly drops to 10atm. The work involved is 4000 J.
(I) Show that the final temperature is greater than a reversible adiabatic expansion at the same pressure.
(II) $C_v=1.5R$, calculate the entropy change during the irreversible expansion.

[3 ½

marks]

QUESTION THREE (20 MARKS)

- (a) Briefly explain the following:

- (i) Carnot cycle [7 marks]
(ii) Carnot refrigerator [1 mark]
(iii) Carnot theorem [½ mark]

- (b) Two moles of a perfect gas underwent the following processes:

A reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0L)

A reversible isochoric change of state from (1.0 atm, 40.0L) to (0.5 atm, 40.0L)

A reversible isothermal compression from (0.5 atm, 40.0L) to (1.0 atm, 20.0L)

- (i) Sketch and label each of the processes on the same P – V diagram. [1 mark]

- (ii) Calculate the total work (w) and the total heat change (q) involved in the above processes. [3

marks]

- (iii) Calculate the change in internal energy, enthalpy and entropy for the overall process [½ mark]

- (c) A heated copper block at 130 loses 340J of heat to the surrounding which are at room temperature of 32. Calculate

- (i) The entropy change of the system (copper block). [½ mark]
(ii) The entropy change of the surrounding. [½ mark]

- (iii) The total entropy change in the universe due to this process. Assume that the temperature of the block and the surroundings remain constant. [½ mark]
- (d) Assuming ideal gas thermodynamic efficiency, calculate the amount of work needed to freeze 180g of water at 0 when the surrounding air is at a temperature of
- (i) 25 [1 mark]
- (ii) 47(Latent heat of fusion of ice is 6.01 KJ mol⁻¹) comment on your answers [½ mark]
- (e) Give a brief explanation of Trouton's rule. [2 marks]
- (ii) Calculate the vapor pressure of a liquid at 25 if its normal boiling point is 80.2 [1 mark]

QUESTION FOUR (20 MARKS)

- (a) (i) Derive the equation given below which shows variation of Gibbs free energy function with temperature at a constant pressure [4 ½ marks]
- (ii) The free energy change (for the reaction is found to be 13.13 KJ at 300K and for it is -60.21JK⁻¹. Calculate for the reaction at 300K. Calculate for the reaction at 300K [1 mark]
- (b) Predict the sign of entropy change for each of the following processes. Give reason(s) for each case.
- (i) [½ mark]
- (ii) [½ mark]
- (iii) Hand boiling of an egg [1 ½ marks]
- (iv) Devitrification of glass [½ mark]
- (c) (i) For a certain reaction Gibbs free energy change (cal /mole)=13580 +16.1T logT-72.59T. Calculate the entropy change in JK⁻¹ mol⁻¹ and the enthalpy change in KJ mol⁻¹ of the reaction at 27 (1 cal = 4.184J)
- (ii) Two moles of a monoatomic gas initially at 4.0 bar and 47 undergo reversible expansion in an insulated container. Calculate the temperature at which

the pressure reduced to 3.0 bar. [1
mark]

(iii) Establish the condition for spontaneous vaporization of water given
Cal mol⁻¹ and = 26 Cal K⁻¹ [1 mark]

(d) (i) Prove that [3 ½ marks]

(ii) The state of a mole of an ideal gas changed from State A (2 P,V) through four
different processes and finally returned to the initial state reversibly as
shown below:

Calculate the total work done by the system and heat absorbed by the system in
the cyclic process. [3
marks]
