

ADSORPTION OF ELECTROLYTES BY OXIDES

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by

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ABSTRACT

The thesis describes the direct measurement of adsorption of electrolytes on some oxide surfaces and electrokinetic measurements made on the same systems.

Oxides with the spinel structure were chosen so that variation of lattice constant and chemical properties could be controlled and the extent of their effects on adsorption examined. A number of spinels were prepared from the pure parent oxides or coprecipitated hydroxides.

The surface areas of some samples of the spinels, prepared for adsorption studies, have been measured by a B.E.T. isotherm method. Propane was used as the adsorbate gas, conveniently giving pressures of the order of 10 cm Hg at solid carbon dioxide temperatures.

The electrokinetic behaviour of two of the spinels, MgAl_2O_4 and NiAl_2O_4 , was studied by the streaming current technique.

Methods of analysing small quantities of solutions of divalent metal electrolytes at low concentration were devised so that the adsorption of these electrolytes could be determined.

The results are less satisfactory than expected; in a number of cases the total cation and anion concentrations did not agree, indicating at least a partial failure of the analytical techniques.

Even within these severe limitations it has been possible to arrive at certain qualitative conclusions. The surfaces of MgAl_2O_4 and NiAl_2O_4 are not chemically inert. Evidence was obtained for the presence of MgCO_3 on an atmospherically aged surface of MgAl_2O_4 , which gave rise to

appreciable concentrations of Mg^{++} in the electrolyte solutions.

$NiAl_2O_4$ had a less soluble surface. Contact between solid and solution always reduced the electrolyte cation concentration; in some cases this was due to precipitation as the hydrated oxide.

The zeta-potential measurements cannot strictly be compared with the adsorption data because leaching alters the state of the oxide surfaces and the pH of the solutions.

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CONTENTS

TITLE PAGE	1.
ABSTRACT	2.
ACKNOWLEDGEMENTS	4.
CONTENTS	5.
SYMBOLS	7.
1. INTRODUCTION	9.
1, i. General	9.
1, ii. Purposes of the work	11.
1, iii. Consideration of practical methods	12.
2. SPINELS	17.
2, i. Properties and structure	17.
2, ii. Review of preparative methods	20.
2, iii. Experimental preparation	21.
3. SURFACE AREA MEASUREMENT	32.
3, i. Review of methods	32.
3, ii. Experimental methods	36.
4. ELECTRIC DOUBLE LAYER	44.
4, i. General	44.
4, ii. Surface ion exchange	54.
4, iii. Zeta-potentials and electrokinetic measurements	56.
4, iv. Experimental determination of zeta-potentials	68.
4, v. Analytical techniques	79.
4, vi. Adsorption measurements	98.

	6.
5. RESULTS	112.
5, i. Surface areas	112.
5, ii. Zeta-potential results	123.
5, iii. Results of adsorption measurements	127.
6. DISCUSSION	142.
7. REFERENCES	156.

SYMBOLS

The following symbols will be used without further definition.
Units are given in the text where they differ from those stated.

a = particle radius, cm.

C = constant.

c = concentration, in g equiv. l^{-1}

d = density, in $g\ cm^{-3}$

e = electronic charge, e.s.u.

K = constant.

k = Boltzmann's constant.

\ln = natural logarithm.

\log = logarithm to the base 10.

M = molecular weight, molarity.

m = milli -

N = Avogadro's number.

n = number of ions per cm^3 (double layer theory); number of moles (surface area measurements).

P = pressure, dynes per cm^2

R = gas constant, ergs per $^{\circ}C$ per mole.

S = surface area, cm^2

T = absolute temperature.

V = volume, cm^3 /

x = distance, cm

z = valency, inclusive of sign.

δ = double layer thickness, cm.

ϵ = dielectric permittivity.

ζ = electrokinetic zeta-potential.

η = viscosity, poises.

H = inverse of double layer thickness, cm^{-1}

μ = micro -

σ = charge density per cm^2

ψ = potential difference between a point in solution near to the surface and a point an infinite distance from the surface.

1. INTRODUCTION

1,i. GENERAL

Much experimental work has been published on the electrokinetic properties of various natural and some synthetic minerals, but no satisfactory general theory has been found for correlating the experimental results with the properties of the solid phase and the ions in solution.

Frequently, the electrokinetic measurements have been used to calculate the extent of adsorption of ions on the surface under consideration; for instance, (1). It must be assumed, in performing these calculations, that there is a general relation between the measured electrokinetic potential and the surface charge and that the surface charge originates from the adsorption of one ion only. The calculated surface charge is that actually on the surface. However, some results recently obtained on non-mineral surfaces indicate that these assumptions are not valid: (2).

There are two reasons for doubting the validity of these assumptions; the exact position of the plane of shear of the electric double layer and the significance of the zeta-potential are unknown, and values of dielectric constant and viscosity of the medium near a charged surface, for which bulk values are used, vary with surface charge density.

Briefly, any electrokinetic measurement consists of the determination of the relative mobility of a solid with respect to a solution. This mobility can be interpreted in terms of a potential difference between the plane of shear of the two phases

and the bulk of solution, viz. the zeta-potential. The zeta-potential can only have significance if this plane of shear is known. There is no independent method of determining this plane, nor is there, in general, any theoretical method of relating zeta to other potentials (e.g. electrode potentials) of the system. The plane of shear has frequently been associated with a certain plane in the model for the electric double layer developed by Gouy (3), Chapman (4) and Stern (5). There is no fundamental reason for this; it is an arbitrary choice and solely a matter of convenience in calculation. Further, there is no fundamental reason for assuming that this plane of shear is independent of factors such as electrolyte concentration and viscosity.

There is a general relation between the net surface charge density and the zeta-potential which is independent of any model or assumption regarding the position of the plane of shear. This is the charge per unit area between the plane of shear and the bulk solution (also it is equal and opposite to the net charge per unit area between the plane of shear and the bulk solid). It is by using such a relation that the adsorption of ions has been calculated. It should be stressed that this value represents the difference between the total cation and the total anion adsorptions within the plane of shear. It is impossible to calculate either of these quantities without resorting to a model for the electric double layer and the associated electrokinetic effects. In view of the uncertainty of the interpretation of electrokinetic measurements and

of the model of the electric double layer, there is no general relation between the net surface charge densities as calculated from the relative mobilities and the true surface charge density or adsorption of ions.

1,ii. PURPOSES OF THE WORK.

One purpose of the present work was to measure, directly, the adsorption of electrolytes on oxide surfaces and to compare the results with those obtained by electrokinetic methods.

A second purpose of this project was to investigate some of the factors affecting the extent of the adsorption. In this respect all previous work has been carried out on individual minerals and synthetic oxides. Comparison of the results for the several oxides is made difficult because not only their chemical constituents but also their crystal lattice structures differ.

The series of oxides known as the spinels was chosen for the experimental investigations. They are compound oxides, e.g. $MgAl_2O_4$, all having the same crystal lattice structure and occur frequently among minerals. Thus, by studying adsorption on several of these oxides, the effect of structural changes, normally present in a series of simple metal oxides, is eliminated from the comparison. Spinel can be readily prepared in a pure form from the parent oxides and in this way lattice dimensions and chemical constitution can be varied in a controlled manner. Hence it is possible to investigate individual rather than overall effects.

The only published work in adsorption and zeta-potentials of materials of the spinel type is that of Anderson (6) and Benton and

Horsfall (7) working with synthetic magnetite.

Several electrolytes, which contained divalent cations that can be incorporated into a spinel lattice, were chosen for the investigation. It was suspected that ion exchange might occur between these cations and divalent lattice ions which latter would then be detectable in the equilibrium solution. Considerable exchange of lattice ions takes place only on fresh precipitates and this has been extensively studied by Kolthoff (8). Only very small and possibly non-equilibrium concentrations of the lattice ions from the spinel would be expected in the electrolyte solutions. Lead salts were also included since from some earlier zeta-potential measurements lead ions appeared to have a high affinity for the surface, yet they cannot occur as lattice ions. Calcium salts were used as a basis of comparison of other electrolytes. Calcium would be expected to be an indifferent ion, the adsorption of which was purely by electrostatic forces. The electrolyte anions, chloride and nitrate were chosen in order to minimise any effect due to specific adsorption of the anion. The former was preferred in the adsorption measurements because it was easier to determine analytically.

1,iii. CONSIDERATION OF PRACTICAL METHODS.

The experimental work consists of three topics which are described together with relevant published data and theoretical considerations. The three topics are: the preparation of the spinels, the determination of surface areas and the measurement of zeta-potentials and adsorption.

The structure of several types of spinel has been briefly reviewed. It was found convenient to describe the structure in terms of an oxygen layer lattice since the oxygen atoms exert a controlling influence on the lattice dimensions.. A number of methods by which a homogeneous mixture of the pure parent oxides might be prepared were tested. Examination of the material after the solid state reaction had been carried out indicated that some of the mixtures were not homogeneous and the methods by which they had been prepared were rejected. A molybdenum sheet element furnace was used to obtain the high temperatures required for the solid state reaction to occur at a satisfactory rate. The fired products were tested for spinel formation by X-ray diffraction and solubility in dilute acids.

The extent of adsorption by a solid from a solution by reason of the electric double layer is related to the surface area of the solid and the volume and concentration of the solution. Hence it was necessary that the surface areas of the spinels be determined. An apparatus was constructed to measure surface areas by means of the Brunauer, Emmett and Teller adsorption isotherm. Propane was used as the adsorbate gas, conveniently giving pressures of the order of 10 cm Hg at the adsorption temperature. This technique has limitations which have been discussed but only comparative values of surface area are required.

As the electric double layer effects constitute the most important part of the work, much consideration has been given to the properties and structure of the electric double layer. Models

of the double layer are discussed and an expression, based on the Gouy model, was derived for the surface charge density at a solid surface.

The various methods of measuring zeta-potentials have been described. A simple form of electro-osmosis cell was constructed but was found to be unsatisfactory and the more sensitive streaming current method was adopted. The streaming current equation was derived and the assumptions regarding surface conductivity considered. The electrokinetic behaviour of two of the spinels, $MgAl_2O_4$ and $NiAl_2O_4$, in a number of electrolyte solutions was studied. The electrolytes, at concentrations between $10^{-5}M$ and $10^{-2}M$, were prepared by dilution of $1M$ stock solutions.

The low concentrations of solutions used in the adsorption experiments, of which, frequently, only small samples were available, meant that many of the simpler analytical techniques could not be used in their usual macro-chemical form. Methods of analysing these small quantities of divalent metal electrolytes at low concentration were devised so that the adsorption of these electrolytes could be determined. At a late stage in the investigation a Cathode Ray Polarograph became available, greatly simplifying the determination of lead, zinc and nickel ions.

A considerable number of adsorption experiments were performed, principally on $MgAl_2O_4$ and $NiAl_2O_4$ spinels. Some preliminary results obtained using spinels prepared at relatively low temperatures suggested that ion exchange might be the principal

mechanism of adsorption. However, further testing on samples sintered at higher temperatures showed that only small amounts of the spinel cations were present in the equilibrium solutions. In the earliest experiments, where only small samples of spinels were available, a number of adsorption tests were performed on each sample. It was discovered that adsorbed ions were not completely removed by washing the sample with distilled water and it was suspected that the state of the surface would no longer be the same. Accordingly, it was decided to use smaller samples of the spinel for only one test each.

The results are less satisfactory than expected; in a number of cases the total cation and anion concentrations did not agree, indicating at least a partial failure of the analytical techniques. Possible causes of failure are considered, low pH readings and the undetected presence of aluminium in the adsorption solutions having very low pH are the most likely, but these cannot explain all the errors. The anion analyses, which were effectively chloride only in all cases, of the final solutions tended to be higher than those of the original solutions and no reasonable explanation of this observation can be offered.

Even within these severe limitations it has been possible to arrive at certain qualitative conclusions. The surfaces of $MgAl_2O_4$ and $NiAl_2O_4$ are not chemically inert. Evidence was obtained which suggested that $MgCO_3$ might be present on an

atmospherically aged surface of $MgAl_2O_4$, which gave rise to appreciable concentrations of Mg^{++} in the electrolyte solutions. $NiAl_2O_4$ had a less soluble surface. Contact between the solid and electrolyte solution always reduced the electrolyte cation concentration; in some cases this was due to the precipitation as the hydrated oxide.

The zeta potential measurements cannot strictly be compared with the adsorption data because the flow of electrolyte through the plug alters the state of the surface. The pH and concentration of the electrolyte in contact with the solid for a zeta-potential measurement are those of the initial solution since sufficient electrolyte is run through the plug to bring this about: in the case of an adsorption experiment these parameters are changed by the adsorption process.

2. SPINELS

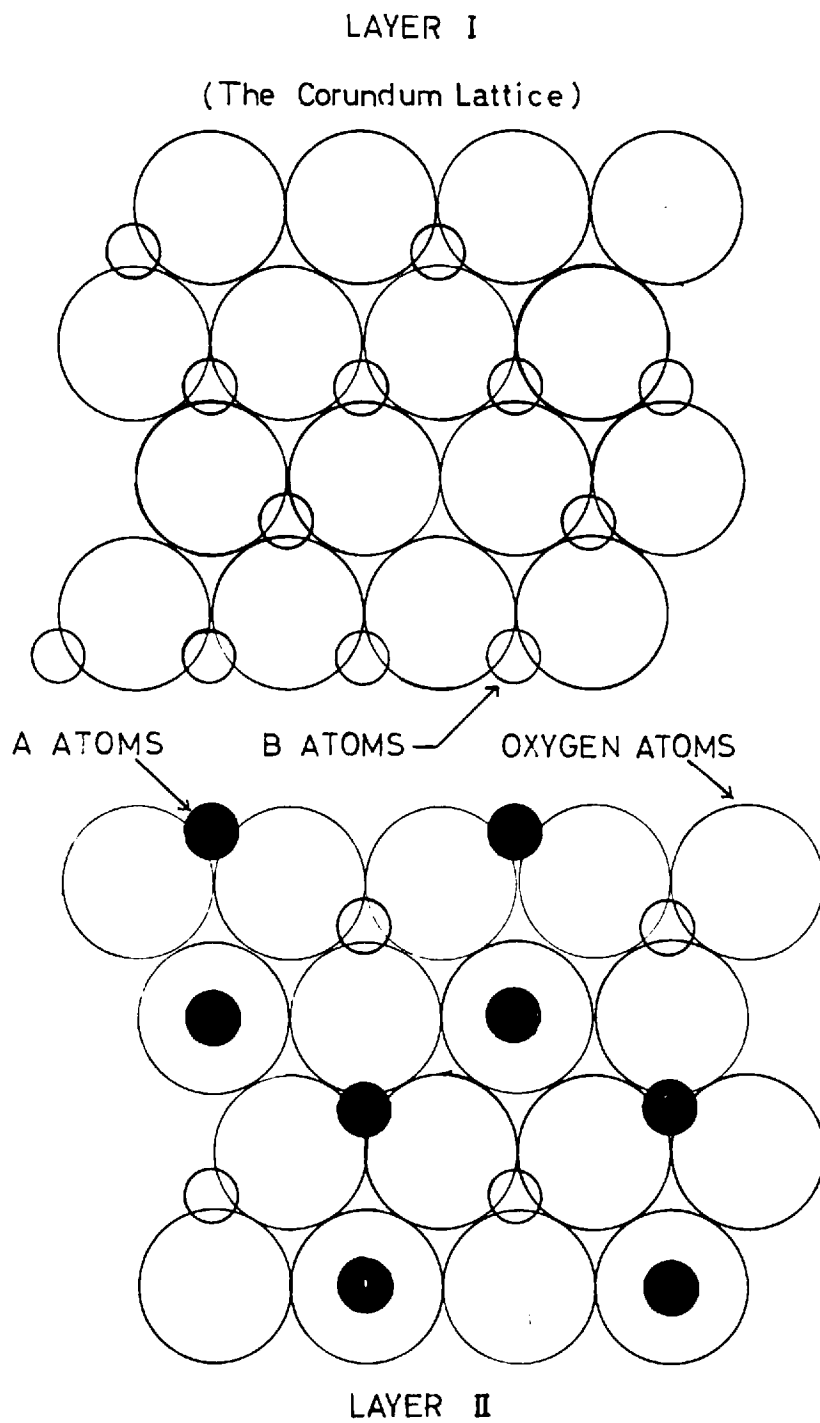
2, i. PROPERTIES AND STRUCTURE.

Spinel is an oxide of general form AB_2O_4 with a well-established crystal structure but many modifications are known. The lattice structure is basically similar to that of diamond, the B atoms occupying the sites of carbon atoms in diamond. In view of the complexity of the spinel crystal lattice, the unit cell contains 32 O atoms, the structure is most conveniently described in terms of a layer lattice. The normal spinel is composed of alternate layers of I (the corundum lattice) and II in Fig. I, which is a projection along a triad axis of the unit cell. The layers are superposed in such a way as to give each A atom four and each B atom six nearest oxygen neighbours and overall cubic close packing for the oxygen atoms.

Certain "inversed" spinels exist in which half the B atoms occupy the tetrahedral lattice sites with the remaining B atoms and the A atoms filling the octahedral lattice sites. Spinel of this type are conveniently represented and distinguished as $B(AB)O_4$ and are exemplified by; $Al^{3+}(Mg^{2+}Fe^{3+})O_4^{2-}$, $Fe^{3+}(Ti^{2+}Fe^{3+})O_4^{2-}$, $Zn^{2+}(Sn^{4+}Zn^{2+})O_4^{2-}$.

Three types of spinel can be obtained depending on the valencies of A and B, viz. A^{2+}, B^{3+} ; A^{4+}, B^{2+} ; A^{6+}, B^{3+} or 2:3, 4:2 and 6:1 spinels. Calculation by Verwey and Hielmann (9) showed that the 2:3 spinels would be most stable in the normal form and 4:2 in the "inversed" form. Experimental evidence bears this out in general, a few 2:3 "inversed" forms are known.

FIG. 1. LAYER PACKING IN SPINELS.



Full details of the structure are given by Wells (10). It is apparent, see Table 1, that the size of the unit cell depends only slightly on A and rather more on B but is mainly governed by the oxygen lattice. The structure is very stable - chemically inert except under extreme conditions.

TABLE 1. LATTICE CONSTANTS OF SOME SPINELS.

All belong to the O_h^7 space group. The length of the side of the unit cell "a" is given in angstrom units.

Type	Formula	a	Formula	a	Formula	a		
2:3	$MgAl_2O_4$	8.090	$MgCr_2O_4$	8.290	$MgFe_2O_4$ (i)	8.342		
			$CdCr_2O_4$	8.59	$CdFe_2O_4$	8.73		
	$CoAl_2O_4$	8.059	$CoCr_2O_4$	8.31	$CoFe_2O_4$	8.36		
					$CuFe_2O_4$ (i)	8.445		
	$FeAl_2O_4$	8.12			Fe_3O_4 (i)	8.37		
	$NiAl_2O_4$	8.045	$NiCr_2O_4$	-	$NiFe_2O_4$ (i?)	8.340		
	4:2	$ZnAl_2O_4$	8.099	$ZnCr_2O_4$	8.323	$ZnFe_2O_4$	8.403	
$CuCo_2O_4$				8.039				
$SnMg_2O_4$				8.58	$SnCo_2O_4$	8.60	$SnZn_2O_4$	8.65
$TiCo_2O_4$				-	$TiZn_2O_4$	8.46		
			$ZnCo_2O_4$	8.108				
1:6	$MoAg_2O_4$	9.26						

(i) indicates "Inversed" 2:3 spinels

2.1.1. REVIEW OF PREPARATIVE METHODS

Considerable data exists on the occurrence of spinels in refractories and slags but only a limited amount is available on their preparation in the pure state without resorting to the addition of mineralizers to increase the rate of conversion from the starting materials. Yamaguchi (11) classified various basic oxides sintered with alumina by the temperature at which conversion to spinel occurred, the spinel being detected by the X-ray powder method. Other workers (12 a-d) have determined the percentage of spinel formed after given times using various methods. That some of these were prepared from fairly coarse material is obvious from the range of their results. The fullest data that can be obtained indicate complete conversion to $MgAl_2O_4$ of a material having a grain size of 0.06 mm. after 10 mins. at 1450°C on a test piece compressed to 10,000 p.s.i.

Dilatorskii (16) gives the colours of several spinels - a useful guide to the degree of conversion. Hild (17) gives a method for the preparation of $ZnAl_2O_4$ and Natta and Passerini (18) for some bivalent cobalt spinels. Methods of preparing spinels containing vanadium (19), gallium (20a-c) and germanium (23) have also been published.

That reactions between solids can take place without the formation of any liquid phase was first demonstrated by Spring (24). Hedvall and his school have made detailed investigations into solid state reactions (25 a-c). Lattice ions near structural defects are less firmly bound than those in the bulk solid and therefore

such ions near the surface are especially active and govern the rate of reaction in the solid state. This occurs to a marked extent during a phase change and the increased reactivity at this stage is known as the Hodvall effect. In the sintering of oxides atmospheric oxygen may exchange with oxide ions near these active sites making these ions especially suitable for initiating the reaction with foreign oxides in a mixture. In addition to this the equilibrium oxygen pressure will determine the stoichiometry of the oxide and hence the number of defects and active sites. Optimum conditions for sintering spinels can, therefore, only be determined after detailed investigation. Although most preparations specify the best time and temperature for conversion, the composition of the atmosphere round the sample is often described in vague terms. Increasing the number of points of contact, by using fine, pressed material, leads to a reduction, often considerable, in both sintering temperature and reaction time (28). The X-ray powder method is used most frequently to determine the extent of spinel formation; other methods that have been used include magnetic spectra (29), radiotracer diffusion (30) and the Hahn emanation method (31).

2.iii. EXPERIMENTAL PREPARATION.

The two stages in the preparation of the spinels were, first, to prepare an intimate mixture of the oxides (or compounds which decompose to the oxides) and second, to carry out the solid state reaction, in which the oxides combined, at high temperatures. The methods used for preparing the intimate mixture were as follows.

Solutions of the nitrates, of known composition, were mixed and evaporated and the solid residues were heated gently to decompose the nitrates. This method proved unsatisfactory because the final stages of the evaporation, under an infra-red lamp, caused spurting and loss of material from the syrupy liquid: only small batches of material could be prepared because of the bulk of the solutions.

The second method tested was to mix the individual oxides in stoichiometric proportions. Analytical Reagent grade oxides were used where available, other oxides were prepared by decomposition of the nitrates where loss of material was of little consequence. The oxides were sieved finer than 200 mesh before weighing and mixing, the mixture was put in a bottle and shaken vigorously before sintering. At the temperatures available with the early furnace this method tended to leave some unreacted metal oxide. With the higher temperatures available in the molybdenum sheet element furnace (Fig. II) reaction appeared to be complete.

A third method tested was to prepare a mixed solution of known composition and to rapidly coprecipitate the hydroxides by addition of aqueous ammonia. Frequently nitrates were used but ammonium aluminium sulphate was used for solutions containing aluminium. The precipitation was carried out rapidly to ensure a homogeneous precipitate. The mixed precipitate was dried, pelleted and fired to the appropriate temperature. Filtering the voluminous precipitate provided the only drawback to this method.

The extent of reaction was estimated, in the majority of cases by the X-ray powder method. Series of X-ray photographs were taken of the individual unfired oxides, unfired mixtures of oxides in stoichiometric proportions and mixtures fired under various conditions. Thus, by comparing the photographs of the individual oxides with the fired and unfired mixtures it was possible to distinguish the main lines of the individual components and the subsequent changes on firing. Under the most favourable conditions the most intense lines of the individual oxides completely disappeared and new ones, corresponding to the various spinels, appeared. This method is sufficiently sensitive to detect less than 5% of unreacted oxides in the mixture. It was hoped that amounts of this order would be contained in the interior of the sintered powders and have no effect on the surface properties of the spinels.

In other cases the solubility in very dilute acid was used to indicate the extent of reaction. The spinels are virtually insoluble in acids whereas any unreacted oxides in the fired mixture, with the possible exception of Al_2O_3 , will be attacked. As only the surfaces of the powder particles were under investigation unreacted material in the interior of the particles was unimportant provided the spinel surface layer was sufficiently thick for the particle to behave as though it were uniform throughout. Thus the reaction was considered to have proceeded to a sufficient extent if acid could not penetrate the outer layer of the particles and leach out considerable amounts of unreacted oxide. Generally,

10^{-3} M hydrochloric acid was used for this test and conductometric measurements or titration with alkali, after about 5 days in contact with the powder, were used to determine the change in concentration. Most of the spinels tested in this way caused a lowering of the acid concentration equivalent to the dissolution of the order of 0.005% of the spinel. This treatment was followed by repeated water washing; the concentration of dissolved electrolyte decreased rapidly but never reached zero. $MgFe_2O_4$ prepared from the parent oxides reacted with the acid very rapidly and no acid was detectable in the solution after 24 hours; presumably the reaction products included Fe_3O_4 and unreacted MgO in large quantities.

Samples of the following spinels were prepared from the mixed oxides for preliminary tests; $MgAl_2O_4$, $MgCr_2O_4$, $MgFe_2O_4$, $NiAl_2O_4$, $ZnAl_2O_4$, $CuAl_2O_4$, $MnAl_2O_4$ and Mg_2TiO_4 . Because of the rapid reaction of the sample of $MgFe_2O_4$ with acid a further sample of this spinel was made from the coprecipitated hydroxides to give a more intimate mixture of the starting materials. This sample proved satisfactory when subjected to the acid leaching test. The samples of $CuAl_2O_4$ and $MnAl_2O_4$ were rejected without further testing on account of their non-uniformity of colour. The sample of Mg_2TiO_4 after a first firing became violet on the outer surface where the reducing atmosphere had penetrated but there was a considerable amount of unreacted material in the interior of the crucible. After mixing

and refiring the lightly compacted mixture under apparently the same conditions as formerly a greyish-green material was obtained. Since the reported colour of Mg_2TiO_4 is violet to black this sample was rejected on the grounds of uncertainty of composition. It is probable that the material was a mixture of the more easily formed $MgTiO_3$ and MgO .

Further tests required the preparation of more material, the higher temperature furnace becoming available at this stage. The methods are detailed below:

$ZnAl_2O_4$. A mixture of zinc and aluminium oxides, finer than 160 mesh, was made up in stoichiometric proportions. Homogeneity was ensured by rotating the bottle containing the mixture for several hours.

A series of six pellets, $\frac{1}{2}$ inch in diameter by 1 inch long, were prepared at pressures ranging from 400 to 2,400 p.s.i. in a Millen Mounting Press. A small quantity of water was used as a binder. The pellets were air dried at $110^\circ C$. The optimum pressure was found to be 1,000 p.s.i. which gave a pellet that remained hard on drying yet without any tendency to bind in the die. The remaining material was made into pellets at this optimum pressure.

The pellets were scraped to remove any iron contamination on their surfaces and fired in air at $1600^\circ C$. Each pellet remained in the hot zone (about 3 inches long) for three hours and was then slowly withdrawn and annealed. The surfaces of the fired pellets were again scraped.

NiAl_2O_4 . The nickel aluminium spinel was prepared by precipitating the hydrous oxides from a solution of nickel nitrate and ammonium aluminium sulphate by the rapid addition of aqueous ammonia. The mixture was dried, lightly pressed and sintered at 1600°C for three hours in air.

MgAl_2O_4 . A series of pellets was prepared for the original spinel by the method used for ZnAl_2O_4 . The optimum pressure was found to be 1200 p.s.i. using a slightly damped mixture of magnesium and aluminium oxides. In view of the higher melting point of this spinel as compared with ZnAl_2O_4 the sintering temperature was increased to $1650\text{--}1700^\circ\text{C}$ for three hours retention in the hot zone of the furnace.

MgCr_2O_4 . To prevent oxidation of the Cr_2O_3 to a complex chromic chromate during the sintering process the effluent "forming gas" from the furnace was passed through the alumina tube used to support the crucibles in the main furnace tube. The ends of the main tube were loosely plugged with a large fireclay crucible above and asbestos wool below. A slightly higher gas flowrate than used for the furnace alone was required to obtain a uniform green product in pellets compressed to 1000 p.s.i. after 3 hours firing. The slow lowering of the crucibles through the furnace had a useful annealing effect in the reducing atmosphere.

The early spinel preparations were carried out in a horizontal tube furnace capable of reaching 1450°C . The recrystallised alumina furnace tube, 2 inches in diameter, was heated by means of

six Crusilite elements fed through a Variac transformer. The measured output power was used as a guide to the temperature attained at equilibrium which was frequently checked with an optical pyrometer.

The main advantage of this furnace was that it could accommodate a 50 ml. crucible, permitting the preparation of large batches of material at a single firing and hence obtaining a uniform product. The lengthy heating up time and limited temperature attainable proved to be the most serious drawbacks.

A molybdenum sheet element furnace (32 a,b), similar to that designed by McRitchie and Ault (34), was adapted for the preparation of further samples of spinels. The general construction can be seen from the diagram, Fig. II. Power was supplied through variable and step-down transformers rated at 6 K.V.A. The heating element consisted of a sheet of molybdenum rolled into a cylinder 1.25 inches diameter connected directly across the output terminals of the transformer. During operation of the furnace, the element was surrounded by an atmosphere of "forming gas", 90% N₂ and 10% H₂ to prevent oxidation.

