"CHEMICAL REACTIVITY
OF COAL
AND
ITS COMPONENTS."

A thesis submitted to the University of Glasgow in fulfilment of the requirements for the degree of Doctor of Philosophy (Faculty of Science).

Rajindra Pal Puri.

B.Sc.(Hons:), M.Sc.
(Panjab), A.R.T.C.,
A.R.I.C., A.M.Inst.F.

May, 1949.

ACKNOWLEDGMENT.

The thanks of the author are due to

Professor W.M. Cumming, O.B.E., D.Sc., F.R.I.C., M.I.Chem.E., F.R.S.E.,

and J.R. Campbell, Esq., B.Sc., Ph.D., A.R.T.C., F.R.I.C., M.Inst.F.,

for suggesting the problem, for their constant valuable advice, guidance and for their sustaining encouragement.

Thanks are also due to Mr. H.V. Mehta, B.Sc., B.Sc.(Tech), A.R.T.C., in collaboration with whom the work on "The application of sulphonated coals to the anodising of aluminium" was carried out.

Department of Technical Chemistry,
Royal Technical College,
Glasgow.

R.P. Puri.

RESUME.

Action of nitric acid (approximately hundred per cent) and fuming sulphuric acid on bituminous coal has been studied.

Action of nitric acid (approximately 100%)

A special technique and apparatus evolved to study the action of nitric acid on coal under controlled conditions is described.

A study of the gaseous products obtained during the reaction has revealed that reaction must be carried for a least 12 hours to obtain a fair yield of the products of the third stage of oxidation.

A detailed study of the water-insoluble product, isolated during this reaction, is given. It is a dark red product with a molecular weight of the order of 160, the lowest so far reported for a coal degradation product of the humic acid type. It has a molecular formula $C_6 H_4 O_4 N$, is a mono basic acid and has one nitro group but evidence to structural formula is inconclusive.

Action of fuming sulphuric acid.

A study of the action of fuming sulphuric acid on coal with respect to the ion exchange properties/

properties introduced in this so called sulphonated coal is given.

An apparatus and procedure for sulphonating the coal under any desired conditions is described. It is shown that with the coal being used, the optimum exchange capacity is obtained by using 20% SO_3 oleum at 110° - 120°C for 3 - 4 hours. Additions of small percentages of approximately 100% HNO_3 are shown to catalyse the sulphonation of coal.

Titration curves of the sulphonated coals, with and without the addition of NaCl, are given. The base-binding capacity of these "insoluble acidoids" is shown to be a function both of pH and ionic strength of the solution. Correlation of the experimental data with Griessbach's theoretical equation is described.

A possible application of the H-ion-exchangers to catalyse the anodizing of aluminium has been studied. It is shown to be a useful catalyst and yields a better anodic film in a shorter time.

CONTENTS.

Page

1. General Introduction. 1

PART I

2. Study of action of nitric acid on coal.

Section 1. Introduction. 6

Section 2. Experimental. 20

I Action of nitric acid on coal 20

(i) Preliminary work. 20
(ii) Apparatus and Procedure. 21

II Study of the gaseous products evolved during the oxidation of coal with nitric acid. 27

(i) Apparatus. 27

III Study of the water-insoluble product 37

(i) Batch production of the product. 37
(ii) Purification and fractionation. 37
(iii) Ultimate composition and Empirical formula. 38
(iv) Molecular weight determination. 39
(a) Cryoscopic method. 39
(b) Cryoscopic method - using Thermistor. 49
(c) Ebulliscopic method. 51
(d) Barger's Osmosis method. 54

(v) Functional groups 63

(1) Groups not containing nitrogen. 63
(a) Carboxyl and Hydroxal groups. 63
(b) Attempted methylation. 71
(c) Attempted esterification. 72

(2) Chemistry of nitrogen in the compound. 74

(vi) Thermal decomposition of the product. 83

Section 3. Discussion of the results. 85

I Study of the gaseous products evolved during the oxidation of coal with nitric acid. 85
II Study of the water-insoluble product 89

(i) General properties. 90
(ii) Ultimate composition and Empirical formula. 91
(iii) Molecular weight. 92
(iv) Molecular formula of the compound. 97
(v) Functional Groups. 97
(a) Groups not containing nitrogen. 98
(b) Nature of nitrogen-containing groups. 101

Section 4. Summary and Conclusions. 110

PART II

3. Study of action of fuming sulphuric acid on coal. 114

Section 1. Introduction. 114

Section 2. Experimental. 127

I Preliminary work. 127

- (i) Sulphuric acid of oleum strength. 127
- (ii) Preparation of coal. 127
- (iii) The reaction. 128

II Apparatus and Procedure. 129

III Method of determination of base-exchange capacity. 133

IV Study of physical and chemical factors on sulphonation. 137

- (i) Effect of temperature 137
- (ii) Effect of Time. 138
- (iii) Effect of concentration of oleum. 138
- (iv) Effect of the nature of sulphonating agent. 143

V Study of titration curves of sulphonated coals. 151

- (i) Preparation of the exchanger for titration. 151
- (ii) Time required for equilibrium between acidoid and alkali. 152
- (iii) Titration of sulphonated coal. 155
- (iv) Titration of known sulphonic acids. 155
- (v) Effect of the ionic strength of the solution on the pH-neutralization curves of Zeo-Karb H.I. 165

VI Study of the application of sulphonated coals to the anodizing of aluminium. 178

- (i) Apparatus and procedure. 179
- (ia) Effect of concentration of sulphuric acid. 183

(ii) Effect of time. 184
(iii) Effect of concentration of sulphonated coal. 184

(iv) Effect of sulphonated coal on the quality of anodizing. 189

Section 3. Discussion of results. 195

I Study of physical and chemical factors on sulphonation of coal. 195

II Study of titration curves of sulphonated coals. 202
Correlation of experimental data with Griessbach's equation. 210

III Anodizing of aluminium as catalysed by sulphonated coal. 230

Section 4. Summary and conclusions. 237
4. Appendix I. 243
5. Appendix II. 257
6. References. 263

7. Additional papers Folder.

"CHEMICAL REACTIVITY OF COAL AND ITS COMPONENTS"

GENERAL INTRODUCTION.

For nearly 200 years mankind has been using coal extensively, our present civilization being largely dependent upon it. Coal, in truth, stands not beside, but entirely above all other commodities. It is the World's leading commodity whether measured in terms of tonnage produced, monetary value or industrial importance. It is the material source of energy of any country - even in the modern atomic age. It is the universal aid - the factor in everything we do. With this almost any feat is possible or easy; without it we are thrown back into the laborious poverty of old times. In spite of this undisputed and probably unrivalled position of coal in our modern civilization, much less is known about its chemical nature than about that of perhaps any other important natural raw material. In fact for a long time many controversial opinions were put forward about its definition and even its origin. Our knowledge of the origin of coal necessarily suffers from the recognized imperfections in the geological record,, and therefore the scientific imagination had often to fill in gaps where precise information or definition is wanting

It/

It is generally accepted, however, that coal has a vegetable origin and any view or theory concerning the factors and conditions operative at the various successive stages in the long transformation process is necessarily somewhat speculative and subject to reservation. Certain well-attested features which stand out prominently in the record may, however, be regarded as more or less common.

It has been, of course, long recognized that coal is a rock. It is not a mineral although in trade, industry and legal affairs it is considered as a mineral. This is because according to Dana(1), our standard authority on the subject, mineral is an inorganic homogeneous substance with a definite composition all of which coal lacks. Anyway it is accepted to be of an organic origin and its widely accepted definition was originally proposed by Stopes and Wheeler (2) and later modified by Fox (3). According to them "coal is defined as a compact stratified mass of metamorphosed plants which in part have suffered arrested decay to varying degrees of completeness, free from all save a very low percentage of other matter."

Chemical reactivity of coal and its components has been studied by various workers mainly with the idea of evolving fresh and novel uses or classification of coal. Although/

Although it has been known for long that coal contains carbon, hydrogen, nitrogen, sulphur, etc., that on carbonization it yields coke, tars and a complex mixture of oxides of carbon, steam, hydro-carbons, hydrogen, ammonia, sulphuretted hydrogen etc.; such facts reveal little concerning the chemical constitution of the coal substance, beyond its organic origin and nature. In fact these facts were the fruits of labour of those who wanted to use the coal rather than study its chemistry. Until recently the research on coal does not seem to have followed the logical deductions anticipated from the source of origin of coal, but that what little is known about it seems largely the result of isolated experiments concerning utilization of coal, often dependent on chance for their success because coal is an extremely difficult and refractory substance to deal with.

Attempts to study the chemical reactivity of coal and its components with a view to obtaining some definite information as to its chemical constitution have been thwarted at the outset by its insolubility and by its resistance to all but the most powerful reagents, which indeed render the main bulk of the coal substance soluble, but which in so doing destroy or profoundly modify the molecular structures of the compounds obtained therein. For this reason the mode of attacking/

attacking the problem most fruitful in results up to date has been an indirect one - destructive distillation - relying for its proofs on a comparitive examination of the behaviour of substances of known constitution under similar treatment. Valuable, even though scanty, information has, however, also been gained by more direct methods of attack by the use of solvents. Use also has been made of reagents to aid in determining the constitution of coal chiefly by the geologists and paleo-botanists, who have found in the partial breakdown of the mass by concentrated acids and oxidants suitable means of isolating organized structures for examination under the microscope. Chemists, on the other hand, have been alternatively dismayed by the complexity of the products of such reactions, or confounded by their apparent simplicity.

Of the many reactions employed to study the chemical reactivity of coal and its components, the action of nitric acid and sulphuric acid (of oleum strength) seem to be of rather greater interest.

1. <u>Action of nitric acid (100% approximately)</u>.

A study of the literature of the work done by various investigators on the action of nitric acid on coal suggests its use as a very effective means, because of its oxidizing properties, to gain an insight into the character of the/

the nuclei structure of the complicated coal molecule. Approximately 100% nitric acid which, though never tried before, has the qualities of a very promising oxidant, was therefore chosen as an interesting reagent for study.

2. Action of Sulphuric Acid.

When coal is treated with concentrated sulphuric acid at temperatures up to 250°C, the product, after the removal of the acid, has base-exchange properties, and a number of patents has been taken out to cover this property. The industrial utility of these "sulphonated coals" has stimulated research on their practical aspects, and the patent literature has grown at a much more rapid rate than the literature devoted to scientific investigations of the action of sulphuric acid on coal or the ion-exchange process as it occurs in these "carbonaceous exchangers". This was the second reaction selected for the study.

The study of the above two reactions which is detailed in the following pages, has been divided into two parts as:-

Part 1 :- This deals with the study of the action of nitric acid (approximately 100%) on coal.

Part 2 :- This deals with the study of the action of sulphuric acid (of oleum strength) on coal and the ion-exchange process of carbonaceous exchanger thus produced.

PART I

STUDY OF THE ACTION OF APPROXIMATELY 100% NITRIC ACID ON COAL.

SECTION 1.

STUDY OF THE ACTION OF APPROXIMATELY 100% NITRIC ACID ON COAL.

INTRODUCTION.

A number of reagents, e.g. atmospheric oxygen, nitric acid, alkaline potassium permanganate, alkaline hypochlorites, hydrochloric acid in presence of potassium chlorate, chromic acid, chlorine, sulphuric acid, etc. has been utilized to aid in the elucidation of the constitution of coal. However, as is evident from the nature of the above mentioned reagents, the majority of these have been oxidants - aerial oxygen and nitric acid being the most commonly employed reagents.

One of the most useful tools available to the chemist for establishing the structure of organic molecules has been "oxidation". In those cases where the substance under investigation is of low molecular weight, identification of its oxidation products may lead immediately to a knowledge of its structure. But the results have been rather less conclusive with substances of high molecular weight e.g. polymers, coal etc. However in certain polymers, as for example, linear diene polymers, such as the natural and synthetic rubbers, where the naturally occurring double bonds offer a ready/

ready opening for attack, oxidation has yielded results of the greatest significance (4).

The chemical and physical properties of bituminous coals indicate tridimensional or net-work structures, and hence a complicated series of oxidative degradation products is to be expected. Oxidation takes place, however, with convenient velocity with a number of oxidizing agents at a temperature such that there is a little probability of internal structural changes, and even with these mild oxidation procedures some eighty per cent of the carbon of typical bituminous coals can be recovered in the form of alkali-soluble products. It is because of the high yield of products of moderate molecular weight and the low temperature required for the reaction that oxidation has been used extensively for investigation of the structure of coal and related substances. Apart from the theoretical interest of these studies, the possibility of obtaining products of commercial value is always present since an important part of the oxidation products consist of poly-carboxylic acids, e.g. mellitic, pyromellitic or picric (obtained by oxidation of coal in liquid suspension either in nitric acid or in alkaline medium by means of gaseous oxygen or potassium permanganate) and acids of this type are finding wide applications in the synthesis of resins, fibres and/

and lacquers. If these acids are esterified, the esters form useful plasticisers for the manufacture of Buna rubber, while if the esters are in turn etherified, suitable lubricating oils are produced.

Oxidation of coals can be further subdivided in three stages as mentioned below (5) :-

1. Surface oxidation:-

No fundamental change in the structure of the coal molecule is made by this mild oxidation which, however, takes place with appreciable velocity in the case of bituminous coals at room temperatures and above. The external groupings are modified, those most readily detached being eliminated as simple oxygenated compounds and their place being taken by carboxyllic groups. According to some these products exhibit peroxidic properties and are believed to consist of a coal-oxygen-water surface complex. Anyway no structural changes take place, carbon dioxide, carbon monoxide and water are formed concomitantly and are usually liberated if this action is prolonged or if the temperature is increased. The rate is a function of the rank of the coal as well as of temperature, oxygen partial pressure and surface area. Superficially the coal is little affected but it does show changes in caking properties, heat of combustion and susceptibility to further oxidation/

oxidation. The presence of acidic surface groups is indicated before any appreciable alkali solubility appears.

2. Humic Acid formation:-

A moderate degree of oxidation will produce sufficient change in the external groupings of the coal molecule to render the matrix of bituminous coal soluble with difficulty in alkalis. However, as oxidation proceeds more groupings from the side chains are eliminated and some of the carboxyllic groups begin to decarboxylate. Mahler (6), for example, passed a slow stream of air during long periods through coals heated to low temperatures and found traces of formic acid, methyl alcohol and acetone and larger quantities of acetic acid were present in the condensed products whilst the coals themselves became increasingly soluble in aqueous potassium hydroxide. This observation supports the view that the limiting condition is reached eventually when all external groupings have been eliminated.

These alkali-soluble, acid insoluble products are designated as "regenerated humic acids". These humic acids are far from homogeneous, but probably are of the same general type of structure, differing chiefly in molecular weight and the point of attachment of the functional groups.

3. Third stage:-

If more drastic oxidation methods are applied or if the process which produced the humic acids of stage 2 is continued for a sufficient length of time, a breakdown of the nuclear structure of the humic acid molecule occurs into lower molecular weight acids soluble in acid and neutral, as well as alkaline, aqueous media. Transformation from stage 2 to stage 3, as in the previous step, is always accompanied by formation of carbon dioxide, until, if the oxidation is sufficiently prolonged, all the carbon appears in that form. The transformation in stage 3 is characterized by definite colour changes which are presumably indicative of internal structural changes. The colour of the aqueous solution of the water - soluble acids range from deep reddish brown to a pale yellow. The intensity of the colour of these organic acids is a function of the extent of the oxidation and hence bears a definite relation to the fraction of the carbon appearing as carbon dioxide. It was noted in America that with a Pittsburgh Seam Bituminous Coal, pale orange to yellow solutions were obtained when approximately fifty per cent carbon of the coal had been converted to carbon dioxide, and colourless solutions were not obtained until more than ninety per cent of the carbon had been so converted, thus indicating the remarkable stability of/

of the molecules containing these chromophoric groups. The nature of the colour - bearing groups in the oxidation products of coal has attracted practically no attention although it seems to be of a great significance. Moreover such diverse oxidizing agents as nitric acid, alkaline potassium permanganate and molecular oxygen all furnish intensely yellow oxidation products. The oxidation products prepared by the pyrolysis of cellulose at moderate temperatures also have a yellow colour.

It may be noted that the greater part of the significant information concerning the structure of coal can be obtained by a thorough study of the oxidative degradation in the stage 3 above. This is because the identification of any simpler compounds resulting from such a break down will help in building back the character of the complicated ulmin molecule. It was for this reason that oxidation of coal to this third stage of oxidation was selected as a suitable method of attack in the problem.

These acids obtained by drastic oxidation of coal may be got in one step, without isolation of humic acids, or in two, involving an intermediate formation of humic acids. That the humic acids are an intermediate product there appears no doubt although in very active oxidation procedures, as is proposed for the present study, their existance may be fleeting. This/

This whole series of so-called "Soluble acids" appears to be between humic acids and the ultimate odixation products viz. carbon dioxide and water, and it is the isolation of these intermediate acids which could help in the elucidation of coal structure.

As already indicated a variety of oxidizing agents has been and can be employed in various media. With the exception of nitric acid, the use of these oxidizing agents in other than alkaline medium results in poor yields of the simpler types of organic acids and the conversion of a large fraction of carbon to carbon dioxide. To obtain the soluble organic acids in good yields it appears to be essential first to degrade the coal structure to units of the humic acid type and then to attack these individually in a homogeneous reaction. The behaviour of oxidizing agents in an acid aqueous medium appears to parallel more closely the heterogeneous gas-solid reaction of oxidizing gases on coal at elevated temperatures, where, except under very special circumstances, the formation of organic acids does not take place. This is probably due to the insolubility of humic acids in acidic aqueous media. But nitric acid constitutes a specific and very important exception which gives these simpler acids in quite good yield probably because, at least in the higher concentrations, humic/

humic acids are soluble in nitric acid. It seems, therefore, that nitric acid gives an effective and efficient method of attack on the coal molecule because of the good yield of the simple acids and the usual ease of the isolation of the degradation products from an acidic medium.

Many investigations dealing with the action of nitric acid on coal and various forms of carbon have been carried out but unfortunately much of the work has been of a qualitative nature. Besides a good part of the investigations have dealt with graphite and various types of carbon rather than with coals, but they are of interest in a general way. The early work with nitric acid was aimed at distinguishing between and classifying different carbonaceous materials such as lignite, coal, coke, amorphous carbon, wood, charcoal and graphite. The products were merely examined qualitatively and described as yellow viscous liquids, humic acids, graphitic acids, and so forth, and in few experiments were definitely characterized products reported and in still fewer the amounts (7).

The action of nitric acid on a variety of carbonaceous materials including coals, has been studied by Donath and his co-workers. Part of this work was carried out to develop methods of distinguishing between different ranks of coal and part to establish the nature of the oxidation products. Nitric/

Nitric acid of specific gravity 1·055 was claimed to distinguish between brown and bituminous coals, the brown coal reacting strongly, the bituminous being unattacked (8). They claim to have isolated a number of aliphatic acids from brown coal viz. oxalic, propionic, butyric and caproic acid. A nitro-product was also mentioned. These workers also suggested the formation of nitroso compound when nitric acid reacted with coal.

Dimroth and Kerkovius (9) made an important contribution to our knowledge of the nature of the nitric acid oxidation products of carbonaceous materials by oxidizing charcoal with nitric acid, converting the acids to Barium salts, and decarboxylating these salts by distillation with Barium hydroxide, Benzene, naphthalene and fluorene were found in the resulting hydrocarbons. This discovery of fluorene is reported to be the first and, to date, the only direct experimental evidence for the presence of highly condensed ring nuclei in the oxidation products of coals or carbons.

Mellitic and Pyro-mellitic acids were obtained, up to a yield of 30% by Meyer and Steiner (10) by oxidation of carbonaceous materials. The same workers (11) later claimed to have isolated mellitic acid in yields up to 40% by refluxing carbonaceous materials with nitric acid of specific gravity 1·51 to which small amounts, 0·2 to 0·5 per cent, of/

of vanadic acid were added as a catalyst. The best yields were obtained from pine and fir charcoal. The yields were small with graphite and little or none with brown and bituminous coals. The yields of the acids obtained were estimated from the weight of crude ammonium salt recovered and purified by conversion to a copper salt.

The action of nitric acid of various concentrations on brown coal has been studied by Marcusson (12a). He found that approximately a third of the nitrogen added in the reaction could be split out again by refluxing with hydrochloric acid; for this reason he suggested that the nitric acid may have been held in oxonium structures.

The oxidation of the humic acids to so called soluble acids have not been studied until recently when Francis and Wheeler (12), Fuch and Stengel (13) and later Howard (14) and co-workers published some work on these lines. Although not much is known about these acids it appears safe to recognize that there lies between the regenerated humic acids and the crystalline, definitely characterizable types, such as oxalic and benzene carboxylic acids, a series of soluble and insoluble acids of varying molecular complexity, characterized by colours ranging from reddish brown to golden yellow, having lower equivalent and molecular weights than humic acids, showing

far/

far greater solubility in solvents like ether, alcohol and acetone, diffusing through parchment or cellophane, either with or without an applied electrical potential, having ultimate compositions indicating cyclic nuclei, and having, like the humic acids, oxygen unaccounted for in either carboxyl or hydroxyl groups, but usually with a very much smaller fraction of total oxygen so unaccounted for.

It appears reasonable to assume that a study of the nuclear structure of these coloured intermediate acids would be of great importance. They are of sufficient complexity so that any facts established would be of significance, and yet they appear simple enough so that available tools could effect a successful attack.

Francis and Wheeler (loc.cit.) seem to be the first workers to oxidize the regenerated humic acids to the soluble-acids stage. A yield of 25 per cent of soluble-acids based on the humic acids, was obtained by the action of 30 per cent nitric acid. Acetic, oxalic, succinic, picric, and pyromellitic acids were definitely identified among the oxidation products, and trimellitic acid was thought to be present. About 3 per cent of picric acid, based on humic acid, was recovered.

Fuchs and Stengel (loc.cit.) have oxidized

humic/

humic acids from Kassler brown coal, with 1:1 nitric acid. About 71·5 per cent conversion to soluble acids has been claimed. These were fractionated and recovered in the form of calcium salts insoluble in 1:1 hydrochloric acid or 1·85N nitric acid, calcium oxalate, silver salt fractions and nitrophenols, the fractions based on the original humic acids being 20·5, 2·78, 43·9 and 4·45 per cent respectively. By conversion of some of these fractions to methyl esters etc. it was found that mellitic, benzene pentacarboxylic, pyromellitic (1, 2, 4, 5 benzene-tetracarboxylic acid), and trimesic (1, 3, 5 benzene tricarboxylic acid) acids were definitely present. About 4·5 per cent of picric acid was also recovered. But, apart from what is mentioned above, neither the free acids nor the methyl esters of the remaining fractions were obtainable in crystalline form.

Recently Juettner, Smith and Howard(loc.cit) studied the prolonged treatment of coal with dilute nitric acid and claim to have obtained about 33 per cent degradation of coal to simpler products even with 1N nitric acid by carrying on the reaction for 32 to 34 days. No pure compounds were isolated from the products, fractionated by solubility in organic solvents with subsequent exhaustive methylation and fractional distillation in a molecular still. Small amounts of mellitic and benzene pentacarboxylic acids were, however, characterized/

characterized as methyl esters using salt fractionation followed by esterification and fractional distillation. Repeated redistillation of the volatile fractions resulted in continued accumulation of resinous, and if temperature was increased, even carbonized residues. This peculiar thermal behaviour of these soluble acids indicate the presence in their nuclear structures of other than simple carbon rings.

In order to learn something of the nature of the nuclei of these acids, a 100 gram sample of these acids was decarboxylated by the Fischer and Schrader (15) method. Hydrocarbons formed were recovered and consisted of those boiling in the benzene range, higher hydrocarbons, and the bomb smelt strongly of cresol and aromatic bases. All these facts point to the presence, even in these simple soluble acids, of nuclei other than the simple benzene ring.

The above review of the work done by various workers in the study of the action of nitric acid on coal suggests that although nitric acid is a very effective means for degrading the coal to soluble acids the resulting products are still quite complex. It was ~~this~~ thought, therefore, that approximately 100% nitric acid, being a stronger oxidizing agent, may be able to unlock the coal molecule and disrupt it gradually in such a fashion as to produce simpler recognizable/

recognizable products, the constitution of which it may be compar~~i~~tively easier to determine. These products, must, however, be of sufficiently large molecular dimensions as to aid in reconstructing the larger molecule from which they may have been split off.

It was decided, therefore, to examine the effect of this strong acid on coal to ascertain if it would prove to be a more fruitful reagent than the ordinary concentrated acid in producing intermediates which could be identified.

SECTION 2.

EXPERIMENTAL.

I Study of Action of 99·9% Nitric Acid on Coal.

(i) Preliminary Work.

(a) Nitric Acid:-

Nitric acid of 99·96% strength was specially obtained for the study of this reaction. The strength of the acid was frequently checked by titration, the acid being weighed in a Lunge-Rey pipette.

(b) Coal:-

High volatile Bituminous coal (Dumbreck coal) was obtained for this study. The coal was ground to a 72 B.S.S. sieve.

