

THE OPEN UNIVERSITY OF SRI LANKA

B.Sc Degree Programme / Stand Alone Course-Level 5 Assignment - II (fest) (Galcell ---) - 2006/2007 CHU 3124/ CHE 5124 Physical Chemistry

(1 1/2 hours)

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1600	Terre	2046

3.30 p.m - 5.60 p.m

This question paper consists of 40 (forty) MCQs

* Answer all 40 questions (46 x 2.5 = 100 marks) Choose the most correct answer to each of the questions and mark this answer with an "X" on the answer script.

*Use a PEN (not a PENCIL) in answering

*Any question with more than one answer will not be counted

*Marks will be deducted for incorrect answers (2.5/6 mark per incorrect answer).

*The use of a non-programmable electronic calculator is permitted.

*Logarithm tables will be provided

Gas constant (R)	$= 8.314 \mathrm{J K^{-1} mol^{-1}}$
Avogadro constant (NA)	$=6.023 \times 10^{23} \mathrm{mol}^{-1}$
Faraday constant (F)	$= 96,500 \text{ C mol}^{-1}$
Planks constant (h)	$= 6.63 \times 10^{-34} \mathrm{J s}$
Velocity of light (c)	$= 3.0 \times 10^8 \text{ m s}^{-1}$
Standard Atmospheric pressure (π)	$= 10^5 \text{Pa} (\text{N m}^{-2})$
$\log_{c}(X)$	$= 2.303 \log_{10}(X)$

1. When an aluminium wire is inserted into a solution of aluminium ions following reactions may take place at the Al(s)/Al³⁺ (aq) interface.

Al(s)
$$\longrightarrow$$
 Al³⁺(aq)+3e⁻ (A)
Al³⁺(aq)+3e⁻ \longrightarrow Al(s) (B)

After some time the rate of (A) will become equal to that of (B).

Electrons involved in reaction (B) reside in the solution phase since Al³⁺ (ag) is in this phase.

(iii) Electrons involved in reaction (A) reside on the aluminium wire.

The correct statements, out of (i), (ii) and (iii) above, are

(a) (i) and (ii) only.

(b) (i) and (iii) only. (c) (ii) and (iii) only.

(d) All (i), (ii) and (iii).

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- may have only two interfaces.
- has at least two electrodes.
- (iii) may have a zero emf.

- (a) (i) and (ii) only.
- (b) (i) and (iii) only.
- (c) (ii) and (iii) only.

- (d) All (i), (ii) and (iii).
- (e) None of the answers (a), (b), (c) or (d), is correct.

The ionic conductor in a Galvanic cell

- cannot be a solid. a
- (ii) may be a molten salt.
- (iii) may be a solution of an electrolyte.

The correct statements, out of (i), (ii) and (iii) above, are

- (a) (i) and (ii) only. (d) Alt (i), (ii) and (iii).
- (b) (i) and (iii) only.
- (c) (ii) and (iii) only.
- (e) None of the answers (a), (b), (c) or (d), is correct.

4. A liquid junction potential may appear

- only at an interface of two immiscible liquid phases.
- (ii) at an interface of two aqueous solutions.
- because of the difference in rates of diffusion of different ions in solutions.

The correct statements, out of (i), (ii) and (iii) above, are

- (a) (i) and (ii) only.
- (b) (i) and (iii) only.
- (c) (ii) and (iii) only.

- (d) All (i), (ii) and (iii).
- (e) None of the answers (a), (b), (c) or (d), is correct
- A cell is constructed by dipping a lead wire in a lead nitrate solution, a silver wire in a silver nitrate solution and bringing the solutions into contact through a porous wall. The electric potential of lead wire is x volts higher than that of the silver nitrate solution. The potential of the silver wire is y volts higher than that of lead nitrate solution. The potential of the silver nitrate solution is z volts higher than that of the lead nitrate solution.

The emf (without considering the sign) of the cell, in volts, is

- x+y-z
- (b) |x-y-z| (c) |x+y+z|

- (e) None of the answers, (a), (b), (c) or (d), is correct.