Temperatures up to 1700°C were obtained with only a modest power input. Fig. III is a temperature/power survey of the furnace. The disadvantages of the earlier furnace were eliminated but the gain was offset to some extent by the limited crucible capacity of 5 ml. To compensate for this and hence ensure a

Key to Figure II

A to F	Flow of casing cooling water.
G	Forming gas input.
H	Forming gas output.
I	Top cap.
J,N,T,V,X	Hollow brass outer casing sections.
K	Conical wedges holding element in contact with M and W.
L	O - ring seals.
M, W	Brass contact cones.
P	Alumina furnace tube.
Q	Molybdenum sheet element.
R	Molybdenum sheet radiation shields.
O	Molybdenum spring clips and spacers.
S	Silica, outer radiation shield.
U	Insulated bushes between casing sections T and V.
Y, Z	Electrical input lugs.

FIG. II. MOLYBDENUM SHEET ELEMENT FURNACE.

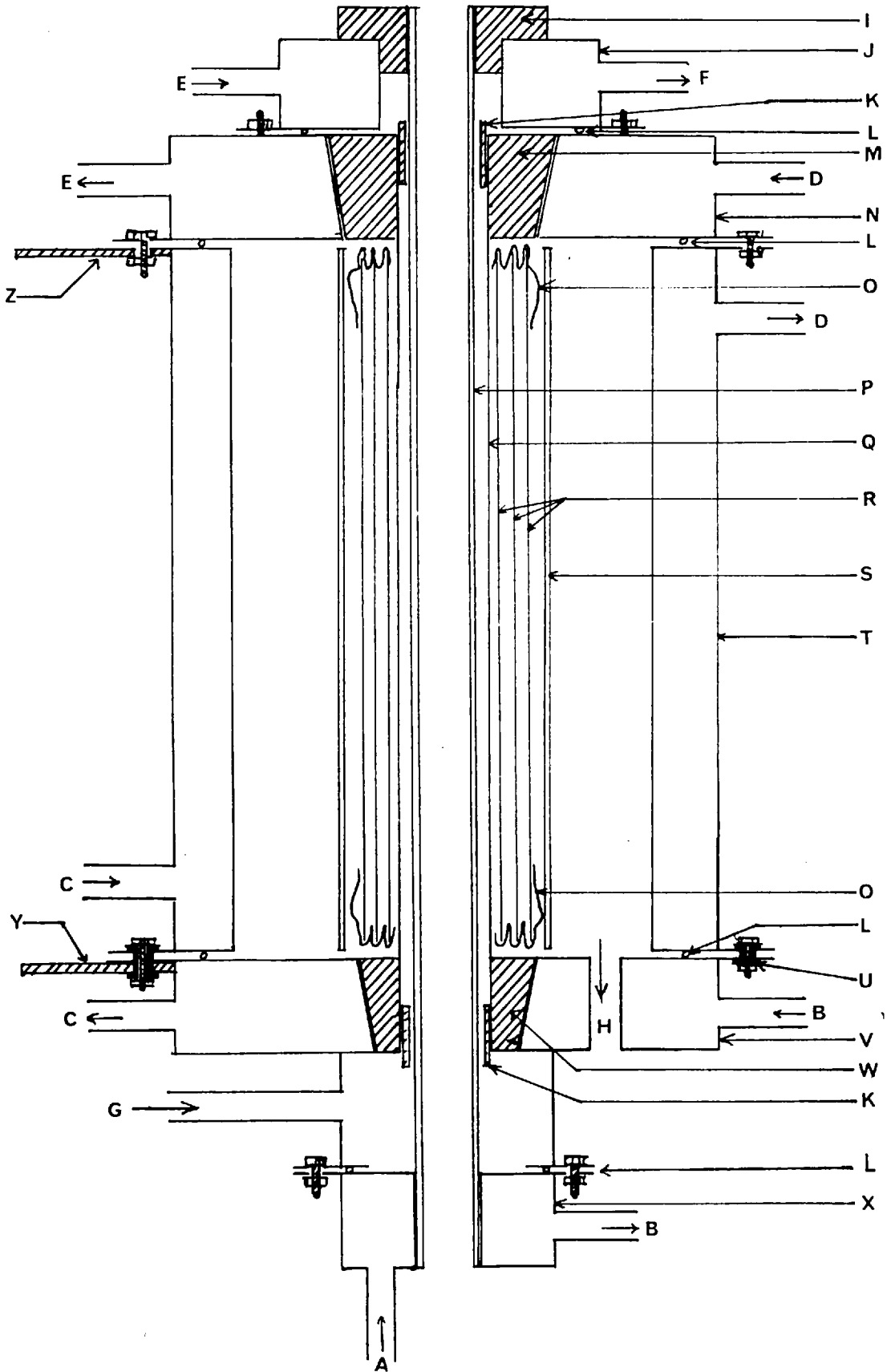
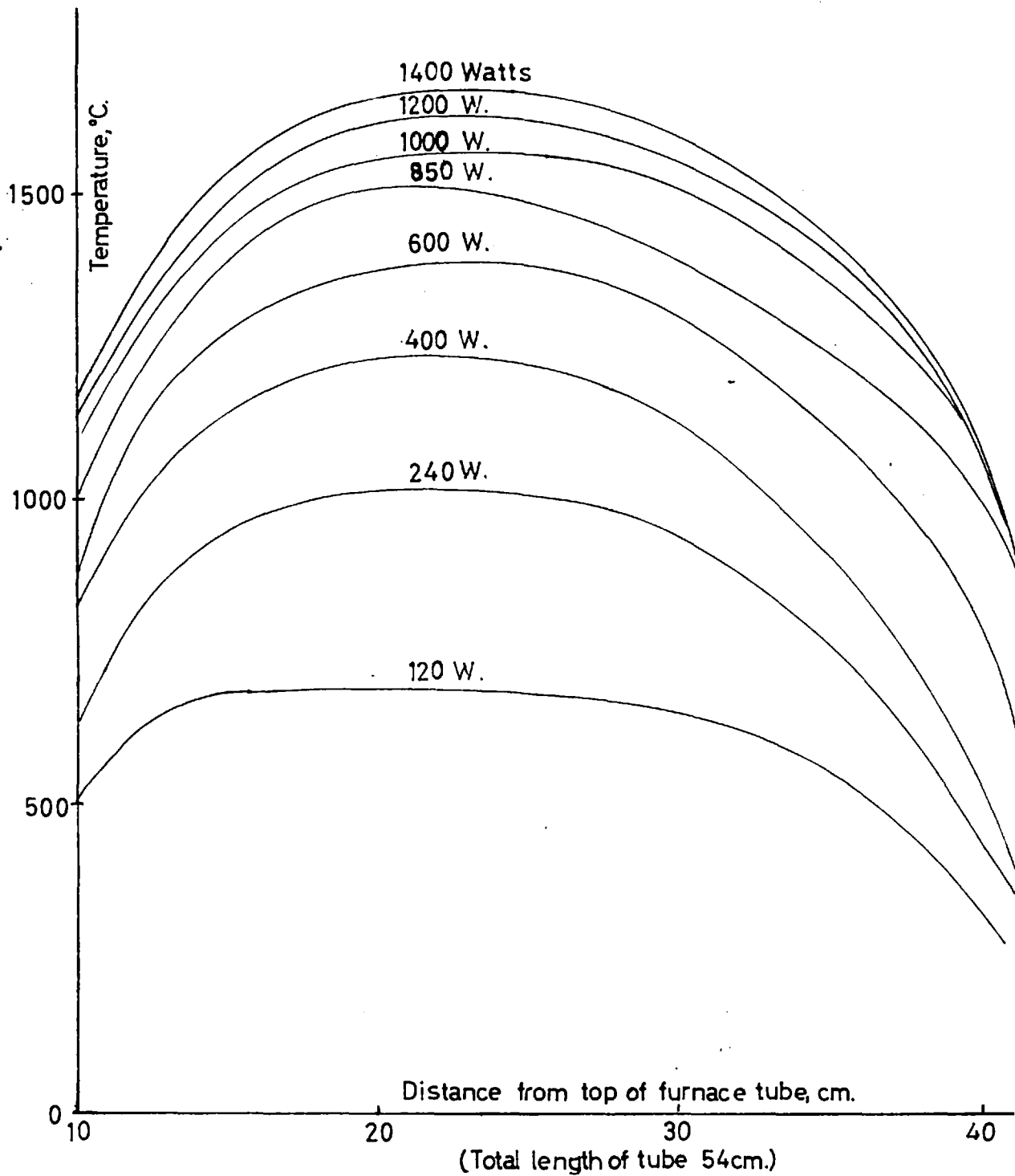


FIG. III. TEMPERATURE/POWER SURVEY OF MOLYBDENUM SHEET
ELEMENT FURNACE.



high degree of uniformity in batch production the furnace was filled with a column of empty crucibles, supported on a $\frac{1}{2}$ inch diameter alumina tube, which were removed at a steady rate from the bottom of the tube once equilibrium was established. Loaded crucibles were simultaneously fed in from the top of the furnace, thus all the contents received the same treatment in their passage down the furnace tube.

3. SURFACE AREA MEASUREMENT

3.1. REVIEW OF METHODS

The extent of adsorption by a solid from a solution by reason of the electric double layer is related to the number of sites for adsorption and the number of ions available to fill those sites or, in other words, the surface area of the solid and the volume and concentration of the solution. These latter two quantities are readily measurable but of the various experimental methods for measuring the surface area of the adsorbent it is necessary to select one which will give the requisite area. It is possible to visualise a solid material containing numerous pores and cracks of varying size. If this material is covered with a monomolecular layer of various adsorbates a measure of its surface area can be obtained. Now if the adsorbate can penetrate the pores and cracks in the solid this internal area will contribute to the total; but if this adsorbate is replaced by a larger molecule certain of the pores and cracks may become impenetrable and no longer add to the measured surface area. Thus, a range of decreasing surface areas could be determined using adsorbates of increasing size.

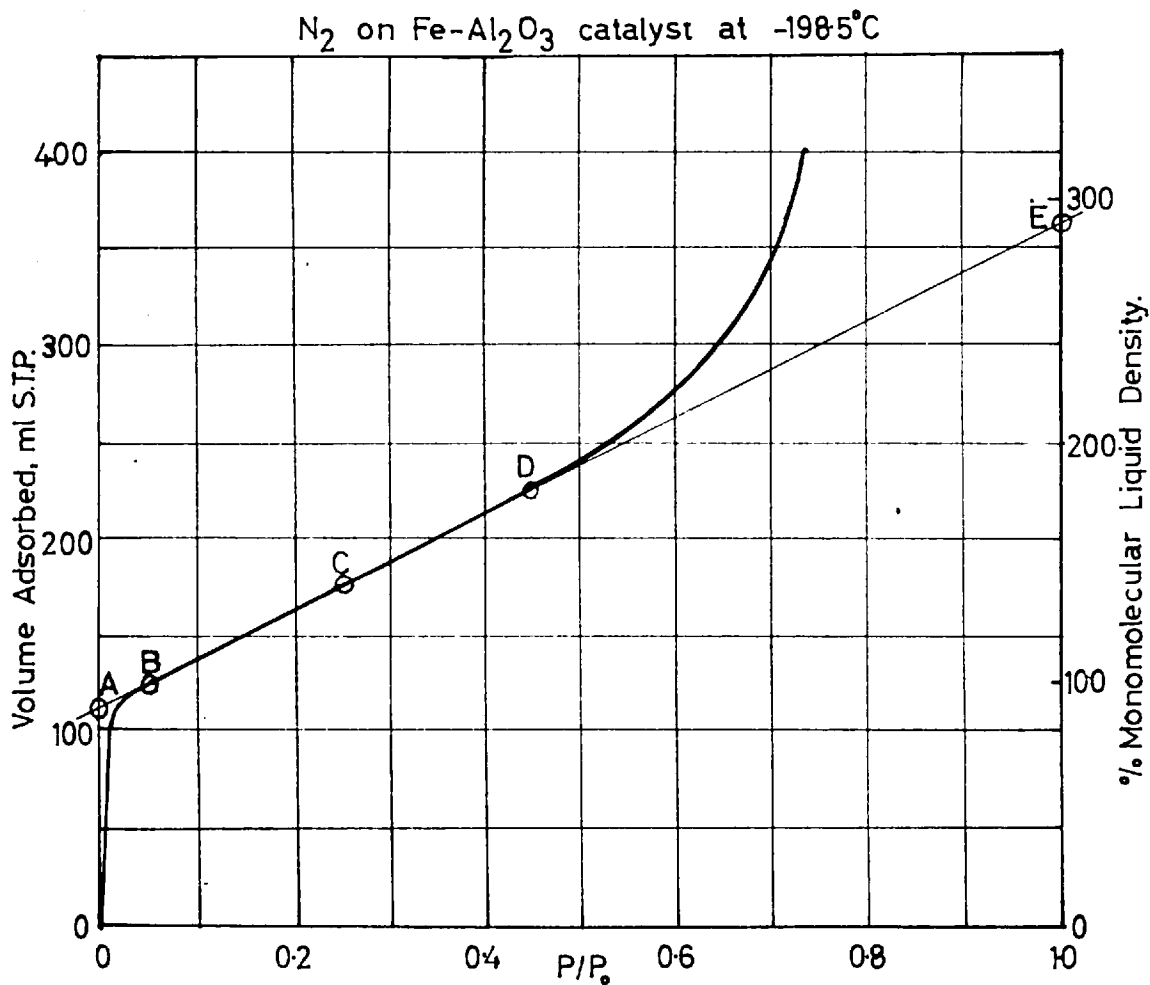
The ideal technique would be to measure the surface area under conditions identical to those of the chosen adsorption system. In cases of adsorption onto a solid from a solution generally, and especially under conditions of low adsorption or surface area, this becomes impracticable as it involves determining very small changes in high solution concentrations. A vapour phase adsorption technique using an adsorbate of similar size to that to be studied in the solution provides a useful alternative.

Early methods of measuring the surface area of powder were generally based on the adsorption from solution of a surface active but chemically inert substance and the estimation of that substance before and after the adsorption experiment. Harkins and Gans (35) used a solution of oleic acid in benzene as their adsorbate solution. Samples of the solution were extracted with alcohol and the oleic acid titrated with NaOH solution. The oleic acid molecules were assumed to be close-packed on the surface and to occupy an area of 20.0\AA^2 , a value based on crystallographic data. The accuracy of this type of method is not very high.

The use of low temperature van der Waals vapour adsorption isotherms was investigated by Brunauer, Emmett and Teller (36 a-d, 40 a) in the early 1930's for determining surface areas. One of their early isotherms is reproduced in Fig. IV and shows the typical S - shape with straight central portion. Surface areas were determined for points A to E; the better reproducibility of point B for a number of adsorbents can be accounted for by its close approximation to the formation of a monolayer. The surface area would be expected to be approximately equal for all gases at a point where the surface is equally covered. This rather empirical approach was soon put on a sound theoretical basis by extending the Langmuir adsorption theory to an infinite number of layers (40 a-c).

From the rates of condensation and evaporation from an infinite number of layers of adsorbed molecules once equilibrium has been attained, an expression was derived for the amount of gas

FIG. IV. EARLY ADSORPTION ISOTHERM OF BRUNAUER, EMMETT & TELLER
(showing points used to calculate surface areas)



required to form a monolayer on the surface. Two assumptions are made: that the energy of adsorption of molecules in the second and subsequent layers is equal to the heat of liquefaction of the adsorbate and that the evaporation and condensation properties of molecules in these layers are the same as in the liquid state.

The isotherm equation then follows

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m} + \frac{C - 1}{V_m \cdot C} \cdot \frac{P}{P_0} \quad 1$$

where P = pressure, V = volume of the gas; P_0 = the saturation vapour pressure; V_m = the volume of gas ^{reduced to N.T.P.} required to form a monolayer and C is a constant. If it is further assumed that the gas is ideal $\frac{V}{V_m} = \frac{n}{n_m}$, where n_m is the total number of moles required to form a monolayer on the adsorbent surface. Then,

$$\frac{P}{n(P_0 - P)} = \frac{1}{n_m C} + \frac{C - 1}{n_m C} \cdot \frac{P}{P_0} \quad 2$$

A plot of $P/n(P_0 - P)$ against P/P_0 should yield a straight line with intercept $1/n_m C$ and slope $(C-1)/n_m C$. If only a limited number of layers can be adsorbed then a modified expression is obtained which for one layer only is the Langmuir type expression

$$P/V = P/cV_m + P/V_m \quad 3$$

and for four or more layers becomes equal to equation 2 which is most applicable for surface area calculations in which P/P_0 lies between 0.05 and 0.35.

Assuming that the average cross-section of the adsorbed molecules is the same as that corresponding to the plane of closest

packing in the solidified gas

$$S = 4 (0.866) (M/4/2 \cdot A \cdot d_s)^{2/3}$$

4

where S = surface area occupied per molecule, M = molecular weight of the adsorbate, A = Avogadro's number and d_s = the density of the solid gas. In many cases the adsorbate is liquid at the temperature of the adsorption and the density of the liquid at this temperature can be substituted for the density of the solid, d_s , with a marked reduction in scatter of the calculated surface areas.

Harkins and Jura (43) developed an absolute calorimetric method of determining the surface area of non-porous powders which did not require any knowledge of the molecular areas. These workers also improved upon the apparatus of Brunauer, Emmett and Teller; the new form of apparatus, Fig. V, gave greatly increased precision and accuracy to the surface area results. Other forms of B.E.T. apparatus have been constructed by Lippens and Hermans (44).

More recent methods of determining surface areas include *use of heats of adsorption of* differential ~~thermal analysis~~ and chromatographic techniques which require complicated and expensive apparatus without any considerable improvement in accuracy over the B.E.T. method; (45 a-d)

3,ii. EXPERIMENTAL METHODS

a) Construction and calibration of the apparatus.

The apparatus is diagrammatically illustrated in Fig. VI and is basically a modified form of the simple apparatus used by Harkins and Jura, Fig. VII. The refined apparatus used by Harkins and Gans incorporated a capillary type mercury cut-off and a pressure

FIG.V. HARKINS' AND JURA'S ADSORPTION APPARATUS

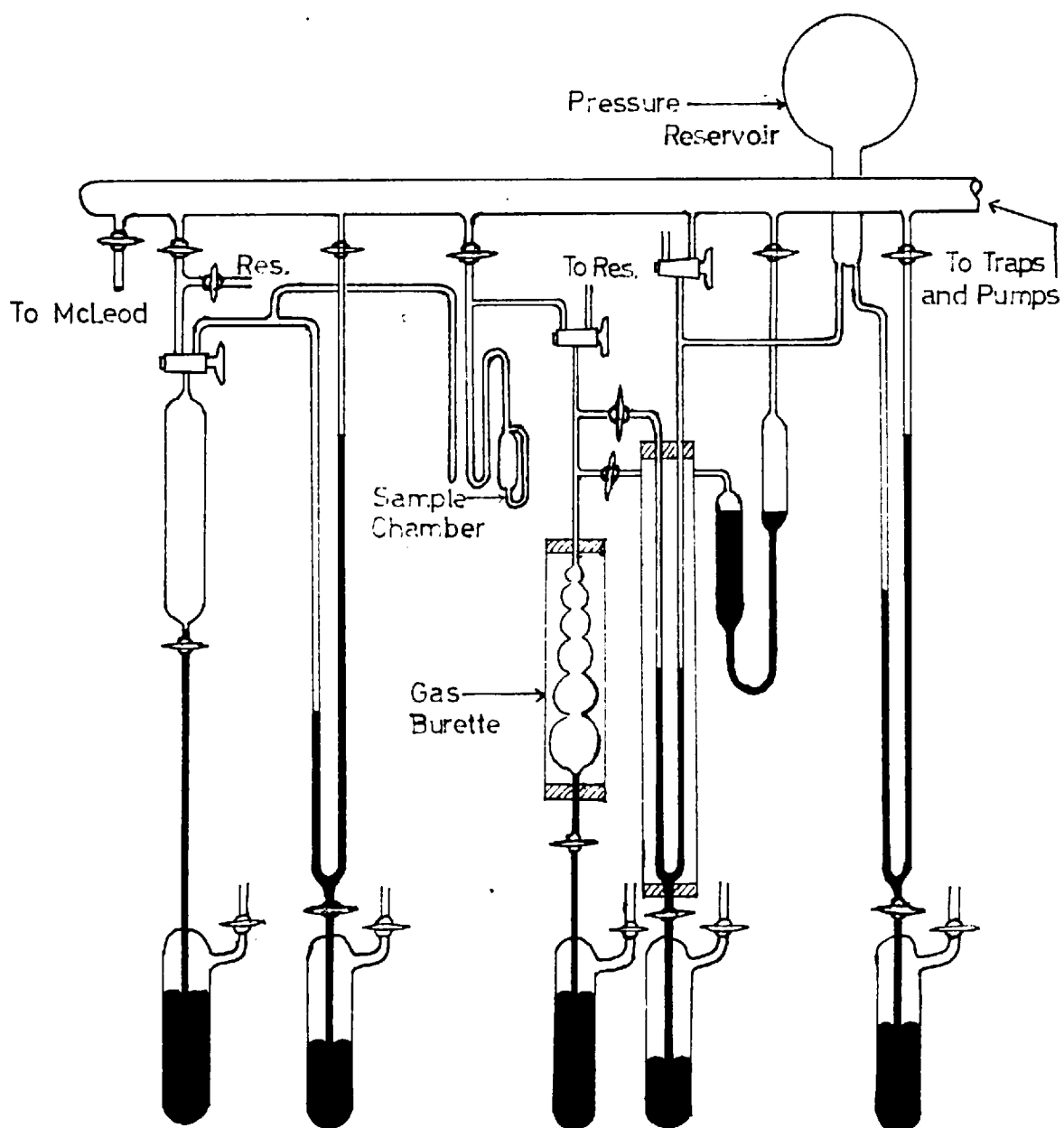


FIG.VI. EXPERIMENTAL ADSORPTION APPARATUS FOR SURFACE AREA MEASUREMENTS.

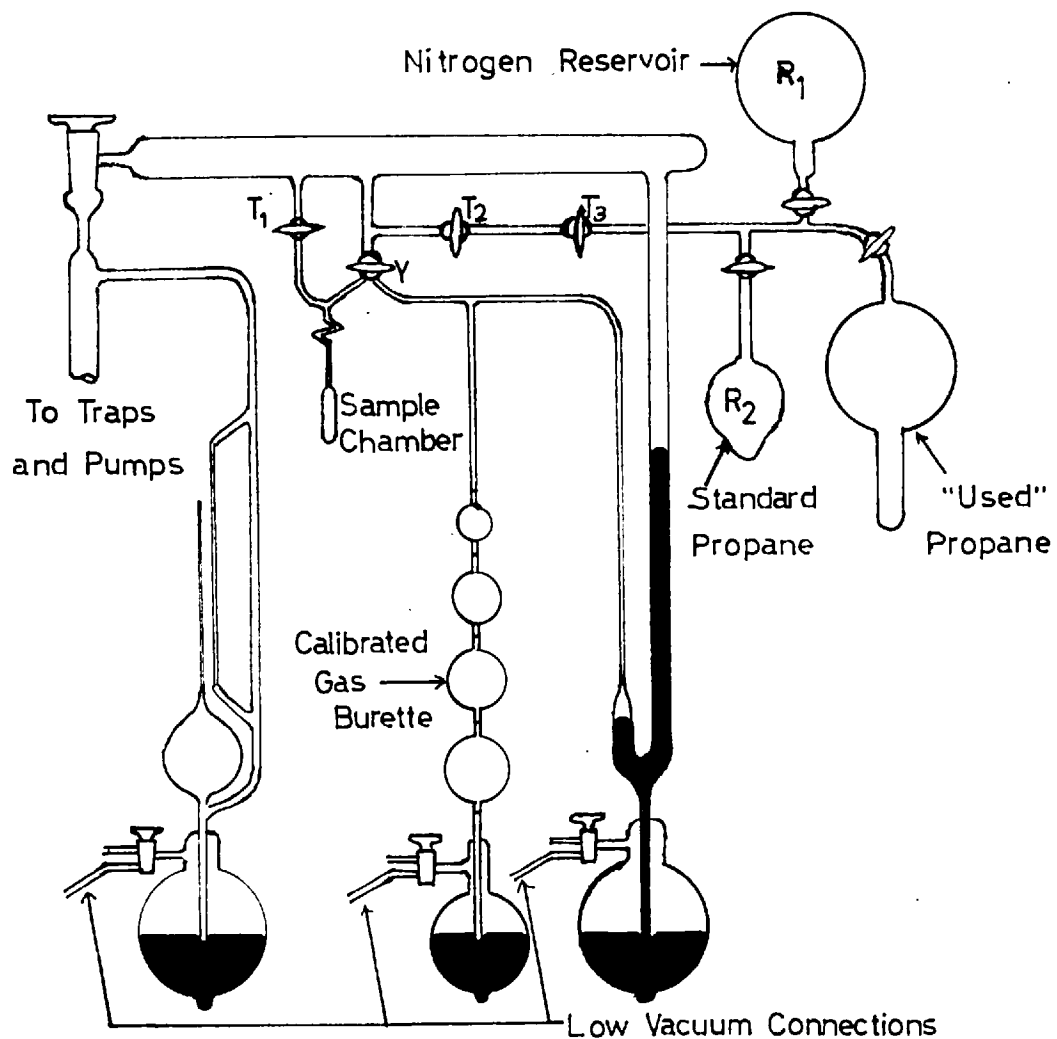
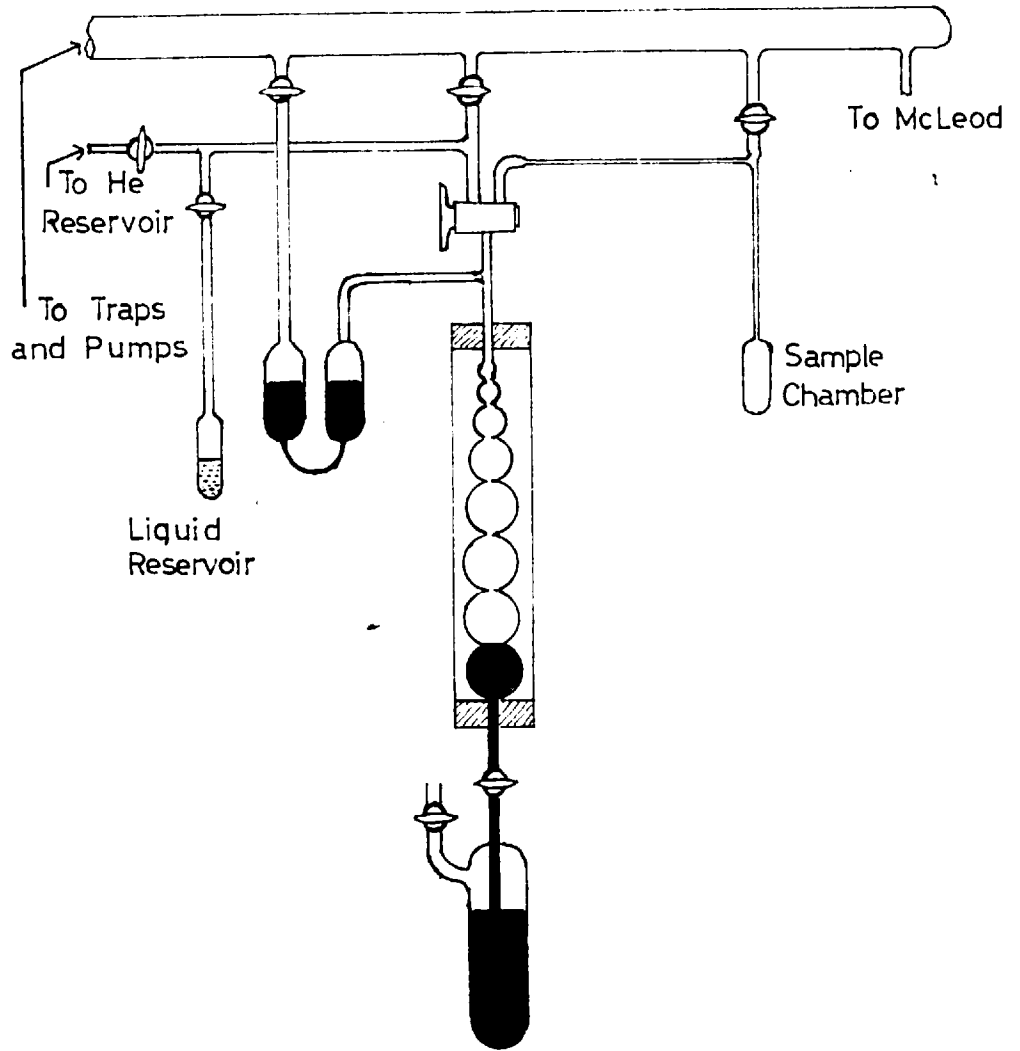


FIG.VII. SIMPLIFIED FORM OF ADSORPTION APPARATUS
USED BY HARKINS AND JURA.



reservoir between the gas burette and high pressure monometer which enabled continuous pressure readings to be made during the adsorption. This feature is absent in the present apparatus but the volume of gas in the adsorption section was held constant by bringing the mercury level to the same fixed lower mark for each pressure measurement.

The actual pressure measurements were taken between the highest parts of the two meniscus. The lower mercury level was adjusted so that the rim of the meniscus coincided with the fixed mark. The manometer arrangement, whereby mercury moves into or out of both limbs simultaneously, rather than from one into the other, was to keep the dead space volume constant and to ensure that both meniscus moved in the same sense, hence making pressure corrections for meniscus height unnecessary. Pressure measurements were found to be considerably affected by the method of illuminating the mercury surfaces. The method finally adopted was to have a pre-focussed torch bulb mounted above and behind the manometer. The light beam was reflected from a small mirror, mounted on an extension arm fitted to the microscope barrel, horizontally across the meniscus into the microscope. This ensured that the angle of illumination remained constant and independent of the mercury level which improved the accuracy and reproducibility of the pressure readings.