(c) The Reaction:-

It was found that when the coal reacted with this nitric acid even at room temperatures, the reaction was very vigorous in the initial stages and copious evolution of gases and nitrogen peroxide fumes took place. The reaction was strongly exothermic at this stage and sometimes resulted even in actual fire in the flask if the locally-developed/

developed reaction heat was not quickly removed by shaking the contents vigorously in a cooling bath. Once the vigour of the initial stage of the reaction was overcome and sufficient nitric acid had been added to give a thin suspension, the reaction proceeded more smoothly. The contents were ultimately refluxed after being brought to the boiling stage with careful and controlled heating necessary since the foam produced used to choke the condenser thus developing an internal pressure and which ultimately led to the contents being suddenly thrown out through the condenser.

A number of preliminary experiments were carried out to overcome the difficulties cited above - and finally the following procedure and apparatus were evolved.

(ii) Apparatus and Procedure:-

(a) Apparatus:-

The apparatus, shown in the figure 1, consisted of a one litre round bottom flask, A, fitted with ground glass equipment which connected it with a water-condenser, F, and a three-way stop cock, G. The three-way stop cock, G, connected the flask with the funnel, E, containing nitric acid or with the atmosphere via BCD as desired.

Thus/

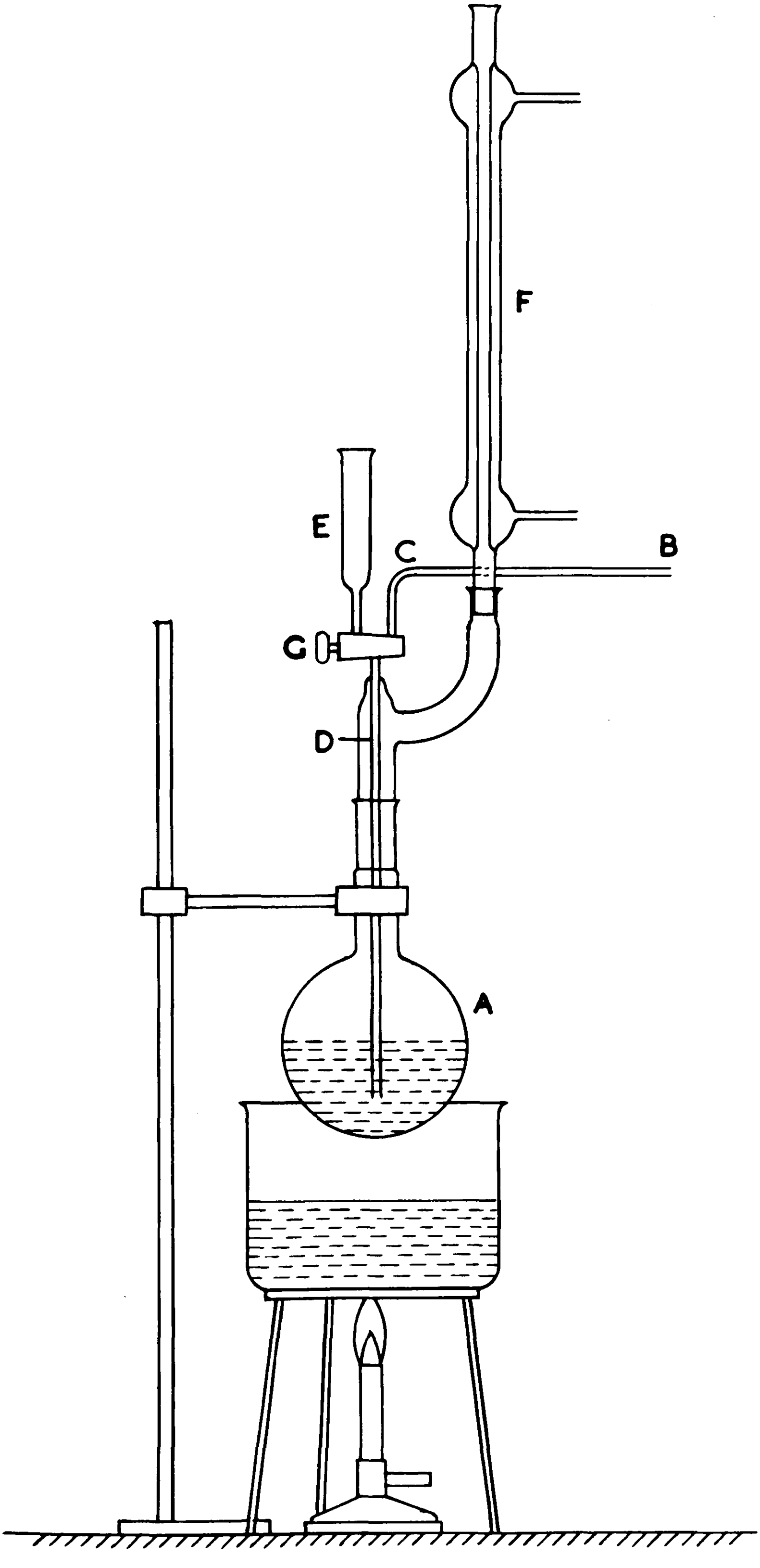


FIGURE I.

APPARATUS FOR ACTION OF NITRIC ACID ON COAL.

Thus nitric acid could be added in small increments at any required interval even when the refluxing was going on. It may be noted that all joints employed were the ground-glass quick-fit type because of their obvious advantages when dealing with such a highly corrosive chemical as 100 per cent nitric acid. The flask was immersed in a water bath which contained the cooling mixture, crushed ice and water, in the initial stages of the reaction and was gradually warmed to the stage of using this as a steam bath.

(b) Procedure:-

A weighed quantity of (50 grams) of the coal of size 72 B.S.S. was placed in the flask which was detached from the apparatus at this stage and enough solid carbon dioxide was added to cool the coal to a sufficiently low temperature. Nitric acid was also cooled by the constant addition of solid carbon dioxide. Cooled nitric acid was then added to the flask, containing the cooled coal, in small increments. The flask was shaken continuously and more solid carbon dioxide was freely added if the flask began to become warmer. In this way the vigour of the initial stages of the reaction tended to become less although the momentary evolution of nitrogen peroxide fumes was still copious. This momentary evolution of

nitrogen/

nitrogen peroxide took place, probably, due to the local heat developed by contact of the nitric acid with coal particles, and this heat was not quickly taken away by the adjoining particles on account of the heterogeneous nature of the medium. However, when enough nitric acid had been added to give a thin paste of coal and acid, the evolution of nitrogen peroxide fumes slackened. The condenser was then fitted on the flask. The apparatus was fixed on the stand with the flask dipping in water bath. The water bath was gradually heated from below taking care that the temperature of the water rose very slowly and smoothly. Sudden or quick rises were avoided as that sometimes increased the vigour of the reaction mixture resulting in foaming of the contents which ultimately led to the contents being thrown out through the condenser. Every now and then the apparatus was unclamped from the stand and given a good shaking by swirling the flask, to avoid any sudden foaming up of the reaction mixture.

When the water began to boil, the water-bath rings were fitted and the flask placed over it appropriately to let the reaction proceed at the temperature of the steam. This refluxing was carried for 27-30 hours, more nitric acid being added after every one hour in the initial/

initial stages of refluxing in increments of about 50 ml. till the requisite quantity had been added. The quantity of nitric acid used was at the rate of 100 ml. per 10 grams of the coal taken.

After refluxing was complete, the contents were allowed to cool. The flask was then detached. All the coal-degradation products were in solution in the acid at this stage. The orange-red viscous solution was then poured into ice cool distilled water which was continuously stirred. A light reddish precipitate was obtained together with orange yellow (with red) tinge solution. Evidently the coal had been degraded into products some of which were soluble in water while others were insoluble and hence were precipitated. The contents were kept overnight at the end of which the precipitated material was removed by filtering through a Buchner funnel, the filtrate being collected separately. The precipitated product was washed free from water soluble compounds and nitric acid. The solid compound was finally dried and freed from traces of nitric acid at 100°C in vacuum for twelve to fourteen hours.

Thus the reaction of nitric acid on coal as described above resulted apparently in the following products:-

(i) Gaseous/

(i) Gaseous products evolved during the reaction which were normally let off to the atmosphere.

(ii) The water-insoluble solid degradation product - The precipitate.

(iii) The water-soluble degradation product - The filtrate.

Products (i) and (ii) above only were further investigated for reasons given in the discussion on the subject. (Page 89).

II Study of the gaseous products evolved during the oxidation of coal with nitric acid.

(i) Apparatus:-

The apparatus used is shown in figure 2. The part of the apparatus used for the action of nitric acid on coal was the same as in Fig. 1 except that the reaction flask was about 250 ml. capacity. The open end of the water condenser, F, was connected to a gas-collecting system. The condenser, F, was connected to two calibrated aspirators, J and J^1 through a stop-cock, H, so that either of these could be connected to collect the gases from the reaction flask. Each of the calibrated aspirators was connected to levelling aspirators, k and k^1 respectively, by means of a rubber delivery tube so that the gases could be sucked in the aspirators J or J^1 from the reaction flask or pushed out through the stop-cocks I or I^1 respectively, by lowering or raising the appropriate levelling aspirator.

(ii) Procedure:-

Ten grams of the coal (72 B.S.) were taken in the flask, A, and the whole apparatus was appropriately fitted up as shown in the Fig.2. Levelling aspirator K^1 was raised to bring the water level up to the stop-cock/

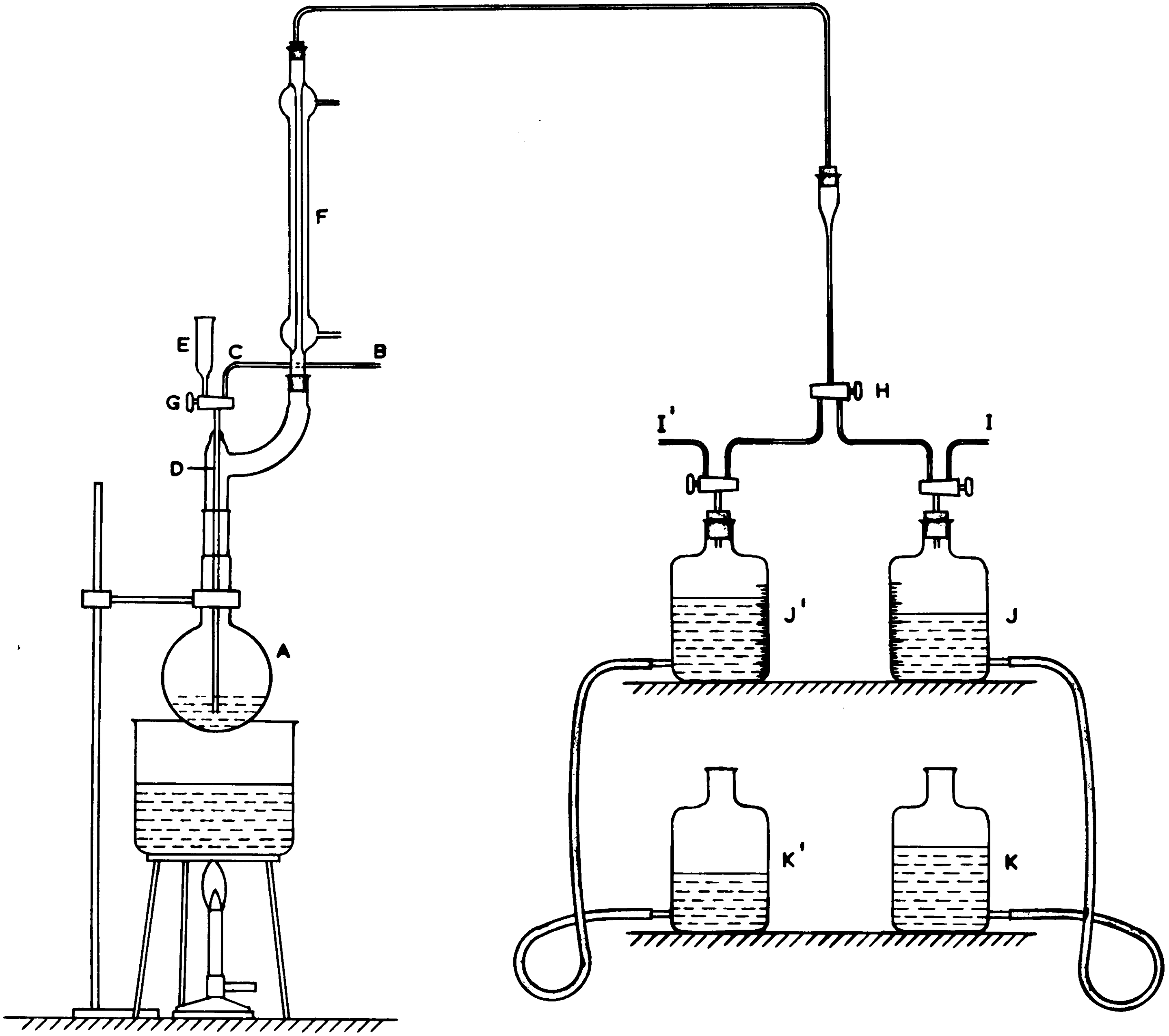


FIGURE 2.

APPARATUS FOR STUDY OF GASEOUS PRODUCTS EVOLVED BY OXIDATION OF COAL WITH NITRIC ACID.

stop-cock, H, the stop-cock, G, being turned in the process, to connect the flask with the atmosphere via BCD, to expel the displaced air. Both stop-cocks H and G were then closed. Both the aspirators J and J^1 were full of water. It was decided to collect gases over water as it would dissolve away any nitrogen peroxide gas coming over thereby also reducing the solubility of carbon dioxide in water.

The respective stop-cocks were turned so as to connect the aspirator J to a nitrogen-cylinder via tube DCB. A slow stream of nitrogen was passed which displaced the air into the aspirator, J, the levelling aspirator, K, being kept at a lower level to exert a suction effect. Stop-cock, H, was then turned and the levelling aspirator, K, was raised to expel this displaced air and nitrogen mixture to atmosphere through stop-cock, J, which was opened during this process. This process of passing the nitrogen and subsequently expelling the collected gases in, J, to atmosphere was repeated thrice to ensure complete substitution of the air in the flask and the condenser etc. by nitrogen.

One hundred cubic centimeters of nitric acid were then added to the flask through the funnel, E, which started the reaction. No solid carbondioxide was used/

used for cooling in this particular experiment as it would have contributed carbon dioxide gas to the gaseous products evolved during the reaction. Moreover as the amount of coal taken was relatively small (10 grams only) the vigour of the reaction in the initial stages was comparatively slight.

For a known time the gas was collected in the aspirator, J, at the end of which the stop-cock, H, was turned to let the gases be collected in aspirator, J^1. In the meanwhile the gases collected in J were let off into the air and the aspirator kept (full of water) ready for the subsequent collection of gases. When 300 ml. of gas had been collected in, J^1, the stop-cock, H, was turned so that the gases were collected in J. In the meanwhile gases from J^1 were transferred to another aspirator through, I^1, for subsequent analysis. At the end of the prescribed time, t, the stop-cock, H, was again turned to connect J^1 which was kept ready to take the fresh gases. The gases collected in the 2nd time-interval, t, were the amounts collected in J^1plus J. For the next period of time for which the gases were to be collected, again the first 300 ml. were collected in J^1 while the rest were collected in J. The gases collected in J^1 only were analysed. (Macpharlane's gas analysis/

analysis apparatus was used in all the analysis). In this way about eight samples were collected, for different times, and were individually analysed.

It is perhaps necessary to explain here why the above experimental procedure was used for the collection and the analysis of the gases evolved. The capacity of the reaction flask, the condenser and the connecting tubes was found by a separate experiment to be about 300 ml., making allowance for about 100 ml. of the nitric acid which was added for the reaction. If the typical case No.1 is/taken (see Table I) 520 ml. of gases were collected in J in the first two minutes. Evidentally this contained 300 ml. of displaced nitrogen, which was originally present in the system, together with 220 ml. of gases evolved in these two minutes. 300 ml. of the gases left in the reaction flask and condenser etc. also represent, in effect, the gases produced in these two minutes. Therefore the 500 ml. collected in J were let off to air, and these 300 ml. were collected in J^1 in the next time-interval. After collection up to 300 ml. mark, the remaining amount of gases, being evolved during that time interval, were collected in J. So while 300 ml. in J^1 did contribute to the total gases evolved in the second time interval, its composition corresponded/

corresponded to the gases evolved in the first time-interval. That explains why the first 300 ml. were always collected in J^1 and rest were collected in J. It may be added that the analysis represented only the average composition of the gases evolved during that time interval. The method becomes particularly less accurate in the last stages of the experiment when during much longer time interval even, the total gases evolved were less than 300 ml. So while only an average value of the composition of the gases evolved during the various time intervals, near the last stages, was obtained by this procedure, it did sufficiently indicate, the progress of the reaction.

The results obtained have been tabulated in Table I on page 33.

In figures 3, 4 and 5 the following curves have been drawn:-

(1) Time and rate of gas evolution.

(2) Time and quantity of gas evolved.

(3) Time and percentage composition of the gases evolved.

T A B L E I.

GASEOUS PRODUCTS EVOLVED DURING OXIDATION OF COAL WITH NITRIC ACID.

No.	Total time in Hours	Gas collected in time interval (ml.)	Total gas collected up to that time (ml.)	Average number of ml. evolved per minute	Analysis of gas evolved		
					% NO.	% CO_2	% N_2
1	1/30	520	520	260	4·0	5·5	90·5
2	7/60	1000	1520	217	6·1	10·1	83·8
3	1/2	400	1920	64	8·9	17·7	73·4
4	2	580	2500	20·8	12·0	39·8	48·2
5	4	300	2800	11·7	26·6	32·6	40·8
6	6	180	2980	8·3	40·1	24·2	35·7
7	12	200	3180	4·4	60·1	16·8	23·1
8	18	120	3300	3·0)	63·2	15·7	21·1
9	30	50	3350	1·9)			

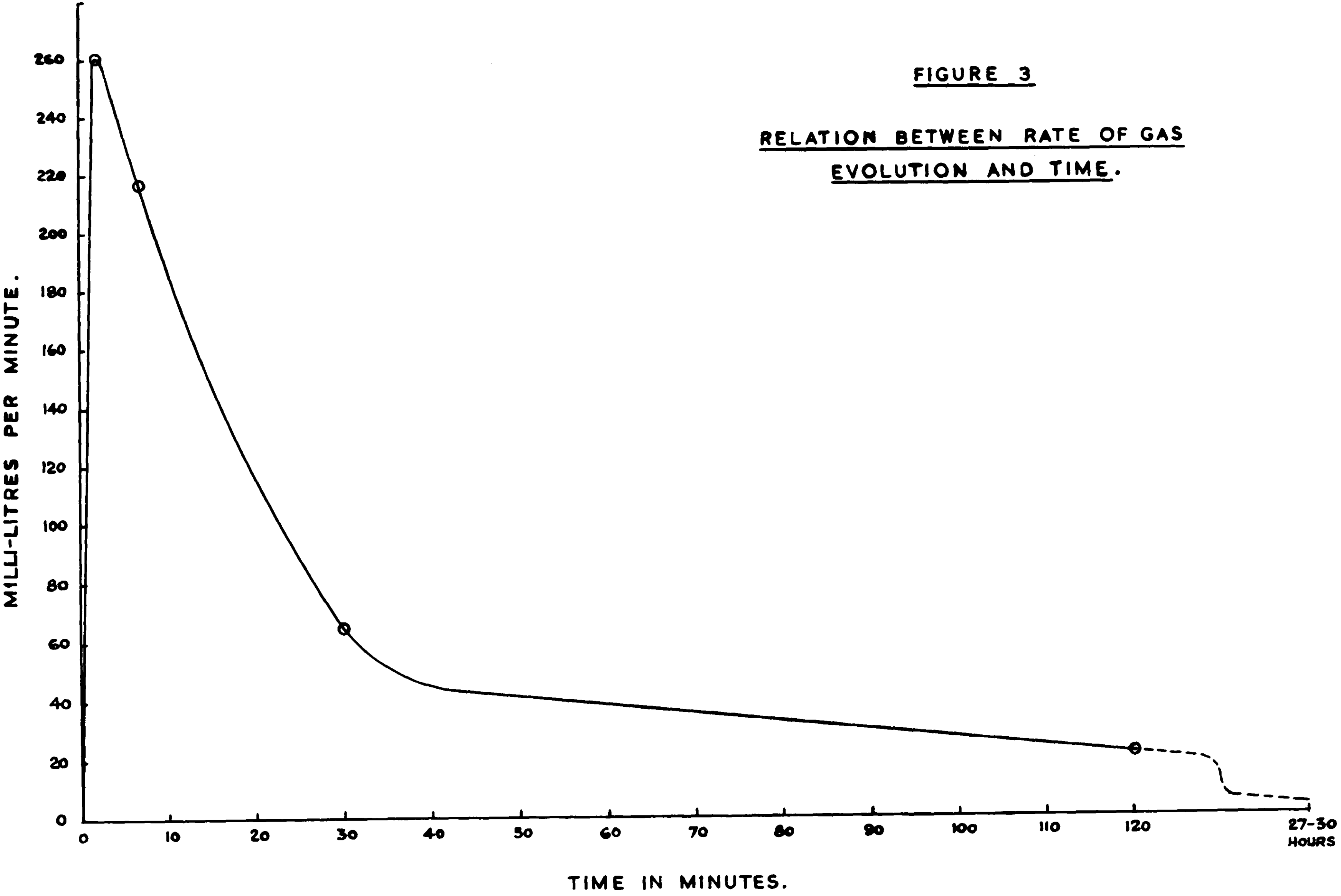


FIGURE 3

RELATION BETWEEN RATE OF GAS EVOLUTION AND TIME.

