ION ADSORPTION BY SOME METAL OXIDES

A Thesis submitted to the University
of London for the Degree of Doctor
of Philosophy

by

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The work described in this thesis consists of investigations into the sorptive behaviour of magnetite and of zirconia in some dilute aqueous electrolyte solutions.

Total sorption at the interfaces $\text{Fe}_3\text{O}_4/\text{NaCl}$, $\text{Fe}_3\text{O}_4/\text{NaNO}_3$, $\text{Fe}_3\text{O}_4/\text{Na}_2\text{SO}_4$, $\text{Fe}_3\text{O}_4/\text{Na}_2\text{HPO}_4$, $\text{Fe}_3\text{O}_4/\text{K}_2\text{CrO}_4$, $\text{ZrO}_2/\text{NaCl}$, $\text{ZrO}_2/\text{HCl}$ and $\text{ZrO}_2/\text{HNO}_3$, has been measured by conductimetric determination of concentration loss from solution when equilibrated with a quantity of the finely divided adsorbent.

A potentiometric technique has been devised and used, in conjunction with conductimetric measurements, to determine the extent of sorption of each ionic species from solutions containing three ions. This technique has been used to measure total sorption at the interfaces $\text{ZrO}_2/(\text{HCl} + \text{HNO}_3)$ and $\text{ZrO}_2/(\text{HCl} + \text{NaCl})$ and to study the phenomena occurring at the $\text{Fe}_3\text{O}_4/\text{HCl}$ interface, in which latter case ferrous ions are released into solution.

Micro-electrophoretic studies at the $\text{ZrO}_2/\text{HCl}$, $\text{ZrO}_2/\text{HNO}_3$ and $\text{ZrO}_2/\text{NaCl}$ interfaces have been made. Electrokinetic potentials and charges in these systems have hence been determined.

The phenomena occurring at the metal oxide/solution interfaces studied have been interpreted in terms of ion exchange and physical sorption processes. Exchange reactions between ions from solution and amphoteric surface hydroxyl groups have been postulated.
Total sorption data have been compared with data obtained, both previously and in the present work, from electrokinetic studies. It is shown that conclusions drawn, regarding adsorbability of ions at these interfaces, from electrokinetic studies, must be regarded with caution unless direct measurements of total sorption are also available.
The work described in this thesis was carried out in the laboratories of the Chemistry Department, Battersea College of Technology, under the direction of Dr. D. P. Benton and the general supervision of the Head of the Department, Dr. J. E. Salmon.

The writer wishes to express his most sincere appreciation of the constant help and encouragement received from Dr. Benton during the course of this work.

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GENERAL INTRODUCTION
When two phases come into contact their interface is a seat of free energy. There will generally be a redistribution of the various components of the system in the interfacial region arising from the tendency of the interfacial free energy to reduce to a minimum. This redistribution is usually covered by the term adsorption.

Again, in general, an electric potential difference is established between the phases. This is associated with the formation of the so-called electrical double layer. That is, there will be an excess of positive charge towards one phase and an excess of negative charge towards the other.

Considering more particularly the interface between a solid and a dilute aqueous electrolyte solution, the electric charge which the surface of the solid acquires usually has its most important origins in ionisation of the solid surface and/or the adsorption of ions.

The adsorption forces can be non-specific of a physical or Van der Waal's type, or a more specific chemical type of interaction. The physical type will be readily reversible whilst the generally much stronger chemisorption may be very irreversible.

The surface charge will cause ions of opposite sign to concentrate near the surface, whilst ions of the same sign will be repulsed.

Helmholtz (1) treated adsorption phenomena in terms of a condenser like electrical double layer but made no suggestions as to its structure. Perrin (2) visualised one plate of the condenser to be on the solid surface with the other plate, composed of attracted ions, concentrated in the
liquid, in a compact layer parallel to the solid surface.

The theory of Gouy (3), Chapman (4), and Debye and Hückel (5) embodied this double layer concept. They also visualised a surface charge on the solid, but considered the attracted ions, because of random thermal motions, to form a diffuse layer with a deficiency of ions of the same sign as the solid surface and an excess of oppositely charged ions. This diffuse layer was considered to be spread out into the liquid phase with the ion excesses and deficiencies reducing with increasing distance from the particle until, at a sufficient distance from the surface, the distribution of ions became that of the bulk solution.

Treating the ions as point charges, the average concentration, $N_i$, of an ion $i$ at any given point in the diffuse layer could be calculated from the electrical potential, $\psi$, at that point using the Boltzmann theorem. Hence:

$$N_i = N_i^B \exp \left( \frac{-Z_i e \psi}{kT} \right)$$

where $N_i^B$ is the concentration of ions, $i$, of valency $Z_i$ in the bulk solution, far from the surface, where $\psi$ is zero, $e$ is the electronic charge, $k$ the Boltzmann constant and $T$ is the absolute temperature.

Combination of the Boltzmann equation with the appropriate form of Poisson's equation for a flat surface, (applicable when the extension of the diffuse layer is small compared with the radius of curvature of the surface),
\[ \frac{d^2 \psi}{dx^2} = -4 \pi \varepsilon \rho \]

where \( \rho \) is the charge density at distance \( x \) from the surface, and \( \varepsilon \) the dielectric constant of the medium, allows the derivation of the charge per unit area, \( \sigma \), of a flat diffuse layer in the form.

\[ \sigma = \left( \frac{\varepsilon kT}{2 \pi} \right)^\frac{1}{2} \left\{ \sum_{N_1} B \left[ \exp \left( \frac{-Z_1 e \psi_0}{kT} \right) - 1 \right] \right\} \]

where \( \psi_0 \) is the potential at the surface.

For a uni-univalent electrolyte this expression reduces to:

\[ \sigma = \left( \frac{2N_B e kT}{T \gamma} \right) \sinh \frac{e \psi_0}{2kT} \]

where \( N_B \) is the electrolyte concentration in the bulk solution.

The Gouy theory, outlined above, suffers from a number of defects. In particular, assuming ions to be point charges does not seem permissible in solutions other than very dilute ones. Bikerman (6) and Verwey and Overbeek (7) have shown that for a double layer potential of 300 mV and a bulk solution concentration of \( 10^{-3} N \) a surface concentration of counter ions of \( 160N \) would be required.

Stern (8) proposed a model of the electrical double layer which incorporates both Perrin (2) and Gouy (3) concepts. He visualised the charge in the liquid phase to be in two parts. One part of approximately a single ion in thickness was considered to be held firmly within a
distance \( d \) of the surface, whilst the remainder of the charge formed a diffuse layer of the Gouy type. The "fixed" layer bore a charge \( \sigma_1 \), whilst the diffuse layer bore a charge \( \sigma_2 \).

According to the Stern theory, the electrical potential, within the "fixed" layer declines linearly as between the plates of an electrical condenser, then tends exponentially, through the diffuse layer, to zero in the bulk solution. Stern proposed an equation containing three terms representing the charge and number of ions in each zone of the electrical double layer. The three terms may be summarised as the surface charge \( \sigma_s \), the charge in the fixed layer \( \sigma_1 \), and the charge in the diffuse layer \( \sigma_2 \).

For the state of overall electro-neutrality:

\[
\sigma_0 = \sigma_1 + \sigma_2
\]

The Stern theory can be considered to be a major improvement upon the Gouy theory. It takes into account the non-zero size of the counter ions, and the specific adsorption of ions. Also a distinction is drawn between \( \psi_0 \), the total potential across the whole electrical double layer (Nernst potential), and the potential across the diffuse part of the double layer \( \psi_d \). This distinction has a great advantage in providing some theoretical basis for the lack of identity between the Nernst potential \( \psi_0 \), at the surface, on the one hand, and the so-called electrokinetic or zeta potential concerned in a variety of phenomena which involve tangential displacement of the liquid with respect to the solid surface, i.e., electrokinetic phenomena.

Electrokinetic phenomena have been known for some time. Application of a shearing force parallel to the interface results in the effects
of streaming potential (Quincke 1859) and sedimentation potential (Dorn 1878), whilst the application of an electric field parallel to the interface causes relative motion, as in electrophoresis (Reuss 1808) and electro-osmosis (Porret 1816). These various effects have been summarised by many authors, e.g. Booth (9).

In general, investigations involving these phenomena are directed towards the determination of the electrokinetic or zeta potential which is the potential at the plane where solvent molecules and counter ions are sufficiently loosely held for their tangential displacement to occur, relative to the solid surface and its more tightly held ions and solvent molecules. The electrokinetic potential has been often identified with $\psi_d$, the potential at the plane separating the Stern and Gouy zones of the electrical double layer, this of course implying that the slipping plane in electrokinetic motion occurs at the boundary between the fixed and diffuse layers of the Stern model. However, various workers have cast some doubt upon the validity of this assumption. For example, Eversole and Lahr (10), (11) have postulated an immobile liquid film up to $100\AA$ thick, whilst Elton (12), (13), who criticised the work of Eversole and Lahr and showed that the experimental error did not justify their conclusions, demonstrated experimentally, for the quartz/dilute aqueous solution interface, that any rigid layer, either ionic or molecular, attached to the interface was less than $25\AA$ thick. These thicknesses are considerably greater than the single ionic diameters envisaged in the Stern theory for the fixed zone of the double
layer. Should the slipping plane be further out in the diffuse layer and not identifiable with the fixed/diffuse layer boundary then $S$ will be numerically less than $\psi_d$.

The location of the slipping plane is important in considerations of the relationship between the electrokinetic potential, $S$, and the extent of ion adsorption. Even if the slipping plane was identifiable with the fixed/diffuse layer boundary, then electrokinetic potential data could only be interpreted in terms of a net charge on either side of this boundary.

Anderson (14) has pointed out that the calculation of adsorption data, from electrokinetic potentials, requires that a number of assumptions be made regarding the structure of the interfacial electric double layer, in particular concerning the location of the electrokinetic slipping plane. The "adsorption" data derived from electrokinetic measurements are usually limited to the net charge of the adsorbed layer on either side of the slipping plane. Rutgers (15) has suggested that the surface charge at the slipping plane is due to a small excess adsorption of ions of one sign in a large total adsorption. Benton, Elton, and Harrison (16) found that whilst the electrokinetic charge at the gold/potassium chloride solution interface is 3 to 5 times greater than that at the gold/hydrochloric acid interface, the total adsorption of hydrochloric acid is 3 to 5 times greater than that of potassium chloride at corresponding bulk solution concentrations.

In general, then, only limited information regarding the distribution
of the total number of adsorbed ions of each sign on either side of the slipping plane can be obtained from electrokinetic measurements alone.

The metal oxide/electrolyte solution interface is of interest apart from a fundamental point of view, in connection with the aqueous corrosion of metals. The presence of an oxide film on the metal may be of importance in determining the nature and rate of corrosion processes and in the mode of action of substances used as corrosion inhibitors.

Anderson (14) attempted a comparison between the inhibiting action and adsorbability of a number of ions on the oxide magnetite, a corrosion product of steel. This author made studies of the electrophoretic behaviour of magnetite suspensions in a number of electrolyte solutions. However, in view of the uncertainties discussed above, any conclusions drawn from such electrokinetic work, regarding the extent of adsorption of ions must be regarded with caution.

A major aspect of the work to be described here is concerned with a comparison of data regarding adsorption from solution, derived from electrokinetic studies, and data derived more directly by measurement of concentration loss from solution.

In much of the work presented in the literature, the phenomena occurring at the metal oxide/aqueous electrolyte solution interface have been interpreted in terms of ion exchange processes.

Exchange between cations and anions from solution with amphoteric surface hydroxyl groups is envisaged, e.g. O'Connor and Buchanan (17),
Kraus, Phillips, Carlson, and Johnson (18) have demonstrated exchange behaviour comparable to that of the synthetic organic exchangers and have successfully used similar theoretical treatments in the interpretation of their findings.

In general, metal oxides, depending upon solution pH can function either as cation or anion exchangers, e.g., Amphlett, McDonald, and Redman (19) demonstrated that, at high pH, thorium is a cation exchanger, whilst at low pH it is an anion exchanger.

O'Connor and Buchanan (17), Johansen and Buchanan (20), and O'Connor, Johansen, and Buchanan (21) have accounted for the surface charge at the metal oxide/aqueous electrolyte interface in terms of dissociations of amphoteric surface hydroxyl groups and their exchange with ions from solution. For hydrated stannic oxide O'Connor and Buchanan (17) and Edwards and Ewers (22) have postulated the dissociations:

\[
\begin{align*}
\text{low pH} & : \\
\text{isoelectric pH} & : \\
\text{high pH} & :
\end{align*}
\]

The dotted line represents the position of the slipping plane. At the isoelectric point both hydrogen ion and hydroxyl ion dissociations are equal and at a minimum and the net surface charge is zero. Increasing pH
facilitates hydrogen ion dissociation and decreasing pH facilitates hydroxyl ion dissociation. Thus anion and cation exchange will depend upon solution pH. Mattson and Pugh (23) have demonstrated that exchange does not occur at the isoelectric pH of metal oxides, but that for a pH other than this value either anion or cation exchange may occur.

The behaviour of hydrogen ions and hydroxyl ions is markedly different than that of other ions. For example, a relatively low hydrogen ion concentration will reverse the sign of a negatively charged metal oxide, whereas a relatively large concentration of a polyvalent cation may otherwise be required for such a charge reversal. Similarly low hydroxyl ion concentrations will cause a negatively charged surface to rapidly become more negative whilst other anions usually have a much smaller effect.

The charge reversal of hydrated stannic oxide in hydrochloric acid solution (17) was attributed to the formation of an entity such as:

\[
\begin{align*}
\text{Sn} & + \cdot \text{Cl}^1 \\
\text{Sn} & + \cdot \text{Cl}^1
\end{align*}
\]

with ionisation of surface chloride groups resulting in a positive charge. However, in sodium hydroxide solution, the formation of the entity:

\[
\begin{align*}
\text{Sn} & \left\langle 0^1 \right. \cdot \text{Na}^+ \\
\text{Sn} & \left. 0^1 \right\rangle \cdot \text{Na}^+
\end{align*}
\]

would give a more negative charge.

O'Connor (17) suggests that both ion adsorption and ion exchange jointly determine the behaviour of the metal oxide/aqueous electrolyte
interface, and that the predominance of either phenomenon depends upon the prevalent conditions.

In initially neutral salt solutions Ghosh (24) observed the release of hydrogen ions from hydrated manganese dioxide and Bhatia and Ghosh (25) observed the release of hydroxyl ions from titanium hydroxide sol. In both cases appreciable changes of pH were noticed. These phenomena were accounted for by an exchange process.

The work to be described in this thesis is concerned with the metal oxide/dilute aqueous electrolyte solution interface. The oxides studied, in particular, were magnetite, Fe$_3$O$_4$, and zirconia, ZrO$_2$.

Sorption in these systems has been studied by measurements of the concentration loss from solution on equilibration with a quantity of the finely divided solid.

For comparison with electrokinetic data on similar systems, the concentration range of interest was below approximately $2 \times 10^{-3}$N. Very sensitive techniques for determination of concentration loss were therefore required and conductimetric and potentiometric methods have been employed.

In general, when referring to the phenomena investigated by concentration loss techniques, the term sorption will be used.
SECTION I

(i) Apparatus

(ii) Materials
APPARATUS

(a) The Cell

The cell used for the work described here is illustrated in Fig. 1. For clarity the diagram shows an expanded view of the cell. In practice, the limbs of the cell were situated at the corners of an equilateral triangle.

The mixing compartment A, of approximately 250 ml. capacity, was 19 cm. long and 5.5 cm. in diameter. At its upper end it carried a B50 ground glass socket, the stopper for which was fitted with a glass stirrer passing through a nylon sleeve. The stopper also carried an inlet tube, fitted with a B10 socket, through which addition or removal of electrolyte solution could be made and through which nitrogen gas could be forced.

The side arm B carried a B24 socket into which the platinum electrodes used for conductivity determinations, could be fitted in a reproducible manner. Side arm B also carried a small inlet tube, fitted with a B7 cone, through which nitrogen gas could be forced.

The side arm C, which was joined to the base of side arm B, carried a B45 socket into which the rubber bung carrying the electrode system for potentiometric measurements could be placed. The rubber bung also carried an inlet tube, bearing a B7 cone, through which nitrogen gas could be passed.

The bottom of side arm B was connected to the main body of the cell by means of a tube which entered the main body of the cell above solution level and terminated about 1 cm. from the bottom of the cell.
The cell, as was all other glassware used in this work, was constructed from Pyrex glass.

Withdrawal of liquid from the cell was effected using the apparatus illustrated in Fig. 2. The conical flask was of 150 ml. capacity, suction being applied to its side arm. The end of the withdrawal tube was hook shaped in order to prevent solid being sucked up in the stream of liquid leaving the cell.

Additions of water were made to the cell from a polythene washbottle, against a counter current of nitrogen.

(b) Conductivity Electrodes

The electrodes were constructed from bright platinum sheet. They were 2 cm. long by 1 cm. wide and 1 cm. apart. Separation was effected by glass spacers and support by means of thick platinum wire sealed into Pyrex glass tubing. Contact between the electrodes and external thick copper leads was by means of mercury contained in the glass tubing. Mercury cups, supported in the thermostat, were used to connect the copper leads to the bridge circuit.

(c) Potentiometry Electrodes

(i) Glass Electrodes

The electrodes used were type G.H.S.33 as supplied by Electronic Instruments Limited. This type of electrode contains an internal metal screen which is connected to the screening of the lead.
Before use, electrodes were soaked in $5 \times 10^{-3} N$ hydrochloric acid at 25 degrees C. for at least a week.

(ii) **Silver-Silver Chloride Electrodes**

The silver-silver chloride electrode was used in preference to the calomel electrode, since the low solubility product of silver chloride ($1.5 \times 10^{-10}$) would cause negligible contamination of the test solution, whereas contamination with potassium chloride from a calomel electrode would have rendered the conductivity measurements useless.

Electrodes were prepared by the method of Brown (26). Each silver-silver chloride electrode was prepared on a 2 cm. length of platinum wire sealed into Pyrex glass tubing.

To obtain a clean surface which plated evenly the platinum wire was successively washed in benzene, concentrated sulphuric acid, distilled water, hot concentrated nitric acid, and finally distilled water. Electrodes were silver plated in batches of six, a total current of 1.2 mA, i.e. 0.2 mA/electrode, was passed for a total time of six hours. A platinum anode was used in preference to a silver one, since the latter polarises readily.

The plating solution was prepared by dissolving 60 gm. of "AnalaR" potassium cyanide in 300 ml. of conductivity water, then adding, slowly, with mechanical stirring, a concentrated solution of "AnalaR" silver nitrate in conductivity water. Silver nitrate was added until a little undissolved silver cyanide remained after stirring for 30 minutes. After cooling, the
solution together with undissolved silver cyanide was made up to 1500 ml. with conductivity water.

After soaking overnight in distilled water, silver chloride was formed on the surface by electrolysis in 0.1N "AnalaR" grade hydrochloric acid using a platinum cathode.

The electrodes, after rinsing, were soaked in conductivity water for 24 hours before being stored in approximately $5 \times 10^{-3}$N hydrochloric acid. Before use electrodes were always allowed to age for at least 3 days. After this time the maximum potential difference between any two electrodes rarely exceeded 0.5 mV. Electrodes showing deviations in excess of this value were discarded.

The electrodes were found to be stable for periods of up to 3 months, although when in use, their useful lifetime was considerably shortened. The onset of instability was marked by irreproducible potentials; changes of the order of 10 to 15 mV occasionally being observed. Usually electrodes were discarded before the commencement of instability.

Before replating, spent electrodes were stripped of silver chloride by means of strong ammonia solution, and of silver with concentrated nitric acid. After washing plating was carried out as described.

For measurements, a glass electrode and a silver-silver chloride electrode were mounted in a rubber bung. The stems of the electrodes were coated with paraffin wax to minimise the retention of solution on removal of the electrode system from the cell.
(d) **Cleaning of Apparatus**

The cell and all other glassware used were degreased by means of the reaction between concentrated nitric acid and ethanol; the reaction being performed in the apparatus concerned. The products of the reaction were rinsed out with distilled water, and all residual reactants and products, being steam volatile, were removed by steaming for 45 minutes. After steaming the apparatus was rinsed out with conductivity water, then filled with conductivity water and left to soak for at least 12 hours. The apparatus was then drained, rinsed out with conductivity water, and dried at 110 degrees C.

The platinum electrodes for conductivity measurements were degreased by washing successively in benzene, concentrated sulphuric acid, then conductivity water, followed by soaking in the latter for at least 12 hours before use. Drying was carried out on filter paper.
(ii) MATERIALS

(a) Conductivity Water

Conductivity water was prepared by passing freshly distilled water through the mixed-bed, ion exchange resin Biodeminrolit supplied by The Permutit Company Ltd.

Two ion exchange columns were used. One column was 40 cm. long and 4 cm. in diameter, it was fitted with a 2 litre reservoir and a 2 litre receiver, the latter being connected to the atmosphere via a soda-lime tube. The other column was 25 cm. long and 2.5 cm. in diameter, it being fitted with a 1 litre reservoir and a delivery tube terminating in a B10 joint. In both cases the reservoir was connected to the column by a tap so that the flow rate could be regulated.

For stock solutions, recrystallisations, and washing, water was used directly from the larger column. However for adsorption runs, conductivity water from the large column was passed through the small column which was connected to the cell by means of the B10 joint on the delivery tube, thus avoiding contact between water and atmosphere.

(b) Nitrogen Gas

"White Spot" oxygen free nitrogen supplied by British Oxygen Company Ltd. was used. The only purification necessary was the removal of dust by means of a glass wool filter.
(c) **Electrolytes**

**Hydrochloric and Nitric Acids**

"AnalalR" grade reagents were diluted to approximately 0.1N using conductivity water. These solutions were then standardised against re-crystallised borax using methyl red indicator (27).

**Sodium Chloride**

"AnalalR" grade reagent was recrystallised three times from conductivity water using a platinum evaporating basin. After drying, the product was heated to dull redness for 15 minutes then cooled in a desiccator. Because of its low temperature coefficient of solubility, "recrystallisation" was carried out by partial evaporation and cooling of a saturated solution.

**Sodium Benzoate**

Laboratory grade reagent was recrystallised from a 95 per cent ethanol - 5 per cent water mixture, the product filtered at the pump, then dried at 110 degrees C.

**Sodium Nitrate, Disodium Hydrogen Phosphate, and Potassium Chromate**

The anhydrous "AnalalR" grade reagents were dried at 110 degrees C and used without further purification.

Stock solutions, approximately 0.1N, of all the above solid reagents were made up by weight, in conductivity water.

For all electrolytes, more dilute solutions, of approximately $5 \times 10^{-3}$N, for addition to the cell during a run, were made up by weight from the 0.1N stock solutions.
(d) **Adsorbents**

**Zirconia**

The material used was high purity (99.99 per cent) zirconia supplied by Johnson Matthey. The hard, white, granular solid was prepared by hydrolysing recrystallised zirconium tetrachloride to the oxychloride followed by precipitation of zirconium hydroxide using ammonia solution. After washing and drying the precipitate was heated in a muffle furnace at 1000 to 1100 degrees C.

The material supplied was crushed to a suitable size using an agate pestle and mortar; all fines being removed by differential sedimentation in conductivity water. The material was dried at 110 degrees C.

**Magnetite**

Three preparations of magnetite were used for the work described here. They were:

I. By the method of Welo and Baudisch (28)

A solution of 3.6 gm. of hydrated ferrous sulphate was added slowly, with stirring, to a solution consisting of 1.04 gm. of sodium hydroxide and 0.8 gm. of potassium nitrate in 200 ml. of distilled water. On standing overnight the green precipitate converted to magnetite. Using a centrifuge the product was repeatedly washed with conductivity water.

II. By the method described by Anderson (14)

An excess of strong ammonia solution was added slowly, with stirring,
to a solution consisting of 11.1 g. of hydrated ferrous sulphate and 21.6 g. of hydrated ferric chloride in 200 ml. of distilled water. Repeated washing with conductivity water caused agglomerated material to peptise, but prolonged washing yielded a colloid-free product. As with preparation I, a centrifuge was used to assist washing.

