RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc (General) Degree in Applied Sciences
First Year - Semester II Examination – October/November 2017

CHE 1302 – PHYSICAL CHEMISTRY I

Answer **FIVE** questions only Time: Three (3) hours

$R = 8.314\ J\ K^{-1}\ mol^{-1}$, $1\ bar = 10^5\ Pa$, $1\ atm = 1.01325 \times 10^5\ Pa$

1.

a) Assuming ideal gas behavior, calculate the root mean square speed of a helium atom (relative atomic mass 4.0) at 298 K.

b) Show that the mean molar translational kinetic energy of an ideal gas is 3/2 RT.

c) Use the laws put forward by Boyles, Charles and Avogadro to show that the Boltzmann constant (k) and the universal gas constant (R) are independent of the nature of gas.

d) Indicate briefly the advantage of using the reduced equation of state instead of the van der Waal's equation of state to describe the behavior of gases.

e) Explain why real gaseous CO_2 and NH_3 can be liquefied very easily at room temperature while it is impossible to liquefy gaseous H_2 and O_2 under similar conditions.

f) Calculate the three critical constants for NH_3 given that the van der Waals constants for this gas are $a = 0.366\ Nm^4\ mol^{-2}$ and $b = 4.3 \times 10^{-5}\ m^3\ mol^{-1}$

(100 marks)

2.

a)

i. What are extensive and intensive properties?

ii. Classify the following into extensive and intensive properties

Enthalpy, density, pressure, heat capacity, molar volume, free energy, kinetic energy, entropy, molecular weight, volume (20 marks)

b) 5 mol of an ideal gas at 400 K and 4 atm pressure undergo expansion isothermally to half the initial pressure. If this expansion take place;

i. Reversibly

ii. Irreversible against zero pressure

iii. Irreversible against 5 atm external pressure

Calculate the work done on the gas by surrounding in each case. (30 marks)

c) 2 mol of an ideal gas is allowed to expand reversibly at a constant temperature of 0 ^{0}C from an initial pressure of 25 atm to final pressure of 0.2 atm.

Calculate

i. The work done w by the system

ii. Internal energy change ΔU of the system

iii. Enthalpy change ΔH of the system

(30 marks)

d) What is the ΔH when 10 mol of H_2O at 20 atm is heated from 30 ^{0}C to 40 ^{0}C?

$C_{p,m}(\text{liquid, } H_2O) = 75 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta H_{\text{Vapourization}} = 47.3 \text{ kJ mol}^{-1}$ at 373 K

$C_{p,m}(\text{gaseuos, } H_2O) = 35.4 \text{ J K}^{-1} \text{ mol}^{-1}$

(20 marks)

3.

a) Define the compressibility factor (z) of a gas and show how the deviation of the behavior of a real gas from ideality can be expressed in terms of the compressibility factor for

i) A given gas at various temperatures

ii) A series of gases at a temperature

(25 marks)

b) Explain what do you understand by the term 'critical temperature' of a gas

(15 marks)

c)

i. Briefly explain the Gibbs free energy criterion for equilibrium and spontaneity in a system

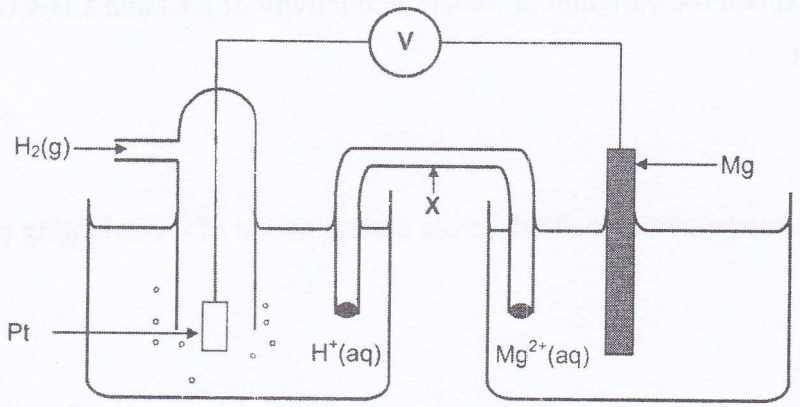
ii. Ammonium chloride dissolves in water at 300 K with a molar increase in enthalpy of 243 k J mol^{-1}. The corresponding molar entropy change for the dissolution is 168.5 kJ mol^{-1}. Calculate the value of ΔG

iii. Deduce whether ammonium chloride will spontaneously dissolve in water at constant pressure and temperature

iv. If this conversion take place reversibly (hypothetically) under condition of constant pressure and constant temperature, calculate the value of ΔG

(60 marks)

4. The galvanic cell represented below consists of a hydrogen half-cell and a magnesium half-cell at standard conditions.



$E^0 (Mg^{2+}/Mg) = -2.37$ V

a) Write down the balanced equation with the help of half cell reactions, for the net (overall) cell reaction taking place in the above cell.

b) Write down the cell notation for the above cell.

c) Calculate the cell potential using Nernst equation and Gibbs free energy change.

d) How will the initial voltmeter reading be affected if the concentration of the electrolyte in the $Mg(s)/Mg^{2+}(aq)$ half-cell is decreased? Explain your answer.

e) What is 'X' in the diagram and its role in this cell?

(40 marks)

f) Write short notes on the following:

(i) Helmholtz electrical double layer

(ii) Liquid junction potential

(iii) $Ag/AgCl/Cl^-$ electrode

(60 marks)

5.

a) The molar conductivity of a solution containing 2.54 g of $CuSO_4$ /L is 91.0 S cm^2 mol^{-1}. What is the resistance of a 100 cm^3 of this solution when placed between two electrodes 1.00 cm apart, each having an area of 1.00 cm^2. (atomic weight: Cu = 63.5, S = 32.0, O = 16.0 g mol^{-1}) (30 marks)

b) Sketch and explain the variation of molar conductivity of KCl and CH_3COOH against concentration. (30 marks)

c) Give detailed experimental method for the determination of the solubility product of $PbSO_4$ (40 marks)

6.

a) One mole of an ideal gas is compressed isothermally but irreversibly at 130 °C from 2.5 to 6.5 bar in a piston/cylinder device. The work required is 30% greater than the work of a reversible isothermal compression. The heat transferred from the gas during the compression flows to a heat reservoir at 25 °C. Calculate the entropy changes of the gas, the heat reservoir, and ΔS_{total}. (30 marks)

b) Derive an equation for the determination of pH of an acid solution by quinhydrone electrode.

(40 marks)

c) The limiting molar conductivities of KCl, KNO_3, and $AgNO_3$ are 14.99 mS m^2 mol^{-1}, 14.50 mS m^2 mol^{-1} and 13.34 mS m^2 mol^{-1} respectively at 25 °C. Calculate the limiting molar conductivity of AgCl at this temperature?

(Hint: The basis for the solution is Kohlrausch's law of independent of ions)

(30 marks)