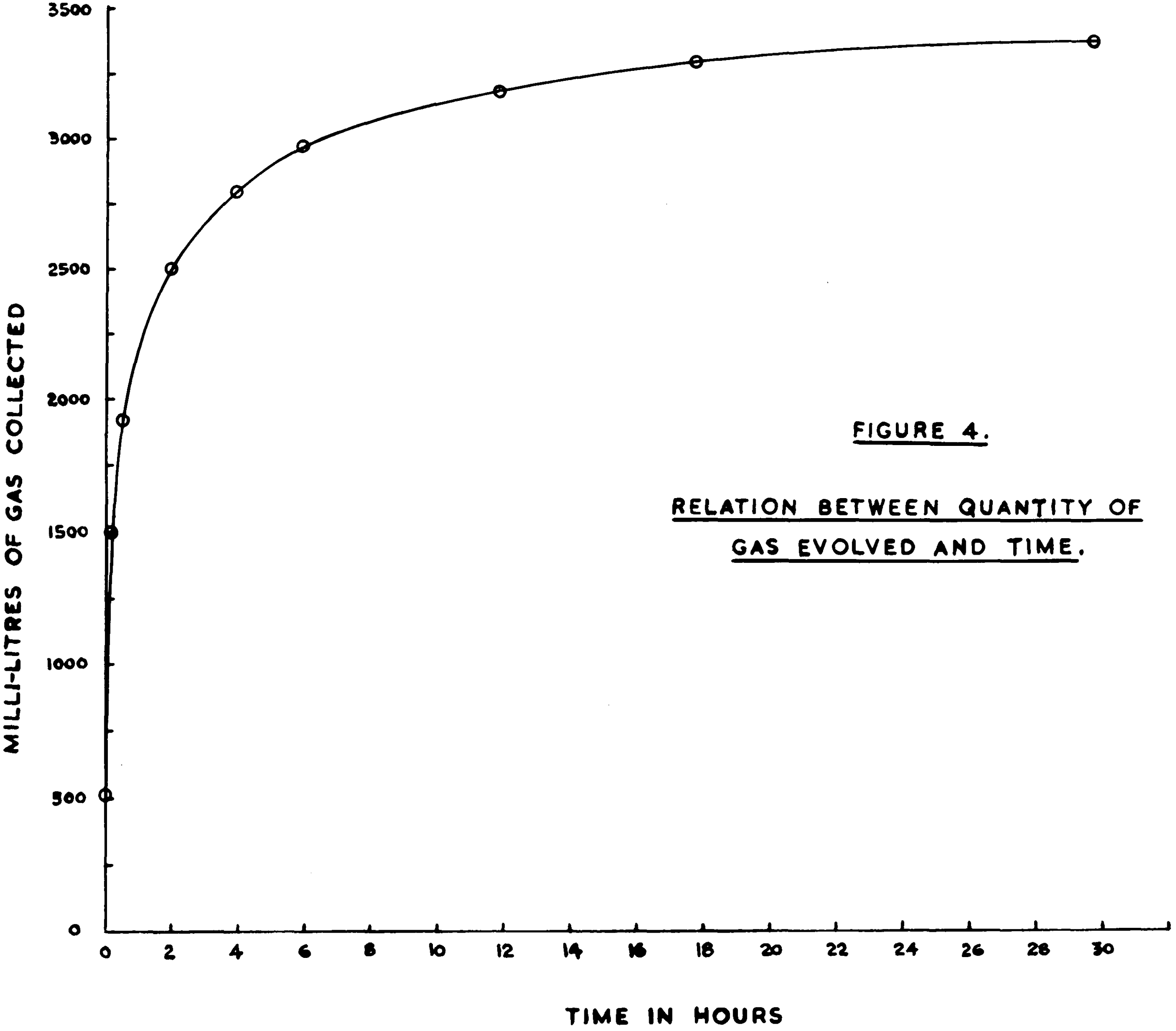
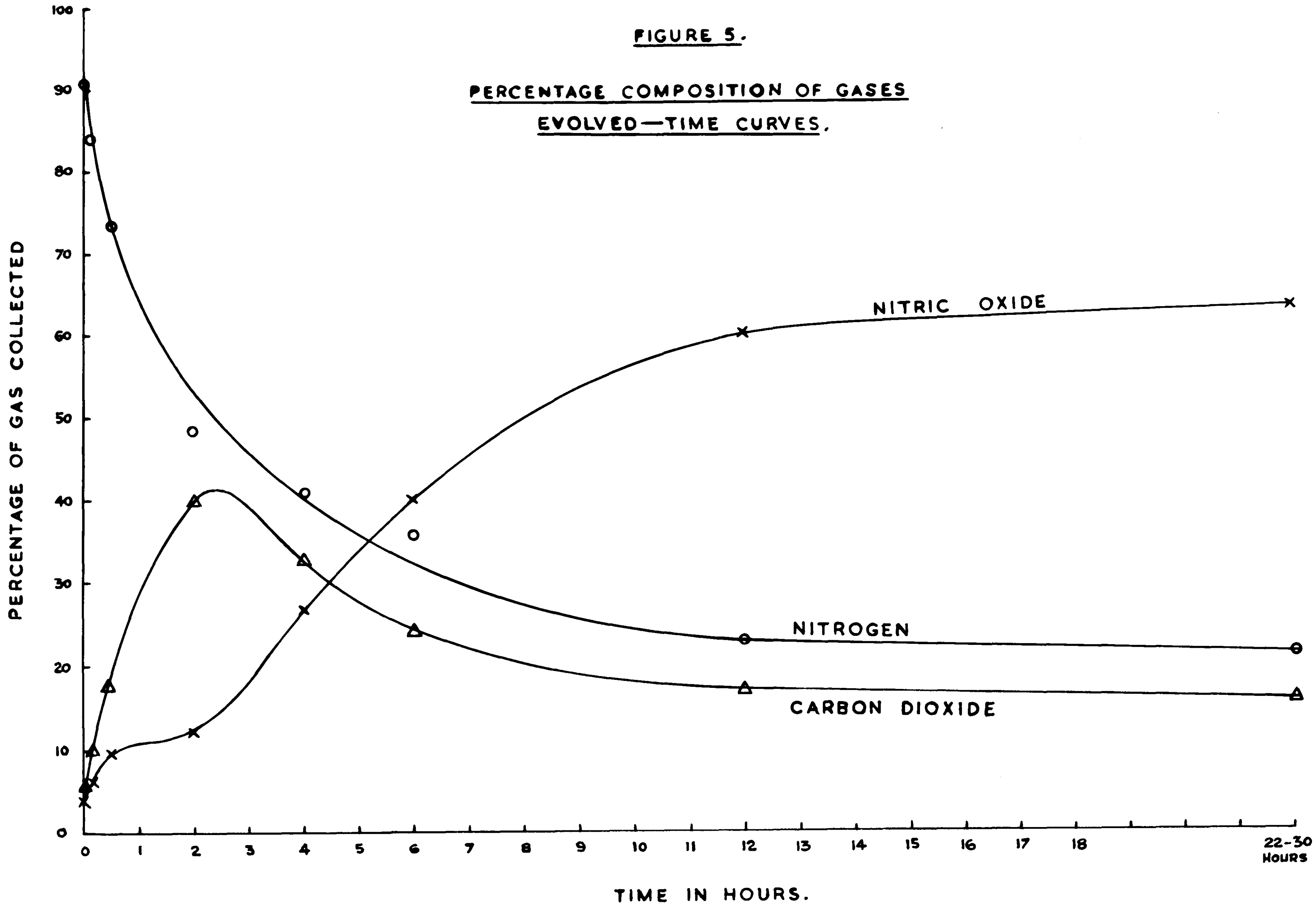


FIGURE 4.

RELATION BETWEEN QUANTITY OF GAS EVOLVED AND TIME.

FIGURE 5.

PERCENTAGE COMPOSITION OF GASES EVOLVED—TIME CURVES.



III Study of the water-insoluble product.

(i) Batch Production of the Product:-

Since this substance formed an important degradation product of coal, it was essential to investigate its composition in order to gain an insight into the character of the nuclear structure of the complicated coal molecule. It was appreciated that this water-insoluble product might probably represent more than one chemical compound of the same general type of structure, differing chiefly in the molecular weight and the points of attachment of the functional groups.

It was essential to have some stock of this water-insoluble product as it formed the starting point for its further study. Consequently a battery of five refluxing apparatus of the type described already on page 21 (fig.1) was set up, each capable of taking a charge of fifty grams. The product was isolated and subsequently purified in the manner as already described on pages 23 - 25.

The product was ground to a fine powder and once again dried at 100°C in vacuum for two hours to remove the last traces of nitric acid.

(ii) Purification and fractionation:-

The product did not show any tendency to/

to crystallize from solution in acetone, alcohol or furfural - the only solvents in which it was freely soluble. Attempts were also made to purify and resolve this into components, if any, by using the Chromotographic technique. But unfortunately no positive results were obtained probably because of the polar nature of the solvents. Fractional precipitation was also tried but with no success. So it was decided to proceed with the investigation and assume the product to be fairly homogeneous because, despite the nature of the mode of its production, its components, if any, were likely to have the same general type of structure. This is because it is a general experience that such degradation products differ mainly in the functional groups, the basic nuclear structure being the same.

(iii) Ultimate composition and empirical formula.

The product obtained was analysed for carbon and hydrogen at the Oxford Laboratories and for nitroge in micro-analytical laboratory of the Royal Technical College, Glasgow. The following composition was found:-

Ultimate Composition.

Carbon	47·53%
Hydrogen	2·76%
Oxygen	40·71%
Nitrogen	9·00%

It should be noted that no claim is made in the following pages that the material isolated has the formula $C_6H_4O_4N$; in fact it is doubtful if such a compound is capable of separate existence. Some slight evidence has been sought as to the composition but the data accumulated has been too meagre to be conclusive.

molecular weight. Because of limited solvents in which the substance was soluble e.g. acetone, alcohol, furfural, pyridine, di and trihydroxy benzenes, it presented a great problem to determine the molecular weight accurately in a number of these. This was because one or the other solvent had melting or boiling point in the range in which a Beckman thermometer or in case of low melting point solvents e.g. pyridine and furfural even a mercury in glass thermometer could not have been used. The following methods were tried, therefore, and each one was specially adapted for the purpose.

(a) Cryoscopic method:-

Because of relative insolubility of the product in the common cryoscopic solvents except those mentioned above, the choice of solvent was rather important. Whereas di and trihydroxybenzenes appeared to be more suitable from/

from the point of view of availability of ther~~/~~mometers, for the cryoscopic measurements, catechol was selected as the most suitable because of its thermal stability and moderate melting point. Lately Smith and Howard (16) used Catechol as a cryoscopic solvent for the determination of the molecular weight of the coal oxidation product which they obtained by prolonged action of 1N nitric acid on bituminous coal.

Apparatus and Procedure:-

The apparatus is shown in fig.6 on page 41. A wide mouthed test-tube (diameter 2·5"), "A" was supported in a 2 litre tall pyrex beaker through an aluminium lid. The beaker contained glycerine and had a stirrer and was used as a heating bath. A large cork placed in the mouth of the test-tube supported a thermometer, "T", for indicating the temperature of the air bath, "A", the standard 15 mm, test-tube, "E", which contained the cryoscopic solvent, a thermometer "F", and a stirrer "G". The thermometer "F" was graduated in tenths and read by means of a lens.

The empty test-tube, "E", was weighed to the nearest milligram and six to eight grams of purified catechal introduced into the bottom of this by means of a short wide-stem funnel. The catechol was fused in a separate glycerine bath maintained at about 125°C after placing the thermometer/

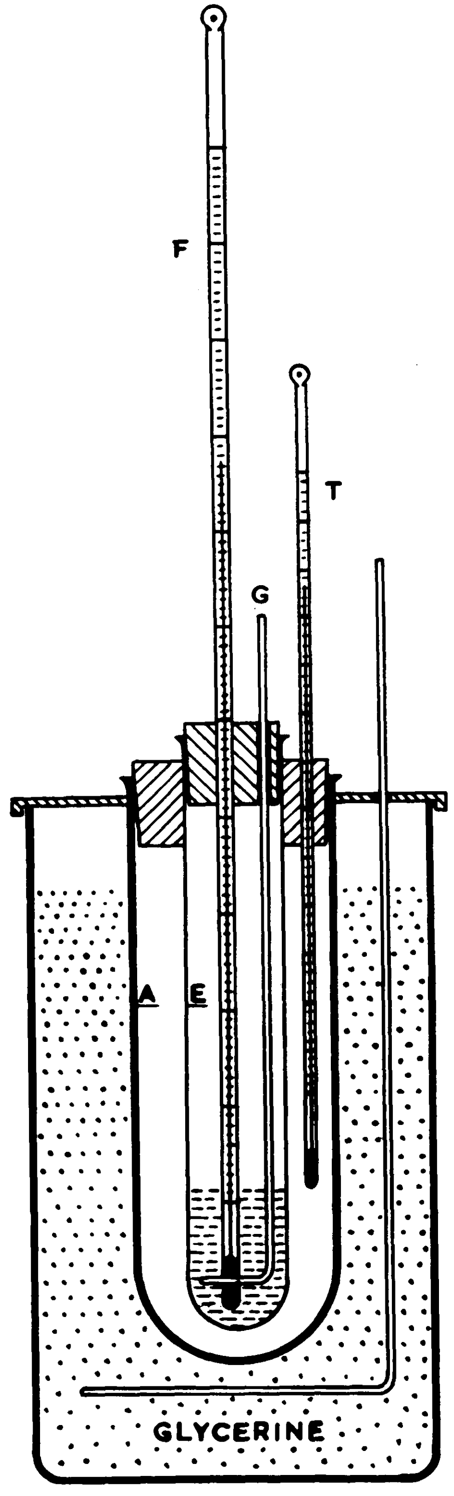


FIGURE 6.

APPARATUS FOR MOLECULAR WEIGHT DETERMINATION BY CRYOSCOPIC METHOD.

thermometer, "F", and the loop stirrer in position. In the meanwhile the temperature of the air-bath, "A", had been brought to about 95-100°C by heating the surrounding glycerine bath. The test-tube, "E", was then placed in the air-bath, "A". Stirring was then started in the test-tube, "E", and the freezing point determined as is done in any standard cryoscopic determination. The freezing points were determined several times for the pure solvent. It was usually found that after the first fusion, the freezing point values were constant. The test-tube was then removed from the air-bath, the catechol melted and thermometer and the stirrer withdrawn from the molten catechol in such a way that catechol did not smear the sides of the tube. Any catechol adhering to the sides, however, was removed by evaporation or wiping with a cotton swab. The thermometer and the stirrer were also cleaned and dried.

After the tube, "E", and contents cooled down to the room temperature, it was weighed. The product - under investigation - was roughly weighed in a paper scoop and was then introduced through a large stemmed funnel reaching nearly the top of the fused catechol. The funnel was removed. The tube containing catechol and the sample was weighed again. The difference in the two weighings corresponded to the amount of/

of the sample taken. The weight of the catechol was obtained by the difference between the weight of the empty tube and that of tube plus catechol. 60 to 100 milligrams of solute were used with 6 to 8 gms. of catechol. The freezing point for the solution was determined in the same way as for the pure solvent.

If K denotes the cryoscopic constant, the molecular weight of the solute is governed by the following formula which was used for calculation of the molecular weights:-

$$M = K\,1000\,\frac{w}{Wdt}$$

where M = molecular weight of the solute
w = weight of the solute taken
dt = depression in the freezing point
W = weight of the solvent taken

w, W and dt was noted from the above experiment and hence molecular weight could be calculated, knowing the value of K.

Cryoscopic constant for Catechol.

The value of the cryoscopic constant for catechol, which was essential for the calculation of the molecular weight by its substitution in the above formula, was stated to be 7·13° per mole per 1000 grams of solvent as given in the "International Critical Tables" (McGraw Hill Book, Co.) (15a). However/

However, the experimental work indicated the average value of 5·9 (described later in this section). Also, a calculation of the molal depression constant of freezing point for catechol was made on thermodynamical basis by using Clapeyron-Clausius equation, as detailed below, and a value of 5·73 was obtained.

Assuming the vapour to obey the ideal gas laws, and its volume to be large in comparison with that of the solid or liquid, and that the Raoult's law is applicable, the following expression relating the molecular weight and depression in freezing point, based on the use of Clapeyron-Clausius equation, can be derived.

$$dT = \frac{RT^2 \quad 1000w}{1000L_f \quad M \quad W} \quad ..... \quad (1)$$

where dT = depression in the freezing point.

R = gas constant

T = freezing point of the solvent in degrees Absolute.

L_f = Latent heat of fusion per gram of solvent

W = weight of the solvent

w = weight of the solute

M = molecular weight of the solute

equation (1) can be written as:-

$$dT = \frac{RT^2}{1000L_f} \quad m \qquad \ldots\ldots \quad (2)$$

$$= Km$$

where m = molality of the solution

K = molal depression constant of freezing point or the cryoscopic constant, for the given solvent.

$$\text{so} \quad K = \frac{RT^2}{1000L_f} \qquad \ldots\ldots \quad (3)$$

In the case of catechol by substituting the values of R, T and L_f in (3) above, the value of K, the cryoscopic constant for catechol, was calculated as:-

R = 1·9871 calories. 1° K/Mol.

T = $377{\cdot}3^\circ$ A

L_f = 49·4 g. calories per gram

$$\text{thus} \quad K = \frac{1{\cdot}9871 \times (377{\cdot}3)^2}{1000 \times 49{\cdot}4}$$

$$= 5{\cdot}73$$

The above value obtained on the theoretical considerations was confirmed experimentally by using Caledon Jade Green (16-17 dimethoxy, dibenzanthrone, $C_{36}H_{20}O_4$: Molecular weight - 516) as solute. This substance was specially selected as it had a sufficiently high molecular weight. Besides on carbonization it is known to/

to give a residual product somewhat similar to that obtained by the carbonization of a coking coal. The results of a typical experiment are given below although these were made in triplicate:-

Caledon Jade green taken = 0·1005 grams = w (weight of solute)
Catechol taken = 7·6430 grams = W (weight of solvent)
Lowering of freezing point = 0·15°C = dt
Molecular weight of Caledon Jade Green = 516·0 = M (molecular weight of solute)

If K denotes the cryoscopic constant, the following relation holds:-

$$M = K\,1000\,\frac{w}{W\,dt}$$

$$\text{so}\quad K = \frac{M\,W\,dt}{1000\,w}$$

substituting the experimental values

$$K = \frac{516 \times 7{\cdot}643 \times 0{\cdot}15}{0{\cdot}1005}$$

$$= 5{\cdot}89$$

An average value of 5·9 was obtained by Howard and Smith (loc.cit.) when they used the following substances as solute:- benzoic acid, salicylic acid, 1 : 3 : 2 - xylenol, B-naphthol, Sym-tribromophenol, resorcinol, phenatol. Consequently/

Consequently the experimentally determined value of K was used throughout in this investigation.

Results:-

The unknown substance was dried in the following three ways.

(1) Dried at 105°C in Vacuum.

(2) Dried at 50°C in vacuum over Phosphorus Pentoxide.

(3) Dried at 120°C in air oven.

The molecular weights of all these samples were determined in the manner explained above and are given in Table II on page 48.

TABLE II

MOLECULAR WEIGHT OF SUBSTANCE BY CRYOSCOPIC METHOD (USING THERMOMETER)

No.	Drying temperature in degrees Centigrade.	Solute in grams.	Solvent in grams.	Percentage concentration of Solute.	Average depression in freezing point °C	Molecular Weight
1.	105 in vacuum	0·0903	7·7825	1·16	0·54	126·8
2.	50 in vacuum over P_2O_5	0·0923	7·9270	1·16	0·43	160·0
3.	120 in air oven	0·1056	7·9194	1·33	0·40	196·7

(b) Application of Thermistor to the determination of the molecular weight by cryoscopic method.

In view of the low values of molecular weight obtained in the previous method, it was decided to check these by as many methods as possible, including the cryoscopic method using furfural and pyridine, these two solvents being selected on account of their low melting points. Means were then sought for determining with accuracy the small temperature changes involved in the cryoscopic method, especially when mercury in glass thermometers were useless at the range of the temperatures in which the freezing points of pyridine and furfural lie. Finally recourse was made to a new temperature measuring instrument, the Thermistor (recently developed by Standard Telephones and Cables Limited, Footscray, Kent) for this purpose. The description of the thermistor and experimental procedure of its application to the determination of the molecular weight of the substance - under investigation - is given as appendix 1 on page 243. Only a brief account of the results obtained is included here.

The results obtained are presented in Table III on page 50. These confirm the low values for the molecular weight obtained by the previous method and by other methods described in the pages to follow. Possibility of interaction/

interaction between solute and the solvent was rather remote at the low temperature at which the investigations were carried out. This doubt which existed in the previous method using catechol as a cryoscopic solvent with higher freezing point was thus eliminated. The electronic amplifying circuit associated with the thermistor used in these experiments was reasonably stable and temperature difference measurements of the order of ±·001°C were possible and were easily reproduced provided allowances were made for the slight variation of the instrument calibration with time and slow drift in the recording meter which is usually associated with the D.C. amplifiers.

TABLE III.

Molecular weight of substance by cryoscopic method (using thermistor)

No.	Solvent	$\frac{dv}{dT}$ Volts/°C	ΔT °C	Molecular Weight X
1	Pyridine	0·0935	0·0375	147·9
2.	Furfural	0·088	0·0237	156·3

X The substance dried at 50° in vacuum over Phosphorus Pentoxide was used in these determinations.

(c) Ebullioscopic Method:-

An improved boiling point apparatus, designed by Cottrell (17) was used in the determination of the molecular weight of the substance in solvent like acetone which could not be used as a cryoscopic solvent. In this apparatus is secured a more perfect equilibrium between the solution and the vapour and the temperature of the equilibrium is accurately determined when both phases are under the same external pressure. Also with this apparatus, the fluctuations of temperature and errors of temperature determinations due to super-heating etc. are avoided.

Apparatus and Procedure:-

The apparatus is shown in fig. 7 on page 52, and consisted of a boiling tube, A, into the neck of which fitted the stopper, B. The walls of the stopper were prolonged downwards so as to form a cylinder enclosing the bulb of the Beckman Thermometer, T, and the branches of the "pump tube", C. The cylinder served as a jacket for the thermometer and prevented the liquid, flowing from the condenser D, coming into contact with the thermometer. The pump tube, C, was divided as shown into three branches, arranged symmetrically, and surrounding the lower end of the thermometer; and the other open ends of the tube were bent so that the/

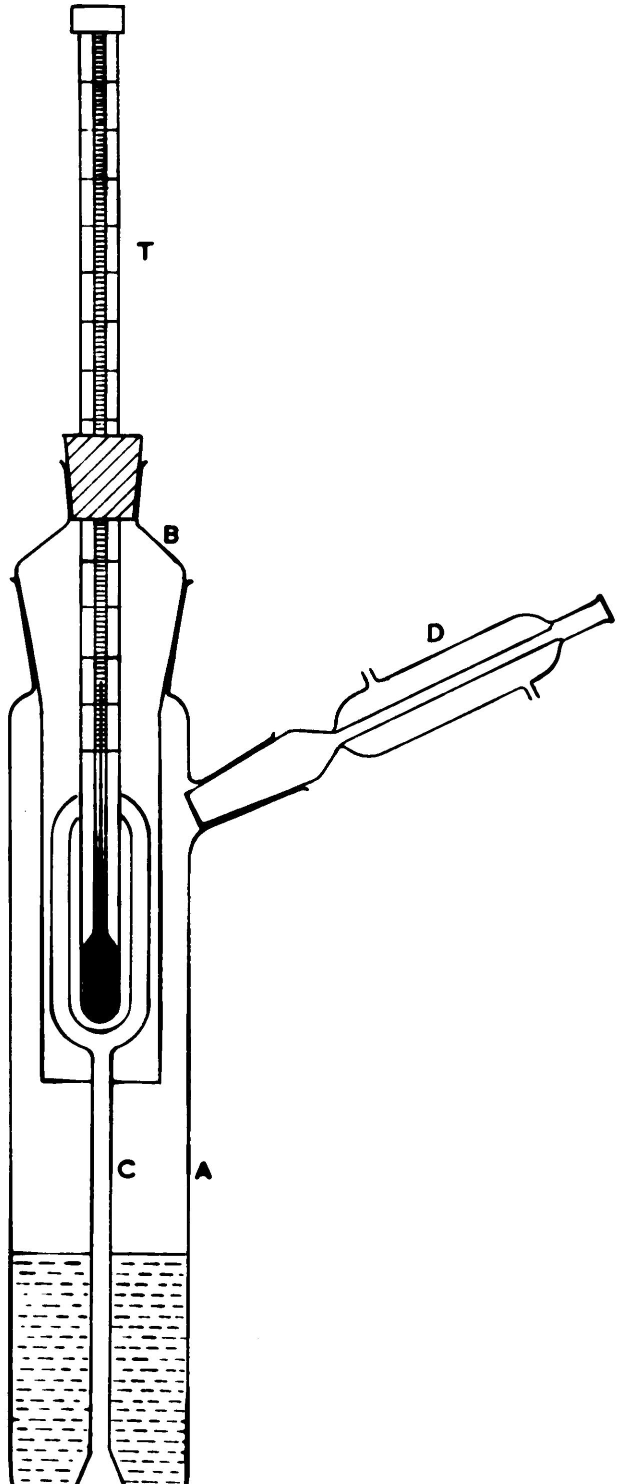


FIGURE 7.

COTTRELL'S BOILING POINT APPARATUS FOR MOLECULAR WEIGHT DETERMINATION.

the openings faced the stem of the thermometer. The funnel of the tube rested on the bottom of the boiling tube.

Known amount of specially dried acetone introduced into the boiling tube was caused to boil by means of a flame protected from draughts. The Beckman thermometer had already been fixed at the boiling point of acetone in the standard way. When the liquid boiled, the bubbles of the vapour which formed under the funnel rose up in the narrow tube carrying with them the liquid which was then projected against the stem of the thermometer. The bulb of the thermometer was, in this way, kept bathed in the boiling liquid which was pumped up by the vapour bubbles and which was in equilibrium with the vapour in the apparatus. By this means a constant temperature (boiling point) was soon obtained, and the temperature remained very steady. After determining the boiling point of the pure solvent, a weighed amount of the substance, the solute, was introduced by way of the condenser, and the boiling point of the solution was determined in the same way as for the solvent.

As in the case of the cryoscopic method, the molecular weights of the substance, as dried under various conditions, were determined. The results were calculated by using the standard expression as:-

$$M =/$$

$$M = K \frac{w}{dt.W.}$$

where M = molecular weight of the solute

w = weight of the solute

W = weight of the solvent

dt = rise in the boiling point.

The results are recorded in Table IV on page 55.

(d) Barger's Osmosis Method(18) :-

This method was employed finally to confirm the previous values of the molecular weight. This was very essential because never before has the isolation of a coal degradation product of the humic acid type, and of such a low molecular weight, been reported.

During an investigation on mushrooms, variations in the vapour pressures of salt solution were noticed, and it was suggested to G. Barger that these might be the basis of a method of molecular weight determination. Barger's method, as it is called now, is based on the principle that if solutions of different concentrations are placed in a closed system, solvent passes from the solution which is osmotically weaker to that which is osmotically stronger, by isothermal distillation; ultimately the same osmotic pressure is set up in both. Thus if a solution of known/

TABLE IV

Molecular weight of the substance by Ebullioscopic Method.

Solvent used = Acetone.

Drying temperature in °C	Solute in grams.	ml. of solvent	wt. of solvent grams	Average elevation in boiling point °C	Molecular weight.
105 in vacuum	0·5282	50·0	39·5	0·156	147·4
50 in vacuum over $P_2 O_5$	0·5116	50·0	39·5	0·128	174·0
120 in air oven	0·5018	50·0	39·5	0·117	186·7

known concentration of the substance to be examined is prepared and tested against comparison solutions of known molecular concentrations, the molecular weight can be calculated. For the determination, small drops of solution of the substance and of the comparison solutions are placed alternately between small air bubbles in a tube. The alteration of the distance between the two menisci of a drop, owing to isothermal distillation, is determined under the microscope by means of an eye-piece micrometer. The comparison solution which shows no osmotic alteration is used for the calculation of the molecular weight of the substance. The method appeared to be of special interest because no elaborate apparatus or technique were required, and a wide range of solvents could be used i.e. in this case acetone, pyridine and furfural. These solvents had also been used for cryoscopic and ebullioscopic measurements. The experimental description of the method is given as appendix 2 on page 257. The results of the experiments, however, are given here.