The gas burette bulbs were calibrated by weighing the volume of mercury which filled them. Temperature corrections, to the nearest 0.1°C , were applied to the density of the mercury.

b) Operational procedure.

About 8 to 10 g of the dry powder whose surface was required were weighed into a sample holder which was then sealed onto the apparatus and then slowly evacuated, care being taken to avoid loss of material. The sample was degassed by heating at 400°C under vacuum for several hours after which it was isolated from the rest of the apparatus by means of the taps T_1 and Y (see Fig. VI). A cooling bath at -78.5°C , maintained by a solid carbon dioxide / alcohol mixture, was placed about the sample chamber and its level was held sensibly constant throughout the experiment.

A gas is required for calibrating the dead space volumes of the apparatus that will not be adsorbed at the temperature of the sample cooling bath. Nitrogen was used for this purpose and was expanded by stages from reservoir R_1 through taps T_2 and T_3 into the gas burette and manometer dead space. A series of pressure and volume measurements were made and, by applying Boyles Law to these readings, the dead space volume V_m , between the uppermost bulb of the gas burette and the fixed mark on the manometer, was calculated. The gas was then allowed to expand through the tap Y into the sample container. A similar series of pressure and volume measurements were made and the additional dead space above the sample was calculated. The value for V_m is a constant for the apparatus but the additional sample dead space must be repeated for each sample.

Propane was used as the adsorbate: N.C.L. sample stated to be better than 99.9% pure. The choice of gas, and the temperature of the adsorption, was originally dictated by the inadequate supply of liquid nitrogen available (at Liverpool). Some justification can be made for using propane on the grounds that the size of the molecule (4×10^{-8} cm. diameter approximately) is nearer in size to an hydrated cation than either krypton or nitrogen which are the preferred adsorbents (molecular diameters 3.14 and 3.15×10^{-8} cm respectively). Also, the relative areas of different samples were more important than absolute values.

The apparatus was again evacuated and the sample degassed. Two similar series of pressure and volume measurements were made with propane, from reservoir R_2 (Fig. VI). With the gas in the burette and manometer only it was possible to calculate the amount present. When the gas was admitted to the sample container 15 minutes were allowed for equilibrium to be reached and the level of the cooling bath was checked. The amount of gas adsorbed accounts for a lowering of the pressure at a given volume.

All pressure readings were taken for increasing and decreasing pressures. Good agreement was obtained indicating that the adsorption was reversible and without hysteresis.

Various values for the saturated vapour pressure of propane, P_0 , at the adsorption temperature are reported or can be calculated from published data (49, and others). This is due to some extent to uncertainty in the exact temperature maintained by a bath of solid carbon dioxide in alcohol. Some propane was condensed at

liquid nitrogen temperatures into an empty sample tube which was then allowed to warm up to the solid CO₂ bath temperature and the saturated vapour pressure was experimentally measured. It was found to be 111.6 mm Hg at this temperature which is close to one of the reported values (50).

An attempt was made to determine the amount of gas adsorbed by an empty sample container (superficial area about 20 cm²). No significant change in the PV terms occurred with the tube open to the adsorbate. Hence it was not necessary to correct the determined adsorption for adsorption due to the container.

The B.E.T. isotherm plot, equation 2, was performed and using a value for the area occupied per molecule of propane, calculated from equation 4, the surface area of the sample was calculated.

A typical series of results for one of these surface area determinations is given in Chapter 5, i.

4. ELECTRIC DOUBLE LAYER

4,i. GENERAL

a) Origin of charges in the double layer.

Surface ionisation and preferential adsorption of one ion from solution are the mechanisms by which an interfacial charge can arise when a solid is placed in a liquid. These effects can be illustrated by reference to the behaviour of systems containing glass and barium sulphate.

The effects on glass of hydrogen and hydroxyl ions are particularly important.

In $10^{-5}N$ alkali,	ζ increases numerically beyond the value in water by 16 mV.
" $10^{-5}N$ acid,	" decreases " " " " " " 80 mV.
" $10^{-5}N$ K ,	" " " " " " " " 20 mV.

These most reasonable explanation of these observations is that ionisation of silicic acid groups occurs and to a greater extent in alkaline than acid solutions.

Barium sulphate systems preferentially release SO_4^{--} ions leading to a positive zeta-potential. This is equivalent to postulating an excess of vacant lattice sites or interstitial ions, possibly due to defects and dislocations. Such systems are characterised by high sensitivity to heavy metal ions and polyvalent cations. These ions form a Stern layer in which they are strongly bound because of their high polarisation energy.

b) Excess ions in solution.

The electric double layer consists of excess ions (or electrons) present on the surface of the solid phase and an equivalent amount of

ionic charge of opposite sign distributed in the solution phase near the interface. The charge on the solid is treated as a surface charge spread out uniformly over the surface. The space charge in solution is considered to be built up by unequal distribution of ions and the solvent is treated as a continuous medium influencing the double layer only through its dielectric constant.

The Gouy-Chapman theory of the distribution of the ions in solution considers the ions as point charges whilst the Stern theory takes account of their finite volume. This latter theory, in the "specific adsorption potential", also accounts for the possibility that ions may be adsorbed through non-coulombic forces.

c) Potentials in the double layer.

Two extreme examples of the interface between a solid and a solution can be envisaged.

1. The interface is completely polarisable. The potential difference between solid and solution may be altered by the application of an external potential difference to the interface. There is no exchange of charged species between the two phases.
2. The interface permits fully reversible exchange of charged species; it is thus an electrode of a galvanic cell. The potential difference between the two phases may be altered by changing the chemical potential of the exchanging species in the solution.

The most extensively studied example of the first type is the interface between mercury and an aqueous solution. The cell may be envisaged as containing a solution, a mercury electrode and a standard hydrogen electrode. The hydrogen cell is assumed to be

ideally reversible and of so small a surface that its adsorption may be neglected. The mercury electrode is assumed to be completely polarised; that is, no ions from solution can be discharged at it, and the concentration of Hg_2 ions is negligible. Consequently, any charge carried to it by an external potential difference remains on the mercury.

For an example of the second type a similar cell may be envisaged in which the mercury electrode has been replaced by a silver-silver iodide electrode. As opposed to the case of the completely polarisable electrode the potential difference of this cell is not a new variable of the system but is completely defined by the composition of the phases present. It is this type of system which is assumed for the spinel-solution system under investigation.

Both treatments give similar expressions for the change in Gibbs free energy of the interface with change in the aqueous phase in terms of the changes in chemical potential of the species present and in the interfacial potential. The difference is that in the case of the completely polarisable electrode the expression applies to all the species present since none can be discharged whilst for the completely reversible electrode adsorbed lattice ions are not included.

The difference in Galvani potential, $\Delta\psi$, between two phases may be defined as the coulombic work required to transfer a species having unit charge from the bulk of one phase to the bulk of the other phase.

The actual work required to transfer a charged species involves not only coulombic work but also chemical work, since there is a difference in chemical potential between the phases. Neither contribution can be determined or calculated independently for two phases, although it can be done for two regions of the same phase. The actual work done in transferring the charged species is the difference in electrochemical potential, $\Delta \bar{\mu}_i$, and the chemical contribution $\Delta \mu_i$, so

$$\Delta \bar{\mu}_i = \Delta \mu_i + z_i e \Delta \psi$$

$$\text{or } \Delta \psi = \frac{\Delta \bar{\mu}_i - \Delta \mu_i}{z_i e} \quad \underline{5}$$

If a reversible exchange of the species between the two phases is possible then equilibrium can be reached, which corresponds to $\Delta \bar{\mu}_i = 0$ and

$$\Delta \psi = -\Delta \mu_i / z_i e \quad \underline{6}$$

If the charged species ^{are} of the major components of a solid phase (e.g. the cation or the anion of an ionic crystalline material) then small changes in concentration in a solution phase will not influence the chemical potential in the solid. The ^{infinitesimal} finite change in chemical potential, $d(\Delta \mu_i)$, brought about by changing the solution concentration of the charged species is

$$d(\Delta \mu_i) = kT d(\ln c_i) \quad \underline{7}$$

$$\text{hence } d(\Delta \psi) = -kT d(\ln c_i) / z_i e \quad \underline{8}$$

Ions which conform to this treatment are known as potential determining ions and their concentration determines $\Delta \psi$.

As a result of the difference in Galvani potential near the interface there will be an orientation of dipoles and redistribution of ions. The two effects may be formally separated such that

$$\Delta\psi = \chi + \psi_0 \quad 2$$

where χ is the part associated with the solid and oriented dipoles and ψ_0 the part associated with the ionic charges in solution. It is convenient to assume that if no major changes occur in the solution or the solid as a result of altering electrolytes and concentrations in the solution that $d\chi=0$, hence

$$d(\Delta\psi) = d\psi_0 = \frac{kT \cdot d(\ln c_i)}{z_i e} \quad 10$$

The fact that ψ_0 varies with c_i in the same way as the Nernst potential is a direct consequence of the close relationship between ψ_0 and the Galvani potential difference developed above. Within the limits of the assumptions made, definite values can be allocated to ψ_0 because one value can be fixed, viz. $\psi_0 = 0$ at the zero point of charge (χ is still finite and of unknown value).

d) Models of the double layer.

The first model of the double layer was proposed, but not used, by Helmholtz in 1879 (51) but the simple condenser model is contrary to the Second Law of Thermodynamics and will not be considered further.

In 1910 Gouy and Chapman independently presented a new

theoretical treatment in which the distribution of the counter ions around the charged surface is based on the Boltzmann distribution. This gives a picture of the double layer similar to that proposed by Debye and Hückel (52) for the ion atmosphere around simple ions. The model corresponds to an equilibrium between the electrical forces responsible for the maintenance of the electric-double layer and the thermal motion tending to maintain homogeneous distribution of the charges in the bulk liquid. The total excess of counter ions in the double layer is equivalent to the number of charges on the particle surface.

The Boltzmann relation gives the concentration of excess ions at x in terms of ψ , however x is itself a function of ψ ; hence before the distribution can be fully defined the relation between ψ and x is required. The number of each kind of ions in the double layer, at a point where the potential is ψ is given by

$$n_i = n_i^0 \exp(-z_i e \psi / kT) \quad 11$$

where n_i^0 is the number of ions of species i in the bulk solution, far from the surface, where $\psi = 0$.

The excess charge per unit volume of liquid is ρ , where

$$\rho = \sum z_i n_i e.$$

$$\text{or } \rho = e \left[\sum_+ z_+ n_+^0 \exp(-z_+ e \psi / kT) - \sum_- z_- n_-^0 \exp(-z_- e \psi / kT) \right] \quad 12$$

Poisson's equation describes the relation between the potential ψ , which changes from a certain value, ψ_0 , at the

interface to zero in the bulk of the solution, the charge density, ρ , and the distance from the interface.

$$\nabla\psi = \frac{-4\pi\rho}{\epsilon} \quad 13$$

Combining equations 12 and 13

$$\nabla\psi = \frac{-4\pi}{\epsilon} \sum z_i n_i^0 \exp(-z_i e \psi / kT) \quad 14$$

For small values of ψ only the first two terms of the exponential expansion need be considered. This corresponds to $z_i \psi < 25\text{mV}$. and the expression becomes

$$\nabla\psi = \frac{-4\pi}{\epsilon} \sum z_i n_i^0 = \frac{-4\pi}{\epsilon} \sum z_i n_i^0 \cdot \frac{z_i e \psi}{kT} \quad 15$$

On account of the electroneutrality of the solution

$$\sum z_i n_i^0 = 0 \quad 16$$

whence

$$\nabla\psi = \frac{4\pi e^2}{\epsilon kT} \sum n_i^0 z_i^2 \cdot \psi \quad 17$$

which is generally written

$$\nabla\psi = \kappa^2 \psi \quad 18$$

in which

$$\kappa^2 = \frac{4\pi e^2}{\epsilon kT} \sum n_i^0 z_i^2 \quad 19$$

and $1/\kappa$ has the dimensions of length and is known as the double layer thickness since it is the plate separation of an equivalent simple condenser.

The summation term can be further expanded

$$\sum n_i^0 z_i^2 = \sum (n_i^0 z_i) z_i = \frac{c \cdot N_e}{10^3} \sum z \quad 20$$

where $\sum z$ is the numerical sum of the valencies and c is the electrolyte concentration in g. equiv. /l. Equation 19 becomes, for 2:1 electrolytes as used in the experimental work described later,

$$K^2 = \frac{12 \pi e^2 c N}{10^3 \epsilon k T} \quad 21$$

This approximate equation does not hold for large potentials when the complete equation must be used.

By restricting the discussion to an infinitely large plane interface the Laplace operator can be simplified to d^2/dx^2 and an expression for ψ as a function of distance from the surface can be derived.

$$\frac{d^2 \psi}{dx^2} = -\frac{4\pi}{\epsilon} \sum z_i n_i^0 \exp(-z_i e \psi / kT) \quad 22$$

$$2 \cdot \frac{d\psi}{dx} \cdot \frac{d^2 \psi}{dx^2} = -\frac{8\pi}{\epsilon} \sum z_i n_i^0 \exp(-z_i e \psi / kT) \cdot \frac{d\psi}{dx} \quad 23$$

Integration gives

$$\left(\frac{d\psi}{dx} \right)^2 = \frac{8\pi kT}{\epsilon} \sum n_i^0 \left[\exp(-z_i e \psi / kT) - 1 \right] \quad 24$$

applying the boundary condition that for $x = \text{infinity}$, $\psi \rightarrow 0$ and $d\psi/dx \rightarrow 0$.

The condition of electroneutrality of the total double layer requires that the surface charge is equal and opposite to the total space charge in solution. This establishes a relation between the surface charge density, σ , and the surface potential, ψ_0 .

$$\sigma = - \int_0^{\infty} \rho \, dx \quad \underline{25}$$

This can be integrated by using Poisson's expression, 13.

$$\sigma = + \int_0^{\infty} \frac{\epsilon}{4\pi} \frac{d^2\psi}{dx^2} \, dx = - \frac{\epsilon}{4\pi} \left(\frac{d\psi}{dx} \right)_{x=0} \quad \underline{26}$$

Combining equations 24 and 25 we find the full expression

$$\sigma = - \left\{ \frac{\epsilon kT}{2\pi} \sum_i n_i^0 \left[\exp(-Z_i e \psi_0 / kT) - 1 \right] \right\}^{1/2} \quad \underline{27}$$

The Gouy theory, discussed above, has one serious defect. The ions are regarded as point charges with the consequence that if n_i^0 is high and ψ_0 is also high, e.g. 200 mV., absurdly high concentrations near the surface are predicted, demonstrating the non-validity of the theory close to the surface.

Stern based his modified theory on the assumption that close to the fixed charge on the surface there is something like a fixed layer of counter ions at a distance δ , which might be of the order of thickness of a hydrated ion. Between the two layers occurs a linear potential drop. Beyond this first layer of ions the diffuse layer, as in the Gouy theory, extends into the solution and the total thickness is the sum of the extension

of the two layers. Stern's theory also includes allowance for the limited number of adsorption sites on the surface and for the "specific adsorption potential" of the ions which includes the influence of all forces other than those of simple coulombic attraction between the charged surface and an ion.

So far nothing has been said about the potential distribution around a spherical particle. Considering the Debye-Hückel approximation for small potentials, the potential ψ_x at a distance x from the surface of a particle, radius a , is

$$\psi_x = \psi_0 \frac{a}{(a+x)} \exp -\kappa x$$

28

For small particles, the potential falls off more rapidly with increasing distance x than in the case of the flat double layer. In the latter case the potential has decreased to 5% of the value at the surface such that $\kappa x = 3$. So providing $\kappa a \gg 3$ the double layer around a curved surface is the same as that for a flat surface. As κ is rarely less than 10^6 cm^{-1} , particles greater than 300 \AA radius may be regarded as plane surfaces.

In assigning numerical values to the terms in the various equations the assumption must be made that ϵ , the permittivity, has the same value in the double layer as in the bulk solution. When there is a high ionic concentration within the double layer this assumption is open to doubt.

4,ii. SURFACE ION EXCHANGE

Only in the simplest cases is the double layer built up from the ions of a single salt. Generally, several types of ions are present, some of which are contributed by the surface after exchanging with ions from the solution. The exchange of true lattice partners is generally only present to any considerable extent in fresh precipitates making equilibrium phenomena difficult to observe although considerable work on this aspect of ion-exchange has been done by Kolthoff. In Kolthoff's examples exchange was considerable because the surface areas of the precipitates were high and bulk exchange occurred in some cases.

The simplest case of ion-exchange is, theoretically, that for a diffuse Gouy layer in which all specificity except valency can be neglected. The ratios of the concentration of ions of equal valency will be the same in the double layer as in the bulk solution. If one of the cations is divalent and the other monovalent the exchange is greatly shifted towards the divalent cation in places of negative potential and vice versa for anions.

Customarily adsorptions are referred to the solvent and the total cations and anions just compensating the surface charge are considered as belonging to the double layer. However, in ion exchange work it is convenient to consider ions bearing the same charge as the surface as having zero

adsorption and an amount of charge equal to the surface charge is considered exchangeable.

Van Os (53) considered a diffuse double layer at a negatively charged plane surface in equilibrium with a solution containing two salts with monovalent anions. One salt has a monovalent and the other a divalent cation. By applying equation 11 to both salts and multiplying by e the excess of positive over negative charge for the two salts can be calculated. By integrating over the whole double layer the ratio of the two excesses is found to depend only upon the surface potential and the concentration ratio in the bulk solution and not on the absolute concentrations. Especially for high negative potentials the distribution is very much in favour of the divalent cation in the double layer; at a surface potential of about -100 mV and for a ratio of divalent to monovalent cations of 1:10 in the bulk liquid this is increased to 2:1 in the double layer.

In most cases of ion exchange a certain specificity of the ions is observed and the simple Gouy theory is no longer applicable. The Stern double layer theory could perhaps be applied, but because most practical ion exchangers do not rely on surface exchange alone this has not been done. In those ion exchangers where the bulk of the material takes part in the exchange process the specificity is much more marked.

An extreme case might be considered in which all the double

layer is concentrated in the Stern layer an equation of the following type holds for the exchange between monovalent ions

$$\frac{n_1}{n_2} = f \cdot \frac{c_1}{c_2} \quad 29$$

where $f = \exp(\frac{\phi_1 - \phi_2}{kT})$, an expression for the difference in the Stern adsorption potentials ϕ_1 and ϕ_2 of the respective ions. Various modifications to this equation have been suggested for exchange between ions of different valency but neither theoretical derivation nor experimental evidence give sufficient information to choose any particular form.

The pH of the solution can play an important part in ion exchange, especially when the exchanging groups are weak acids or bases. Only when the exchanging groups are strongly acidic can a direct comparison be made between the exchange of metal and hydrogen ions in the diffuse part of the double layer.

4,iii. ZETA POTENTIALS AND ELECTROKINETIC EFFECTS

a) Electrokinetic phenomena and slipping-plane considerations.

Ion exchange is probably the most important practical application of the electric double layer but there are a number of others; Furstenau (54) has shown a high degree of correlation between contact angle, adsorption density, flotation recovery and zeta potential. The only experimental method of investigating the electric double layer is by means of electrokinetic measurements.

Electrokinetic phenomena involve both electricity and a tangential movement of two phases along each other. They may arise from an external electric field directed along the phase boundary and resulting in movement; or from movement of the phases over each other, resulting in an electric field. The first type is exemplified by electro-osmosis and electrophoresis, and the second type by sedimentation and streaming potentials.

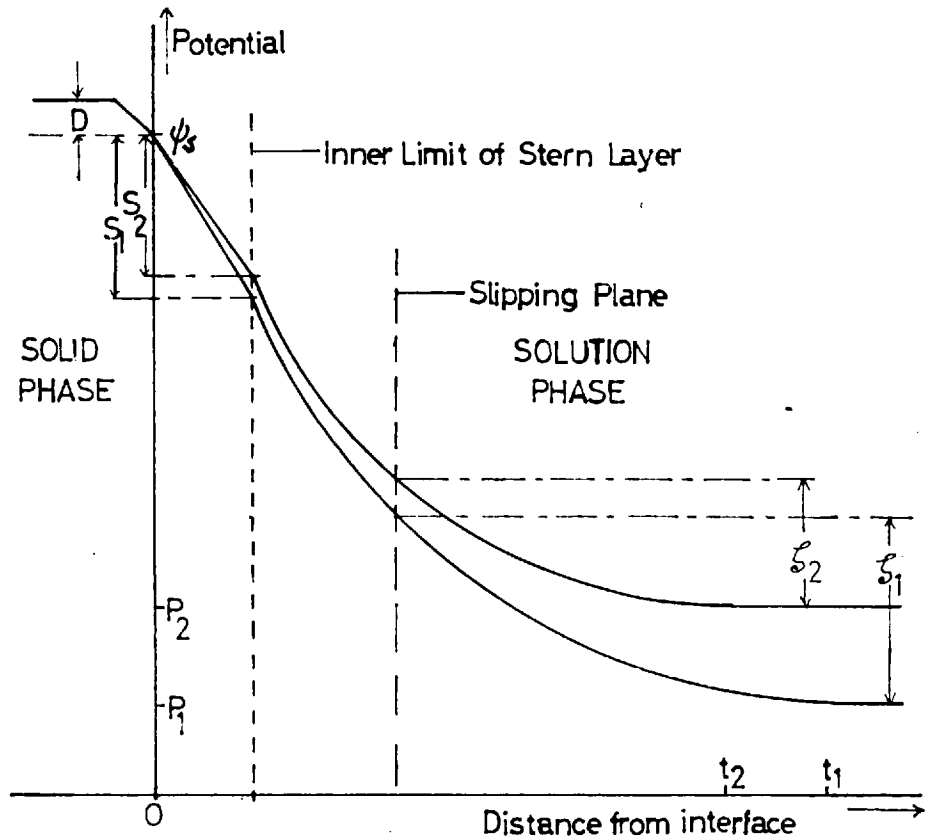
For both kinds of electrokinetic phenomena it appears that the potential in the slipping-plane between the fixed and the flowing liquid is determinative. This potential is called the zeta-potential (ζ).

The slipping-plane does not occur at the physical boundary between the two phases but further out into the solution phase. The potential at this plane must, therefore, always be smaller than the surface potential ψ_0 . Overbeek (55) suggests that the slipping-plane might occur at the junction of the Stern and Gouy layers. For very small concentrations this would lead to the zeta-potential becoming very close to ψ_0 and thus explain that at these low concentrations only potential determining electrolytes have any influence on ζ . At higher concentrations the compression of the Gouy layer would explain the lowering of ζ . Stern adsorption potentials would account for differences between different electrolytes of the same valency type and the

reversal of charge by adsorption of ions. The experimental evidence tends to suggest that the slipping-plane is situated somewhere in the Gouy layer. Also there is no real evidence that the position of the slipping-plane will not change with change in concentration or electrolyte.

That part of the double layer between the particle surface and the slipping-plane will not suffer any distortion when the diffuse double layer is subjected to shear by an external mechanical or electrical force, being firmly held by the electrostatic forces of the particle. A few speculative attempts have been made to elucidate the thickness of this adhering layer. Eversole et al (56 a,b) tried to calculate t (see Fig. VIII) on the basis of electrokinetic data available in the literature. It was assumed that the charge on the particle surface is equal to the total excess charge in the double layer less that part in the sheared-off layer. ζ as well as ψ_δ occur in this equation; the latter is successfully eliminated in terms of ζ for two concentrations, this assumes that both δ and t are unaffected by the change in ionic strength. The t values obtained for monovalent ions vary between 10 and 70 Å, depending on the material and the method of determining ζ . Bickerman (58 a,b) postulated that the fixed layer may be restrained by protrusions on the surface and that this surface roughness would then explain the higher values of t . Kramer and Freise (60 a,b) examined

FIG.VIII.EFFECT OF CONCENTRATION ON THE
DOUBLE LAYER.



P_1, P_2 , potentials of bulk solutions of concentrations c_1 and c_2
where $c_1 < c_2$.

S_1, S_2 , Stern adsorption potentials

t_1, t_2 , thickness of the double layers

ξ_1, ξ_2 , zeta potentials

ψ_s , surface potential, D is due to the double layer
within the bulk solid.

ion exchange resin particles; they found t to vary with the valency of the counterions. In NaCl t was of the order of 10 Å compared with up to 200 Å in $AlCl_3$.

Other attempts to measure t have been made by Derjaguin et al (62 a-h); the method used in all these experiments was based on a direct measurement of the adhering layer between plates, plate and bubble and between two bubbles. The measured thickness need not necessarily be identical with those previously described. The method helps to clarify the idea of a firmly attached multilayer of water molecules and ions on a charged surface. It appears that the surfaces exert a certain force on the surrounding liquid and ions but it is difficult to say anything definite about the true cause of the observations. The static effects can be ascribed to the pressure of the electric double layers but it is not clear to what extent the molecules surrounding the charged solid are immobilized.

Grahame (70) has shown that ions within the slipping plane lose all or part of their hydration shells by reason of their close proximity to the surface. In addition some other ions, not in direct contact with the surface, are included; these ions probably have their crystalline hydration form, given by the Goldschmidt co-ordination number as shown by Bernal and Fowler (71). Some ions of this latter type may, further from the surface, take on part of the hydration shells of the "bound"

ions. These various hydration states finally merge into the bulk form of the ions.

b) Derivation of the streaming current equation.

The relations between the electrokinetic phenomena and the zeta-potential can be derived without any exact structural knowledge of the electric double layer other than the potential distribution as developed by Stern.

When liquid is forced through a porous plug by an external pressure a potential difference, the streaming potential, is set up across the ends of the plug. If the ends of the plug, or rather the electrodes between which the plug is contained, are shorted together the streaming current flows through the short circuit in preference to the liquid. In practice, this short circuit is replaced by a low resistance galvanometer as in the experimental technique discussed in 4,iv.

Consider the flow of liquid through a single capillary of length l and radius a , large compared with δ , the thickness of the double layer.

A potential E_s volts is generated by the liquid flow in the electric double layer near the wall of the capillary. Providing the flow is laminar its profile is parabolic and is given by the classical equation for laminar flow:

$$v = \frac{P}{4\eta l} (a^2 - r^2)$$

where in the tube, at any distance r from the centre, the linear velocity of flow of the liquid, of viscosity η , is

v , under the pressure P .

By differentiation, the velocity gradient at and very close to the wall is:

$$\left(\frac{dv}{dr}\right)_{r=a} = -\frac{P \cdot a}{\eta \cdot 2 \cdot l} \quad 31$$

Provided the electric double layer is thin in comparison with a , the velocity at any distance $x = a - r$ from the wall of the tube is given by

$$v = \int_0^x \left(\frac{dv}{dx}\right)_{x=0} dx = \frac{Pax}{2\eta l} \quad 32$$

Provided η is constant within the double layer. A similar equation, with a different value of dv/dx , will be true of flow in the laminar sublayer near the wall even if the flow is so fast as to be turbulent elsewhere. The theory, therefore, remains valid if the ionic double layer lies within this laminar layer. Since by definition the charge carried per second by the liquid, the streaming current I_s , is

$$2\pi a \int_0^a \rho \cdot v \cdot dx \quad 33$$

Substitution of ρ from Poisson's equation and of v from equation 32 gives

$$I_s = -\frac{Pa^2}{4 \cdot l \cdot \eta} \int_0^a D \frac{d^2 \psi}{dx^2} \cdot x \cdot dx. \quad 34$$

If D is also independent of x , i.e. independent of the

presence of the electric double layer, integration by parts gives

$$I_s = -\frac{PDa^2}{4\eta l} \left\{ \left[x \cdot \frac{d\psi}{dx} \right]_{x=0}^{x=a} - \left[\psi \right]_{x=0}^{x=a} \right\} \quad 35$$

and, since $d\psi/dx = 0$ and $\psi = 0$ when $x=a$ (the radius of the tube being so much greater than δ) and since also $\psi = \zeta$ when $x=0$, this reduced to:

$$I_s = -\frac{P \cdot D}{4\pi\eta} \cdot \zeta \cdot \left(\frac{\pi a^2}{l} \right) \quad 36$$

If D and η vary with field strength in the double layer, it can be shown (72) that

$$I_s = -\frac{Pa^2}{4\pi l} \int_0^{\zeta} \frac{D}{\eta} d\psi \quad 37$$

When a low resistance galvanometer is connected across the ends of the capillary the return circuit can be visualised as two resistances in series, the capillary and the galvanometer of resistances R and R_G respectively. In the steady state the streaming potential across the plug E_s , is balanced by the current flowing through these resistances and measured on the galvanometer as I_G .

$$E_s = I_s R = I_G R + I_G R_G \quad 38$$

$$I_s = I_G \frac{R+R_G}{R} \quad 39$$

$$\text{Rearranging, } \zeta = \frac{4\pi\eta}{P \cdot D} \cdot I_G \cdot \frac{R+R_G}{R} \cdot \left(\frac{l}{\pi a^2} \right) \quad 40$$

Because of the accumulation of ions in the double layer, there is a conductance path along the surface of the capillary and the resistance of the return path through the capillary can be expressed as

$$\frac{1}{R} = \frac{\pi a^2 \kappa}{l} + \frac{2 \pi a \kappa_s}{l} \quad 41$$

where κ and κ_s are the specific bulk and surface conductivities respectively.

