

CHUKA



UNIVERSITY

UNIVERSITY EXAMINATIONS

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

CHEM 821: ADVANCED CHEMICAL THERMODYNAMICS

STREAMS: MSC CHEM

TIME: 3 HOURS

DAY/DATE: WEDNESDAY 08/04/2020

11.30 A.M. – 2.30 P.M.

INSTRUCTIONS:

- Answer ALL questions.

QUESTION ONE (15 MARKS)

- Express Dieteric and Redlich-Kwong equation in the virial form and obtain expression for the Boyle temperature in each case. (7 marks)
 - Derive an equation for the coefficient of thermal expansion $\{\alpha = \frac{1}{v} (\frac{dv}{dT})_P\}$ for a gas that obeys soave-Redlich-Kwong equation. (3 marks)
 - Develop an equation of real gas that obeys Berthelot equation and relates entropy with temperature, volume, heat capacity at constant volume and van der Waal's constants. (5 marks)

QUESTION TWO (15 MARKS)

- Discuss by what physical mechanism the adiabatic steps of the Carnot cycle can get an irreversible character. (2 marks)
 - For isopropanol vapour at 400°C the following equation is available. $Z = 1 - 4.93 \times 10^{-4}P - 15.46 \times 10^{-6}P^2$ where P is in bars. Estimate the fugacity at 100 bars and 400°C . ($3\frac{1}{2}$ marks)
 - A 40% mole by methanol-water solution is to be prepared. How many m^3 of pure methanol (molar volume $50.8 \times 10^{-6}m^3/mol$) and pure water

(molar volume = $20.082 \times 10^{-6} \text{ m}^3/\text{mol}$) are to be mixed to prepare 3.2 m^3 of desired solution. The partial molar volume of methanol and water in 40% solution are $44.68 \times 10^{-6} \text{ m}^3/\text{mol}$. $21.84 \times 10^{-6} \text{ m}^3/\text{mol}$ respectively. (3½ marks)

(ii) Use Redlich Kister test to verify whether the following data is consistent.

X_1	Y_1	Y_2
0.0	0.576	1.00
0.2	0.655	0.985
0.4	0.748	0.930
0.6	0.856	0.814
0.8	0.950	0.626
1.0	1.00	0.379

X = mole fraction

y = activity coefficients

(6 marks)

QUESTION THREE (15 MARKS)

3. (a) For the reaction

$\text{C}_2\text{H}_4 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{C}_2\text{H}_4\text{O}$, develop equation for ΔH^0 , K and ΔG^0 , Find ΔG^0 at 550 k.
 c_p (cal/mol k) data

$$\text{C}_2\text{H}_4 = 3.68 + 0.0224T$$

$$\text{O}_2 = 6.39 + 0.0021T$$

$$\text{C}_2\text{H}_4\text{O} = 1.59 + 0.00332T$$

Standard heat of reaction ΔH_{298}^0 $\text{C}_2\text{H}_4\text{O} = -12190$ and $\text{C}_2\text{H}_4 = -12500$, cal/mol
and $\Delta G_{298}^0 = -19070$ cal/mol. (7 marks)

(b) The system Pb (m. pt 327°C) and Sb (m. pt 631°C) exhibits a simple eutectic at 86% Pb (by mass) and 246°C . Breaks in the cooling curves in thermal analysis were found for the following compositions.

$T^\circ\text{C}$	550	500	400	300	296
Mass % Pb	30	44	66	80	96

Draw a tentative phase diagram for the system and label it. Calculate the amount of antimony that crystallizes out from 20Kg of melt containing 35% Pb by mass after cooling to a temperature of 400°C . How much is the maximum amount of Sb that can be recovered from the melt. (6 marks)

- (c) Discuss the advantages of a modulated temperature differential scanning calorimeter (MTDSC). (2 marks)
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