"AnalaR" grade reagents were used for preparations I and II.

III. By the method of David and Welch (29)

Mond Carbonyl Iron Powder (Grade MCP) and high purity (99.99 per cent) ferric oxide (Johnson Matthey) were intimately mixed in stoichiometric proportions and heated in a current of purified argon at 960 degrees C for 6 hours. After cooling and thoroughly mixing, the product was again heated at 960 degrees C for 6 hours in a current of purified argon.

Purification of the argon, supplied by British Oxygen Company Ltd., was effected by passing it through a trap immersed in solid carbon dioxide, concentrated sulphuric acid, anhydride, copper gauze at 600 degrees C and finally over a mixture of quicklime (40 per cent by weight) and magnesium powder at 600 degrees C.

(e) Weight of Magnetite per Unit Volume of Suspension

Magnetite preparations I and II, on which the major part of the sorption work on magnetite was carried out, were only available in the form of suspensions. Precipitated magnetite, after drying does not re-disperse on shaking with water, also on drying at 110 degrees C, oxidation.
occurs. Consequently it was necessary to devise a method whereby the weight of magnetite used in a sorption run could be determined.

It was found that for a well stirred magnetite suspension, equal volumes of solution, as removed with a pipette, contained equal weights of magnetite. The agreement between weights of magnetite for equal volume portions of the same suspension was better than 0.5 per cent. This was determined by drying equal volumes of magnetite from the same suspension.

The technique used was to take a mechanically stirred suspension containing about 2 gm. magnetite per 100 ml. of water. Using a pipette, 50 ml. portions of suspension were placed in the cell and two weighed evaporating basins, the sample placed in the cell being the second of the three portions. The portions in the evaporating basins were dried to constant weight at 110 degrees C; thus the weight of magnetite used in a given sorption run could be determined.
SECTION II

(i) Conductimetric Measurements
(ii) Potentiometric Measurements
(iii) Determination of Extent of Sorption
(iv) Desorption Measurements
(1) CONDUCTIMETRIC MEASUREMENTS

(a) Measurement of Resistance

Cell resistances were measured using a conventional Wheatstone bridge type of circuit. The oscillator supplying a frequency of 1000 c.p.s. and the null point detector were incorporated in one instrument supplied by Airmec Laboratories. The detector unit consisted of an amplifier and a D.C. microammeter. The bridge circuit used is shown in Fig.3. The metre wire AB was of about 20 ohms resistance, X was a non-inductive, 0.1 per cent grade, variable resistance box supplied by H. W. Sullivan Ltd. of range 0 - 10,000 ohms in 0.1 ohm stages. M was a variable condenser, of continuous range up to 0.1 μF, and r₁ and r₂, fixed resistances each of 100 ohms resistance. r₁ and r₂ were embedded in tubes of paraffin wax and immersed in the thermostat. The sliding contact C was a transparent perspex cube, of 4 cm. side, with a single strand of fine wire tightly stretched around it.

Measurement of resistances greater than 10,000 ohms

To measure resistances greater than 10,000 ohms r₁ was shorted out of the circuit with a piece of thick copper wire. The circuit was calibrated by connecting an accurately known resistance R in place of the cell and determining the balance points on the bridge wire for various values of X. A graph of X/R against bridge wire reading was then constructed. It was then possible to find any cell resistance by reading off the value of X/R corresponding to the bridge wire reading and using the equation:
Unknown resistance = \( \frac{X}{X/R \text{ from bridge wire reading}} \)

It was thus possible to measure resistances of over 10^6 ohms, but in practice values in excess of 5 \( \times \) 10^5 ohms were rarely measured.

**Measurement of resistances less than 10,000 ohms**

First, the electrical centre of the bridge wire was determined by replacing the cell with a known resistance and setting \( X \) to the same value as this resistance. The bridge wire reading for balance then gave the electrical centre of the bridge wire. With the sliding contact set in this position cell resistances could be measured directly using the resistance box \( X \).

By this means resistances in the range 400 to 10,000 ohms could be measured with the required sensitivity.

Using these techniques it was thus possible to measure resistances in the required range of 400 to 5 \( \times \) 10^5 ohms, with an accuracy of 0.1 per cent.

(b) Determination of Cell Constant

Since the same cell was to be used over the wide concentration range of 2 \( \times \) 10^-5 to 2 \( \times \) 10^-3 N it was necessary to determine the cell constant at a number of concentrations throughout the range. This was because of variations in cell constant with concentration (The Parker Effect)(30).

The cell was calibrated for each electrolyte and also for mixed
electrolytes where appropriate. Calibration was effected by carrying out a run in the absence of adsorbent.

From data obtained in this manner it was possible to calculate the cell constant, \( \gamma \), for a single electrolyte using the relationship:

\[
\frac{\gamma}{R} = K = \frac{c \Lambda}{10^3}
\]

where \( R \) is the cell resistance, \( c \) the electrolyte concentration, \( \Lambda \) the equivalent conductance of the electrolyte at concentration \( c \), and \( K \) the specific conductance.

The equivalent conductances were calculated from the limiting form of the Onsager equation:

\[
\Lambda = \Lambda_0 - (A + B \Lambda_0) \sqrt{c}
\]

where \( \Lambda_0 \) is the equivalent conductance at infinite dilution, and \( A \) and \( B \) constants peculiar to uni-univalent electrolytes. Values of \( \Lambda_0 \), \( A \), and \( B \) are given in Appendix I.

For electrolyte mixtures the cell constant was calculated assuming that the equivalent conductance depends on the total ionic strength of the medium. That this assumption is essentially correct was demonstrated by the fact that cell constants for single electrolytes and for mixtures, were in agreement.

At concentrations less than approximately \( 2 \times 10^{-5} \) N the cell constant was found to fall sharply and at concentrations above approximately \( 1 \times 10^{-2} \) N it increased slowly; between these values it was found to remain constant.
That polarisation due to using bright platinum electrodes, was not occurring, was confirmed by carrying out a series of resistance measurements for various electrolyte solutions using oscillators operating at 1000 c.p.s. and 1500 c.p.s. Identical resistance measurements were obtained for the two frequencies at all pertinent electrolyte concentrations.

(c) Solvent Correction

It is necessary to correct measured conductivities for the contribution made to them by the solvent and any impurities which it may contain.

In the conductivity water used the major conducting impurity present was likely to be carbon dioxide in the form of carbonic acid. The equilibrium:

\[ \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \]

gives rise to a conducting solution. The second dissociation:

\[ \text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \]

is so small as to be negligible (31).

It was necessary to correct conductances, measured in the salt solutions used, for the contribution due to dissolved carbon dioxide. Corrections were made by subtracting the reciprocal resistance of the water in equilibrium with adsorbent at the commencement of the run, from the reciprocals of the resistances measured during the run.

In solutions of strong acids, the dissociation of carbonic acid is suppressed by the common ion, that is the hydrogen ion, and its contribution to conductivities may be neglected in strong acid solutions of concentration greater than approximately \(2 \times 10^{-5}\)N (31).
(ii) POTENTIOMETRIC MEASUREMENTS

(a) Measurement of E.M.F.

E.M.F.'s were determined using a conventional potentiometer circuit. The circuit, illustrated in Fig. 4, incorporated a Tinsley potentiometer, type 3367B and a Vibron electrometer model 33B as null point detector.

One of the requirements of the potentiometric cell upon which E.M.F. measurements were made is that only a very low current should be drawn from it in order that it may function reversibly. The Vibron electrometer is a high resistance instrument, possessing a resistance of $10^{13}$ ohms. Consequently the current drawn from the cell is of the order of $2 \times 10^{-14}$ amps. Another advantage of the Vibron is that it has a good zero stability. This stability is achieved by conversion of the direct current from the electrode system to alternating current before amplification; alternating current amplifiers having better zero stability than direct current amplifiers.

To obtain reproducible potentials it was necessary to stand both electrometer and potentiometer on earthed copper sheeting. The metal frame supporting the cell was also connected to earth.

The G.H.S.33 glass electrode is specifically designed for use with electrometers of the Vibron type; it having internal metal screening as well as a screened lead. To eliminate the capacitance effects which occur in high resistance circuits, the glass electrode was connected directly to the electrometer thus avoiding discontinuity of screening.
FIG. 4

GLASS ELECTRODE

STANDARD CELL

Ag/AgCl ELECTRODE
(b) Precautions Required for Reproducible Electrode Behaviour

Measurements of E.M.F. were made on the cell

Glass Electrode | Solution containing $H^+$ and $Cl^{-}$ | AgCl/Ag.

The E.M.F. of such a cell is given by the expression:

$$ E = \frac{RT}{F} \ln a_H + a_{Cl^-} + \text{constant} $$

where the constant is characteristic of the solution and reference electrode within the glass membrane of the glass electrode.

In the solutions of interest in this work (up to concentrations of $2 \times 10^{-3} \text{N}$), ionic concentration adequately represents ionic activity and E.M.F. measurements have been used to determine the $C_{H^+}C_{Cl^-}$ concentration product.

All measurements were made with reference to a solution of constant composition in which the electrodes were stored. This reference solution, which contained only the electrolytes present in the test solution, was of ionic strength of about $5 \times 10^{-3} \text{N}$. After each determination of E.M.F. on the test solution, the E.M.F. of the reference solution was determined, and the difference $\Delta E$, used to derive the product of hydrogen and chloride ion concentrations. On transference from reference solution to test solution, and vice versa, the electrodes were washed with conductivity water thermostatted at 25 degrees C, then dried on filter paper. Waxing the electrode stems minimised solution losses from the test solution.

To reduce the effect of concentration gradients at the glass electrode, and thus minimise response times solutions were blown back and
forth between mixing and measuring compartments a number of times before a measurement was made.

Using this technique it was possible to obtain reproducibility of potential to better than 0.1 mV.

Calibration of the electrode system was made by carrying out a run in the absence of adsorbent. A plot of $\Delta E$ against $\log_{10} C_H + C_{Cl^-}$ was used as the calibration. The graph so obtained was a straight line of slope 58.1, which is in quite good agreement with the theoretical value of $\frac{RT}{F}$ of 59.16. However, at $C_{H^+}C_{Cl^-}$ products of less than $2 \times 10^{-9}$ some deviation from linearity occurred. As a precaution, the electrode system was recalibrated at intervals of 3 to 4 weeks, but on no occasion did the calibration alter for a given reference solution.

Solutions of pure hydrochloric acid, hydrochloric acid/nitric acid, and hydrochloric/sodium chloride mixtures all gave the same calibration graph using the same reference solution in each case.

**Electrode Behaviour**

The reproducibility of potentiometric cells of the type used in this work is very dependent upon electrode behaviour. Factors such as temperature changes, electrode care, and asymmetry potential are at once important since they determine this behaviour.

(i) *Asymmetry Potential*

If, in the potentiometric cell used in this work, the test solution consisted of pure hydrochloric acid of concentration equal to that inside
the glass electrode membrane, then, since the two half cells constituting
the system should have equal and opposite E.M.F.'s, the system would be
expected to have zero E.M.F. However, in practice, this is not the case,
a small potential, usually in the range 0 to 2 mV being obtained. This is
due to the asymmetry potential of the glass electrode. The asymmetry
potential varies with time but is usually constant over the space of a few
hours. It is due to factors such as chemical degradation or dehydration
of the glass surfaces, curvature of the electrode bulb, or surface scratches.

Strictly the E.M.F. $E_t$ of the electrode system in the test solution
used is given by:

$$E_t = E_a + \frac{RT}{F} \ln \frac{C_{H^+}(t)C_{Cl}^-(t)}{C_{H^+}(r)C_{Cl}^-(r)} + A$$

where $E_a$ is the asymmetry potential, $Ae$ constant and subscript $t$ refers
to ionic species in the test solution.

If it is assumed that the asymmetry potential is the same for solu-
tions of similar ionic type and pH, then the E.M.F. of a reference solution
is given by:

$$E_r = E_a + \frac{RT}{F} \ln \frac{C_{H^+}(r)C_{Cl}^-(r)}{C_{H^+}(r)C_{Cl}^-(r)} + A$$

where subscript $r$ refers to ionic species in the reference solution.

Subtracting $E_r$ from $E_t$ gives:

$$E_t - E_r = \Delta E = \frac{RT}{F} \ln \frac{C_{H^+}(t)C_{Cl}^-(t)}{C_{H^+}(r)C_{Cl}^-(r)} - \frac{RT}{F} \ln \frac{C_{H^+}(r)C_{Cl}^-(r)}{C_{H^+}(r)C_{Cl}^-(r)}$$

which for a reference solution of constant composition gives:
\[ \Delta E = \frac{RT \ln C_{H^+}(t)}{F} C_{Cl}(t) + B \]

where \( B \) is a constant.

Consequently by referring all measurements to a reference solution and working in terms of \( \Delta E \), the asymmetry potential may be eliminated (32).

(ii) Temperature Effects

If the temperature at which measurements on the test solution are made differs from that at which the electrode system is calibrated then the slope factor \( RT/F \) will be different in each case and errors in interpreting E.M.F. measurements will arise.

Zero shift occurs when reference and test solutions are at different temperatures. The constant term \( A \) in the E.M.F. equations will then be different for the two solutions and the point at which \( \Delta E \) becomes zero will depend upon the temperatures of the two solutions.

Another problem, presented by temperature changes during storage or washing of the glass electrode, is that of hysteresis (32). That is, changes in glass electrode potential do not immediately follow temperature variations, there being a time lag until the correct E.M.F. is attained. In part, at least, this hysteresis may reside in the inner reference electrode. Hysteresis effects are less important for the outer reference electrode although they can occur for it on cooling from a high to a low temperature.

Errors due to temperature changes were avoided by, at all times working at a constant temperature, storing the electrode system at this
temperature, and washing with water heated to this temperature.

(iii) Electrode Response

Since the mechanism of the glass electrode has been fairly well established as one of ion exchange (32), it is necessary for an equilibrium to be set up between electrode and test solution before stable, drift-free measurements can be made. To minimise response times, the electrode system was stored in a solution of similar ionic strength and composition to that in which it was used, e.g. pure hydrochloric acid for pure hydrochloric acid test solutions and equinormal electrolyte mixtures for mixed electrolyte solutions. The storage solution also served as reference solution in the elimination of asymmetry potentials.

Poor response may also be obtained if the silver chloride layer of the silver-silver chloride reference electrode is too thick (33).
(iii) DETERMINATION OF EXTENT OF SORPTION

(a) Experimental Procedure

The cell was set up with a rubber bung closing the potentiometric side arm. A known weight of adsorbent was introduced to the main compartment and the apparatus flushed out with nitrogen gas. Approximately 100 gm. of conductivity water was then introduced and equilibrated with the solid. The water was then removed, while flushing the cell with nitrogen gas. Washing with conductivity water was continued in this manner until the lowest possible conductance was obtained for the water in equilibrium with the solid. The amount of water, finally in equilibrium with the solid, was determined by weighing. The cell was then mounted in a brass frame, in an oil thermostat, operating at 25 degrees + 0.01 degrees C, and controlled by a mercury-toluene regulator. The conductance of water in equilibrium with adsorbent was measured after temperature equilibrium was attained. Addition of stock electrolyte solution was then made from a weight burette, and the adsorbent equilibrated with the electrolyte solution; intermittent stirring being used. After all solid material had sedimented out, the clear solution was forced into the side arms by means of a small positive pressure of nitrogen gas.

If potentiometric measurements were to be made, the potentiometric electrode system was introduced into the cell immediately before forcing solution into the side arms. After conductimetric and potentiometric
measurements had been made a pressure of nitrogen gas was applied in order to return the solution to the main compartment. This procedure of blowing solution back and forth was repeated until reproducibility of measurement was obtained. In the case of potentiometric measurements, the electrode system was returned to its reference solution immediately after the equilibrium determination of E.M.F. had been made.

Further addition of stock electrolyte solution was made in stages so as to obtain equilibrium solution concentrations in the range \(2 \times 10^{-5}\) to \(2 \times 10^{-3}\) N.

(b) Calculation of Results

Equilibrium concentrations of the ions in solution were determined as follows.

(i) Single Electrolyte Solutions

The conductimetric method alone was used in these cases. Equilibrium concentrations were determined from measured solution resistances, after solvent correction, using the results of prior calibration in the absence of adsorbent (Section II, (i) b).

For the case of hydrochloric acid solutions the potentiometric method was also applied, the equilibrium concentration of hydrogen and of chloride ions being given by:

\[
C_{H^+} = C_{Cl^-} = C_{H^+Cl^-}
\]

where the product \(C_{H^+Cl^-}\) was determined from the measured E.M.F. and the
results of prior calibration in the absence of adsorbent (Section II,(ii)b).

(ii) Mixed electrolyte solutions

In solutions containing three ionic species (e.g. HNO₃/HCl or HCl/NaCl) conductimetric and potentiometric measurements were made. The specific conductance, \( K \), of the equilibrium solution was determined from the measured resistance and the appropriate cell constant obtained from prior calibration in the absence of adsorbent (Section II, (i) b). The concentration product, \( X = C^+ C^- \), was determined from E.M.F. measurement (Section II, (ii) b). Then:

\[
10^3 K = C^+ H^+ + C^- Cl^- + C_i i^- \quad - (1)
\]

\[
X = C^+ HCl \quad - (2)
\]

and from the requirement of electroneutrality:

\[
C^+ = C^- + NC_i = 0 \quad - (3)
\]

where \( C \) is the concentration, in equivalents per litre, \( \lambda \) the equivalent ion conductance, and \( n \) is \( \pm 1 \) according to whether ion"i" is a cation or anion.

Simultaneous solution of equations (1), (2), and (3) then allowed calculation of the equilibrium concentration of each ionic species.

The dependance of equivalent ion conductance upon the ionic strength of the solution necessitated the employment of a method of successive approximation to obtain the correct values for use in equation (1).

Equations (1), (2), and (3) were first solved for values of \( C^+ \), \( C^- \), and \( C_i \) using equivalent ion conductance values applicable to the ionic strength of
the solution, if no sorption had taken place. The calculation was then repeated using equivalent ion conductance values applicable to the ionic strength corresponding to the first derived values of \( C_H \), \( C_{Cl} \), and \( C_i \). Successive repetition of the process gave final correct values of the equilibrium concentrations. In general, two such successive approximations sufficed.

Finally the extent of sorption of each ionic species was obtained using the equation:

\[
\alpha = \frac{(C_0 - C_E) \, V \, N}{10^3 \, W}
\]

where \( \alpha \) is the number of ions sorbed per gram of adsorbent, \( C_0 \) is the concentration (gm. ions/litre) if no sorption had occurred, \( C_E \) is the concentration (gm. ions/litre) in equilibrium with \( W \) grams of adsorbent, \( V \) is the weight of equilibrium solution in grams, and \( N \) is Avogadro's number.
(iv) DESORPTION MEASUREMENTS

At the end of each sorption run, the degree of reversibility of the sorption process was investigated.

A measured weight of solution was removed from the cell; the cell flushed out with nitrogen gas and conductivity water added to the cell to make the total volume of solution present up to approximately 110 ml. After equilibration, conductance measurements were made and any release of sorbed solute calculated.
SECTION III

Sorption by Synthetic Magnetite

(i) Sorption from Salt Solutions

(ii) Magnetite in Hydrochloric Acid Solutions
(i) SORPTION FROM SALT SOLUTIONS

Sorption from Sodium Chloride Solutions

Sorption studies from sodium chloride solutions in the concentration range $2 \times 10^{-5}$ to $2 \times 10^{-3}$M have been made on magnetite preparations I, II, and III using the conductivity loss technique. Studies have also been made for sodium chloride concentrations up to $5 \times 10^{-3}$M using conductimetric titrations to determine equilibrium solution concentrations. The sorption measurements at these higher concentrations were made on preparation I.

(a) Sorption at Equilibrium Concentrations Below $2 \times 10^{-3}$M

For preparations I, II, and III sorption measurements were made by adding portions of stock electrolyte solution to a magnetite suspension. In all cases sorption was found to be instantaneous.

Results for preparations I and II are shown in Tables 1, 3 and 4, and illustrated graphically in Fig. 5 where $a$ is the number of ions sorbed per gram of magnetite and $C_e$ is the equilibrium electrolyte concentration expressed in gram moles per litre.

It can be seen that preparations I and II exhibit a steady increase in sorption with electrolyte concentration and at equilibrium concentrations greater than $10^{-4}$M preparation I obeys the Freundlich isotherm $d = k_1 C_e^{k_2}$ where $k_1$ and $k_2$ are constants. The greater sorptive powers of preparation I may be attributed to its smaller particle size. Examination with an optical microscope showed preparation I to be homodisperse with particle diameters of 1-2µ whilst the diameters of particles of preparation II lay in the
Fe$_3$O$_4$ / NaCl Solution

PREP. I  ORUNI  ORUN II  ORUN II
PREP. II  ABATCH'A  ORUN II

FIG. 5

LOG$_{10}$ C$_E$

20.0  19.0  18.0  17.0

LOG$_{10}$ (tons/yr)
range 3-50μ but predominantly between 3 and 10μ.

The extent of sorption per unit weight by different batches of preparation I was found to be quite reproducible, whereas the extent of sorption exhibited by preparation II was found to vary from batch to batch. Sorption measurements were also attempted on magnetite preparation III. A very much smaller sorption per unit weight of solid was indicated than in the case of preparations I and II. The magnitude of the sorption was, however, too small to be measured accurately by present techniques. The particles were of 5-20μ diameter and, on geometric surface area considerations, might be expected to have sorptive properties comparable to those of preparation II. That this is not the case would suggest that the more flocculent, less dense precipitation preparations of magnetite have greater sorptive properties than the compact and much denser dry preparation III. This will, however, be discussed more fully in Section III, (i)(i).

(b) Desorption of Sodium Chloride

The reversibility of the sorption process was investigated in the cases of preparations I and II. At the end of a sorption run a portion of the solution in the cell was removed and replaced by conductivity water. The conductance of the solution after equilibration of the system enabled the amount of sodium chloride desorbed to be calculated. This dilution process was repeated until the equilibrium solution concentration fell to approximately 10^{-4}M. At this point desorption investigations were discontinued because of the uncertainty involved in the solvent correction.
For sodium chloride solutions the sorption process was found to be irreversible, no removal of sodium chloride from the solid, on dilution of the equilibrium solution, being detected.

(c) Sorption at Equilibrium Concentrations between $10^{-4}$ and $5 \times 10^{-1}$M.

These measurements were made on magnetite preparation I.

In view of the magnitude of sorption from solutions of sodium chloride and the fact that at $2 \times 10^{-3}$M equilibrium concentration there appeared to be no indication that the sorptive properties of the solid were approaching saturation, it was of interest to measure the extent of sorption from solutions of higher concentration. This was carried out by determination of chloride ion concentration in the solution in equilibrium with magnetite preparation I, by conductimetric titration with standard silver nitrate solution. Conductimetric titration was selected as the method of analysis in preference to indicator methods for these solutions.

The procedure adopted was essentially that of Vogel (27). Silver nitrate solution standardised against sodium chloride was used for analysis. Two standard silver nitrate solutions of concentrations approximately 1N and $10^{-1}$N were prepared, the latter being obtained by dilution of the former. Duplicate titrations were carried out on each solution. From the equilibrium concentrations determined in this manner and the known initial concentration before equilibration with magnetite the sorption of chloride ion per gram of magnetite was calculated in each case.

