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Adsorption of Anions on PBO_2 in a Leclanche Dry Cell

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Abstract: A study of the adsorption of alkaline anions on lead (IV) oxide (PbO_2) used as cathode material in dry cell has been carrying out. The absorption method by potentiometric titrations were adopted for different anions at four different concentrations of the anions in augment solution. The results of the analysis obtained showed that lead (iv) Oxide (PbO_2) can be used in dry cell as a depolarizer when blended with alkaline anions particularly the sulphate (SO_4^{2-}) ion as compared with NO_3^-, Cl^- and Br^- ions, respectively some graphs were plotted in addition to some fear ones necessary for both the determination of the surface areas of PbO_2. Also the adsorption of alkaline anion on PbO_2 is in accordance with Longmuir Freundlich and Tamkin isotherms.

Key words: Adsorption, alkaline anions, lead (IV) oxide, concentration of anions, surface area, PH of solution

INTRODUCTION

Electrochemical cells are cells in which current (faradaic current) flow from one electrode to another and are classified into two cells. That is Galvanic and Electrolytic cells. However, this research is on adsorption properties of lead (IV) oxide in a dry cell (Galvanic) (Kubasov, 1987).

A dry cell is one in which chemical reactions occur spontaneously at the electrodes when conductor is connected across them. And chemical energy is converted into electrical energy. These types of cells are widely known as batteries. Cell is a unit of a battery and is non-rechargeable primary cell. An example is the leclanche (Zn-MnO_2) cell on which this work is based.

Leclanche cell is improved types of primary cell known in the past as voltaic and pile invented by Alessandre Volta. The cell consist of a zinc container which acts as the anode (positive pole), the center terminal made up of a carbon rod acts as the cathode (negative pole) and the electrolyte which consist of powered carbon Zinc chloride, ammonium chloride, water, lead (iv) oxide and an inert tiller in the form of paste. A porous line placed between the Zinc container and the paste prevents contact and serves as a salt bridge which allows the flow of ions (Meyers, 1987).

A number of reactions may occur when the cell is in use. Usually the operating voltage of a dry cell is in range of 0.9-1.4 volts. The following reaction occurs at the cathode:

$$2PbO_2 + 2NH_4^+ + 2e^- \rightarrow Pb_2O_3 + 2NH_3 + H_2O$$

At the anode:

$$Zn + 4NH_3 \rightarrow Zn(NH_3)_4^{2+} + 2e^-$$

The hydrogen ions formed by the hydrolysis of water in the first half of the reaction gain electrons to become hydrogen molecules and cluster at the vicinity of the carbon rod. This called polarization. The PbO_2 present in the paste act as a depolarizer by using up the hydrogen ions that is formed at the cathode and presenting it from forming hydrogen gas (Antropon, 1972).

The overall cell reaction is the sum of the reactions at the two electrodes:

$$Zn + H_2O + 2PbO_2 \rightarrow Pb_2O_3 + H_2O + ZnO$$

The adsorption method by potentiometric titrations will be adopted. This will however, assist in establishing the better concentration suitable for adsorption from the analysis that will eventually evolve.

Adsorption involved the transfer of a constituent of a fluid (liquid or gaseous) to the surface of a liquid/solid phase. When a liquid molecule is adsorpted on the surface of a solid, it settles on it much like a condensing molecule and is then held on the surface by attractive forces such as Vander Waal force. Also in some cases depends on the chemical natures of the molecule and the surface

However, adsorption is the preferential concentrations of a species at the interface between phases. This term rather than absorption is used when no surface penetration occurs. Adsorption results from

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disequilibrium forces associated with surface molecules of a solid or liquid. The high potential energy of these molecules is lowered by the attraction of freeing substances. The adsorbed substances show increased reactivity. An adsorption phenomenon is divided into two main classes: Physical adsorption and chemical adsorption (or, chemisorptions) (Aloko, 2000).

Physical adsorption arises from intermolecular forces involving permanent dipole, induced dipole and qradrapole interaction. It involves Vander Waal or secondary valence it is akin to condensation. Chemisorptions, on the other hand, involves a chemical interaction with attendant transfer of electron between the adsorbent and the adsorbing species (adsorb ate).
Adsorption is obtained from the formula given below (Dyer, 1994)

$$Q = \Delta VC/S*1000 \quad (1)$$

In principal, one can apply Gibb's equation to the problem of adsorption at the solid-solution interface. In this case, the surface concentration "u" will equal (N/A), where A is the specific area of the solid and (dv/dc) refers to the change interfacial tension with solute concentration.