6. In a cell diagram

- a solid vertical line represents a boundary between two miscible liquids.
- the boundary between two aqueous solutions may be represented by a dashed vertical line.
- (iii) the chemical species in a single phase may be written in any order.

- (a) (i) and (ii) only.
- (b) (i) and (iii) only.
- (c) (ii) and (iii) only.

- (d) All (i), (ii) and (iii).
- (e) None of the answers (a), (b), (c) or (d), is correct.

- 7. A cell is constructed by dipping a magnesium wire in a magnesium chloride solution, a copper wire in a copper sulphate solution and bringing the solutions into contact through a porous wall. Possible cell diagrams for this cell are
 - $Mg(s) Mg^{2+}(aq): Cu^{2+}(aq), SO_4^2$ (aq) Cu(s)(i)
 - Mg(s) Mg²⁺ (aq), Cl (aq): Cu²⁺ (aq) Cu(s) (ii)
 - $Mg^{2+}(aq) Mg(s) Cu(s) Cu^{2+}(aq)$ (iii)

(a) (i) and (ii) only.

(b) (i) and (iii) only. (c) (ii) and (iii) only.

(d) All (i), (ii) and (iii).

(e) None of the answers (a), (b), (c) or (d), is correct

- 8. When writing down a cell diagram
 - always one has to find out the (+)ve and (-)ve terminals first
 - one has to make sure that the spontaneous cathode appears at the right hand
 - in general, one does not need information about the spontaneity of the (iii) chemical reactions involved.

The correct statements, out of (i), (ii) and (iii) above, are

(a) (i) and (ii) only.

(b) (i) and (iii) only.

(c) (ii) and (iii) only.

(d) Alt (i), (ii) and (iii).

(e) None of the answers (a), (b), (c) or (d), is correct.

- 9. According to IUPAC conventions, the cell reaction corresponding to a cell diagram
 - always has oxidation taking place at the electrode on the right hand side.
 - always has the cathodic half reaction taking place at the electrode on the left hand side.
 - does not have to be spontaneous.

The correct statements, out of (i), (ii) and (iii) above, are

(a) (i) and (ii) only.

(b) (i) and (iii) only. (c) (ii) and (iii) only.

(d) Alt (i), (ii) and (iii).

(e) None of the answers (a), (b), (c) or (d), is correct.

- 10. When a Galvanic cell is connected to a load
 - oxidation takes place at the (+)ve terminal. (i)
 - (ii) electrons in the external circuit flows from the spontaneous anode to spontaneous cathode.
 - (iii) spontaneous cathode is at a higher electric potential than the spontaneous anode.

The correct statements, out of (i), (ii) and (iii) above, are

(a) (i) and (ii) only.

(b) (i) and (iii) only.

(c) (ii) and (iii) only.

(d) Alt (i), (ii) and (iii)。

11. Anode, cathode and cell reactions corresponding to the cell diagram $Fe(s) | Fe^{2+}(aq) : Ag^{+} | Ag(s)$, respectively, are

(i)
$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^{-}$$

(ii)
$$Ag(s) \longrightarrow Ag^{+}(aq) + e^{-}$$

(iii)
$$\operatorname{Fe}(s) + 2 \operatorname{Ag}^{+}(aq) \longrightarrow \operatorname{Fe}^{2+}(aq) + 2 \operatorname{Ag}(s)$$

The correct statements, out of (i), (ii) and (iii) above, are

(a) (i) and (ii) only. (b) (i) and (iii) only. (c) (ii) and (iii) only.

(d) All (i), (ii) and (iii). (e) None of the answers (a), (b), (c) or (d), is correct.