Provided the bulk conductivity is large compared with the surface conductivity equation 40 can be extended to a plug of arbitrary geometry. The restrictions, that the pore radius is large and the particles of which the plug is composed are large compared with δ , still apply.

The equation then becomes

$$\zeta = - \frac{4 \pi \eta}{P, D} \cdot I_e \cdot \frac{R + R_G}{R} \cdot k \quad 42$$

where k , the plug constant, is equal to $R \kappa$ providing that the surface conductivity can be neglected. In the presence of electrolytes of increasing concentrations the contribution of the surface conductivity to the total becomes vanishingly small and the ratio of the resistance of the cell containing the plug filled with electrolyte solution to that of the cell

containing solution only becomes constant. This limiting ratio is the plug constant, k .

c) Summary of experimental methods of zeta-potential determination.

Electrophoresis can be defined as the study of particle motion with respect to a bulk liquid under the influence of an applied electric field. The microscopic or ultramicroscopic method, in which single particles are observed, is applicable for particles in the size range 0.1μ to 10μ . For colloidal molecules the moving boundary method (73) can be used; a mass of particles is observed. The results for non-spherical particles, particularly proteins, were given a theoretical interpretation by Overbeek (74). Sols of ThO_2 and CuO have been investigated electrophoretically (75 a-d). Anderson has also investigated synthetic magnetite using microelectrophoresis, a modified form of the microscopic method in which only very small quantities of the sol are required.

In 1931, Henry (79) studied the effect of an electric field on a large single particle suspended in an electrolyte solution. The high experimental errors, mainly associated with the particle suspension system, have prevented further development of this technique.

Electro-osmosis consists of the movement of bulk solution under an applied field with respect to a fixed

solid in the form of a plug. Particle sizes are slightly larger than for electrophoresis and to avoid surface conductance effects it is convenient to use solutions of 10^{-4} M and upwards. Douglas has used this method for fluorspar and iceland spar (80a,b) [#]

Sedimentation potentials (Dorn effect) are set up when solid particles move with respect to a bulk liquid. The difficulty in controlling the flow of the solid and the measurement of the small potentials produced have meant that this effect has been little used to determine electrokinetic potentials. Elton and his co-workers (82 a-j) have recently investigated this technique more thoroughly but only results for silica, with a high zeta-potential, have been published.

Streaming potentials are set up when bulk liquid is forced through a fixed plug of material. The particle sizes need be neither uniform nor very small and a large range of electrolyte concentrations can be used though the potentials become very small at high concentrations. Wood (92) and Gortner (93) derived equations from which the zeta potentials may be calculated. The theory has been criticised by Bull (94). The technique has been used by numerous workers for a variety of fibrous and powdered

[#] These two papers form an interesting comparison of changing the anion but unfortunately impurities in the natural specimens and difference in crystal structure make exact comparison impossible.

materials (95 a-g). Bolt (102) has shown that errors introduced by using values of bulk viscosity and dielectric constant, rather than the values in the electric double layer, are in opposite senses and for small potentials, $\zeta \ll 25$ mV, cancel.

The zeta-potentials calculated from streaming potential and electro-osmotic measurements are equal, as shown by Biefer (103), providing that observations of electro-osmotic velocity are corrected for the leak-back of solution through the pores of the plug under the extra pressure of the liquid transported.

The equations for streaming potential and electro-osmosis, in single capillaries including corrections for surface conductance, are

$$\zeta = \frac{4\pi\eta}{D} \left(\kappa + \frac{2\kappa_s}{a} \right) \frac{E_s}{P} \text{ - streaming potential} \quad 43$$

$$\text{and } \zeta = \frac{4\pi\eta}{D} \left(\kappa + \frac{2\kappa_s}{a} \right) \frac{u}{i} \text{ - electro-osmosis} \quad 44$$

$$\therefore E_s i = uP \quad 45$$

where E_s is the streaming potential under a pressure P and u is the electro-osmotic volume flow rate produced by a current i . This relation has frequently been tested and it also holds if $\int D/\eta$ is replaced by $\int_0^{\zeta} D/\eta \cdot d\psi$, provided only that the velocity gradient very near the wall is non-turbulent in both cases.

If the streaming potential is applied across a galvanometer of known resistance the streaming current can be measured. This method is less sensitive to electrolyte concentration (for a given zeta-potential) than streaming potential measurements. O'Connor has used this method to determine the zeta-potential of natural scheelite (104).

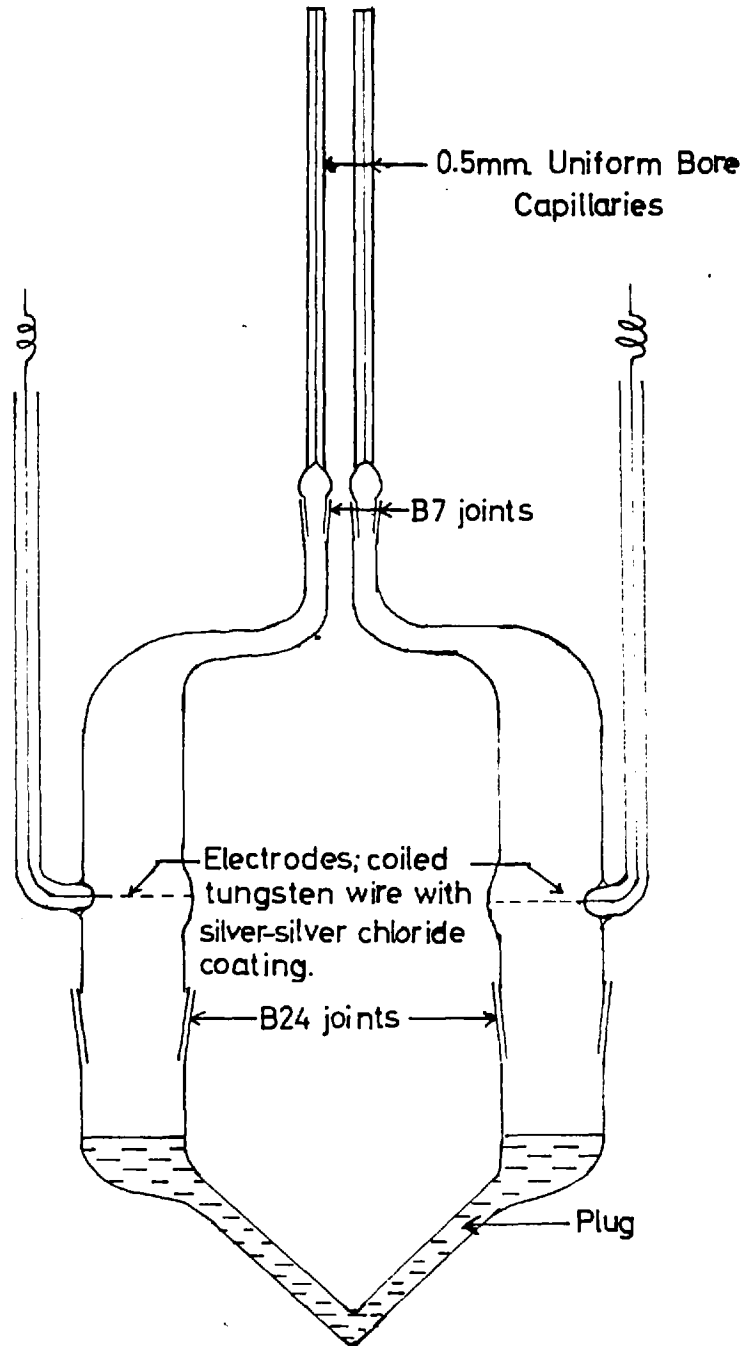
Electrocapillary and capacity measurements provide the most complete information about the electric double layer but this technique is confined to irreversible electrodes, mercury being the most studied. The electroviscous and ballioelectric effects, although due to electrokinetic phenomena, are too difficult to handle mathematically to provide a suitable method of measuring zeta-potentials.

4,iv. EXPERIMENTAL DETERMINATION OF ZETA-POTENTIALS.

a) Electro-osmotic measurements.

A closed circuit streaming potential apparatus used for some previous determinations of zeta-potentials of $MgAl_2O_4$ spinel was abandoned because of the difficulty in preventing the powdered material, which formed the plug, leaking back through the platinum gauze electrodes. A simple V-shaped electro-osmosis cell was constructed as in Fig. IX in which the plug was formed by allowing the

FIG. IX. ELECTRO-OSMOSIS CELL.



material under investigation to settle through the electrolyte in the cell. It was hoped that this form of packing would reproduce should the plug be disturbed. The whole apparatus was immersed in a water bath thermostatted at 25°C.

After constructing several prototypes the plug section was finally made from two 5 cm lengths of $\frac{1}{4}$ inch bore glass tubing with a 90° angle between them. This angle was formed by grinding the ends of the sections to 45° and fusing, care being taken not to distort the tubing. This arrangement gave the best compromise between solution flow rate and plug stability.

The upper parts of the electrode arms were bent so that both capillaries, of 0.5 mm precision bore tubing, could be observed in the microscope eyepiece simultaneously. The original electrodes consisted of copper gauze intermeshed with a tungsten lead sealed through the wall of the apparatus and plated first with silver and then with silver chloride but this treatment did not prevent copper from entering the solution. A coil of well annealed tungsten wire (0.01 in. diameter) was substituted and silver plated followed by anodisation in KCl solution until chlorine was evolved, exposing only unreactive tungsten. Part of the silver chloride coating

was removed, by reversing the anodising current, and then the electrodes were further anodised at a lower current density to give an increased surface area of silver chloride.

To avoid contamination from grease polytetrafluoroethylene sleeves were used at the cone and socket joints. These were not entirely satisfactory because of uneven stretching and it was found that wetting the surfaces of the joints with the cell electrolyte solution gave a watertight seal.

A potential of 120V across an MgAl_2O_4 plug in water developed a pressure difference of only 2 mm. across the capillaries which took some two hours to reach equilibrium when the viscous and electro-osmotic flows become equal. An increased pressure difference can only be obtained at the expense of additional time to reach equilibrium. The equilibrium level could have been obtained from the rate of approach to equilibrium although this was also slow. Because the viscous flow rate was so low it took a considerable time before a change of concentration could be effected. At this period results of early adsorption measurements became available, indicating the presence of material dissolved from the solid. It was therefore decided that this method should be abandoned in favour of one in which only uncontaminated electrolyte solution passes through the plug.

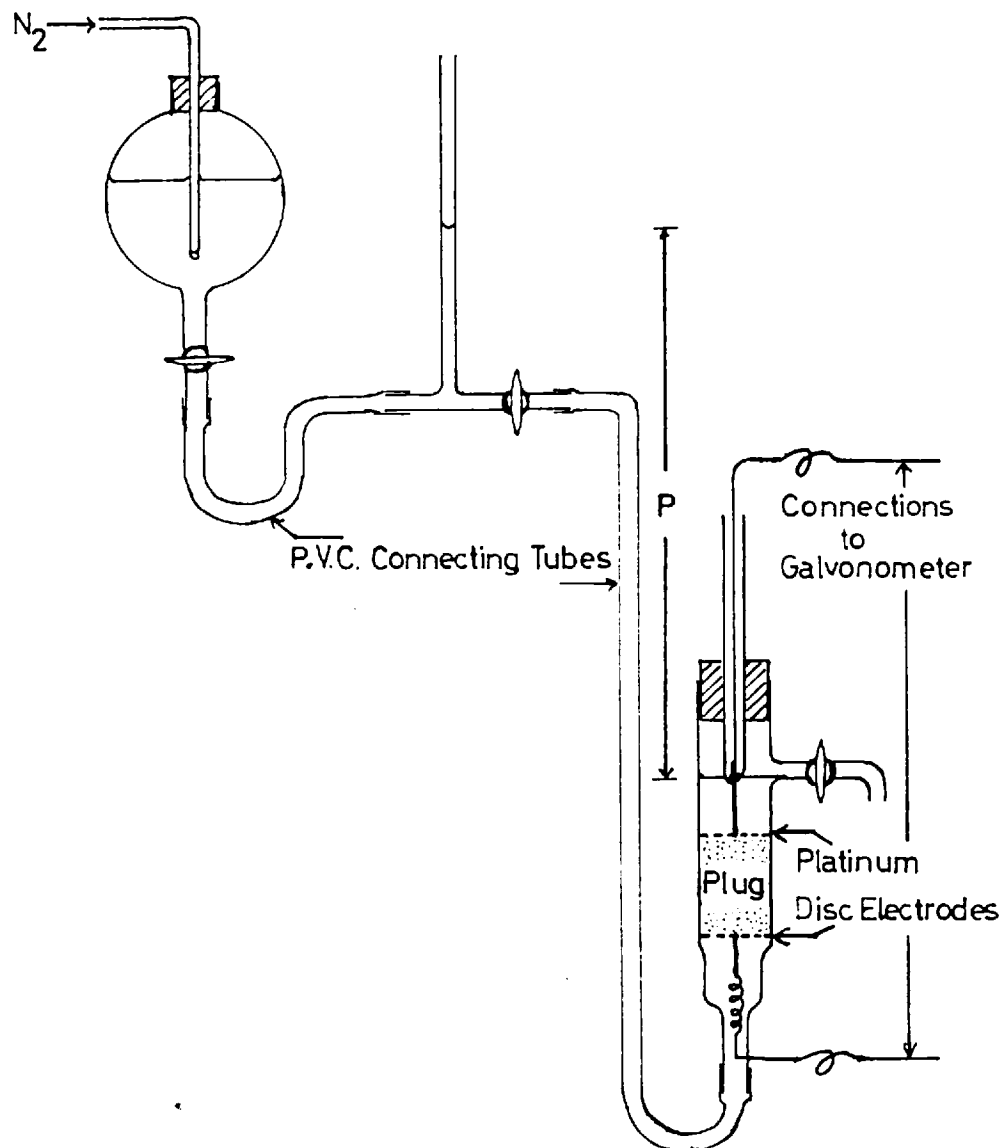
b) Streaming current measurements.

The streaming current apparatus (Fig. X) consisted of a solution reservoir fitted with a constant head device, a manometer and the plug section. The plug section was comprised of a vertical glass tube with a slight constriction on which rested a platinum disc pierced with numerous fine holes. The plug was packed on this disc and a second similar disc pressed tightly on the plug. Connections from the two discs were taken to a sensitive galvanometer.

To ensure uniform packing of the plug the following standard technique was adopted. The cell was filled with water, the lower electrode only being in position, and a thin layer of -60 mesh spinel fraction was added. The bulk of the plug, consisting of 60 - 120 mesh material, was then added slowly with constant tapping of the cell walls to assist settling and prevent channelling, until a depth of 1 cm. was attained. A thin upper layer of coarse material was finally added and the upper electrode inserted to hold the whole plug firmly in place.

Five litres of distilled water were run through the apparatus to condition the plug. The upward flow of solution through the plug was to minimise washing out of the finer particles. The behaviour of the galvanometer

FIG.X. STREAMING CURRENT APPARATUS.



when the flow was stopped and during the decay of polarisation was followed. A series of 1M solutions of various electrolytes were prepared for use in the apparatus after suitable dilution. The range of concentrations studied was 10^{-5} to 10^{-2} M. The solutions were run through the plug in order of increasing then decreasing concentration followed by double-distilled water. The current change when the flow of solution through the plug was stopped was measured several times. The connections from the galvanometer to the cell were reversed and the measurements repeated.

It appeared that the streaming current in water varied considerably for any plug. This was found to be due to absorption of atmospheric CO_2 into the water. Accordingly all the solutions were freed from carbon dioxide by bubbling nitrogen through the double-distilled water used in the dilution of the electrolyte stock solutions and by maintaining an atmosphere of nitrogen in the reservoir of the apparatus. All recorded results were obtained in this manner unless otherwise stated.

c) Washing the plug.

It has been shown (Horsfall and Benton, Private Communication) that adsorbed electrolytes on metal oxides are not readily desorbed in water, even electrolytes which are not expected to exert specific adsorption or potential

determining effects. These workers found that the adsorption process could be reversed by washing the solids with boiling water.

This effect was not observed from the streaming current measurements indicating that the amount adsorbed was small. However, to ensure complete removal of the adsorbed ions the plug was washed with about 1l. boiling, double-distilled water between ^{successive treatments with} electrolyte solutions.

d) Polarisation effects.

In early streaming current observations, it had been noticed occasionally that the galvanometer required a few seconds to reach its maximum deflection, returning slowly to the zero position. To check whether this could be due to polarisation effects at the cell electrodes an external polarising potential was applied to the cell. The implication is that, if the polarisation decays rapidly, the deflection recorded by the galvanometer will be the difference between that proportion of the streaming current returning through the galvanometer and the current caused by the polarisation decay, hence any zeta-potential calculations would be invalidated. The external polarisation was supplied by a 2V accumulator wired in series with a resistance of about 1 megohm across the cell electrodes. This produced a galvanometer deflection of about 20 divisions

($0.1\mu\text{A}$). The rate of deflection of the galvanometer and the apparent streaming current were unchanged by the polarisation. Changing the polarity and magnitude of the applied potential had no effect. When no solution was flowing, switching on the polarising circuit caused a rapid deflection of the galvanometer which returned to zero very slowly when the polarising potential was removed, i.e. the polarisation decays only slowly. No change in the apparent streaming current could be detected when the solution flow through the plug was stopped and the external polarisation circuit was broken simultaneously,

c) Surface conductivity.

In low concentrations of electrolytes surface conductivity contributes a small, though significant, part to the total conductance of the streaming current return path which consists of the surface, bulk solution and the external circuit all connected in parallel. The surface conductivity arises from two separate causes; firstly, there is an excess of ions in the double layer over the bulk solution concentration and their motion in the electric field gives rise to part of the total, the ionic mobility contribution; secondly, the electrokinetic movement itself provides the electro-osmotic contribution (which is not observed in high frequency a.c. fields where electro-

osmosis cannot develop) this is basically a displacement of the free charge in the double layer.

The effects of surface conductivity of the plug materials tested were corrected for by determining the apparent conductivity of various concentration of KCl in the cell with the plug in place. In high concentrations of electrolyte the contribution to the total conductivity from the surface becomes negligible. By measuring the resistance of the plug containing high concentrations, up to 0.2M, of KCl a limiting value of the cell constant, k , was found. k is defined by the equation

$$k = R.C / R_G$$

46

where R is the measured resistance of the plug and R_G the measured resistance of the solution using a dip cell with constant C to correct the measured solution resistance to specific resistance. The limiting value of k is a measure of the bulk conductivity alone. At lower concentrations the value of k is decreased by the surface conductance effects; however, to a good approximation it is the limiting value which is required in equation 42 used for the calculation of zeta-potentials.

$$\zeta = \frac{4\pi\eta}{D} \times I_g \times \frac{R+R_g}{R} \times \frac{k}{P} \quad 42$$

where ζ = zeta-potential in c.s.u.

η = viscosity of the solution in poises.

D = dielectric constant of the solution.

I_g = galvanometer current in c.s.u.

R = plug resistance in ohms.

R_g = galvanometer resistance in ohms.

P = pressure head in dynes cm^{-2}

k = limiting cell constant.

Inserting the requisite conversion factors into the equation it becomes

$$\zeta = 1.696 \times 10^3 \times I_g \times \frac{R+R_g}{R} \times k \text{ at } 26^\circ\text{C} \quad 47$$

where ζ is in millivolts, I_g is in microamps. and P is the pressure head in cm. of solution.

Certain corrections were applied before calculating a value for the zeta-potential;

(i) The measured pressure was reduced by the frictional loss of hydrostatic head. This was experimentally determined as the hydrostatic head required to produce a given flowrate through the apparatus in the absence of a plug; it was found to be proportional to the flowrate. The correction normally amounted to less than 1% of the total pressure.

(ii) Temperature fluctuations between solutions were allowed for, to the nearest 0.5°C , in the constant used in equation 47.

(iii) After standing for several days, the plug sometimes became highly compacted and the flow-rate became very low. In such cases the plug was disturbed slightly to improve the flow-rate and the cell constant was redetermined with approximately 0.2M KCl solution.

4.v. ANALYTICAL TECHNIQUES

a) Determination of aluminium.

A method of determining aluminium gravimetrically in which hydroxyl ions are produced in situ and the aluminium hydroxide precipitated from a chloride solution, Willard and Tang (105), was used in the analysis of solutions of aluminium salts from which the original spinels were prepared. It was not possible to reduce the scale of this determination to cover the very small amounts of aluminium leached from the fired spinels.

To determine the amount of aluminium extracted from the spinels a method using ethylenediaminetetraacetic acid (E.D.T.A) was devised. The solution was boiled with excess E.D.T.A., cooled and, a) the aluminium determined by back-titration of the excess E.D.T.A. at pH5 or, b)

magnesium and aluminium determined at pH 10 or, c) magnesium alone determined at pH 10 by omitting the boiling. Initial tests were made with 10^{-2} M solutions of magnesium and aluminium and the back titration was accomplished potentiometrically using mercurous nitrate solution and a static mercury drop electrode. The end point using this method was too indistinct for good reproducibility and the titrating solution was changed to ferrous ammonium sulphate. The titration curves then obtained were of a flat Z shape, apparently due to the combined effect of two redox potential changes and again the end point could not be located accurately.

A further variation was tried; the titration was carried out with a zinc nitrate solution and the end point detected using a mixture of potassium ferro- and ferri-cyanides as a redox indicator with a platinum wire electrode. This was entirely satisfactory for 10^{-2} M but not for 10^{-4} M solutions. The aluminium solutions were evaporated down and the zinc concentration was increased to 10^{-3} M giving some improvement to the end point for aluminium alone. The very small quantities of aluminium extracted from the spinel were, however, usually within the titration error. The results for magnesium when determined by a type c) titration and by the difference between b) and c) titrations differed by more than the

experimental error. In order to reduce this discrepancy, the point in the process at which the indicator and buffer were added was varied as were the concentrations and amounts added; but no satisfactory method could be developed. In view of the extremely small amounts of aluminium extracted from the spinel it was decided to neglect this ion in the adsorption determinations.

b) Determination of zinc using dithizone.

A standard solution of zinc was prepared by dissolving a known weight of the A.R. oxide in the minimum quantity of hydrochloric acid and diluting accurately to approximately 10^{-6} M. Samples of this standard solution were taken to give up to 5% of zinc, 1 ml. of pH 10 buffer (1M NH_4OH / 1M NH_4Cl) was added and the volume was brought to 100 mls. by the addition of distilled water. 10 ml. of a 0.001% solution of recrystallised dithizone in carbon tetrachloride was added to this solution after transferring to a shaking funnel and the mixture was shaken vigorously for five minutes. Samples of the carbon tetrachloride layer were run into 1 cm. spectrophotometer cells and the optical density of the solution was measured at 530 and 625 $m\mu$. No reproducible results were obtainable for either 530 $m\mu$, viz. the zinc dithizonate absorption peak or 625 $m\mu$, viz. the dithizone in the carbon tetrachloride absorption peak.

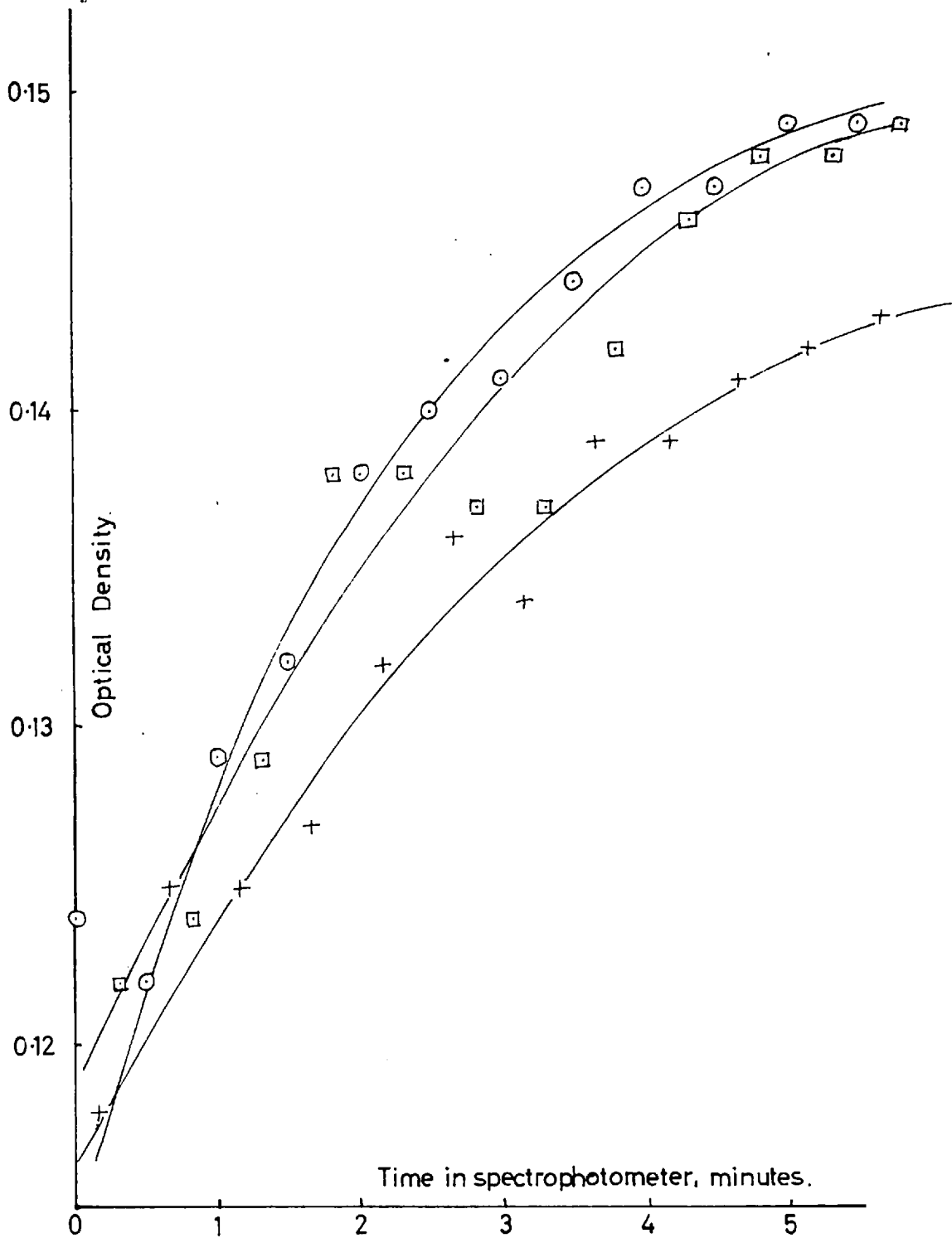
This lack of reproducibility - the solutions turn yellow - was investigated by following the spectrophotometric behaviour of three [↓]simultaneously extracted (samples) of from distilled water. The rate of decomposition, as shown by the change in optical density of the solution, would be expected to be equal for all three samples:- The graphs (Fig. XI) show this not to be so. Therefore the possibility of taking absorption measurements after any given time interval was not practicable. The possibility that impurities in the dithizone were catalysing the decomposition means that fresh solutions and standardisations would be necessary for each series of measurements. Accordingly the method was abandoned.

c) Determination of divalent cations with E.D.T.A.

Divalent cations at the concentrations investigated could be determined satisfactorily by titration with E.D.T.A. using standard compleximetric indicators. The titrations showed that glassware cleaned with chromic acid retained considerable quantities of titratable chromium even after several rinses and also that some of the electrolyte solutions used, slowly removed calcium ions from the walls of the glass containers. Adsorption experiments were then carried out whenever possible in polythene bottles and the titrations in fused silica beakers to minimise these possible sources of contamination.

FIG.XI. OPTICAL BEHAVIOUR OF ZINC DITHIZONATE IN CCl_4 SOLUTIONS.

Three Blank Solutions Compared.



It was decided to use a back-titration method since this allowed the determination of a large number of ions without undue difficulties arising from blocking of the indicator, as in the direct titration of copper using E.D.T.A. with Eriochrome Black T indicator. Even with a back titration care had to be exercised to prevent local concentrations of copper ions blocking the indicator.

Schematic analytical procedures, based on methods devised by Flaschka (106) were drawn up for the analysis of Pb^{++} , Mg^{++} , Ca^{++} , Cu^{++} , Ni^{++} and Zn^{++} in the presence of Mg^{++} , Ni^{++} , Zn^{++} or Cr^{++} which might have been leached from the spinels initially investigated, Table 2. Most titrations were carried out at pH10 with Eriochrome Black T indicator; other pH's and various masking agents enabled the same method to differentiate between the ions. Copper, nickel and zinc can be masked by the addition of excess KCN solution; the zinc, unlike copper and nickel, is released from its cyanide complex by the addition of formaldehyde. These ions can be titrated at pH5: titration at pH6.5 was used for the determination of nickel in the presence of copper, and in these cases PAN indicator was used.

To an aliquot of the sample solution, usually 25 ml., was added a measured excess of 10^{-3}M E.D.T.A. Buffer, and masking agents when required, were next added and followed

Table 2.

Schematic procedure for compleximetric titrations.

