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4 SEM TDC CHM M 1 (N/O)

2016

(May)

CHEMISTRY

(Major)

Course : 401

(Physical Chemistry—I)

The figures in the margin indicate full marks for the questions

(New Course)

Full Marks : 48
Pass Marks : 14

Time : 2 hours

1. Select the correct answer : 1×5=5

(a) Li^+ has a smaller ionic mobility than K^+ because of the

(i) larger size of Li^+

(ii) larger radius to charge ratio of Li^+

(iii) greater degree of hydration of Li^+

(iv) smaller nuclear charge of Li^+

(b) Which of the following is not a good conductor of electricity?

(i) NaCl (aq)

(ii) NaCl (s)

(iii) NaCl (molten)

(iv) Silver metal

(c) The primary cells are

(i) rechargeable

(ii) not rechargeable

(iii) everlasting

(iv) None of the above

(d) Standard electrode potentials of three metals X, Y and Z are $-1{\cdot}2$ V, $+0{\cdot}5$ V and $-3{\cdot}0$ V respectively. The reducing power of these metals will be

(i) $Z > X > Y$ (ii) $X > Y > Z$

(iii) $Y > Z > X$ (iv) $Y > X > Z$

(e) 2 moles of an ideal gas at 27 °C temperature are expanded reversibly from 2 L to 20 L. If the value of R is taken as 2 cal $K^{-1}mol^{-1}$, then the entropy change will be

(i) 92·1 (ii) 0

(iii) 4 (iv) 9·2

(Continued)

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

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

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

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

(d) In conductometric titration, the titre should be always very much concentrated than the solution to be titrated. Explain why.

(e) Give one example each of electrode concentration cell and electrolyte concentration cell.

(f) Write the physical significance of Helmholtz free energy and Gibbs free energy.

(g) Calculate the entropy increase in the evaporation of a mole of water at 100 °C.

(Heat of vaporization = 540 cal g^{-1})

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UNIT—I

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

(a) Deduce an expression for the entropy changes associated with the changes in temperature and pressure of an ideal gas. 4½

(b) *(i)* State Carnot theorem. 1

(ii) A Carnot engine works between the temperatures 27 °C and 127 °C. Calculate the efficiency of the engine. 1½

(iii) Predict whether at 27 °C, the following reaction is spontaneous or not : 2

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$$

Given $\Delta H = +9080\ J mol^{-1}$ and $\Delta S = +35 \cdot 7\ J\ K^{-1} mol^{-1}$.

(c) *(i)* State and explain Nernst heat theorem. 2

(ii) Describe the third law of thermodynamics. 2½

UNIT—II

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

(a) *(i)* Represent the variation of equivalent conductance of KCl and CH_3COOH with dilution graphically and give explanation for such variation. 5

(ii) Define the term transference number. 2

(b) Explain Wien effect and Debye-Falkenhagen effect. 3½+3½=7

(c) *(i)* Define molar conductivity and equivalent conductivity. 4

(ii) The equivalent conductances at infinite dilution (λ_0) of HCl, CH_3COONa and NaCl are 426·16, 91·0 and 126·45 $ohm^{-1} cm^2 g\ eqvt^{-1}$ respectively. Calculate λ_0 of acetic acid. 3

UNIT—III

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

(a) What is liquid junction potential? Derive an expression for it. 5

(b) What are fuel cells? Discuss how the e.m.f. is generated in a hydrogen-oxygen fuel cell. 5

(c) (i) A solution of $CuSO_4$ is electrolysed for 10 minutes with a current of 1·5 amperes. What is the mass of copper deposited at the cathode? (Atomic mass of copper = 63·56 u) 4

(ii) Define standard electrode potential. 1

(Old Course)

Full Marks : 48
Pass Marks : 19

Time : 3 hours

1. Select the correct answer : 1×5=5

(a) In the lead-acid battery, during charging, the cathode reaction is
(i) formation of $PbSO_4$
(ii) reduction of Pb^{2+} to Pb
(iii) formation of PbO_2
(iv) deposition of Pb at the anode

(b) Li^+ has a smaller ionic mobility than K^+ because of the
(i) larger size of Li^+
(ii) larger radius to charge ratio of Li^+
(iii) greater degree of hydration of Li^+
(iv) smaller nuclear charge of Li^+

(c) Which of the following is not a good conductor of electricity?
(i) NaCl (aq)
(ii) NaCl (s)
(iii) NaCl (molten)
(iv) Silver metal

(d) Standard electrode potentials of three metals X, Y and Z are $-1{\cdot}2$ V, $+0{\cdot}5$ V and $-3{\cdot}0$ V respectively. The reducing power of three metals will be

(i) $Z > X > Y$

(ii) $X > Y > Z$

(iii) $Y > Z > X$

(iv) $Y > X > Z$

(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 questions : 2×5=10

(a) Explain how the solubility product of a salt can be determined by e.m.f. measurement.

(b) Write the difference between galvanic cell and electrolytic cell.

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

(Continued)

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

(e) The molar conductivities at infinite dilution of KCl, KNO_3 and $AgNO_3$ at 298 K are

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

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

and $0{\cdot}013334\ \Omega^{-1}m^2mol^{-1}$

respectively. What is the molar conductivity of AgCl at infinite dilution at this temperature?

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

UNIT—I

3. Answer any *two* of the following questions : 7×2=1

(a) (i) Define specific and molar conductance. Explain why specific conductance decreases with dilution but molar conductance increases. 2+3

(ii) Represent variation of equivalent conductance of KCl and CH_3COOH with dilution graphically.

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

(ii) Describe any one method for determining the transport number of an ion. 3

(c) Explain Wien effect and Debye-Falkenhagen effect. 3½+3½=7

UNIT—II

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

(a) (i) Derive Nernst equation. 3

(ii) Calculate the e.m.f. of the cell

$Ag(s)|Ag^{+}(a=0\cdot1)||Zn^{2+}(a=0\cdot1)|Zn(s)$

Given

$E^{\circ}_{Ag/Ag^{+}} = 0\cdot799V, E^{\circ}_{Zn^{2+}/Zn} = -0\cdot763V$

Is the reaction spontaneous? 2

(b) What are fuel cells? Discuss how the e.m.f. is generated in a hydrogen-oxygen fuel cell. 5

(Continued)

(c) (i) What is liquid junction potential? How can it be minimized? 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

UNIT—III

5. Answer any *three* of the following questions : 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

$N_2(g)+O_2(g) \rightleftharpoons 2NO(g);\ \Delta H = 180\cdot75$ kJ

(b) Write the effect of temperature and pressure on chemical potential.

(c) Derive Duhem-Margules equation.

(d) Deduce the relationship between ΔG° and K_C of a reversible reaction.

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