The above experiment was carried using three different solvents viz. pyridine, acetone and furfural. In order to illustrate the method of calculation actual variations in the dimensions of the droplets are given (in Table V on page 58) of one typical experiment viz. 1% solution of/

of the substance and 0·04M comparison solution, using pyridine as solvent in both cases.

In the way shown in Table V on page 58 the total change in each drop of all the experiments is calculated. In the tables of all the results which follow the total change in a drop, from the time of start to the time the osmotic equilibrium was obtained, is given; and not the actual variations in the dimensions of the droplets. These results are tabulated in Tables VI, VII and VIII on pages 59, 60 and 61 respectively.

It will be noted from all these tables that an order of the molecular weight is obtained which, of course, confirms the figures obtained by the cryoscopic and ebullioscapic methods.

Average values for the molecular weight of the substance, as obtained by all these methods, are presented together in Table IX on page 62.

TABLE V.

Solvent = Pyridine
Concentration of solution of substance under investigation = 1%
Concentration of comparison solution = 0·04M

Time in Hours	Size of Drop number * (in micrometer scale divisions)				
	II	III	IV	V	VI
0	67	52	75	55	63
4	67	52	75	55	63
24	69	50	78	53	64
48	72	48	82	50	66
72	75	46	86	48	68
96	77	43	89	45	70
120	77	43	89	45	70
Total change in each drop	+10	-9	+14	-10	+7

Increase denoted by + Decrease denoted by -

* II, IV and VI are drops of solution containing substance under investigation; III and V are drops of the comparison solution.

TABLE VI

Molecular weight of the substance by Osmosis method. (Solvent - Pyridine)

Concentration of the solution of the substance - under investigation - in Pyridine = 1%
Comparison substance = Azobenzene.

Molar concentration of comparison solution.	Time in Hours to attain osmotic equilibrium	Size of Drops numbers * (in micrometer scale divisions)					Aggregate change	Drops II, IV, VI increased or decreased denoted by + or - respectively
		II	III	IV	V	VI		
·03M	120	+15	-14	+11	-13·5	+10	64·5	+
·04M	120	+10	-9	+14	-10	+7	50	+
·05M	120	+5	-2·5	+6·5	-2·5	+4	20·5	+
·06M	120	-4	+1	-2	+1	-2	10	-
·07M	120	-7	+9	-6	+7	-8	37	-
·08M	120	-10	+11	-11	+12	-9	53	-

* II, IV and VI are drops of solution containing substance under investigation; III and V are drops of the comparison solution.

It is clear from the table that 1% solution of the substance is isotonic with 0·05 - ·06M solution of azobenzene. From this the molecular weight is between $\frac{1\times10}{\cdot05}=200$, & $\frac{1\times10}{\cdot06}=166\cdot6$

TABLE VII

Molecular weight of the substance by Osmosis method. (Solvent - Acetone)

Concentration of the solution of the substance - under investigation - in acetone = 1·0%
Comparison substance = Azobenzene.

Molar concentration of the comparison solution.	Time in Hours to attain the osmotic equilibrium.	Size of Drops numbers * (in micrometer scale divisions)					Aggregate change	Drops II, IV, VI increased or decreased denote by + or - respectively.
		II	III	IV	V	VI		
·03M	24	+16·5	-14·0	+16·0	-15·6	+10·0	72·1	+
·04M	24	+13·0	-12·0	+9·0	-8·0	+7	49·0	+
·05M	24	+2·0	- 3·0	+4·5	-3·0	+3·0	15·5	+
·06M	24	- 2·0	+5·0	-3·0	+4·0	-4·0	18·0	-
·07M	24	-14·0	+16·0	-12·0	+11·0	-10·0	63·0	-
·08M	24	-20·0	+17·5	-16·0	+22·0	-18·0	93·5	-

* II, IV and VI drops are of solution containing the substance under investigation; III and V are drops of the comparison solution.

It is seen from the above table that the osmotic pressure of the 1·0% solution of the substanc under investigation corresponds with that of a 0·05-0·06M solution. From this the molecular weight of the substance is between $\frac{1 \times 10}{\cdot 05} = 200$; and $\frac{1 \times 10}{\cdot 06} = 166{\cdot}6$

TABLE VIII

Molecular weight of the substance by Osmosis method. (Solvent - Furfural).

Concentration of the solution of the substance - under investigation - in furfural = 1·0%
Comparison substance = Azobenzene.

Molar concentration of the comparison solution.	Time in Hours to attain the osmotic equilibrium.	Size of Drops numbers * (in micrometer scale divisions)					Aggregate change	Drops II, IV, VI increased or decreased denoted by + or - respectively.
		II	III	IV	V	VI		
·04M	96	+12·0	-10·0	+10·0	-8·0	+12·0	52·0	+
·05M	96	+5·0	- 4·0	+3·0	-3·0	+7·0	22·0	+
·06M	96	- 2·0	+2·0	-1·0	+1·0	-3	9·0	-
·07M	96	- 9·0	+8·0	-7·0	+9·0	-8	41·0	-
·08M	96	-18·0	+14·0	-17·0	+13·5	-14	76·5	-

* II, IV and VI are drops of solution containing substance under investigation;
III and V are drops of the comparison solution.

It is clear from the table that 1% solution of the substance is isotonic with 0·05 - 0·06M solution. From this the molecular weight of the substance lies between

$$\frac{1 \times 10}{\cdot 05} = 200; \quad \text{and} \quad \frac{1 \times 10}{\cdot 06} = 166{\cdot}6$$

TABLE IX

Molecular weight of the substances by different methods.

	MOLECULAR WEIGHTS BY			
Solvent	Cryoscopic-method using		Ebullioscopic method	Osmosis method.
	Thermistor	Thermometer		
Pyridine	147·9	-	-	166 - 200
Furfural	156·3	-	-	166 - 200
Catechol	-	160	-	-
Acetone	-	-	174	166 - 200

IV FUNCTIONAL GROUPS

1. Groups not containing nitrogen.

(a) Carboxyl and Hydroxy groups:-

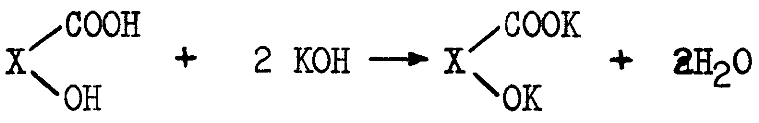
The next important step in the further investigation of the product, after having determined the molecular weight, is the detection and estimation of the functional groups.

The substance under investigation gave a qualitative response to the presence of acidic groups, but it was difficult to be certain, as is the case with substances of the humic acid type, whether it contained carboxyl groups or phenolic groups or both. Besides it is known by common experience that oxidation products of coal are acids and they usually contain carboxyl and hydroxyl groups. An aqueous suspension of the acid has a pH of 4, and can be titrated electrometrically directly with alkali using a glass electrode (19). Ubaldini and Siniramed (20) have used this method in a different way, both to determine the carboxyl as well as the Phenolic groups. The same authors proposed that if such an acid is refluxed with calcium carbonate in aqueous calcium acetate and the evolved carbon dioxide is weighed, the acid group could be evaluated. However Ubaldini's method was used/

used and is described below:-

Procedure:-

About 0·3 grams of the substance were weighed accurately and placed in a round bottomed flask. 10 ml. of 95·0% alcohol were added to moisten the contents followed by the addition of 50 ml. of 0·2118N alcoholic potash solution which was also made in 95% alcohol. The alkali acted upon the carboxyl and the phenolic groups to give the corresponding potassium salt according to the equation:-



$$\mathrm{X}<\begin{matrix}\mathrm{COOH}\\ \mathrm{OH}\end{matrix} + 2\ \mathrm{KOH} \longrightarrow \mathrm{X}<\begin{matrix}\mathrm{COOK}\\ \mathrm{OK}\end{matrix} + 2\mathrm{H_2O}$$

X stands for unknown radical.

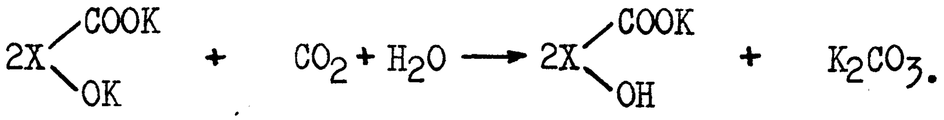
95% alcohol solution was deliberately employed as the potassium salt of the substance was insoluble in 95% alcohol. Since this resulted in a heterogeneous system, the attainment of equilibrium was slow. So the contents were refluxed for an hour to complete the above reaction. After cooling, the contents were transferred to a 100 ml. measuring flask. 95% alcohol was used for washing down the contents and making up the volume of the suspension to 100 ml. The whole mixture was allowed to stand overnight to allow the precipitate of the potassium salt of the substance/

stance to settle.

10 ml. of the coloured supernatant liquid were pipetted out. As the solution was dark coloured the excess unused alkali was back-titrated against standard acid electrometrically using a glass electrode. A small amount of phenolphthalein was also added to the liquid which was to be titrated. In carrying the titration, the titrating liquid, the standard acid in this case, was run in small quantities at a time from the burette into the solution to be titrated, the solution being kept well-stirred by means of a stirrer. As the titration approached the equivalence point, which was indicated both by the indicator and the pH readings, the titrating liquid was added in smaller and smaller amounts.

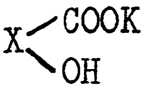
The pH values were plotted against the volume of the titrating acid. Two typical curves are shown in the figure 8 on page 69. Since it was a titration of strong alkali (excess unused one) against strong acid, the usual curves with sharp inflection were obtained. The results of two typical titrations are given in Table X on page 68. From the knowledge of the amount of standard alkali used up by the acid, the total acidity could be calculated.

The insoluble Potassium salt of the substance from the above experiment was filtered on a filter paper and washed with 95% alcohol, till the filtrate was free from alkali, as indicated by the absence of appearance of a red colour with phenolphthalein. It was finally washed with 75% alcohol. This precipitate was then suspended in 50 ml. of 75% alcohol in a beaker and dried carbon dioxide gas was bubbled through it for about half an hour. If the substance had contained a phenolic group, the following reaction would have taken place(20a):-



$$2X\begin{matrix}\diagup COOK\\ \diagdown OK\end{matrix} + CO_2 + H_2O \longrightarrow 2X\begin{matrix}\diagup COOK\\ \diagdown OH\end{matrix} + K_2CO_3.$$

Thus Potassium Carbonate equivalent to the phenolic acidity would have been liberated. The contents of the beaker were then transferred to a measuring flask and made up to 100 ml. with 75% alcohol. This was because



$X\begin{matrix}\diagup COOK\\ \diagdown OH\end{matrix}$ is supposed to be insoluble in 75% alcohol while potassium carbonate is soluble. The contents were again left overnight. 10 ml of the supernatant layer were pipetted out and titrated, as before, against standard acid electrometrically using glass electrode. No acid was used up at all showing thereby the absence of any Potassium Carbonate and hence of the phenolic groups.

<u>Results</u>:-/

Results:-

From the knowledge of the amount of standard alkali used by the substance, the equivalent weight of the acid can be calculated by the following formula.

$$E = \frac{W}{N \times Y}$$

where E = Equivalent weight of the substance.

W = Weight of the substance in milligrams.

N = Normality of Potassium hydroxide used.

Y = Ml. of Potassium hydroxide equivalent to total acidity of the substance.

As the substance did not show any acidity due to phenolic group, the total acidity exhibited by the substance was assumed to be entirely due to - COOH groups. The results of the equivalent weight thus calculated by using the above formula are given in Table XI on page 70.

As the molecular weight of the substance lay between 150-200 and the equivalent is of the order of 138 (from table XI on page 70) it may be safely concluded that the substance is mono-basic and that no phenolic group is present in the structure. The small difference between the values for the molecular and equivalent weight of the substance is due to the fact that the substance probably consists of a mixture of molecular species anologous to a homologous series.

TABLE X.

Titration curves of the substance.

Substance taken in case (1) = 0·2982 gms.
Substance taken in case (2) = 0·3000 gms.

Ml. of 0·2118N alcoholic KOH added in each case = 50 ml.
39·8 ml. of standard acid = 50 ml. of 0·2118N KOH.

Ml. of standard acid used.	pH in case I	pH in case II
0·0	11·58	11·50
1·0	11·48	11·11
2·0	11·14	10·91
2·2	10·98	10·78
2·4	10·82	10·15
2·6	10·26	9·03
2·7	9·14	7·73
2·8	7·85	5·62
2·9	5·60	4·62
3·0	4·58	4·10
3·1	4·02	3·85
3·2	3·78	3·60
3·4	3·50	3·43
3·6	3·35	3·23
4·0	3·11	3·00
5·0	2·84	2·80

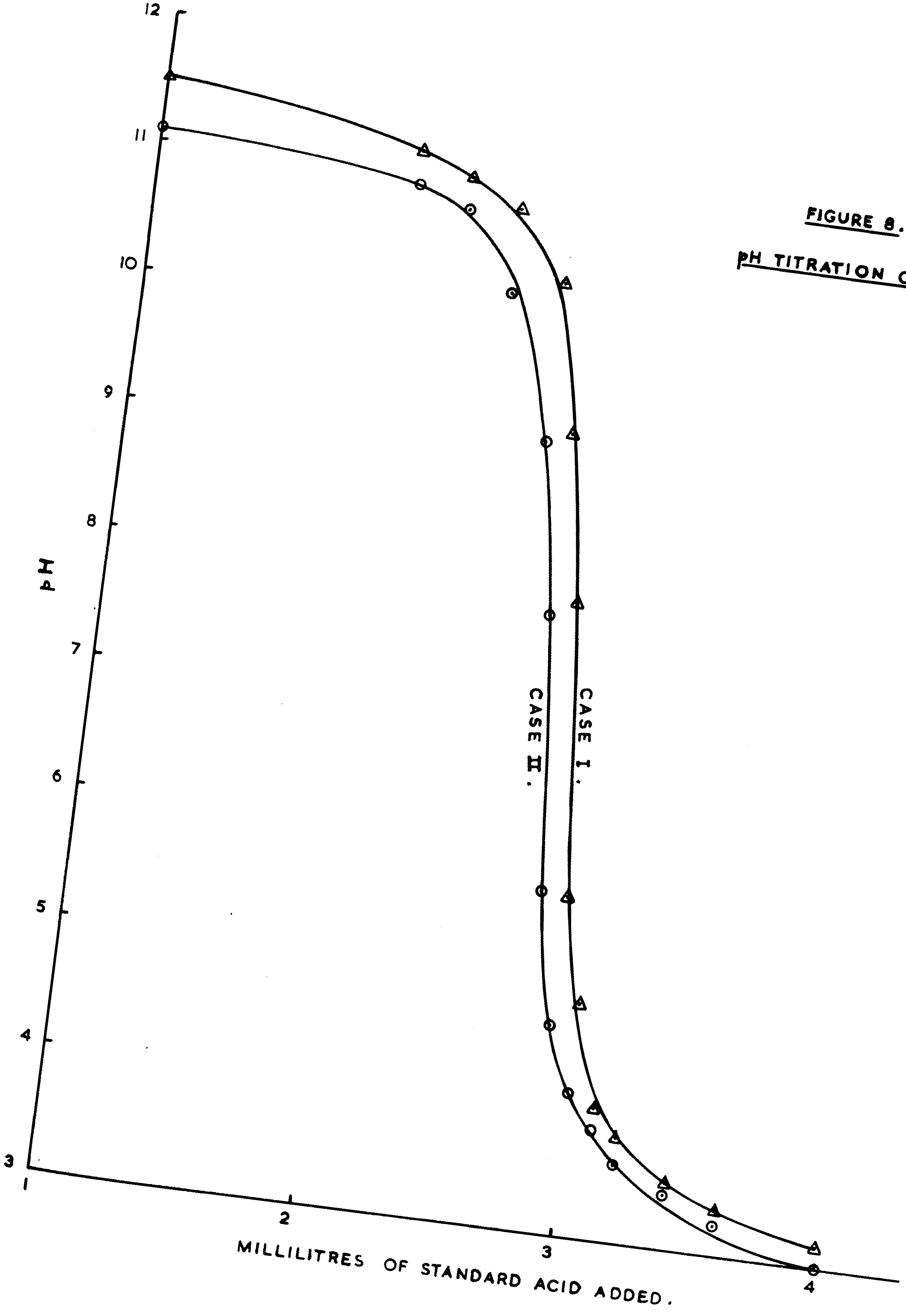


FIGURE 8.

pH TITRATION CURVE.

TABLE XI

Equivalent weight of the substance.

50 ml. of 0·2118N KOH ≡ 35·8 ml. of standard acid.

Weight of substance taken in grams.	*Ml.of standard acid for back titration of 10 ml.of solution.	Ml.of standard acid for back titration of 100 ml. of solution.	Ml.of standard acid equivalent to alkali used up. ≡	Ml.of 0·2118N KOH used up.	Equivalen weight.
0·2982	2·85	28·5	7·3	10·2	138·0
0·3000	2·75	27·5	8·3	11·6	122·1

* This was obtained from the pH acid titration curves in figure 8 on page 69.

(b) Attemped methylation:-

In order to find if the compound, under investigation, had any -OH group repeated methylation was tried using aqueous, methyl alcohol and ethyl alcohol media at the boiling points. It was found, however, that the resulting product recovered was always the original product and gave negative tests by Zeisel's method for methoxy groups. A typical experiment of methylation is described below in brief:-

10 gms. of the substance were taken in about 50 ml. of methyl alcohol containing 6 gms. of sodium hydroxide. The mixture was cooled and 20 gms. of dimethyl sulphate were added in small increments. The mixture was then refluxed for about 2 hours at the boiling point of methyl alcohol. The mixture was then cooled, excess alkali added to destroy the excess of dimethyl sulphate. The contents were then acidified with hydrochloric acid. Methyl alcohol was distilled off. The compound was filtered and washed free of chloride ion. The resulting product on submitting to Zeisel's method gave negative results for methoxy group.

The compound obtained above was subjected to further methylation in aqueous media at the temperature of steam but yielded no positive results. It was concluded therefore that the -OH group is not present in the molecule.

(c) Attempted Esterification of the Compound:-

As the substance was acid in nature, it was decided to attempt to esterify it and fractionate and characterize the esters if possible. Many unsuccessful attempts were made to make a methyl ester of the substance, using various possible methods of esterification. A typical experiment is very briefly described below:-

In a 250 ml. round bottomed flask 10 grams of the substance, 50 ml. of absolute methyl alcohol and 5 grams of concentrated sulphuric acid (2·7 ml.) were taken. a few chips of porous porcelain were added and the reflux condenser fixed on the flask. The contents were refluxed for about 4-5 hours. At the end the alcohol was distilled off in a water bath and the contents left in the flask were allowed to cool. The residue was then poured into a beaker containing about 200 ml. of cold water and the precipitate was filtered and washed free of all acidity. (The filtrate contained no oily liquid; nothing was extracted by shaking with an organic solvent). The precipitate was dried and tested for esterification by hydrolysis. It gave negative results showing absolute absence of any ester-formation.

The

The afore-mentioned process was tried by varying the time of esterification, and also by using methyl alcohol and dry hydrochloric acid but no success was achieved.

2. CHEMISTRY OF NITROGEN IN THE COMPOUND.

According to the molecular formula (which happens to be the same as the empirical formula in this case since molecular weight is the same as the empirical weight), $C_6 H_4 O_4 N$, the substance contained a nitrogen atom. Curiously enough it did not respond to any qualitative test for a nitrogen - containing group except that it did give off ammonia on treatment with alkali under different conditions. Charmbury and co-workers (21) have made an interesting study to determine indirectly the nature of such nitrogen-containing groups. Since it is quite possible that nitrogen in the compound, under investigation, even though present in the form of some known groups may not be responding to the standard known methods because of some structural manifestations, the technique used by the above workers (loc.cit.) was adopted to make an indirect study of the nature of these nitrogen containing group or groups.

Four variations in the method of treating the substance were employed. Procedure (1) consisted of determining (a) the amount of ammonia liberated from the substance by vigorous oxidation with alkaline permanganate; (b) the amount of nitrogen converted to the nitrate ion, and (c) the amount of carbon oxidized to carbon dioxide and volatile acids. Procedure (2) consisted of determining the amount of nitrogen in the substance which could be distilled as ammonia by alkaline hydrolysis before oxidizing them with permanganate and continuing as in procedure (1). Procedure (3) consisted of alkaline hydrolysis, followed by alkaline reduction with zinc, and continuing as in procedure (1). Procedure (4) consisted of alkaline hydrolysis and reduction in one operation, and then following procedure (1).

Procedure 1:-

(a) Estimation of nitrogen liberated as Ammonia. on alkaline permanganate oxidation.

25 grams of Potassium hydroxide and 35 grams of Potassium permanganate were dissolved in about 300 ml. of distilled water and introduced into a 2-litre flask which was fitted with a Kjeldahl trap and condenser, a dropping funnel and a stop-cock to equalize the changes in pressure within the flask. 2•5 grams of the substance were dissolved in alkali (50 ml. of 12% potassium hydroxide) and were introduced dropwise through the dropping funnel into the flask into boiling alkaline permanganate. 10 ml. of saturated boric acid diluted to about 100 ml. with distilled water were taken in a tall 400 ml. beaker and placed under the/

the condenser so that the four-opening bubbler, which was attached to the end of the condenser to aid in the absorption of ammonia, dipped in the boric acid solution. The ammonia which was distilled was thus neutralized by boric acid and the condensate was collected in the beaker till about 300 ml. had been collected. The distillate was then titrated against 0·1N sulphuric acid for ammonia.

Sufficient water was then added to the flask through the dropping funnel, keeping the stop-cock open to atmosphere to equalize the pressure inside and outside the flask. The stop-cock was then closed and the contents were again distilled, and the ammonia and the condensate were collected in the same manner. The distillate was again titrated against 0·1N sulphuric acid to determine the ammonia liberated. This process was repeated till 300 ml. of the distillate required less than 0·5 ml. of 0·1N sulphuric acid. This indicated the end of the reaction. A total of 20 hours was required to complete the reaction.

(b) Extent of Carbon Oxidation:-

After the reaction (a) above had been completed, the contents of the flask were cooled and 60 ml. of 50% sulphuric acid were introduced into the flask. The contents/

contents were again distilled and the volatile acids and water were collected in a 500 ml. flask attached to the condenser, while the carbondioxide gas, produced during the course of this distillation was dried by passing through two bubblers containing concentrated sulphuric acid, then through a tower containing fused calcium chloride. The gas was finally absorbed in a weighed U-tube filled with "Carbesol" and a potash bulb containing Potassium hydroxide solution. The Potash-bulb was protected against carbondioxide absorption from atmosphere by means of a guard U-tube filled with "Carbesol". The distillation was carried at a slow and steady rate, although in the initial stages the liberation of carbon dioxide was rather copious. All the carbon dioxide was carried into the U-tube and potash absorption bulb at the end of the run by forcing carbon dioxide-free nitrogen through the stop-cock in the flask. This swept all the carbon dioxide in the system through the absorption bulb. The amount of carbon dioxide was obtained from the increase in weight of the potash absorption bulb and the U-tube containing "Carbesol". The volatile acids, collected in the flask, were titrated against the standard 0·1N sodium hydroxide and calculated as acetic acid.

(c)/

(c) Determination of Nitrate ion produced.

The nitrate ion produced in the reaction (a) was quantitatively determined by filtering off the manganese dioxide produced in (b). The precipitate was thoroughly washed. The filtrate and the washings were returned to the flask and reduced by adding 25 grams of 20-mesh zinc and an additional 25 ml. of concentrated sulphuric acid. When the reduction was complete, 120 grams of potassium hydroxide were added and ammonia distilled into boric acid and titrated as before.

Procedure 2:-

2·5 grams of the substance were dissolved in 300 ml. of 10% Potassium hydroxide solution and introduced into the 2-litre flask in the apparatus as described in procedure (1). The contents were then distilled intermittently until the titration of 300 ml. of the distillate, collected as described in procedure (1), required 0·5 ml. or less of 0·1N sulphuric acid. About sixteen hours were required for the completion of the above reaction.

The contents were then cooled and 10 grams of Potassium permanganate dissolved in water were added into the flask. The contents were again distilled and the ammonia evolved collected. When the colour of the potassium/

potassium permanganate was discharged, 5-grams more of potassium permanganate were added and the contents again distilled for ammonia. In this way 5 gram portions of potassium permanganate dissolved in water were added to the flask again and again until the colour of the permanganate persisted in the solution and no more ammonia distilled. A total of 30 grams of potassium permanganate were required and it took 21 hours to complete the reaction.

The amount of carbon oxidized to carbon dioxide and volatile acids; and the amount of nitrogen converted to nitrate ion were also determined in the same way as described in procedure (1).

Procedure 3:-

2·5 grams of the substance were introduced into the flask (same apparatus as in procedure (1)) and 300 ml. of 10% potassium hydroxide were added. The contents were distilled till no more ammonia was evolved. Then 25 grams of zinc dust were added after the contents had cooled down and the stopper immediately replaced. Distillation was carried on till no more evolution of ammonia took place as indicated by the titre value of 300 ml. of the distillate being less than 0·5 ml. of 0·1N sulphuric acid. Water was added in the flask as and when required as described in the procedure (1). A/

A total of 32 hours was required to complete this reaction.