Ions determined		Titration required
Cr ³⁺	Ca ²⁺	Ca at pH12, cold; Ca + Mg at pH10, cold; Ca + Mg + Cr at pH10, hot.
	Cu ²⁺	Cu at pH5 (PAN) cold; Mg at pH10 with xs. KCN, cold; Mg + Cr at pH10, xs. KCN, hot.
	Pb ²⁺	Pb at pH8, cold; Pb + Cr at pH8, hot; Mg + Pb + Cr at pH10, hot.
	Mg ²⁺	Mg at pH10, cold; Cr at pH8, hot; (Mg + Cr at pH10, hot).
	Ni ²⁺	Ni + Mg at pH10, cold; Ni + Mg + Cr at pH10, hot; Mg + Cr at pH10 with xs. KCN, hot.
	Zn ²⁺	Zn + Mg at pH10, cold; Ni + Mg + Cr at pH10, hot; Mg at pH10 with xs. KCN, cold.
Mg ²⁺	Ca ²⁺	Ca at pH12, Ca + Mg at pH10.
	Cu ²⁺	Cu at pH5 (PAN); Mg at pH10 with xs. KCN.
	Pb ²⁺	Pb at pH8; Pb + Mg at pH10.
	Mg ²⁺	Mg at pH10.
	Ni ²⁺	Mg at pH10 with xs. KCN; Mg + Ni at pH10.
	Zn ²⁺	Mg at pH10 with xs. KCN; Mg + Zn at pH10.

Table 2 (continued).

Ions determined		Titration required
Ni ²⁺	Ca ²⁺	Ca at pH10 with xs. KCN; Ca + Ni at pH10.
	Cu ²⁺	Ni at pH6.5 (PAN); Cu + Ni at pH5 (PAN).
	Pb ²⁺	Pb at pH10 with xs. KCN; Pb + Ni at pH10.
	Mg ²⁺	Mg at pH10 with xs. KCN; Mg + Ni at pH10.
	Ni ²⁺	Ni at pH10.
	Zn ²⁺	Zn + Ni at pH5 (PAN); Zn at pH10 with xs. KCN followed by xs. formaldehyde.
Zn ²⁺	Ca ²⁺	Ca at pH10 with xs. KCN; Ca + Zn at pH10.
	Cu ²⁺	Zn + Cu at pH5 (PAN); Zn at pH10 with xs. KCN followed by xs. formaldehyde.
	Pb ²⁺	Zn + Pb at pH10; Pb at pH10 with xs. KCN.
	Mg ²⁺	Zn + Mg at pH10; Mg at pH10 with xs. KCN.
	Ni ²⁺	Zn + Ni at pH5 (PAN); Zn at pH10 with xs. KCN followed by xs. formaldehyde.
	Zn ²⁺	Zn at pH10.

For titrations at pH's below 7 PAN indicator (1-(2-Pyridylazo)-2-naphthol) was used, all other titrations were carried out using Eriochrome Black T indicator.

by the indicator in solid form in sufficient quantity to give a faint, but readily discernible, colour. The titrant, a $10^{-3}M$ solution of lead or zinc nitrate, was then run in until the colour change occurred; blue to purple for Eriochrome Black T at pH10. The mean of two titres agreeing to within 0.1 ml was taken as the end-point. No satisfactory calcium titrations at pH12 were obtained and masking agents were found to give large blank corrections reducing the accuracy of the titrations.

d) Polarographic determinations.

Lead, zinc and nickel analyses were latterly much simplified and speeded up by the use of a Southern Instruments K1000 Cathode Ray Polarograph. 0.1M KNO_3 was found suitable as a supporting electrolyte when the cations under investigation were about $10^{-4}M$. When Zn^{++} and Ni^{++} occurred in the same solution the peaks overlapped in KNO_3 , but a supporting electrolyte 0.1M with respect to both NH_4OH and NH_4Cl was found to give satisfactory separation of the two peaks.

Spurious maxima were observed in some solutions and one drop of 0.1% freshly prepared gelatin solution added to the 5 ml. or so of solution under test was found to be satisfactory in suppressing them without introducing a volume correction.

The calibration plots of peak height in microamps vs. concentration are shown in Figs. XII, XIII, XIV. Calcium and magnesium cannot be determined by this method.

e) Determination of calcium and magnesium.

The determination of calcium in the presence of magnesium at concentrations near $10^{-3}M$ was found to be unsatisfactory with Murexide indicator at pH 12 in the E.D.T.A. titrations. New complexometric indicators were tried; "Calcien" (yellow \rightarrow fluorescing yellow) gave difficulty under ordinary conditions of illumination in detecting the exact point at which fluorescence starts and Patton and Reeder's Indicator (red \rightarrow blue) was oxidised very quickly at the pH of the titration and gives a variable colour change.

The determination was performed spectrophotometrically in a Unicam SP 600 spectrophotometer. The reagent employed was di-(o-hydroxyphenylimino)-ethane in alcoholic solution at pH 12.6, using the method employed by Kerr (107). The bright red colour of the complex took a few minutes to develop but was stable for about 30 minutes. Beer's law is obeyed up to $40 \mu g$ of calcium, Fig. XV. An attempt was made to repeat the determination at pH 10 where, by comparison with E.D.T.A. complexing, it was hoped that magnesium might also complex. The solutions tested developed a uniform yellow colour with no trace of the red

FIG.XII. POLAROGRAPHIC CALIBRATION FOR LEAD SAMPLES.

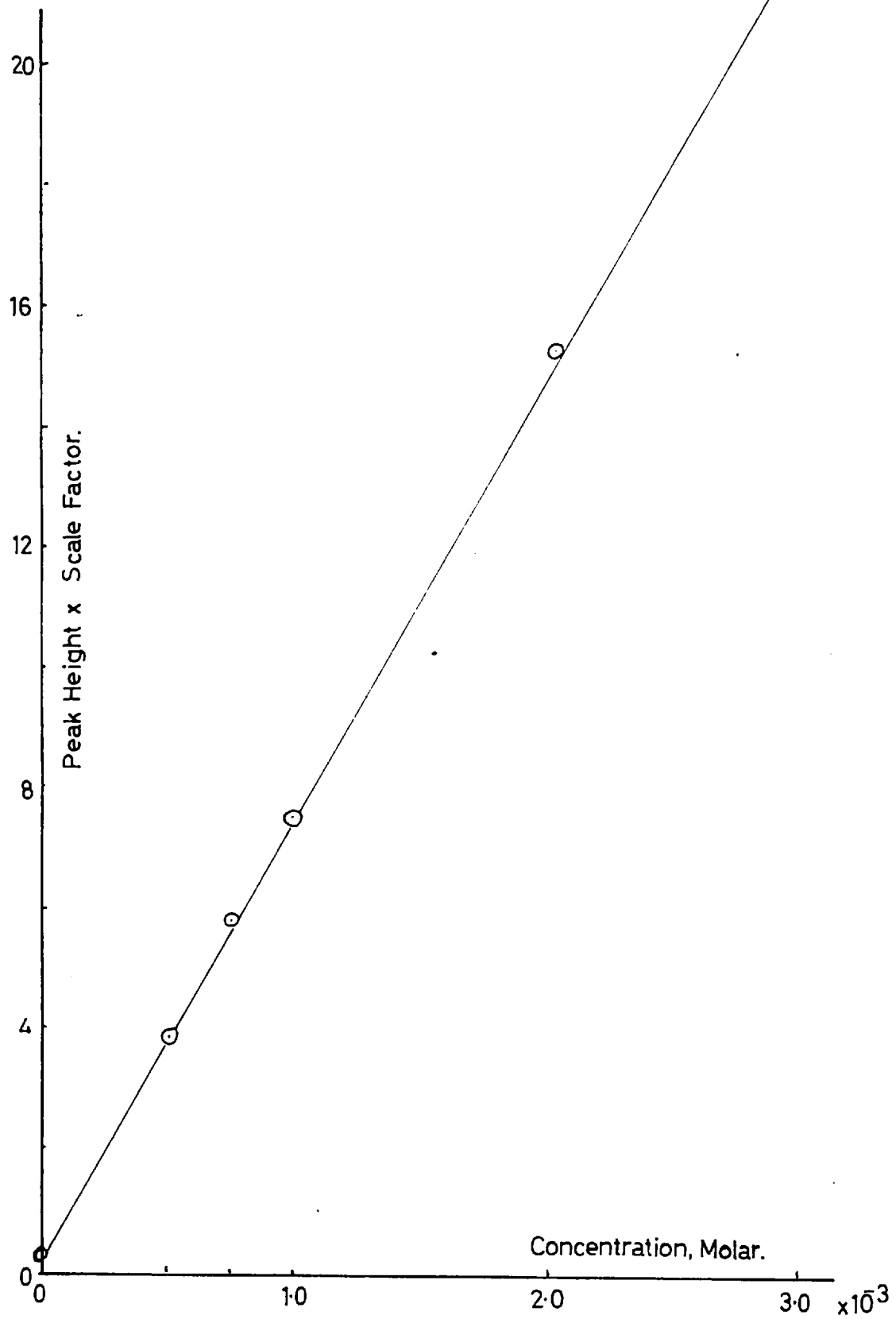


FIG.XIII. POLAROGRAPHIC CALIBRATION FOR ZINC SAMPLES.

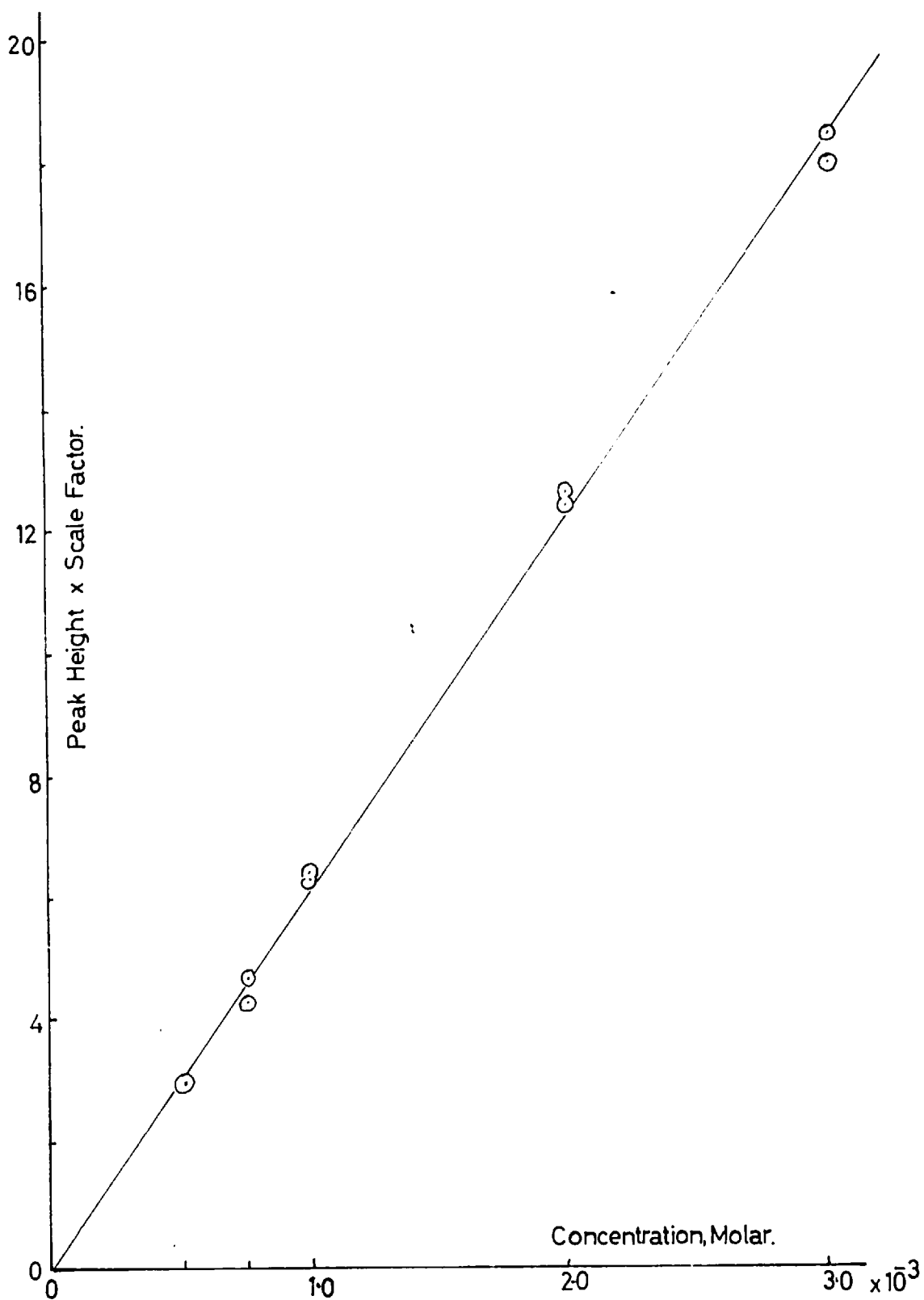


FIG. IV. POLAROGRAPHIC CALIBRATION FOR NICKEL SAMPLES.

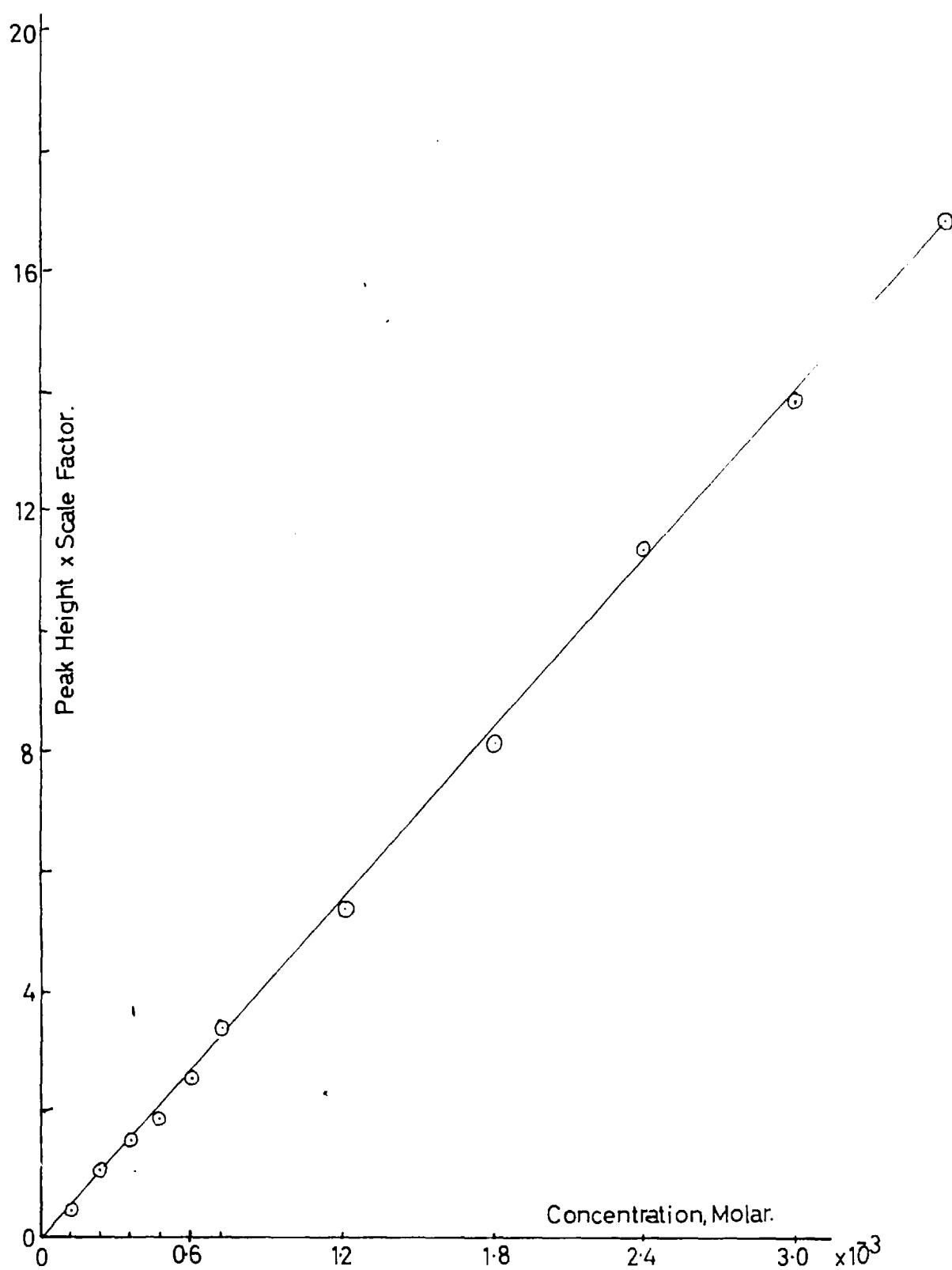
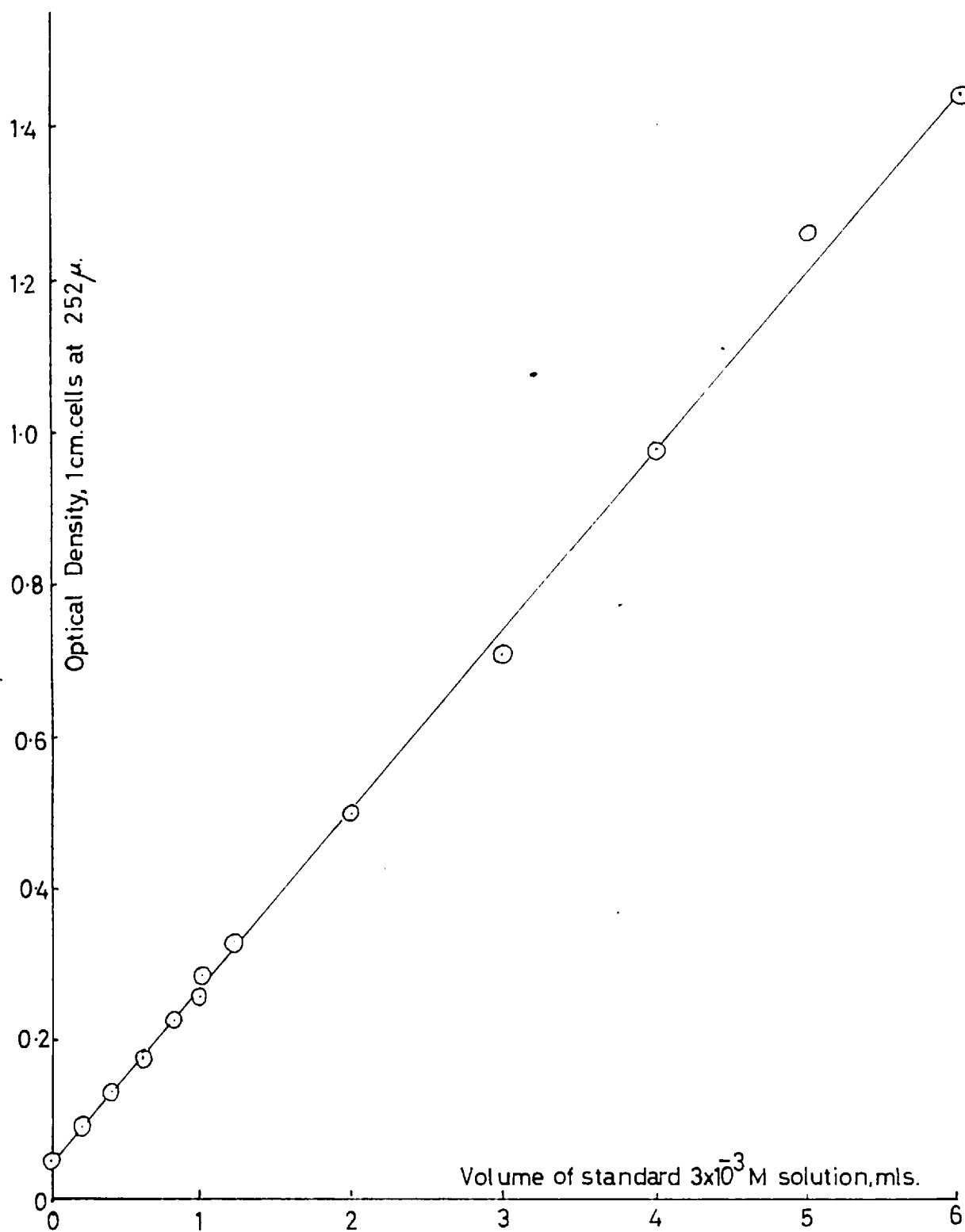


FIG.XV. SPECTROPHOTOMETRIC STANDARDISATION OF CALCIUM.



colour of the complex even after standing for 24 hours.

Magnesium, therefore, had to be determined titrimetrically. It was thought advisable to determine the total cations and find magnesium by difference rather than attempting a direct determination by the addition of masking agents. As little as 1% of total cations as Mg^{++} in $10^{-3}M$ solutions could be determined: less than this could be detected but was not accurately measureable.

f) Perchlorate determinations.

To avoid excessive complication of the adsorption results it was necessary to use a univalent anion for which the surface has little specific affinity. Nitrates were used in the earliest experiments but when full analysis of the adsorption solutions was required, it became necessary to use an anion which could be determined. A scheme of analysis was drawn up for perchlorate ion which is not adsorbed.

A gravimetric method of determining the ion as nitron perchlorate was tried (103). To avoid excessive dilution of the reagents, since the nitron perchlorate is appreciably soluble, the determination was carried out in semi-micro filter beakers. However, the reduction in scale from macro to semi-micro quantities led to unacceptably large variations in standard determinations and the method was abandoned.

g) Analysis of chloride ion.

The technique adopted for the final series of adsorption measurements required precise analyses of small volumes of solution of which only 1 ml. samples were available for anion determinations. Test analyses were satisfactorily completed on the potentiometric titration of chloride ion with mercurous nitrate. The end-point of the titration corresponded to almost complete precipitation of the chloride as mercurous chloride.

The apparatus consisted of a pool of mercury containing some mercurous chloride placed in a 5 ml. tall form beaker. A platinum wire sealed into a thin glass tube made connection with the mercury pool. 1ml. of the unknown chloride solution, between 5×10^{-4} and 3×10^{-3} M, was pipetted into the beaker. A salt bridge consisting of a cotton thread soaked in saturated ammonium nitrate solution made the connection from the solution to a saturated KCl/calomel electrode. The potential across the two electrodes was measured on a Pye pH - and millivoltmeter. The mercurous nitrate solution, about 4×10^{-3} M, was added from an "Agla" micrometer syringe with a capillary tip placed below the surface of the solution in the beaker. Mixing was accomplished by placing the titration beaker on a rotating table, the stationary electrodes and capillary

tip providing sufficient agitation. The mercurous nitrate solution was added in 0.005 ml. portions at 90 second intervals.

The potential vs. volume curves were plotted, Fig. XVI shows typical examples, but a more rapid determination of the end-point was made from the differential curve. A graph of the change in potential for a 0.01 ml. addition vs. the total volume, e.g. Fig. XVII which corresponds to the curves shown in Fig. XVI, shows a peak change of the order of 80 mV. at the end-point.

Carbonate interferes unless the pH of the solution is low. One drop of 10^{-1} M HNO_3 was added to each titration to prevent the precipitation of the highly insoluble mercurous carbonate.

The mercurous nitrate solution was standardised by titration in the above manner against a 10^{-3} M solution of KCl made up by weight. The reproducibility of the titration, on this scale, was $\pm 10^{-4}$ moles/litre at all concentrations used. Tests for reproducibility and accuracy of location of the end-point were satisfactorily carried out with solutions of lead and copper chlorides.

Measurement of the pH of the solutions with a Pye pH Meter completed the determination of the composition of the electrolyte solutions before and after adsorption.

FIG. XVI. POTENTIOMETRIC TITRATION OF CHLORIDES WITH MERCUROUS NITRATE.

Potential vs. Volume.

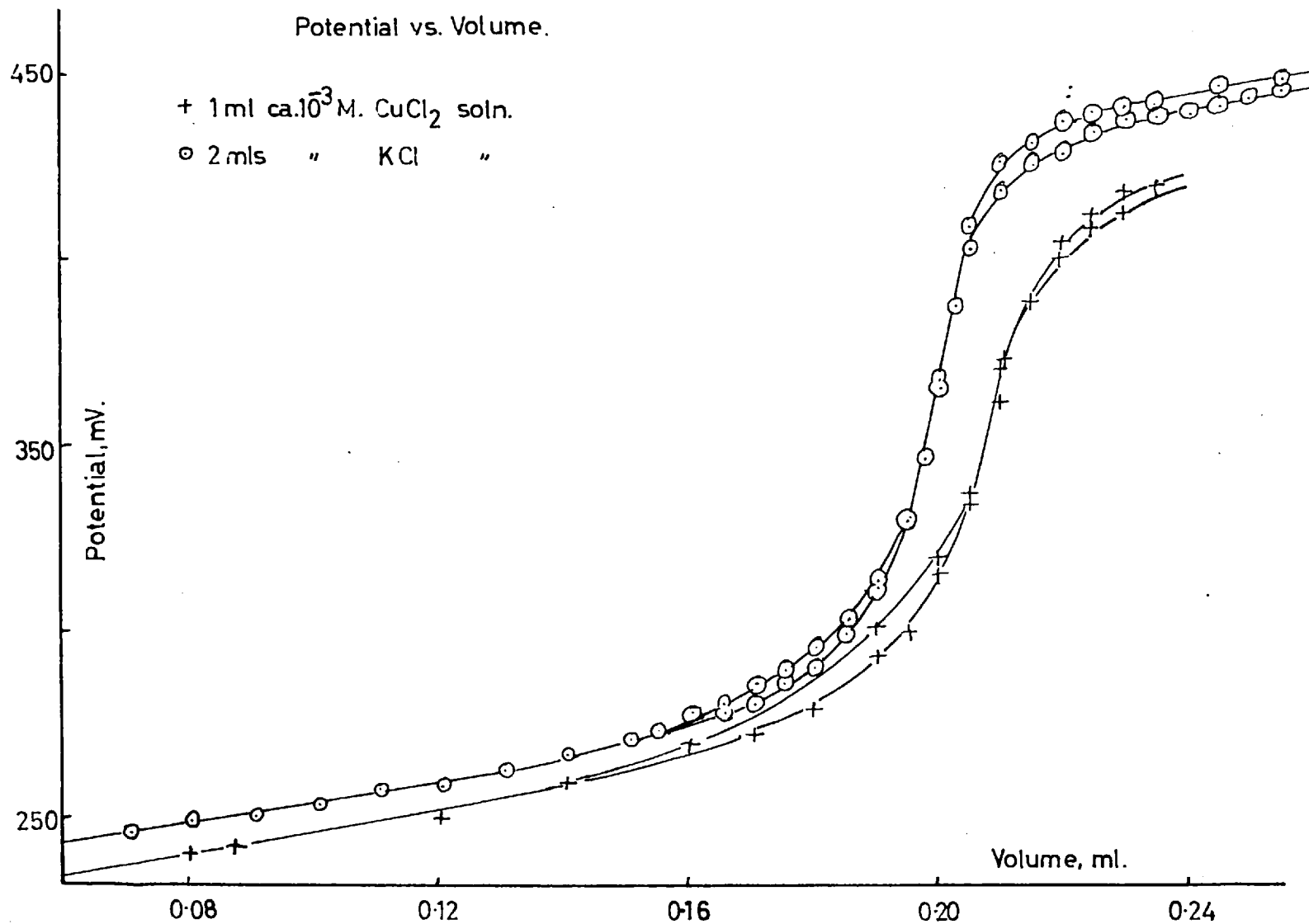
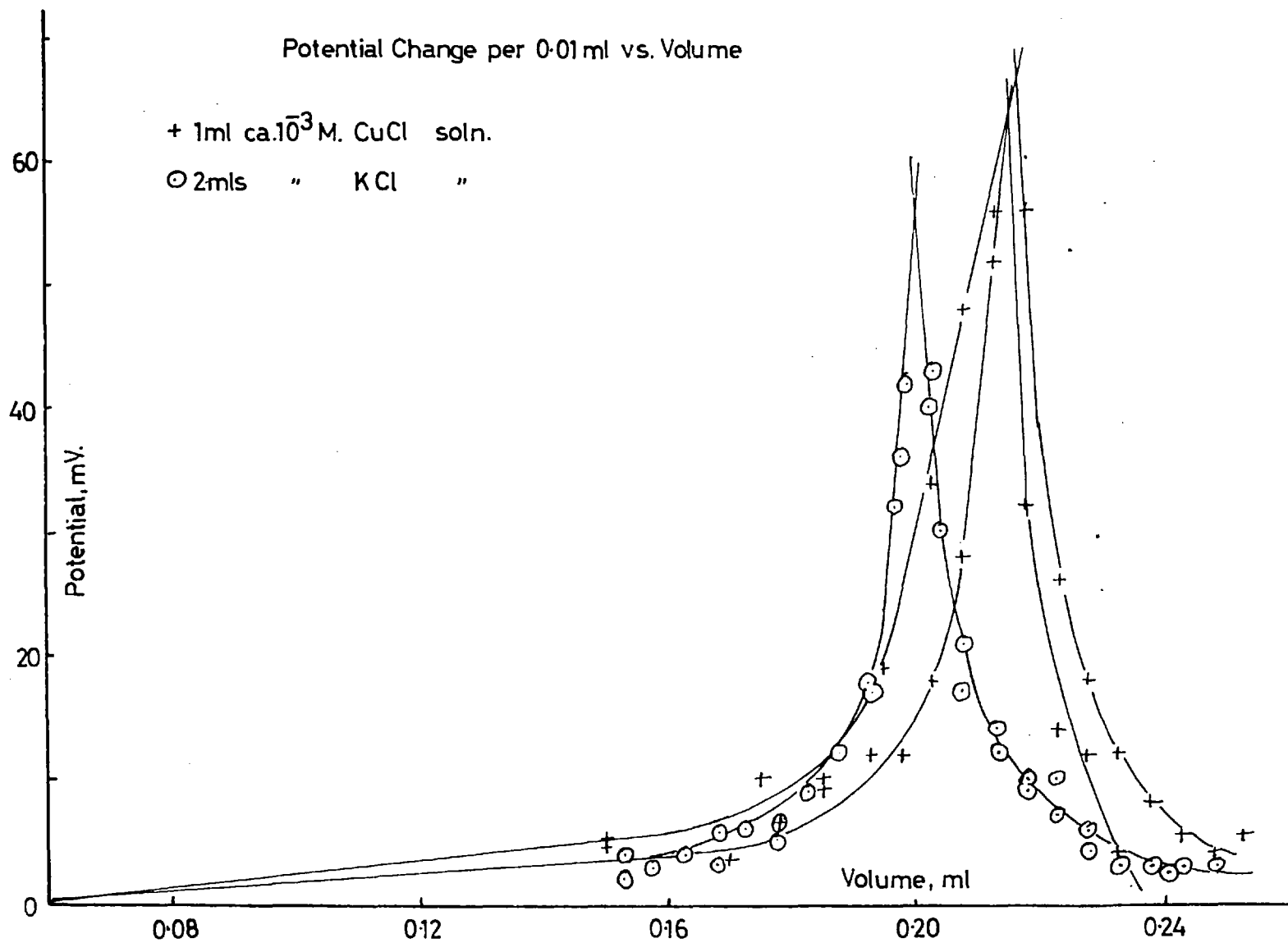


FIG. XVII. POTENTIOMETRIC TITRATION OF CHLORIDES WITH MERCUROUS NITRATE.



