ADVANCED LEVEL PHYSICAL CHEMISTRY PROBLEMS

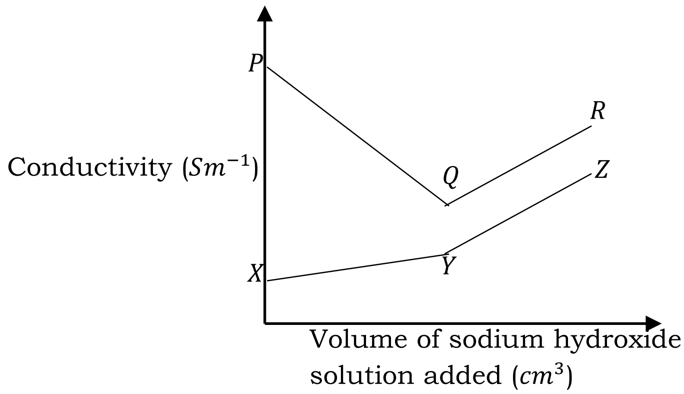
CHAPTER 11: ELECTROCHEMISTRY

1. (a). (i), State Kohlrausch's law of independent migration of ions
   (ii). The molar conductivities of potassium nitrate, potassium cyanide and nitric acid at infinite dilution are 145, 156 and 421 $\Omega^{-1}cm^2mol^{-1}$ respectively. Calculate the molar conductivity of hydrocyanic acid at infinite dilution.
   (b). Explain how the molar conductivity of the following solutions would vary with concentration.
   (i). Sodium hydroxide
   (ii). Aqueous ammonia
   (c). The ionic conductivities of sodium and hydroxide ions are 4.95×10^{-3} and 1.98×10^{-2} $\Omega^{-1}cm^2$ respectively. Calculate the molar conductivity of 0.1M sodium hydroxide solution.
   (d). Briefly outline practical applications of conductivity measurements in
   (i). Volumetric analysis
   (ii). Study of complexes

2. (a). (i), State Kohlrausch's law of ionic conductivity at infinite dilution.
   (ii). Calculate the molar conductivity of methanoic acid at infinite dilution given that the molar conductivity of sodium methanoate, sodium chloride and hydrochloric acid at infinite dilution are 9.5×10^{-2}, 1.26×10^{-1} and 4.26×10^{-1} Sm^2mol^{-1} respectively.
   (b). Ionic conductivities of silver and chloride ions at infinite dilution are 6.2×10^{-2} and 7.6×10^{-2} Scm^2mol^{-1} respectively at 298K. the electrolytic conductivity of silver chloride solution at 298K is 1.22×10^{-4} Sm^{-1}. Calculate the solubility of silver chloride at 298K in gl^{-1}.
   (c). Name one practical application of ionic conductivity apart from determination of solubility of electrolytes

3. (a). Explain the term molar conductivity of an electrolyte
   (b). Sketch a graph to show how the molar conductivity of barium hydroxide varies with concentration in aqueous solution
   (c). given that the molar conductivities of barium hydroxide, barium chloride, and ammonium chloride at infinite dilution are 457.6, 240.6 and 129.8 $\Omega^{-1}m^2mol^{-1}$ respectively. Calculate the molar conductivity of ammonia solution at infinite dilution

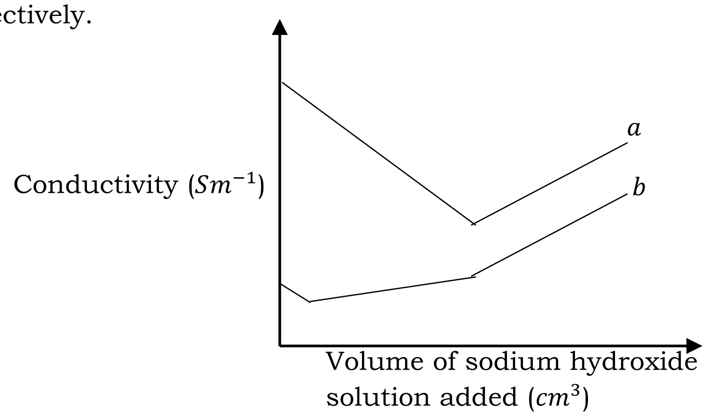
4. (a). (i), State Faraday's law of electrolysis.
   (ii). A current of 2A was passed for 30 minutes through a cell containing dilute sulphuric acid and hydrogen was collected at the cathode. Determine the volume of the gas collected. (1F = 96500 C)
   (b). Graphs PQR and XYZ show variation of the conductivities of solutions formed when 0.1M hydrochloric and 0.1M ethanoic acid were respectively titrated with 0.1M sodium hydroxide solution. Account for the differences in the shapes of the graphs.