It is often possible to represent experimental result over a limited range by an empirical isotherm or suggested by Freundlich (David *et al*., 1981).

$$N = KC^{a} \quad (2)$$

Where K and a are constants. These constant have no physical significance but can be evaluated by a plot of log N versus log C. however, Eq. 2 fails to predict the behaviour usually absorb at low or is often directly proportional to C and at high concentrations. At low concentrations or is often directly proportional to C and at high concentrations N usually approaches a constant limiting value which is independent of C. much efforts has been devoted to developing a theory of adsorption from which would explain the observed experimental facts. In some simple system a theory derived by Langmuir can be applied. This theory is restricted to cases where only lower of molecule can be adsorbed at the surface (Moore, 1992).

The Langmuir isotherm can be derived from either kinetic or equilibrium arguments and is most commonly applied to the chemisorptions of gasses. The equation appropriate to adsorption from solution is given by

$$Q = KC/1+KC \quad (3)$$

Where Q is the fraction of solid surface covered by adsorbed molecules and K is a constant at constant temperature

$$\text{But } Q = N/N_m \quad (4)$$

Where N is the number of moles adsorbed per gram of solid at an equilibrium solute concentration C and N_m is the number of moles per gram required to form a monolayer substituting Eq. 4 and 3 we have;

$$C/N = C/N_m+1/KN_m \quad (6)$$

If the Langmuir isotherm is an adequate desorption of the adsorption process, then a plot of C/N versus C will yield a straight line with slope $1/N_m$. if the area occupied by an adsorbed molecules on the surface is known, the specific area, A (in square meters per gram) is given by

$$A = N_m N_{o\sigma} *10^{-20} \quad (7)$$

Where N_o is Avogadro's number and σ is given in square Armstrong. If adsorption isotherm is determined at several different temperatures, one would predict that the shapes of the C/N versus C plots should all be the same if the number of adsorption site (N) is dependent on temperature which is usually true. However, the intercepts should change with temperature, since K is a function of temperature (Moore, 1992).

This study is aimed at investigating the depolarizing ability of MnO_2 partially substituted with PbO_2; and then determine the adsorption of some (alkaline ions) on lead (IV) oxide, PbO_2 in order to increase either its depolarizing effectiveness or its voltage output. And the adsorption isotherm upon which the adsorption properties of PbO_2 related to shall be determined.

MATERIALS AND METHODS

Chemicals and equipments used: The chemical used in the adsorption from solution experiment for the determination of specific area of PbO_2 and that used for the potentiometric titration are presented in Table 1 while Table 2 contains information about the equipment used in the different experiments.

Experimental procedure

Procedure for the determination of surface area of lead (IV) oxide: One hundred mililitier of acetic acid solution each of concentrations 0.0215, 0.03, 0.06, 0.09, 0.12 and 0.15 M were measured with a pipette and added to seven

Table 1: List of chemicals

Chemicals	Source	Comments
Lead II Oxide (PbO_2)	BOH chemical LTD Poole England	Laboratory reagent (Analytical)
Sodium Hyroxide (NaOH)	CHE PROHA chemical Netherlands	Laboratory reagent (Analytical)
Phenolphthalein	May and Baker LTD DAGENHAM England	Laboratory chemical
Potentiometric titration	BDH chemicals	Laboratory reagent
Distilled water	FUT Minna, Nigeria	Laboratory used
Sodium Nitrate ($NaNO_3$)	INTERCHEM (U.K)	Laboratory chemical (Analytical)
Sodium Sulphate, Na_2SO_4	"	"
Sodium Chloride, NaCL	"	"
Sodium Bromide, NaBr	"	"
Nitrogen gas	Supplied in cylinders	Analytical/Industrial

The Nitrogen gas was used to; Provide an inert environment in the titrating vessel and thus inhibit side reactions, Drive off oxygen and carbon dioxide, which might be present in the vessel, Nitrogen takes the place of oxygen molecules present in the aqueous solutions and performs its function by providing the necessary electrons that make up the quantity of oxygen needed in PbO_2 molecule

