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RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (General) Degree in Applied Sciences
First Year Semester II Examination – February /March 2019

CHE 1302 –PHYSICAL CHEMISTRY I

Answer **Five** questions only. Time: 03 hours

Universal Gas Constant (R) = 8.314 J K^{-1} mol^{-1}, Faraday constant (F) = 9.65 x 10^4 C mol^{-1}
Use of a non-programmable calculator is permitted.

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1. (a) Define the following terms:
   (i) Chaotic motion. (ii) Elastic collision.

   20 marks

   (b) 1 mol of O_2 molecules is confined in a container and struck each of its walls each second. Calculate:
   (i) Total force that the molecules exert on the wall if there speed is 500 m s^{-1}.
   (ii) The pressure of the gas if the area of each wall is 20 cm^2.
   (iii) Root mean square speed.

   30 marks

   (c) What is liquefaction of gas? Draw a fully labeled diagram and discuss the Andrews isotherms for CO_2 at (i) a temperature much above the critical temperature (ii) a temperature at the critical temperature and (iii) a temperature much below the critical temperature.

   50 marks

2. (a) The van der Waals equation of state represents the behavior of gases well when they deviate moderately from ideality.

   (i) Explain briefly, the corrections made by van der Waals to pressure and volume in the ideal gas equation.
   (ii) Calculate the pressure needed to confine 1 mol of CO_2 gas to a volume of 0.5 L at 298 K using van der Waals equation. (a = 3.592 L^2 atm mol^{-2} b = 0.0427 L mol^{-1})
   (iii) What pressure would be needed if CO_2 gas behaved ideally?
   (iv) Predict the relative size of the van der Waals constants for the gases, H_2, CH_4 and SO_2

   50 marks

(b) The derivative of pressure with respect to volume of the van der Waals equation is given by:

$$\frac{\partial P}{\partial V} = RT\frac{\partial}{\partial V}\left(\frac{1}{V-b}\right) - a\frac{\partial}{\partial V}\left(\frac{1}{V^2}\right)$$

At the critical point, show that $V_c = 3b$, $P_c = \frac{a}{27b^2}$, $T_c = \frac{8a}{27bR}$

50 marks

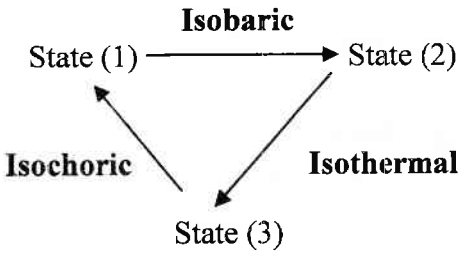
3. (a) Explain the terms:
(i) thermodynamic reversibility. (ii) state variable.

20 marks

(b) (i) State the first law of thermodynamics

20 marks

(ii) One mole of an ideal gas is subjected to a reversible cycle from state (1) to state (2) and then to state (3) and finally to state (1) as illustrated below. Cp = (5/2)R, C_V = (3/2)R



Fill in the blanks in the two tables given below

Table 1

State	P(atm)	V (dm3)	T (K)
1	1.0		298
2			596
3			

Table 2

Process	q(J)	w(J)	U(J)	H(J)
1→2				
2→3				
3→1				

60 marks

4. (a) One mol of an ideal gas is allowed to expand reversibly and isothermally at 27 ^{0}C until is volume is tripled. Calculate ΔS_{sys} and ΔS_{uni}.

20 marks

(b) One mol of ice is melted at 0 ^{0}C and 1.0 atm pressure to form liquid water. The heat of fusion of ice is 6.0 kJ mol^{-1}. Calculate ΔU, ΔH, ΔS, ΔG, q and w for this process. (Density of ice = 0.917 g cm^{-3}, density of water = 0.99 g cm^{-3})

40 marks

(c) Write down FOUR equations that can be used to determine the Gibbs free energy change for the following reaction.

$CuSO_4(aq) + Zn\,(s) \rightarrow ZnSO_4(aq) + Cu\,(s)$ 20 marks

(d) From the first law of thermodynamics, show that C_p-C_v = R

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p \qquad \left(\frac{\partial U}{\partial T}\right)_v = C_v$$

20 marks

5. (a) Define the following terms:
(i) standard electrode potential. (ii) liquid junction potential.

20 marks

(b) A galvanic cell was constructed employing the following half-reactions:

$Cu^{2+} + 2e^- \leftrightharpoons Cu \quad E^0 = +0.34$ V

$Sn^{2+} + 2e^- \leftrightharpoons Sn \quad E^0 = -0.14$ V

The cell was composed of aqueous solutions of 0.1 mol dm^{-3} Sn^{2+} and 0.1 mol dm^{-3} Cu^{2+}.

(i) Write down the net cell reaction when the cell operates
(ii) Calculate the cell potential for the process at 298 K. Is the reaction spontaneous?
(iv) Calculate the maximum work (ΔG) available from this system.

30 marks

(c) (i) Explain with appropriate equations, how you could use the quinhydrone electrode to measure the pH of a solution.

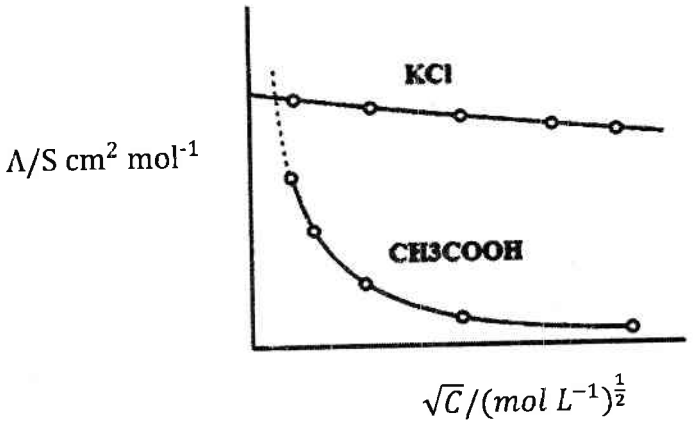
30 marks

(d) Compare and contrast the characteristics of standard hydrogen electrode and silver/silver chloride electrode. 20 marks

6. (a) 0.5 mol dm^{-3} solution of NaCl is placed between two electrodes 1.5 cm apart and having an area of each 3.0 cm^2 offered a resistance of 25.0 ohms. Calculate the molar conductivity of NaCl solution.

25 marks

(b) Explain the variation of molar conductivity of the two electrolytes as shown in the following plot.



25 marks

(c) Describe how you would determine the solubility product of AgCl at 25 ^{0}C, using a conductivity measurement method.

25 marks

(d) The limiting molar conductivities of KCl, KNO_3, and $AgNO_3$ are 14.99 $mSm^2\ mol^{-1}$, 14.50 $mSm^2\ mol^{-1}$ and 13.34 $mSm^2\ mol^{-1}$ respectively at 25°C. Calculated the limiting molar conductivity of AgCl at this temperature.

25 marks