Equal volumes of a magnetite suspension of known weight of solid/unit
volume, were placed in weighed 150 ml. conical flasks previously blown out with nitrogen. Suitable weights of stock sodium chloride solution were now added and conductivity water to make the total volume up to approximately 120 ml. added. After weighing, the stoppered flasks were suspended in a thermostat at 25 degrees C and shaken at frequent intervals. After about two hours the supernatant liquid was removed to flasks, previously rinsed out with some of the supernatant liquid and flushed out with nitrogen. Analysis of the solution was then carried out as follows:

A known weight of the sodium chloride solution together with an excess of ethyl alcohol was placed in a conductivity cell previously blown out with nitrogen. The cell and contents were then brought to temperature equilibrium at 25 degrees C in an oil thermostat. Additions of standard silver nitrate solution were now made from a weight burette, the conductance of the resultant solution being determined after each addition. Care was taken to obtain equilibrium, chemical and thermal, as indicated by constancy of bridge reading. An excess of standard silver nitrate solution was added. A plot of conductance against amount of added silver nitrate solution gave two intersecting straight lines, the point of intersection of which gave the end point of the titration. Curvature of the plot near the end point, due to the solubility of silver chloride (this effect being especially pronounced for the more dilute equilibrium solutions) was eliminated by extrapolation. The solubility of the silver chloride precipitate was lowered, with a consequent shortening of the required extrapolation,
by the addition of ethyl alcohol to the solutions. Another advantage of using an alcoholic medium was that the silver chloride precipitate coagulated (except at the lower concentrations studied when it gave the solution an opalescent appearance). In the absence of alcohol the precipitate remained finely divided sticking to the electrodes and the cell wall.

The cell used, Fig. 6, was a conventional type of conductivity cell consisting of a cylindrical Pyrex vessel 15 cm long and 4 cm in diameter into which fitted a B40 stopper carrying a pair of platinum electrodes each of 4 cm² area and 0.5 cm apart, being separated by glass spacers at each corner. There was also a B10 quickfit joint, attached to the stopper, through which additions of solution could be made. Conductance measurements were made using the bridge circuit described in Section I.

Results are shown in Table 2 and illustrated graphically in Fig. 7, where the results obtained by conductivity loss measurements at concentrations below 2 x 10⁻³ M are included. Log α, where α is the number of ions of each sign sorbed per gram of solid, is plotted against the logarithm of the equilibrium electrolyte concentration. It can be seen that the sorption from sodium chloride solution by magnetite preparation I obeys a Freundlich isotherm at concentrations up to 5 x 10⁻¹ M.

(d) Sorption from salt solutions by magnetite preparation II

Sorption from a range of salt solutions by magnetite preparation II has been studied using the conductance loss technique. Preparation II was
chosen for this work since direct comparison of the results could then be
made with electrophoretic data available for the preparation (14).

The salts studied were sodium sulphate, sodium nitrate, sodium
benzoate, disodium hydrogen phosphate and potassium chromate.

(e) Comparison of extent of sorption by different batches of preparation II.

The extent of sorption of a given electrolyte varied from batch to
batch; it was thus necessary to standardise different batches with respect
to a particular electrolyte.

Standardisation of each batch of magnetite was carried out by sodium
sulphate sorption runs, when parallel sorption isotherms were obtained.
The parallelism of the sorption was confirmed for two batches A and B by
means of sodium chloride sorption runs. Results for batches A and B
are given in Tables 3, 4, 5, and 6, and illustrated in Fig.8 where log $\alpha$
is plotted against the logarithm of the equilibrium electrolyte concen­
tration. $\alpha$ is the number of anions sorbed per gram of magnetite. In
the case of sodium chloride $\alpha_{Na^+} = \alpha_{Cl^-}$ but for sodium sulphate
$\alpha_{Na^+} = 2\alpha_{SO_4^{2-}}$.

In the work presented here all sorption isotherms were determined
on one batch of magnetite, with the exception of that of sodium nitrate.
However, using sodium sulphate standardisation isotherms to derive a simple
proportionality factor, it was possible to correct the sodium nitrate
isotherm for direct comparison with the other salts.
### TABLE I

Fe$_3$O$_4$ (Preparation I) - NaCl

#### RUN I

Weight of Magnetite $= 0.187$ gm.

<table>
<thead>
<tr>
<th>Initial Concentration $C_o$ (M)</th>
<th>Equilibrium Concentration $C_E$ (M)</th>
<th>Weight of Solution $V$ (gm.)</th>
<th>$a_{Na^+} = a_{Cl_1}$ (ions/gm. Fe$_3$O$_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4.102 \times 10^{-5}$</td>
<td>$3.996 \times 10^{-5}$</td>
<td>132.64</td>
<td>$4.53 \times 10^{17}$</td>
</tr>
<tr>
<td>$7.216 \times 10^{-5}$</td>
<td>$6.990 \times 10^{-5}$</td>
<td>133.44</td>
<td>$9.76 \times 10^{17}$</td>
</tr>
<tr>
<td>$1.768 \times 10^{-4}$</td>
<td>$1.719 \times 10^{-4}$</td>
<td>136.17</td>
<td>$2.18 \times 10^{18}$</td>
</tr>
<tr>
<td>$4.889 \times 10^{-4}$</td>
<td>$4.680 \times 10^{-4}$</td>
<td>145.04</td>
<td>$9.80 \times 10^{18}$</td>
</tr>
<tr>
<td>$8.830 \times 10^{-4}$</td>
<td>$8.411 \times 10^{-4}$</td>
<td>158.02</td>
<td>$2.13 \times 10^{19}$</td>
</tr>
<tr>
<td>$1.329 \times 10^{-3}$</td>
<td>$1.257 \times 10^{-3}$</td>
<td>175.84</td>
<td>$5.68 \times 10^{19}$</td>
</tr>
</tbody>
</table>

#### RUN II

Weight of Magnetite $= 0.186$ gm.

<table>
<thead>
<tr>
<th>Initial Concentration $C_o$ (M)</th>
<th>Equilibrium Concentration $C_E$ (M)</th>
<th>Weight of Solution $V$ (gm.)</th>
<th>$a_{Na^+} = a_{Cl_1}$ (ions/gm. Fe$_3$O$_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.490 \times 10^{-5}$</td>
<td>$2.426 \times 10^{-5}$</td>
<td>108.57</td>
<td>$2.27 \times 10^{17}$</td>
</tr>
<tr>
<td>$6.018 \times 10^{-5}$</td>
<td>$5.803 \times 10^{-5}$</td>
<td>109.22</td>
<td>$7.60 \times 10^{17}$</td>
</tr>
<tr>
<td>$1.102 \times 10^{-4}$</td>
<td>$1.058 \times 10^{-4}$</td>
<td>110.16</td>
<td>$1.59 \times 10^{18}$</td>
</tr>
<tr>
<td>$2.407 \times 10^{-4}$</td>
<td>$2.297 \times 10^{-4}$</td>
<td>112.68</td>
<td>$4.01 \times 10^{18}$</td>
</tr>
<tr>
<td>$4.317 \times 10^{-4}$</td>
<td>$4.138 \times 10^{-4}$</td>
<td>116.59</td>
<td>$6.75 \times 10^{18}$</td>
</tr>
<tr>
<td>$8.850 \times 10^{-4}$</td>
<td>$8.366 \times 10^{-4}$</td>
<td>127.04</td>
<td>$1.99 \times 10^{19}$</td>
</tr>
<tr>
<td>$1.748 \times 10^{-3}$</td>
<td>$1.593 \times 10^{-3}$</td>
<td>151.11</td>
<td>$7.13 \times 10^{19}$</td>
</tr>
</tbody>
</table>
### TABLE 2

**Fe₃O₄ (Preparation I) - NaCl (Conductimetric Titration)**

#### RUN I

<table>
<thead>
<tr>
<th>Initial Concentration $C_o (M)$</th>
<th>Equilibrium Concentration $C_e (M)$</th>
<th>Weight of Solution $V$ (gm.)</th>
<th>$\alpha_{\text{Na}^+} = \alpha_{\text{Cl}^-}$ (ions/gm. Fe₃O₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5.427 \times 10^{-4}$</td>
<td>$5.170 \times 10^{-4}$</td>
<td>137.05</td>
<td>$1.08 \times 10^{19}$</td>
</tr>
<tr>
<td>$1.297 \times 10^{-3}$</td>
<td>$1.195 \times 10^{-3}$</td>
<td>119.16</td>
<td>$3.71 \times 10^{19}$</td>
</tr>
<tr>
<td>$3.277 \times 10^{-3}$</td>
<td>$3.042 \times 10^{-3}$</td>
<td>125.09</td>
<td>$9.19 \times 10^{19}$</td>
</tr>
<tr>
<td>$9.170 \times 10^{-3}$</td>
<td>$7.702 \times 10^{-3}$</td>
<td>119.68</td>
<td>$5.39 \times 10^{20}$</td>
</tr>
<tr>
<td>$1.526 \times 10^{-2}$</td>
<td>$1.597 \times 10^{-2}$</td>
<td>129.04</td>
<td>$1.03 \times 10^{21}$</td>
</tr>
<tr>
<td>$3.610 \times 10^{-2}$</td>
<td>$3.139 \times 10^{-2}$</td>
<td>119.07</td>
<td>$1.72 \times 10^{21}$</td>
</tr>
</tbody>
</table>

#### RUN II

<table>
<thead>
<tr>
<th>Initial Concentration $C_o (M)$</th>
<th>Equilibrium Concentration $C_e (M)$</th>
<th>Weight of Solution $V$ (gm.)</th>
<th>$\alpha_{\text{Na}^+} = \alpha_{\text{Cl}^-}$ (ions/gm. Fe₃O₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3.592 \times 10^{-2}$</td>
<td>$3.072 \times 10^{-2}$</td>
<td>127.77</td>
<td>$1.66 \times 10^{21}$</td>
</tr>
<tr>
<td>$8.213 \times 10^{-2}$</td>
<td>$6.990 \times 10^{-2}$</td>
<td>130.97</td>
<td>$4.02 \times 10^{21}$</td>
</tr>
<tr>
<td>$2.039 \times 10^{-1}$</td>
<td>$1.782 \times 10^{-1}$</td>
<td>121.94</td>
<td>$3.84 \times 10^{21}$</td>
</tr>
<tr>
<td>$5.603 \times 10^{-1}$</td>
<td>$4.470 \times 10^{-1}$</td>
<td>125.58</td>
<td>$3.57 \times 10^{22}$</td>
</tr>
</tbody>
</table>
Table 3

Fe₃O₄ (Preparation II) - NaCl

**Batch A**

Weight of Magnetite = 1.19

Weight of Water = 115.55 g.m.

<table>
<thead>
<tr>
<th>Initial Concentration C₀ (M)</th>
<th>Equilibrium Concentration Cₑ (M)</th>
<th>Weight of Solution V (g.m.)</th>
<th>α⁺NaCl = α⁻Cl⁻ (ions/gm. Fe₃O₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.881 x 10⁻⁵</td>
<td>2.742 x 10⁻⁵</td>
<td>116.05</td>
<td>6.05 x 10¹⁶</td>
</tr>
<tr>
<td>5.856 x 10⁻⁵</td>
<td>5.661 x 10⁻⁵</td>
<td>116.56</td>
<td>1.15 x 10¹⁷</td>
</tr>
<tr>
<td>1.171 x 10⁻⁴</td>
<td>1.148 x 10⁻⁴</td>
<td>117.59</td>
<td>1.32 x 10¹⁷</td>
</tr>
<tr>
<td>2.348 x 10⁻⁴</td>
<td>2.325 x 10⁻⁴</td>
<td>119.71</td>
<td>1.41 x 10¹⁷</td>
</tr>
<tr>
<td>3.989 x 10⁻⁴</td>
<td>3.964 x 10⁻⁴</td>
<td>122.80</td>
<td>1.55 x 10¹⁷</td>
</tr>
<tr>
<td>7.108 x 10⁻⁴</td>
<td>7.059 x 10⁻⁴</td>
<td>129.14</td>
<td>3.20 x 10¹⁷</td>
</tr>
<tr>
<td>1.117 x 10⁻³</td>
<td>1.104 x 10⁻³</td>
<td>138.43</td>
<td>8.67 x 10¹⁷</td>
</tr>
</tbody>
</table>
Fe₃O₄ (Preparation II) - NaCl

**TABLE 4**

**BATCH B**

**RUN I**

Weight of Magnetite = 0.87 gm.

Weight of Water = 109.94 gm.

<table>
<thead>
<tr>
<th>Initial Concentration C₀ (M)</th>
<th>Equilibrium Concentration Cₑ (M)</th>
<th>Weight of Solution V (gm.)</th>
<th>αₙa = αₙa⁺[^1] (ions/gm. Fe₃O₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.744 x 10⁻⁵</td>
<td>3.490 x 10⁻⁵</td>
<td>110.43</td>
<td>1.95 x 10¹⁷</td>
</tr>
<tr>
<td>7.356 x 10⁻⁵</td>
<td>7.082 x 10⁻⁵</td>
<td>110.91</td>
<td>2.11 x 10¹⁷</td>
</tr>
<tr>
<td>1.505 x 10⁻⁴</td>
<td>1.475 x 10⁻⁴</td>
<td>111.95</td>
<td>2.30 x 10¹⁷</td>
</tr>
<tr>
<td>3.101 x 10⁻⁴</td>
<td>3.071 x 10⁻⁴</td>
<td>114.15</td>
<td>2.32 x 10¹⁷</td>
</tr>
<tr>
<td>6.581 x 10⁻⁴</td>
<td>6.527 x 10⁻⁴</td>
<td>119.28</td>
<td>4.48 x 10¹⁷</td>
</tr>
<tr>
<td>1.044 x 10⁻³</td>
<td>1.032 x 10⁻³</td>
<td>125.53</td>
<td>9.94 x 10¹⁷</td>
</tr>
<tr>
<td>1.310 x 10⁻³</td>
<td>1.292 x 10⁻³</td>
<td>130.25</td>
<td>1.62 x 10¹⁸</td>
</tr>
</tbody>
</table>

**RUN II**

<table>
<thead>
<tr>
<th>Initial Concentration C₀ (M)</th>
<th>Equilibrium Concentration Cₑ (M)</th>
<th>Weight of Solution V (gm.)</th>
<th>αₙa = αₙa⁺[^1] (ions/gm. Fe₃O₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.804 x 10⁻⁵</td>
<td>3.551 x 10⁻⁵</td>
<td>113.74</td>
<td>2.00 x 10¹⁷</td>
</tr>
<tr>
<td>8.438 x 10⁻⁵</td>
<td>8.172 x 10⁻⁵</td>
<td>114.38</td>
<td>2.11 x 10¹⁷</td>
</tr>
<tr>
<td>1.269 x 10⁻⁴</td>
<td>1.240 x 10⁻⁴</td>
<td>114.97</td>
<td>2.37 x 10¹⁷</td>
</tr>
<tr>
<td>2.177 x 10⁻⁴</td>
<td>2.150 x 10⁻⁴</td>
<td>116.24</td>
<td>2.14 x 10¹⁷</td>
</tr>
<tr>
<td>4.237 x 10⁻⁴</td>
<td>4.192 x 10⁻⁴</td>
<td>119.24</td>
<td>3.75 x 10¹⁷</td>
</tr>
<tr>
<td>8.562 x 10⁻⁴</td>
<td>8.485 x 10⁻⁴</td>
<td>126.08</td>
<td>6.79 x 10¹⁷</td>
</tr>
<tr>
<td>1.346 x 10⁻³</td>
<td>1.336 x 10⁻³</td>
<td>134.84</td>
<td>9.55 x 10¹⁷</td>
</tr>
</tbody>
</table>
Fe$_3$O$_4$/NaCl SOLUTION

**FIG. 7**

- **LOG$_{10}$ (ions/gm)**
- **LOG$_{10}$ C$_e$**

- ○ CONDUCTIVITY LOSS RUN I
- ○ CONDUCTIVITY LOSS RUN II
- □ CONDUCTIMETRIC TITRATION RUN I
- □ CONDUCTIMETRIC TITRATION RUN II
Sorption from Sodium

(f) Sorption from Sodium Chloride, Sodium Nitrate, and Sodium Sulphate Solutions

In all cases sorption was instantaneous and desorption experiments indicated the sorption to be irreversible under the experimental conditions. The sorption isotherms of sodium nitrate and of sodium chloride are almost identical. The sorption isotherm of sodium sulphate indicates a sorption about 2-3 times as great as that occurring from sodium chloride and sodium nitrate solutions at the lower concentrations, the differences being somewhat larger at higher concentrations.

Results for the three salts are shown in Tables 4, 6, and 7, together with the sodium sulphate calibration data, for sodium nitrate sorption, which is given in Table 8.

(g) Sorption from Sodium Benzoate Solutions

Magnetite was found to show no detectable sorption from solutions of sodium benzoate; the conductivity of solution in contact with magnetite being identical to that of solution in the absence of magnetite.

(h) Sorption from Potassium Chromate and Disodium Hydrogen Phosphate Solutions

Sorption behaviour from solutions of these salts was found to be quite different from the behaviour exhibited by the other electrolytes studied.

The sorption in both cases was a slow process taking up to 6 hours for equilibrium to be attained. For both electrolytes at equilibrium
concentrations greater than $5 \times 10^{-5}$M, the magnetite peptised to yield a colloid which became so dense at equilibrium concentrations of approximately $2 \times 10^{-4}$M that adsorption runs had to be discontinued at this point.

The large degree of sorption taking place at the higher equilibrium concentrations of these electrolytes is, doubtless due in part, to the increase in available sorbing sites formed on peptisation of the absorbent. Notwithstanding the peptisation of the solid, the sorption isotherms were found to be fairly reproducible.

Results for potassium chromate and disodium hydrogen phosphate are shown in Tables 9 and 10.

The sorption of both these electrolytes appears to be quite reversible, desorption experiments indicating that although some hysteresis occurs the desorption approximately follows the sorption isotherm. The desorption process was, like the sorption process, rather slow, taking up to 5 hours for equilibrium to be reached in both cases. Due to the presence of colloidal material in the solution at the end of a run, the desorption experiments, which involved removal of this colloid with solution, were of necessity only semi-quantitative.

It is of interest to note that in the desorption process of both electrolytes fresh colloid was still produced on dilution of solution until the equilibrium solution concentration was less than $5 \times 10^{-5}$M.

The results for all the salts studied are illustrated in Fig. 9.
where $a$ is the number of anions sorbed per gram of magnetite and $C_e$ is the equilibrium electrolyte concentration expressed in gram moles per litre. The results for sodium nitrate have, in this figure, been corrected by applying a correcting factor of 1.17 to the results shown in Table 7. Here $a$ (cation) = $a$ (anion) for the 1 : 1 electrolytes and $a$ (cation) = 2$a$ (anion) for the 1 : 2 electrolytes.

It can be seen that at all concentrations the sorption of potassium chromate is greater than that of sodium sulphate being slightly greater at $10^{-5}$M and about 20 times as great at $10^{-4}$M equilibrium concentration.

The sorption isotherm for disodium hydrogen phosphate intersects the isotherms of sodium nitrate and sodium chloride at an equilibrium concentration of approximately $6 \times 10^{-5}$M and that of sodium sulphate at approximately $10^{-4}$M. However, at all concentrations the sorption is less than that of potassium chromate. At concentrations below approximately $5 \times 10^{-5}$M the sorption of disodium hydrogen phosphate was too small for accurate measurements using the present techniques.
TABLE 5

Fe₂O₄ (Preparation II) - Na₂SO₄

**BATCH A**

**RUN I**

Weight of Magnetite = 1.19 gm.
Weight of Water = 109.40 gm.

<table>
<thead>
<tr>
<th>Initial Concentration</th>
<th>Equilibrium Concentration</th>
<th>Weight of Solution</th>
<th>aSO₄⁻ (ions/gm. Fe₂O₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₀ (M)</td>
<td>Cₑ (M)</td>
<td>V (gm.)</td>
<td></td>
</tr>
<tr>
<td>2.064 x 10⁻⁵</td>
<td>1.719 x 10⁻⁵</td>
<td>110.01</td>
<td>1.92 x 10¹⁷</td>
</tr>
<tr>
<td>4.066 x 10⁻⁵</td>
<td>3.653 x 10⁻⁵</td>
<td>110.61</td>
<td>2.30 x 10¹⁷</td>
</tr>
<tr>
<td>8.464 x 10⁻⁵</td>
<td>7.939 x 10⁻⁵</td>
<td>111.95</td>
<td>2.97 x 10¹⁷</td>
</tr>
<tr>
<td>1.848 x 10⁻⁴</td>
<td>1.764 x 10⁻⁴</td>
<td>115.12</td>
<td>5.10 x 10¹⁷</td>
</tr>
<tr>
<td>3.327 x 10⁻⁴</td>
<td>3.173 x 10⁻⁴</td>
<td>120.14</td>
<td>9.35 x 10¹⁷</td>
</tr>
<tr>
<td>4.884 x 10⁻⁴</td>
<td>4.644 x 10⁻⁴</td>
<td>125.93</td>
<td>1.53 x 10¹⁸</td>
</tr>
<tr>
<td>6.991 x 10⁻⁴</td>
<td>6.602 x 10⁻⁴</td>
<td>134.71</td>
<td>2.65 x 10¹⁸</td>
</tr>
</tbody>
</table>

**RUN II**

Weight of Magnetite = 1.19 gm.
Weight of Water = 106.43 gm.

<table>
<thead>
<tr>
<th>Initial Concentration</th>
<th>Equilibrium Concentration</th>
<th>Weight of Solution</th>
<th>aSO₄⁻ (ions/gm. Fe₂O₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₀ (M)</td>
<td>Cₑ (M)</td>
<td>V (gm.)</td>
<td></td>
</tr>
<tr>
<td>1.743 x 10⁻⁵</td>
<td>1.388 x 10⁻⁵</td>
<td>106.93</td>
<td>1.92 x 10¹⁷</td>
</tr>
<tr>
<td>3.475 x 10⁻⁵</td>
<td>3.062 x 10⁻⁵</td>
<td>107.43</td>
<td>2.24 x 10¹⁷</td>
</tr>
<tr>
<td>6.880 x 10⁻⁵</td>
<td>6.385 x 10⁻⁵</td>
<td>108.43</td>
<td>2.71 x 10¹⁷</td>
</tr>
<tr>
<td>1.311 x 10⁻⁴</td>
<td>1.245 x 10⁻⁴</td>
<td>110.32</td>
<td>3.68 x 10¹⁷</td>
</tr>
<tr>
<td>2.657 x 10⁻⁴</td>
<td>2.540 x 10⁻⁴</td>
<td>114.61</td>
<td>6.80 x 10¹⁷</td>
</tr>
<tr>
<td>4.531 x 10⁻⁴</td>
<td>4.313 x 10⁻⁴</td>
<td>121.18</td>
<td>1.33 x 10¹⁸</td>
</tr>
<tr>
<td>6.935 x 10⁻³</td>
<td>6.539 x 10⁻⁴</td>
<td>130.80</td>
<td>2.61 x 10¹⁸</td>
</tr>
</tbody>
</table>
TABLE 6

Fe$_3$O$_4$ (Preparation II) - Na$_2$SO$_4$

**BATCH B**

Weight of Magnetite = 0.87 gm.

Weight of Water = 113.42 gm.