4.vi. ADSORPTION MEASUREMENTS.

a) Preparation of samples for adsorption studies.

For the preliminary tests the sample was ground to finer than 60 mesh in an agate mortar and the fines were removed by sedimentation.

The sample was brought into equilibrium with double-distilled water and the concentration of ions leached from the oxide was determined. Leaching was continued until the ion concentration reached a minimum value (which was never found to be zero for $MgAl_2O_4$ spinel). In some cases leaching was carried out with very dilute acid solutions (approximately $10^{-3}M$), *see page 23*.

It was found that after the first leaching treatment only the divalent cation was removed from the oxide. The first leaching removes a small amount of trivalent ion, but not in stoichiometric ratio with the divalent ion, and is probably removed in the form of a soluble salt formed by reaction with alkali metal contaminants of the original oxides.

After the leaching treatment all samples were quickly washed with double-distilled water and dried at $110^{\circ}C$ in air.

Some of the extractions were followed by continuous conductivity measurements. The interpretation of these

measurements and their subsequent conversion into concentrations was rather difficult and the proposed use of this technique for following the adsorption process was abandoned.

b) Early investigations.

To establish the most convenient concentration for adsorption studies an experiment was carried out in which the change of adsorption with concentration of electrolyte could be studied. 100 ml. $10^{-2}M$ lead nitrate solution were shaken up with a 4g sample of $MgAl_2O_4$ spinel. After standing for 24 hours a sample of the solution was removed and a known amount of double-distilled water added and the mixture shaken. Back titration with E.D.T.A. of the sample of solution gave a measure of the amount of lead removed from the solution and adsorbed on the spinel. The new theoretical concentration of the lead remaining in the diluted solution in contact with the spinel was calculated (this included the lead ions already adsorbed) and the procedure of sampling and diluting was repeated several times. Solutions approximately $10^{-3}M$ indicated a total adsorption of about 25% of the lead on the 4g sample of spinel. These values had to be regarded as only approximate because of cumulative titration errors and insufficient knowledge regarding the reversibility of the adsorption.

The first full series of adsorption experiments were carried out on weighed amounts of the samples, between 5 and 10 g, which were brought into contact with 100 ml. of solutions of various electrolytes ($\text{Pb}(\text{NO}_3)_2$, MgCl_2 , ZnSO_4 and CaCl_2) of concentration approximately 10^{-3}M , for at least two hours in polythene bottles. The mixture was filtered by a sintered glass filter crucible (porosity 4). The solutions were analysed for cations volumetrically with E.D.T.A. both before and after adsorption. The titrations were carried out in fused silica beakers.

The results for NiAl_2O_4 , ZnAl_2O_4 and MgCr_2O_4 prepared from the fired oxides and MgAl_2O_4 and MgFe_2O_4 from the coprecipitated hydroxides suggested that ion-exchange was a major mechanism in the adsorption process. Up to half the electrolyte cations were adsorbed (1 to 5 μ moles/g) and were largely replaced by the divalent lattice ions. There were several cases in which overall adsorption or desorption was found but the concentrations rarely exceeded 6 μ moles/g.

A sample of MgFe_2O_4 prepared from the fired oxides was found to give complete exchanging of electrolyte cations in all cases. It appears that this sample consisted of a mixture of Fe_3O_4 and MgO , which latter undergoes the

exchange reactions. Results from this sample were discarded. Large amounts of material extracted from a spinel sample throw doubt on its constitution and such results must be treated with caution.

Since no constant solid / solution ratio was used, because of the varying weights of the spinel samples, no direct correlation of these results is possible. Such a correlation can only be obtained when the equilibrium concentrations of the solutions in contact with the spinel are the same.

As a consequence of the ion exchange mechanism apparent in the above adsorption experiments a series of tests was made to check the adsorption/extraction concentration ratio. The sample of $MgAl_2O_4$ spinel used previously was washed with double-distilled water, dried in air at $110^\circ C$ and contacted with 100 ml. $10^{-3}M$ lead nitrate solution. The lead and magnesium concentrations were determined after the solution had been in contact with the spinel for four different periods. Although the total amount of lead adsorbed varied with the time the solution was in contact with the spinel a constant ratio of 1.05 for lead adsorbed to magnesium extracted was found: i.e. an overall adsorption.

c) Extraction of ZnAl_2O_4 .

Attempts were made to measure the amount of metal ion that could be extracted from ZnAl_2O_4 spinel in water and dilute nitric acid solutions.

Four samples of ZnAl_2O_4 approximately 1.8 g. each were placed in polythene bottles. 25 ml. of water was added to each of two of the samples and 25 ml. dilute nitric acid ca. 10^{-3}M , to each of the others. To one of the samples containing water was added 1g "Zeo-Karb 225" ion-exchange resin in the sodium form and to one of the samples containing acid was added 1g of the same resin in the hydrogen form. The bottles were agitated in a flask shaker for about 20 hours over the course of a week.

After a week the mixtures were filtered. 1g of the sodium form of the ion-exchange resin was added to the aqueous extract of that sample which had contained no resin and likewise 1g of the hydrogen form to the acid extract. These were left in contact for about 3 hours and filtered off. The other samples of resin were separated from the spinel by screening. The spinel samples and extracts were discarded. The ion-exchange resin samples were eluted with 25 ml. 5% NaCl solution and the extract titrated with 10^{-3}M E.D.T.A. at pH 10.

Those extracts to which the resin was added after filtering off the spinal were not titratable (less than $0.05 \mu\text{moles}$). The aqueous extract which contained the ion-exchange resin throughout (Na form) contained 80 micromoles of titratable ion and the acidic extract which contained the ion-exchange resin throughout (H form) contained 160 micromoles of titratable ion. This indicated that there was a very small amount of zinc in solution, in equilibrium with the solid spinel. In an acidic solution the amount present was greater.

d) Adsorption studies on NiAl_2O_4 .

Further tests were carried out to investigate more closely the adsorption of lead, magnesium, zinc and calcium ions by nickel aluminium spinel and the subsequent removal of adsorbed ions. The NiAl_2O_4 spinel was chosen because it had shown low nickel desorption in the preliminary tests and was, therefore, abnormal. The oxide was prepared by coprecipitation from nickel nitrate and ammonium aluminium sulphate with final sintering at 1400°C . A batch of about 100g was ground to minus 200 mesh and was washed with dilute nitric acid (ca. 10^{-2}M) followed by several changes of distilled and double-distilled water. During the washing fines were removed by decantation as before. The batch was then dried at 110°C in air. Five portions (A to E, Table 7) were taken

of between 10 and 20g. each and adsorption of ions from approximately $10^{-3}M$ solutions of the electrolytes used previously was determined. The total amount of electrolyte adsorbed was about 10% of the original amount. After each adsorption the supernatant liquid was filtered off as before and the portion of the spinel washed several times with double-distilled water and dried at $110^{\circ}C$ in air.

The adsorption experiments were arranged to study the reproducibility of adsorption on similar surfaces and the effect on adsorption of pretreating the surface with the same or a different electrolyte. Thus, sample A had three treatments with Pb^{++} followed by one of Mg^{++} , sample B had one treatment each of Pb^{++} and Mg^{++} and sample C one of Mg^{++} only. Samples D and E were treated with Zn^{++} and Ca^{++} respectively.

In no test was nickel detected in the supernatant liquid in amounts greater than the experimental error, i.e. one drop of the titrating solution. This indicated the absence of any significant ion-exchange with this material contrary to the indications of the preliminary experiments (where the adsorption was near the lower limit of measurement).

The marked decrease in adsorption with repetition

and the effect of the surface pretreatment on a second ion, viz. Mg^{++} , could be due to either the surface retaining some of the adsorbed ions or to alteration of the original surface by the adsorption and washing process. Attempts were made to detect any lead retained, after washing the samples, by secondary X-ray emission. However, small unclassified peaks are found in the region of the main lead emission peaks even on a sample of "Specpure" nickel oxide used as a blank. These peaks could not be accurately reproduced in magnitude and any small amounts of lead present would be masked by the variation in these peaks. Count rates, at the angles for the maxima of lead secondary emission, also gave inconclusive results.

The $NiAl_2O_4$ samples used previously were mixed together and washed with dilute nitric acid (ca. $10^{-2}M$) followed by prolonged soaking in several changes of double-distilled water. The batch was dried in air at $110^{\circ}C$ and material finer than 120 mesh was used to study the effect of electrolyte concentration on adsorption.

Portions of a 1M stock solution of lead nitrate were diluted and 100 ml. of 3×10^{-4} , 10^{-3} , 2×10^{-3} , 4×10^{-3} and $10^{-2}M$ solutions were mixed with 10 g samples of the $NiAl_2O_4$ in polythene bottles. 100 ml. of distilled water was added to a further sample (No. 6, Table 9) and filtered

off after 24 hours. This sample was then dried in air at 110°C and placed in a polythene bottle with 100 ml. 10^{-3}M solution. This served as a blank indicating whether or not pre-treatment with water alone (as opposed to lead nitrate solutions) had any effect on the subsequent adsorption of ions.

In order to determine whether hydrogen or hydroxyl ions were involved in the adsorption, the pH of the solutions before and after adsorption was measured; steady readings were generally obtained. Since an increase in pH of about 0.2 units, independent of lead concentration, occurred during the adsorption some lead nitrate solutions were titrated with sodium hydroxide solution. The amount of NaOH required to produce an increase of 0.2 units over the original pH of the lead nitrate solution was determined and compared with the amounts calculated to produce the same change if the lead nitrate solution behaved as a strong acid. The experimental results were inconsistent and could not be used to interpret the pH changes occurring as a result of adsorption.

e) Final series.

Fresh samples of MgAl_2O_4 and NiAl_2O_4 spinels were prepared for the final series of adsorption experiments. In view of the apparent gradual decrease in the adsorption

capacity of the NiAl_2O_4 observed in the earlier experiments it was thought advisable that each sample should be used once only. The fired batches of spinel were ground finer than 300 mesh; independent surface area measurements were made on samples of the MgAl_2O_4 and NiAl_2O_4 which were obtained by careful multipoint sampling from the whole batch (100g) divided into four quarters.

2g of the spinel was accurately weighed out into a 15 ml centrifuge tube and 10 ml of the required electrolyte was added from a pipette. The tube was closed with a polythene stopper and agitated for a set period, normally 48 hours. Before removing any samples for analysis the tube and contents were centrifuged for 10 mins. A 5 ml. sample was withdrawn for the cation determinations, 2 ml. of the polarographic supporting electrolyte were added and the mixture made up to 25 ml. with double distilled water. A 5 ml. sample of this new solution was used to determine the sum of the metal ions by back-titration with E.D.T.A. and a 10^{-3}M solution of the original electrolyte. Further 5 ml. samples were used to determine cations polarographically. Of the solution remaining in the centrifuge tube only about 3 mls. could be removed. The pH of this small quantity was measured and 1 ml samples were used for the chloride determinations.

The first electrolyte to be investigated was lead chloride. Lead chloride was precipitated from a solution of A.R. lead nitrate by the slow addition of A.R. hydrochloric acid. The precipitate was washed several times with water and dried in air at 110°C . Solutions 10^{-3}M , $2 \times 10^{-3}\text{M}$ and $3 \times 10^{-3}\text{M}$ in PbCl_2 were made up by weight and solutions $5 \times 10^{-4}\text{M}$ and $7.5 \times 10^{-4}\text{M}$ were made up by dilution of portions of the two most concentrated solutions.

Preliminary tests were carried out, using the 10^{-3}M solution, to establish the time required to reach equilibrium. Three samples were made up for each spinel and analyses were performed after 4, 13 and 25 hours. The mixtures were not agitated during the adsorption. There appeared to be no difference between the solutions analysed after 13 and 25 hours. A full test was then carried out for all five concentrations of electrolyte and the solutions were analysed after 48 hours with agitation. With few exceptions the total anion and cation concentrations were within 10% of each other.

A further group of adsorption experiments was made using zinc chloride solutions at the same concentrations as for PbCl_2 . The zinc chloride solutions were prepared by dissolving the A.R. zinc oxide in A.R. hydrochloric

acid and diluting with double-distilled water. Entirely different behaviour was observed, compared with lead chloride adsorption; only three of the analyses showing satisfactory agreement, an excess of chloride ion was indicated in the others. The final pH of the solution appeared to control the discrepancy in some way.

At this stage it was suspected that the spinels might have adsorbed water and carbon dioxide since being fired, i.e. the surface retains the properties of the simple oxides of magnesium and nickel, and that hydroxyl ions were causing a lower pH measurement or carbonate ions were reporting a chloride ions through insufficient acidification of those titrations. It would require of the order of 0.01% free chloride ion in the solid to provide the measured excess by solubility alone.

A further test was made on the adsorption of $10^{-3}M$ $PbCl_2$ solution on $MgAl_2O_4$ spinel freshly heated to about $900^\circ C$. The behaviour was similar to that observed with the unheated spinel except that the final solution became strongly alkaline.

A fresh solution of zinc chloride was prepared by adding dilute hydrochloric acid to a boiling aqueous suspension of zinc oxide until the last trace of solid just dissolved so that the pH of the solution might be kept as

high as possible. The spinels were heated to about 900°C before weighing out into the adsorption tubes. The general behaviour was as with the more acid solutions but the analytical results were in much closer agreement both before and after the adsorption.

Solutions of nickel and calcium chloride were then tested. Nickel chloride solutions 6×10^{-4} and 3×10^{-3} M were made up by dissolving the A.R. nickel oxide in boiling hydrochloric acid and diluting the stock solution. These solutions were strongly acid and the total cations were considerably in excess of the chloride ions both before and after adsorption.

CaCl_2 solutions of the same concentrations were made up by dissolving calcium carbonate in dilute hydrochloric acid and making up with double-distilled water to the required volume. There was an anomalous increase in the calcium concentration in the two dilute solutions which would appear to indicate that some of the extracted magnesium and nickel was reporting as calcium although this was not confirmed by the spectrophotometric determinations on calibration solutions.

To complete each series of adsorption vs. concentration experiments a value for the "solubility" in water was required. Tests were made on the unheated spinels

using water that had been allowed to absorb carbon dioxide from the atmosphere and on both heated and unheated spinels with nitrogen saturated water.

5. RESULTS

5.i. SURFACE AREAS.

a) A typical calculation.

The results recorded here are those for an 8g sample of NiAl_2O_4 used in the last series of adsorption measurements. The sample was degassed under vacuum for $1\frac{1}{2}$ hours at 400°C .

The calibration of the gas burette, found by weighing mercury running out of the bulbs, was 0, 10.488, 28.409, 69.705 and 158.150 ml at the calibrated marks. The manometer dead space, V_m , had been calculated as 6.294 ml from several previous runs with nitrogen. The results of the first stage of the propane adsorption and the total dead space volume determination using nitrogen (Tables 4 and 3 respectively) have been used to demonstrate the method of calculation.

The bracketed result in Table 3, which is significantly different from the others, has been omitted from the calculation of a mean value of V_g . The choice of results for the ΔPV and ΔP stages of the calculations, indicated at the left hand side of the ΔPV column, ensures that each measurement is used twice only and that as large a range of values as possible is scanned. Early calculations using adjacent pressure and volume results gave a non-symmetrical distribution of values of V_g which became constant as ΔP increased. Calculation of all possible PV combinations gives no further improvement in accuracy.

After evacuating then degassing the sample, propane was introduced into the manometer section and further pressure and volume measurements were made.

TABLE 3. Determination of total dead space volume, V , using nitrogen. $T = 22^{\circ}\text{C}$.

Volume of gas, ml.	Mercury Levels		P cm Hg	PV	ΔPV	ΔP	$\frac{\Delta PV}{\Delta P}$
	Upper	Lower					
1) V_S	18.578	0.114	18.464	0	(1/3) 172.783	12.382	13.954
2) V_{S+} 10.488	10.631	0.111	10.520	110.334	(2/5) 124.045	9.038	13.725
3) V_{S+} 28.409	6.210	0.128	6.082	172.784	(3/4) 41.350	3.010	13.738
4) V_{S+} 69.705	3.186	0.114	3.072	214.134	(4/2) 103.800	7.448	13.937
5) V_{S+} 158.150	1.637	0.145	1.482	234.378	(5/1) (5/9) 234.378	16.982 17.074	13.802 13.749
6) V_{S+} 69.705	3.204	0.120	3.084	214.970	(6/8) 104.206	7.477	13.937
7) V_{S+} 28.409	6.216	0.129	6.087	172.926	(7/5) 61.453	4.605	(13.345)
8) V_{S+} 10.488	10.689	0.128	10.561	110.764	(8/7) 62.162	4.474	13.894
9) V_S	18.686	0.130	18.566	0	(9/6) 214.970	15.472	13.894

Mean value of $\frac{\Delta PV}{\Delta P} = V_S = 13.848 \pm 0.094$ ml.

TABLE 4. Determination of the amount of propane in the system,
 $T = 22.8^{\circ}\text{C}$. (Propane confined to manometer section).

Volume of gas, ml.	Mercury Levels		P' cm Hg	$P'V$	V' , ml.	$(PV)'$
	Upper	Lower				
V_m	18.165	0.105	18.060	0	6.294	113.670
$V_m + 10.488$	6.950	0.122	6.828	71.641	16.782	114.587
$V_m + 28.409$	3.402	0.108	3.294	93.580	34.703	114.312
$V_m + 69.705$	1.610	0.106	1.504	104.81	75.999	114.302
$V_m + 158.150$	0.864	0.178	0.686	108.49	164.444	112.809
$V_m + 69.705$	1.678	0.169	1.509	105.18	75.999	114.682
$V_m + 28.409$	3.408	0.104	3.304	93.860	34.703	114.659
$V_m + 10.488$	6.957	0.126	6.831	71.655	16.782	114.638
V_m	18.419	0.137	18.272	0	6.294	115.004

$$\text{Mean } (PV)' = 114.296 \pm 0.672$$

From the PV values it is possible to calculate ΔPV , ΔP and a further value of V_m as before. The previously determined value calculated for V_m , 6.294 ml, has been used here to give a total volume V' . If it were much in error this would lead to a systematic variation in $(PV)'$ which would indicate whether V_m was too small or too large.

TABLE 5. Adsorption measurements. $T = 22.5^{\circ}\text{C}$.

(Propane allowed 15 mins. to reach equilibrium before pressures were measured).

Volume of gas, ml.	Mercury Levels		P'' , cm. Hg.	$(PV)''$
	Upper	Lower		
13.848 ($=V_s+V$)	3.074	0.114	2.960	40.990
24.336	2.102	0.119	1.983	48.258
42.257	1.466	0.123	1.343	56.751
83.553	0.922	0.114	0.808	67.511
171.998	0.590	0.132	0.458	78.775
83.553	0.959	0.132	0.827	69.098
42.257	1.524	0.144	1.380	58.315
24.336	2.167	0.132	2.035	49.524
13.848	3.077	0.106	2.971	41.142

$(PV)''$ is now a measure of the gas remaining in the apparatus. The difference between this and $(PV)'$ from Table 4 is a measure of the gas adsorbed. From a knowledge of the temperature of the measured gas, 295.7°K , and the gas constant in appropriate units, i.e. P in cm. Hg, V in ml and T in $^{\circ}\text{K}$, the actual amount of gas adsorbed in moles is calculated. The terms then required to plot the B.E.T. isotherm expression, equation 2, are then calculated, Table 6.

TABLE 6. Calculations for B.E.T. isotherm plot.

$(PV) - (PV)''$	$n \times 10^5$	$(P_0 - P)$	$n(P_0 - P) \times 10^5$	$P/n(P_0 - P) \times 10^5$	P/P_0
73.306	3.976	8.198	32.595	0.09081	0.2653
66.038	3.582	9.175	32.865	0.06034	0.1777
57.545	3.121	9.815	30.633	0.04384	0.1204
46.785	2.537	10.350	26.258	0.03077	0.0724
35.521	1.927	10.700	20.619	0.02221	0.0410
45.198	2.451	10.331	25.321	0.03266	0.0741
55.981	3.036	9.778	29.686	0.04649	0.1237
64.772	3.513	9.123	32.049	0.06350	0.1824
73.153	3.968	8.187	32.486	0.09145	0.2663

The slope s and intercept i are measured from the graph, Fig. 20, and n_m is calculated from equation 2.

$$s = \frac{0.1283 - 0.010}{0.40} \times 10^5 = 0.2975 \times 10^5$$

$$i = 0.01 \times 10^5$$

$$s/i = C - 1 = 29.75$$

$$C = 30.75$$

$$n_m = \frac{C-1}{s \cdot c} = \frac{29.75}{30.75 \cdot 0.2975} \times 10^{-5} = 32.53 \mu \text{ moles}$$

From equation 4 S, the surface area occupied by each propane molecule, is calculated (assuming spherical molecules).

$$\begin{aligned}
 S &= 4(0.866) \left(\frac{M}{4} \sqrt{\frac{2}{3}} \right)^{2/3} \\
 &= 4 \times 0.866 \left(\frac{44.09}{4} \times 1.414 \times 6.025 \times 10^{23} \times 0.6259 \right) \\
 &= 26.1 \text{ sq. } \text{Å}^2
 \end{aligned}$$

The surface area of the sample can now be deduced:

$$\text{Area} = 26.1 \times 10^{-16} \times 32.53 \times 10^{-6} \times 6.025 \times 10^{23} \div 8$$

$$\underline{\underline{\text{Area} = 6393 \text{ cm}^2\text{g}^{-1}}}$$

b) Results for various spinel samples.

The surface areas of some of the NiAl_2O_4 samples used for adsorption studies, Chapter 4,vi,d), have been determined as well as the area of a similar, untreated sample. The results are shown in Table 7 and the B.E.T. isotherms in Fig. XVIII.

TABLE 7.

Sample	No. of pretreatments	Surface area (cm^2g^{-1}).
A	4	8000
B	2	7200
C	1	6500
F	0	7300

The experimental error in the determination of n_m is of the order of $\pm 4\%$. This would be equivalent to a variation of $\pm 1\text{ml}$ in V_S , the combined dead space volumes of the sample chamber and the manometer, Fig. XIX. The variation in surface area of these samples is thus not related to the number of processes previously undergone by the samples, i.e. loss of the fine particles in filtrations and drying.

Independent surface area measurements were made on three 8g. samples of the MgAl_2O_4 and on two 8g samples of NiAl_2O_4 used in

FIG. VIII. B.E.T. ISOTHERMS FOR VARIOUS NiAl_2O_4 SAMPLES.

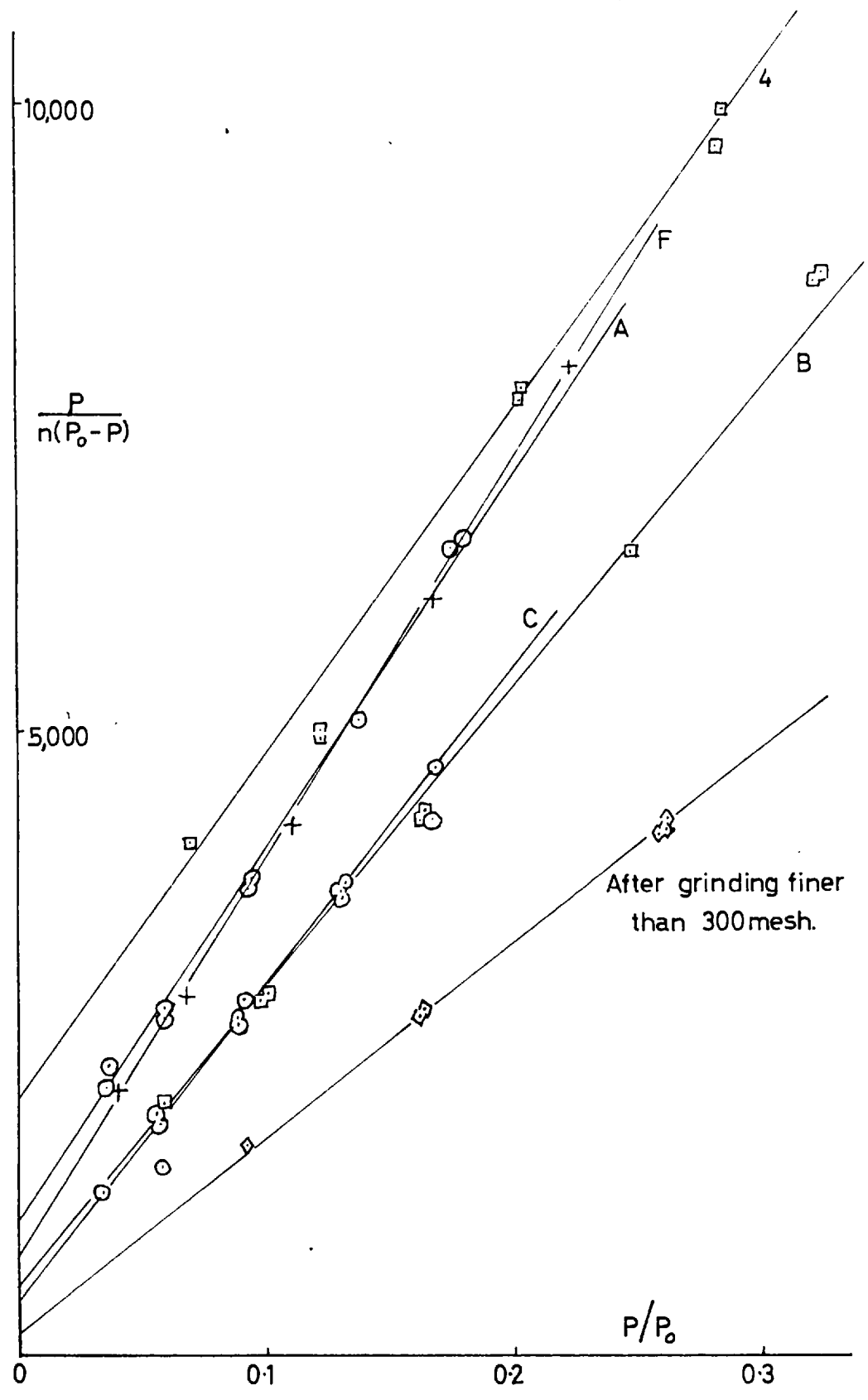
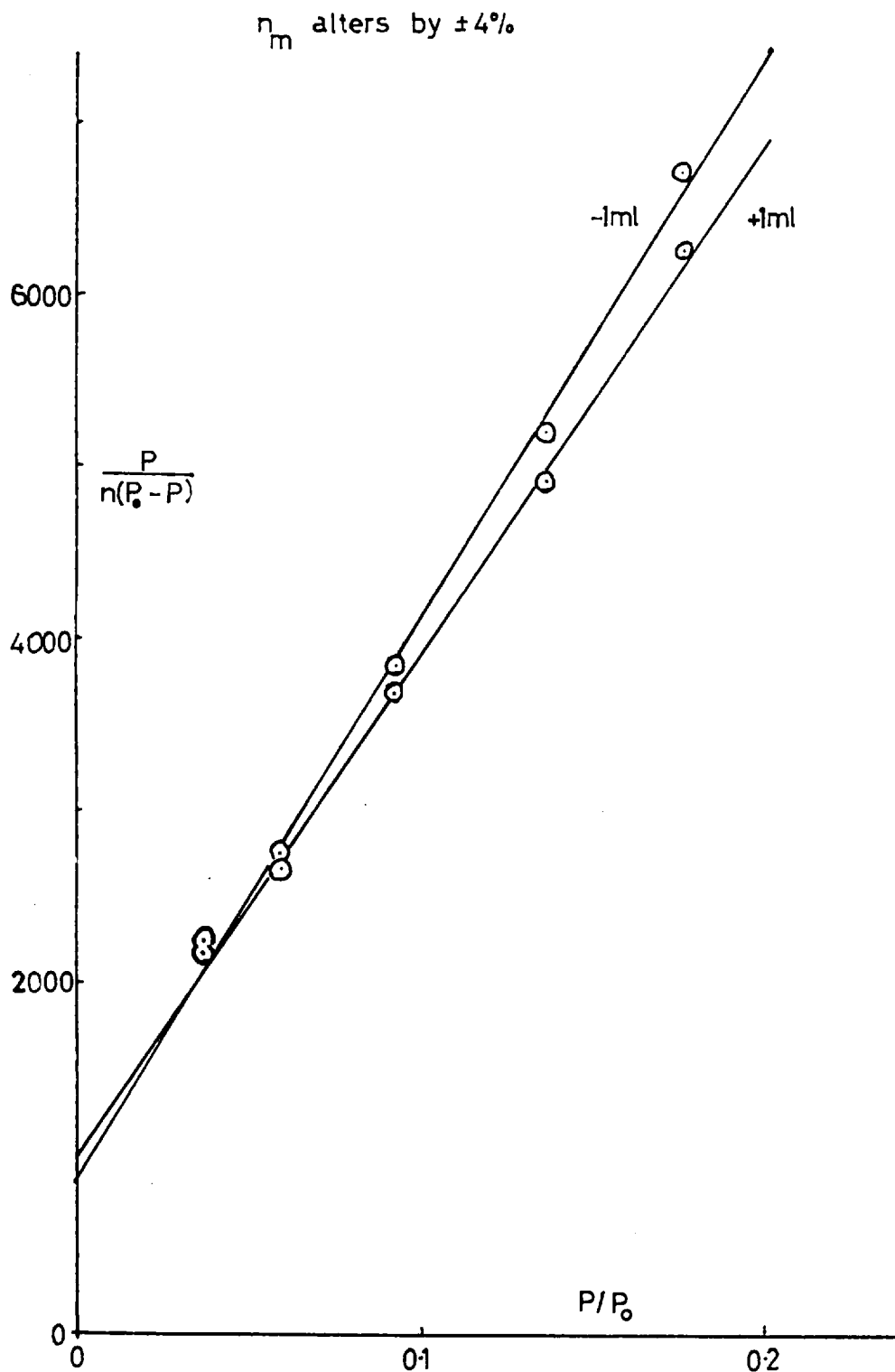


FIG. XIX. ERRORS IN B.E.T. ISOTHERMS; EFFECT OF A ± 1 ml VARIATION IN THE TOTAL DEAD SPACE VOLUME OF THE APPARATUS.



the final series of adsorption measurements. The samples were obtained by multipoint sampling from the whole of each batch of oxide (100g) divided into four quarters. The results for the two nickel samples were in excellent agreement and gave an area of $6390 \text{ cm}^2 \text{ g}^{-1}$, Fig. XXI. The results for the three magnesium spinel samples were not in such good agreement and they were 6250, 6680 and $7480 \text{ cm}^2 \text{ g}^{-1}$, with a mean of $6800 \text{ cm}^2 \text{ g}^{-1}$. Fig. XXI illustrates the B.E.T. isotherm plots for the MgAl_2O_4 samples. Curve (ii) indicates more scatter of the individual points than was usually obtained. The variation is a little greater than that expected from inaccuracies in the gas adsorption measurements.