12. The charge numbers of the cell reactions

(i)
$$2 \text{Al}(s) + 3 \text{Cu}^{2+}(aq) \longrightarrow 2 \text{Al}^{3+}(aq) + 3 \text{Cu}(s)$$

(ii)
$$Al(s) + \frac{3}{2} Cu^{2+}(aq) \longrightarrow Al^{3+}(aq) + \frac{3}{2} Cu(s)$$

(iii)
$$\frac{1}{2}$$
 Mg(s) + Ag⁺(aq) \longrightarrow $\frac{1}{2}$ Mg²⁺(aq) + Ag(s)

respectively, are

- (a) 6, 6, 2. (b) 3, 3, 2. (c) 6, 3, 2.
- (d) 6, 3, 1. (e) None of the answers (a), (b), (c) or (d), is correct.
- 13. The charge number of the cell reaction $A + B \rightarrow C + D$ is 6. If the relative molecular mass of the product C is 120, the mass of C produced during the passage of 1 faraday of electrons is
 - (a) 120 g.
- (b) 40 g.
- (c) 30 g

- (d) 20 g.
- (e) 60 g.
- 14. At 298 K and 1 bar, the electric potential (relative to some standard level) of copper and zinc electrodes of a Daniell cell are $0.340 \,\mathrm{V}$ and $-0.763 \,\mathrm{V}$, respectively, when the copper and zinc ion concentrations are equal to $1.0 \,\mathrm{mol}\,\mathrm{dm}^{-3}$. The emfs assigned to the cell diagrams,

$$Cu(s)$$
 $Cu^{2+}(aq)(1.0 \text{ mol dm}^{-3})$ $Zn^{2+}(aq)(1.0 \text{ mol dm}^{-3})$ $Zn(s)$ and

$$Zn(s) | Zn^{2+}(aq)(1.0 \text{ mol dm}^{-3}) : Cu^{2+}(aq)(1.0 \text{ mol dm}^{-3}) | Cu(s),$$

at 298 K and 1 bar, respectively, are

- (a) -1.103 V,1.103 V.
- (b) 1.103 V, -1.103 V.
- (c) -0.423V, 0.423V
- (d) 0.423 V, -0.423 V.
- (e) 0.340 V, -0.763 V.

15.	resistances a	t equilibrium we	determine the emf of a cell. The lengths of the ere found to be 25.0 cm and 30.0 cm with the cell are espectively. The emf of the test cell was	nd a
	(a) 1.2 V. (d) 1.0 V.	(b) 1.5 V. (e) 0.7 V.	(c) 0.8 V.	

16. The spontaneous cell reaction in a Daniell cell of emf 1.1 V (at 298 K and 1 bar) is $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$. When it is connected to a battery, with a voltage greater than 1.1 V, such that the positive terminal of the battery is connected to the copper electrode and the negative terminal to the zinc electrode

no reaction will take place within the Daniell cell since the voltage of the battery opposes its emf.

the reaction $Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s)$ may take place within (ii) the Daniell cell.

(iii) electrons may flow from the battery into the zinc electrode.

The correct statements, out of (i), (ii) and (iii) above, are (c) (ii) and (iii) only. (a) (i) and (ii) only. (b) (i) and (iii) only. (e) None of the answers (a), (b), (c) or (d), is correct. (d) All (i), (ii) and (iii).

Consider the following electrodes.

 $Mn(s) Mn^{2+}(aq)$

 $Pb(s) | PbSO_4(s) | SO_4^{2-}(aq)$

(iii) $Zn(s) H^{+}(aq), Zn^{2+}(aq)$

Definitely the chemically reversible electrodes, out of (i), (ii) and (iii), are

(a) (i) and (ii) only. (d) All (i), (ii) and (iii). (b) (i) and (iii) only.

(c) (ii) and (iii) only.

(e) None of the answers (a), (b), (c) or (d), is correct.

Half reactions of the redox electrodes, Pt(s) MnO₄⁻(aq), Mn²⁺(aq), H⁺(aq), $Pt(s) | Cr_2 O_7^{2-}(aq), Cr^{3+}(aq), H^+(aq) \text{ and } Pt(s) | ClO_4^-(aq), ClO_3^-(aq), H^+(aq),$ respectively, are

 $MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$

 $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$

(iii) $ClO_4^-(aq) + 2H^+(aq) + 2e^- \longrightarrow ClO_3^-(aq) + H_2O$

The correct statements, out of (i), (ii) and (iii) above, are

(a) (i) and (ii) only.

(b) (i) and (iii) only.

(c) (ii) and (iii) only.

(d) All (i), (ii) and (iii).