5. (a). State Kohlrausch's law of independent conductivity of ions.
   (b). Some ionic mobilities at infinite dilution at 25Some ionic mobilities at infinite dilution at 25°C of hydroxide, chloride, ammonium and sodium ions are 198.6, 76.4, 73.6 and 50.1 $\Omega^{-1}cm^2$. Calculate the molar conductivity of ammonium hydroxide at infinite dilution.
   (c). The ionic radii and ionic conductivities at infinite dilution of some ions are shown below

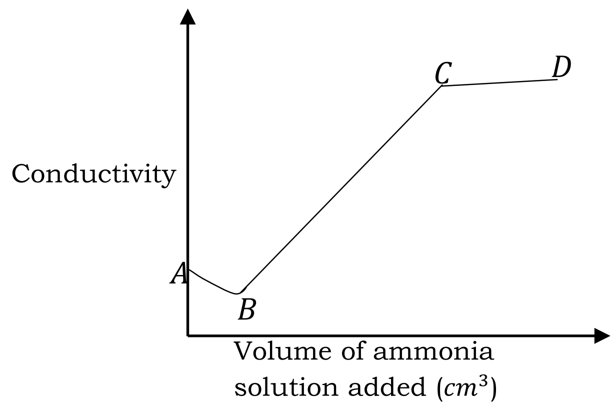
Ion	Ionic radius (nm)	Ionic conductivity ($\Omega^{-1}cm^2$)
Li^+	0.060	38.7
Na^+	0.095	50.1
K^+	0.133	73.5

   Explain the trend in ionic conductivities
   (d). The diagram below shows curves 'a' and 'b' obtained when aqueous sodium hydroxide was gradually separately to equimolar solutions of hydrochloric acid and ethanoic acid respectively.



   Explain the shapes of each curve

6. (a). Define the following terms
   (i). Conductivity
   (ii). Molar conductivity
   (b). The graph below shows changes in the conductivity when 0.01M methanoic acid was titrated with 0.1M ammonia solution.



(c). At 25°C, the molar conductivity of silver nitrate, potassium nitrate and potassium chloride are 133.4,145.0 and 149.9 $\Omega^{-1}cm^2mol^{-1}$ respectively. At the same temperature, the conductivity of a saturated solution of silver chloride and pure water are 3.14×10^{-6} and 1.6×10^{-6} $\Omega^{-1}cm^{-1}$.

(i). Calculate the solubility of silver chloride in moles per dm^3.

(ii). Determine the solubility product of silver chloride at 25°C.

(d). The ionic conductivities of rubidium and sodium ions are 78.3 and 50.1 $\Omega^{-1}cm^2mol^{-1}$ respectively. Explain the difference in the values gives.

7. (a). The molarity of a sample of hydrochloric acid about 0.1M was determined accurately by measuring the conductivity of the solution as 1.0M sodium hydroxide solution was added to 50cm^3 of the acid. The results were as follows.

Conductivity ($\Omega^{-1}cm^{-1}$)	4.1	3.3	2.4	1.7	1.5	1.8	2.2	2.5
Volume of 1.0M sodium hydroxide solution (cm^3)	1	2	3	4	5	6	7	8

(i). Plot a graph of conductivity against volume of 1.0M sodium hydroxide

(ii). Determine from the graph the volume of 1.0M sodium hydroxide used to reach end point

(iii). Calculate the molarity of hydrochloric acid.

(b). Name one other application of conductivity measurements.

8. (a). The molar conductivities of sodium hydroxide solutions of different concentrations are shown in the table below

Concentration (moldm^{-3})	0.01	0.04	0.09	0.16	0.25	0.36
Molar conductivity ($\Omega^{-1}cm^2mol^{-1}$)	238	230	224	217	210	202

(i). Draw a graph of molar conductivity against the square root of concentration.