Table 2: List of equipments

Equipment	Source	Comment
50 mL beaker	SIMAX Czechoslovakia	Analytical (Fragile)
250 mL Erlenmeyer	Czechoslovakia	"
50 mL burette	TECHNICO England	"
100 mL titration	SCHOTT MAIN 2	"
25 mL pipette	TECHCELOR W- Germany	"
Analytical Balance AE160	OHAUS U.S.A	Analytical
PH meter EIL (7045/46)	JENWAY U.K	"
Hot plate magnetic stirrer	Corning Germany	"
Magnetic follower	Corning Germany	Analytical
Weighing Balance	OHAUS Corporation JEORHAM PARK U.S.A	"
1000 mL Volumetric Flask	JAY Tech England "	
250 mL Conical Flask	PYREX England	"
10 mL Pipette	TECHCOLOUR West Germany	"
Tripod stand and Clamp	TECHNICO England	"

250 mL Erlenmeyer flasks. Then 2 g of the lead (IV) oxide was added to the flask containing, a given concentration of the acetic acid.

The 7 flasks were then Stoppard with rubber cork and each flask was shaken intermittently for a period of 30 min and was put into a water bath at 250°C to stand for 24 h.

After 24 h, the equilibrium was reached the solutions were filtered into seven separate conical flasks, the first 10 mL of the filtrate for each of the mixtures was discarded as a precaution against adsorption of the acid by the filter paper.

Then, two 25 mL portion of each decanted solution (alignments) was taken with pipette and titrated against 0.1 M sodium hydroxide solution using phenolphthalein as the indicator. The same procedure was repeated for the remaining concentration of the acetic acid solutions. However, a 10 mL burette was used for 0.015 and 0.03 M solutions in the titration from the titre values, the new concentrations of the acetic acid solutions were calculated. Thus, the numbers of moles present before and after adsorption were similarly calculated and the difference obtained.

These values were used to calculated values for C/N and hence a plot of C/N versus C was drawn. The slope of the straight line obtained, was calculated and used for the calculation of the adsorption area of lead (IV) oxide.

Procedure for potentiometric titration: To a clean dry 100 mL beaker, a little of 1M Sodium Sulphate solution was added to rinse the beaker. The 50 mL of the 1 m solution of Sodium Sulphate was measured with a 50 mL pipette and transferred into the beaker and a magnetic follower placed inside to provide a continuous stirring. The beaker was placed on a magnetic stirrer, which was connected to power source. A reference electrode and indicator electrode (built into one holder) connected to a pH meter was hanged into the solution in the beaker. Then a nitrogen gas jet regulated by a gauge from the nitrogen gas cylinder was inserted into the solution in the beaker such that the gas outlet is immersed in the solution. In addition, a burette filled with 0.1 M Nitric acid solution was also placed such that its tip was directly pointed to the solution in the 100 mL beaker. After which the magnetic stirrer was switched on and the nitrogen gas regular opened to provide a continuous gas jetting into the solution (bubbling).

After a while when the pH meter was stabilized and the initial pH reading without the 0.1 M solution of Nitric was noted. Subsequently, 0.5 mL of the titrant (acid) were added from the burette and the pH reading noted for every two minutes after each addition, when the indicator electrode had reached a constant value. The 0.5 mL increment and the corresponding pH reading were noted for a total of 10 mL additions when no significant change

was observed in the reading. At the end, both the magnetic stirrer and the pH meter were switched off and the solution mixture disposed.

Similarly, another 50 mL of the 1M Sodium Sulphate solution was pipette into the beaker and 2 g of lead (IV) oxide added. The magnetic follower was then inserted into the beaker and the whole set-up was arranged after stabilizing the pH meter with distilled water. The same procedure was repeated for a total of 10 mL of 0.5 mL addition of the 0.1 M Nitric acid solution.

Subsequent solution of Sodium Nitrate; $NaNO_3$, Sodium Bromide; NaBr and Sodium Chloride, NaCl were tried both with and without lead (IV) oxide PbO_2.

The volumetric readings of the 0.1 M HNO_3 and their corresponding pH readings for all the sets of titrations carried out were tabulated. Graphs were plotted for each set of reading (both pH of solutions with and without PbO_2) and for all concentrations of different anions.