19.	Under a certain set of conditions a Galvanic cell was found to have a zero cmf. W
	 (i) the cell reaction is at equilibrium under these conditions. (ii) there will be no current in a load when it is connected to this cell. (iii) both electrodes are at the same electric potential.
	The correct statements, out of (i), (ii) and (iii) above, are (a) (i) and (ii) only. (b) (i) and (iii) only. (c) (ii) and (iii) only. (d) All (i), (ii) and (iii). (e) None of the answers (a), (b), (c) or (d), is correct
20.	The aqueous phase in a lead-lead sulphate electrode is saturated with (i) lead sulphate. (ii) sulphate ions. (iii) lead chloride.
	The correct statements, out of (i), (ii) and (iii) above, are (a) (i) and (ii) only. (b) (i) and (iii) only. (c) (ii) and (iii) only. (d) All (i), (ii) and (iii). (e) None of the answers (a), (b), (c) or (d), is correct.
21.	A glass electrode
	(i) is <u>not</u> a chemically reversible electrode.
	(ii) may be made to be sensitive to ions other than H'(aq).
	(iii) usually has a buffer solution in contact with the inner surface of the glass membrane.
	The correct statements, out of (i), (ii) and (iii) above, are (a) (i) and (ii) only. (b) (i) and (iii) only. (c) (ii) and (iii) only. (d) Alt (i), (ii) and (iii). (e) None of the answers (a), (b), (c) or (d) is correct

- 22. A salt bridge is customarily used to bring electrical contact between the electrolytic phases of two electrodes in constructing a galvanic cell.
 - (i) In a salt bridge we use KCI since K⁺(aq) and CI⁻(aq) have nearly equal ionic mobilities.
 - (ii) In a salt bridge we use agar to minimise the mixing of the electrolyte in electrode and KCl solution in salt bridge due to convection.
 - (iii) The potential differences created at the two salt-bridge/half-cell-electrolyte liquid junctions are nearly equal and opposite.

The correct statements, out of (i), (ii) and (iii) above, are.
(a) (i) and (ii) only.
(b) (i) and (iii) only.
(c) (ii) a

(d) All (i), (ii) and (iii).

(b) (i) and (iii) only. (c) (ii) and (iii) only.

- 23. (i) The total liquid junction potential in a cell with a salt bridge is nearly zero. (ii) Strictly speaking, a salt bridge makes a cell chemically irreversible.
 - (iii) A chemically reversible electrode may be used with a salt bridge to construct a chemically reversible cell.

- (a) (i) and (ii) only. (b) (i) and (iii) only. (c) (ii) and (iii) only.
- (d) All (i), (ii) and (iii). (e) None of the answers (a), (b), (c) or (d), is correct.
- 24. $\Delta G = -n FE$, where E is the emf of assigned to a cell diagram and ΔG is the Gibbs free energy of the corresponding cell reaction, may be
 - (i) derived using a thermodynamically reversible discharge process of a cell.
 - (ii) applied to a cell with a non-zero liquid junction potential.
 - (iii) applied to a cell with a salt bridge.

The correct statements, out of (i), (ii) and (iii) above, are

- (a) (i) and (ii) only. (b) (i) and (iii) only. (c) (ii) and (iii) only.
- (d) All (i), (ii) and (iii). (e) None of the answers (a), (b), (c) or (d), is correct.
- 25. Under standard conditions and at 298 K, the emfs assigned to the cell diagram $Zn(s) \left| Zn^{2+}(aq) \right| Cu^{2+}(aq) \left| Cu(s) \text{ is } 1.103 \text{ V.} \text{ What is the standard Gibbs free} \right|$ energy of $Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s)$ at 298 K?
 - (a) 112.9 kJ.
- (b) -112.9 kJ.
- (c) 212.9 kJ.

- (d) -212.9 kJ.
- (e) 122.9 kJ
- 26. A particular cell reaction, at 300 K and 2 bar, has a Gibbs free energy change of 447.3 kJ. Under the same conditions, the emf assigned to the corresponding cell diagram is -1.545 V. If F = 96,500 C mol⁻¹ charge number of the cell reaction is
 - (a) 1
- (b)
- (c) 3

- (d) 4
- (e) None of the answers (a), (b), (c) or (d), is correct.
- 27. In $a_X = \gamma_X \left(\frac{c_X}{c^0}\right)$, which gives the activity a_X of an ionic species X,
 - (i) c_X is the molar concentration of the species X.
 - (ii) in general, the value of γ_X depends on the particular ionic species.
 - (iii) c⁰ is always unity irrespective of the units.

