KOLEJ UNIVERSITI TUNKU ABDUL RAHMAN

FACULTY OF APPLIED SCIENCES AND COMPUTING

ACADEMIC YEAR 2013/2014

MARCH/APRIL EXAMINATION

CHEMISTRY AACB4114(A)
Thermodynamics and Electrochemistry

MONDAY, 14 APRIL 2014 TIME: 9.00 AM - 11.00 AM (2 HOURS)

ADVANCED DIPLOMA IN SCIENCE
(CHEMISTRY AND BIOLOGY)

Instructions to Candidates:

Answer **ALL** questions. All questions carry equal marks.

AACB4114(A) THERMODYNAMICS AND ELECTROCHEMISTRY

Physical constants and units conversion factors:

Universal gas constant, $R = 8.314\ J\ K^{-1}\ mol^{-1}$
$1\ F = 96500\ C\ mol^{-1}$
$1\ J = 1\ C\ V$

Q 1 . (a) (i) Define "chemical potential".

(ii) Using thermodynamic arguments, prove that when two phases in a system are in equilibrium, the chemical potentials of a substance present in both phases must be the same; otherwise a spontaneous flow of substance will occur.

(2, 6 marks)

(b) (i) Explain clearly the meaning of "colligative properties" of dilute solutions.

(ii) Account for the origin of ONE of the colligative properties of a dilute solution in terms of the modification of chemical potential of the solvent by addition of the solute.

(5, 6 marks)

(c) At 15 °C, an aqueous solution containing 1 mol of NaOH in 4.6 mol of water has a vapour pressure of 4.474 mmHg whereas pure water has a vapour pressure of 12.788 mmHg.

Calculate the following:

(i) the activity coefficient of water in the solution,

(ii) the difference between the chemical potential of water in the solution and that of pure water.

(3, 3 marks)
[Total : 25 mark]

Q2. (a) Give a brief account of ONE of the following:

(i) adsorption of gases on solids,

(ii) lyophilic sols.

(12 marks)

(b) Explain clearly what is meant by the statement that " the standard redox potential (ε^{o}) of the Zn^{2+}/Zn couple is -0.76 V" .

(4 marks)

Q2(Continued).

(c) The emf of the electrochemical cell

$$\text{Cd} \;\Big|\; \begin{array}{c}\text{Saturated solution}\\ \text{CdSO}_4\,(s),\ \text{Hg}_2\text{SO}_4\,(s)\end{array} \;\Big|\; \text{Hg}$$

is given by the expression

$$\varepsilon\,(V) = 0.6708 - 1.02 \times 10^{-4}\,(T - 298) - 2.4 \times 10^{-6}(T - 298)^2$$

where T is the thermodynamic temperature.

(i) Write the electrode reactions and overall cell reaction.

(ii) Calculate the values of ΔG and ΔS for the cell reaction at 318 K.

(2.5, 6.5 marks)
[Total: 25 marks]

Q3. (a) Describe briefly, with the aid of a suitable diagram, the concentration-dependence of of the molar conductivities of strong and weak electrolytes.

Name two examples of each type of electrolyte.

(6 marks)

(b) Write a concise account on **EITHER** the Onsager equation **OR** the Arrhenius theory of electrolytic conduction.

(12 marks)

(c) At 281 K, the conductivity of a saturated solution of lead sulphate is $1.84 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ and that of the water used is $1.40 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$. The limiting molar conductivity of Pb^{2+} and SO_4^{2-} ions are 122.0 and 136.0 $\Omega^{-1}\ cm^2\ mol^{-1}$ respectively. Calculate the solubility of lead sulphate at 281 K. State clearly any assumption made in your calculation.

(7 marks)
[Total : 25 marks]

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Q4. (a) Derive the Phase Rule from thermodynamic arguments. State clearly any assumption(s) made in the derivation.