The surface areas correspond to a spherical particle diameter of approximately 2μ whereas the actual particles would be expected to have a diameter of about 30μ . (Very small particles were removed by decantation before the surface area and adsorption measurements were made). This indicates that the actual particles consisted of sintered aggregates of smaller particles giving a large internal surface. This was confirmed by the fact that grinding a sample of NiAl_2O_4 that had been treated with $10^{-3} \text{ M Pb}(\text{NO}_3)_2$ (Sample 4, Table 9) from all less than 200 mesh to all less than 300 mesh produced ~~only~~ a smaller change in surface area; *than would be expected* 5800 to $9700 \text{ cm}^2 \text{ g}^{-1}$.

Part of this finely ground batch appeared more grey than the rest and it was suspected that this might be due to contamination

FIG.XX. B.E.T. ISOTHERM FOR TWO SAMPLES OF NiAl_2O_4 SPINEL

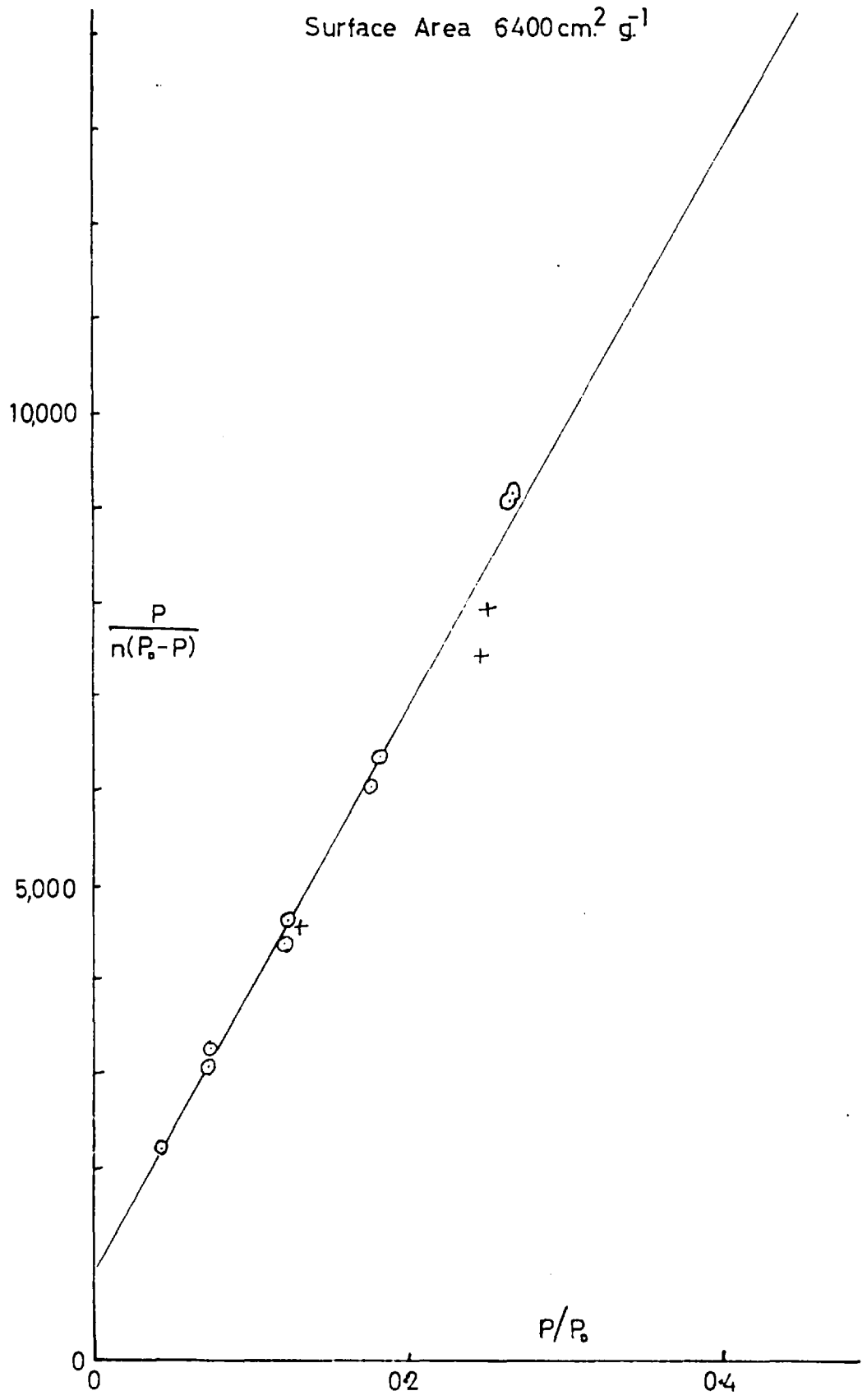
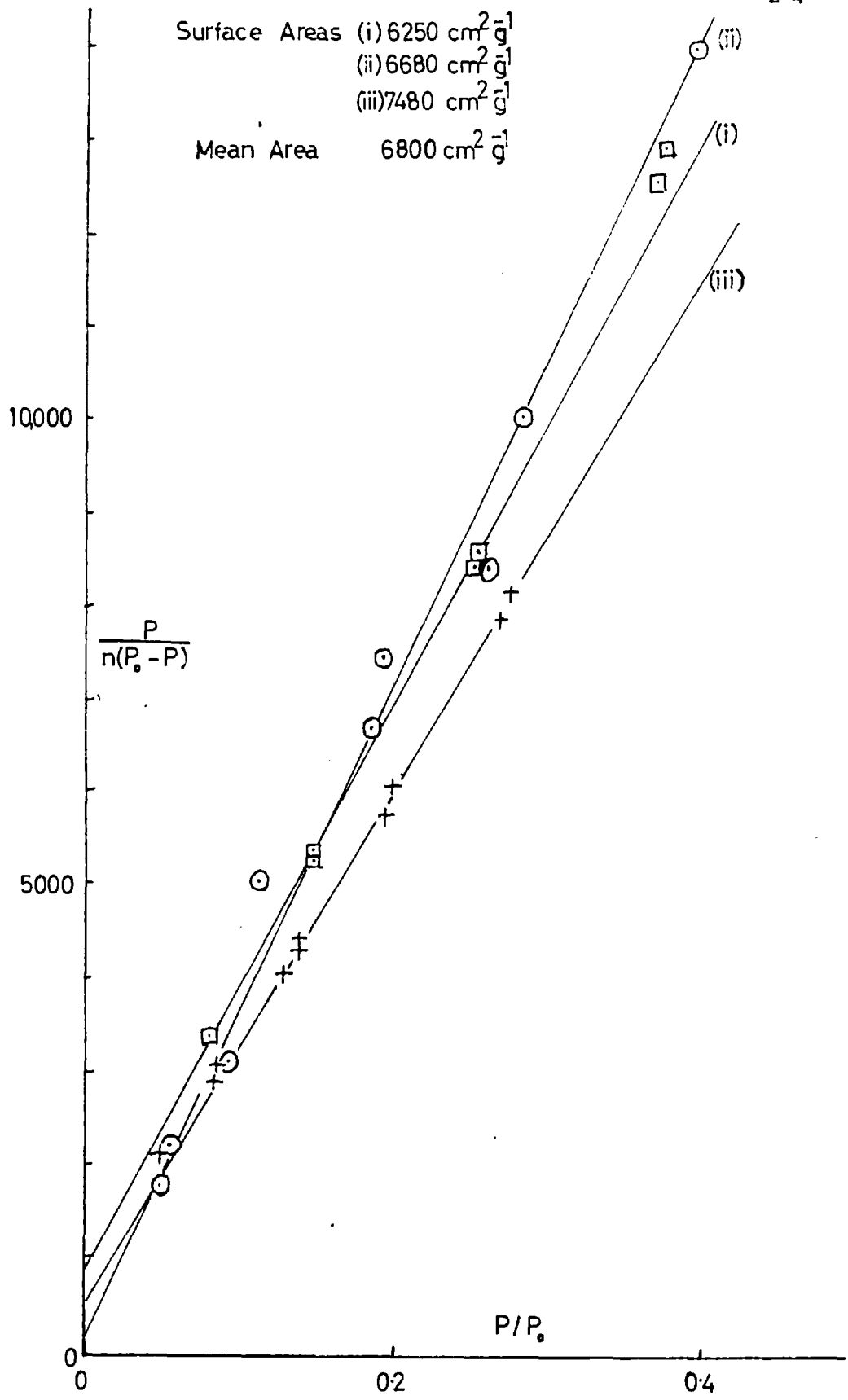


FIG. XXI. B.E.T. ISOTHERMS FOR THREE SAMPLES OF $MgAl_2O_4$ SPINEL

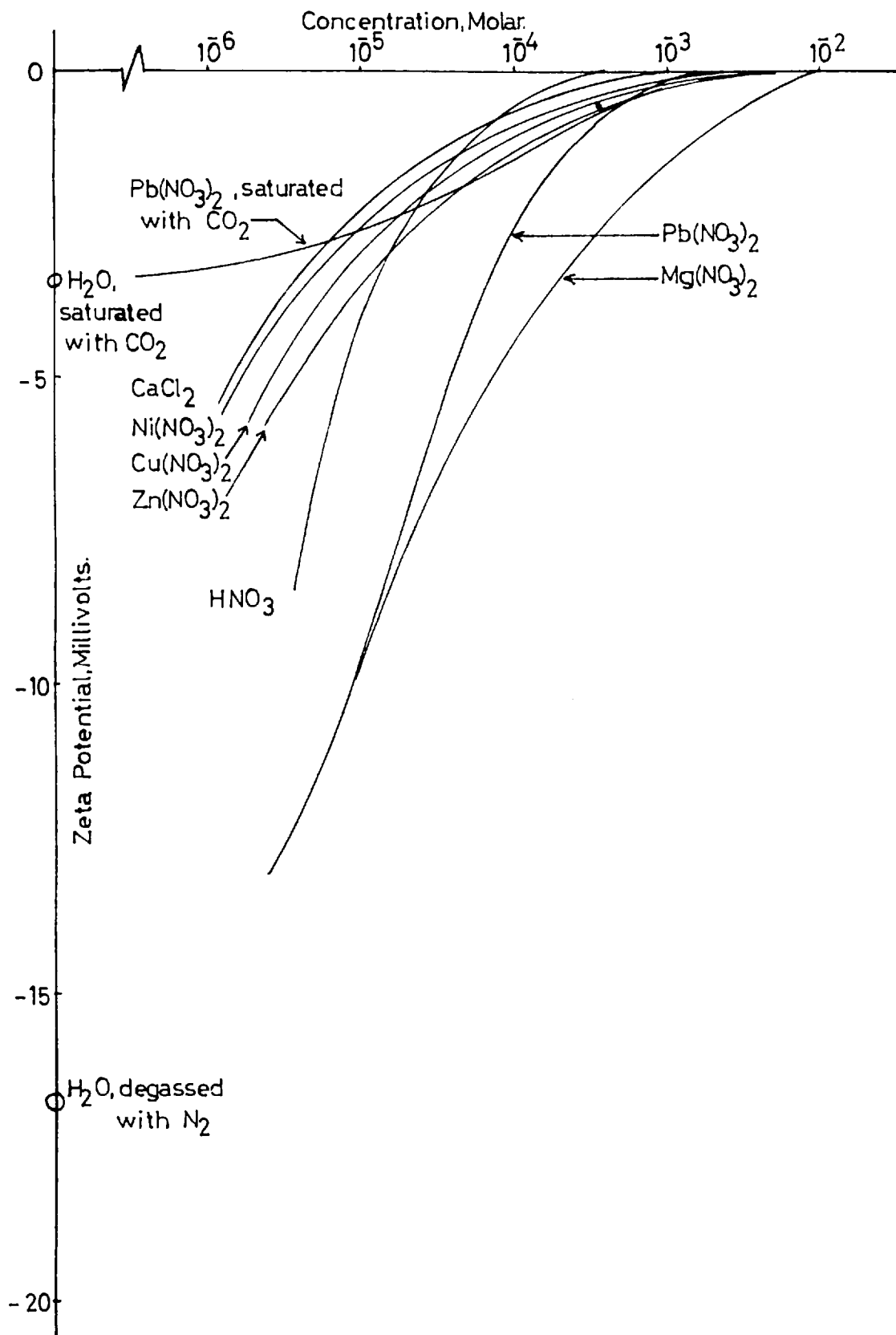


by porcelain from the "Vibrator" vibratory ball mill used for the grinding. Examination of the powder under high magnification showed that the particles retained their blue colour down to a diameter of approximately 10μ and then changed to greyish white. Undoubtedly some silica impurities would still be present in the final material although the very fine particles were separated from the main bulk of the powder by beaker decantation of the spinel in water.

5,ii. ZETA-POTENTIAL RESULTS.

Anderson (109) and Benton (110) have shown how the various parts of the curves of zeta-potential versus concentration may be interpreted and their explanations are widely used although there is still some diversity of opinion as to the best method of expressing the electrokinetic data (111, a-d). The general interpretation of the results is in terms of two groups of ions; potential determining ions and surface indifferent ions. This second group can be further subdivided into surface active and surface inactive indifferent ions. Hydrogen, hydroxyl and solid lattice groups are generally regarded as being potential determining in that a change in their concentration will produce a more marked change in zeta-potential than an equivalent concentration change of any other ion.

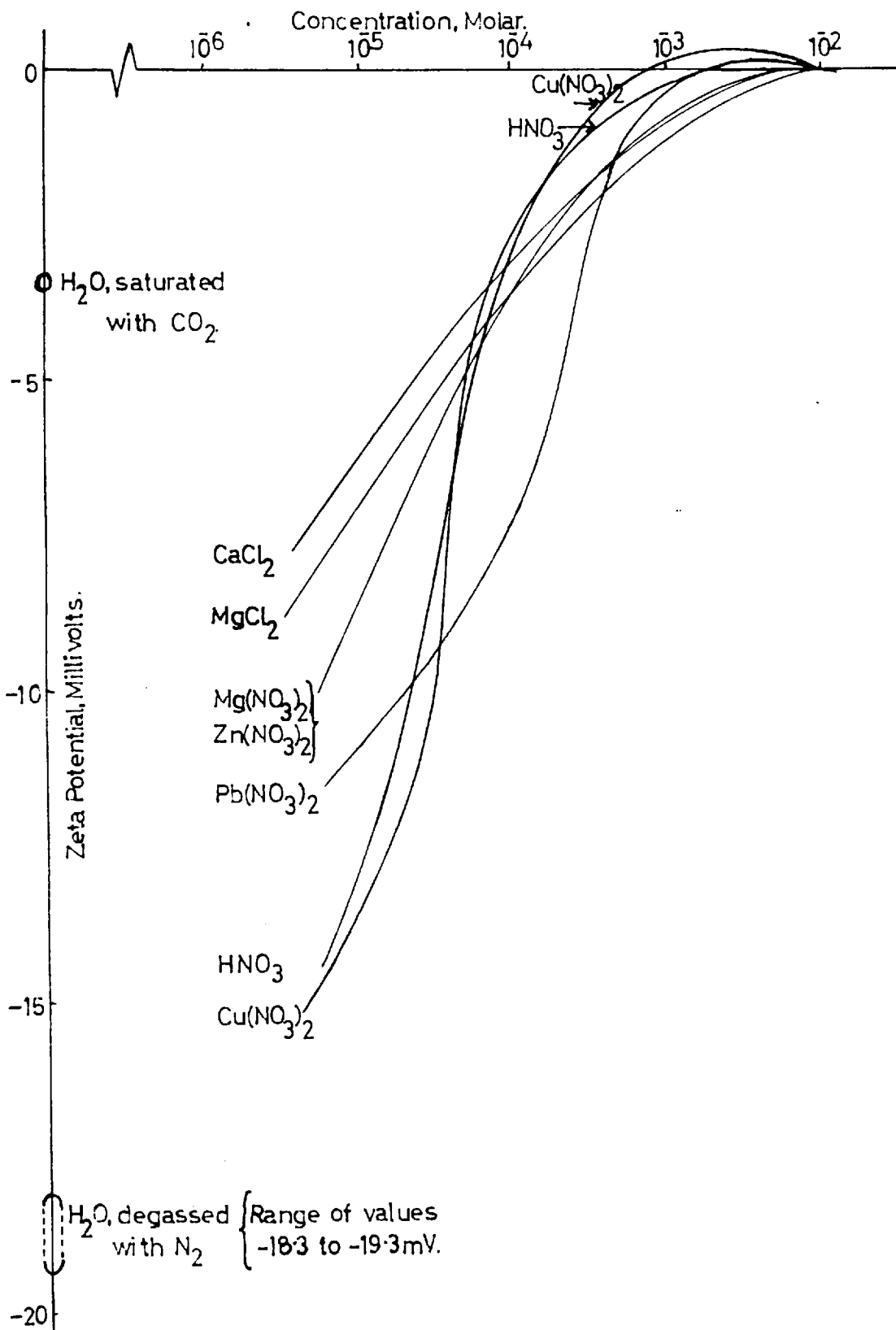
Fig. XXII shows the variation of zeta-potential with concentration for $MgAl_2O_4$. The curves also show the considerable effect of carbon dioxide dissolved in water on the zeta-potential.

FIG. XXII. ZETA POTENTIALS OF $MgAl_2O_4$ SPINEL.

Of the electrolytes likely to prove potential determining nitric acid shows a marked tendency to reduce the negative potential, but in no solution was a positive potential detected. This effect is typical of all oxides. The curve for $Mg(NO_3)_2$ is remarkable; it shows that this electrolyte produces the smallest change in zeta-potential at a given concentration.

Calcium chloride was included in the investigation since, by analogy with the alkali metal ions, Ca^{++} might be expected to be a surface inactive indifferent cation whose adsorption was purely by electrostatic forces and whose influence on the zeta-potential was mainly due to a reduction in the thickness of the diffuse part of the double layer. Other divalent ions, which can fit into the lattice, might be expected to adsorb by a part physical and a part chemical mechanism and hence have a greater effect. It is therefore of particular interest that this electrolyte should be the most effective in reducing the negative zeta-potential.

The results for $NiAl_2O_4$, shown in Fig. XXIII, are similar, but the order of effectiveness of the ions is slightly changed. Small positive potentials were found for $Cu(NO_3)_2$. When a potential determining ion such as H^+ changes the sign of zeta the surface charge as well as the double layer charge must change sign but when a surface active indifferent ion (Cu^{++} in this instance) causes this change then there must be a higher charge in the Stern layer than at the surface: a triple layer is formed. Such ions

FIG. XXIII. ZETA POTENTIALS OF NiAl_2O_4 SPINEL.

must be bound by chemical as well as electrostatic forces. Solutions of nickel nitrate and lead nitrate which had not been outgassed with nitrogen gave irreproducible and irreversible results which bore no resemblance to the curves for outgassed solutions.

Five litres of double-distilled water, freed from CO_2 by outgassing with nitrogen and having a $\text{pH} = 7.00$, were run through the NiAl_2O_4 plug and the streaming current was measured several times. The zeta-potential was calculated and values between -18.3 and -19.4 mV were obtained. Similarly a further 5 litres of water were saturated with CO_2 ; the zeta-potential in this solution was found to be -3.5 mV. Corresponding values for the MgAl_2O_4 plug were -15.0 to -16.7 mV and -3.5 mV respectively.

5,iii. RESULTS OF ADSORPTION MEASUREMENTS.

The results of the adsorption experiments on NiAl_2O_4 samples A to E (4,vi.d) are shown in Table 8. The figures are the calculated adsorptions in micromoles of the stated ion per g of sample. The treatment numbers indicate the order in which the adsorptions were carried out on a particular sample. In no test was nickel detected in the equilibrium solution in amounts greater than the experimental error, i.e. one drop of the titrating solution. This indicates the absence of any significant ion exchange with this material, contrary to the indications of the earliest experiments.

TABLE 8.

Sample	Treatment 1	2	3	4
A	Pb ⁺⁺ 0.90	Pb ⁺⁺ 0.61	Pb ⁺⁺ 0.32	Mg ⁺⁺ 0.20
B	Pb ⁺⁺ 0.87	Mg ⁺⁺ 0.25		
C	Mg ⁺⁺ 0.61			
D	Zn ⁺⁺ 1.5			
E	Ca ⁺⁺ 1.1			

The results, Table 8, are summarised below.

A.1 and B.1 show that adsorption on similar surfaces is reproducible to within the expected experimental error.

A.1, 2 and 3 show the marked decrease in adsorption capacity with repetition. This indicates that continual treatment with electrolytes and wash water alters the state of the surface. A.4, B.2 and C.1 indicate the effect of pretreating the surface on a second ion, viz. Mg⁺⁺. These two effects may be due to the surface retaining some of the adsorbed ions rather than alteration of the original surface by the adsorption and washing process. D.1 and E.1 show that the adsorption of Zn⁺⁺ and Ca⁺⁺ is comparable with those of Pb⁺⁺ and Mg⁺⁺.

Table 9 (overleaf) shows the results of the effect of electrolyte concentration, $\frac{Pb(NO_3)_2}{\wedge}$, on adsorption on NiAl₂O₄. These results also show that the adsorption capacity of the spinel had decreased.

TABLE 9.

Sample	Before Adsorption		After Adsorption		Amount adsorbed mole/g
	Concentration (M)	pH	Concentration (M)	pH	
1	9.815×10^{-3}	4.35	9.805×10^{-3}	4.56	1.0
2	4.020×10^{-3}	4.68	3.966×10^{-3}	4.82 [±]	0.54
3	2.025×10^{-3}	4.89	1.994×10^{-3}	5.01 [±]	0.31
4	1.005×10^{-3}	5.10	0.998×10^{-3}	5.20	0.07
5	3.041×10^{-4}	5.31	2.932×10^{-4}	5.40	0.11
6	1.005×10^{-3}	5.10	0.980×10^{-3}	5.12	0.25

The two pH values marked \pm slowly increased by about 0.1 pH unit.

Insufficient solution was available to repeat the analysis of the solution from Sample 4 which gives an anomalous result (Sample 6 was pretreated with water but is otherwise similar). The probable error on the amount adsorbed at 10^{-3} M is $\pm 0.05 \mu$ mole g^{-1} .

Tables 10 to 14 show the results obtained by contacting various electrolyte solutions with the two oxides $MgAl_2O_4$ and $NiAl_2O_4$ in the final series of adsorption measurements. Tables 11a, 12a, 13a and 14a give the detailed analytical results obtained in each case. Tables 11b, 12b, 13b and 14b give a summary of the total electrolyte concentrations after various adsorption experiments. In the latter tables the values of "cations" and "anions" for each solution should be equal. Overall increases or decreases of electrolyte concentrations are possible and the significance of these will be discussed later.

The oxides were contacted with double-distilled water and the resulting solutions analysed in the same way as in the adsorption measurements. Table 15 shows the results and they clearly indicate the different nature of the surfaces and freshly heated oxides and also the effect of carbon dioxide dissolved in water.

The surface charge density calculated from the zeta-potential of NiAl_2O_4 in $10^{-3}\text{M Pb}(\text{NO}_3)_2$ solution is about 10.5×10^{11} charges per sq. cm. which is nearly 80 x the value calculated from the adsorption measurements. The possible explanations for the discrepancy between chemical and electrokinetic values of the surface charge density, discussed in Chapter 6, suggest that the pH of the solution should decrease. In fact the pH is observed to increase (Table 9) by about 0.2 pH units independent of concentration. The results of some titrations of lead nitrate versus sodium hydroxide solutions were plotted. The amount of NaOH solution required to produce an increase of 0.2 pH units over the original pH of the lead nitrate solution was determined. This was compared with the amounts calculated to produce the same change if the lead nitrate solution behaved as a strong acid. If hydrolysis of the lead ions occurred or some weak acid were present (pH of water about 5.6) the quantity of NaOH required would increase. The experimental results were inconsistent and could not be used to interpret the pH changes occurring as a result of adsorption, Fig. XXIV.

FIG. XIV. TITRATION OF LEAD NITRATE SOLUTIONS.

NaOH added to increase pH by 0.2 units in 100 ml $\text{Pb}(\text{NO}_3)_2$ at concentrations as noted in milliequivalents/litre.

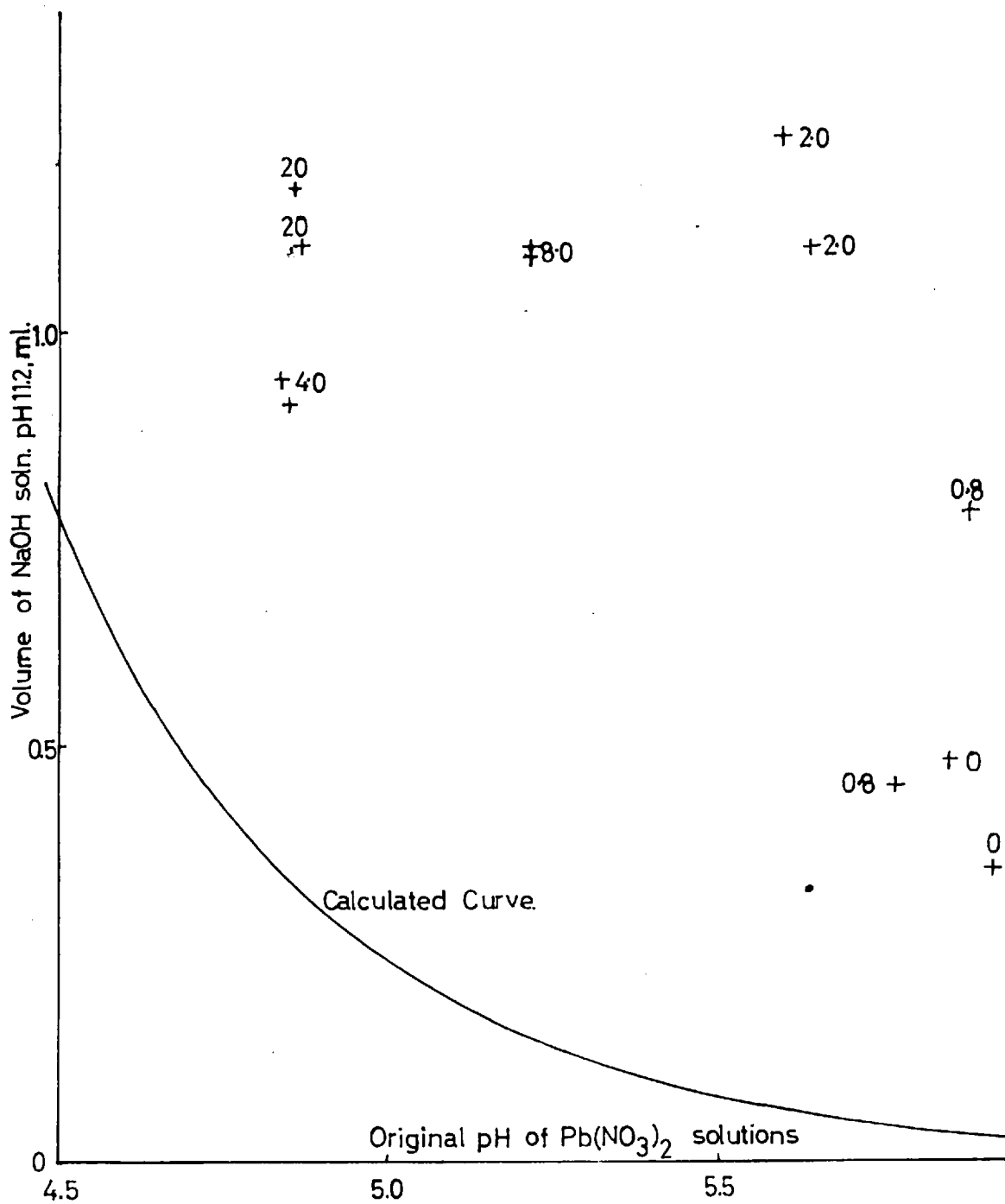


Table 10

Adsorption of PbCl_2 on aged spinels MgAl_2O_4 and NiAl_2O_4

Origin of Solution No.	Time in contact, hours.	Concentration, milli-equivalents per litre						
		Pb^{++}	pH	H+	Ni^{++} or Mg^{++}	Total cations	$\text{Cl}^- = \text{Total anions}$	$\Sigma M - \Sigma A$
Initial Solution 1	0	2.00	5.43	0	0	2.00	2.15	-0.15
Contacted 2 with aged 3 MgAl_2O_4 4	4	1.48	5.62	0	0.50	1.98	1.95	+0.03
	13	1.10*	5.97	0	0.92	2.02	2.29	-0.27
	25	1.10*	6.00	0	0.88	1.98	2.19	-0.21
Contacted 5 with aged 6 NiAl_2O_4 7	4	1.59	5.05	0.01	0	1.60	2.19	-0.59
	13	1.67	5.75	0	0	1.67	2.22	-0.57
	25	1.67	5.80	0	0	1.67	2.19	-0.52

$\Sigma M - \Sigma A = \text{Total cations} - \text{total anions.}$

* But later experiments for Pb^{++} on MgAl_2O_4 showed $[\text{Pb}^{++}] = 0$ after adsorption, Table 11(a).