RESULTS AND DISCUSSION

After several test have been carried out on the samples, the results obtained are tabulated in Table 3.

The following charts below are titre values from the potentiometric adsorption of 0.1M HNO_3 against different concentrations of aqueous solution of different anions (that is SO_4^{2-}, NO_3^-, CL^- and Br^-).

Determination of surface area of PbO_2: The volumetric analysis (titration) between the various concentration of acetic acid including the control show a gradual increase in the titre value of 0.1 M NaOH, thus, reflecting increasing concentration of the acetic acid. This can be observed in Table 3. Similarly, a plot of C/N versus C gave a straight line and the slope (N_m) was used for the determination of the surface area of the PbO_2 as shown in Fig. 1. The results shows that PbO_2 has a surface area of 1264.83 m g^{-1}.

Effects of concentration of anions on adsorption: The adsorption of the different anions concentration and of course the plots of the adsorption, Q versus Log C (Fig. 2) shows that the lower the concentration of the anions, the higher the adsorption of the anions. This is a complete deviation from the fact that the higher the concentration of the anions (greater gradient) the higher the adsorption of the adsorbate. The fact is that the higher the concentration of the anions, the less is the kinetic energy of the anions and the changes of being adsorbed with time. However, the lower is the concentration of the anions; the higher is the chances of being adsorbed as a result of lesser concentration of the anions.

Table 3: Results for the determination of specific area of lead (IV) oxide, PbO_2

	Control						
Initial Conc. of Acetic acid (M)	0.03	0.015	0.03	0.06	0.09	0.12	0.15
Volume of acetic acid used (Ml)	25.00	25.00	25.00	25.00	25.00	25.00	25.00
Volume of 0.1M NaOH (mL) (Ave)	7.50	8.20	9.50	22.20	31.50	42.60	48.20

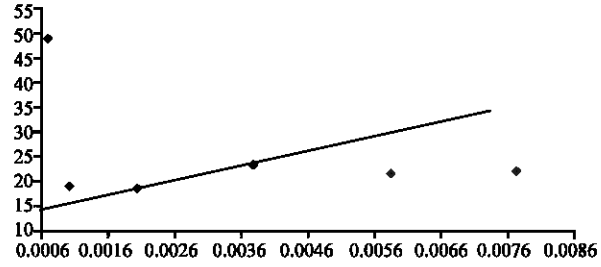

Fig. 1: Plot of C/N Versus concentration (Mole)

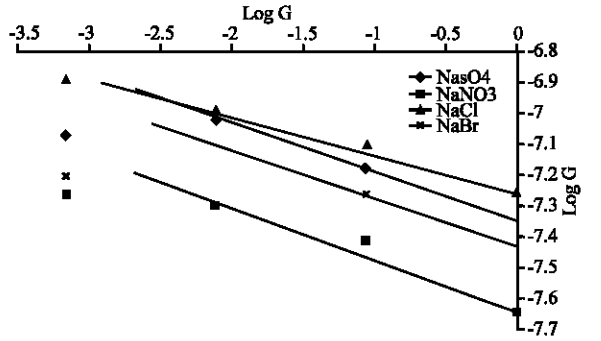

Fig. 2: Showing calculated Log C versus Log G

Effects of concentration of anions on surface charge, (E): Results obtained for the surface charge (E) as shown in Fig. 3, show that the lower the concentration of the anions, the higher is the surface charge posed on the PbO_2 .Similarly, the surface charge of the different concentrations of the anions with respect to the change in volume of the anions at selected pH (6), also show that the lower the concentration of the anions, the higher is the surface charge, this was clearly observed in Fig. 3 by all anions except in negligible instance where a slight deviation occurred. On comparing the calculated surface charges of the anions base on:

- Different concentration for each of the anion shows that

  SO_4^{2-} : 0.01M > 1m $ 0.001M > 0.1M
  NO_3^- : 0.001M > 0.01M > 0.1M > 1M
  Cl^- : 0.001M > 0.01M > 0.1M > 1M
  Br^-: 1M > 0.01M > 0.001M > 0.1M