(9 marks)

(b) Deduce the number of degrees of freedom in each of the following:

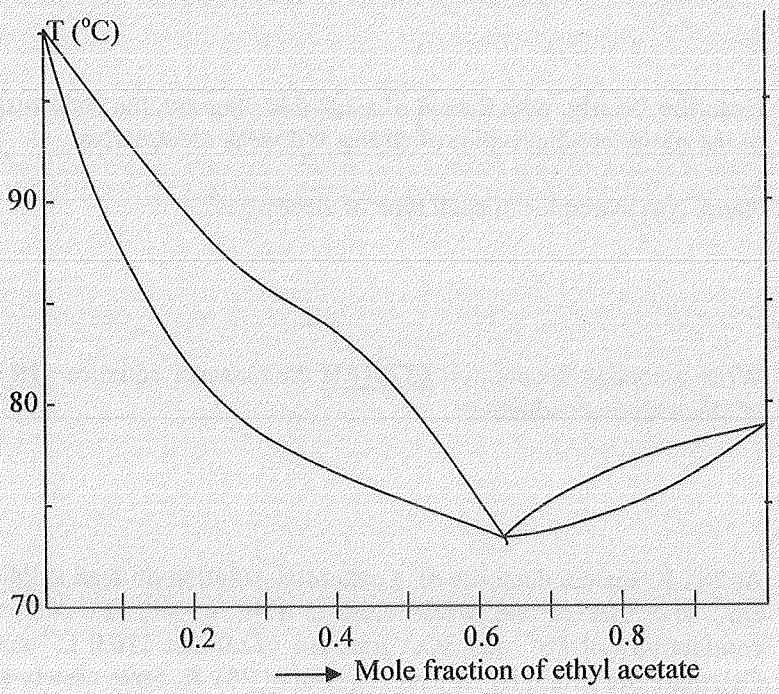
(i) an aqueous solution of KCl,

(ii) the equilibrium: $Fe\ (s) + H_2O\ (g) \rightleftharpoons FeO\ (s) + H_2\ (g)$.

Show all your workings clearly.

(2.5, 2.5 marks)

(c) The boiling point-composition diagram for ethyl acetate/water system is shown below. A solution containing 0.500 mole fraction is boiled in an open beaker until the boiling point rises by 5 °C.



(i) Determine graphically the composition of the solution when the boiling was stopped, and the initial and final boiling points.

(ii) If the vapour had been collected and condensed, what would be the average composition of the distillate?

(iii) Sketch the corresponding vapour pressure-composition diagram for ethyl acetate/water system. Label the diagram completely.

(4, 4, 3 marks)
[Total: 25 marks]

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APPENDIX

Formulas:

1. $Y_m = \overline{Y}_1 + \chi_2 (dY_m / d\chi_2)$
2. $d(\ln P)/dT = \Delta H_v / RT^2$
3. $\Delta G_M = RT \Sigma n_i \ln \chi_i$
4. $[\partial(G/T) / \partial T]_p = - H / T^2$
5. $\Delta T_b = R(T_b)^2 \chi_2 / \Delta H_v$
6. $\Delta T_f = R(T_f)^2 \chi_2 / \Delta H_f$
7. $1/\Lambda = 1/\Lambda_o + C\Lambda / K_d\Lambda_o^2$
8. $\Lambda_i = |z_i|Fu_i = t_i\Lambda$
9. $\varepsilon = \varepsilon^o - (RT/nF) \ln (a_L^{\ell} a_M^{m} / a_A^{a} a_B^{b})$

   At 298 K, $\varepsilon = \varepsilon^o - (0.05915/n) \log (a_L^{\ell} a_M^{m} / a_A^{a} a_B^{b})$
10. $I = (\frac{1}{2}) \Sigma m_i z_i^2$
11. $\eta_{sp} / C = [\eta] + k[\eta]^2 C$
12. $\Gamma_2 = - (a_2 / RT)(d\gamma / da_2)$
13. $V = bPV_m / (1 + bP)$