<table>
<thead>
<tr>
<th>Initial Concentration</th>
<th>Equilibrium Concentration</th>
<th>Weight of Solution</th>
<th>$^{\text{a}}$SO$_4$ (ions/gm. Fe$_3$O$_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_0$ (M)</td>
<td>$C_E$ (M)</td>
<td>V (gm.)</td>
<td>(a$_{Na^+}$ = 2$a_0$SO$_4$)</td>
</tr>
<tr>
<td>$2.467 \times 10^{-5}$</td>
<td>$2.057 \times 10^{-5}$</td>
<td>114.04</td>
<td>$3.25 \times 10^{17}$</td>
</tr>
<tr>
<td>$4.999 \times 10^{-5}$</td>
<td>$4.498 \times 10^{-5}$</td>
<td>114.68</td>
<td>$3.92 \times 10^{17}$</td>
</tr>
<tr>
<td>$1.112 \times 10^{-4}$</td>
<td>$1.051 \times 10^{-4}$</td>
<td>116.29</td>
<td>$5.33 \times 10^{17}$</td>
</tr>
<tr>
<td>$2.289 \times 10^{-4}$</td>
<td>$2.181 \times 10^{-4}$</td>
<td>119.46</td>
<td>$8.96 \times 10^{17}$</td>
</tr>
<tr>
<td>$5.396 \times 10^{-4}$</td>
<td>$5.120 \times 10^{-4}$</td>
<td>128.76</td>
<td>$2.47 \times 10^{18}$</td>
</tr>
<tr>
<td>$8.029 \times 10^{-4}$</td>
<td>$7.556 \times 10^{-4}$</td>
<td>137.86</td>
<td>$4.49 \times 10^{18}$</td>
</tr>
</tbody>
</table>
### TABLE 7

Fe₃O₄ (Preparation II) - NaNO₃

#### RUN I

<table>
<thead>
<tr>
<th>Initial Concentration Cₒ(M)</th>
<th>Equilibrium Concentration Cₑ(M)</th>
<th>Weight of Solution V (gm.)</th>
<th>αₙa = αₙO₃ (ions/gm.Fe₃O₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.105 x 10⁻⁵</td>
<td>5.725 x 10⁻⁵</td>
<td>116.45</td>
<td>2.09 x 10¹⁷</td>
</tr>
<tr>
<td>1.369 x 10⁻⁴</td>
<td>1.331 x 10⁻⁴</td>
<td>117.45</td>
<td>2.07 x 10¹⁷</td>
</tr>
<tr>
<td>2.634 x 10⁻⁴</td>
<td>2.597 x 10⁻⁴</td>
<td>119.20</td>
<td>2.64 x 10¹⁷</td>
</tr>
<tr>
<td>6.275 x 10⁻⁴</td>
<td>6.188 x 10⁻⁴</td>
<td>124.45</td>
<td>5.10 x 10¹⁷</td>
</tr>
<tr>
<td>9.825 x 10⁻⁴</td>
<td>9.668 x 10⁻⁴</td>
<td>130.05</td>
<td>9.20 x 10¹⁷</td>
</tr>
<tr>
<td>1.498 x 10⁻³</td>
<td>1.467 x 10⁻³</td>
<td>139.14</td>
<td>2.04 x 10¹⁸</td>
</tr>
</tbody>
</table>

#### RUN II

<table>
<thead>
<tr>
<th>Initial Concentration Cₒ(M)</th>
<th>Equilibrium Concentration Cₑ(M)</th>
<th>Weight of Solution V (gm.)</th>
<th>αₙa = αₙO₃ (ions/gm.Fe₃O₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.050 x 10⁻⁵</td>
<td>5.670 x 10⁻⁵</td>
<td>121.25</td>
<td>2.11 x 10¹⁷</td>
</tr>
<tr>
<td>1.289 x 10⁻⁴</td>
<td>1.250 x 10⁻⁴</td>
<td>122.19</td>
<td>2.24 x 10¹⁷</td>
</tr>
<tr>
<td>2.631 x 10⁻⁴</td>
<td>2.588 x 10⁻⁴</td>
<td>124.10</td>
<td>2.51 x 10¹⁷</td>
</tr>
<tr>
<td>5.408 x 10⁻⁴</td>
<td>5.348 x 10⁻⁴</td>
<td>128.23</td>
<td>3.62 x 10¹⁷</td>
</tr>
<tr>
<td>1.043 x 10⁻³</td>
<td>1.028 x 10⁻³</td>
<td>136.46</td>
<td>9.63 x 10¹⁷</td>
</tr>
</tbody>
</table>
TABLE 8

$Fe_3O_4$ (Preparation II) - $Na_2SO_4$

Weight of Magnetite = 1.28 gm.
Weight of Water = 105.80 gm.

<table>
<thead>
<tr>
<th>Initial Concentration $C_0(M)$</th>
<th>Equilibrium Concentration $C_E(M)$</th>
<th>Weight of Solution $V(gm.)$</th>
<th>$a_{SO_4^2-}$ (ions/gm. $Fe_3O_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3.134 \times 10^{-5}$</td>
<td>$2.539 \times 10^{-5}$</td>
<td>106.53</td>
<td>$2.98 \times 10^{17}$</td>
</tr>
<tr>
<td>$7.303 \times 10^{-5}$</td>
<td>$6.536 \times 10^{-5}$</td>
<td>107.53</td>
<td>$3.88 \times 10^{17}$</td>
</tr>
<tr>
<td>$1.721 \times 10^{-4}$</td>
<td>$1.609 \times 10^{-4}$</td>
<td>109.98</td>
<td>$5.80 \times 10^{17}$</td>
</tr>
<tr>
<td>$3.761 \times 10^{-4}$</td>
<td>$3.553 \times 10^{-4}$</td>
<td>115.38</td>
<td>$1.13 \times 10^{18}$</td>
</tr>
<tr>
<td>$6.884 \times 10^{-4}$</td>
<td>$6.479 \times 10^{-4}$</td>
<td>124.77</td>
<td>$2.37 \times 10^{18}$</td>
</tr>
</tbody>
</table>
TABLE 9

Fe₃O₄ (Preparation II) - K₂CrO₄

**RUN I**

Weight of Magnetite = 0.87 gm.
Weight of Water = 104.79 gm.

<table>
<thead>
<tr>
<th>Initial Concentration</th>
<th>Equilibrium Concentration</th>
<th>Weight of Solution</th>
<th>αCrO₄⁻ (ions/gm. Fe₃O₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₀ (M)</td>
<td>Cₑ (M)</td>
<td>V (gm.)</td>
<td></td>
</tr>
<tr>
<td>1.490 x 10⁻⁵</td>
<td>1.081 x 10⁻⁵</td>
<td>105.29</td>
<td>2.99 x 10¹⁷</td>
</tr>
<tr>
<td>3.076 x 10⁻⁵</td>
<td>2.489 x 10⁻⁵</td>
<td>105.83</td>
<td>4.32 x 10¹⁷</td>
</tr>
<tr>
<td>6.830 x 10⁻⁵</td>
<td>5.440 x 10⁻⁵</td>
<td>107.13</td>
<td>1.06 x 10¹⁸</td>
</tr>
<tr>
<td>1.422 x 10⁻⁴</td>
<td>8.655 x 10⁻⁵</td>
<td>109.79</td>
<td>4.24 x 10¹⁸</td>
</tr>
<tr>
<td>2.622 x 10⁻⁴</td>
<td>1.375 x 10⁻⁴</td>
<td>114.40</td>
<td>9.90 x 10¹⁸</td>
</tr>
</tbody>
</table>

**RUN II**

Weight of Magnetite = 0.87 gm.
Weight of Water = 122.30 gm.

<table>
<thead>
<tr>
<th>Initial Concentration</th>
<th>Equilibrium Concentration</th>
<th>Weight of Solution</th>
<th>αCrO₄⁻ (ions/gm. Fe₃O₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₀ (M)</td>
<td>Cₑ (M)</td>
<td>V (gm.)</td>
<td></td>
</tr>
<tr>
<td>1.888 x 10⁻⁵</td>
<td>1.463 x 10⁻⁵</td>
<td>123.04</td>
<td>3.64 x 10¹⁷</td>
</tr>
<tr>
<td>3.916 x 10⁻⁵</td>
<td>3.212 x 10⁻⁵</td>
<td>123.85</td>
<td>6.05 x 10¹⁷</td>
</tr>
<tr>
<td>8.285 x 10⁻⁵</td>
<td>6.320 x 10⁻⁵</td>
<td>125.63</td>
<td>1.72 x 10¹⁸</td>
</tr>
<tr>
<td>1.564 x 10⁻⁴</td>
<td>9.880 x 10⁻⁵</td>
<td>128.75</td>
<td>5.15 x 10¹⁸</td>
</tr>
<tr>
<td>3.456 x 10⁻⁴</td>
<td>2.469 x 10⁻⁴</td>
<td>137.52</td>
<td>9.40 x 10¹⁸</td>
</tr>
</tbody>
</table>
### TABLE 10

$\text{Fe}_3\text{O}_4$ (Preparation II) - $\text{Na}_2\text{HPO}_4$

#### RUN I

Weight of Magnetite = 0.87 gm.

Weight of Water = 119.87 gm.

<table>
<thead>
<tr>
<th>Initial Concentration $C_0$ (M)</th>
<th>Equilibrium Concentration $C_E$ (M)</th>
<th>Weight of Solution $V$ (gm.)</th>
<th>$a\text{HPO}_4^-$ (ions/gm. $\text{Fe}_3\text{O}_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3.816 \times 10^{-5}$</td>
<td>$3.853 \times 10^{-5}$</td>
<td>120.93</td>
<td>$1.24 \times 10^{17}$</td>
</tr>
<tr>
<td>$8.300 \times 10^{-5}$</td>
<td>$8.155 \times 10^{-5}$</td>
<td>122.20</td>
<td>$2.63 \times 10^{18}$</td>
</tr>
<tr>
<td>$1.759 \times 10^{-4}$</td>
<td>$1.456 \times 10^{-4}$</td>
<td>124.91</td>
<td>$8.00 \times 10^{18}$</td>
</tr>
<tr>
<td>$4.115 \times 10^{-4}$</td>
<td>$3.245 \times 10^{-4}$</td>
<td>132.36</td>
<td>$3.45 \times 10^{18}$</td>
</tr>
</tbody>
</table>

#### RUN II

Weight of Magnetite = 0.87 gm.

Weight of Water = 114.54 gm.

<table>
<thead>
<tr>
<th>Initial Concentration $C_0$ (M)</th>
<th>Equilibrium Concentration $C_E$ (M)</th>
<th>Weight of Solution $V$ (gm.)</th>
<th>$a\text{HPO}_4^-$ (ions/gm. $\text{Fe}_3\text{O}_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4.277 \times 10^{-5}$</td>
<td>$4.204 \times 10^{-5}$</td>
<td>115.67</td>
<td>$5.85 \times 10^{16}$</td>
</tr>
<tr>
<td>$9.080 \times 10^{-5}$</td>
<td>$8.650 \times 10^{-5}$</td>
<td>116.98</td>
<td>$3.50 \times 10^{17}$</td>
</tr>
<tr>
<td>$2.020 \times 10^{-4}$</td>
<td>$1.606 \times 10^{-4}$</td>
<td>120.10</td>
<td>$3.45 \times 10^{18}$</td>
</tr>
<tr>
<td>$4.267 \times 10^{-4}$</td>
<td>$3.210 \times 10^{-4}$</td>
<td>126.97</td>
<td>$9.30 \times 10^{18}$</td>
</tr>
</tbody>
</table>
SURFACE CHARGE (electrons/cm²) x 10⁻²

a. NaCl
b. Na benzoate
c. Na₂SO₄
d. K₂CrO₇
e. Na₂HPO₄

FIG. 10
(i) Discussion

The results presented here for total sorption from various pure unbuffered electrolyte solutions have been compared with the "adsorption" data obtained by Anderson (14) from electrokinetic potential measurements using a micro-electrophoretic technique. The results are directly comparable since in both cases the measurements refer to magnetite preparation II. Anderson's results for the relevant electrolyte solutions are reproduced graphically in Fig. 10, where $\sigma$ is the surface charge in electronic charge/cm$^2$ and $C_e$ the equilibrium electrolyte concentration expressed in gm.moles/litre. $\sigma$ has been interpreted by Anderson in terms of ions "adsorbed" per unit area of adsorbent.

Comparing the data presented in Figs. 9 and 10, it is apparent that an entirely different picture of the relative "adsorbabilities" of the various anions studied is given. The most striking contrast is between the similarity of the electrophoretic data for the benzoate, chloride, and sulphate solutions and the lack of corresponding similarity in the total sorption data. Electrophoretic data would appear to indicate that benzoate and sulphate are "adsorbed" to a similar degree, but in total sorption measurements the sorption of benzoate is so small as not to be measureable, whilst a large sorption of sulphate occurs.

Anderson concluded, apparently on the basis of the continuous increase of positive surface charge with increasing concentration of sodium chloride solution, that chloride ion is not adsorbed by magnetite. The
present work demonstrates that such a conclusion is ill advised. It is suggested that electrophoretic "adsorption" data merely reflect the charge (which indeed is likely to be a net charge) arising from ions at either side of a relatively non-reentrant slipping surface around a particle. Yet a large number of ions may be sorbed in the reentrant regions of the particles and these play little part in determining the properties of the interface governing electrophoretic particle mobility. The fact that sorption from sodium benzoate solutions was not detected by the present technique may arise from the inability of the large benzoate ion to penetrate the reentrant regions of the magnetite. This would also be supported by the fact that the total sorption by magnetite preparation III, which is a hard, compact material, was so small as not to be measurable with any degree of accuracy, whereas electrophoretic studies yielded similar data (35) to that obtained by Anderson for preparation II.

Presumably the precipitated magnetites, preparations I and II, due to their more flocculent, less dense nature contained far larger amounts of reentrant surface than preparation III. Hence, if an ion was sufficiently small to enter these more internal regions of the solid a much greater degree of total sorption would occur than if it was too large and could only occupy sites on the external surfaces.

On the basis of total sorption measurements the following anion sorption series can be derived:

$$(\text{benzoate})^- < \text{Cl}^- < \text{NO}_3^- < \text{SO}_4^2^- < \text{CrO}_4^{2-}$$
It is not possible to place the $\text{HPO}_4^{\text{-}}$ ion in this series since its degree of sorption, relative to other anions, appears to be concentration dependent.

Absolute surface area measurements have not been made upon any of the magnetite preparations in view of the fact that different sorbed species will have different amounts of "reentrant surface" available to them and consequently the available surface area for one sorbed species is not the same as for another sorbed species. Rather all measurements have been referred to a given batch of magnetite as already described.
(ii) MAGNETITE IN HYDROCHLORIC ACID SOLUTION

Attempts were made to determine sorption by magnetite from solutions of hydrochloric acid in the concentration range $2 \times 10^{-5} \text{N}$ to $2 \times 10^{-3} \text{N}$. The magnetite studied was preparation II, a heat dried modification of preparation II, and preparation III.

It has been demonstrated that all the preparations of magnetite studied, on treatment with hydrochloric acid solutions, released ferrous ions into solution, the release of ferric ions not being detected. Mechanisms whereby ferrous but not ferric ions may be released into solution have been considered.

(a) Magnetite, Preparation II/HCl solution

A sorption run was carried out as described previously (Section II, (iii), small additions of stock hydrochloric acid solution being made to magnetite in equilibrium with conductivity water. Determinations of sorption were attempted by the simultaneous use of conductimetric and potentiometric techniques.

During the course of the measurements it was found that colloidal material separated from the solid, the amount of colloid formed increasing with increase in acid concentration. The colloidal suspension was found to be very stable with time, although the colloidal particles could be removed from the electrolyte solution by a strong magnetic field or by neutralisation of the acid.

Interpretation of the conductimetric and potentiometric measurements
in terms of simple loss of hydrochloric acid from solution gave results showing lack of agreement between the two methods. It was at first thought that possibly the presence of colloidal material affected the behaviour of the glass electrode, and work with preparation II was abandoned in favour of preparations IIA (see below) and III.

Later work showed that the major reason for this apparent discrepancy between conductimetric and potentiometric measurements was due to the release into solution of ferrous ions.

(b) Magnetite, Preparation IIA/HCl solution

It was found that preparation II could be obtained in a form which did not peptise in hydrochloric acid solution by the following treatment. The well washed precipitate (preparation II) was separated by centrifugation and heated in a Pyrex boat at 300-400 degrees C for 30 minutes in a rapid stream of nitrogen. The resultant hard lumps of magnetite were ground, by means of an agate pestle and mortar, to give particles in the size range 5-20 μ.

As with preparation II, sorption determinations were attempted by the simultaneous use of conductimetric and potentiometric techniques, and a sorption run in the hydrochloric acid concentration range 2 x 10^{-5} to 2 x 10^{-3}N was carried out.

Although no colloidal material was obtained in this case, equilibrium acid concentrations, as calculated separately on the basis of simple loss of hydrochloric acid from solution from conductimetric and potentiometric
measurements were again found to differ widely. The results suggested the presence of a third ion in solution. This ion was suspected to be either the ferrous or the ferric ion, or possibly both. Spot tests, given in Appendix II, showed the presence of ferrous ions but not of ferric ions.

The conductimetric and potentiometric measurements obtained for this type of sorption run, on preparation IIA, was therefore interpreted using the equations:

\[
\begin{align*}
\dot{10^3K} &= C_H \lambda_H + C_{Cl} \lambda_{Cl} + C_{Fe} \lambda_{Fe} \\
\epsilon (E.M.F.) &= C_H C_{Cl} \\
C_H + C_{Fe} &= C_{Cl}
\end{align*}
\]

where \( C_{Fe} \) is the ferrous ion concentration. All concentrations are expressed in equivalents per litre. Values of the equivalent ion conductances, used in these calculations, are given in Appendix I.

Results of these measurements on preparation IIA are given in Table II, where the equilibrium solution composition has been interpreted in terms of hydrogen, ferrous, and chloride ion concentrations.

(c) Repeated Exchange of Hydrochloric Acid Solution over Magnetite Preparation IIA

It was thought that the removal of ferrous ions from magnetite might be a simple "leaching out" process leaving a \( \gamma \)-ferric oxide skeleton (Section III,(ii),d). To test this hypothesis it was attempted to "exhaust" a sample of preparation IIA of ferrous ions by repeated
TABLE II

Magnetite (Preparation IIA) - HCl solution

Weight of Magnetite = 5.49 gm.
Weight of Water = 114.46 gm.

<table>
<thead>
<tr>
<th>Weight of Solution V (gm.)</th>
<th>Initial HCl Concentration $C_o$ (Normal)</th>
<th>$C_{H^+}$ (Normal)</th>
<th>$C_{Cl^-}$ (Normal)</th>
<th>$C_{Fe^{++}}$ (Normal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>116.06</td>
<td>$1.088 \times 10^{-4}$</td>
<td>$1.45 \times 10^{-7}$</td>
<td>$1.050 \times 10^{-4}$</td>
<td>$1.049 \times 10^{-4}$</td>
</tr>
<tr>
<td>118.23</td>
<td>$2.349 \times 10^{-4}$</td>
<td>$7.690 \times 10^{-7}$</td>
<td>$2.117 \times 10^{-4}$</td>
<td>$2.109 \times 10^{-4}$</td>
</tr>
<tr>
<td>121.82</td>
<td>$4.345 \times 10^{-4}$</td>
<td>$2.430 \times 10^{-6}$</td>
<td>$3.666 \times 10^{-4}$</td>
<td>$3.642 \times 10^{-4}$</td>
</tr>
<tr>
<td>128.36</td>
<td>$7.688 \times 10^{-4}$</td>
<td>$9.765 \times 10^{-6}$</td>
<td>$5.615 \times 10^{-4}$</td>
<td>$5.517 \times 10^{-4}$</td>
</tr>
<tr>
<td>138.08</td>
<td>$1.208 \times 10^{-3}$</td>
<td>$3.603 \times 10^{-5}$</td>
<td>$8.002 \times 10^{-4}$</td>
<td>$7.642 \times 10^{-4}$</td>
</tr>
<tr>
<td>140.21</td>
<td>$3.734 \times 10^{-3}$</td>
<td>$1.136 \times 10^{-4}$</td>
<td>$2.611 \times 10^{-3}$</td>
<td>$2.497 \times 10^{-3}$</td>
</tr>
<tr>
<td>143.32</td>
<td>$7.298 \times 10^{-3}$</td>
<td>$1.651 \times 10^{-4}$</td>
<td>$5.485 \times 10^{-3}$</td>
<td>$5.320 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
equilibration with fresh hydrochloric acid solution. The procedure was as follows:

A known weight of preparation IIIA was equilibrated with a known weight (approximately 100 gm.) of approximately $5 \times 10^{-n}$ N hydrochloric acid. The equilibrium concentrations of the three ionic species, i.e., hydrogen, chloride, and ferrous ions, were then determined by the simultaneous use of conductimetric and potentiometric techniques. Next, as much as possible of the supernatant liquid was removed, weighed, and replaced with a similar weight of hydrochloric acid of the same concentration as that initially used. Again the equilibrium concentrations of the three ions were determined. This procedure was repeated several times.

In the early stages equilibrium was attained in times of approximately one hour, this time lengthening to approximately twenty hours in the later stages. The run was discontinued after 20 exchanges of solution, at which time the magnetite had been treated with approximately 2 litres of the original hydrochloric acid solution. Results for a selection of points are illustrated in Table 12.

It can be seen from Tables 11 and 12 that the removal of hydrogen ion from solution was very large. That the interpretation of the potentiometric and conductimetric measurements was essentially correct was supported by a number of subsidiary measurements. The equilibrium hydrogen ion concentrations shown in Table 12 have been confirmed by measurement of pH,
TABLE 12

Repeated HCl Exchange over Magnetite (Preparation IIA)

Weight of Magnetite = 2.56 gm.
Concentration of HCl Solution = 4.695 x 10^{-4} N

<table>
<thead>
<tr>
<th>Stage</th>
<th>Total Weight of Solution Added (gm.)</th>
<th>$C_{H+}$ (Normal)</th>
<th>$C_{Cl^-}$ (Normal)</th>
<th>$C_{Fe^{++}}$ (Normal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Equilib.</td>
<td>120</td>
<td>1.45 x 10^{-5}</td>
<td>4.45 x 10^{-4}</td>
<td>4.30 x 10^{-4}</td>
</tr>
<tr>
<td>5th &quot;</td>
<td>600</td>
<td>1.94 x 10^{-5}</td>
<td>4.53 x 10^{-4}</td>
<td>4.34 x 10^{-4}</td>
</tr>
<tr>
<td>10th &quot;</td>
<td>1100</td>
<td>2.49 x 10^{-5}</td>
<td>4.61 x 10^{-4}</td>
<td>4.36 x 10^{-4}</td>
</tr>
<tr>
<td>15th &quot;</td>
<td>1600</td>
<td>7.37 x 10^{-5}</td>
<td>4.60 x 10^{-4}</td>
<td>3.86 x 10^{-4}</td>
</tr>
<tr>
<td>20th &quot;</td>
<td>2100</td>
<td>8.55 x 10^{-5}</td>
<td>4.63 x 10^{-4}</td>
<td>3.78 x 10^{-4}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Stage</th>
<th>$C_{Fe^{++}}$ (Colorimetric)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.20 x 10^{-4}N</td>
</tr>
<tr>
<td>5</td>
<td>4.46 x 10^{-4}N</td>
</tr>
<tr>
<td>10</td>
<td>4.44 x 10^{-4}N</td>
</tr>
<tr>
<td>15</td>
<td>3.42 x 10^{-4}N</td>
</tr>
<tr>
<td>20</td>
<td>3.32 x 10^{-4}N</td>
</tr>
</tbody>
</table>
after the removal of the solutions from the cell, using a glass electrode in conjunction with a saturated calomel electrode. Also the calculated ferrous ion concentrations have been confirmed by direct colorimetric determination with o-phenanthroline reagent, using a Unicam S.P.500 spectrophotometer at a wavelength of 500 μm. The procedure was as described by Vogel (27).

A standard solution of ferrous sulphate, approximately 10^{-3} N, was made up in conductivity water. Portions were diluted to a number of different concentrations, and in each case a predetermined amount of 0.2M sodium acetate solution was added to bring the pH to 3.5 ± 1 (determined in duplicates using bromophenol blue as indicator). 10 ml. portions of each solution were taken and to each was added 1 ml. of 10 per cent hydroxylamine hydrochloride solution and 1 ml. of 0.1 per cent o-phenanthroline solution. After standing for one hour the optical densities of the solutions, contained in 1 cm. silica cells, were measured.

The results are shown in Table 12. It is seen that these determinations confirm well the calculated ferrous ion concentrations in the solutions removed from the magnetite in the "exchange" experiments.

(d) Magnetite Preparation III/HCl solution

Metal oxides when heated strongly or prepared at high temperatures are, in many cases, more resistant to acid attack than the corresponding oxide prepared at low temperatures and which has not been subjected to strong heating. Preparation III was a high temperature dry preparation,
TABLE 13

Magnetite (Preparation III)/HCl (Conductance - Time)

Weight of Magnetite = 4.20 gm.
Weight of HCl Solution = 127.32 gm.
Concentration of HCl Solution = $3.42 \times 10^{-4} N$

Conductance of HCl Solution in Absence of Magnetite

= $1.451 \times 10^{-4} \text{ ohm}^{-1} \text{ cm.}^{-1}$

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>Conductance of HCl Solution $K(\text{ohm}^{-1} \text{cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.395 \times 10^{-4}$</td>
</tr>
<tr>
<td>2</td>
<td>$1.381 \times 10^{-4}$</td>
</tr>
<tr>
<td>3</td>
<td>$1.361 \times 10^{-4}$</td>
</tr>
<tr>
<td>4</td>
<td>$1.353 \times 10^{-4}$</td>
</tr>
<tr>
<td>5</td>
<td>$1.347 \times 10^{-4}$</td>
</tr>
<tr>
<td>6</td>
<td>$1.341 \times 10^{-4}$</td>
</tr>
<tr>
<td>7</td>
<td>$1.335 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
prepared in an attempt to obtain a sample of magnetite resistant to attack by hydrochloric acid.