The residue was then oxidized with 10-gram, subsequently with 5-gram - lots of potassium permanganate in the same manner as described in procedure 2, i.e. till no more ammonia distilled and the colour of the permanganate persisted in the contents of the flask. 50 grams of Potassium permanganate and 26 hours were required to complete this reaction.

The extent of oxidation of the carbon to carbon dioxide and volatile acids; and the conversion of nitrogen to nitrate ion was also studied in the same manner as described in procedure (1).

Procedure 4:-

2·5 grams of the substance were taken in the flask containing 60 grams of potassium hydroxide dissolved in 300 ml of water (same apparatus as in procedure 1). 25 grams of zinc dust were added to it and the contents were then boiled. This was carried on till no more ammonia distilled over. Procedure for collecting the distillate and addition of more water when required were the same as in procedure (1). It required 72 hours to complete this reaction.

After cooling the contents, 10-grams of potassium permanganate dissolved in 300 ml. of water were

added/

added to it and oxidation carried on as described in procedure (2) and (3). More permanganate in lots of 5 grams was added till no more ammonia distilled over and the contents retained the permanganate colour. A total of 50 grams of permanganate and 28 hours were required to complete the reaction.

The extent of the oxidation of the carbon to carbon dioxide and volatile acids; and of nitrogen to nitrate was also studied in the same way as described in the procedure (1).

Results:-

The results of these experiments are presented in Table X11 on page 82.

TABLE XII

	Percent total nitrogen* converted to					Percent total carbon * oxidized to		
Procedure	NH_3 by alkaline hydrolysis	NH_3 by alkaline reduction	NH_3 by alkaline oxidation	NO_3^- by alkaline oxidation	Total nitrogen recovered	CO_2	Volatile acids	Total carbon recovered
1	-	-	4·9	79·4	84·3	95·3	0·7	96·0
2	4·2	-	18·6	61·2	84·0	87·0	5·3	92·3
3	4·7	16·4	60·8	5·2	87·1	89·4	3·8	93·2
4	-	19·2	58·7	6·7	84·6	80·5	2·1	82·6

* figures for nitrogen and carbon converted to NH_3, NO_3^-, CO_2 and volatile acids etc. are expressed as percentage of the original nitrogen and carbon present in the substance under investigation.

vi. STUDY OF THE THERMAL DECOMPOSITION OF THE PRODUCT.

In order to study the thermal decomposition of the compound at various temperatures the Gray-King low temperature carbonisation apparatus was used in a manner described below:-

5 grams of the product crushed to pass 72. B.S.S. were introduced into the weighed carbonizing tube and spread evenly by gentle tapping. An ignited and weighed asbestos wool plug was pushed into its mouth to act as a filter for the gases that might be evolved. The charged tube was then placed in the appropriate position in the furnace while all arrangements had been made appropriately for collection of gas, tar and ammonia, if any in the normal way. The furnace was then gradually heated and at a temperature of about 200°C, the substance decomposed with an explosive violence giving out a copious outburst of gases. Some gas was collected in the aspirator including the displaced air but most of the gases were lost owing to the displacement of the rubber stopper by the explosion. Repeated attempts were made to regulate this decomposition but the substance decomposed spontaneously at temperatures near 200°C. The gases collected in the aspirator were analysed. The results of/

of a typical experiment are given in Table XIII given below.

TABLE XIII

Analysis of decomposition gases.

Carbon dioxide	20·2%
Carbon monoxide	50·2%
Oxygen	2·0%
Nitrogen	27·6%

If the oxygen be due to the displaced air in the mixture, 2% of oxygen roughly corresponds to about 10% nitrogen. Thus the nitrogen corresponding to thermal decomposition is 17·6%

SECTION 3.

DISCUSSION OF RESULTS.

I Study of the gaseous products evolved during the Oxidation of coal with nitric acid.

This particular aspect of the problem was studied to follow, if possible, the course the reaction takes with time. A close study of the results which have been presented in Table I, figures 3, 4 and 5 on pages 33-36 respectively brings out the following interesting points.

(i) It may be noted from figure 3 that the velocity of the gas evolution rises suddenly and approaches a maximum at the end of about two minutes. It begins to fall rapidly after two minutes and at the end of about thirty minutes begins gradually to approach the lower minimum, till after about 4 hours it becomes constant for all practical purposes.

As is clear from figure 4 nearly half the amount of the total gas is liberated in the first seven minutes. While very small amounts of carbon dioxide and nitric oxide are liberated, nitrogen forms the bulk of the gas (fig.5) viz. 90·5% at the end of two minutes and about 84% at the end of seven minutes. This obviously suggests that/

that oxidation involving direct addition of oxygen is taking place since nitrogen oxides are being reduced directly to molecular nitrogen. Probably it corresponds to the first-stage oxidation, referred to as surface-oxidation on page 8 which is characterized by the addition of oxygen and the formation of oxygen-containing groups. These are believed to have acidic and peroxidic properties and are believed to consist of a coal-oxygen-water surface complex.

(ii) From seven minutes onwards, the velocity of gas evolution goes on falling quite rapidly up to about 30 minutes. Even at the end of 30 minutes the gas evolved contains 73·4% of nitrogen while the percentages of carbon dioxide and nitric oxide begin to increase. This stage probably represents the gradual change to second-stage of oxidation (refer page 9) which is characterized by the more easily detachable groupings being eliminated to form oxygenated compound i.e. carbon dioxide whilst the coal molecule becomes definitely of acidic character. It may be noted, however, that after about two and a half hours, the amount of carbon dioxide being liberated becomes a maximum, - the amount of nitric oxide also becomes appreciable; while the amount of nitrogen falls appreciably. This probably indicates the second-stage of oxidation at its peak when carbon/

carbon dioxide and water are given up concomitantly and profusely. It may thus be observed that while up to 30 minutes, the surface-oxidation merges into the second-stage oxidation, the latter goes on up to about 2.1/2 hours.

(iii) It is from about two and a half hours upwards that evolution of carbon dioxide begins to decline while the nitrogen is already declining at a constant rate. It is also at this stage that nitric oxide begins to rise at a rapid pace suggesting thereby a more regulated oxidation presumably indicative of internal structural changes - the third stage of oxidation (refer pages10-11).

(iv) It may be noted that after about twelve hours the rates of evolution of all gases,except NO,decline. The evolution of nitric oxide becomes a maximum but constant; It is also at this stage that we approach the flat portion of all the curves in figures 3, 4 and 5 suggesting that the transformation to the soluble acid stage of the last traces of partially oxidized coal is in progress. Also oxidation probably degrades the compounds still further without much evolution of gases.

It may be safely concluded from the above discussion that to get a good yield of the products formed in the third stage of oxidation, the one we aimed at, the/

the reaction must be carried out for at least twelve hours.

As observed above, although practically no more gases are evolved after about twelve hours of reaction further degradation may still be going on which can be judged only by observing the change in colour from deep hazy brown to clear red with an orange tinge which is of course rather difficult to perceive. However, the reaction was carried on for 30 hours in all cases to get the maximum yield of finally degraded product, and no dependence was made on the colour changes of the reaction mixture.

II STUDY OF THE WATER-INSOLUBLE PRODUCT.

As already observed in the experimental presentation of the action of nitric acid on coal, the resulting products can be classified as:-

(i) Gaseous products (which have already been discussed in the previous pages 85-88)

(ii) Water-soluble compounds.

(iii) Water-insoluble product.

It is obvious from the review of the literature (pages 13-18) that the water-soluble compounds have been investigated by many workers. With the exception of some unidentifiable materials, these contain mellitic, pyromellitic and other benzene carboxylic acids, picric, oxalic and other known acids in varying proportions depending upon the method of oxidation. The insoluble product, isolated in the above reaction, however, appeared to be of humic acid type but since it had been prepared by the oxidation of coal using approximately 100% nitric acid as an oxidant and because of its good solubility in acetone, alcohol, pyridine and furfural it was thought it may be a mixture of sufficiently degraded compounds. It was thought that it might consist of the compounds immediately preceding the benzenoid acids in the scheme of oxidation and hence most desirable/

desirable to forge another link in the chain between the benzene carboxylic acids and the original humic acids.

It was with these views in mind that the detailed study of the insoluble product was taken up in preference to the study of water-soluble compounds which, as explained above, might have contained the various benzenoid acids, in various proportions.

(i) General Properties:-

The product was dark-red in colour. It was insoluble in water but soluble in alcohol, acetone, furfural, pyridine, and di and trihydroxy benzenes. It did not crystallize from the solution in any of these solvents but could be recovered en masse on evaporating the solvent. Attempts to resolve it into its components, if any, did not meet with any success, although crystallization, chromotographic separation and fractional precipitation were tried. However, it is a general experience that such degradation products obtained from coal, although far from homogeneous, have probably the same nuclear structure differing chiefly in the point of attachment of functional groups. So it was decided to proceed with further investigation on this product taking it to be fairly homogeneous for the purpose of this investigation because its components, if any, were likely to have the same general type of structure.

(ii) Ultimate composition and Empirical formula:-

Ultimate composition being a rather insensitive property, it is perhaps not surprising that the carbon, hydrogen and oxygen contents of coal oxidation products from a variety of sources do not vary greatly though this does not hold good strictly if the oxidation is carried for a prolonged time or if more drastic oxidation methods are applied as in this case. The carbon-hydrogen ratio is lower than that obtained by some of the other workers, e.g. C-H ratio of the product isolated is 17·2:1 against 22·4:1 obtained by Francis (12) and Wheeler for the product obtained by oxidation of coal with hydrogen peroxide followed by alkali extraction, 19·6:1 for the product obtained by the prolonged action of 1N nitric acid on coal by Smith and Howard (16) and 18·8:1 obtained for the product by action of 16N nitric acid on coal followed by extraction with furfural, followed by solution in alkali by Fuchs and Sandhoff (22). This probably indicates the presence of condensed cyclic structure but of less complexity in this compound. However, ultimate composition is not a very sensitive property for such deductions.

As much as 9·0% nitrogen has entered the molecule of the degradation product which is nearly the highest figure obtained to date, the previous figure being of the order of 5·9% as reported by Fuchs and Sandhoff (loc.cit.). The possible nature of these nitrogen-containing groups is discussed later (pages 101-109)

The empirical formula, calculated from the ultimate composition, is $C_6 H_4 O_4 N$ with an empirical weight of 154. Though strictly it is not justified to calculate the mepirical formula of a product which may be a mixture but, as explained already on page 90, for subsequent investigation this is taken to be a single compound.

The molecular formula must be $(C_6 H_4 O_4 N)n$ where n is a whole number; it follows that the molecular weight must be the whole number product of 154. This incidentally, provides a useful check over the molecular weight determinations as made by known standard methods.

(iii) Molecular weight.

Before further investigation could have been done on the product it was essential to determine accurately its molecular weight. The determination of the molecular weight of such a product was complicated by the fact that none of the solvents available for the cryoscopic or/

or ebullioscopic methods within the normal range of application of a Beckmann thermometer could be considered suitable for use with this product. Acetone (B.P. 56°C), for example, did appear to dissolve the substance but doubt existed whether the mixture was a true solution or a colloidal dispersion; also the binary solvent, acetone-water, was much more effective than acetone alone, despite the fact that the substance was insoluble in water. Furfural (M.P.-38·7°C), di and trihydroxy benzenes (for example catechol M.P. 104·3°C) and pyridine (M.P. - 42°C) were good single solvents. In using any of these solvents it was essential to adopt means to measure small temperature changes at 104°C on the one hand and between -35°C) and -50°C) on the other. Mercury in glass thermometers could be used for the former temperature but would have been unsuitable for use with pyridine and furfural. Since low values of molecular weight were obtained in the preliminary determinations, it was decided, therefore, to check these by as many methods as possible.

Preliminary experiments which were then repeated accurately were done by using the cryoscopic method employing catechol as the cryoscopic solvent and an average figure of 160 was obtained for the molecular weight which is the lowest so far reported for any coal-degradation product of this type.

The/

The results of these experiments tabulated in Table II on page 48 seem to preclude the possibility of loosely bound water being a factor in the low results obtained. Solvation causes low values, but for a substance of molecular weight of, say 1200 to give an apparent value of 160, more than three fourths of the solvent must be bound to the solute. At a concentration of 1 gram per 100 grams of catechol as the solvent, molecular weight 110, each mole of the solute, molecular weight 1200 would have to bind more than 800 moles of solvent. This evidently seems highly improbable.

Another possible cause of low values would be chemical condensation with or without the elimination of water. In the latter case, a product of higher molecular weight is expected, so the possibility is ruled out. In the former case, however, if the solute reacts with catechol with the formation of water, the apparent molecular weight of the solute will be quite low. Such a reaction is possible but opposed to it is the fact that low values for molecular weight are obtained immediately. Solution in catechol takes place in a few minutes. If the sample is free from sorbed water, as it was, it is difficult to see how the first value can be too low unless a condensation reaction takes place immediately/

immediately, although it may be too high due to incomplete solution. It seemed, therefore, that the low value obtained must be quite correct. However, to confirm the low figure obtained recourse was made to other possible methods using different solvents. These were Ebullioscopic and Osmosis methods which have been described on pages 51 - 57. Cryoscopic method using pyridine and furfural as solvents (M.P. -42°C and $-38{\cdot}7^{\circ}$C respectively), which have melting point below the range of mercury in glass thermometer, was also used, in which a new temperature measuring intrument, the Thermistor (fig. 32 on page 245) (recently developed by the Standard Telephones and Cables Ltd., Footscray, Kent) was employed and proved to be a reliable and accurate instrument.

All these measurements confirmed the low value of the molecular weight of the substance. Although the values of molecular weight obtained by colligative methods such as freezing point, boiling point and osmotic pressure (all of which were employed) are particularly sensitive to the presence of small weight per centage of low molecular-weight species, the values probably represent an average because the solute possibly consists of a series of molecular sizes analogous to a polymeric homologous series.

In/

In this case it may be mentioned that molecular weight of coal-degradation products of this type have been variously reported as from 300 to 1250 when determined by physical methods and from 680 to 1600 by chemical methods. The very considerable variations in these values of molecular weight reported may be ascribed in part to the molecularly heterogeneous nature of the materials under investigation, partly to peculiar specific molecular properties and partly to the different stage of degradation the particular product has been brought to in a particular oxidation process. While various investigators including Oden (23), Fuchs (24), Thiessen and Engelder (25), Samec and Pirkmaier (26) reported coal degradation products of rather high molecular weight, Smith and Howard (16) are reported to have isolated products by prolonged action of 1N nitric acid on Pittsburgh Seam bituminous coals which were found to be soluble in dihydroxy phenols, such as catechol, and cryoscopic measurements in this solvent led to average values around 300.

Thus it may be noted that a product of humic-acid type with the lowest molecular-weight, so far reported, has been isolated which may be of a general structure immediately preceding the benzenoid acids in the scheme of/

of oxidation. This is because, evidence indicating the position of any compound in the series of oxidation products is conveniently provided by the molecular weight of the compound which, of course, decreases with increasing degradation. Therefore its general structure might provide the missing but useful link between the benzenoid acids and the humic acids.

(iv) Molecular formula of the compound:-

As already described on page 92 the empirical formula of the compound is $C_6 H_4 O_4$ N with an empirical weight of 154; the molecular weight can only be n x 154. Since the molecular weight determinations have yielded the figures ranging from 150-200, it may be assumed that correct molecular weight should be 154 and hence same as the empirical weight. So the molecular fomula will also be the same as the empirical, i.e. $C_6 H_4 O_4$ N. Conclusive evidence leading to the structural formula of such a compound is lacking.

(v) Functional groups.

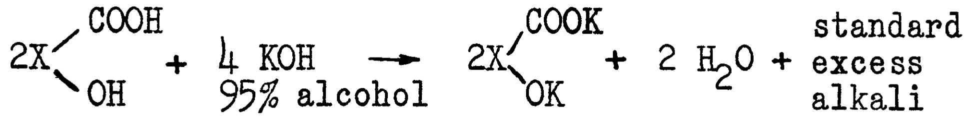
It will be observed from the ultimate composition (refer page 38) that the substance contains about 40·7% of oxygen and 9% of nitrogen, corresponding to 4 atoms of oxygen and one of nitrogen in the molecular formula $C_6 H_4 O_4$ N. (refer page 97). The next step, therefore, was to/

to find how this oxygen and nitrogen are distributed in the substance i.e. the determination of various functional groups.

(a) Groups not containing nitrogen:-

Relatively little work has been done in the determination of the functional groups in humic acids and other oxidation products obtained from bituminous coals. Generally all the oxidation products are acids and contain carboxyl and hydroxyl groups. The substance under investigation decomposed a solution of sodium bicarbonate showing thereby that it may contain both carboxyl and hydroxyl groups. This is because phenolic groups alone cannot decompose a 5% solution of sodium bicarbonate. Consequently the substance may be or may not be a hydroxy acid. An aqueous suspension of the substance had a pH of about 4 and for determining its total acidity it could be directly titrated against standard alkali but since in a hetergeneous system of this kind, the attainment of equilibrium is slow, it is preferable to dissolve the substance in an excess of standard alkali and to determine the excess by back titration (19). This method as modified by Ubildini (loc.cit.) was used which gives the carboxyl and the phenolic hydroxyl groups in one step. The method which is described on pages 64 - 66 is based on the principle illustrated by the following equations:-

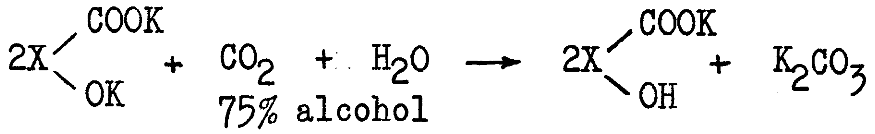
If X is the unknown radical in the substance which has a carboxyl and a phenol - OH group, then on treatment with excess of standard alkali, the following reaction will take place:-



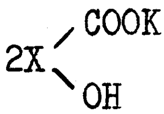
$$2X\begin{matrix}\text{COOH}\\ \text{OH}\end{matrix} + \underset{95\%\ \text{alcohol}}{4\ \text{KOH}} \longrightarrow 2X\begin{matrix}\text{COOK}\\ \text{OK}\end{matrix} + 2\ H_2O + \text{standard excess alkali}$$

Thus the back titration of the excess alkali gives the total acidity due to both - COOH and - OH group. 95% alcohol is used to make the potassium salt of the substance insoluble so that the excess alkali can be titrated.

This precipitate of Potassium salt of the substance, washed free of alkali, is suspended in 75% alcohol solution and dry carbon dioxide is bubbled through it which liberates an equivalent amount of potassium carbonate from the potassium ions attached to the phenolic group according to the following equation(20a):-



$$2X\begin{matrix}\text{COOK}\\ \text{OK}\end{matrix} + \underset{75\%\ \text{alcohol}}{CO_2 + H_2O} \longrightarrow 2X\begin{matrix}\text{COOK}\\ \text{OH}\end{matrix} + K_2CO_3$$

Thus Potassium carbonate equivalent to the phenolic group is liberated and is soluble in 75% alcohol whereas the precipitate of  $2X\begin{matrix}\text{COOK}\\ \text{OH}\end{matrix}$ remains insoluble. The potassium carbonate can be titrated and can give the acidity due to phenolic group. Thus/

Thus the carboxyl groups can then be calculated knowing the total acidity and the molecular formula as described on pages 66 - 67.

It was established by this means that the substance, under investigation, is a mono basic acid with no phenolic groups at all. Absence of the phenolic groups was further confirmed by the fact that all attempts at methylation failed (refer page 71). As the molecular formula of the substance is $C_6 H_4 O_4 N$, all the four oxygen atoms are accounted for since it contains one - COOH group and one nitro group ($-NO_2$) as discussed on pages 101 - 109. This, therefore, further confirmed the absence of any hydroxy group.

It may be observed here that during the methylation process, with methyl alcohol and dimethyl sulphate (page 71) or during direct esterification using methyl alcohol and sulphuric acid (page 72), no esterification took place at all. This peculiar behaviour of the substance, with such a low molecular weight, to refuse to yield a crystalline form of the acid or its methyl ester is somewhat similar to the behaviour of some of the so-called "soluble acids" (refer page 10 & 15-18) which are reddish-yellow soluble coloured acids obtained during the degradation of coal, and the elucidation of the structure of which has been attempted by/

by many workers with little success. Like some of the soluble acids it seems to lie between the regenerated humic acids and the crystalline well-defined, definitely characterizable types such as benzene carboxylic acid and oxalic acid etc., shows greater solubility in organic solvents than the regenerated humic acids, has an ultimate composition indicative of the cyclic nucleus with all its oxygen accounted for. It also shows, like them, marked thermal instability - in fact it decomposes with almost an explosive violence probably due to the presence of a nitrogroup (see pages 106, and 107).

(b) Nature of nitrogen-containing groups:-

Although the substance - under investigation, was finally confirmed to be of reasonably low molecular weight, the standard qualitative tests for identification of nitrogen-containing groups did not yield anything positive except that when boiled with alkali-solution, small amounts of ammonia were liberated (27). This behaviour was a bit strange and hence the chemistry of nitrogen in the compound was studied indirectly by observing the action of alkaline potassium permanganate on the substance under a variety of conditions (21) as described on pages 75 - 81. The results have been presented in Table XII on page 82.

It may be noted from the Table XII that results/

results of procedure 1 indicate the presence of two types of nitrogen in the molecule of the substance. The first one is 4·9% which must be obviously in a reduced state since it was evolved as ammonia even under the conditions of oxidation with alkaline permanganate. The second one which is 79·4%, must be in a higher state of oxidation as it was liberated as nitrate ion. Results of procedure 2 indicate the liberation of 4·2% of ammonia, approximately the same as in the case of procedure1 by alkaline permanganate oxidation, while a part of the remaining nitrogen, 18·6%, appeared as ammonia on subsequent oxidation with alkaline permanganate. This shows that this amount of nitrogen has been reduced to such a point where it is evolved as ammonia on subsequent alkaline permanganate oxidation. The results might suggest that 4·2% nitrogen evolved as NH_3 by boiling alkali may be on account of some internal oxidation-reduction reaction in which the oxidized nitrogen played the same part as the alkaline potassium permanganate in procedure 1. Subsequent results, however, as obtained in the procedures 3 and 4 do not justify this conclusion. This is because in procedure 3, 16·4% nitrogen was evolved by alkaline reduction after the substance had already been subjected to alkaline hydrolysis and in procedure 4, 19·2%, was evolved by boiling with alkali and zinc/

zinc dust. The difference i.e. 3•8% is nearly equal to the amount liberated by alkaline oxidation and alkaline hydrolysis i.e. 4•9 and 4•2% respectively. Therefore it is obvious that this quantity of nitrogen i.e. 4•2 - 4•9% must be in such a form as can be liberated directly by alkaline hydrolysis rather than by internal oxidation-reduction reaction.

It may also be noted from the Table XII that in procedure 1 the quantity of nitrogen oxidized to nitrate ion, 79•4%; in procedure 2 the amount of nitrogen liberated in the form of ammonia by permanganate oxidation and as nitrate ion, 79•8%, and in procedure 3 the total nitrogen reduced by zinc and alkali and evolved as ammonia together with that evolved on permanganate oxidation, 77•2%, are fairly close to each other. This indicates fairly quantatitive nature of these reactions.

It becomes important to find out in what reduced form 4•2 - 4•9% nitrogen could exist so as to liberate ammonia on alkaline hydrolysis and also on alkaline permanganate oxidation. The fact that a reduced form of nitrogen may be liberated as ammonia on alkaline permanganate oxidation has been demonstrated by Charmbury and his co-workers (loc.cit.). They showed that about 88% of the nitrogen in amino-acetic acid was liberated as ammonia on alkaline/

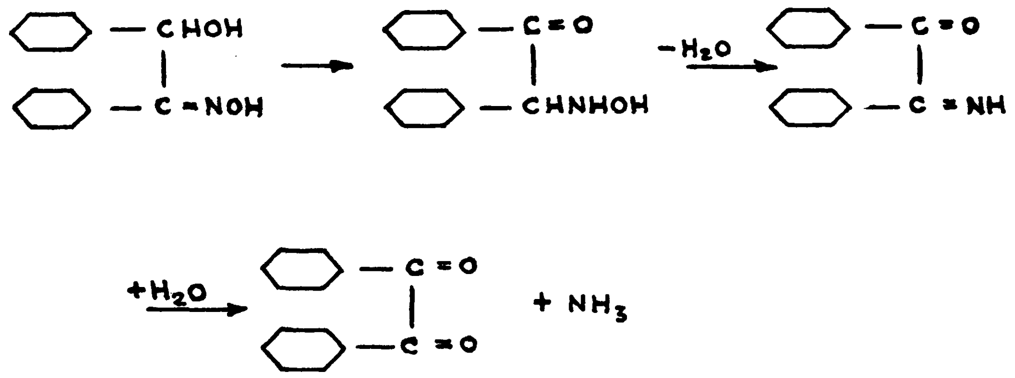
alkaline permanganate oxidation, while in the case of more resistant p-amino benzoic acid, only about 67% of the amino nitrogen was released as ammonia. At the same time 1·0% nitrogen in amino-acetic acid and 8·4% in amino-benzoic acid was converted to nitrate ion. A nitro compound, viz. nitrobenzoic acid gave only 0·2% nitrogen as ammonia under the similar conditions while about 40% was oxidized to give nitrate ion. The low yield of nitrate ion from p-nitrobenzoic acid was attributed to the resistance of the compound to oxidation, the oxidation being only 21% of total carbon content of nitrobenzoic acid. These amino-acids were, however, shown to give practically negative results for ammonia when subjected to alkaline hydrolysis, e.g. amino-acetic acid evolved 0·6% of nitrogen as ammonia while p-aminobenzoic acid yielded none at all. Therefore this 4·2 - 4·9% of nitrogen evolved as ammonia on alkaline oxidation and alkaline hydrolysis could not be due to an amino group.