- (a) (i) and (ii) only.
- (b) (i) and (iii) only.
- (c) (ii) and (iii) only.

- (d) All (i), (ii) and (iii).
- (e) None of the answers (a), (b), (c) or (d), is correct.

28. An electrolyte MaXb dissociates fully, in a solution as

 $M_a X_b \rightarrow c M^{2+}(aq) + \left[M_{ac} X_b\right]^{2-}(aq)$. The activity coefficients of the cationic and anionic species produced are γ_+ and γ_- , respectively. The mean activity coefficient of the electrolyte in this solution is

- (a) $\gamma_{\pm} = \gamma_{+}^{a} \gamma_{-}^{b}$
- (b) $\gamma_{\pm} = \left[\gamma_{+}^{a} \gamma_{-}^{b} \right]^{\frac{1}{a+b}}$
- (c) $\gamma_{\perp} = \gamma_{\perp}^{c} \gamma_{\perp}$
- (d) $\gamma_{\pm} = \left[\gamma_{+}^{c} \gamma_{-} \right]^{1/c+1}$
- (e) $\gamma_{\pm} = \left[\gamma_{+}^{a} \gamma_{-}^{b} \right]^{1/a+b+c}$
- 29. The activity coefficients of aluminium and chloride ions, in a solution, are 0.75 and 0.90 respectively. The mean activity coefficient of AlCl₃ in this solution is nearly equal to
 - (a) 0.860 (d) 0.785
- (b) 0.547 (e) 660
- (c) 0.380

- 30. The standard state of
 - (i) a substance is independent of temperature.
 - (ii) an ideal gas is reached when the pressure of it is equal to 1 bar.
 - (iii) an ionic species cannot be prepared experimentally.

The correct statements, out of (i), (ii) and (iii) above, are

- (a) (i) and (ii) only.
- (b) (i) and (iii) only.
- (c) (ii) and (iii) only.

- (d) Alt (i), (ii) and (iii).
- (e) None of the answers (a), (b), (c) or (d), is correct.
- 31. In general, E⁰ in Nernst equation
 - (i) is independent of temperature.
 - (ii) is the emf assigned to a cell reaction when the <u>reactants</u> are in their standard states <u>irrespective</u> of the state of the products.
 - (iii) depends on the cell reaction under consideration.

The correct statements, out of (i), (ii) and (iii) above, are

- (a) (i) and (ii) only.
- (b) (i) and (iii) only.
- (c) (ii) and (iii) only.
- (d) All (i), (ii) and (iii). (e) None of the answers (a), (b), (c) or (d), is correct.
- 32. The emf assigned to the cell diagram

 $Mg(s) Mg^{2+}(aq)(a = 0.5) Mg^{2+}(aq)(a = 1.5) Mg(s)$, at 300 K and 1 bar is;

- (a) 0.014 V
- (b) -0.014 V
- (c) 0.000 V

- (d) -0.028 V
- (e) 0.028 V

33. At 300 K and 2 bar, the emf assigned to the cell diagram

$$Mg(s) Mg^{2+}(aq) (a_{Mg^{2+}} = x) CI^{-}(aq) (a_{CI^{-}} = b) AgCl(s) Ag(s)$$

is 2.6050 V when x = 0.5 and 2.5960 V when x = 1.0. (The standard emf for this cell diagram is E^0). Using only this data one

- (a) can evaluate E0 but cannot evaluate b.
- (b) can evaluate b but cannot evaluate E°.
- (c) can evaluate both E and b.
- (d) cannot evaluate either E⁰ or b.
- (e) cannot evaluate any quantity involving both E⁸ and b.
- 34. The emf assigned to the reaction

 $PbI_2(s) + Zn(s) \rightarrow Pb(s) + Zn^{2+}(aq) + 2I^-(aq)$, at 298 K and 1 bar, is equal to 0.407 V, when the activities of zinc and iodide ions are 0.75 and 0.80 respectively. The thermodynamic equilibrium constant of the above reaction at 298 K and 1 bar is