As with preparations II and IIA, preparation III when treated with hydrochloric acid solutions released ferrous ions into solution. Again no trace of ferric ions could be detected in solution.

The solid, like preparation IIA, did not peptise on treatment with hydrochloric acid.

The release of ferrous ions proceeded much more slowly than in the case of the precipitated magnetites. The results indicated an initial rapid sorption from solution followed by a slow process or processes as ferrous ions were released into solution. This is illustrated by results shown in Table 13 and illustrated in Fig. 11, for the addition of approximately 100 ml. of $3.42 \times 10^{-4}$ N hydrochloric acid solution to a sample of magnetite preparation III. The changes taking place were followed by the conductivity loss technique. In Fig. 11, the specific conductance of the electrolyte solution is plotted against time. The initial conductance of the hydrochloric acid solution in the absence of adsorbent was calculated using the limiting form of the Onsager equation.

It was not possible to discover whether or not the first stage was pure sorption followed by release of ferrous ions in the second stage, because use of the potentiometric method would have rendered the time scale meaningless.

A further experiment of the exchange type was carried out on
preparation III. A quantity of solid was soaked in several changes of approximately 0.5N hydrochloric acid over a period of several weeks. The solid was then washed in conductivity water, acetone, ether, and air dried. X-ray examination of this material showed no change in crystallographic structure of the solid. This point is discussed more fully at a later stage (Section III, (ii), e).

(e) Examination of Magnetite Preparations by X-ray Crystallography

The X-ray powder diffraction technique has been employed to study both the chemical composition and crystallographic structure of the various preparations of magnetite used in the work described here. The principal impurity encountered in precipitated magnetite was found to be α-ferric oxide.

The percentages of iron in magnetite (72.4 per cent) and α-ferric oxide (69.9 per cent) are sufficiently close to make extremely accurate chemical analyses necessary for the estimation of small amounts of α-ferric oxide in magnetite. Low values of iron in magnetite would be obtained not only through partial oxidation to ferric oxide, but also, in the case of precipitated magnetites, because of the retention of water even after prolonged drying (29). Except in the case of preparation III, this latter phenomenon would cause excessive errors in the estimation of α-ferric oxide.

X-ray powder method

The Bragg reflection formula, for reflection or diffraction of X-rays at the planes of a crystal, is $n\lambda=2d \sin \Theta$, where $n$ is an integer, $d$ is the crystal spacing, $\lambda$ the wavelength of incident X-rays and $\Theta$
the angle of incidence of the X-rays. For a single stationary crystal
\( \Theta \) is constant and an X-ray photograph will be formed by the reflection
from different crystal planes. However, in powder photography, monochromatic radiation is used together with a powder of randomly orientated crystals which give many values of \( \Theta \). Instead of spots being formed on
the photographic plate for the various crystal planes as with a single
crystal, concentric rings are produced. If instead of a wide plate only
a strip of film is used, approximately straight lines are obtained. The
number and spacing of these lines will depend upon the fact that every
crystalline substance has its own characteristic atomic structure which
gives an X-ray diffraction pattern peculiar to the substance.

The experimental technique was to coat a glass fibre with finely
ground magnetite powder using Canada balsam as adhesive. This was mounted
on a rotating spindle, and a strip of photographic film, in the form of a
cylinder placed round the sample, there being a hole in the middle of the
film to permit entry of X-rays. The film was contained in a Hilger 9 cm.
powder camera using cobalt K (\( \alpha \)) radiation.

Powder photographs obtained in this manner were initially examined
for freedom from impurities by comparison with the powder photographs given
by Rooksby (36). Otherwise comparisons were made against photographs,
for a magnetite preparation III free from \( \alpha \)-ferric oxide, and for \( \alpha \)-ferric
oxide.

The interpretation of powder photographs was by visual comparison
against photographs of pure iron oxides. Magnetite and α-ferric oxide have quite different X-ray powder diffraction patterns. Estimations of the α-ferric oxide content of magnetite specimens were also made by comparison.

The various preparations of magnetite employed in the work described here were examined as described above. The preparations and their treatment, if any, before examination were as follows:

(a) Preparation II washed in conductivity water, acetone, ether and air dried.
(b) Preparation II treated as in (a) followed by heating to 300-400 degrees C in a rapid stream of nitrogen.
(c) Preparation IIIA.
(d) Preparation III.

The investigations revealed that:

(a) contained traces of α-ferric oxide, (b) contained rather more α-ferric oxide than did (a), (c) contained a considerable percentage of α-ferric oxide (estimated 30 per cent) whilst no batch of preparation III contained more than trace amounts of α-ferric oxide.

These results would appear to indicate that heating to 300-400 deg. C in the absence of oxygen can still cause oxidation of magnetite to α-ferric oxide providing that water is present. Welch (29) found that the presence of water was of importance in the oxidation of magnetite to α-ferric oxide. At temperatures below 400 degrees C magnetite prepared by precipitation and
dried by heating in a current of argon, on oxidation gave \( \gamma \)-ferric oxide with no \( \alpha \)-ferric oxide, whereas a dry preparation, identical with preparation III, gave \( \alpha \)-ferric oxide on oxidation at temperatures as low as 185 degrees C. Conversion of \( \gamma \)-ferric oxide to the \( \alpha \)-form occurs readily at 400 degrees C (36) and the oxidation of magnetite to \( \alpha \)-ferric oxide as in preparation IIA can be represented as:

\[
\text{Heat} \quad \frac{H_2O + O_2}{\text{Fe}_3\text{O}_4} \quad \frac{\text{Heat}}{\gamma - \text{Fe}_2\text{O}_3} \quad \frac{\text{Heat}}{\alpha - \text{Fe}_2\text{O}_3}
\]

At small crystallite size, the X-ray diagram of magnetite is indistinguishable from that of \( \gamma \)-ferric oxide without careful measurement of the lattice parameters (36). The diagrams from preparation II and its modifications were too diffuse in the pertinent region for such analysis to be performed. Consequently the presence or absence of \( \gamma \)-ferric oxide could not be detected. It is not impossible, therefore, that preparation II contains a proportion of \( \gamma \)-\text{Fe}_2\text{O}_3.

Preparation III gave a sharp diffraction pattern. Because it was prepared at 960 degrees C, which is considerably higher than the temperature at which the transition \( \gamma \)- to \( \alpha \)-ferric oxide occurs, there is no possibility of any \( \gamma \)-ferric oxide being present.

(f) \( \alpha \)-Ferric Oxide/HCl solution

In view of the fact that preparation IIA contained appreciable quantities of \( \alpha \)-ferric oxide and preparation III traces of this oxide (Section III, (ii),b) the behaviour of this material in hydrochloric acid
solutions has been investigated by conductimetric measurements. No traces of either ferrous or ferric ions were found to be released into solution.

α-ferric oxide was prepared as follows. Ferric hydroxide was precipitated from a boiling 0.5N solution of "Analar" grade ferric chloride using a slight excess of ammonia solution. The liquid was boiled for several minutes after precipitation. The filtered ferric hydroxide was well washed with hot 1 per cent ammonium nitrate solution by centrifugation and decantation followed by ignition in a vitreous crucible at 1000 degrees C. The resultant solid was crushed and ground to give particles of diameter 1-2μ.

Results for sorption from hydrochloric acid solution by α-ferric oxide are shown in Table 14 and illustrated in Fig.12, where α represents the numbers of hydrogen and chloride ions removed from solution per gram of absorbent and C_E is the equilibrium hydrochloric acid concentration.

Equilibrium times varied from one hour at low acid concentrations to approximately 20 hours for 10^{-3}N hydrochloric acid. Also at the higher acid concentrations some peptisation of the solid occurred.

The measurements made on α-ferric oxide indicated that, when present in magnetite, it made no contribution to any processes occurring other than that of sorption. The only magnetite containing α-ferric oxide in appreciable quantities was preparation IIIA, hence it was only in this case that it can be looked upon as having made a significant contribution to the sorption process. In all cases it can be assumed that α-ferric oxide played no part in the chemical process or processes occurring.
### TABLE 14

\( \alpha-\text{Fe}_2\text{O}_3 - \text{HCl} \)

Weight of \( \alpha \)-Ferric Oxide = 5.73 gm.

Weight of water = 114.55 gm.

<table>
<thead>
<tr>
<th>Initial Concentration ( C_0 ) (Normal)</th>
<th>Equilibrium Concentration ( C_E ) (Normal)</th>
<th>Weight of Solution ( V ) gm.</th>
<th>( a_{\text{Cl}} ) ions/gm. ( \alpha\text{-Fe}_2\text{O}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 6.465 \times 10^{-6} )</td>
<td>( 2.985 \times 10^{-6} )</td>
<td>114.73</td>
<td>( 4.20 \times 10^{16} )</td>
</tr>
<tr>
<td>( 1.761 \times 10^{-5} )</td>
<td>( 8.498 \times 10^{-6} )</td>
<td>115.04</td>
<td>( 1.10 \times 10^{17} )</td>
</tr>
<tr>
<td>( 4.680 \times 10^{-5} )</td>
<td>( 2.149 \times 10^{-5} )</td>
<td>115.85</td>
<td>( 3.08 \times 10^{17} )</td>
</tr>
<tr>
<td>( 1.127 \times 10^{-4} )</td>
<td>( 5.410 \times 10^{-5} )</td>
<td>117.74</td>
<td>( 7.26 \times 10^{17} )</td>
</tr>
<tr>
<td>( 3.471 \times 10^{-4} )</td>
<td>( 2.298 \times 10^{-4} )</td>
<td>125.00</td>
<td>( 1.54 \times 10^{18} )</td>
</tr>
<tr>
<td>( 8.030 \times 10^{-4} )</td>
<td>( 6.360 \times 10^{-4} )</td>
<td>141.75</td>
<td>( 2.49 \times 10^{18} )</td>
</tr>
</tbody>
</table>
Magnetite has the inverse spinel structure with 24 iron ions distributed in the holes between 32 cubic close packed oxygen ions. One third of the cations are ferrous ions, the remainder ferric ions.

In the inverse spinel structure the unit cell can be considered as \( \text{A}_8\text{B}_{16}\text{O}_{32} \) with the oxide ions in a close packed cubic arrangement, where \( \text{A} \) are the cations occupying the tetrahedral holes and \( \text{B} \) the cations occupying the octahedral holes. In the normal spinel structure, as to be expected from radius ratio considerations, divalent cations occupy \( \text{A} \) sites whilst trivalent cations occupy \( \text{B} \) sites, an example of this being \( \text{Co}_3\text{O}_4 \). However, in magnetite, which has an inverse spinel structure the ferrous ions occupy half the octahedral holes whilst the ferric ions are equally distributed between octahedral and tetrahedral holes. Due to this distribution of ions in the magnetite lattice, the formula is usually written as \( \text{Fe}^{3+}\text{Fe}^{2+}\text{Fe}^{3+}\text{O}_{4} \), this being preferred to \( \text{Fe}^{2+}\text{Fe}^{3+}\text{O}_{4} \), since it indicates the equivalence in crystallographic positioning of \( \text{Fe}^{2+} \) and one half of the \( \text{Fe}^{3+} \) ions (37)(38).

The spinel structure has also been accepted for \( \gamma \)-ferric oxide, e.g. (39). \( \gamma \)-ferric oxide always contains the elements of water. On the basis of these facts it has been suggested that the structure of \( \gamma \)-ferric oxide either lies between \( \text{Fe}_8^{3+}[\text{Fe}_{12}^{3+}\square_{1/4}(\text{OH})_{12}]_{0.28} \) and \( \text{Fe}_8^{3+}[\text{Fe}_{13.1/3}\square_{22/3}]_{0.32} \) (29) or between \( \text{Fe}_8^{3+}[\text{Fe}_{12}^{3+}]_{0.32} \) and \( \text{Fe}_8^{3+}[\text{Fe}_{1,1/3}\square_{22/3}\text{Fe}_{12}^{3+}]_{0.32} \) (40). \( \square \) represents cation vacancies.

\( \alpha \)-ferric oxide has the corundum structure which has a unit cell of 6
oxygen atoms forming an octahedral group around the metal atom and 4 metal atoms surrounding each oxygen atom. It gives an X-ray powder photograph completely different to those of magnetite and \( \gamma \)-ferric oxide.

Thus the experimental work presented here shows that only ferrous ions and no ferric ions are released into solutions of hydrochloric acid, and that after prolonged soaking of magnetite in 0.5N hydrochloric acid solution the inverse spinel structure is retained. Possible mechanisms consistent with these facts have been considered.

**Consideration of possible mechanisms**

(1) It is suggested that there is an initial sorption of hydrogen ions followed by combination of hydrogen ions with oxygen ions situated at surface defects resulting in the removal of oxygen either as hydroxyl ions or as water molecules. This would leave the solid with a net positive charge which results in the release of ferrous ions into solution leaving a solid which will tend towards a \( \gamma \)-ferric oxide skeleton as the removal of ferrous ions proceeds.

That ferrous ions are removed in preference to ferric ions may be due to the relative electrostatic bond strengths of the cations. Assuming, to a first approximation, that the charge on each cation is dissipated on oxygen ions which are its immediate neighbours then the cation charge divided by the cation coordination number can be used as a measure of electrostatic bond strength.

The coordination number of cations, in tetrahedral sites is 4, and
in octahedral sites is 6. Thus for ferric ions in tetrahedral sites the electrostatic bond strength can be represented as $3/4$ and in octahedral sites as $3/6$, but for ferrous ions in octahedral sites as $2/6$. Hence it can be seen that ferrous ions are held in the lattice by weaker bonds than those holding ferric ions. Thus the bonds holding ferric ions in the lattice may be sufficiently strong to prevent their release into solution.

This mechanism can be represented as:

1. $\text{H}^+ (\text{solution}) \rightarrow \text{H}^+ (\text{sorbed})$.

2. $\text{H}^+ (\text{sorbed}) + \text{O} (\text{lattice}) \rightarrow \text{OH}^\cdot (\text{solution})$.

3. $2\text{H}^+ (\text{sorbed}) + \text{O} (\text{lattice}) \rightarrow \text{H}_2\text{O} (\text{solution})$.

4. $\text{Fe}_3\text{O}_4^{2+} (\text{solid}) \rightarrow \text{Fe}^{2+} (\text{solution}) + \gamma-\text{Fe}_2\text{O}_3$ type network (solid).

The slowing down of the process, in the repeated exchange experiment, may be simply a reflection of the reduction in the number of oxygen ions situated at surface defects as the reaction proceeds. Further it may reflect the time required for ferrous ions to diffuse to the surface of the solid. It may be noted that Evans and Pryor (41) suggested a similar mechanism for the dissolution of a-ferric oxide in dilute hydrochloric acid. (2) This mechanism postulates the release of ferrous ions into solution accompanied by the formation of hydrogen gas which may remain sorbed by the solid. The process suggested is that hydrogen ions are sorbed from solution, and withdraw electrons from the solid to give hydrogen gas which remains occluded by the solid. Electrons may be produced by the conversion of
ferrous ions to ferric ions. The lability of electrons in magnetite has been demonstrated by Verwey (42). The resultant positive charge on the solid results in the release of ferrous ions into solution.

The mechanism is then:
1. $\text{H}^+(\text{solution}) \rightarrow \text{H}^+(\text{sorbed})$.
2. $2\text{H}^+(\text{sorbed}) + 2\text{e} \rightarrow \text{H}_2(\text{sorbed})$.
3. $2\text{Fe}^{2+}(\text{solid}) \rightarrow 2\text{Fe}^{3+}(\text{solid}) + 2\text{e}$.
4. $\text{Fe}^{2+}(\text{solid}) \rightarrow \text{Fe}^{2+}(\text{solution})$.

It is suggested that sorbed hydrogen ions initiate the process and that the final product would be a $\gamma$-ferric oxide skeleton. The slowing down of the process could again be due to the diffusion of ferrous ions from the interior of the solid to the surface.

There is a well established possible analogy for this mechanism in the sodium tungsten bronzes which are formed by treating sodium tungstate with reducing agents at high temperature. These compounds over the composition range in which they are cubic have crystal lattices in which not all the places available as sites for sodium ions need be occupied. Their composition varies between the limits $\text{Na}_0.3 \text{WO}_3$ and $\text{NaWO}_3$ (37). Removal of sodium ions from the system is accompanied by a corresponding conversion of $\text{W}^{5+}$ to $\text{W}^{6+}$ within the lattice (37), (43).

Mechanisms (1) and (2) are quite similar but mechanism (1) requires that three times as much ferrous ion be released into solution as by mechanism (2). The investigation of the total amount of ferrous ions released would
be the only way in which the correct mechanisms could be selected. Un-
fortunately the release of ferrous ions soon becomes so slow that the length
of time which would be required for such investigations would be prohibitively
long.

Anderson (14) studied the behaviour of magnetite in solutions con-
taining suitable mixtures of hydrochloric acid, sodium chloride, and sodium
hydroxide by an electrophoretic technique. He concluded that the effect of
pH was attributable to its influence on the effect of dissociation of basic
groups on the magnetite surface. This interpretation was found to be
least satisfactory at low pH values.

In electrophoretic experiments a very small quantity of solid is
equilibrated with a relatively great volume of electrolyte solution, with the
result that the phenomena made apparent by the work described here (in which
the ratio weight of solid to volume of solution is relatively enormous)
would lead to negligible changes in the nature of the equilibrium solution.
However, from the point of view of the structure of the solid and the nature
of its surface these phenomena must be of equal importance in the inter-
pretation of electrophoretic data.

The work presented here thus shows that phenomena occur, in the
system, which would not be detected in electrophoretic examination. Since
these phenomena affect the surface structure of the solid material they
should be taken into account in any interpretations of electrokinetic data.
SECTION IV

ZIRCONIA IN ELECTROLYTE SOLUTIONS

IV A. Electrophoretic Studies
IV B. Total Sorption Studies
Studies of total sorption by zirconia from single and mixed electrolyte solutions have been made in the concentration range $2 \times 10^{-5}$ to $2 \times 10^{-3}$ N. Sorption from pure sodium chloride and pure nitric acid solutions has been investigated by means of the conductivity loss technique. Sorption from pure hydrochloric acid solution, from solutions containing equal proportions of sodium chloride and hydrochloric acid, and from various mixtures of nitric and hydrochloric acids, has been studied by the simultaneous use of potentiometric and conductimetric techniques.

No electrokinetic information for zirconia was available in the literature. Consequently micro-electrophoretic studies, as described in Section IV A, were made on zirconia in pure solutions of sodium chloride, nitric acid, and hydrochloric acid in the concentration range $10^{-5}$ to $10^{-2}$ N.
IV A. MICROELECTROPHORETIC STUDIES ON ZIRCONIA

(i) Introduction

The theoretical treatment of the motion of a particle, suspended in an ionic liquid, under an applied electric field, i.e., electrophoresis, was first considered by Helmholtz (44) who showed that the electrophoretic velocity of a particle is proportional to the electrokinetic potential at the interface.

Smoluchowski (45) assumed that electrophoresis was simply the reverse of electroosmosis and derived the same equation for relative motion of solid and liquid for both phenomena. Smoluchowski's equation may be written, for electrophoresis:

\[ V_E = \frac{\varepsilon \zeta \, E}{4 \pi \eta} \]

where \( V_E \) is the particle velocity under an applied field strength \( E \) in a liquid of dielectric constant \( \varepsilon \) and coefficient of viscosity \( \eta \), and \( \zeta \) is the electrokinetic potential.

Assumptions made in the derivation of this equation were:

1) That the usual hydrodynamic equations of motion for a viscous fluid hold in both the double layer and the bulk of the liquid.
2) That the motion is "streamline", that is, the inertia terms are negligible in the hydrodynamics.
3) That the applied field may be considered as simply superimposed on the field due to the double layer.

4) That the conductance, dielectric constant, and viscosity of the liquid in the double layer may be considered to have the same values as in the bulk of the liquid.

5) That the particles are non-conducting.

6) That the particle dimensions are large, i.e., the particle radius of curvature at any point is large compared with the thickness of the double layer.

Debye and Hückel (46), using the methods of their theory of strong electrolyte solutions, confirmed the proportionality between particle velocity and electrokinetic potential, for small spherical particles where the double layer extension was large compared with particle radius, but obtained a different factor of proportionality. Their equation may be written:

\[ V_E = \frac{\varepsilon E}{6\pi \eta} \]

Henry (47), in a detailed analysis of the problem, gave a theoretical treatment of electrophoretic motion which covered all sizes of spherical particles on the basis of the assumptions 1-4, above, made by Smoluchowski, with the further assumption that the electric distribution in the ion atmosphere was of the Debye-Hückel exponential type. Henry derived a general equation:

\[ V_E = \frac{\varepsilon E}{4\pi \eta} f(Ka) \]
where \( f(K_a) \) is a function of the particle radius \( a \), and reciprocal double layer thickness \( K \). He further showed that for large values of \( K_a (>100) \) the value of \( f(K_a) \) tends to unity and becomes independent of particle shape and size. Then Smoluchowski's equation is obtained. For small values of \( K_a (<1) \) the value of \( f(K_a) \) is dependant upon particle shape and for spheres tends to \( 2/3 \). Then Hückel's equation applies.

The essential difference between the approaches of Smoluchowski and Debye and Hückel is found in the geometry of the applied electric field. The former treatment took into account the deformation of the applied field by the particle; that of Debye and Hückel did not.

Although the Henry treatment of the problem vindicated the Smoluchowski equation:

\[
V = E_E = \frac{E_E}{4\pi \eta}
\]

for particles of all shapes and sizes where \( K_a \) is large, an essential supposition was still that the electric field due to the double layer and the applied electric field may be simply superimposed on each other. This is not strictly correct. Two factors should be considered:

(1) Due to the fact that the particle and the outer part of the double layer, having opposite charges, move in opposite directions, the symmetry of the double layer is distorted. Time is taken for its restoration, "the time of relaxation", and the outer part of the double layer lags behind the particle, retarding the electrophoretic motion. The relaxation effect has been analysed by Booth (48) and by Overbeek (49).
In using the Smoluchowski equation for calculation of electrokinetic potentials from measured electrophoretic velocities, the correction required to account for the relaxation effect is proportional to the second and higher powers of the electrokinetic potential. Such corrections tend to zero for small values of $S$. For electrokinetic potentials of the order encountered in the present work, in uni-univalent electrolyte solutions such corrections would be very small ($\approx 1$ per cent).

(2) Due to the existence of the double layer at the particle/solution interface, there is generally a greater concentration of ions near the interface than in the bulk solution. This results in an enhanced conductance in the region of the interface, i.e., surface conductance, which can modify the electrophoretic velocity by altering the potential distribution of the applied field. This effect has been analysed by Booth (50) and by Henry (51). In the case of very small particles ($\lesssim 1 \mu$ diameter) and high values of $S$ considerable corrections to the measured electrophoretic velocity are required. Again, however, corrections required in the present work, using larger particles, and where electrokinetic potentials were low (0 – 30 mV), would be small.

Electrophoretic velocities of zirconia particles in solutions of sodium chloride, hydrochloric acid, and nitric acid (concentration range $0 - 10^{-2}$ N) have been measured using a micro-electrophoretic technique. Electrokinetic potentials have been calculated using the Smoluchowski equation. Net charges on either side of the slipping plane have been
calculated using the equation (General Introduction)

\[ \sigma = \left[ \frac{2\pi \varepsilon R \kappa T}{I} \right]^\frac{1}{2} \sinh \frac{e \varepsilon}{2kT} \]

values of \( \left[ \frac{2\pi \varepsilon R \kappa T}{I} \right]^\frac{1}{2} \) and of \( \frac{e \varepsilon}{2kT} \) for 20°C are given in Appendix I, together with values of \( \eta \) and \( \varepsilon \).
(ii) **Apparatus**

The majority of micro-electrophoretic studies, described in the literature, have been carried out in a cell mounted horizontally. However, work in progress in this laboratory has indicated that errors may arise, in the use of such apparatus, from deformation of the symmetry of the electroosmotic flow of the solution (see below), caused by sedimentation of particles on to the floor of the cell.