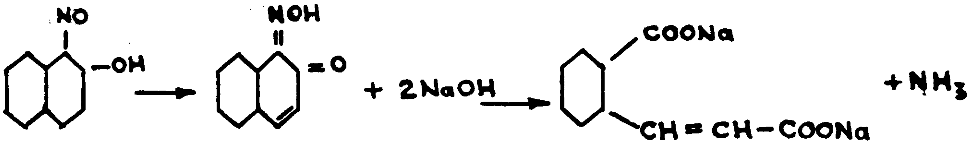
The possibility of the presence of such groups as cyanide, amide or quarternary - ammonium type, which are known to liberate ammonia on alkaline hydrolysis is practically ruled out in view of the use of approximately 100% nitric acid - a very strong oxidizing agent - for the isolation of this product.

It/

It was shown, however, by Charmbury and co-workers (loc.cit.) that compounds containing oxime and nitroso groups do yield ammonia on alkaline hydrolysis as well as on permanganate oxidation, e.g. a-benzoin oxime and a-nitroso-B-naphthol evolved about 87% and 80% respectively of the nitrogen content as ammonia on boiling with alkali. a-Benzoin oxime yielded about 68% of nitrogen as ammonia on alkaline permanganate oxidation. The following explanation for this behaviour of these two compounds was suggested by them:- "a-benzoin oxime and a-nitroso-B-naphthol would be expected to be hydrolysed by boiling alkali to hydroxal-amine. However, since hydroxal-amine will not distil from an alkaline solution and is rapidly oxidized by permanganate, the liberation of ammonia indicates that this substance is the primary product of the reaction rather than hydroxylamine". The following equations, propounded by them, explain the direct elimination of ammonia from both these compounds:-

(1)





The above results are very similar to those obtained in the case of the compound - under investigation, suggesting thereby that this 4·2 - 4·9% of nitrogen might be in the form of nitroso or iso-nitroso group which is more likely rather than an oxime group because of liberation of large amounts of nitric oxide during its preparation by oxidation of coal with nitric acid (ref. fig.5) on page 36.

The remaining nitrogen i.e. 79·4% converted to nitrate ion by treatment with alkaline potassium permanganate must be in the form of nitro or nitrate ester group - the only other groups at a higher oxidation level than the nitroso or isonitroso level which are likely to be introduced by the nitric acid treatment. The formation of the nitrate ester is, however, improbable because of the method of the preparation of the compound. So the rest of this nitrogen is in the form of a nitro compound. It will be interesting here to refer to the study of the thermal decomposition of the compound described on pages 83-84. The substance decomposed almost in a sudden explosive form, the resulting gases of decomposition having the following composition/

composition:-

Carbon Dioxide	20·2%
Carbon Monoxide	50·2%
Oxygen	2·0%
Nitrogen	27·6%

Since the gases collected included the displaced air also, and reckoning the oxygen to be due to air only, about 10% nitrogen must be subtracted from the above value since it must have been contributed by air. So 17·6% nitrogen were evolved by the compound.

The above thermal decomposition is somewhat similar to the decomposition of nitro compounds e.g. trinitro phenol (picric acid) a well known explosive, when suddenly heated or detonated by means of fulminate of mercury, is known to decompose according to the equation (28)

$$2C_6H_2(NO_2)_3\,OH \quad = \quad 12CO + H_2 + 3N_2 + 2H_2O$$

The carbon dioxide liberated by the compound probably results from decarboxylation of the carboxyl group.

It could be safely concluded, therefore, that the 79·4% of the nitrogen liberated as nitrate ion by alkaline permanganate oxidation in procedure (1) is in the form of a nitro-group.

It/

It may be noted from the Table XII on page 82 that on reduction of the substance 16·4% of nitrogen was liberated as ammonia (in procedure 3) while 60·8% remained and was liberated as ammonia on alkaline oxidation. Considering that the nitro-group on complete reduction would give an amino-group which ordinarily does not hydrolyse to ammonia on boiling with alkali, it seems more likely that certain structural changes in the compound favour the elimination of ammonia from some intermediate product. One possible explanation would be that during the reduction of the nitro-group, a stage of intermediary nitroso or oxime group is giving rise to ammonia by the action of boiling alkali. It may be that a part of this intermediate nitroso or oxime compound is acted upon by alkali while the rest gets reduced to the amino-stage before alkali gets time to hydrolyse it.

To sum up the above discussion, the nitrogen in the substance - under investigation - is present in two distinct forms i.e. (1) 79·4% in the form of nitro group which is liberated as nitrate ion on oxidation with alkaline permanganate and (2) 4·2 - 4·9% at the less oxidized nitroso or isonitroso level which is liberated as ammonia not only by alkaline permanganate but also by alkaline hydrolysis. This/

This is when the total nitrogen recovered in these forms is about 84 - 85% of the total nitrogen present in the compound.

It may be recalled that the molecular formula (refer page 97) of the substance is $C_6 H_4 O_4 N$ which indicates that nitrogen only in one form could be present in the compound. The discussion in the foregoing pages, however, has revealed the presence of two distinct forms of nitrogen viz. majority at the nitro group level and a very small percentage at the nitroso or isonitroso level. It is possible, therefore, that the product may contain small amounts of a substance which has the same general structure but has nitrogen oxidized to the nitroso or iso-nitroso level, whereas the bulk of the product is a pure nitro-body. That is to say the nitroso-compound should be regarded, for all practical purposes, as an impurity in the main nitro-compound.

SECTION IV

SUMMARY and CONCLUSIONS.

A detailed study has been made of the action of nitric acid, approximately hundred per cent, on bituminous coal. A special technique and apparatus evolved to study the reaction under controlled conditions has been described. In this solid carbon dioxide was used to cool the reaction mixture and minimised the risks of fires to which such reaction is prone because of the highly exothermic nature of the reaction.

Three types of products were obtained by such a reaction which was carried on for 30 hours.

(i) Gaseous products.
(ii) Water-insoluble product.
(iii) Water-soluble product.

A study of (i) has been made which has confirmed the standard three stages of oxidation in coal. It was found that, in order to obtain a fair yield of the products of the third stage of oxidation which is indicative of the structural degradation in coal, reaction must be carried over at least 12 hours.

The water-soluble product has not been studied because, as shown by a review of the literature, the water-soluble compounds obtained under such conditions generally/

generally contain benzenoid acids and some unidentifiable materials.

The water-insoluble product, however, has been studied in detail as it appeared, in so far as could be judged from some of its physical properties and mode of its production, that it might consist of the compounds immediately preceding the benzenoid acids in the scheme of oxidation and consequently most desirable to forge another link in the chain between the benzene carboxylic acids and the original humic acids.

This product is dark red in colour, is insoluble in water but soluble in alcohol (partially), acetone, furfural, pyridine, di and trihydroxy benzenes. It refuses to be fractionated by fractional crystallization, chromatographic separation and fractional precipitation. Since such degradation products consist of a series of molecular species, probably of same nuclear structure differing chiefly in the attachment of functional groups, this product was assumed to be fairly homogeneous for further investigation.

The product is found to have a molecular formula of $C_6 H_4 O_4 N$ with an ultimate composition with all its oxygen accounted for, as it is a monobasic acid with one nitrogroup in the structure. The determination of the molecular/

molecular weight of this substance by cryoscopic, ebullioscopic and osmosis methods has been described. In two of the determinations, by the cryoscopic method in pyridine and furfural as solvents, a new device for measuring small changes in temperature of the order of $\pm \cdot 001^{\circ}C$, the Thermistor, has been used which is given as appendix I. The product has a molecular weight of the order of 160 which is the lowest so far reported, the previous lowest being 300 as reported by Smith and Howard (loc.cit.) on a product obtained by prolonged action of 1N nitric acid on bituminous coal. The low molecular weight of the product is itself an evidence of its position in the series of oxidation degradation products since the molecular weight decreases with increasing degradation.

Since the product does not respond to qualitative tests for groups containing nitrogen an indirect study of the chemistry of nitrogen, on the lines similar to those used by Charmbury and co-workers (loc.cit.) has been made. It has led to the conclusion about the presence of a nitro-group. The fact that the product is thermally unstable and decomposes at about 200°C with almost explosive violence confirms the presence of a $-NO_2$ group.

The most peculiar observation, however, is its refusal to yield a methyl ester (although it is a monobasic/

monobasic acid) and to crystallize. Both these attempts were made with a view to fractionating it into its components, if any, and to characterize its methyl esters by distillation. This behaviour, however, is not new when one deals with degradation products of coal which somehow always tend to exhibit an anomolous behaviour. A close analogy is provided by the so-called soluble acids (refer pages 10-13 + 15-18) which are reddish yellow soluble coloured acids obtained during the degradation of coal and elucidation of the structure of which has been attempted by many investigators with little success.

It may be concluded, therefore, that by action of such a strong oxidant as approximately hundred per cent nitric acid on coal, a product has been isolated which

(i) has a molecular weight of the order of 160.

(ii) is a monobasic acid.

(iii) has nitrogen in the form of a nitro group.

But the complete evidence leading to the structural formula of such a compound is lacking. It appears, therefore, that the substance may be in such a state that it leads to these simple conclusions, but in fact, is of a sufficiently complex nature. It is only hoped, therefore, that some of the facts established about this apparently simple coal degradation product would be of some significance.

PART II

STUDY OF ACTION OF FUMING SULPHURIC ACID ON COAL.

PART II.

STUDY OF ACTION OF FUMING SULPHURIC ACID ON COAL.

SECTION 1.

INTRODUCTION.

The action of sulphuric acid on coal has been characterized as chiefly that of an oxidizing agent, although some sulphur is found in the product. Oxidizing reactions in this direction were carried out mainly with a view to isolate some degradation products so that the structure of these might lead to build back the complicated coal-molecule structure. It was, however, a work of much qualitative nature and only small amounts of definitely characterized products were obtained.

It was found as early as 1845 by Marchard (29) that carbon dioxide and sulphur dioxide were the main products along with small amounts of organic acids when concentrated sulphuric acid reacted on coals. Giraud (30) in 1894 reported obtaining a yield of about 5 per cent of pyromellitic acid (1, 2, 4, 5, - benzene tetra carboxyllic acid) by/

by distilling bituminous coal with concentrated sulphuric acid. Philippi and Thelen (31) reported higher yields of pyromellitic acid using metallic mercury as catalyst. Interesting information about the oxidizing action of concentrated sulphuric acid on coal arose recently from the observation that, unless very prolonged periods were employed, Kjeldahl's method gave low values for nitrogen determinations. These were explained by Beet (32) to be due to the formation of more pyridine carboxyllic acids, resistant to sulphuric acid.

A number of workers employed mixtures of sulphuric acid with chromates, permanganates, and chlorates for oxidizing coal (33, 34, 35, 36, 37, 38) and reported having obtained only carbon dioxide and carbon monoxide as the chief products with the formation of neglegible amounts of complex oxygen-containing compounds. It will be noted that these oxidizing reactions with sulphuric acid yielded only small amounts of characterized products and unfortunately much of the work has been entirely qualitative.

A rather interesting observation was made that coal on treatment with concentrated sulphuric acid at temperatures up to 250°C absorbed a good amount of acid. The resulting product was found to have base-exchange properties.

Base-exchange is a phenomenon exhibited by substances insoluble in solvents and aqueous solutions. These substances have their cations that ionize in polar solvents and are capable of exchanging these cations with ions which may be present in solution surrounding them, without any visible change in the solid structure. Their chief usefulness is dependent upon this characteristic, since they form a fixed matrix with available randomly distributed charges which may be used for many types of exchange reactions. The general reaction may be expressed by the equation,

$$AE + B \rightleftharpoons BE + A$$

in which E is an exchanger (an anion) and A and B are positively charged. These substances behave chemically like other familiar ionic substances, with the exception that, for the most part, their compounds are highly insoluble.

The first observations on base-exchange phenomena are generally accredited to J.T. Way (39), who studied the adsorption of cations by soils about a century ago and to Eichorn (40) who discovered that the bases were mutually exchangeable. Subsequent researches were devoted to base-exchange occurring in zeolites. All of these substances contain alkali or alkaline earth metals, and it is these metals which ionize and exchange with ions in solutions.

They/

They have also a highly porous structure or else a very large exposed surface to permit these ions to get in and out. Lamberg (41), Eichorn (loc.cit.), and Gans (42) studied these mineral exchangers exhaustively, and later Gans (43) made commercial application of zeolites to water softening. Indeed, the zeolites became so much associated with ion-exchange that term "Zeolite" was extended to include all ion-exchanging substances. This usage persists today even for sulphonated coals which are referred to as "Carbonaceous Zeolites" or "Carbonaceous Exchangers". The instability of these siliceous exchangers in acidic media and the search for other cation exchangers stimulated studies on the cation exchange adsorbents based upon naturally occurring organic materials. Thus Fischer and Fuchs (44) suggested that water could be softened by using the sodium humates of brown coal. Barrowman's work (45) on water-softening was followed by disclosures that acid-treated humic substances could be used for the removal of cations from water (46), and that sulphonated tannins (47), coal, lignite (48), and other organic materials (49, 50) could be used for a similar purpose. These carbonaceous exchangers proved to be a considerable advance over the zeolites (51) both in their increased exchange capacity and their stability in acids. In-organic zeolites/

zeolites are stable at a pH near neutrality and so cannot be employed successfully for reactions involving hydrogen ions or in basic solutions.

As in the case of the siliceous exchangers, the industrial utility of these compounds stimulated research on their practical aspects, and the patent literature began to grow at a very fast rate (52, 53, 54). The main attention was focused on producing carbonaceous exchangers with a high base-exchange capacity using different types of sulphonating agents of different concentration at different temperatures. Thus United Water Softeners Ltd. (55) developed a method of treating peat, lignite, coal and even anthracite with sulphuric acid, or with chlorosulphonic acid to give a material of good base-exchange capacity. Material of higher base-exchange capacity (56) was claimed to have been prepared by treating the material, either during or after the preparation, with an alkali sulphite or bisulphite or with an aldehyde such as formaldehyde. One part of coal treated with sulphur trioxide (less than two parts) in liquid sulphurdioxide at -10° to -15°C was claimed to give a material of very high exchange capacity (57). The use of sulphuric acid, sulphur trioxide or amidosulphonic acid, in the presence of a mercury salt was found to give still better results (58).

Thus many improvents have been made both with respect to getting materials with increased base-exchange capacities, and more desirable physical properties. The real stimulus to the ion-exchange industry was given in 1935 when Adams and Holmes published their classic paper on purely synthetic organic cation and anion exchange resins, and described for the first time, anion exchange reactions(59). This discovery opened a new era in the chemistry of synthetic resins since the vast array of resins which have been prepared may now be re-assessed on the basis of chemical properties, rather than on the basis of physical properties, which have formed the criterion of their industry so far. These synthetic ion-exchange resins have a higher exchange capacity than the sulphonated coals. Although the "sulphonated coals" do not have the capacity of the newer sulphonic acid resins, these are cheaper and definitely have better chemical stability (60). Thus work on production of cheaper carbonaceous exchangers with higher exchange-capacity is still a matter of interest and has been attempted in the study detailed in part II of this thesis.

Owing to the finding of manifold new uses, in industry, of the base exchange materials besides the traditional water-softening, the patent literature has grown at/

at a much more rapid rate than the literature devoted to scientific investigations of the ion-exchange process as it occurs in these ion-exchangers. However several significant papers have appeared which presage interesting investigations in this field. As detailed later in this thesis, some work on the physical study has been attempted, and it may be useful to preface that with a very brief review of the ion exchange theory with respect to the work contributed in that direction.

Ion-Exchange Theory:-

An Ion-exchange material may be defined as an insoluble substance containing labile ions which are exchangeable with ions in the surrounding solution without any visible physical change in the structure of ion-exchange material. These materials are available for exchange of both cations and anions and are called as cation and anion exchangers respectively. A grain of the cation exchanger magnified sufficiently would probably resemble a sponge whose walls are studded at intervals with fixed negative ions (which are believed to be $[\mathrm{Al\ Si_3O_8}]^-$ in the case of zeolite exchangers) due to sulphonic and/or carboxyl groups in the more recent carbonaceous and resinous exchangers. Positive sodium or hydrogen ions, depending upon the fact that the exchanger is for sodium cycle or hydrogen cycle, hover in the internal passages/

passages and around the surface of the sponge. If such a body of an exchanger is placed in another salt solution, e.g. calcium chloride solution, calcium ions can diffuse through the body of this sponge but for every one calcium ion, two sodium ions or two hydrogen ions (whatever is the case) must come out to maintain neutrality within the body of the exchanger. Thus the reaction proceeds by exchange of equivalent amounts of ions. Exchange is a typical reversible process and for the above example the following equation may be written:-

$$Ca^{++} + 2(Na^{+}Ex^{-}) \rightleftharpoons 2\,Na^{+} + (Ca^{++}Ex_2^{-})$$

If the equilibrium obeys the law of mass action, as some believe it does, the following equation would hold good:-

$$\frac{(Na^{+})^2 \text{ solution} \quad (Ca^{++}) \text{ Exchanger}}{(Ca^{++}) \text{ solution} \quad (Na^{+})^2 \text{ Exchanger}} = \text{A constant}$$

The value of the equilibrium constant depends upon the exchanger and is generally more than one in above case, e.g. it was found to be three in a typical exchanger studied by Walton(51). This shows that exchanger prefers to take calcium ions to sodium ions, other things being equal. In general an exchanger is more attracted to the ions which have higher valency and are less hydrated in solution (61, 62). Ionic radius has also been correlated with the equilibrium constant in/

in that the larger the unsolvated ion, the better it is held by the exchanger (61). The equilibrium constant is not much affected by the temperature (63). Schubert (64) has applied the law of mass action to ion-exchange equilibria employing the solid solution principle of Vaneslow (65) for evaluating the activities of solid phase components. However this method was extended utilizing the Duhem relation described by Kielland (66).

Thus although these workers have done work of significance in this field of the study of mechanism of the exchange reactions on ion-exchangers, it has not received so much attention as has been devoted to work describing the immense possibilities of the industrial application of these materials. This is rather unfortunate since a complete understanding of the process cannot be had until an exhaustive study of the equilibria in static systems is obtained, and the theories of exchange, which have been developed for siliceous exchangers, have been applied in this field.

A very instructive study in this field has been contributed by Griessbach (67). He seems to be the only investigator who has formulated equations similar to the Jenny and Wiegner equation (68), for the exchange equilibria of/

of a hydrogen-exchanger, i.e. exchangers which exchange metallic ions in the surrounding solution with hydrogen ions. He showed that it should be possible to characterize different types of exchangers by means of well-defined constants, a definite step toward an understanding of base-exchange phenomena. However it may be noted that his results are presented graphically only, so it is possible to draw qualitative conclusions only. Besides all his data was obtained by titration of exchangers in presence of one concentration (.01N) of neutral salt only. In view of this and the work of Steinhardt and Harris (69) on the base-combining capacity of wool who showed that it was a function of pH and ionic strength, it was felt that Griessbach's work could be carried further by studying the variations in the pH neutralization curves of a carbonaceous exchanger as the ionic strength of the solution is changed, since the base-binding capacity of the exchanger should be a function of this variable. A part of the work detailed in the pages to follow deals with this physical aspect of the hydrogen ion-exchangers.

As already mentioned, the uses of ion-exchangers in the realm of industry have grown at such a tremendous rate and have become so voluminous in number that it has practically resulted in the addition of a new unit process/

process to those already available in the chemical industry. The possible applications of this unit process increase as the commercially available materials are improved by further research and development. In most of their uses, however, the following is the underlying principle:- The materials, as it were, act as ionic sieves, concentrating ions within themselves in an insoluble form, from which they can be subsequently liberated by eluting agents in the regeneration process. A novel use of hydrogen-exchangers, however, has been to use these as catalysts in the reactions catalysed by the hydrogen ions. These, insoluble acids, have the obvious advantages over the use of soluble acids, that they can be easily removed from the reaction mixture by, for example, simple filtration or decantation. The fact that the exchangers can be used repeatedly, with periodic regeneration with acids, offsets the initial costs. Catalytic processes involving hydrogen exchangers reported in the literature include the hydrolysis of starch to glucose (70), esterification and ester interchange, acetal synthesis, alcoholysis, and ester hydrolysis (71) and other many such applications.

An interesting application of the carbonaceous hydrogen-exchanger, based on its ionization to give H^+ ions, has been studied as it is applied to the "anodic oxidation" of/

of aluminium. Anodic oxidation (72) is an electrolytic process for thickening the oxide film present on all aluminium surfaces. This process is applied for various reasons e.g. to provide a key for painting, to provide an insulating coating and dyeing (73) for decorative purposes etc. The commercial processes for the anodic oxidation of aluminium and its alloys are based on the use of either chromic acid (72) sulphuric acid (74) or oxalic acid (75) as an electrolyte. Since carbonaceous hydrogen-exchanger is capable of ionizing to give a steady concentration of H-ions it was thought that its use alone or in conjunction with the acid electrolyte would provide an interesting subject for study with a view to improving the film of oxide formed on Aluminium as, the acid electrolyte alone goes on decreasing in strength, with continued anodic oxidation process, on account of its dissolving action on the oxide. The study has been detailed in Section 2 of Part II of this thesis.

Thus the above review is sufficiently indicative of the fact that the progress in the field of ion-exchange has been appreciable for the past few years and it is imperative that many more applications and uses will be found for this unit operation, the more we become acquainted with the fundamentals of the phenomenon of ion-exchange. It is/

is with this principle in view that the work, described on the pages to follow, has been attempted including the topics mentioned in the text of this introduction.

SECTION 2.

EXPERIMENTAL AND RESULTS.

I Preliminary Work.

(i) Sulphuric Acid of Oleum strength.

Oleum (20% SO_3) was obtained for the study of this reaction. Oleums containing different percentages of sulphur trioxide, required for any particular investigation, were made by mixing this oleum with the required quantities of concentrated sulphuric acid. The strengths were checked by the use of Lunge-Rey pipette for weighing a known amount of the acid and subsequent titration against a standard alkali.

(ii) Coal:-

Bituminous coal of high volatile matter content from Dumbreck Colliery was selected. It was crushed to size 25-40 B.S.S. This size is the one recommended for coal-sulphonation experiments because material of this size when packed in a column, provides the requisite permeability for liquids which may be required to flow through the columns. Besides if the exchange capacity of various products is to be compared, it seemed quite essential that the testing procedure should include a narrow size limit of the product which, in turn,/

turn, depends to quite an extent on the size of the starting material.

(iii) The Reaction:- (Hitherto referred as sulphonation of coal)

It was found when oleum was added to coal, a violent reaction took place with evolution of copious fumes containing sulphur dioxide and some sulphur trioxide. But gradually the reaction became less vigorous especially when sufficient oleum had been added to give a sort of suspension of coal in the acid. The contents had to be brought to the ultimate temperature of sulphonation rather slowly to avoid any sudden evolution of gases which might have resulted in the contents of the reaction mixture being thrown out of the sulphonation pot. It was found that agitation of the contents by the use of a stirrer was very essential to get a smooth and uniform product. On the other hand it was important to carry the stirring very slowly to avoid the breaking up of coal particles.

After a number of preliminary experiments, the following apparatus and procedure were finally evolved:-

II Apparatus and Procedure:-

The apparatus, as shown in Fig.9 on page 130 consisted of a cast-iron sulphonation pot, A, of capacity of about 1200 ml. The vessel, A, was lined with lead-sheet, B, as shown in the figure. It had a lid, C, which could be tightly screwed on to the top of the sulphonation pot. Through the collar in the centre of the lid passed a cast-iron rod, R, which carried four blades. This rod could be rotated, as a stirrer, at a small controlled speed by gearing the pulley, fixed at its top-end to an electric motor. The blades were made of such a shape that the coal-oleum suspension was forced down slowly to the bottom and rose up again along the sides. This was essential because normally coal tends to float up in the acid for a fairly long time in the initial stages of sulphonation.

The lid, C, had an inlet, I. which could be closed, if so desired, with screw cap and lead washer.. The lid also had a thermometer pocket, P, which was made of such a length that its bottom end stayed nearly in the centre of sulphonation pot when the lid had been secured on to the pot. The temperature of the reaction could be measured by the thermometer, T, which was immersed in oil in the thermometer pocket, P.