- (a) 2.8×10^{13}
- (b) 5.4×10^6
- (c) 8.5×10^{26}

- (d) 5.0×10^{12}
- (e) 6.4×10^6
- 35. The thermodynamic equilibrium constant of the reaction $2Ag(s) + 2Br^{-}(aq) + PbSO_4(s) \rightarrow 2AgBr(s) + SO_4^{2-}(aq) + Pb(s)$ at 298 K and 1 bar, is 5.329×10^{-15} . At 298 K and 1 bar, what is the emf assigned to the cell diagram $Pb(s) | PbSO_4(s) | SO_4^{2-}(aq) | Br^{-}(aq) | AgBr(s) | Ag(s)$ when the activities of sulphate and bromide ions are unity?
 - (a) -0.4219 V
- (b) 0.2110 V
- (c) 0.4219 V

- (d) -0.2110 V
- (e) 0.3110 V.
- 36. Activity coefficient, γ_z , of an ionic species, of charge number Z, in aqueous solution, may be estimated using
 - (i) $\log(\gamma_z) = -AZ\sqrt{1}$
 - (ii) $\log(\gamma_z) = -\frac{AZ^2\sqrt{1}}{1+aB\sqrt{1}}$
 - (iii) $\ln(\gamma_z) = -CZ^2\sqrt{I}$

where A, a, B & C are constants and I is the ionic strength of solution.

- (a) (i) and (ii) only.
- (b) (i) and (iii) only.
- (c) (ii) and (iii) only.

- (d) Alt (i), (ii) and (iii).
- (e) None of the answers (a), (b), (c) or (d), is correct

- 37. (i) Debye-Huckel limiting law (for activity coefficient of an ionic species) is applicable over a wider range of ionic strengths than the Debye-Huckel extended law.
 - (ii) The constant A in Debye-Huckel laws for activity coefficient depends on temperature of the solution and the dielectric constant of the solvent.
 - (ii) The <u>constant B</u> in Debye-Huckel extended law for activity coefficient depends on temperature of the solution and the dielectric constant of the solvent.

- (a) (i) and (ii) only. (d) All (i), (ii) and (iii).
- (b) (i) and (iii) only. (c
- (c) (ii) and (iii) only.
- (e) None of the answers (a), (b), (c) or (d), is correct
- 38. The ionic strength, I, of a solution of electrolytes is defined by

$$1 = \frac{1}{2} \sum_{n} c_n Z_n^2$$
. Here

- it is sufficient to perform the summation only over the cationic species in the solution since the charge due to cations and anions has to be equal in a neutral solution.
- (ii) c_n is the molar concentration of ionic species n.
- (iii) Z_n is the charge number of ionic species n.

- (a) (i) and (ii) only.
- (b) (i) and (iii) only.
- (c) (ii) and (iii) only.

- (d) All (i), (ii) and (iii).
- (e) None of the answers (a), (b), (c) or (d), is correct
- 39. The ionic strength of an aqueous solution which is 0.5 mol dm⁻³ in Al(NO₃)₃ and 0.75 mol dm⁻³ in MgCl₂ is
 - (a) 10.5 mol dm^{-3}
- (b) $10.5 \times 10^3 \text{ mol m}^{-3}$
- (c) $5.25 \times 10^3 \text{ mol m}^{-3}$
- (d) $5.25 \times 10^{-3} \text{ mol m}^{-3}$
- (e) $15.5 \,\mathrm{mol \, dm^{-3}}$.
- 40. The ionic strength of an aqueous solution of $Ba(NO_3)_2$ and NaCl is 2.75 mol dm⁻³. If the concentration of $Ba(NO_3)_2$ is 0.75 mol dm⁻³ what is that of NaCl?
 - (a) $1.63 \, \text{mol dm}^{-3}$
- (b) 3.25 mol dm^{-3}
- (c) 0.5 mol dm^{-3}
- (d) $1.0 \, \text{mol dm}^{-3}$
- (e) $2.70 \, \text{mol dm}^{-3}$