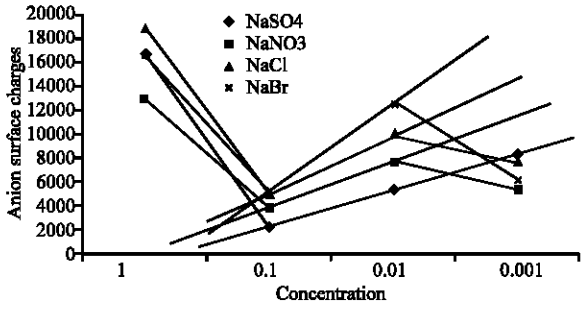

Fig. 3: Plots of surface charges of anions against concentrations

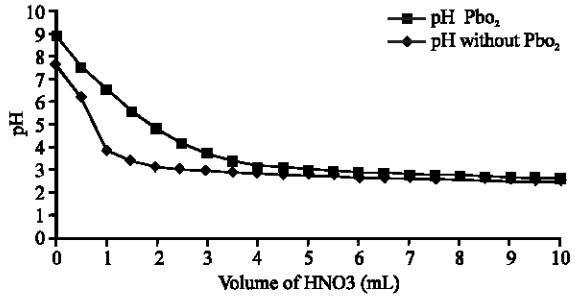

Fig. 4: Plots for 0.01M Na2SO4 pH reading against the volume of 0.1M HNO3

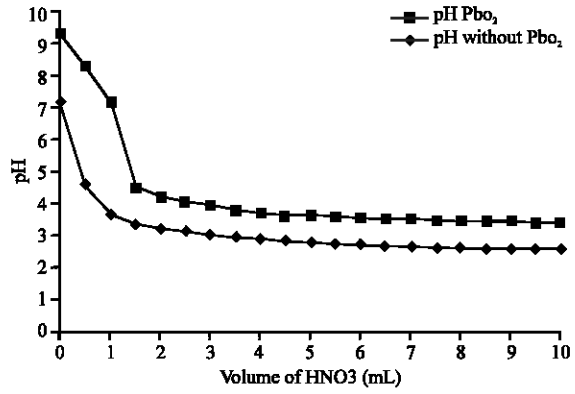

Fig. 5: Plots of 0.01M NaNO3 pH reading against the volume of 0.1M HNO3

Thus, the surface charge (as calculated) of 0.01 M SO_4^{2-} is higher than those of 1 M, 0.001 M and 0.1 M while that of 0.001 M NO_3^- is higher than those of 0.01, 0.1 and 1 M. Similarly, the surface charge of 0.001 M Cl^- is higher than those of 0.01, 0.1 and 1 M. also the surface charge of 1 M Br^- is higher than those of 0.01, 0.001 and 0.1 M.

- Surface charges of some concentration of the anions shows that

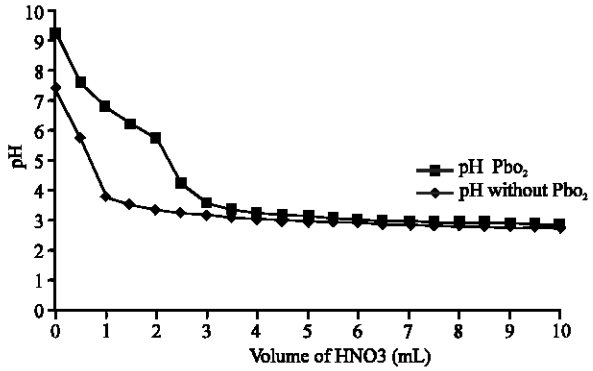

Fig. 6: Plots of 0.01 M NaCl pH reading against the volume of 0.1M HNO3

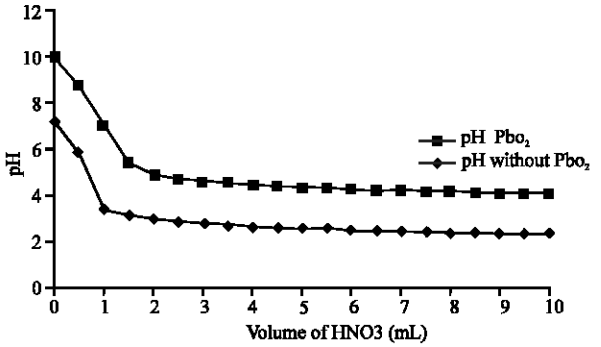

Fig. 7: Plots of 0.01M NaBr pH reading against the volume of 0.1M HNO3

For 1M, SO_4^{2-} Br^- > Cl^- > NO_3^-
For 0.1M, SO_4^{2-} > Cl^- > Br^- > NO_3^-
For 0.01M, SO_4^{2-} > Cl^- > Br^- > NO_3^-
For 0.001M, SO_4^{2-} > Cl^- > Br^- > NO_3^-