Note. Concentration units; milli-equivalents per litre = milli-normal.

Table 11a

Adsorption of Lead Chloride on MgAl_2O_4 and NiAl_2O_4

Origin of Solution		Concentration, milli-equivalents per litre						
		No.	Pb^{++}	pH	H^+	Ni^{++} or Mg^{++}	Cl^-	Total cations
Initial Solutions	1	1.00	5.76	0	0	1.02	1.00	1.02
	2	1.50	5.58	0	0	1.44	1.50	1.44
	3	2.00	5.39	0	0	2.2	2.0	2.2
	4	4.0	5.39	0	0	3.9	4.0	3.9
	5	6.0	5.22	0	0	5.9	6.0	5.9
Contacted with aged MgAl_2O_4	1	0	7.51	0	1.21	1.30	1.21	1.30
	2	0	7.65	0	1.61	1.86	1.61	1.86
	3	0	7.61	0	2.2	2.2	2.2	2.2
	4	0	7.37	0	4.5	4.4	4.5	4.4
	5	0	7.46	0	6.2	6.5	6.2	6.5
Fresh PbCl_2 solution CO_2 free	3a	1.92	5.67	0	0	2.10	1.92	2.10
Contacted with fresh MgAl_2O_4	3a	0	9.50	0	2.3	2.2	2.3	2.3 #
Contacted with aged NiAl_2O_4	1	0.54	5.88	0	0.12	1.20	0.66	1.20
	2	1.00	5.90	0	0.42	1.84	1.42	1.84
	3	1.47	5.77	0	0.52	1.96	1.99	1.96
	4	3.6	5.64	0	0.54	3.9	4.2	3.9
	5	4.7	5.48	0	0.84	6.2	5.5	6.2

Includes a concentration of 0.1 corresponding to OH^-

Table 11b

Adsorption of Lead Chloride on $MgAl_2O_4$ and $NiAl_2O_4$, Summary of Solution Data

Original Soln. No.	Concentration, milli-equivalents per litre							
	Initial		Final, aged $MgAl_2O_4$		Final, fresh $MgAl_2O_4$		Final, aged $NiAl_2O_4$	
	cations	anions	cations	anions	cations	anions	cations	anions
1	1.00	1.02	1.21	1.30	-	-	<u>0.66</u>	<u>1.20</u>
2	1.50	1.44	<u>1.61</u>	<u>1.86</u>	-	-	<u>1.42</u>	<u>1.84</u>
3	2.0	2.2	2.2	2.2	-	-	1.99	1.96
3a	1.92	2.10	-	-	2.3	2.3	-	-
4	4.0	3.9	4.5	4.4	-	-	4.2	3.9
5	6.0	5.0	6.2	6.5	-	-	5.5	6.2

Table 12a

Adsorption of Zinc Chloride from Acid Solution on $MgAl_2O_4$ and $NiAl_2O_4$

Origin of Solution No.	Concentration, milli-equivalents per litre							
	Zn ⁺⁺	pH	H ⁺	Ni ⁺⁺ or Mg ⁺⁺	Cl ⁻	Total cations	Total anions	
Initial Solution	1	1.00	3.20	0.63	0	2.1	1.63	2.1
	2	1.50	3.00	1.00	0	3.1	2.5	3.1
	3	2.0	2.68	2.1	0	4.1	4.1	4.1
	4	4.0	2.53	3.0	0	9.4	7.0	9.4
	5	6.0	2.32	4.8	0	13.3	10.8	13.3
Contacted with aged $MgAl_2O_4$	1	0.02	8.3	0	3.5	3.0	3.5	3.0
	2	0.02	8.83	0	4.2	3.3	4.2	3.3
	3	0.02	8.27	0	5.9	4.5	5.9	4.5
	4	1.83	7.00	0	8.5	9.0	10.3	9.0
	5	2.4	7.00	0	10.7	13.0	13.1	13.0
Contacted with aged $NiAl_2O_4$	1	0.88	5.22	0	0.80	2.1	1.68	2.1
	2	1.48	4.96	0	0.92	3.2	2.4	3.2
	3	2.1	4.50	0	0.84	4.3	2.9	4.3
	4	3.9	3.17	0.7	1.14	9.2	5.1	9.2
	5	5.8	3.30	0.5	1.06	13.0	6.9	13.0

Table 12b

Adsorption of Zinc Chloride from Acid Solution on $MgAl_2O_4$ and $NiAl_2O_4$,
 Summary of Solution Data

Original Solution No.	Concentration, milli-equivalents per litre					
	Initial		Final, aged $MgAl_2O_4$		Final, aged $NiAl_2O_4$	
	cations	anions	cations	anions	cations	anions
1	<u>1.6</u>	<u>2.1</u>	<u>3.5</u>	<u>3.0</u>	<u>1.68</u>	<u>2.1</u>
2	<u>2.5</u>	<u>3.1</u>	<u>4.2</u>	<u>3.3</u>	<u>2.4</u>	<u>3.2</u>
3	4.1	4.1	<u>5.9</u>	<u>4.5</u>	<u>2.9</u>	<u>4.3</u>
4	<u>7.0</u>	<u>9.4</u>	10.3	9.0	<u>5.1</u>	<u>9.2</u>
5	<u>10.8</u>	<u>13.3</u>	13.1	13.0	<u>6.9</u>	<u>13.0</u>

Table 13a

Adsorption of Zinc Chloride from Less Acid Solution on MgAl_2O_4 and NiAl_2O_4

Origin of Solution No.	Concentration, milli-equivalents per litre							
	Zn ⁺⁺	pH	H ⁺	Ni ⁺⁺ or Mg ⁺⁺	Cl ⁻	Total cations	Total anions	
Initial Solutions	1	1.00	4.40	0.04	0	1.05	1.04	1.05
	2	1.50	4.19	0.07	0	1.47	1.57	1.47
	3	2.0	4.04	0.09	0	2.0	2.1	2.0
	4	4.0	3.70	0.20	0	4.1	4.2	4.1
	5	6.0	3.53	0.30	0	6.2	6.3	6.2
Contacted with fresh MgAl_2O_4	1	0.20	7.78	0	0.88	1.81	1.08	1.81
	2	0	7.78	0	2.4	2.0	2.4	2.0
	3	0.03	8.28	0	2.4	2.6	2.4	2.6
	4	0.90	7.28	0	3.6	4.5	4.5	4.5
	5	3.1	6.77	0	4.5	6.8	7.6	6.8
Contacted with fresh NiAl_2O_4	1	0.77	7.04	0	0	1.24	0.77	1.24
	2	1.18	7.00	0	0.05	1.81	1.23	1.81
	3	1.67	6.90	0	0.05	2.4	1.72	2.4
	4	3.8	6.73	0	0.07	4.4	3.9	4.4
	5	6.0	6.56	0	0.14	6.8	6.1	6.8

Table 13b

Adsorption of Zinc Chloride from Less Acid Solution on MgAl_2O_4 and NiAl_2O_4 ,
 Summary of Solution Data

Original Solution No.	Concentration, milli-equivalents per litre					
	Initial		Final, fresh MgAl_2O_4		Final, fresh NiAl_2O_4	
	cations	anions	cations	anions	cations	anions
1	1.04	1.05	<u>1.08</u>	<u>1.81</u>	<u>0.77</u>	<u>1.24</u>
2	1.57	1.47	<u>2.4</u>	<u>2.0</u>	<u>1.23</u>	<u>1.81</u>
3	2.1	2.0	2.4	2.6	<u>1.72</u>	<u>2.4</u>
4	4.2	4.1	4.5	4.5	3.9	4.4
5	6.3	6.2	7.6	6.8	6.1	6.8

Table 14a.

Adsorption of NiCl_2 and CaCl_2 on MgAl_2O_4 and NiAl_2O_4

Origin of Solution No.	Concentration, milli-equivalents per litre							
	Ni ⁺⁺ or Ca ⁺⁺	pH	H+	Mg ⁺⁺ or Ni ⁺⁺	Cl ⁻	Total cations	Total anions	
Initial NiCl_2 Solutions	1	1.20	2.40	4.0	-	1.16	5.2	1.16
	2	6.00	1.95	11.2	-	6.6	17.2	6.6
Contacted with aged MgAl_2O_4	1	0.12	6.45	0	6.1	2.0	6.2	2.0
	2	4.85	5.70	0	22.9	7.7	27.8	7.7
Contacted with aged NiAl_2O_4	1	1.48	3.10	0.79	-	2.0	2.3	2.0
	2	6.2	2.20	6.3	-	10 [‡]	12.5	10 [‡]
Initial CaCl_2 Solutions	1	1.20	3.87	0.14	0	1.29	1.34	1.29
	2	6.0	3.19	0.65	0	6.4	6.7	6.4
Contacted with aged MgAl_2O_4	1	1.50	7.30	0	0.70	2.4	2.2	2.4
	2	5.8	7.00	0	1.76	6.8	7.6	6.8
Contacted with aged NiAl_2O_4	1	1.40	6.30	0	0	2.0	1.40	2.0
	2	2.8	5.23	0	3.8	7.1	6.6	7.1

‡ This is an estimated figure, the solution was spoiled just before the end point was reached.

Table 14b

Adsorption of NiCl_2 and CaCl_2 on MgAl_2O_4 and NiAl_2O_4 ,
Summary of Solution Data

Solution No.		Concentration, milli-equivalents per litre					
		Initial		Final, aged MgAl_2O_4		Final, aged NiAl_2O_4	
		cations	anions	cations	anions	cations	anions
NiCl_2	1	<u>5.2</u>	<u>1.16</u>	<u>6.2</u>	<u>2.0</u>	2.3	2.0
	2	<u>17.2</u>	<u>6.6</u>	<u>27.8</u>	<u>7.7</u>	12.5	10 *
CaCl_2	1	1.34	1.29	2.2	2.4	<u>1.40</u>	<u>2.0</u>
	2	6.7	6.4	7.6	6.8	6.6	7.1

* This is an estimated value, the solution was spoiled just before the end point was reached.

Table 15

Treatment of $MgAl_2O_4$ and $NiAl_2O_4$ with water for 48 hours
 (Concentrations in milli-equivalents/litre)

Condition of spinel and water	pH	Mg^{++} or Ni^{++}	Equivalent $Hg_2(NO_3)_2$
Water + atmos. CO_2 initial	5.7	0	0.30
After contact with aged $MgAl_2O_4$	7.75	0.84	-
After contact with aged $NiAl_2O_4$	6.80	0.12	-
Water degassed with nitrogen	7.00	0	0.01
After contact with aged $MgAl_2O_4$	7.59	0.76	0.08
After contact with fresh $MgAl_2O_4$	10.36	2.8	0.08
After contact with aged $NiAl_2O_4$	6.90	0.12	0.05
After contact with fresh $NiAl_2O_4$	7.08	0.01	0.03

"Equivalent $Hg_2(NO_3)_2$ " represents anions determined by the mercurous nitrate titration method.

6. DISCUSSION

The 80-fold difference between surface charge densities for NiAl_2O_4 in 10^{-3} M $\text{Pb}(\text{NO}_3)_2$ calculated from early adsorption and electrokinetic measurements, can be interpreted as follows:

1. It can be concluded that the determination of adsorption from zeta-potentials may not be possible in this case.
2. The difference between the adsorption and the electrokinetic measurements may arise from one of the following phenomena:-

(i) The high positive charge due to the measured adsorption of cations is almost balanced by adsorption of anions into the fixed part of the double layer.

(ii) The cations lost from the solution might exchange with hydrogen ions from water adsorbed on the surface. The pH of the solution will decrease in this case and also in case (i) if OH^- is adsorbed.

(iii) The adsorbed cations might undergo ion exchange with cations from the spinel - but the analytical results of these early adsorption series indicated that this was not so.

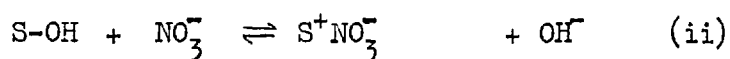
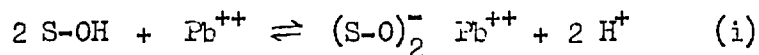
The next series of adsorption experiments (lead nitrate at various concentrations adsorbed on NiAl_2O_4 spinel) in which the pH's of the solutions were measured, showed increases in pH ruling out interpretations 2 (i) and 2 (ii).

The overall adsorption is possibly the result of both true adsorption and surface ion-exchange. Considering the

true adsorption process, the solution can be regarded as being divided into three regions; (a) that part between the solid surface and the slip plane (corresponding to the zeta-potential) (b) the diffuse double layer extending from the slip plane to the bulk solution and (c) the bulk solution. In the case of lead nitrate adsorption there will be Pb^{++} , H^+ , OH^- and NO_3^- ions in all three regions of the solution. The measured zeta-potential of + 5 mV in $10^{-3}\text{M Pb}(\text{NO}_3)_2$ solution indicates that there is an excess of cations in the fixed layer; $\sum z_i n_i$ is positive, where z_i and n_i are the valency and number respectively of the four ionic species. In the diffuse double layer, region (b), there must be an excess of anions such that $\sum z_i n_i$ for this region exactly balances that for the fixed layer. The bulk solution is electrically neutral, i.e. $\sum z_i n_i = 0$.

If the pH of the bulk solution is to increase as a result of this adsorption process the number of hydroxyl ions in the bulk solution must increase. This can only occur if the ratio $\text{OH}^-/\text{NO}_3^-$ is less in region (a) than in the rest of the solution or, conversely, if the ratio $\text{H}^+/\text{Pb}^{++}$ is greater in regions (a) and (b) than in (c).

It is suggested that the second process, surface ion-exchange, involves the reactions



where S-OH represents the hydrated surface. Reactions of this type will have no effect on the net surface charge. Reaction (i) will contribute to the measured uptake of Pb^{++} . If reaction (ii) is more favoured than reaction (i) there will be a net increase in hydroxyl ion concentration in the bulk solution.

Two methods are available to obtain further information about these two processes. Either use the measured change of pH in conjunction with the measurements of zeta-potential and lead ion adsorption or values for the total uptake of the anion together with the other measurements may be utilised. Each method, together with certain assumptions about the diffuse part of the double layer, provides enough data to calculate the number of ions in each part of the solution and on the surface. The measurements of change in pH have already been pointed out as unsatisfactory and hence the second method, involving full analysis of the adsorption solutions, was adopted for the final series of adsorption experiments.

Inspection of Tables 10 and 11b to 14b shows that of sixty-four solutions on which "complete analysis" was performed, twenty solutions gave analyses in which anions apparently exceeded cations by significantly more than the experimental error of 10%. A further eight solutions gave analyses corresponding to a significant excess of cations. These twenty-eight results are underlined in Tables 10 and 11b to 14b.

Accepting the electroneutrality law two possible explanations are left, either the analyses were grossly in error or they were not complete. If the results are to have any value it is necessary to establish the probable cause of the discrepancy in each case.

There are four instances in which anions apparently exceed cations in the original solutions; they are all strongly acidic solutions of zinc chloride (Table 12b). The most likely source of error is in the pH measurement giving a low hydrogen ion concentration. An error of 0.2 pH units on these four samples would entirely account for the discrepancy. Although this error is greater than expected, it is possible in unbuffered solutions. In the less acid solutions of $ZnCl_2$ (prepared from the same oxide sample) the hydrogen ion concentration is a much smaller part of the total cations and so any error in the pH measurement is less noticeable.

Dealing next with the fourteen cases giving anomalous results after adsorption on $NiAl_2O_4$ spinel. Table 12b shows that all five of the final, more acid zinc chloride solutions, after contact with the $NiAl_2O_4$, have anions far in excess of cations. The discrepancy increases with concentration of zinc and hydrogen ions from 15% to 40%. The final pH of these solutions varied from 5 to 3 and it is likely that the assumption that no aluminium dissolves from the spinel is no

longer correct. Comparison of the anion analyses for the original and final solutions shows good agreement. It is reasonable to assume that the cations unaccounted for are Al^{+++} which would not be detected in the polarographic determination of zinc and nickel. The concentration of Ni^{++} is a guide to the amount of solid attacked by the acid solution. Assuming that three equivalents of Al^{+++} dissolve for each of Ni^{++} (based on the ratio $Al:Ni = 2:1$ in the oxide) the maximum concentration of Al^{+++} possible is more than enough to account for the differences except at the highest concentration of $ZnCl_2$.

The results for the less acid zinc chloride solutions after contact with fresh $NiAl_2O_4$ (Table 13b), again indicate that the anion concentrations exceed the corresponding cation concentrations. The differences here are approximately constant and independent of zinc or hydrogen ion concentration. The final pH of the solutions was sufficiently high to keep aluminium out of solution. No reasonable and simple explanation can be suggested for these discrepancies.

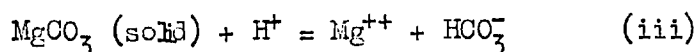
Nickel chloride solutions (Table 14b) should yield results comparable to the zinc chloride solutions. Inspection of Table 14b shows that there is no similarity, neither are the anion nor the cation analyses self-consistent. Although small errors in pH measurements and the presence of Al^{+++} in the final solutions may partly account for the major dis-

crepancies they cannot account for the total differences. Similarly, the results of contacting low concentration lead chloride solutions with NiAl_2O_4 (Tables 10 and 11b) are difficult to understand. These results and those of Table 13b discussed earlier cannot be interpreted and they must cast some doubt on the analytical procedures used, particularly that for nickel.

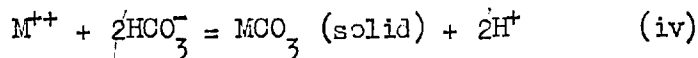
Generally, the results of contacting the various electrolyte solutions with MgAl_2O_4 show better agreement than those for NiAl_2O_4 . Five of the ten anomalous results are in those two groups which are already in considerable doubt: the more acid zinc chloride (Table 12b) and the acid nickel chloride solutions (Table 14b). Three of these results are only just outside the likely experimental error and may be the result of an accumulation of errors all in the same sense (Table 10, solutions 3 and 4 and Table 11b, solution 2). The remaining pair of results are for the low concentration solutions of the less acid ZnCl_2 . In solution 1 (Table 13b) it would appear by comparison with other solutions of this group that the anion analysis was seriously in error. In solution 2 it is more likely to be the cation analysis which is at fault. Again no satisfactory explanation can be offered for these results.

Where aged MgAl_2O_4 was used and the final solution was at pH of 6.5 or greater there may have been a contribution to the total anions from HCO_3^- which was not determined. As will be

discussed later, there is some evidence that the aged $MgAl_2O_4$ had some carbonate on the surface; this will dissolve in the acid solutions and, if the final pH is high, the reaction may be written



Of these ions H^+ and Mg^{++} are determined but HCO_3^- is not which will result in an apparent excess of cations. It is difficult to estimate the quantity of bicarbonate which may remain because, in the early stages of adsorption and in the chloride estimation the solution is acid and some carbon dioxide may be evolved as gas and in the later stages of adsorption when the solution becomes neutral or alkaline the reaction



may occur, where M^{++} is the electrolyte cation. This reaction will remove bicarbonate from the solution and, following reaction (iii), will tend to restore the cation-anion balance that is determined. Only the more acid solutions of zinc chloride gave consistently high total cation analyses after contact with aged $MgAl_2O_4$ (Table 12b), other solutions did not give consistent results. The less acid zinc chloride solutions were only used in conjunction with freshly heated $MgAl_2O_4$ where no carbonate is expected.

The anion analyses (which were effectively chloride only in all cases) of the final solutions tended to be higher than those of the original solutions. Of forty final solutions

examined, thirty-one gave a final chloride ion analysis higher than that of the original solutions; in fifteen cases the difference was greater than the probable experimental error. In only one case was the experimental error exceeded in the other direction and then only by a small amount. The effect appears to be real and not restricted to any particular solutions. The possibilities why this should occur are (a) the chloride analysis fails after contact between solution and solid but not before (b) chloride, or another ion precipitated by mercurous nitrate in acid solution, is extracted from the solid or (c) the solution becomes concentrated. When a solution without solids was subjected to the same treatment as in the adsorption measurements no decrease in weight was observed thus eliminating possibility (c). Treatment of the spinels with water in a similar manner showed that no appreciable chloride or other comparable ion was extracted although some chloride ions originating from the saturated calomel electrode used in the pH measurement will appear in the solution. However, as the same technique was used for the water treatment samples and no significant quantity of chloride ion appeared in these solutions (Table 15), it is reasonable to assume that this was not the source of the increase in chloride ion concentration. It is difficult to see why the analytical method should work on the original solutions and not on the final solutions which differed only

by the presence of low concentrations of Ni^{++} or Mg^{++} whilst Pb^{++} , Zn^{++} etc. were already present in the original solutions. Again there appears to be no reasonable explanation of this observation.

Summarising the preceding discussion of the validity of the adsorption measurements the position is:-

(i) the analyses are less certain than was expected from the original testing and calibration:

(ii) the results for the more acid zinc chloride solution and the nickel chloride solution are unreliable;

(iii) the results for all measurements involving the oxide NiAl_2O_4 are doubtful, probably because the nickel analysis was at fault,

(iv) the anion (chloride) concentration apparently increased as a result of contact with the spinels for no obvious reason.

Even within these severe limitations it is possible to arrive at some qualitative conclusions about the interaction of the electrolytes with the two oxides. First, it is quite clear that the oxides do not have inert surfaces, ions originally in the oxide lattice appear in the solution in all cases. The higher concentration of Mg^{++} in the final solutions indicate that the magnesium spinel is more reactive than the nickel spinel, although the surface areas of the two oxides were comparable.

The action of CO_2 -free double-distilled water (Table 15) on these spinels gives an indication of what is happening in the case of electrolytes. The freshly heated magnesium spinel gives an alkaline solution and a quantity of magnesium dissolves of the same order as the amount of magnesium available in the oxide surface. If the surface layer is assumed to be $\frac{1}{2}$ unit cell thick, i.e. one hypocube of the cell, then four magnesium atoms are associated with a surface area of $65.4 \times 10^{-16} \text{ cm}^2$ (from X-ray diffraction data). The concentration of magnesium expected in the final solution can now be calculated as follows:-

$$\text{Magnesium in surface} = \frac{6800 \times 4 \times 10^{16}}{65.43} \times \frac{10^{-23}}{6.023} \text{ moles } \cancel{\text{cm}^2}$$

Since the spinel is present to the extent of 2g per 10 mls. of solution Mg^{++} expected in solution

$$= \frac{68 \times 4 \times 10^{-5}}{65.43 \times 6.023} \times 200 \text{ moles/litre}$$

$$= \frac{68 \times 4 \times 10^{-5}}{65.43 \times 6.023} \times 200 \times 2000 \text{ milliequivalents/litre}$$

Mg^{++} expected in solution = 2.76 milliequivalents / litre.

Mg^{++} found in solution = 2.8 milliequivalents / litre.

Apparently the solid is chemically attacked by the water and magnesium oxide dissolves until equilibrium between solid magnesium hydroxide, magnesium ions and hydroxide ions is reached. As the free energy of formation of the spinels from the primary oxides is small, the activity of MgO in MgAl_2O_4

is not far from unity so the equilibrium reached is virtually the same as that for pure MgO . The primary oxide is completely converted to $Mg(OH)_2$ in the presence of water. Calculation shows that the results for fresh $MgAl_2O_4$ in contact with water are in good agreement with the solubility product of $Mg(OH)_2$, which is approximately 1×10^{-11} . The residual aluminium hydroxide is probably hydrolysed to a hydrated oxide which remains insoluble and attached to the surface of the spinel.

In the case of the unheated $MgAl_2O_4$ with CO_2 -free water the pH increased to 7.6 and less magnesium dissolved. This is consistent with the surface being predominantly magnesium carbonate. If the surface were predominantly magnesium hydroxide the final pH of the solution would lead one to expect an extremely high concentration of magnesium in the solution; the magnesium ion concentration determined, $0.38 \times 10^{-3}M$, is in better accord with the solubility of magnesium carbonate (solubility product 2.6×10^{-5}). The carbonate in solution is not detected by the mercurous nitrate titration carried out in acidified solution.

The $NiAl_2O_4$ shows the reverse tendency, more Ni^{++} is dissolved from the aged solid than from the freshly heated material. It is possible that heating temporarily renders the surface less reactive in a kinetic sense rather than a thermodynamic sense. The slow action of adsorbed water and

CO₂ from the atmosphere converts the surface to hydrated nickel oxide or basic nickel carbonate, either of which reach equilibrium with water more rapidly. As might be expected, less nickel dissolves than magnesium and the final solution is barely alkaline. Horsfall and Benton (7) in their work on synthetic magnetite similarly found that water leached ferrous iron from the solid spinel.

When electrolytic solutions were used with MgAl₂O₄ essentially the same initial processes occurred as with water. Magnesium oxide dissolved to give a more alkaline solution which caused precipitation of the metal cation as a hydrated oxide or basic carbonate, depending on whether the oxide was fresh or aged. In the case of lead chloride the precipitation was complete and the final pH was approximately that reached in water. This was confirmed by slow titration of the lead solution with alkali; precipitation of the lead was virtually complete at a pH of 10. With acid electrolytes precipitation was not complete and the pH did not reach such a high value as in water. Probably the amount of magnesium oxide which could be leached in forty-eight hours was limited. This also confirms that there was no appreciable excess of unreacted magnesium oxide present in the fired spinel since this would have reacted much more rapidly.

In the case of NiAl₂O₄ greater quantities of nickel were extracted from the unheated oxide, particularly by the

acid solutions. The heated oxide showed less tendency to react. Whether or not precipitation of the metal cation occurred cannot be deduced from these results.

The results of the zeta-potential measurements cannot strictly be compared with the adsorption data because the pH of the solutions and, probably, the state of the oxide surface were not the same in the two series of measurements. In zeta-potential measurements the electrolyte solution was passed through the plug until no change was observed in the streaming current. This probably corresponds to a more complete leaching of the oxide than occurred in the adsorption measurements, although the time of contact was much shorter. This is more likely to be the case with $MgAl_2O_4$ than $NiAl_2O_4$. The final surface must resemble hydrated aluminium oxide rather than spinel and the solution will be at a pH at or very near to the pH of the original solution. Any precipitation of the metal cation of the electrolyte which occurred in the first stage of flow will be reversed as further more acid, original solution is streamed through the plug.

The important conclusion of this work is that the interaction of metal oxides of the spinel type with divalent cation electrolytes is much more complex than simple adsorption of the electrolyte. Leaching of the oxide surface is the dominant feature, particularly where the more basic oxides such as $MgAl_2O_4$ are concerned. Ageing of the oxide by air containing

water vapour and carbon dioxide produces a marked change in $MgAl_2O_4$ and a significant change in $NiAl_2O_4$. Zeta-potential measurements made on oxides of this type must be interpreted with great caution because the surface existing at the time of measurement is very different from that of the original oxide.

In order to make a comparison of electrokinetic and chemical values of adsorption more quantitative results will be necessary. This will entail a very thorough investigation of the analytical procedures. Equally necessary will be careful control of the previous treatment of the oxides and, if possible, identification of the surface species produced by the electrolyte-oxide contact. Little of further value to such a lengthy programme could be achieved in the short time available to the author, so the decision was made to conclude the present investigation at this stage.

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