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**4 SEM TDC CHM M 1 (N/O)**

**2019**

( May )

CHEMISTRY

( Major )

Course : 401

**( Physical Chemistry )**

*The figures in the margin indicate full marks for the questions*

( New Course )

*Full Marks* : 48

*Pass Marks* : 14

*Time* : 2 hours

**1.** Choose the correct answer : 1×5=5

*(a)* The efficiency of a heat engine working between 273 K and 373 K is

*(i)* 26·8

*(ii)* 1·0

*(iii)* 0·366

*(iv)* 0·268

(b) The amount of charge required for reduction of 1 mole of $Cu^{2+}$ to Cu is

(i) 96500 C

(ii) 48250 C

(iii) 193000 C

(iv) 24125 C

(c) Which of the following statements is not true for conductometric titrations?

(i) Coloured solutions can be titrated.

(ii) No indicator is required.

(iii) A strong acid can be titrated with a strong base.

(iv) A weak acid can be titrated with a weak base.

(d) A cell reaction occurs spontaneously, if

(i) $\Delta G$ is negative, $E_{cell}$ is positive

(ii) $\Delta G$ is positive, $E_{cell}$ is negative

(iii) both $\Delta G$ and $E_{cell}$ are positive

(iv) both $\Delta G$ and $E_{cell}$ are negative

(e) The electrode that is not suitable for determining the pH of a strongly basic solution is

(i) calomel electrode

(ii) glass electrode

(iii) quinhydrone electrode

(iv) hydrogen electrode



( Continued )

**2.** Answer the following questions : 2×5=10

*(a)* Show that entropy is produced in the irreversible process.

*(b)* Explain the variation of specific and molar conductance with dilution.

*(c)* Explain why $Cd^{2+}$ ion in aqueous $CdI_2$ solution shows abnormal transference number.

*(d)* Explain how the use of $NH_4NO_3$ in agar bridge minimizes the liquid-junction potential.

*(e)* How do you prepare a normal calomel electrode?

**3.** Answer any *two* questions from the following : 4½×2=9

*(a)* Deduce an expression for efficiency of a Carnot engine working between two temperatures $T_1$ and $T_2$.

*(b)* For one mole of an ideal gas, derive the expression for entropy change due to simultaneous changes in temperature and volume.

*(c)* Prove that entropy of mixing of two or more ideal gases is always positive.

**4.** Answer any *two* questions from the following : 7×2=14

*(a)* *(i)* What do you mean by transference number of ions? Discuss the moving boundary method for determination of transference number of ions. 1+4=5

*(ii)* A saturated solution of AgCl at 20 °C has a conductivity of $3{\cdot}41\times10^{-6}$ ohm$^{-1}$ cm$^{-1}$. The conductivity of water used was $1{\cdot}60\times10^{-6}$ ohm$^{-1}$ cm$^{-1}$. Determine the solubility of AgCl.
(Given, $\lambda^{\circ}_{Ag^+} = 61{\cdot}92$ ohm$^{-1}$ cm$^2$,
$\lambda^{\circ}_{Cl^-} = 76{\cdot}34$ ohm$^{-1}$ cm$^2$) 2

*(b)* *(i)* Explain with a suitable example how a precipitation reaction can be studied by conductometric titration. 2

*(ii)* Define cell constant. What is its unit? Explain how cell constant of a particular conductivity cell can be measured. The specific conductivity of an $N/10$ solution of KCl at 25 °C is 0·002765 mho cm$^{-1}$. If the resistance of a cell containing this solution is 400 ohms, what is the cell constant? 1+½+2+1½=5



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(c) (i) Explain the variation of strong electrolyte with concentration in the light of asymmetry effect and electrophoretic effect. 4

(ii) Explain why graphical method fails to determine molar conductance at infinite dilution for weak electrolytes. How can molar conductance at infinite dilution for weak electrolyte be measured? 1+2=3

5. Answer any *two* questions from the following : 5×2=10

(a) (i) What are concentration cells? Derive an expression for EMF of the following electrolyte concentration cell : 1+3=4

$$H_2(1\text{ atm}) \left| H^+(a_1) \right\| H^+(a_2) \left| H_2\ (1\text{ atm}) \right.$$

(ii) Draw the potentiometric titration curve involving strong acid and strong base. 1

(b) (i) What is hydrogen electrode? How can pH of a solution be measured with the help of hydrogen electrode? 1+3=4

(ii) Define liquid-junction potential. 1

(c) (i) What are storage cells? Discuss the charging-discharging processes in a lead storage cell. 1+2=3

(ii) Calculate the EMF of the following cell : 2

$$Mg(s)\left|Mg^{2+}\ (0{\cdot}1\ M)\right\|Ag^{+}\ (0{\cdot}001\ M)\left|Ag(s)\right.$$

Given,

$$E^{\circ}_{Mg^{2+}|\,Mg} = -2{\cdot}37\ V$$

$$E^{\circ}_{Ag^{+}|\,Ag} = 0{\cdot}80\ V$$

( Old Course )