The/

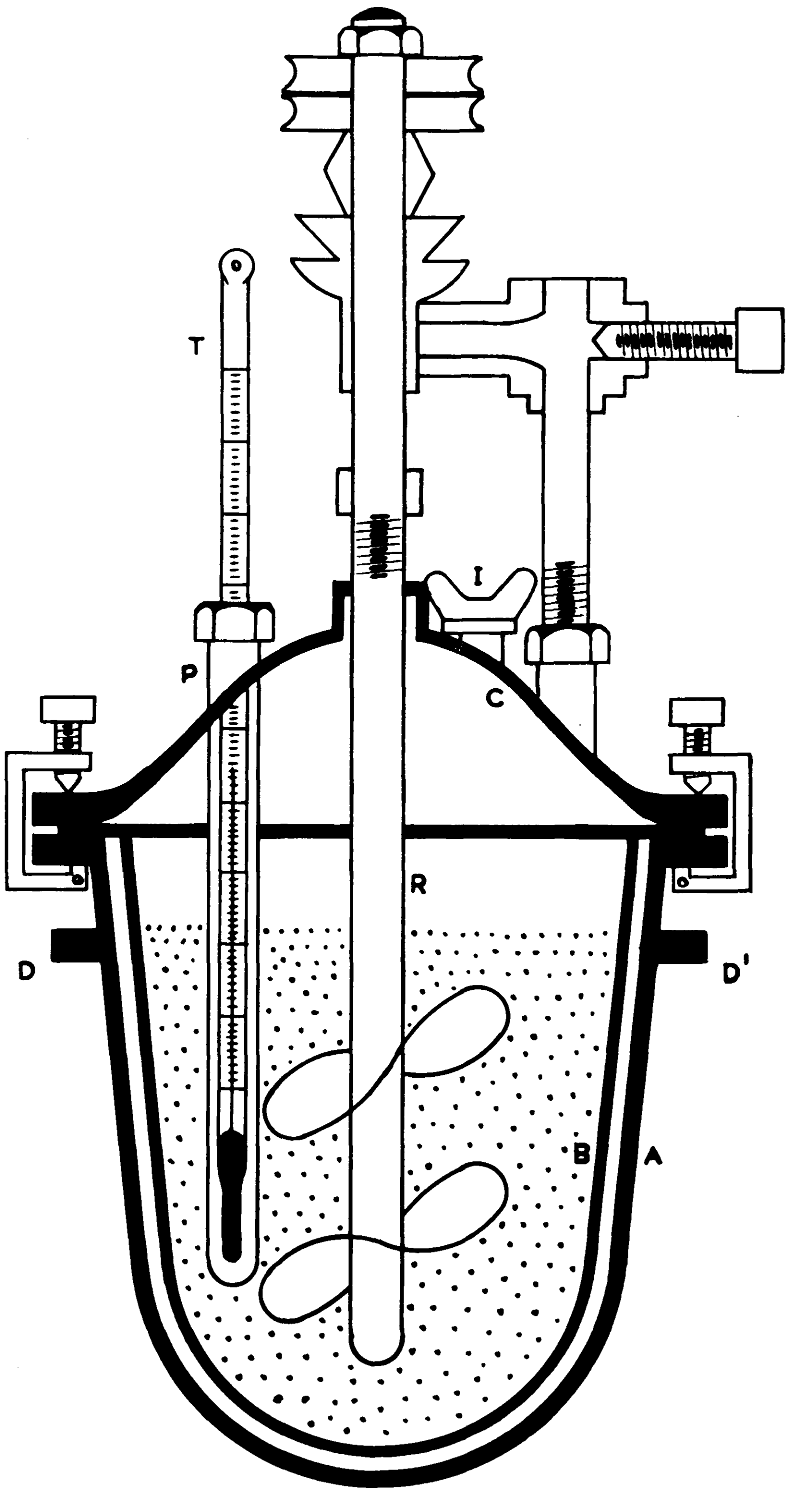


FIGURE 9.

SULPHONATION POT.

The whole sulphonation-pot, could be immersed in an oil bath by using the circular projection DD^1 for supporting the apparatus in the oil bath. The temperature of the oil bath could be controlled within ±3°C. Since stirring was done throughout the process, the whole of the material could be maintained at a uniform temperature.

70 grams of coal of size 25-40 B.S.S. were introduced into the clean and dry sulphonation pot. The lid was tightly screwed on to the top of the pot. The pot was then supported in an iron tripod in a fume-chamber. 750 ml. of the oleum of requisite strength were introduced, in small increments into the pot through the inlet, I, using a small glass funnel. The contents were gradually stirred by rotating the pulley with the hand (from outside). For the first few minutes - 10 to 15 minutes - there was an evolution of copious white fumes which became less later. This was probably due to the development of local heat when oleum came in contact with the coal particles and there was not enough liquid to conduct the heat away.

When all the acid had been added and the reaction had apparently subsided (this required about 20-25 minutes), the sulphonation pot was supported in the oil bath and an electric motor switched on to work the stirrer at the required/

required slow speed of about 30 revolutions per minute. The low speed was to avoid any breaking of the coal particles. The oil-bath was then heated and when the contents of the sulphonation pot had reached the reaction temperature, the time was noted and sulphonation carried on for the desired time. During this process nothing happened which desired any special attention. Fumes were always coming out of the mouth, I.

After the sulphonation had been carried on in the desired circumstances and time, the sulphonation-pot was taken out from the oil-bath and the contents allowed to cool in air. As a rule it was left overnight. In the morning, the lid was removed and the sulphonated material along with the excess of acid was transferred on to a piece of stainless-steel gauze, 15" square, and the excess acid allowed to drain into a porcelain trough.

After nearly all the acid had been drained the material on the gauze was suddenly immersed in a big trough containing cold tap-water. The coal particles were allowed to settle and the supernatent black wash was decanted off. In this way the contents were washed several times till the wash was absolutely clear. The treated coal was then transferred on to the clean gauze and allowed to drain/

drain after which the material was transferred to a clean tray, spread evenly and allowed to air-dry.

This was the general procedure which was followed in all the sulphonation experiments unless otherwise mentioned.

(III) Determination of Base-exchange capacity:-

Several methods for the determination of base-exchange capacity of ion-exchangers have been employed in Great Britain and America but most of these have been developed and used for commercial use of these materials. These methods of test comprise the determination of the operating exchange and not the total exchange capacity, because in practice it is not customary to operate ion-exchange softeners until they are completely exhausted. But, as is obvious, for the study of fundamentals of the process, an absolute exchange capacity is more desirable. Consequently Ensminger's method (76) was modified and adapted to suit the present determinations. The method followed is described below:-

Five grams of the treated coal were weighed into a 250 ml. beaker. 100 ml. tap water were added and the exchanger allowed to stand for an hour so that the material got to its normal swelling. It was then transferred/

transferred to a filter paper in a funnel with the help of a stream of 0·5N hydrochloric acid from a wash bottle, after the initial water had been decanted off. The material was then leached with excess of the regenerating acid viz. one litre of 0·5 normal hydrochloric acid. Excess of acid was used to ensure complete regeneration of the material to H-ion. The contents of the funnel were then washed with distilled water until the filtrate gave a negative test for Cl' ion. The coal sample was then transferred to 600 ml. beaker and 400 ml. of N/1 barium acetate solution, the pH of which had been brought to 5·0 by addition of requisite amount of acetic acid and which also contained 0·5% n-butyl alcohol, were added. Throughout this procedure barium acetate solution brought to a pH of 5 and containing 0·5% n-butyl alcohol was used as results of exchange capacity obtained at this pH are nearer to the results obtained by using neutral monovalent salts (76). The adsorption of barium ions, probably being divalent, is more than monovalent cations like sodium, ammonium (51,77). The addition of 0·5% n-butyl alcohol lowers the surface tension of the solution and brings about a more rapid equilibrium between exchanger and solution as a result of more rapid wetting.

The sample was left in contact with

this/

this barium acetate solution for about half an hour, at the end of which the supernatent liquid was decanted off and fresh 400 ml. of N/1 barium acetate were added. The contents were then left overnight. Next morning the supernatent liquid was decanted off and the coal sample was transferred to a filterpaper in a funnel. The filterpaper and the funnel had already been weighed. The contents of the filterpaper were then leached with about 600 ml. of N/1 barium acetate solution. When all the barrium acetate solution had been used up, the material was further leached with about 600 ml. of N/10 barium acetate solution. The leaching solution was always used in a small wash bottle and care was taken to wash all the sides of the funnel with N/10 barium acetate to ensure complete removal of N/1 barium acetate solution. When the last portion of N/10 solution drained through, the funnel was weighed with the sample and the filterpaper. The weight of the funnel, filterpaper, and the sample being washed with 0·1N solution minus the dry weight of the combination was equal to the millilitres of excess 0·1N barium acetate solution present in the filter paper, coal-sample and adhering to sides of the funnel.

The excess 0·1N barium acetate and

the adsorbed barium (i.e. Ba in the coal as a result of exchange of H ion with Ba) were leached out with about 800 ml. of 0·5N hydrochloric acid. The leached barium solution was made up to one litre. An aliquot amount was then pipetted out and the barium precipitated as barium sulphate. The precipitate was left overnight, filtered, ignited and weighed in the standard way. From this total barium present in one litre could be calculated. The total barium thus determined minus the quantity present as 0·1N barium acetate solution gave the maximum exchange capacity of the sample which was expressed in milli-equivalents per 100 gram.

Preliminary experiments done in duplicate revealed that the results were quite reproducible within ±2% of the original value.

IV. Study of the Physical and Chemical factors in sulphonation of coal.

General facts known about "sulphonation" indicate that the properties of the products resulting from sulphonation of coal may depend upon a number of factors. These factors may not only affect the degree of sulphonation but also the course of the reaction. Some of the more important of these factors were studied in the following order:-

(i) Temperature of the reaction.
(ii) Time of the reaction.
(iii) Concentration of the sulphonating agent.
(iv) Nature of the sulphonating agent.

(i) Study of the Effect of Temperature:-

During the course of the study of the effect of temperature on the reaction, and hence on the base-exchange capacity of the resulting product, the same procedure as described on page 131 was followed, keeping the concentration of the sulphonating agent, oleum in this case, and the time of reaction constant. Oleum (20% sulphur trioxide) was used and the reaction was carried on for four hours. A total of/

of seven experiments were performed at temperatures of 60, 75, 90, 100, 110, 120 and 150°C. The product was isolated, in each case, in the same manner as described in the standard sulphonation procedure on page 131 and the base-exchange capacity of the resulting products were determined by the standard method described.

The results have been tabulated in the Table XIV on page 139 and are plotted in figure 10 on page 140

(ii) Study of the effect of time:-

In these experiments concentration of the sulphonating agent and the temperature were kept constant. Oleum (20% sulphur trioxide) was used and sulphonation was carried at 120 degrees centigrade (found best from the study of effect of temperature on page 137). The time of the reaction was varied as 1, 2, 3 and 4 hours. Sulphonation of coal and the determination of the base exchange capacities of the resulting products were carried in the standard way as described on pages 131 and 133 respectively.

The results obtained have been presented in Table XV on page 141 and figure 11 on page 142.

(iii) Study of the effect of concentration of the sulphonating agent:-

From the previous experiments it was found that the effect of temperature and time could be nearly eliminated/

TABLE XIV

Effect of Temperature on Sulphonation of Coal.

Coal taken = 70 gms.
Oleum (20% SO_3) used = 700 ml.

Time of Reaction = 4 hours.
25 ml. of approximately 0·1N barium acetate ≡ 0·2461 gms of Ba SO_4

Temperature of Reaction.	Total Ba SO_4 precipitated from 5 grams of sample.	Excess Barium Acetate in filter paper and S-coal sample etc.	≡ Ba SO_4	True adsorbed Barium as Ba SO_4/ 5 gms. of sample.	Adsorbed Barium /100 gms. of sample.	Base-exchange capacity m.e./100 grams of sample.
°C	grams	grams	grams	grams	grams	
60	0·3068	6·673	0·0657	0·2411	2·84	41·3
75	0·4326	5·944	0·0585	0·3741	4·40	64·1
90	0·6348	6·206	0·0611	0·5737	6·75	98·3
100	0·8280	5·975	0·0589	0·7691	9·06	131·8
110	0·9170	6·827	0·0672	0·8498	10·00	145·6
120	0·9455	6·958	0·0685	0·8770	10·32	150·3
150	0·9635	6·522	0·0642	0·8993	10·59	154·1

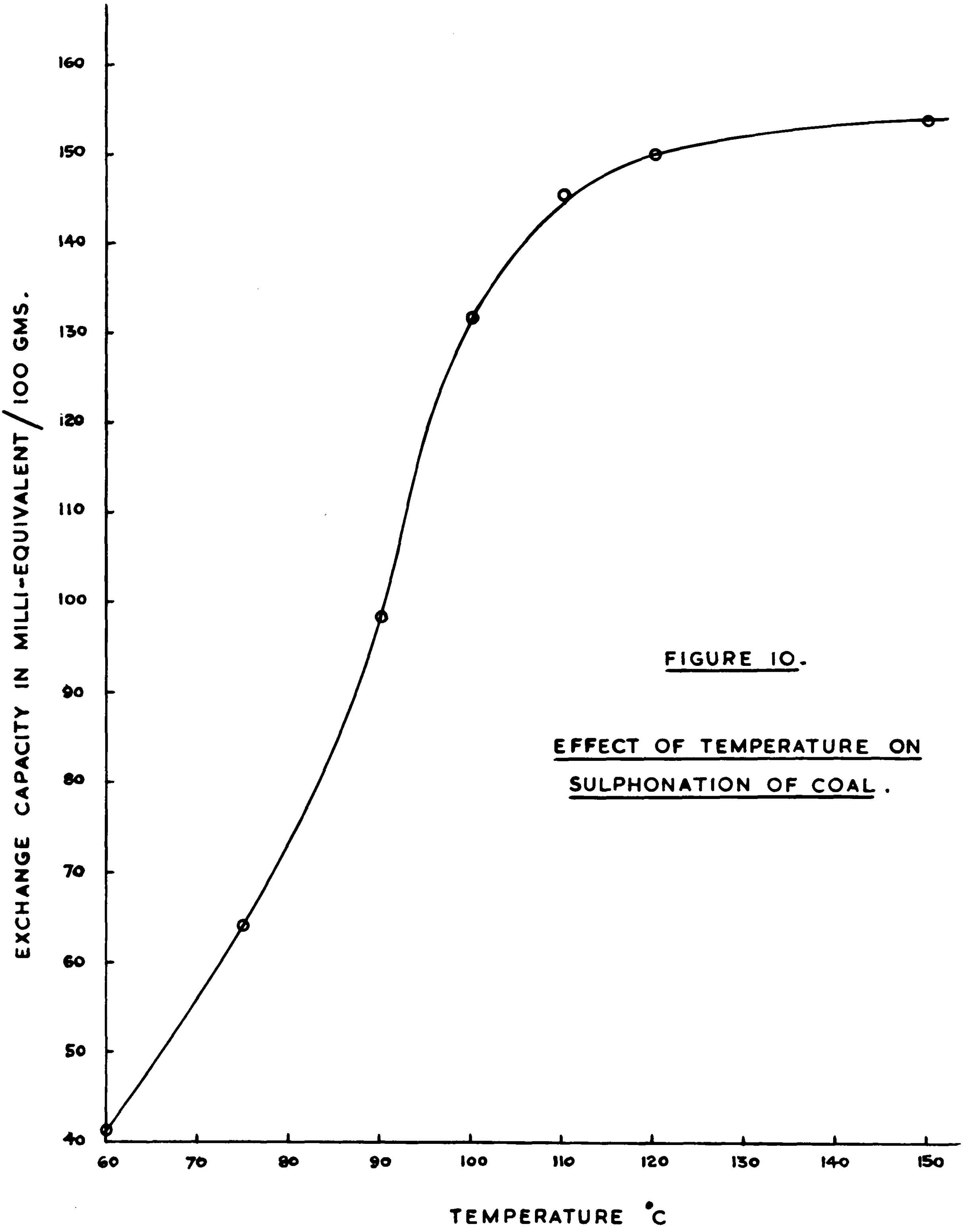


FIGURE 10.

EFFECT OF TEMPERATURE ON SULPHONATION OF COAL.

TABLE XV

Effect of Time on Sulphonation of Coal.

Coal taken = 70 gms.
Oleum (20% SO_3) used = 700 ml.

Temperature of reaction = 120 degrees centigra
25 ml.of approximately 0·1N barium acetate ≡ 0·2461 gms. of Ba SO_4

Time of Reaction	Total Ba SO_4 precipitated from 5 grams of sample.	Weight of excess Barium Acetate (Approximately 0·1N) in filter paper and S-coal sample etc. ≡	Ba SO_4	True adsorbed Barium as Ba SO_4/5 gms. of sample.	Adsorbed Barium/ 100 grams of sample.	Base-Exchange capacity m.e./100gms. of sample.
Hours	grams	grams	grams	grams	grams	
1	0·5364	6·286	0·0619	0·4745	5·59	81·3
2	0·8020	6·359	0·0626	0·7394	8·70	126·7
3	0·9085	6·623	0·0652	0·8433	9·93	144·5
4	0·9455	6·958	0·0685	0·8770	10·32	150·3

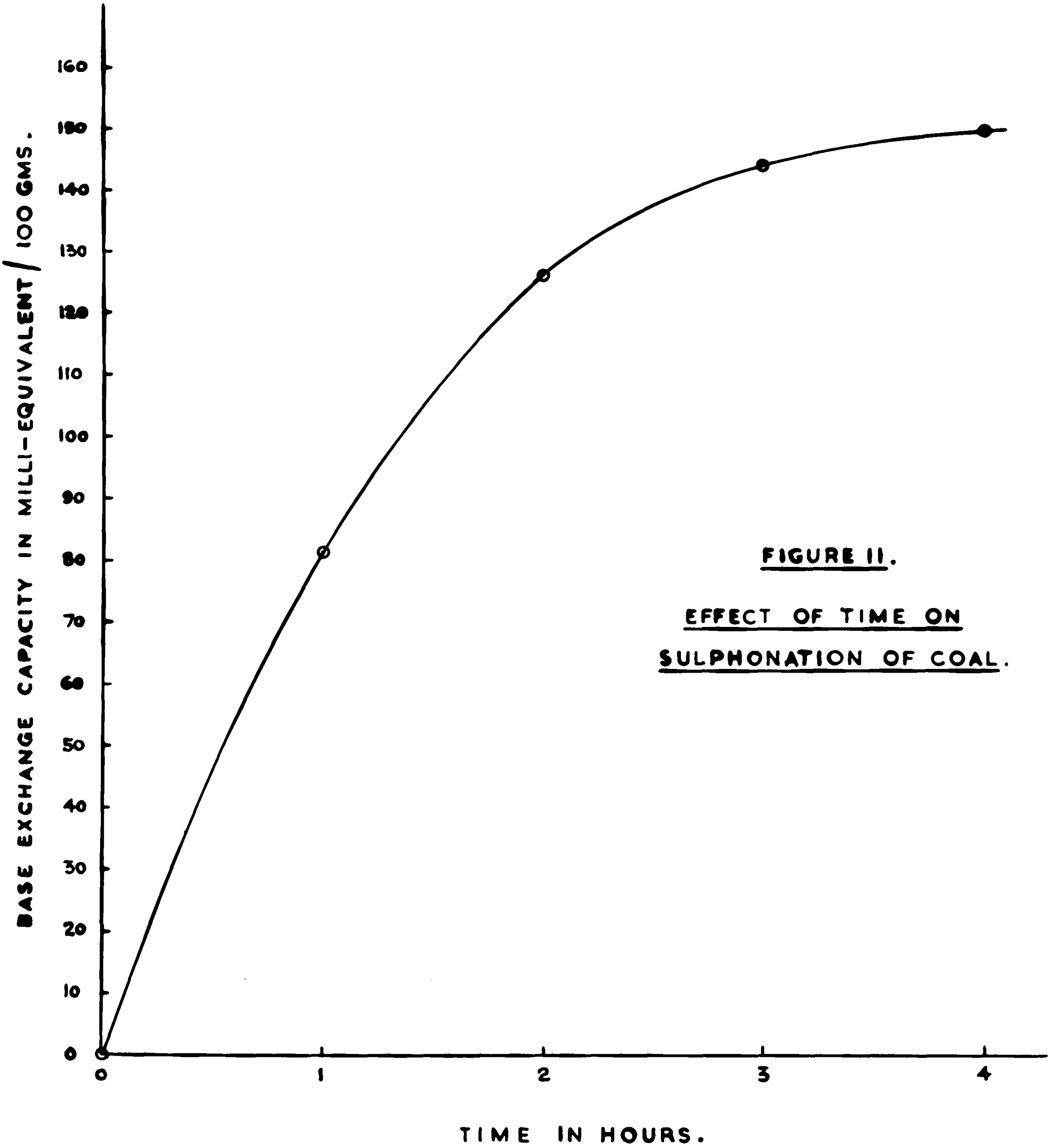


FIGURE II.

EFFECT OF TIME ON SULPHONATION OF COAL.

eliminated provided the reaction was carried for 3-4 hours at a temperature of about 120°C. Keeping these constant six experiments were performed using oleum containing 0·0, 4, 8, 12, 16 and 20% sulphur trioxide. The sulphonation and the determination of base-exchange capacities of resulting products were carried as described on pages 131 and 133 respectively.

The results obtained have been presented in Table XVI on page 144 and figure 12 on page 145

(iv) <u>Study of the effect of the nature of the sulphonating agent</u>:-

It is well recognized in the manufacture of ion-exchangers from coal that coal is probably sulphonated as well as oxidized. This is because concentrated sulphuric acid and sulphur trioxide excercise an oxidizing action also and this characteristic is accentuated at higher temperatures. Since the introduction of carboxyl groups, in coal, by oxidation is known to contribute to the exchange phenomenon,(44) it was thought desirable to use a sulphonating agent which would simultaneously oxidize and sulphonate coal. Whereas number of such processes(78,79), with better results, have already been patented, never before use has been made of approximately 100% nitric acid and oleum mixture. Nitric acid of this strength/

TABLE XVI

Effect of concentration of oleum on sulphonation of coal.

Coal taken = 70 gms.
Temperature of Reaction = 120°C
Time of Reaction = 4 hours.
ml. of oleum used = 700 ml.
25 ml. of approximately 0·1N barium acetate ≡ 0·2461 gms. of Ba SO_4

Percentage of SO_3 in oleum.	Total Ba SO_4 precipitated from 5 grams of sample.	Weight of excess Barium Acetate (approximately 0·1N) in filter paper and S-coal sample etc.	≡ Ba SO_4	True adsorbed Barium as Ba SO_4/5 gms. of sample.	Adsorbed Barium/ 100 grams of sample	Base-Exchange capacity m.e./100 grams of sample.
	grams	grams	grams	grams	grams	
0	0·4418	6·226	0·0613	0·3805	4·48	65·2
4	0·5356	6·746	0·0664	0·4692	5·53	80·4
8	0·5764	6·329	0·0623	0·5141	6·05	88·1
12	0·7635	6·533	0·0643	0·6992	8·23	119·8
16	0·8935	6·837	0·0673	0·8262	9·73	141·6
20	0·9455	6·958	0·0685	0·8770	10·32	150·3

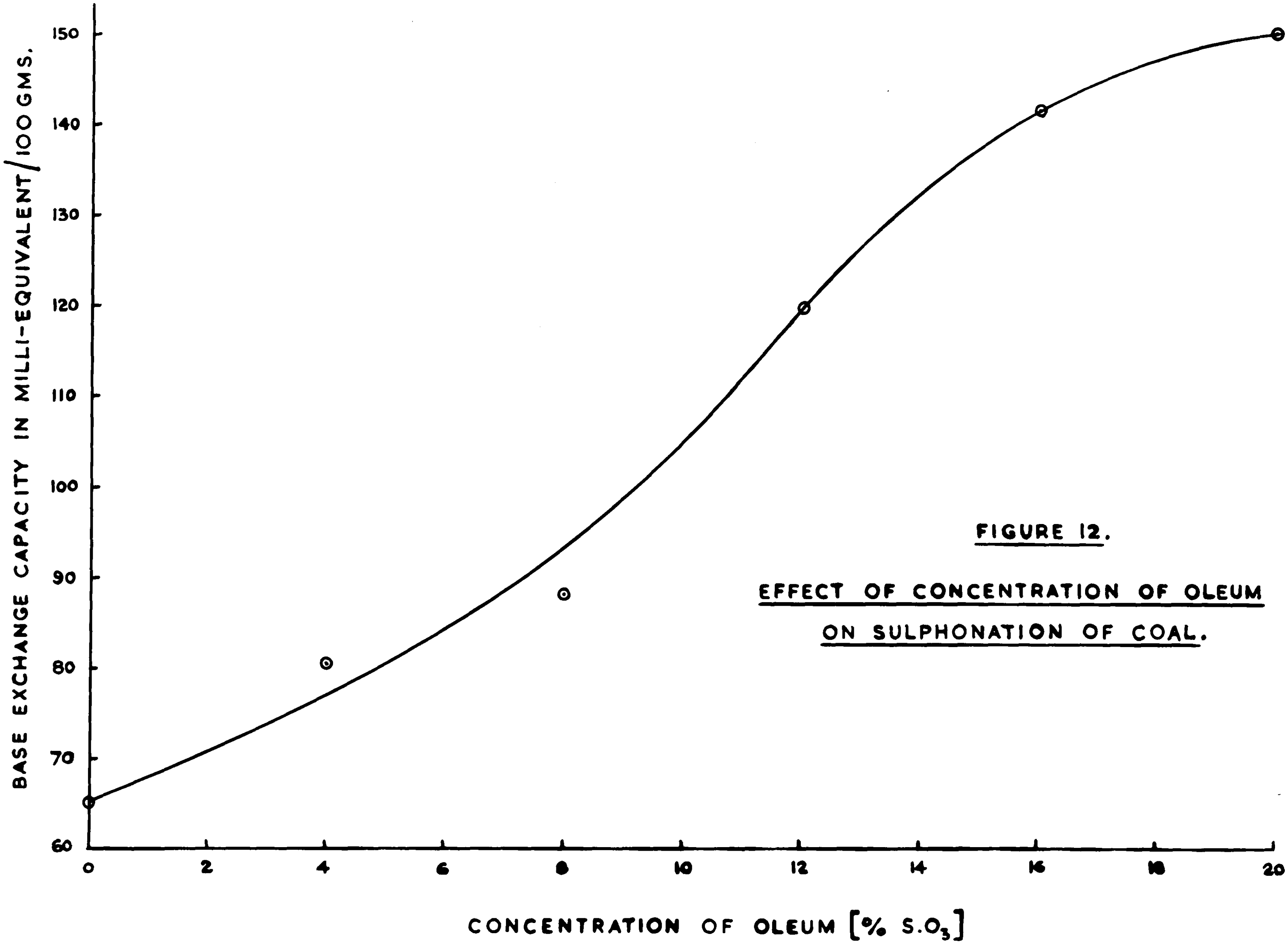


FIGURE 12.

