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University Examinations 2024/2025

FIRST YEAR FIRST SEMESTER EXAMINATION FOR THE DEGREE MASTER OF SCIENCE IN CHEMISTRY

SCH 7113: ADVANCED CHEMICAL THERMODYNAMICS

DATE: JANUARY 2025 **TIME: 3 HOURS**

INSTRUCTIONS: *Answer question **one** and any other **two** questions*

QUESTION ONE (30 MARKS)

a) Give the definition of a real gas (2 marks)

b) Explain the term 'partial pressure' and explain why Dalton's law is a limiting law. (4 marks)

c) Explain how the perfect gas equation of state arises by combination of Boyle's law, Charles's law, and Avogadro's principle. (6 marks)

d) In an industrial process, nitrogen is heated to 500 K in a vessel of constant volume. If it enters the vessel at 100 atm and 300 K, what pressure would it exert at the working temperature if it behaved as a perfect gas? (8 marks)

e) The van der Waals equation of state for real gas is expressed as follows:

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

(i) Explain the constants a and b (4 marks)

(ii) By multiplying both sides of the equation

$$(V_m - b)V_m^2,$$

We obtain:

$$V_m^3 - \left(b + \frac{RT}{p}\right)V_m^2 + \left(\frac{a}{p}\right)V_m - \frac{ab}{p} = 0$$

Given that a = 3.610 clm^6 atm mol^{-2} and b = 4.29 x 10^{-2} dm^3 mol^{-1} use this expression to estimate the terms b+RT/p, a/p and ab/p for CO_2 at 500 K and 100 atm. (6 marks)

QUESTION TWO (15 MARKS)

a) At 100 ^oC and 16.0 kPa, the mass density of phosphorus vapor is 0.6388 kg m^{-3}. What is the molecular formula of phosphorus under these conditions? (10 marks)

b) Derive an expression for the expansion coefficient of a perfect gas. (5 marks)

QUESTION THREE (15 MARKS)

a) Discuss the molecular interpretation of heat and work (6 marks)

b) Discuss the molecular interpretation of the Joule - Thomson effect (9 marks)

QUESTION FOUR (15 MARKS)

a) The partial molar volumes of two liquids A and B in a mixture in which the mole fraction of A is 0.3713 are 188.2 cm^3 mol^{-I} and 176.14 cm^3 mol^{-1}respectively. The molar masses of the A and B are 241.1 g mol^{-I} and 198.2 g mol^{-I}. What is the volume of a solution of mass 1.000 kg give that:?

Total volume $V = n_A V_A + n_B V_B = (n(x_A V_A + x_B V_B)$

Total mass $m = n_A M_A + n_B M_B$

$= n(x_A M_A + (1 - x_A)M_B$ where $n = n_A + n_B$

$$\frac{m}{x_A M_A + (1 - x_A)M_B} = n$$ (5 marks)

b) Give a detailed account of the Debye-Huckel limiting law (10 marks)