*Full Marks* : 48

*Pass Marks* : 19

*Time* : 3 hours

**1.** Choose the correct answer : 1×5=5

*(a)* The relation between equivalent conductance ($\Lambda_e$) and molar conductance ($\Lambda_m$) for $Al_2(SO_4)_3$ is

*(i)* $\Lambda_e = \Lambda_m$

*(ii)* $\Lambda_e = \frac{1}{2}\Lambda_m$

*(iii)* $\Lambda_e = \frac{1}{3}\Lambda_m$

*(iv)* $\Lambda_e = \frac{1}{6}\Lambda_m$

*(b)* The effect of high potential gradient on conductivity is known as

*(i)* asymmetry effect

*(ii)* electrophoretic effect

*(iii)* Wien effect

*(iv)* Debye-Falkenhagen effect

*(c)* A cell reaction occurs spontaneously, if

*(i)* $\Delta G$ is negative, $E_{cell}$ is positive

*(ii)* $\Delta G$ is positive, $E_{cell}$ is negative

*(iii)* both $\Delta G$ and $E_{cell}$ are negative

*(iv)* both $\Delta G$ and $E_{cell}$ are positive

(d) The amount of charge required for reduction of 1 mole of $Cu^{2+}$ to Cu is

(i) 96500 C

(ii) 48250 C

(iii) 193000 C

(iv) 24125 C

(e) For an ideal solution, the value of activity coefficient is

(i) 0

(ii) 1

(iii) >1

(iv) <1

**2.** Answer the following questions : 2×5=10

(a) Explain the variation of specific and molar conductance with dilution.

(b) Explain why transference number of $Cd^{2+}$ shows abnormal behaviour in aqueous $CdI_2$ solution.

(c) Write the differences between electrolytic and galvanic cells.

(d) Explain how a standard hydrogen electrode is prepared.

(e) What is fugacity? Write its physical significance. 1+1=2



( Continued )

**3.** Answer any *two* questions from the following : 7×2=14

*(a)* *(i)* Explain why graphical method fails to determine molar conductance at infinite dilution for weak electrolytes. How Kohlrausch's law is applicable for determination of such value? Explain with a suitable example. 2+2=4

*(ii)* What is cell constant? The resistance of a conductivity cell containing 0·001 *M* KCl solution at 298 K is 1500 ohm. What is the cell constant if conductivity of 0·001 *M* KCl solution at 298 K is $0{\cdot}146\times10^{-3}\ S\,cm^{-1}$? What is its molar conductance? 1+1+1=3

*(b)* *(i)* Conductivity of 0·00241 *M* acetic acid is $7{\cdot}896\times10^{-5}\ Scm^{-1}$. Calculate its molar conductivity. If $\Lambda_m^\circ$ for acetic acid is $390{\cdot}5\ S\,cm^2\,mol^{-1}$, what is its dissociation constant? 3

*(ii)* Write short notes on Wien effect and Debye-Falkenhagen effect. 2+2=4

(c) (i) Define transference number of ions of an electrolyte. Calculate the transference number of $H^+$ and $Cl^-$ from the following data obtained by moving boundary method, using $CdCl_2$ as the indicator electrolyte; concentration of HCl solution is 0·1 *M*, mass of Ag deposited in the coulometer is 0·1209 g, movement of boundary is 7·50 cm and cross-section of the tube is 1·24 $cm^2$. 1+2=3

(ii) Define ionic mobility. Derive a relationship between ionic mobility and ionic conductance. 1+3=4

4. Answer any *two* questions from the following : 5×2=10

(a) (i) What is meant by the term reference electrode? Explain with suitable example one oxidation-reduction electrode. 1+2=3

(ii) Write electrode reaction and calculate the e.m.f. of the cell : 2

$$Cu\left|Cu^{2+}\ (a=0\cdot05\ M)\right\|Ag^{+}\ (a=0\cdot01\ M)\left|Ag\right.$$

Given,

$$E^{\circ}_{Cu^{2+}|Cu} = -0\cdot337\ V$$

$$E^{\circ}_{Ag^{+}|Ag} = 0\cdot799\ V$$



( Continued )

(b) (i) Discuss how pH of a solution can be determined by using quinhydrone electrode. 4

(ii) Draw the potentiometric titration curve involving strong acid and strong base. 1

(c) (i) What is liquid-junction potential? How can it be minimized? 1½+1½=3

(ii) Discuss the charging-discharging processes in a lead storage cell. 2

5. Answer any *three* questions from the following : 3×3=9

(a) State Le Chatelier's principle. Discuss the effect of change of temperature and pressure on the following equilibrium : 1+2=3

$$N_2O_4(g) \rightleftharpoons 2NO_2(g);\ \Delta H = +59{\cdot}0\ kJ$$

(b) Derive van't Hoff equation in the form

$$\frac{d\ln K_c}{dT} = \frac{\Delta E}{RT^2}$$ 3

(c) Define activity and activity coefficient. How can the behaviour of ideal and non-ideal solution be determined from activity coefficient? 1+1+1=3

(d) Derive Gibbs-Duhem equation. 3

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