(ii). Explain the shape of the graph

(iii). Determine the value of molar conductivity at infinite dilution of sodium hydroxide and indicate its units

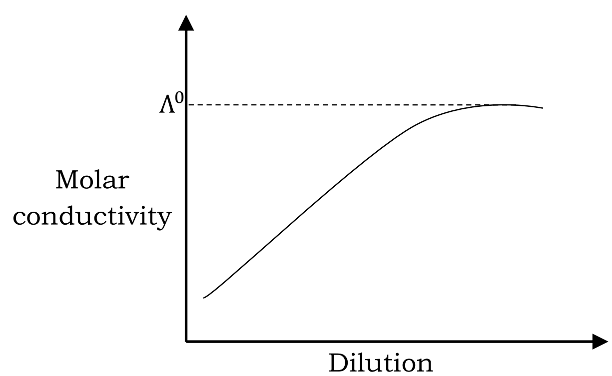
(b). Using the same conductivity cell, the resistance of a 0.1M potassium chloride and 0.1M bromoethanoic acid solutions were found to be 24.96 and 66.50Ω respectively. The conductivity of potassium chloride is 0.01164 $\Omega^{-1}cm^{-1}$ while the molar conductivity of bromoethanoic acid at infinite dilution is 389 $\Omega^{-1}cm^2mol^{-1}$. Determine

(i). The cell constant of the cell
(ii). The molar conductivity of the 0.1M bromoethanoic acid
(iii). The pH of 0.1M bromoethanoic acid.

9. (a). Explain what is meant by the following terms
(i). Molar conductivity
(ii). Electrolytic conductivity
(b). State the relationship between the conductivities above
(c). Draw sketch graphs to show how the molar conductivity of the following vary with concentration
(i). Strong electrolyte
(ii). Weak electrolyte
(d). Explain the shapes of the graphs in (c)
(e). The table below shows the variation of the conductivity with volume of ammonia when two inert electrodes connected to a conductivity meter were immersed in 50 cm^3 of 0.025M zinc nitrates solution and 2 cm^3 portions of 0.5M ammonia added at intervals

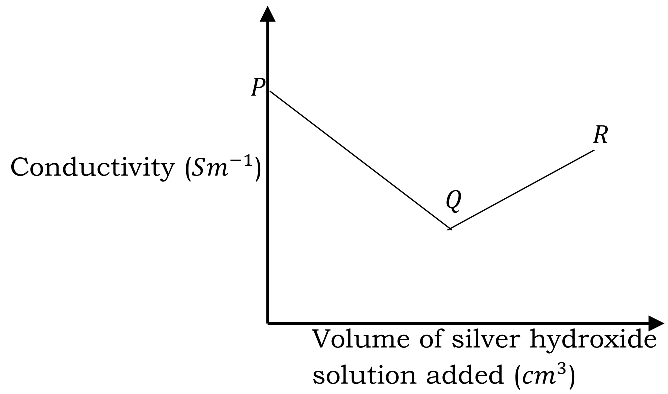
Volume of ammonia (cm^3)	0	2	4	6	8	10	12	14
Conductivity ($\Omega^{-1}cm^{-1}$)	1.2	1.16	1.12	1.08	1.05	1.04	1.06	1.1

10. (a). State three factors that can affect the molar conductivity of electrolytes
(b). The graph below shows the variation of molar conductivity of a strong electrolyte with dilution



Briefly explain the shape of the graph
(c). The molar conductivity of nitric acid, potassium nitrate and potassium fluoride are 421, 145 and 129 $\Omega^{-1}cm^2mol^{-1}$ calculate
(i). The molar conductivity of hydrofluoric acid at infinite dilution
(ii). The dissociation constant, K_a, of a 0.1M hydrofluoric acid solution. (the electrolytic conductivity of hydrofluoric acid is $3.15 \times 10^{-5}\ \Omega^{-1}cm^{-1}$)

11. (a). The conductimetric curve for the titration of hydrochloric acid and silver hydroxide is given below



Explain the shape of the curve XYZ

(b). The molar conductivities of silver nitrate, potassium nitrate, and potassium chloride are 134, 143.2 and 140.8 $\Omega^{-1}cm^2mol^{-1}$ respectively. Calculate the

(i). Molar conductivity of silver chloride at infinite dilution

(ii). The solubility product, K_{sp}, of silver chloride at 25°C. (the electrolytic conductivity of water and that of saturated solution of silver chloride are 5.5×10^{-8} and $1.934 \times 10^{-6}\Omega^{-1}m^{-1}$)

12. (a). State two factors that can affect the molar conductivity of an electrolyte.

(b). The molar conductivity of potassium hydroxide at various concentrations are given in the table below.

Molar conductivity ($\Omega^{-1}cm^2mol^{-1}$)	238	230	224	217	210
[KOH]/ moldm^{-3}	0.01	0.04	0.09	0.16	0.25
$\sqrt{[KOH]}/\ mol^{1/2}dm^{-3/2}$					

(i). Complete the table above

(ii). Draw a graph of molar conductivity against the square root of the concentration of potassium hydroxide

(iii). Explain the shape of the graph

13. (a). State Kohlrausch's law od independent ionic migration and state how it can be used to obtain the molar conductivity of ethanoic acid at infinite dilution.