Nicol (35) has developed a micro-electrophoresis apparatus in which the cell is mounted vertically, thus avoiding asymmetric sedimentation on the walls of the cell. This apparatus has been used in the present work.

The assembly used is shown in Fig. 13. It consisted of a pyrex electrophoresis tube, of the type used by Mattson (52), mounted vertically. The tube consisted of a 20 cm. length of pyrex tube of a uniform bore of 0.125 cm. diameter. Two sides of the tube were ground optically flat; the faces after grinding being at right angles to each other. At each end, the electrophoresis tube was fitted with B10 joints by means of which it was attached to the upper and lower electrode compartments. The upper electrode compartment was joined to a reservoir of 50 ml. capacity via a tap. The lower electrode compartment was joined to a 2-way tap through which the system could either be drained or filled. Filling was from a 50 ml. reservoir mounted at the same height as the reservoir above the electrophoresis cell. A tap at the bottom of the inlet tube enabled
this part of the system to be efficiently drained.

The electrodes were sealed into B10 stoppers by means of which they could be mounted in the electrode compartments, contact with the electrical circuit being made via mercury cups.

The electrodes were of platinum sheet and were cm. long by 1 cm. wide. Polarisation effects were minimised by plating them with grey platinum from a 5% chloroplatinic acid solution containing a trace of sodium acetate. Plating was effected by passing the current from two 2-volt accumulators through the solution for 5 minutes, then reversing the current for a further 5 minutes. After washing thoroughly and allowing to dry the electrodes were heated to dull redness in a bunsen flame.

Prior to plating, the platinum electrodes were cleaned in the same manner as the platinum wires used in the preparation of silver-silver chloride electrodes (Section I, c, (ii) ) in order to obtain a surface which plated evenly.

No thermostatting of the apparatus was used, but on all occasions when measurements were made the temperature of the solution was noted in order that the correct values of the dielectric constant and viscosity of the solution could be employed in calculation of electrokinetic potentials. Since temperature changes have little effect on electrokinetic potential Smith (53) and only small temperature changes occurred during the course of the experiments no significant errors were likely to be introduced by lack of strict temperature control.
The assembly was rigidly mounted by the use of well anchored clamps.

The potential applied to the cell was supplied by two H.T. dry batteries which together were capable of supplying 180 volts. The voltage drop between the electrodes was recorded by means of a voltmeter, a 10KΩ potentimeter enabling the applied voltage to be controlled, and a two way switch enabling the polarity of the system to be reversed.

A potential of 150 volts giving a potential gradient of 6.25 volts/cm. was applied to the cell. No polarization of the electrodes occurred under the voltage gradient, in the solutions studied.

Illumination for the cell was provided by a microscope lamp supplied by J. Swift and Co. Ltd. The light from a 6 volt, 24 watt bulb passed through a condenser system, an iris diaphragm and a focussing system before impinging upon one of the optically ground surfaces of the cell.

The microscope used for observations on particles within the electrophoresis cell was supplied by J. Swift and Co. Ltd. It possessed a course adjustment and a fine, calibrated, adjustment. The stage and condenser system was removed from the microscope which was mounted horizontally. Observations were made perpendicular to, and through one of the optically ground faces of the cell and at right angles to the source of illumination. When in use, the microscope was fitted with a X10 objective and a X20 Telaugic eyepiece containing a graticule ruled in squares.
(iii) **Determination of Electrophoretic Velocity**

(a) **Location of Stationary Level**

An electrical double layer exists at the cell wall/solution interface. As a result of this double layer the application of an electric field to the system causes a displacement of solution relative to the cell wall. This is the electro-osmotic effect.

Since the solution moves along the cell wall in a closed system, a return flow of solution occurs down the centre of the tube. At some layer, between the axis and cell wall there exists a motionless layer of liquid. The true electrophoretic velocity may only be determined for particles in this stationary layer.

Mattson (52) has shown that, for a tube of cylindrical bore, the stationary layer is at a distance of 0.707 a from the axis of the tube, where a is the tube radius.

The tube radius was determined by measuring the length of a column of a known weight of mercury in the tube.

Knowing the tube radius it was possible to calculate the position of the stationary layer and thus focus the microscope so that only particles in this layer were observed. This was done by focussing the microscope on the inside of the cell wall then, by using the microscope fine adjustment "racking in" a calculated distance.

Due to the fact that the cell wall formed a plano-convex lens which affected the optics of the system, the distance that the microscope was "racked in" was not the simple linear distance between the inside of the
cell wall and the stationary layer. The distance "racked in" was calculated using the formula given by Henry (54):

Racking distance from inside wall to stationary level =

$$\frac{\mu_1 a X}{\mu_3 a + X (\mu_2 - \mu_3)}$$

where $X = 0.293a$, and $\mu_1$, $\mu_2$, and $\mu_3$ are respectively the refractive indices of air, the cell material, and the solution.

(b) Calibration of Microscope Fine Adjustment

Calibration of the microscope fine adjustment was effected by measuring the thickness of a microscope slide of known refractive index. A slide scratched on both sides was used. The microscope was focussed on the scratch on the upper side then on the scratch on the lower side of the slide, and the amount of movement of the fine adjustment noted. The thickness of the slide was determined by means of a screw micrometer accurate to $10^{-4}$ cm. This procedure was repeated several times and the average taken.

(c) Calibration of Eyepiece Graticule

The eyepiece graticule was calibrated using a stage micrometer slide. For the optical system used the side of each ruled square on the graticule corresponded to $56 \mu$.

(d) Experimental Procedure

Before use, the apparatus, with electrodes removed and electrode compartments sealed with B10 stoppers, was cleaned with a freshly reacted
mixture of nitric acid and ethyl alcohol. After thoroughly washing out with hot distilled water, the electrodes were replaced and the apparatus rinsed out with conductivity water. After filling and soaking for 2 hours with conductivity water, the apparatus was drained before filling and soaking with electrolyte solution of appropriate normality for a further 15 minutes. The system was then drained before filling with the suspension to be investigated. Care was taken that no air bubbles should be trapped in the system. After closing both the 2-way tap and the tap above the electrophoresis tube, the tube was aligned correctly by removing the microscope eyepiece and adjusting the tube until it passed centrally through the microscope field of view. The eyepiece was now replaced and the microscope focussed on the stationary layer.

The velocities of 40 particles were then measured and the mean taken. Velocities were determined by measuring the time required for a particle to traverse one square of the eyepiece graticule. In the method used it was necessary to time each particle first with one electrode positive then with the other electrode positive. This was accomplished by the use of two stop watches so that continuous observation of each particle could be maintained for each pair of velocity determinations.

(e) The Determination of Electrophoretic Velocity from Observed Velocities

If \( V_G \) is the velocity of a particle under the influence of gravity alone, \( V_T \) the velocity with the top electrode positive and \( V_B \) the velocity with the bottom electrode positive, then the electrophoretic velocity, \( V_E \),
is given by:

\[ V_T = V_E + V_G \quad \ldots \ldots (1) \]

\[ V_B = -V_E + V_G \quad \ldots \ldots (2) \]

Subtracting equation (2) from equation (1) in order to eliminate \( V_G \) gives:

\[ 2V_E = V_T - V_B \]

which can be written as:

\[ V_E = \frac{1}{2} k \left[ \frac{1}{T_T} - \frac{1}{T_B} \right] \]

where \( T \) represents the time required for the particle to traverse a known distance, i.e., one division of the microscope eyepiece graticule, and subscripts \( T \) and \( B \) refer to electrode polarities; as for \( V_T \) and \( V_B \), \( k \) is a constant for the optical system.
(iv) Materials

(a) Zirconia

The hard granular material was ground up, in an agate pestle and mortar until the particle size was approximately 1-2 μ diameter, boiled in conductivity water and dried at 110°C.

A stock suspension was prepared by shaking 1.26 gm. of solid with 100 ml. of conductivity water.

(b) Electrolyte Solutions

Electrolyte solutions of 10^-2, 10^-3, 10^-4, and 10^-5 N were prepared by dilution of 0.1 N stock solutions.

(c) Suspensions

Suspensions were prepared by adding 0.4 ml. of stock suspension, from a pipette to 100 ml. of electrolyte solution of appropriate concentration. The suspensions were shaken mechanically for not less than one hour before use.
(v) Results

The electrophoretic mobilities of zirconia in conductivity water and pure solutions of sodium chloride, hydrochloric acid and nitric acid have been determined. Electrolyte concentrations of $10^{-2}$, $10^{-3}$, $10^{-4}$, and $10^{-5}$ N were used.

The electrophoretic mobilities have been used to calculate the zeta potentials and hence the electrokinetic charges of zirconia in the above electrolyte solutions.

For the reasons given in Section IV A, (a), results have not been corrected for surface conductance or relaxation effects.

In conductivity water the zeta potential recorded ranged from $-25.7$ mV. to $-32.8$ mV.

Results for pure electrolyte solutions are shown in Table (15), and illustrated in Figs. 14 and 15. In Fig. 14 the electrokinetic potential, $\phi$, is plotted against the logarithm of the electrolyte concentration and in Fig. 15 the charge density, $\sigma'$, is plotted against the logarithm of the electrolyte concentration.

From Figs. 14 and 15 it can be seen that there is a reversal of the sign of the surface charge in pure acids which occurs at $10^{-4}$ N in nitric acid and at $10^{-3}$ N in hydrochloric acid. For sodium chloride solution it can be seen that there is a steadily increasing surface charge with electrolyte concentration.
### TABLE 15

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<thead>
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<th>Concentration</th>
<th>Electrophoretic Mobility</th>
<th>$\mathcal{S}$</th>
<th>$\sigma$</th>
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<td>(mV)</td>
<td>(electrons/cm$^2$)</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>2.69</td>
<td>+37.7</td>
<td>+1.91 x $10^{12}$</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>2.62</td>
<td>+36.4</td>
<td>+5.75 x $10^{12}$</td>
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</table>

#### Nitric Acid

#### Hydrochloric Acid

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<th>Electrophoretic Mobility</th>
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<th>$\sigma$</th>
</tr>
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<td>(Normal)</td>
<td>($\mu$ sec$^{-1}$ volt$^{-1}$ cm.)</td>
<td>(mV)</td>
<td>(electrons/cm$^2$)</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>1.77</td>
<td>-25.5</td>
<td>-1.21 x $10^{11}$</td>
</tr>
<tr>
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<td>0.65</td>
<td>-9.4</td>
<td>-1.40 x $10^{11}$</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>1.99</td>
<td>+28.2</td>
<td>+4.10 x $10^{12}$</td>
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</table>

#### Sodium Chloride

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Electrophoretic Mobility</th>
<th>$\mathcal{S}$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Normal)</td>
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<td>(mV)</td>
<td>(electrons/cm$^2$)</td>
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<td>$10^{-4}$</td>
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<td>1.26</td>
<td>-17.1</td>
<td>-2.54 x $10^{12}$</td>
</tr>
</tbody>
</table>
(vi) Discussion

Charge reversal on metal oxide surfaces by acids has been accounted for by O'Connor, Johansen, and Buchanan (17), (20), (21), in terms of anion exchange with surface hydroxyl groups. They suggested that in addition to the exchange mechanism, the process of physical adsorption also occurs, and that the relative importance of either process depends upon the ions present in solution and in particular upon the presence of hydrogen or hydroxyl ions. Anderson (55), working with thoria, considered the dissociation of surface hydroxyl groups to be equivalent to the adsorption of hydrogen and hydroxyl ions on a giant zwitterion represented by $\text{Th}^+ - \text{O}^-$.

The surface charge variations in the electrolyte solutions investigated can be satisfactorily explained in terms of ion exchange and physical adsorption.

Considering first the cases of hydrochloric and nitric acids. The zeta potential of zirconia in water is negative indicating dissociations of the type:

$$\text{Zr} \quad \text{OH} \quad \text{Zr} \quad \text{OH} \quad \text{Zr} \quad \text{O}^- \quad \text{H}^+$$

Addition of acid initially represses this type of dissociation, then at higher acid concentrations exchange of surface hydroxyl groups with the anions of the acid takes place. At low acid concentrations the surface charge becomes slightly more negative due to an excess of anions.
being physically sorbed from solution onto the stationary side of the
slipping plane. However, as the hydrogen ion concentration increases,
ionisation of hydroxyl groups occurs with subsequent anion exchange, giving
ionised surface compounds of the type:

\[ \text{Zr} + \text{Cl}' \quad \text{and} \quad \text{Zr} + \text{NO}_3' \]

This results, at higher acid concentrations, in an overall positive
surface charge.

It is of interest to note that the isoelectric point of zirconia
occurs at a lower concentration in nitric acid than in hydrochloric acid.
Mattson (23) suggests that anions such as chloride and nitrate are more
covalently bound than the hydroxyl ion and that it is the degree of
dissociation of the complex compounds formed between metal oxide and anion
which determines the isoelectric pH. For nitrate and chloride ions the
difference of isoelectric pH suggests that the nitrate ion is held by a
bond less covalent in character than that holding the chloride ion. This
is in accord with the complex chemistry of these ions where it is generally
observed that a nitrate compound is more ionic in nature than the correspond­
ing chloride compound. This point will be discussed more fully in the
General Discussion.

In sodium chloride solutions the zeta potential at the zirconia
interface shows a slight negative maximum, before becoming less negative
at the higher electrolyte concentrations. However, the surface charge
becomes increasingly more negative as the electrolyte concentration
increases. Anderson (55) in consideration of the case of thoria, explained similar behaviour as due either to the suppression of surface hydroxyl group dissociations or to variations in the position of the slipping plane (both by ionic strength effects), or alternatively because of chloride ion adsorption. Modi and Furstenau (56) suggested that, in the case of corundum, such phenomena were caused by compression of the double layer, whilst O'Connor (21) attributed such behaviour, on corundum, to cation exchange accompanied by the physical adsorption of ions.

In the case of zirconia, the pH of the pure sodium chloride solutions was close to the isoelectric point. As electrophoretic measurements in conductivity water showed, the zirconia surface was negatively charged. This negative charge indicates that cation exchange would be favoured. Hence, it is likely, that cation exchange, together with some degree of physical sorption is the reason for the increase in negative surface charge with increase in sodium chloride concentration.
IV B - TOTAL SORPTION STUDIES ON ZIRCONIA

(a) Sorption from Sodium Chloride Solutions

No sorption from pure sodium chloride solutions, in the concentration range $2 \times 10^{-5}$ to $2 \times 10^{-3}$ N, was detected using the conductivity loss technique. Measured conductances of sodium chloride solutions in equilibria with zirconia were found to be identical with those in the absence of zirconia.

The smallest sorption detectable with reasonable accuracy by this technique, for the system used here, was approximately $10^{15}$ ions/gm. at $10^{-5}$ N equilibrium solution concentration rising to approximately $10^{17}$ ions/gm. at $10^{-3}$ N equilibrium solution concentration. Any sorption by zirconia from sodium chloride solutions was therefore less than such values. (See General Discussion).

(b) Sorption from Hydrochloric Acid Solutions

Sorption from hydrochloric acid solutions in the concentration range $2 \times 10^{-5}$ N to $2 \times 10^{-3}$ was measured by the simultaneous use of potentiometric and conductimetric techniques.

Sorption measurements were carried out on two samples of zirconia which were identical except in particle size. The particle size ranges were:

Sample I: Predominantly 200-500 $\mu$ diameter particles containing appreciable amounts of 20-50 $\mu$ diameter particles.
Sample II: Mainly 400-600 μ diameter particles with very little finer material.

In both cases, before use, the material was washed several times with hot conductivity water followed by drying at 110°C.

Results for both samples I and II are shown in Tables (16), (17), and (18), and illustrated in Fig.16, where \( \alpha \) is the number of chloride ions taken up per gram of zirconia and \( C_E \) is the equilibrium hydrochloric acid concentration expressed in normality. It can be seen that good agreement is obtained between the results obtained by the two experimental techniques. The results for Sample I and Sample II are in a constant ratio over the whole concentration range, which is doubtless a reflection of the fact that the number of available sorbing sites for a given electrolyte is proportional to the particle size.

The sorption of hydrochloric acid is not instantaneous, about two hours being required for equilibrium between solid and solution. The major part of the sorption occurred in a few minutes.

At 25°C the sorption is only partly reversible, this being illustrated in Table 19, where the amounts of chloride ions remaining sorbed after several dilutions of the solution at the end of a sorption run are compared with the amounts sorbed at the corresponding equilibrium concentration during the sorption run.

It was found that all sorbed chloride could be removed by repeated washing with boiling conductivity water. Only after this treatment could
TABLE 16

ZrO$_2$ (Sample I) - HCl

Run I

Weight of Zirconia = 11.54 gm.
Weight of Water = 102.66 gm.

<table>
<thead>
<tr>
<th>Conductimetric</th>
<th>Potentiometric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Concentration $C_0$ (Normal)</td>
<td>Initial Concentration $C_0$ (Normal)</td>
</tr>
<tr>
<td>6.750 x 10$^{-5}$</td>
<td>6.750 x 10$^{-5}$</td>
</tr>
<tr>
<td>1.345 x 10$^{-4}$</td>
<td>1.345 x 10$^{-4}$</td>
</tr>
<tr>
<td>3.827 x 10$^{-4}$</td>
<td>3.827 x 10$^{-4}$</td>
</tr>
<tr>
<td>1.406 x 10$^{-3}$</td>
<td>1.406 x 10$^{-3}$</td>
</tr>
<tr>
<td>2.189 x 10$^{-3}$</td>
<td>2.189 x 10$^{-3}$</td>
</tr>
</tbody>
</table>
TABLE 17

\( \text{ZrO}_2 \) (Sample I) - HCl

**Run II**

Weight of Zirconia = 10.45 gm.
Weight of Water = 119.59 gm.

<table>
<thead>
<tr>
<th>Initial Concentration ( C_0 ) (Normal)</th>
<th>Equilibrium Concentration ( C_E ) (Normal)</th>
<th>Weight of Solution ( V ) (gm.)</th>
<th>( a_{Cl} ) (ions/gm.ZrO(_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.757 ( \times 10^{-5} )</td>
<td>2.074 ( \times 10^{-5} )</td>
<td>119.94</td>
<td>( 4.72 \times 10^{16} )</td>
</tr>
<tr>
<td>8.449 ( \times 10^{-5} )</td>
<td>6.431 ( \times 10^{-5} )</td>
<td>120.65</td>
<td>( 1.40 \times 10^{17} )</td>
</tr>
<tr>
<td>1.710 ( \times 10^{-4} )</td>
<td>1.343 ( \times 10^{-4} )</td>
<td>121.76</td>
<td>( 2.58 \times 10^{17} )</td>
</tr>
<tr>
<td>3.544 ( \times 10^{-4} )</td>
<td>2.913 ( \times 10^{-4} )</td>
<td>124.18</td>
<td>( 4.52 \times 10^{17} )</td>
</tr>
<tr>
<td>7.015 ( \times 10^{-4} )</td>
<td>6.036 ( \times 10^{-4} )</td>
<td>129.04</td>
<td>( 7.29 \times 10^{17} )</td>
</tr>
<tr>
<td>1.068 ( \times 10^{-3} )</td>
<td>9.376 ( \times 10^{-4} )</td>
<td>129.37</td>
<td>( 9.76 \times 10^{17} )</td>
</tr>
<tr>
<td>1.451 ( \times 10^{-3} )</td>
<td>1.287 ( \times 10^{-3} )</td>
<td>129.71</td>
<td>( 1.23 \times 10^{18} )</td>
</tr>
<tr>
<td>2.005 ( \times 10^{-3} )</td>
<td>1.792 ( \times 10^{-3} )</td>
<td>130.21</td>
<td>( 1.60 \times 10^{18} )</td>
</tr>
<tr>
<td>Initial Concentration ( C_0 ) (Normal)</td>
<td>Equilibrium Concentration ( C_E ) (Normal)</td>
<td>Weight of Solution ( V ) (gm.)</td>
<td>( q_{Cl}^{(ions/gm, ZrO_2)} )</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>----------------------------------------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>2.757 ( \times 10^{-5} )</td>
<td>2.374 ( \times 10^{-5} )</td>
<td>119.94</td>
<td>2.65 ( \times 10^{16} )</td>
</tr>
<tr>
<td>8.449 ( \times 10^{-5} )</td>
<td>6.457 ( \times 10^{-5} )</td>
<td>120.65</td>
<td>1.39 ( \times 10^{17} )</td>
</tr>
<tr>
<td>1.710 ( \times 10^{-4} )</td>
<td>1.324 ( \times 10^{-4} )</td>
<td>121.76</td>
<td>2.71 ( \times 10^{17} )</td>
</tr>
<tr>
<td>3.544 ( \times 10^{-4} )</td>
<td>2.917 ( \times 10^{-4} )</td>
<td>124.18</td>
<td>4.56 ( \times 10^{17} )</td>
</tr>
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<td>7.015 ( \times 10^{-4} )</td>
<td>6.053 ( \times 10^{-4} )</td>
<td>129.04</td>
<td>7.16 ( \times 10^{17} )</td>
</tr>
<tr>
<td>1.068 ( \times 10^{-3} )</td>
<td>9.387 ( \times 10^{-4} )</td>
<td>129.37</td>
<td>9.68 ( \times 10^{17} )</td>
</tr>
<tr>
<td>1.451 ( \times 10^{-3} )</td>
<td>1.278 ( \times 10^{-3} )</td>
<td>129.71</td>
<td>1.29 ( \times 10^{18} )</td>
</tr>
<tr>
<td>2.005 ( \times 10^{-3} )</td>
<td>1.801 ( \times 10^{-3} )</td>
<td>130.21</td>
<td>1.53 ( \times 10^{18} )</td>
</tr>
</tbody>
</table>
TABLE 18

ZrO₂ (Sample II) - HCl

Weight of Zirconia = 16.83 gm.
Weight of Water = 119.83 gm.