The comparison above, shows that the surface charges of the SO_4^{2-} anions is higher than those of the Cl^-, Br^- and NO_3^- in all the concentrations, while the surface charge of the Cl^- ion is higher than those of the Br^- and NO_3^- ions except for 1 m where that of Br^- ion is greater than those of Cl^- and NO_3^- ions, respectively. However, in all the concentrations, the surface charge of the NO_3^- ion turns out to be the least. The plots of the surface charges, E versus the concentration, C (Fig. 3) shows that SO_4^{2-} ion took a distinct lead. However, a complete deviation was observed for Cl^-, NO_3^- Br^- for the SO_4^{2-} ion, increase in concentration shows a remarkable in the surface charge. The plots of Fig. 2 shows that 'n' and 'k' constants to be positive and thus confirms that they agree with Tomkin, Freundlich and Langmuir isotherms.

Effects of pH on lead (iv) oxide, PbO_2: As the titration proceeds with additional volume of the titrant at interval

of 2 min, a sudden but gradual decrease of the pH become more pronounced with lead (IV) oxide, PbO_2. That is the PH value tends towards greater acidity. Generally, the starting pH values of the titrand in each of the concentrations of the anions, is greater with lead (IV) oxide than those without lead (IV) oxide. This is expected, since the oxide itself is alkaline. As a result, the plots of pH values versus volumes (mL) of the titrant fall below those solutions without PbO_2. This is because the addition of PbO_2 into the titrant results in increase in the pH valued but this suddenly decreases as the hydrogen ions of the titrant gets absorbed unto the PbO_2, there by decreasing the anion concentration from the solution making the solution tends towards acidity due to less anion in solution. The tabulated pH values with successive increase in the volume of the titrant and the corresponding plots of the concentrations of the anions show that at a stage there will be no further change in the pH values (Fig. 4-7). This is possible because when all the adsorption sites have been fully covered by the anions, further addition will not yield any change in the pH values of both the solution with $Pb0_2$ and without $Pb0_2$.

CONCLUSION

The results obtained and its analysis showed that lead (IV) oxide, $Pb0_2$ can be used in dry cell as a depolarizer if properly blended with alkaline anions particularly the Sulphate, $S0_4^{2-}$ ion. This is because their presence will increase the surface changes which in effect results in enhanced voltage out put and extension of the cells life span due to its greater surface change. The investigation shows that the use of $S0_4^{2-}$ ion can be justified because of the consistency in its surface changes at different concentration compared with $N0_3^-$ Cl^- and Br^- ions. Also, the adsorption of alkaline anion on $Pb0_2$ is in accordance with langmuir freundlich and tomkin isotherms as both isotherms drawn from the result gave the constants 'n' and 'k' corresponding to the slope and the intercept (all positive), respectively.

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REFERENCES

Aloko, D.F., 2000. The Adsorption properties of elements on chemical current source. A seminar paper on the PhD work delivered on the 12th march, 2000 at the F.U.T Minna.

Antropon, L.I., 1972. Theoretical Electrochemistry, (2nd Edn.), More Publishers Moscow, pp: 37-40.

David, P.S. *et al.*, 1981. Experiments in physical chemistry, (4th Edn.), Mc Graw- Hill Book Company, USA, pp: 332-337.

Dyer, C.K., 1994. Journal of Power Source, Elsevier Book Co., 54: 49.

John, W.H., 1992. Chemistry for changing times macmillan Pub. Company, York, pp: 237-91.

Kubasov, V., 1987. Introduction to Electrochemistry, Mir Publishers, pp: 10-11.

Meyers, A.R., 1987. Encyclopedia of physical science and technology. (2nd Edn.), Vol. 2 and 5, Academic Press INC, New York, pp: 487-506 and 587-618.

Moore, W.J., 1992. Physical chemistry (4th Edn.), Prentice-Hall Engle Word Chiffs, N.J., pp: 484-487.

Netkon, M. and P. Porter, 1968. Advanced level physics, (6th Edn.), Heinemann Educational Books, London, pp: 241.