(b). Explain the following observations

(i). the electrolytic conductivity of 0.2M hydrochloric acid is greater than that of 0.1M hydrochloric acid

(ii). The molar conductivity of 0.2M hydrochloric acid is less than that of 0.1M hydrochloric acid

(iii). The molar conductivity of 0.5M ethanoic acid is less than that of 0.5M hydrochloric acid

(c). Determine the degree of dissociation of aqueous ammonia whose electrolytic conductivity is $5.364 \times 10^{-7}\Omega^{-1}m^{-1}$ given that the molar conductivities of ammonium and hydroxide ions at infinite dilution are 98 and 200 $\Omega^{-1}cm^2mol^{-1}$.

14. (a). Explain what is meant by the term molar conductivity at infinite dilution
    (b). Describe how the molar conductivity at infinite dilution of sodium ethanoate can be determined
    (c). The molar conductivities of sodium chloride, hydrochloric acid and sodium hydroxide are 126.5, 426.2 and 248.4$\Omega^{-1}cm^2mol^{-1}$ .The electrolytic conductivity of water at 298K is $5.364 \times 10^{-7}\Omega^{-1}m^{-1}$. If one mole of water has a volume of 18cm^3, calculate the
        (i). Degree of ionisation of water
        (ii). Ionic product of water
    (d). Ethanoic acid is titrated with sodium hydroxide.
        (i). Sketch a graph showing the variation of conductivity with volume of sodium hydroxide added
        (ii). Explain the shape of your graph.
    (e). Calculate the degree of dissociation of a 0.2M ethanoic acid whose electrolytic conductivity is $1.473 \times 10^{-6}\Omega^{-1}m^{-1}$ given that the molar conductivities at infinite dilution of magnesium chloride, hydrochloric acid and magnesium ethanoate are 258, 426 and 202$\Omega^{-1}cm^2mol^{-1}$.

15. (a). The molar ionic conductivities of some ions is given below

Ion	Li^+	H^+	K^+	Na^+	Mg^{2+}	Cl^-	$\bar{O}H$
Molar conductivity at infinite dilution ($\Omega^{-1}cm^2mol^{-1}$)	38	350	74	50	106	76	200

        (i). Explain why the ionic molar conductivity of lithium ion is smaller than at of potassium ion
        (ii). Explain why the ionic conductivity of sodium ions is less than that of magnesium ions
        (iii). Calculate the conductivity of 0.01M hydrochloric acid
        (iv). If the hydrochloric acid has been exactly half neutralised with 1M sodium hydroxide solution, calculate the conductivity of the resulting solution.
    (b). The resistance of a 0.1M solution of potassium chloride is found to be 31. If the conductivity of this solution of potassium chloride is $1.29 \times 10^{-2}\Omega^{-1}m^{-1}$.
        (i). Determine the cell constant
        (ii). Using the same cell, the resistance of a 0.1M solution of silver nitrate was 36.7 Ω. Calculate the conductivity of this solution.
    (c). Calculate the conductivity of a solution made by adding
        (i). 50cm^3 of 0.1M sodium hydroxide to 25cm^3 of 0.1M hydrochloric acid
        (ii). 25cm^3 of 0.1M sodium hydroxide to 25cm^3 of 0.1M hydrochloric acid
        (iii). 25cm^3 of 0.1M sodium hydroxide to 50cm^3 of 0.1M hydrochloric acid
        (the ionic molar conductivities of sodium, chloride, hydroxide and hydrogen ions are 50, 76, 200 and 350 $\Omega^{-1}cm^2mol^{-1}$).

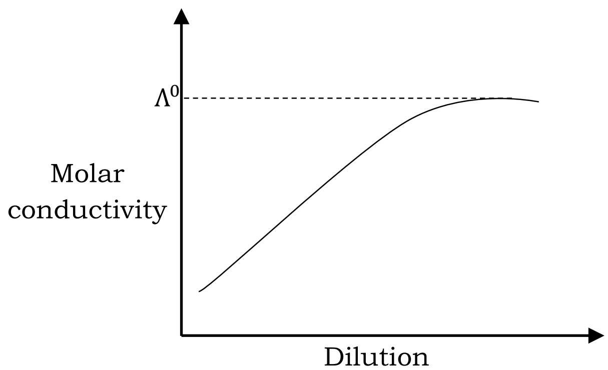
16. (a). State and explain the factors that determine the magnitude of electrolytic conductivity of a
        (i). Strong electrolyte
        (ii). Weak electrolyte
    (b). A solution of an electrolyte of concentration 0.02M has a resistance of 0.357 Ω in a cell of cell constant 1.5 Ωm^{-1}. Calculate the