<table>
<thead>
<tr>
<th>Conductimetric</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Concentration C₀ (Normal)</td>
<td>Equilibrium Concentration Cₑ (Normal)</td>
<td>Weight of Solution V (gm.)</td>
<td>HCl (ions/gm.ZrO₂)</td>
</tr>
<tr>
<td>3.500 x 10⁻⁵</td>
<td>2.780 x 10⁻⁵</td>
<td>120.21</td>
<td>3.10 x 10⁻¹⁶</td>
</tr>
<tr>
<td>7.803 x 10⁻⁵</td>
<td>5.844 x 10⁻⁵</td>
<td>120.69</td>
<td>8.46 x 10⁻¹⁶</td>
</tr>
<tr>
<td>1.628 x 10⁻⁴</td>
<td>1.237 x 10⁻⁴</td>
<td>121.63</td>
<td>1.70 x 10⁻¹⁷</td>
</tr>
<tr>
<td>2.916 x 10⁻⁴</td>
<td>2.287 x 10⁻⁴</td>
<td>123.09</td>
<td>2.78 x 10⁻¹⁷</td>
</tr>
<tr>
<td>5.385 x 10⁻⁴</td>
<td>4.474 x 10⁻⁴</td>
<td>125.99</td>
<td>4.11 x 10⁻¹⁷</td>
</tr>
<tr>
<td>1.072 x 10⁻³</td>
<td>9.459 x 10⁻⁴</td>
<td>132.75</td>
<td>5.99 x 10⁻¹⁷</td>
</tr>
<tr>
<td>1.566 x 10⁻³</td>
<td>1.410 x 10⁻³</td>
<td>139.70</td>
<td>7.80 x 10⁻¹⁷</td>
</tr>
<tr>
<td>2.042 x 10⁻³</td>
<td>1.860 x 10⁻³</td>
<td>147.13</td>
<td>9.58 x 10⁻¹⁷</td>
</tr>
<tr>
<td>Initial Concentration $C_0$ (Normal)</td>
<td>Equilibrium Concentration $C_E$ (Normal)</td>
<td>Weight of Solution $V$ (gm.)</td>
<td>$\alpha_{Cl}$ (ions/gm.ZrO$_2$)</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>---------------------------------</td>
<td>----------------------------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>$3.500 \times 10^{-5}$</td>
<td>$2.773 \times 10^{-5}$</td>
<td>120.21</td>
<td>$3.13 \times 10^{16}$</td>
</tr>
<tr>
<td>$7.803 \times 10^{-5}$</td>
<td>$5.929 \times 10^{-5}$</td>
<td>120.69</td>
<td>$8.10 \times 10^{16}$</td>
</tr>
<tr>
<td>$1.628 \times 10^{-4}$</td>
<td>$1.240 \times 10^{-4}$</td>
<td>121.63</td>
<td>$1.69 \times 10^{17}$</td>
</tr>
<tr>
<td>$2.918 \times 10^{-4}$</td>
<td>$2.265 \times 10^{-4}$</td>
<td>123.09</td>
<td>$2.88 \times 10^{17}$</td>
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<tr>
<td>$5.385 \times 10^{-4}$</td>
<td>$4.472 \times 10^{-4}$</td>
<td>125.99</td>
<td>$4.12 \times 10^{17}$</td>
</tr>
<tr>
<td>$1.072 \times 10^{-3}$</td>
<td>$9.322 \times 10^{-4}$</td>
<td>132.75</td>
<td>$6.65 \times 10^{17}$</td>
</tr>
<tr>
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<td>$1.411 \times 10^{-3}$</td>
<td>139.70</td>
<td>$7.75 \times 10^{17}$</td>
</tr>
<tr>
<td>$2.042 \times 10^{-3}$</td>
<td>$1.862 \times 10^{-3}$</td>
<td>147.13</td>
<td>$9.48 \times 10^{17}$</td>
</tr>
</tbody>
</table>
TABLE 19

Desorption of HCl from ZrO$_2$

<table>
<thead>
<tr>
<th>Equilibrium Concentration (Normal)</th>
<th>Desorption Curve $\alpha_{\text{Cl}}$ (ions/gm. ZrO$_2$)</th>
<th>Sorption Curve $\alpha_{\text{Cl}}$ (ions/gm. ZrO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.0 \times 10^{-3}$</td>
<td>$-</td>
<td>$1.64 \times 10^{18}$</td>
</tr>
<tr>
<td>$2.2 \times 10^{-4}$</td>
<td>$1.38 \times 10^{18}$</td>
<td>$3.8 \times 10^{17}$</td>
</tr>
<tr>
<td>$6.7 \times 10^{-5}$</td>
<td>$1.12 \times 10^{18}$</td>
<td>$1.5 \times 10^{17}$</td>
</tr>
<tr>
<td>$3.6 \times 10^{-5}$</td>
<td>$1.00 \times 10^{18}$</td>
<td>$8.1 \times 10^{16}$</td>
</tr>
</tbody>
</table>
ZrO₂/HCl SOLUTION

LOG₁₀ a₀ (ions/gm)

LOG₁₀ Cₑ

FIG 16

X + o POTENTIOOMETRIC
○ □ △ CONDUCTIMETRIC
○ x SAMPLE I RUN I
□ + SAMPLE I RUN II
△ o SAMPLE II
sorption isotherms be reproduced. This is consistent with the findings of Amphlett (19), in connection with ion exchange on zirconia in more concentrated electrolyte solutions, who found that zirconia after exchange with various anions could be returned to the hydroxy form by treatment with boiling water.

(c) Sorption from Mixed Solutions of Hydrochloric Acid and Sodium Chloride

Sorption from solutions, containing equimolar quantities of sodium chloride and hydrochloric acid, was studied, in the concentration range $2 \times 10^{-5}$ to $2 \times 10^{-3}$ N, with respect to chloride ions, by the simultaneous use of conductimetric and potentiometric techniques.

Sorption runs were carried out as previously described (Section II, (iii)), small additions of a solution containing equimolar quantities of sodium chloride and hydrochloric acid being made to conductivity water in equilibrium with zirconia.

Results were calculated by solution of equations (1), (2), and (3) of Section II.

Calculated values of the equilibrium concentrations of sodium ions were found, within the limits of experimental error, to be the same as the initial concentrations.

Results for zirconia, Sample I, are shown in Tables 20 and 21, and illustrated in Fig. 17 where $a$ represents the number of chloride ions sorbed from solution per gram of zirconia and $C_E$ is the equilibrium hydrogen ion concentration. In Fig. 17 the full curve is the sorption isotherm for pure
hydrochloric acid solutions and the points represent sorption from the mixed solutions.

Since no sorption of sodium ions occurred, in Tables 20 and 21 sorption is expressed in terms of hydrochloric acid sorption.

It can be seen that the sorption of chloride ions is apparently governed by hydrogen ion concentration and not dependent on total chloride ion concentration.

(d) Sorption from Nitric Acid Solutions

Sorption from nitric acid solutions by zirconia, Sample II, in the concentration range $2 \times 10^{-5}$ to $2 \times 10^{-3}$ N was measured by means of the conductivity loss technique.

Results are shown in Table 22 and illustrated in Fig. 18, where $\alpha$ is the number of nitrate ions taken up per gram of zirconia and $C_E$ is the equilibrium concentration of nitric acid expressed in normality.

It can be seen that the results fit a Freundlich isotherm, $\alpha = k_1 C_E^{k_2}$ where $k_1$ and $k_2$ are constants.

As with hydrochloric acid the major part of the sorption process occurred almost instantaneously, with approximately two hours being required for equilibrium between solid and solution to be reached.

The reversibility of the sorption process was similar to that for hydrochloric acid.
(e) **Sorption from Mixed Solutions of Hydrochloric and Nitric Acids**

(i) Sorption of chloride and nitrate ions, by zirconia Sample II, from solutions in the concentration range $2 \times 10^{-5}$ to $2 \times 10^{-3}$ N with respect to hydrogen ions has been studied by the simultaneous use of conductimetric and potentiometric techniques.

After equilibration of a known weight of zirconia with a known weight of conductivity water, additions were made of a stock solution containing hydrochloric and nitric acids in a known concentration ratio. Measurements were then made as previously described (Section II, (iii)).

(ii) **Calculation of Results**

Equilibrium concentrations of hydrogen, chloride, and nitrate ions were calculated by solving the equations:

$$10^2K = C_H \lambda_H + C_{NO_3} \lambda_{NO_3} + C_{Cl} \lambda_{Cl} \quad \text{..... (1)}$$

$$C_H \cdot C_{Cl} = f \text{ (E.M.F.)} \quad \text{......................... (2)}$$

$$C_H = C_{Cl} + C_{NO_3} \quad \text{......................... (3)}$$

as described in Section II.

The solution of these equations, for the case of two anions, is sensitive to small errors in the experimentally measured quantities. This sensitivity was found to be reflected in considerable scatter of the calculated values of equilibrium nitrate ion concentrations, $C_{NO_3}$.
TABLE 20

ZrO₂ (Sample I) - Sodium Chloride/Hydrochloric Acid Solution

Run I

Weight of Zirconia = 10.24 gm.
Weight of Water = 114.83 gm.

Initially: \[ \frac{\text{Concentration H}^+}{\text{Concentration Na}^+} = 1.0 \]

<table>
<thead>
<tr>
<th>Initial HCl Concentration ( C_0 ) (Normal)</th>
<th>Equilibrium HCl Concentration ( C_E ) (Normal)</th>
<th>Weight of Solution ( V ) (gm)</th>
<th>( a_{Cl} ) (ions/gm.ZrO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.771 \times 10^{-5}</td>
<td>1.389 \times 10^{-5}</td>
<td>115.18</td>
<td>2.59 \times 10^{16}</td>
</tr>
<tr>
<td>3.776 \times 10^{-5}</td>
<td>2.793 \times 10^{-5}</td>
<td>115.58</td>
<td>6.69 \times 10^{16}</td>
</tr>
<tr>
<td>7.260 \times 10^{-5}</td>
<td>5.337 \times 10^{-5}</td>
<td>116.27</td>
<td>1.32 \times 10^{17}</td>
</tr>
<tr>
<td>1.359 \times 10^{-4}</td>
<td>1.028 \times 10^{-4}</td>
<td>117.56</td>
<td>2.24 \times 10^{17}</td>
</tr>
<tr>
<td>2.705 \times 10^{-4}</td>
<td>2.116 \times 10^{-4}</td>
<td>120.39</td>
<td>4.17 \times 10^{17}</td>
</tr>
<tr>
<td>5.403 \times 10^{-4}</td>
<td>4.512 \times 10^{-4}</td>
<td>126.50</td>
<td>6.63 \times 10^{17}</td>
</tr>
<tr>
<td>8.289 \times 10^{-4}</td>
<td>7.219 \times 10^{-4}</td>
<td>133.77</td>
<td>8.41 \times 10^{17}</td>
</tr>
<tr>
<td>1.154 \times 10^{-3}</td>
<td>1.015 \times 10^{-3}</td>
<td>143.03</td>
<td>1.17 \times 10^{18}</td>
</tr>
</tbody>
</table>
TABLE 21

ZrO$_2$ (Sample I) - Sodium Chloride/Hydrochloric Acid Solution

**Run II**

Weight of Zirconia = 9.92 gm.
Weight of Water = 121.29 gm.

Initially: \( \frac{\text{Concentration } H^+}{\text{Concentration } Na} = 1.0 \)

<table>
<thead>
<tr>
<th>Initial HCl Concentration ( C_o ) (Normal)</th>
<th>Equilibrium HCl Concentration ( C_e ) (Normal)</th>
<th>Weight of Solution ( V ) (gm.)</th>
<th>( a_{Cl} ) (ions/gm.ZrO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.800 x 10^{-5}</td>
<td>1.471 x 10^{-5}</td>
<td>121.66</td>
<td>2.43 x 10^{16}</td>
</tr>
<tr>
<td>3.679 x 10^{-5}</td>
<td>2.790 x 10^{-5}</td>
<td>122.06</td>
<td>6.60 x 10^{16}</td>
</tr>
<tr>
<td>7.199 x 10^{-5}</td>
<td>5.651 x 10^{-5}</td>
<td>122.80</td>
<td>1.16 x 10^{17}</td>
</tr>
<tr>
<td>1.532 x 10^{-4}</td>
<td>1.246 x 10^{-4}</td>
<td>124.55</td>
<td>2.17 x 10^{17}</td>
</tr>
<tr>
<td>2.925 x 10^{-4}</td>
<td>2.480 x 10^{-4}</td>
<td>127.67</td>
<td>3.45 x 10^{17}</td>
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<tr>
<td>8.022 x 10^{-4}</td>
<td>7.122 x 10^{-4}</td>
<td>140.55</td>
<td>7.68 x 10^{17}</td>
</tr>
<tr>
<td>1.118 x 10^{-3}</td>
<td>1.021 x 10^{-3}</td>
<td>149.93</td>
<td>8.84 x 10^{17}</td>
</tr>
</tbody>
</table>
$ZrO_2/(HCl + NaCl)$ SOLUTION

O RUNI
O RUNII

$\alpha (\text{ions/gm}) \times 10^{-6}$

$\log C_e$

FIG 17
TABLE 22

ZrO₂ (Sample II) HNO₃

Weight of Zirconia = 16.66 gm.
Weight of Water = 125.07 gm.

<table>
<thead>
<tr>
<th>Initial Concentration C₀ (Normal)</th>
<th>Equilibrium Concentration Cₑ (Normal)</th>
<th>Weight of Solution V (gm.)</th>
<th>aₐₙₒ³ (ions/gm.ZrO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.590 x 10⁻⁵</td>
<td>1.411 x 10⁻⁵</td>
<td>125.38</td>
<td>8.12 x 10¹⁵</td>
</tr>
<tr>
<td>4.004 x 10⁻⁵</td>
<td>3.360 x 10⁻⁵</td>
<td>125.86</td>
<td>2.93 x 10¹⁶</td>
</tr>
<tr>
<td>8.125 x 10⁻⁵</td>
<td>6.729 x 10⁻⁵</td>
<td>126.69</td>
<td>6.40 x 10¹⁶</td>
</tr>
<tr>
<td>1.705 x 10⁻⁴</td>
<td>1.437 x 10⁻⁴</td>
<td>128.51</td>
<td>1.25 x 10¹⁷</td>
</tr>
<tr>
<td>3.500 x 10⁻⁴</td>
<td>3.026 x 10⁻⁴</td>
<td>132.34</td>
<td>2.27 x 10¹⁷</td>
</tr>
<tr>
<td>6.500 x 10⁻⁴</td>
<td>5.773 x 10⁻⁴</td>
<td>139.29</td>
<td>3.66 x 10¹⁷</td>
</tr>
<tr>
<td>1.018 x 10⁻³</td>
<td>9.215 x 10⁻⁴</td>
<td>148.85</td>
<td>5.19 x 10¹⁷</td>
</tr>
<tr>
<td>1.328 x 10⁻³</td>
<td>1.215 x 10⁻³</td>
<td>158.01</td>
<td>6.46 x 10¹⁷</td>
</tr>
<tr>
<td>2.031 x 10⁻³</td>
<td>1.873 x 10⁻³</td>
<td>159.06</td>
<td>9.09 x 10¹⁷</td>
</tr>
</tbody>
</table>
However, it was found that calculated values of $C_{\text{Cl}}$ and $C_H$ gave little scatter from linearity when their logarithms were plotted against that of the initial hydrogen ion concentration, $C_H^0$.

i.e. $\log C_{\text{Cl}} = a + b \log C_H^0$

and $\log C_H = f + g \log C_H^0$

The constants $a, b, f, g$, were therefore determined by the method of least squares and hence corrected values of $C_{\text{Cl}}$ and $C_H$ obtained.

Values of $C_{\text{NO}_3}$ were then calculated, using equation (3), from this smoothed data for $C_H$ and $C_{\text{Cl}}$.

To illustrate the method used, complete calculation for sorption by zirconia, Sample II, from solutions containing approximately equal proportions of hydrochloric and nitric acids, is given in Appendix III.

(iii) Results

Results calculated from "corrected" data are presented in Tables 23, 24, and 25, and in Figs. 19, 20, and 21, for solutions containing hydrochloric and nitric acids in the approximate proportions of 1:3, 1:1, and 3:1. $\alpha$ represents the number of anions sorbed per gram of zirconia and $C_E$ is the equilibrium hydrogen ion concentration expressed in normality.

In all cases slight variations in chloride ion to nitrate ion concentrations occurred as sorption proceeded. The limits of the concentration ratios have been indicated on the appropriate figures.
The results show that the relative extent of sorption of chloride and nitrate ions is a function both of hydrogen ion concentration and of anion fraction in solution. The general tendency for relatively greater sorption of the anion present in greater concentration in solution is superimposed upon an increased preference for sorption of chloride ion as the pH of the solution is lowered.
TABLE 23

ZrO₂ (Sample II) - HCl/HNO₃ (1:3)

Weight of Zirconia = 16.14 gm.
Weight of Water = 117.20 gm.

<table>
<thead>
<tr>
<th>Chloride (Normal)</th>
<th>Hydrogen (Normal)</th>
<th>Nitrate (Normal)</th>
<th>Weight of Solution V (gm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.434 x 10⁻⁵</td>
<td>3.532 x 10⁻⁵</td>
<td>4.966 x 10⁻⁵</td>
<td>117.90</td>
</tr>
<tr>
<td>2.813 x 10⁻⁵</td>
<td>7.447 x 10⁻⁵</td>
<td>1.026 x 10⁻⁴</td>
<td>118.64</td>
</tr>
<tr>
<td>5.13 x 10⁻⁵</td>
<td>1.455 x 10⁻⁴</td>
<td>1.968 x 10⁻⁴</td>
<td>119.99</td>
</tr>
<tr>
<td>9.04 x 10⁻⁵</td>
<td>2.786 x 10⁻⁴</td>
<td>3.690 x 10⁻⁴</td>
<td>122.52</td>
</tr>
<tr>
<td>1.766 x 10⁻⁴</td>
<td>5.943 x 10⁻⁴</td>
<td>7.709 x 10⁻⁴</td>
<td>128.84</td>
</tr>
<tr>
<td>2.418 x 10⁻⁴</td>
<td>8.472 x 10⁻⁴</td>
<td>1.089 x 10⁻³</td>
<td>134.30</td>
</tr>
</tbody>
</table>
## TABLE 23 (Cont'd)

### Sorption of Ions

<table>
<thead>
<tr>
<th>Initial Chloride Concentration (Normal)</th>
<th>Initial Nitrate Concentration (Normal)</th>
<th>$\alpha_{\text{Cl}}$ (ions/gm. ZrO$_2$)</th>
<th>$\alpha_{\text{NO}_3}$ (ions/gm. ZrO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.439 \times 10^{-5}$</td>
<td>$4.174 \times 10^{-5}$</td>
<td>$2.20 \times 10^{14}$</td>
<td>$2.83 \times 10^{16}$</td>
</tr>
<tr>
<td>$2.957 \times 10^{-5}$</td>
<td>$8.576 \times 10^{-5}$</td>
<td>$6.38 \times 10^{15}$</td>
<td>$5.00 \times 10^{16}$</td>
</tr>
<tr>
<td>$5.652 \times 10^{-5}$</td>
<td>$1.639 \times 10^{-4}$</td>
<td>$2.34 \times 10^{16}$</td>
<td>$8.25 \times 10^{16}$</td>
</tr>
<tr>
<td>$1.056 \times 10^{-4}$</td>
<td>$3.064 \times 10^{-4}$</td>
<td>$6.96 \times 10^{16}$</td>
<td>$1.27 \times 10^{17}$</td>
</tr>
<tr>
<td>$2.199 \times 10^{-4}$</td>
<td>$6.377 \times 10^{-4}$</td>
<td>$2.08 \times 10^{17}$</td>
<td>$2.22 \times 10^{17}$</td>
</tr>
<tr>
<td>$3.098 \times 10^{-4}$</td>
<td>$8.986 \times 10^{-4}$</td>
<td>$3.41 \times 10^{17}$</td>
<td>$2.74 \times 10^{17}$</td>
</tr>
</tbody>
</table>
TABLE 24

\( \text{ZrO}_2 \) (Sample II) - \( \text{HCl/HNO}_3 \) (1:1)

Weight of Zirconia = 14.09 gm.
Weight of Water = 102.84 gm.

**Equilibrium Concentrations**

<table>
<thead>
<tr>
<th>Chloride (Normal)</th>
<th>Hydrogen (Normal)</th>
<th>Nitrate (Normal)</th>
<th>Weight of Solution V (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 3.436 \times 10^{-5} )</td>
<td>( 6.180 \times 10^{-5} )</td>
<td>( 2.744 \times 10^{-5} )</td>
<td>103.90</td>
</tr>
<tr>
<td>( 5.970 \times 10^{-5} )</td>
<td>( 1.114 \times 10^{-4} )</td>
<td>( 5.170 \times 10^{-5} )</td>
<td>104.71</td>
</tr>
<tr>
<td>( 1.050 \times 10^{-4} )</td>
<td>( 2.032 \times 10^{-4} )</td>
<td>( 9.820 \times 10^{-5} )</td>
<td>106.19</td>
</tr>
<tr>
<td>( 1.690 \times 10^{-4} )</td>
<td>( 3.381 \times 10^{-4} )</td>
<td>( 1.691 \times 10^{-4} )</td>
<td>108.37</td>
</tr>
<tr>
<td>( 2.904 \times 10^{-4} )</td>
<td>( 6.026 \times 10^{-4} )</td>
<td>( 3.122 \times 10^{-4} )</td>
<td>112.78</td>
</tr>
<tr>
<td>( 4.305 \times 10^{-4} )</td>
<td>( 9.183 \times 10^{-4} )</td>
<td>( 4.878 \times 10^{-4} )</td>
<td>118.36</td>
</tr>
</tbody>
</table>
TABLE 24 (Cont'd)

<table>
<thead>
<tr>
<th>Initial Chloride Concentration (Normal)</th>
<th>Initial Nitrate Concentration (Normal)</th>
<th>$\alpha_{\text{Cl}}$ (ions/gm.$\text{ZrO}_2$)</th>
<th>$\alpha_{\text{NO}_3}$ (ions/gm.$\text{ZrO}_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.378 x $10^{-5}$</td>
<td>1.326 x $10^{-5}$</td>
<td>2.50 x $10^{16}$</td>
<td>4.91 x $10^{16}$</td>
</tr>
<tr>
<td>3.283 x $10^{-5}$</td>
<td>3.159 x $10^{-5}$</td>
<td>4.56 x $10^{16}$</td>
<td>6.96 x $10^{16}$</td>
</tr>
<tr>
<td>6.313 x $10^{-5}$</td>
<td>6.075 x $10^{-5}$</td>
<td>8.41 x $10^{16}$</td>
<td>9.37 x $10^{16}$</td>
</tr>
<tr>
<td>1.214 x $10^{-4}$</td>
<td>1.168 x $10^{-4}$</td>
<td>1.43 x $10^{17}$</td>
<td>1.07 x $10^{17}$</td>
</tr>
<tr>
<td>2.892 x $10^{-4}$</td>
<td>2.783 x $10^{-4}$</td>
<td>2.63 x $10^{17}$</td>
<td>9.46 x $10^{16}$</td>
</tr>
<tr>
<td>5.562 x $10^{-4}$</td>
<td>5.352 x $10^{-4}$</td>
<td>4.18 x $10^{17}$</td>
<td>2.94 x $10^{16}$</td>
</tr>
</tbody>
</table>
**TABLE 25**

ZrO₂ (Sample II) - HCl/HNO₃ (3:1)

<table>
<thead>
<tr>
<th>Chloride (Normal)</th>
<th>Hydrogen (Normal)</th>
<th>Nitrate (Normal)</th>
<th>Weight of Solution V (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.767 x 10⁻⁵</td>
<td>4.797 x 10⁻⁵</td>
<td>1.030 x 10⁻⁵</td>
<td>105.61</td>
</tr>
<tr>
<td>7.568 x 10⁻⁵</td>
<td>9.977 x 10⁻⁵</td>
<td>2.409 x 10⁻⁵</td>
<td>106.29</td>
</tr>
<tr>
<td>1.679 x 10⁻⁴</td>
<td>2.213 x 10⁻⁴</td>
<td>5.34 x 10⁻⁵</td>
<td>107.96</td>
</tr>
<tr>
<td>2.904 x 10⁻⁴</td>
<td>3.873 x 10⁻⁴</td>
<td>9.69 x 10⁻⁵</td>
<td>110.22</td>
</tr>
<tr>
<td>5.105 x 10⁻⁴</td>
<td>6.902 x 10⁻⁴</td>
<td>1.797 x 10⁻⁴</td>
<td>114.51</td>
</tr>
<tr>
<td>7.603 x 10⁻⁴</td>
<td>1.038 x 10⁻³</td>
<td>2.78 x 10⁻⁴</td>
<td>119.75</td>
</tr>
</tbody>
</table>

Weight of Zirconia = 14.28 gm.

