CHUKA  **UNIVERSITY**

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

CHEM 821: ADVANCED CHEMICAL THERMODYNAMIC

STREAMS: MSC (CHEM) **TIME: 3 HOURS**

DAY/DATE: MONDAY 05/08/2019 **2.30 PM – 4.30 PM**

INSTRUCTIONS:

ANSWER ALL QUESTIONS

USEFUL DATA

1. (a) (i) Discuss thermal analysis in phase diagram. [4 marks]

(ii) Construct the isothermal equilibrium diagram for aternary system composed of water and two salts having a common ion which does not form a compound. [2 marks]

(iii) Discuss the system in Q 1a(ii) and give two examples of such a system. [4 marks]

(iv) Explain how the diagram in Q1a(ii) is helpful in understanding the principle of isothermal fractional crystallization. [2 marks]

(b) The melting points of metals A and B are and respectively. They form an intermetallic compound C, containing 75 percent of A which melts at . Mixtures containing 20 percent and 90 percent of A melt at constant temperatures at and respectively.

(i) Draw an approximate equilibrium diagram and label each area to indicate the equilibrium involved. [4 marks]

(ii) Explain what happens on cooling liquid mixture containing 50% of A. [1 ½ marks]

(iii) Describe the effect of melting a mixture of zinc in a lead – silver alloy. [½ mark]

(c) For isopropanol vapour at the following equation is available. where P is in bars. Estimate the fugacity at 50 bars and

2. (a) (i) Derive the general expression of fugacity for liquids at constant temperature. [2 marks]

(ii) Liquid chlorine at has a vapour pressure of 0.77M pa, fugacity 0.7M pa and molar volume /kg mole. Calculate the fugacity at 10 mpa and [2 marks]

(iii) A terinary gas mixture contains 20 mole % A, 35 mole% B and 45 mole % C at 60 atmand . The fugacity coefficients of A, B and C in this mixture are 0.7, 0.6 and 0.9. Calculate the fugacity of the mixture. [2 marks]

(b) (i) Deduce whether the equation given below is thermodynamically consistent

X = mole fraction [6 marks]

(ii) Derive an equation for dependence of enthalpy change on temperature for the reaction.

Coefficients in heat capacity equations [5 marks]

Substance	Temperatur e range /K					
	50 – 100	3.6297	-1.7943	0.6579	-0.6007	0.17861
	50 – 100	3.259	1.356	-1.502	-2.374	1.056
Cgraphite	50 – 400	-1.30031	21.18944	-10.16834	26.66831	-25.41989

(iii) From the data given below estimate the variation of the molar heat capacity of nitrogen with pressure at ordinary temperature and pressure.
Heat capacities of Nitrogen (Cp) at
1atm pressure in Cal deg^{-1} Mol^{-1}

6.449	1.413	-0.0807

Joule-Thermson coefficient for nitrogen at in deg
[3 marks]

3. (a) (i) For isopropanol vapour at 200 the following equation is available. where P is in bars. Estimate the fugacity at 50 bars and 200 [2 marks]

(ii) State three major effects of solute and solvent properties in the Debye-Hückel model for dilute solution of strong electrolytes. [2 marks]

(b) (i) Express Berthelot and Dieteric equations in the viral form and obtain an expression for the boyle temperature in each case. [5 marks]

(ii) The pressure exerted by molecules of a gas in 2 litre vessel is 1.52 cm Hg. Calculate the temperature of the gas if the gas

(I) Ideal [1 ½ marks]
(II) Van dar Waals [1 ½ marks]
(III) Dieterici [2 marks]

With the same

(c) (i) Explain how critical volume of a given gas can be determined. [2 marks]

(ii) If the temperature above which van der Waals gas cannot be liquefied is 32.3 and minimum pressure to be applied at that temperature for liquefaction be 48.2 atm.

(I) Determine the diameter of gas molecule. [2 marks]

(II) Calculate "a" and hence pressure of 60gm of the gas at 27 with a volume of 2 litres if its molecular weight is 30. [2 marks]