(i). The electrolytic conductivity of the electrolyte
(ii). The molar conductivity of the electrolyte

(c). Calculate the conductivity of the resultant solution when 20cm^3 of sulphuric acid is exactly half neutralised by sodium hydroxide.
(the ionic molar conductivities of sodium, sulphate, hydroxide and hydrogen ions are 50, 160, 200 and 350 $\Omega^{-1}cm^2mol^{-1}$

(d). State the applications of conductimetric titrations

17. (a). The graph below shows the variation of molar conductivity of hydrochloric acid with dilution



(i). Explain the shape of the graph
(ii). On the same axes, sketch and explain the shape of the graph if ethanoic acid was used instead of hydrochloric acid

(b). The table below shows the variation in molar conductivity of sodium hydroxide with concentration

Concentration (moldm^{-3})	0.01	0.04	0.09	0.16	0.25	0.36
Molar conductivity ($\Omega^{-1}cm^2mol^{-1}$)	238	230	224	217	210	202

(i). Plot a graph of molar conductivity against the square root of concentration
(ii). Explain the shape of the graph
(iii). Determine the value of molar conductivity at infinite dilution for sodium hydroxide

(c). Sketch a graph to show how the molar conductivity of ethanoic varies with square root of concentration. Explain the shape of the graph

(d). The ionic radii and molar conductivity at infinite dilution at 20°C of lithium and caesium ions are given below

Ion	Li^+	Cs^+
Ionic radius (nm)	0.06	0.17
Molar ionic conductivity $\Omega^{-1}cm^2mol^{-1}$	33.5	68.1

Explain the difference in ionic conductivity

18. (a). (i). State Kohlrausch's law of independent ionic migration.
(ii). 2.72g of anhydrous zinc chloride was dissolved in water and the solution made up to one litre. The electrolytic conductivity was found to be $5.176 \times 10^{-3}\Omega^{-1}cm^{-1}$ at 25°C.

Determine the molar ionic conductivity of chloride ions at this temperature ($Zn = 65; Cl = 35.5$; the molar conductivity of zinc chloride at infinite dilution and the molar ionic conductivity of zinc ions are respectively 206 and 54 respecttvely)

(b). (i). Draw sketch graphs to show how molar conductivities of the following compounds vary with concentration

- Copper(II) sulphate
- Hydrofluoric acid

(ii). Explain the shape of the graphs you have sketched in (b) (i)

(c). the table below shows how the molar conductivity of lithium chloride in water at 25°C varies with dilution, $\frac{1}{C}$, where C is concentration.

Dilution ($mol^{-1}dm^3$)	2000	1000	500	200	100	20
Molar conductivity ($\Omega^{-1}cm^2mol^{-1}$)	113.2	112.5	111.5	109.4	107.3	100.1

(i). plot a graph of molar conductivity of lithium chloride against dilution at 25°C.

(ii). Explain the shape of the graph

(iii). Using the graph, estimate the molar conductivity of lithium chloride at infinite dilution at 25°C.

18. (a). Explain what is meant by the molar conductivity

(b). Molar conductivities at infinite dilution for some compounds at 25°C are given in the table below

Compound	Λ_c ($\Omega^{-1}cm^2mol^{-1}$)
$Na_2C_2O_4$	248
H_2SO_4	860
Na_2SO_4	260
$(NH_4)_2SO_4$	308

Calculate the molar conductivity at infinite dilution for

(i). $H_2C_2O_4$

(ii). $(NH_4)_2C_2O_4$

(c). Explain your answers in (b)

(d). State two applications of conductivity measurements

19. (a). Define electrolytic conductivity

(b). Calculate the molar conductivity of a solution containing 0.095g of anhydrous magnesium chloride in a litre of solution at 25°C. (the electrolytic conductivity of magnesium chloride is $2.58 \times 10^{-4}\Omega^{-1}cm^{-1}$)

(c). Calculate the solubility of lead(II) chloride in gl^{-1}, given that the electrolytic and molar conductivities of lead(II) nitrate solution are 2.62×10^{-4} $\Omega^{-1}cm^{-1}$ and 138 $\Omega^{-1}cm^2mol^{-1}$ respectively.