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**4 SEM TDC CHM M 1**

**2013**

( May )

CHEMISTRY

( Major )

Course : 401

**( Physical Chemistry—I )**

*Full Marks* : 48

*Pass Marks* : 19

*Time* : 3 hours

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

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

*(a)* Conductivity of 0·01 *M* NaCl solution is 0·00147 $ohm^{-1} cm^{-1}$. If extra 100 ml of water is added to the above solution, then this conductivity

*(i)* increases

*(ii)* decreases

*(iii)* remains unchanged

*(iv)* first increases and then decreases

(b) The precipitate of $CaF_2$ ($K_{sp}=1{\cdot}7\times10^{-10}$) is obtained when equal volumes of the following are mixed

(i) $10^{-4}$ $M$ $Ca^{2+}$ and $10^{-4}$ $M$ $F^-$

(ii) $10^{-2}$ $M$ $Ca^{2+}$ and $10^{-2}$ $M$ $F^-$

(iii) $10^{-8}$ $M$ $Ca^{2+}$ and $10^{-3}$ $M$ $F^-$

(iv) $10^{-10}$ $M$ $Ca^{2+}$ and $10^{-10}$ $M$ $F^-$

(c) The amount of silver (atomic mass = 108) deposited from a solution of silver nitrate when a current of 965 coulombs was passed is

(i) 10·8 g

(ii) 0·108 g

(iii) 1·08 g

(iv) $1{\cdot}08\times10^3$ g

(d) Given, $E^{\circ}_{(Cr^{3+}|Cr)} = -0{\cdot}72$ V and $E^{\circ}_{(Fe^{2+}|Fe)} = -0{\cdot}42$ V. The potential for the cell

$$Cr|Cr^{3+}(0{\cdot}1\ M)||\ Fe^{2+}(0{\cdot}01\ M)|Fe$$

is

(i) –0·26 V

(ii) 0·26 V

(iii) 0·339 V

(iv) –0·339 V

(e) Which of the following equilibria is not affected by pressure changes?

(i) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(ii) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(iii) $2O_3(g) \rightleftharpoons 3O_2(g)$

(iv) $2NO_2(g) \rightleftharpoons N_2O_4(g)$

**2.** Answer any *five* of the following : 2×5=10

(a) Calculate the equivalent conductivity of 1 $M$ $H_2SO_4$ solution whose conductivity is $26 \times 10^{-2}$ ohm$^{-1}$ cm$^{-1}$.

(b) Equivalent conductance of an electrolyte at finite concentration is less than that an infinite dilution. Explain.

(c) Explain why lithium ions move slower than potassium ions in water under an electric field.

(d) How will you determine the hydrolysis constant of aniline hydrochloride by conductance measurement?

(e) How will you prepare a normal calomel electrode?

(f) Write the chemistry of recharging of the lead storage battery, highlighting all the materials that are involved during discharging.

(g) The cell in which the following reaction occurs

$$2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(s)$$

has $E^{\circ}_{cell} = 0{\cdot}236\ V$ at 298 K. Calculate the standard Gibbs' free energy of the cell reaction.

(h) What is fugacity? Write its physical significance.

## UNIT—I

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

(a) (i) What are ionic mobilities? Derive a relation between ionic mobilities and molar ionic conductances. 1+3=4

(ii) What is meant by abnormal transport number of an ion? Under what condition an aqueous solution of $CdI_2$ shows the negative transport number of $Cd^{2+}$ ion? 1+2=3

(b) (i) Explain Kohlrausch law of independent migration of ions. The molar conductivities at infinite dilution of KCl, $KNO_3$ and $AgNO_3$ at 298 K are—

$$0{\cdot}01499\ \Omega^{-1}\,m^2\,mol^{-1};$$

$0{\cdot}01450\ \Omega^{-1}\,m^2\,mol^{-1}$;

$0{\cdot}01334\,\Omega^{-1}\,m^2\,mol^{-1}$

respectively. What is the molar conductivity of AgCl at infinite dilution at this temperature? 1+2=3

*(ii)* Explain clearly what is meant by asymmetric effect and electrophoretic effect. 2+2=4

*(c)* *(i)* Define specific and molar conductance. Explain why specific conductance decreases with dilution, but the molar conduction increases. 4

*(ii)* The conductivity of a saturated solution of a sparingly soluble salt *MX* in water at 298 K is $1{\cdot}887\times10^{-4}$ ohm$^{-1}$ m$^{-1}$. The molar conductivity of *MX* at infinite dilution at this temperature is $138{\cdot}3\times10^{-4}$ ohm$^{-1}$m$^{-2}$mol$^{-1}$. Calculate the solubility and the solubility product of *MX* at this temperature. 3

UNIT—II

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

*(a)* *(i)* Define standard electrode potential. Derive an expression for the e.m.f. of an electrode. 1+2=3

*(ii)* Discuss with diagram the variation of the e.m.f. during the potentiometric titration of a strong acid with a strong base. 2

*(b)* *(i)* What is liquid junction potential? How can it be minimized? 3

*(ii)* Calculate the standard reduction electrode potential of the $Ni^{2+}|Ni$ electrode when the cell potential for the cell

$$Ni|Ni^{2+}\ (1\ M)||\ Cu^{2+}\ (1\ M)|Cu$$

is 0·59 V.
(Given, $E^{\circ}_{Cu^{2+}|\,Cu} = 0{\cdot}34$ V) 2

*(c)* *(i)* What are fuel cells? Discuss how the e.m.f. is generated in a hydrogen-oxygen fuel cell. 3

*(ii)* Discuss how the quinhydrone electrode can be used to determine the pH of a solution. 2

UNIT—III

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

*(a)* With the help of Le Chatelier's principle, work out the condition which would favour the formation of nitric oxide in the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g); \quad \Delta H = 180{\cdot}75 \text{ kJ}$$

*(b)* Explain the term chemical potential. Derive Gibbs-Duhem equation for two-component system.

*(c)* Derive van't Hoff equation in the form

$$d(\ln K_p) / dT = \frac{\Delta H^\circ}{RT}$$

*(d)* Derive an expression for the change of Gibbs' potential for the following gaseous reaction :

$$aA + bB + ... \rightleftharpoons cC + dD + ...$$

*(e)* Explain clearly that the fugacity of a gas can both be less than or more than the pressure. Why is the fugacity of helium or hydrogen always more than the pressure?

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