RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (General) Degree in Applied Sciences
First Year Semester II Examination– April / May 2015

CHE 1302 – PHYSICAL CHEMISTRY I

Answer any **FIVE** questions. Time: 03 hours

$R = 8.314\ J\ mol^{-1}\ K^{-1}$, $F = 9.65 \times 10^4\ C\ mol^{-1}$

1. (a) Briefly explain the following:
   (i) Thermodynamic reversibility and irreversibility
   (ii) Joule Thomson expansion of an ideal gas and a real gas
   (iii) Thermodynamically Open system and an isolated system

   (b) 2 mol of an ideal gas at 300 K and 6.0 atm pressure undergo expansion isothermally to half the initial pressure. If this expansion takes place
   (i) irreversibly against zero external pressure
   (ii) irreversibly against ~~zero~~ 3.0 atm pressure
   (iii) reversibly

   Calculate the work done by the gas on the surrounding in each case.

   (c) Give the conditions of ΔG for a (i) spontaneous (ii) non-spontaneous and (iii) equilibrium process.

2. (a) State the 2nd law of Thermodynamics

   (b) Calculate the entropy change per mole of substance in each of the following cases.
   (i) The freezing of isobutene at – 159 ^{0}C, ΔH (Solid→ liquid) = -4540 J mol $^{-1}$
   (ii) The vaporization of water at its normal boiling point of 100°C , ΔH (liquid→ vapour) = 40.66 kJ mol $^{-1}$
   (iii) Compression reversibly and isothermally of an ideal gas from a volume of 10 dm^3 to 2dm^3

   (c) At 300 K and 1.0 atm pressure the entropies of graphite and diamond are 5.69 and 2.43 J $mol^{-1}K^{-1}$, respectively and the heat of combustion (ΔH) to CO_2 are -394 and -396 kJ mol $^{-1}$. Calculate the free energy change (ΔG) at 1.0 atm and 300K of the reaction C(graphite) → C(diamond)

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3. (a) Briefly explain the following:
   (i) Standard electrode potential
   (ii) Electro motive force of an electrochemical cell
   (iii) Cell without transference

   (b) Write down the net cell reaction for each of the following cell representation
   (i) $Zn/Zn^{2+}// Cu^{2+}/Cu$
   (ii) $Pt/H_2(g)/HCl\ (aq)/AgCl(s)/Ag$
   (iii) $Mn/MnCl_2\ (aq)/Cl_2(g)/Pt$

   (c) A galvanic cell consists of a Cr^{3+}/Cr half-cell with unknown $[Cr^{3+}]$ and a Ni^{2+}/Ni half-cell with $[Ni^{2+}] = 1.20$ mol dm^{-3}. The electromotive force of the cell at 25°C was measured to be 0.55 V. What is the concentration of Cr^{3+} in the Cr^{3+}/Cr half-cell?
   E^0 for $Cr^{3+}(aq)/ Cr(s) = -0.74$ V, $Ni^{2+}(aq) / Ni(s) = -0.24$ V

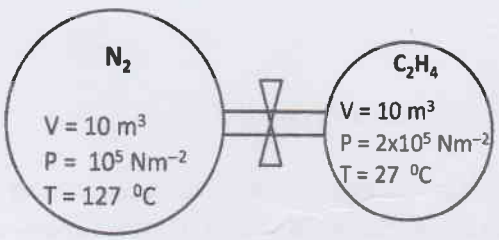
4. (a) Explain with necessary equations, how you would employ a quinhydrone electrode to measure the pH of a solution.

   (b) The conductance of 0.0075 mol dm^{-3} solution of KCl is $1.49\times 10^3\ \mu\Omega^{-1}$. If the cell constant is 105 m^{-1}, calculate the conductivity and molar conductivity.

   (c) The 0.0185 mol dm^{-3} solution of acid HA has the conductance $2.34 \times 10^2\ \mu\Omega^{-1}$. If the cell constant is 105 m^{-1} and molar conductivity at infinite dilution is 391×10^{-4} S m^2 mol^{-1}, calculate the dissociation constant of the acid.

5. (a) Assuming that a given gas obeys the van der Waals equation of state, calculate the work done by "n" moles of gas expanding from a volume V_1 to V_2 at a temperature T.

   (b) Bulbs **A** and B are connected through a tap. Tap is initially closed. **A** contains only gaseous $N_2(g)$ and B contains only gaseous $C_2H_4(g)$. Each exist under the conditions



   The tap is opened and the gases in the two bulbs are allowed to mix freely and completely. However the temperature if each bulb and its gaseous contains is kept unchanged at its initial value.

   (i) Calculate the final P of the gaseous mixture in the bulb B.
   (ii) Calculate the partial pressure of C_2H_4 gas in final gaseous mixture in bulb A.

   (c)(i) Define the "Critical Temperature (Tc)" of a system.

   (ii) Calculate the three critical constants for CO_2 given that the van der Waals constants for this gas are a = 0.366 N m^4 mol^{-2} and $b = 4.3\times10^{-5}$ m^3 mol^{-1}.

$$Tc = \frac{8a}{27Rb} \qquad Pc = \frac{a}{27b^2} \qquad Vc = 3nb$$

6. (a) 24.69 g of $CuSO_4.5H_2O$ crystals were dissolved in water and the solution made up to 1 dm^3. This solution was electrolyzed between Pt electrodes by a current of 0.500 A for 40 minutes. How many cm^3 of 0.100 mol dm^{-3} $Na_2S_2O_3$ solution will be required to use up the I_2 liberated by excess KI from 25 cm^3 of the copper solution after electrolysis?. How many cm^3 of the thiosulphate solution would have been required if Cu electrodes had been used in place of Pt. In the reaction, Cu^{2+} is reduced to Cu^+ and I^- is oxidized to I_2. $S_2O_3^{2-}$ is oxidized to $S_4O_6^{2-}$ by I_2.

(Relative atomic weights: Cu = 63.5, S = 32.0, O = 16.0, H = 1.0)

(b) Derive the relationship between C_p and C_v given below. Use the relationships

H = U + PV and U = f (T V)

$$C_p - C_v = \left(\frac{\partial V}{\partial T}\right)_p \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]$$