Weight of Water = 104.93 gm.
### TABLE 25 (Cont'd)

**Sorption of Ions**

<table>
<thead>
<tr>
<th>Initial Chloride Concentration (Normal)</th>
<th>Initial Nitrate Concentration (Normal)</th>
<th>$\frac{a_{Cl}}{\text{ions/gm.ZrO}_2}$</th>
<th>$\frac{a_{NO}_3}{\text{ions/gm.ZrO}_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.360 x 10^{-5}</td>
<td>1.432 x 10^{-5}</td>
<td>2.64 x 10^{16}</td>
<td>1.79 x 10^{16}</td>
</tr>
<tr>
<td>8.655 x 10^{-5}</td>
<td>2.843 x 10^{-5}</td>
<td>4.88 x 10^{16}</td>
<td>1.95 x 10^{16}</td>
</tr>
<tr>
<td>1.901 x 10^{-4}</td>
<td>6.244 x 10^{-5}</td>
<td>1.02 x 10^{17}</td>
<td>4.10 x 10^{16}</td>
</tr>
<tr>
<td>3.253 x 10^{-4}</td>
<td>1.069 x 10^{-4}</td>
<td>1.62 x 10^{17}</td>
<td>4.65 x 10^{16}</td>
</tr>
<tr>
<td>5.675 x 10^{-4}</td>
<td>1.864 x 10^{-4}</td>
<td>2.76 x 10^{17}</td>
<td>3.39 x 10^{16}</td>
</tr>
<tr>
<td>8.394 x 10^{-4}</td>
<td>2.757 x 10^{-4}</td>
<td>4.00 x 10^{17}</td>
<td>-</td>
</tr>
</tbody>
</table>
$ZrO_2/(HCl+HNO_3)$ SOLUTION

\[
\text{HCl conc.} = \frac{0.28}{0.72 - 0.78}
\]

\[
\text{HNO}_3\text{conc.}
\]

○ HCl
○ HNO$_3$

FIG. 19
\( Z = O_2 / (HCl + HNO_3) \) SOLUTION

\[ \frac{HCl \text{ conc.}}{HNO_3 \text{ conc.}} = \frac{0.73}{0.27} - \frac{0.73}{0.22} \]

\[ \text{O HCl} \]
\[ \text{O HNO}_3 \]

Fig. 21

\( \log_{10} C_e \)
(f) Discussion

Sorption by zirconia from solutions of pure and of mixed electrolytes, has been studied. It has been demonstrated that sorption from pure nitric acid solutions is slightly less than that from pure hydrochloric acid solutions. Sorption of sodium ion from solution has not been detected. It has been shown that in solutions of sodium chloride and hydrochloric acid sorption is independent of anion concentration but is pH dependent. For solutions containing both nitric and hydrochloric acids, anion sorption has been shown to depend upon anion fraction and upon pH.

Consideration of the data for total sorption by zirconia from solutions of hydrochloric and nitric acids (Tables 20 and 22) in conjunction with corresponding electrokinetic charge data (Table 15) indicates that, as in the case of magnetite (Section III, (i), (b)), the sorption process must be occurring on regions of the particles reentrant to the electrokinetic slipping plane. This will be discussed in more detail later (See General Discussion).

As already stated (Section IV A, (vi)), O'Connor, Johansen, and Buchanan have treated the surface of metal oxides as possessing amphoteric, ionising, hydroxyl groups which can exchange with either cations or anions in solution. Total sorption measurements on zirconia as described in the present work can be explained on this basis.

Kraus (18) has shown, for zirconia in sodium chloride solutions, approximately 0.1 N, that equal sodium and chloride ion exchange occurs
in the region of pH 7 and that increasing chloride ion exchange accompanied
by decreasing sodium ion exchange is to be expected with decreasing pH and
vice versa with increasing pH. Amphlett (19) has observed similar behaviour
but found the point of minimum sodium chloride exchange to be at pH 9.
Prasad and Doy (57) have demonstrated that if thoria is precipitated from
a solution of its chloride using less than the theoretical amount of alkali,
it will have a greater anion sorption capacity than thoria precipitated using
the theoretical amount of alkali. Thus, it is likely that the results of
Kraus and Amphlett reflect the difference in the modes of preparation of
zirconia. Mattson (23) has shown that zirconia, precipitated by sodium
hydroxide solution, has an isoelectric pH of 6.7. In solutions in the
region of pH 7 surface hydroxyl group dissociation will be at a minimum.
Consequently in this region sorption will be low. Sorption measurements
from pure sodium chloride solutions were made at a pH of approximately 7,
and as expected, sorption was not detected.
Sorption from pure acid solutions can be considered as a simple
exchange of the acid anion with a surface hydroxyl group. The dependance
of the extent of sorption upon pH may be considered to be due to the
promotion, by hydrogen ions, of hydroxyl group ionisation, thus providing
positive sites for anion sorption, by exchange. The number of sites
available for sorption would thus depend upon hydrogen ion concentration.
Superimposed upon this effect would be the effect of the anion being sorbed.
In Section IV A, (vi), it has been suggested that sorbed nitrate ions are
held to the zirconia surface by a bond which is more ionic in character than that which holds the chloride ion. If this is the case then zirconia surfaces in nitric acid solutions would possess a more positive charge than those surfaces in hydrochloric acid. This positive surface charge would, then, tend to reduce the extent of hydroxyl ion dissociation thereby reducing the number of sites available for anion sorption.

Hence the extent of sorption or exchange can be considered to be governed by surface hydroxyl group dissociations, the magnitude of which dissociations depending upon two factors:

(a) Hydrogen ion concentration which promotes surface hydroxyl group dissociation.

(b) The ionic character of the bond between anion and adsorbent which determines the ease with which surface hydroxyl group dissociation may occur.

In addition to this exchange process it is likely that physical sorption will occur to some extent. The exchange process is probably dominant at higher acid concentrations (Section IV A, (vi) ).

For solutions containing both nitric and hydrochloric acids, hydrogen ions will again promote surface hydroxyl group dissociation. However both nitrate and chloride ion sorption would now modify this dissociation.

In solutions containing a preponderance of nitric acid, the sorption of nitrate ions was greater than that of chloride ions until the pH reached approximately 3.2. This was most likely due to a concentration effect
with the larger concentration of nitrate ions making their sorption more probable than that of chloride ions. However at higher solution concentrations the more covalent nature of the bond between zirconia and the chloride ion offsets this concentration effect.

Physical sorption of ions, may, especially at the lower solution concentrations, be important. This would explain the greater sorption of nitrate than of chloride ions from solutions of low concentration containing equal proportions of the two ions. At higher solution concentrations where the exchange process is more important chloride ion sorption again predominated. In fact at these higher solution concentrations nitrate ions were removed from the solid, presumably by exchange with chloride ions. This, again would be a reflection of the more covalent bonding of the chloride ions.

When a predominance of hydrochloric acid was present in solution, the sorption of chloride ions was, at all solution concentrations, greater than that of nitrate ions, with nitrate ions again being removed by exchange with chloride ions at high solution concentrations. Probably the greater chloride ion concentration outweighed the preference for physical sorption of nitrate ions exhibited at low solution concentrations.

From solutions containing sodium chloride and hydrochloric acid, the number of sites available for ion exchange, was again a function of hydrogen ion concentration, but the extent of chloride exchange was only dependant
upon the ionic character of the zirconia-chloride bond, and thus the process was independent of chloride ion concentration. Sodium ion sorption, by exchange, would be negligible in these solutions since acid dissociations of the surface groups would be repressed.

For exchange processes as postulated above, hydroxyl ions, exchanging with anions would combine with hydrogen ions to give water molecules. Thus the exchange sorption of anions in acid solutions would be expected to be, and was found to be irreversible by dilution of the solution.
GENERAL DISCUSSION AND CONCLUSIONS
The work presented in this thesis has been concerned with the behaviour of zirconia and of magnetite in various electrolyte solutions. It has been shown that precipitated magnetite sorbed large amounts of salt from pure salt solutions whereas sorption by zirconia from pure sodium chloride solution was too small to measure. No significant change in solution pH was observed after sorption, nor were any ions from the adsorbent detected in either case. In dilute hydrochloric acid solutions, magnetite released ferrous but not ferric ions into solution. No zirconium ions were detected in solution using Alizarin-S reagent (see Appendix II), after treatment of zirconia with hydrochloric and nitric acids. Considerable sorption, by zirconia, from acid solutions was observed.

Total sorption data have been compared with the electrophoretic data of Anderson (14) for magnetite, and with the electrophoretic data presented in Section IVA,(v) for zirconia.

The variation of electrokinetic charge and potential with solution pH, in the case of magnetite, was treated by Anderson (14) in terms of a basic dissociation of surface hydroxyl groups. The electrokinetic adsorption data was interpreted in terms of a Langmuirian adsorption of hydroxyl ions on positively charged surface sites. The same author (55), in a study of the electrophoretic behaviour of thoria dispersions, considered both acidic and basic dissociations of surface hydroxyl groups to occur and that these processes were equivalent to the adsorption of hydroxyl ions and of hydrogen ions on to a zwitterion form of the surface.
represented by >Th\(^+\) - O\(^-\). The result of application of the Langmuir iso-
therm to adsorption on a surface >M\(^+\) - O\(^-\) is, of course, equivalent to
the application of the law of chemical equilibrium to a heterogeneous
dissociation. Thus, the Langmuir equation for hydrogen ion adsorption
may be written:

\[
\frac{1}{\Theta_H} = 1 + \frac{K}{C_H}
\]

where \(\Theta_H\) is the fraction of negative sites
occupied by hydrogen ions when the concentration near the surface is \(C_H\),
and \(K\) is a constant. Application of the law of chemical equilibrium to:

\[
M + OH \rightleftharpoons M^+ - OH + OH^-
\]
gives:

\[
K_1^1 = \frac{[OH^+][M^+ \cdot OH]}{[M \cdot OH]}
\]

where \(OH^+ = \frac{K}{C_H}\) and the ratio \(\frac{\Theta_H}{1 - \Theta_H}\) measures the equilibrium active mass
ratio \(\frac{[M^+ \cdot OH]}{[M \cdot OH]}\)

i.e. \(K_1^1 = K \frac{H}{C_H} \cdot \frac{H}{1 - \Theta_H}\)

Hence:

\[
\frac{1}{\Theta_H} = 1 + \frac{K}{K_1^1 C_H} = 1 + \frac{K}{C_H}
\]
Anderson (55) used electrokinetic charge data as a measure of adsorption of hydrogen, chloride, and hydroxyl ions by thoria. Effective ionic concentrations near the surface were calculated from bulk solution concentrations, $C_p$, using the Boltzmann expression:

$$C_i(\text{surface}) = C_{iB} \exp \left( -\frac{Z_i e \Phi}{kT} \right)$$

where $Z_i$ is the valency of ion $i$.

Of particular interest here is this author's treatment for solutions of hydrochloric acid. Because of considerable chloride ion adsorption, values of $\Theta_H$ could not be obtained directly from electrokinetic data (these only giving the net charge on either side of the shear plane). It was assumed, however, that the fraction of positive sites occupied by chloride ions was determined entirely by the concentration of chloride ions near the surface. Values of $\Theta_H$ could then be obtained as differences between values of the surface charge in hydrochloric and in sodium chloride solutions at given values of chloride ion concentration near the surface.

However, the present total sorption measurements, on the analogous case of zirconia, have shown that from pure sodium chloride solutions the sorption is negligible, at least relative to the very large sorption from hydrochloric acid solution, and that sorption of chloride ions from solutions containing sodium chloride and hydrochloric acid is a pH dependent function and not determined by chloride ion concentration.

Thus, as stated in Section IVB (f), the zirconia must be regarded
in the hydrated form, take up of chloride ions only occurring after removal of equivalent hydroxyl groups in acid solution. At the natural pH in pure sodium chloride solution hydroxyl group removal, and hence exchange occurs to an extent not measureable. Chloride ion sorption is thus predominantly governed by pH.

None of the total sorption data obtained satisfies a Langmuirian model. This is not surprising for a number of reasons. In the first place, the Langmuir model describes a process occurring on independent sites whereas the processes occurring are thought to involve interdependent sites (see Section IVB (f)).

Probably the most important reason, however, arises from the sorption that must occur on sites on "internal surface regions" (see Section IVB (f)). The effective concentration of ions near the surface cannot then have the same value at all regions, and the expression:

\[ C_i(\text{surface}) = C_{iB} \exp \left( -\frac{Z_e \xi}{kT} \right) \]

will only apply to surface regions where dissociation occurs "across" the relatively non-reentrant electrokinetic slipping surface. It may be noted here that Nancollas and Patterson (58) found that the rate of ion exchange on thoria was controlled by diffusion into the particles.

Sorption from pure salt solutions by magnetite and by zirconia is likely to occur mainly by simultaneous anion and cation exchange. Since, for both adsorbents, the pH values of the salt solutions used were near the
iso-electric points, the magnitude of the exchange, relative to that in acid or alkaline solutions, would be expected to be small. This was found to be so for sorption by zirconia from pure sodium chloride solutions (Section IVB (f)). Indications were that similar behaviour does, in fact, occur on magnetite, where for magnetite, preparation III, sorption from pure sodium chloride solutions was too small to be accurately measureable (Section III,(i),(a)), but a large sorption from hydrochloric acid was indicated (Section III,(ii),(d)). In pure salt solutions, near the iso-electric point, a slight predominance of either cation or anion exchange may be expected; the surface charge depending upon the predominant type of exchange. That only a slight predominance of either cation or anion exchange was occurring was shown by the fact that no significant changes in solution pH was found after equilibrating pure salt solutions with adsorbent. The large sorption by precipitated magnetite, preparations I and II (Section III (i)) is thought to be a reflection on their relatively open porous structures.

The exchange mechanism postulated for sorption on metal oxides, requires that surface hydroxyl groups shall initially be present. The presence of hydroxyl groups on γ-alumina, even after prolonged heating, has been demonstrated by Peri and Hannan (59). Using an infra-red absorption technique they detected the presence of three types of hydroxyl groups which appeared to be ionically bound. That more than one type of hydroxyl group can be present on metal oxides suggests that cation and anion exchange may occur on different sites.
Exchange behaviour on metal oxides can be explained by treating the metal oxide as a gigantic complex compound. Emeleus and Anderson (43) suggested that zirconium can, in solution, form entities such as \[(\text{ZrO}_2)_n \text{Zr(OH)}^2_2\]²⁺. Thus, by analogy, the structure of zirconia in the absence of exchange may be considered to approximate to entities of the form \[(\text{ZrO}_2)_n (\text{Zr(OH)}_2)_m\]°. If an exchanging anion X be present in solution, then reactions such as:

\[
[(\text{ZrO}_2)_n (\text{Zr(OH)}_2)_m]^0 + 2p \text{HX} \rightarrow [(\text{ZrO}_2)_n (\text{Zr(OH)}_2)_m-p (\text{ZrOX}_2)_p]^0 + 2p \text{H}_2\text{O}
\]

can be envisaged, with partial ionisation of the latter entity to:

\[
[(\text{ZrO}_2)_n (\text{Zr(OH)}_2)_m-p (\text{ZrO}_2)_p-q (\text{ZrO})^q_2]^{q+} + qX^-
\]
determining the surface charge. Slight hydroxyl group dissociations of this type would be charge determining in conductivity water. Similar behaviour would occur for cation exchange. Magnetite would exhibit similar behaviour in salt solutions except that complexes would contain approximately equal amounts of exchanged anion and cation, predominance of either form of exchange being small since solution pH showed no significant change after contact with adsorbent.

In solution chemistry, chloride complexes with zirconium are slightly more stable than the corresponding nitrate complexes (60). This is in agreement with the behaviour of zirconia in solutions consisting of pure hydrochloric and nitric acids and their mixtures, where it has been
suggested that total sorption and surface charge phenomena depend upon the relative ionic characters of zirconium-nitrate ion and zirconium-chloride ion bonds (Sections IVA (v), and IVB (e)).

The magnitude of sorption on precipitated magnetite from pure salt solutions parallels the stability of iron complexes with the anions present in these solutions in the cases of chloride, sulphate, and nitrate ions. Here the order of sorption and of stability constants is : $\text{SO}_4^2->\text{Cl}^->\text{NO}_3^-$. Sorption by magnetite from solutions of disodium hydrogen phosphate and of potassium chromate is complicated by the fact that these solutions are, by nature, slightly alkaline. The presence of hydroxyl ions, thus present, would favour cation exchange giving, at low solution concentrations, a less positive surface, and, at higher solution concentrations, a negative surface, as was observed by Anderson (14). Also on dilution of solution in equilibrium with the magnetite, the presence of hydroxyl ions would favour reversibility of the reaction involving anions, and indeed reversibility of the sorption process was observed (Section III,(i),(d)). In the case of the neutral chloride, nitrate, and sulphate solutions, absence of hydrogen and hydroxyl ions in solution prevented reversibility of the sorption process.

It is to be concluded that electrophoretic "adsorption" data merely reflect the charge (which indeed is likely to be a net charge) arising from ions at either side of a relatively non-reentrant slipping surface around a particle. A large number of ions may be sorbed in
the reentrant regions of the particles and these play little part in de-
termining the properties of the interface governing electrophoretic
c particle mobility. The extent of sorption or relative sorbability of
different ions, derived from electrokinetic studies must be considered
with caution, unless taken in conjunction with studies of total sorption,
particularly in any application such as comparison with the corrosion
inhibiting properties of ions (14).

Ion exchange and associated physical sorption gives a satisfactory
explanation of the phenomena occurring at the metal oxide/aqueous
electrolyte solution interface.
APPENDICES
APPENDIX I

(a) Constants

- **e**: Electronic Charge  \( 4.802 \times 10^{-10} \) e.s.u.
- **F**: The Faraday  \( 9.6488 \times 10^4 \) coulombs.
- **k**: Boltzmann's Constant  \( 1.38 \times 10^{16} \) erg.deg.\(^{-1}\)
- **N**: Avogadra Number  \( 6.03 \times 10^{23} \)
- **R**: Gas Constant  \( 1.985 \) cal.deg.\(^{-1}\)mole.\(^{-1}\)
- **π**: 3.142
- **\( \lambda_{Fe^{++}} \)**: Ionic Conductance of Ferrous Ions 56
- **\( \lambda_{H^+} \)**: Ionic Conductance of Hydrogen Ions 349.8
- **\( \lambda_{Cl^-} \)**: Ionic Conductance of Chloride Ions 76.3

(b) Constants for Onsager Limiting Law (61)

At 25°C, the constants in the equation \( \Lambda = \Lambda_o - (A + B \Lambda_o) \sqrt{C} \) are:

- **A** = 60.65
- **B** = 0.2300
- **\( \Lambda_o(\text{HCl}) \)** = 426.16
- **\( \Lambda_o(\text{HNO}_3) \)** = 421.27
- **\( \Lambda_o(\text{NaCl}) \)** = 126.45
APPENDIX I (Contd.)

(c) Viscosity and Dielectric Constant of Water

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Viscosity (Centipoises)</th>
<th>Dielectric Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>1.0559</td>
<td>81.10</td>
</tr>
<tr>
<td>19</td>
<td>1.0299</td>
<td>80.75</td>
</tr>
<tr>
<td>20</td>
<td>1.0050</td>
<td>80.36</td>
</tr>
<tr>
<td>21</td>
<td>0.9810</td>
<td>80.01</td>
</tr>
<tr>
<td>22</td>
<td>0.9575</td>
<td>79.64</td>
</tr>
</tbody>
</table>

(d) Factors for Calculations of Electrokinetic Potential from Electrokinetic Charge

\[ \sigma = \left[ \frac{2N_B \varepsilon kT}{n} \right]^{\frac{1}{2}} \]

for 20°C, with \( \sigma \) in e.s.u./cm.\(^2\), \( N_B \) in ions/cm.\(^3\), \( \varepsilon \) in millivolts:

\[ \frac{e}{2kT} = 1.979 \times 10^{-2} \]

<table>
<thead>
<tr>
<th>Concentration (Normal)</th>
<th>( \left[ \frac{2N_B \varepsilon kT}{n} \right]^{\frac{1}{2}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1 \times 10^{-5} )</td>
<td>( 1.115 \times 10^2 )</td>
</tr>
<tr>
<td>( 1 \times 10^{-4} )</td>
<td>( 3.524 \times 10^2 )</td>
</tr>
<tr>
<td>( 1 \times 10^{-3} )</td>
<td>( 1.115 \times 10^3 )</td>
</tr>
<tr>
<td>( 1 \times 10^{-2} )</td>
<td>( 3.524 \times 10^3 )</td>
</tr>
</tbody>
</table>
APPENDIX II

Spot Tests (62)

(a) Ferrous Iron

Reagent : 0.1% solution of o-phenanthroline in water.

Test : One drop of faintly acid test solution added to one drop of reagent, gives a red colouration in the presence of ferrous ions.

Sensitivity : Concentrations of ferrous ions of $5 \times 10^{-6}$ M detectable.

(b) Ferric Iron

Reagent : 1% solution of ammonium thiocyanate solution in water.

Test : One drop of test solution added to one drop of reagent gives a red colouration in the presence of ferric ions.

Sensitivity : Concentrations of ferric ions of $10^{-6}$ M detectable.

(c) Zirconium

Reagent : 1% aqueous solution of alizarin-S (sodium alizarin sulphonate).

Test : One drop of test solution, acidified with hydrochloric acid, added to one drop of reagent gives a red precipitate in the presence of zirconium ions.

Sensitivity : Concentrations of zirconium ions of $10^{-4}$ M detectable.
APPENDIX III

Least Squares Calculation for Sorption by Zirconia, Sample II, from an Approximately 1:1 Mixture of Hydrochloric and Nitric Acids.

For a dependant variable $y$ and an accurately known quantity $x$, related in the form $y = a + bx$, where $a$ and $b$ are constants, the normal equations for $n$ observations are:

$$\sum y = na + b\sum x$$
$$\sum xy = a\sum x + b\sum x^2$$

See for example Paradine and Rivett (63).

Here $\log C_{Cl}$ is the dependant variable and $\log C_H^o$ the accurately known quantity $x$, where $C_{Cl}$ is the equilibrium chloride ion concentration and $C_H^o$ the initial hydrogen ion concentration.

Computing values of $\sum \log C_{Cl}$, $\sum \log C_H^o$, $\sum (\log C_H^o)^2$ and $\sum (\log C_H^o) (\log C_{Cl})$:

<table>
<thead>
<tr>
<th>$C_H^o$</th>
<th>$C_{Cl}$</th>
<th>$\log C_H^o$</th>
<th>$\log C_{Cl}$</th>
<th>$(\log C_H^o)^2$</th>
<th>$(\log C_H^o)(\log C_{Cl})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$7.845 \times 10^{-5}$</td>
<td>$3.484 \times 10^{-5}$</td>
<td>$-4.105$</td>
<td>$-4.458$</td>
<td>$16.851$</td>
<td>$18.300$</td>
</tr>
<tr>
<td>$2.423 \times 10^{-4}$</td>
<td>$1.014 \times 10^{-4}$</td>
<td>$-3.616$</td>
<td>$-3.994$</td>
<td>$13.075$</td>
<td>$14.442$</td>
</tr>
<tr>
<td>$3.920 \times 10^{-4}$</td>
<td>$1.663 \times 10^{-4}$</td>
<td>$-3.407$</td>
<td>$-3.779$</td>
<td>$11.608$</td>
<td>$12.875$</td>
</tr>
<tr>
<td>$6.766 \times 10^{-4}$</td>
<td>$2.891 \times 10^{-4}$</td>
<td>$-3.170$</td>
<td>$-3.539$</td>
<td>$10.049$</td>
<td>$11.219$</td>
</tr>
<tr>
<td>$1.007 \times 10^{-3}$</td>
<td>$4.424 \times 10^{-4}$</td>
<td>$-2.997$</td>
<td>$-3.354$</td>
<td>$8.982$</td>
<td>$10.052$</td>
</tr>
</tbody>
</table>
APENDIX III (Contd.)

\[ \sum \log C^0 = -21.158 \quad \sum \log C_1 = -23.342 \]
\[ \sum (\log C^0)^2 = 75.488 \quad \sum (\log C^0)(\log C_1) = 83.182 \]

Thus the normal equations are:

\[-23.342 = 6a - 21.158b + 83.182 = -21.158a + 75.488b \]

Solving for \(a\) and \(b\)

\[ a = -0.3962 \quad \text{and} \quad b = 0.9909 \]

Hence the equation of the straight line relationship between \(\log C^0\) and \(\log C_1\) is:

\[ \log C_1 = -0.3962 + 0.9909 \log C^0 \]

Similarly, the equation of the straight line relating \(\log C^0\) and \(\log C_H\) is:

\[ \log C_H = 0.134 + 1.058 \log C^0 \]

Hence "corrected" values of equilibrium hydrogen and chloride ion concentrations were obtained.

For this particular sorption run the "corrected" equilibrium concentrations are shown in Table 24, Section IVB.
REFERENCES

4. Chapman, Phil. Mag., 1913, (6), (25), 475.
References (Contd.)

35. Nicol, Private Communication.
References (Contd.)


46. Hückel, Physik. Z. 1924, (25), 204.


References (Contd.)