EFFECT OF CONCENTRATION OF OLEUM ON SULPHONATION OF COAL.

strength had been specially obtained for study detailed in part I of this thesis and so it was thought desirable to study the effect of mixture of nitric acid and oleum which is given in the following lines:-

Study of the effect of nitric acid (approximately 100%) on sulphonation of coal with oleum:-

In this study oleum (20% sulphur trioxide) and approximately 100% nitric acid were employed throughout.

Preperation of the sulphonating agent:-

A mixture of oleum and nitric acid was used as the sulphonating agent. The requisite quantity of nitric acid was taken in a cylinder and the appropriate quantity of oleum was added to it in small increments with constant stirring. It was essential to add oleum to nitric acid to ensure a speedy mixing as the latter was much lighter then the former.

The mixing was rather an exothermic process, probably due to presence of any small traces of moisture in nitric acid, and so the mixture had to be allowed to cool (for about 15-20 minutes) in air before it could be used in the reaction.

Procedure/

Procedure:-

The same procedure as described before was followed. The violence of the reaction, in this case, however was far greater and for several minutes evolution of copious brown and white fumes was noticed. The acid mixture had to be added in smaller increments and it took about 25-40 minutes for the contents of reaction to be brought to a stage, when sufficient acid had been added, to give a kind of suspension. The reaction was much calmer afterwards and outwardly followed similar lines as with oleum.

Mixtures containing zero to 12% nitric acid in the nitric acid-oleum mixture (by volume) were tried. It was not possible to try more than this as the initial stages of the reaction with 13% nitric acid were so violent and exothermic that the contents were thrown out and there was a flash of light. Moreover, as will be seen later on in the discussion of this part on pages 199 – 201 , it was not desirable to use such a high percentage of nitric acid in the sulphonating agent.

The results of these twelve experiments have been presented in Table XVII and figures 13 and 14 on pages 148, 149 and 150 respectively.

TABLE XVII

Effect of oleum - nitric acid mixture on sulphonation of coal.

Coal taken = 70 grams. Time of Reaction = 4 hours.
Temperature of Reaction = 120°C Amount of sulphonating mixture used = 700 ml.
25 ml. of approximately 0·1N barium acetate ≡ 0·2531 gms. of $BaSO_4$

Percentage of approximately 100% nitric acid in oleum (20% SO_3) - nitric acid mixture.	Total $BaSO_4$ precipitated from 5 grams of sample.	Excess Barium Acetate in filter paper and S-coal sample etc.	≡ $BaSO_4$	True adsorbed Barium as $BaSO_4$/ 5 gms. of sample.	Adsorbed Barium/ 100 grams of sample	Base-Exchange capacity m.e./ 100 grams of sample.	Percentag increase in the B.E. capacity using value of 0·0% nitric acid as standard
%	grams	grams	grams	grams	grams		%
0	0·9455	6·958	0·0685	0·8770	10·32	150·3*	-
1	0·9855	6·616	0·0670	0·9185	10·81	157·3	4·7
3	1·0495	6·150	0·0623	0·9872	11·62	169·1	12·5
5	1·2160	6·632	0·0671	1·1489	13·53	196·9	31·0
7	1·3015	6·074	0·0615	1·2400	14·60	212·4	41·3
9	1·2360	6·716	0·0680	1·1680	13·75	200·2	33·2
10	1·2660	6·786	0·0687	1·1973	14·09	205·1	36·4
11	1·1920	5·920	0·0599	1·1321	13·32	194·0	29·1
12	1·2315	6·934	0·0702	1·1613	13·68	199·0	32·4

* This figure and the corresponding figures for the $BaSO_4$ precipitate etc. are reproduced from the previous table viz. from Table XVI.

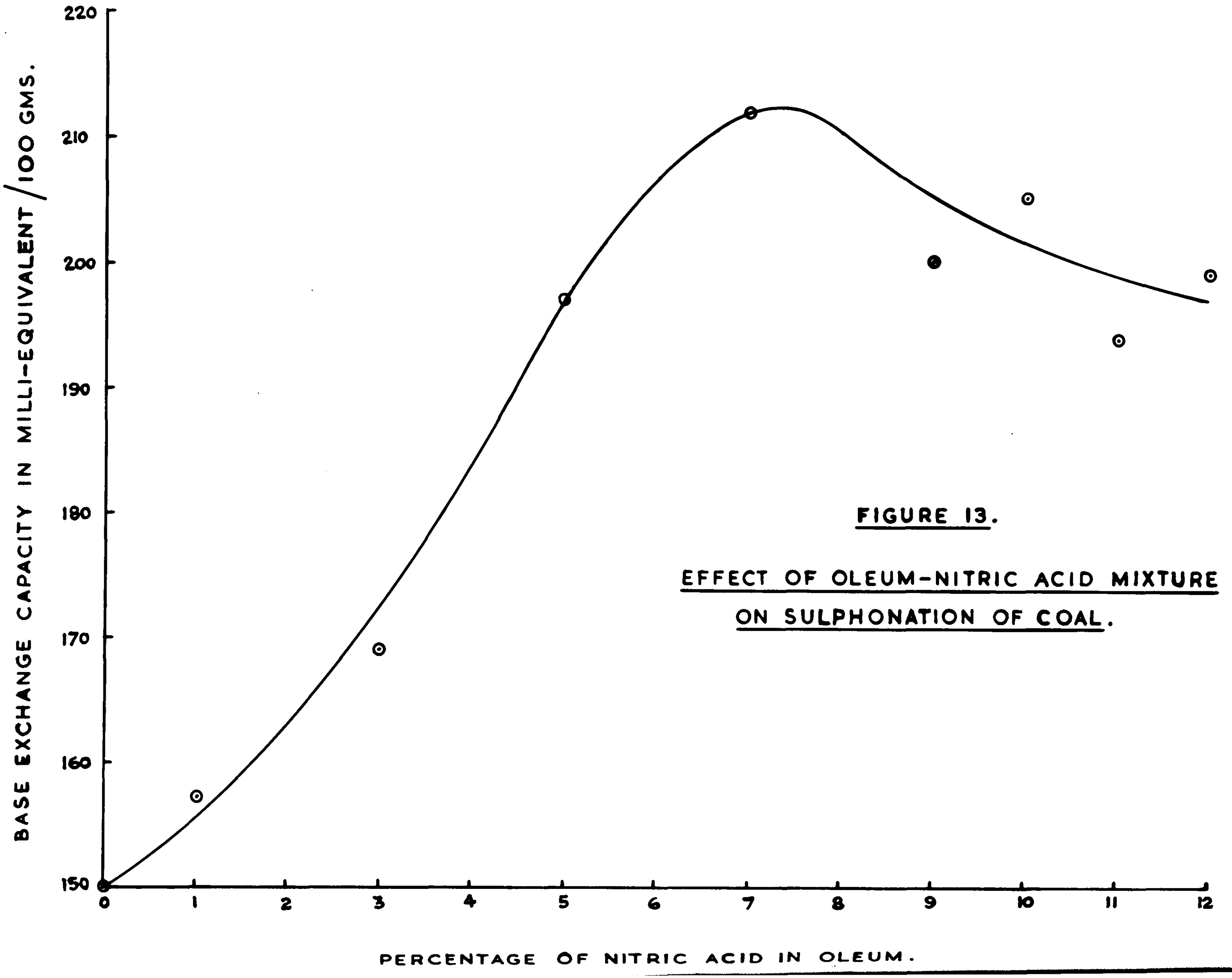


FIGURE 13.

EFFECT OF OLEUM-NITRIC ACID MIXTURE ON SULPHONATION OF COAL.

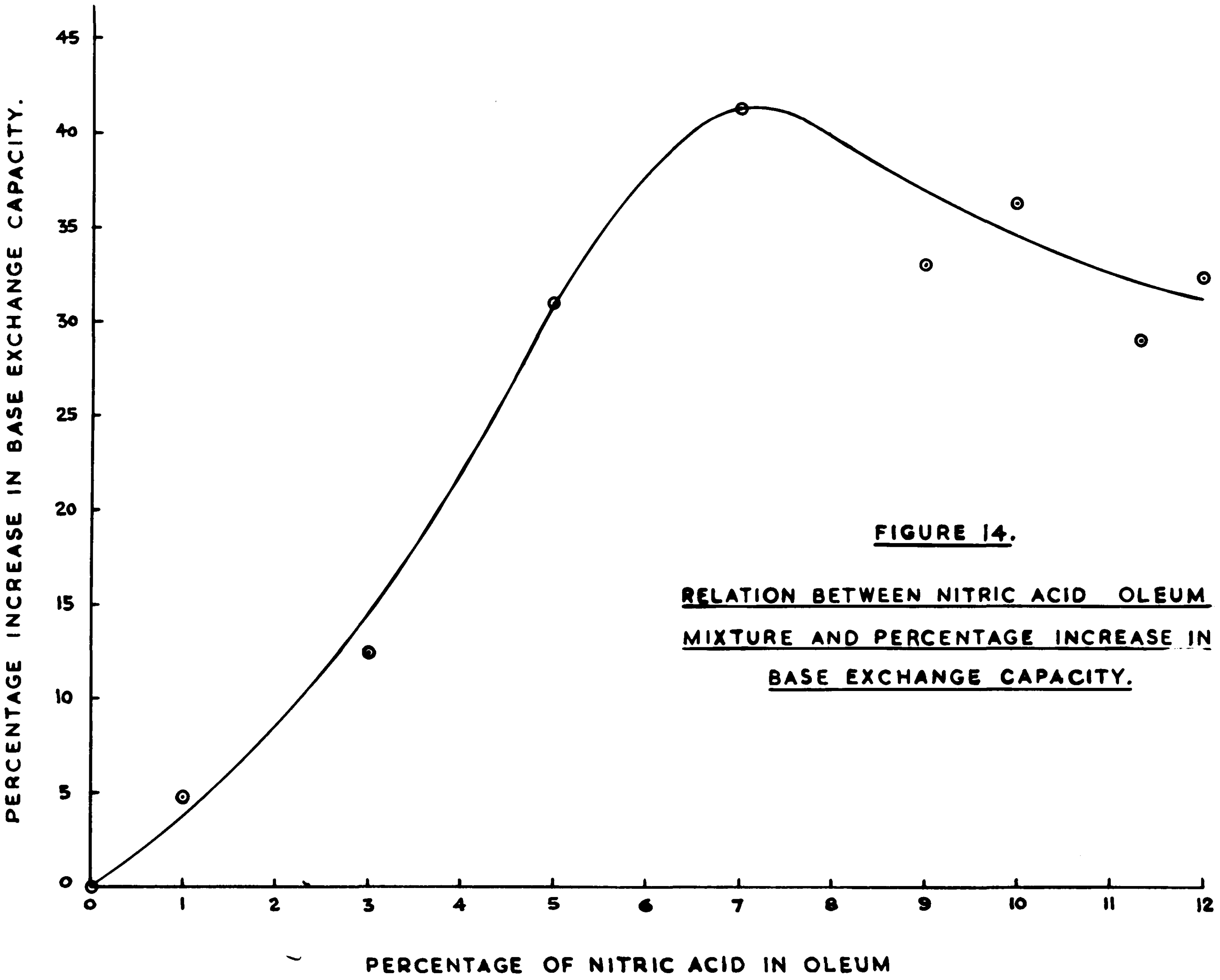


FIGURE 14.

RELATION BETWEEN NITRIC ACID OLEUM MIXTURE AND PERCENTAGE INCREASE IN BASE EXCHANGE CAPACITY.

V. Study of Titration curves of sulphonated coals.

It is known fact that sulphuric acid treated coals exhibit base-exchange properties due to possible introduction of sulphonic acid groups into their structure. It is also known that oxidation along with sulphonation gives material of higher base-exchange capacity(78,79) - possibly due to introduction of carboxyl along with sulphonic acid groups. Thus, in view of the fact that the base-exchange phenomenen may be due to these acid groups in the sulphonated coal and Griessbach's work on the study of titration curves of synthetic H-ion exchangers (loc.cit.), it was thought that the study of the neutralization of these insoluble acidoids may furnish interesting and useful results. The problem was thus studied in the manner mentioned in the following pages.

(i) Preparation of the exchanger for titration.

All the samples to be studied were soaked in distilled water for about two hours. This was done to allow the material to swell up to its maximum capacity which probably is the ideal condition for the base exchange. The samples were then transferred to respective funnels and leached with the requisite quantity of the regenerating liquid - 0·5N HCl in this case. When the material in each funnel had been regenerated/

regenerated it was washed with distilled water till the filtrate gave negative test for chloride ion as tested by silver nitrate. The samples were then air dried and used in all subsequent experiments.

(ii) Time required for equilibrium between acidoid and alkali.

One gram portions of one of the sulphonated coals, prepared in the manner stated above, were taken in seven glass bottles (of capacity about 100 ml.). Ten millilitres of water were added to each of these bottles and material allowed to swell for about two hours. Increasing amounts of 0·1N sodium hydroxide solution were then added into the various samples and the total volume of the solution, in each case, was made to 50 ml. with distilled water. All the mixtures were shaken, after putting in the respective corks, for a few minutes. The pH value of each mixture was determined by the glass electrode almost immediately and after varying intervals of time. The results obtained have been shown in Table 18 and plotted in figure 15 on pages 153 and 154 respectively.

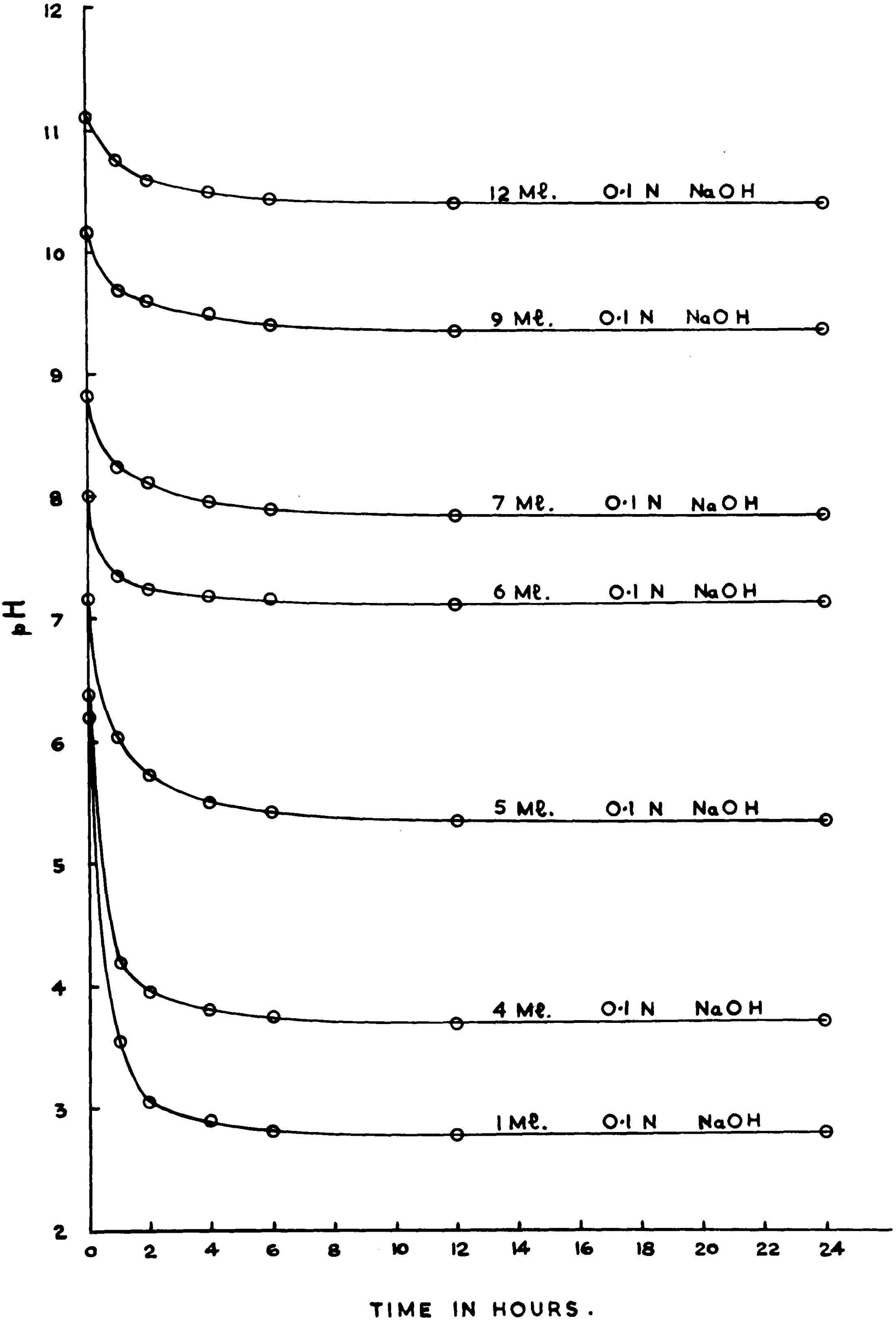
TABLE XVIII

Time required for equilibrium between sulphonated coal and alkali.

Ml. of 0·1N alkali added	pH after time in hours						
	0	1	2	4	6	12	24
1	6·21	3·54	3·04	2·90	2·81	2·78	2·78
4	6·36	4·18	3·94	3·82	3·75	3·70	3·70
5	7·16	6·02	5·72	5·50	5·42	5·35	5·35
6	8·00	7·34	7·24	7·20	7·16	7·13	7·13
7	8·82	8·24	8·14	7·96	7·90	7·85	7·85
9	10·16	9·68	9·59	9·49	9·42	9·38	9·38
12	11·10	10·75	10·60	10·50	10·46	10·41	10·41

FIGURE 15.

TIME REQUIRED FOR EQUILIBRIUM BETWEEN SULPHONATED COAL AND ALKALI.



(iii) Titration of sulphonated coal.

The general procedure followed for the titration was to take one gram portions of the sample, prepared as explained previously, in different and arranged bottles. 10 ml. of distilled water were added in each of the bottles and the sulphonated coal was allowed to swell for about two hours. Then increasing amounts of standard alkali were added in the different numbered bottles. Water was then added in each of these to make the volume to 50 ml. This was done to avoid any deviation in pH value which may be caused by difference in volume in each case. After corking, the bottles were well shaken for several minutes and then were left overnight to ensure the attainment of equilibrium between the sulphonated coal and the alkali (refer prvious experiment page 152) The pH value of the suspension, in each bottle, was then determined by the glass electrode.

Results of titration of two typical sulphonated coals, obtained in the manner stated above, are given in Table XIX and in figures 16 on pages 156 and 157 respectively.

(iv) Titration of known sulphonic acids.

In order to interpret the pH-neutralization curves of two sulphonated coals obtained in the previous experiment/

TABLE XIX

Titration of Sulphonated Coals.

Amount of sample taken in each case = 1 gm.

Normality of alkali used = 0·1N NaOH

Ml.of N/10 NaOH added	S-Coal NoI pH	S-Coal No.II pH
0	2·52	2·44
1	2·75	2·70
2	3·22	2·85
3	3·51	3·10
4	3·62	3·61
5	5·3	-
6	7·12	5·42
7	7·82	6·22
8	8·71	7·44
9	9·38	8·02
10	9·81	9·25
12	10·41	10·15
14	11·20	10·72
16	11·38	11·20
20	11·58	11·42

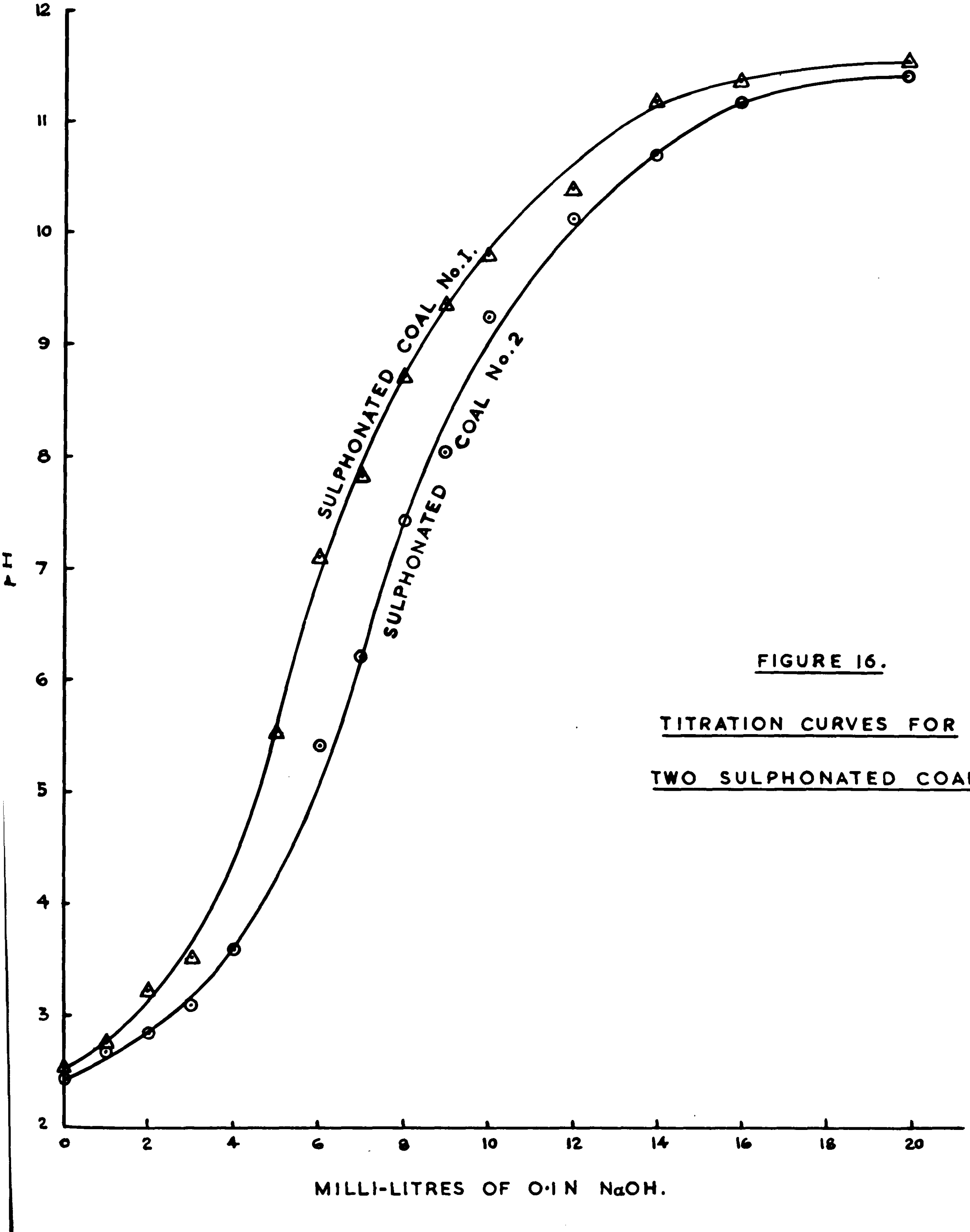
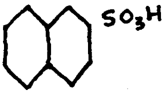
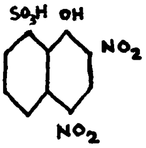
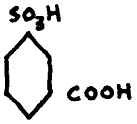
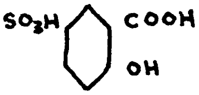


FIGURE 16.

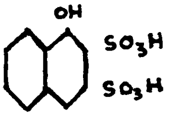
TITRATION CURVES FOR TWO SULPHONATED COALS.

experiment, it was thought desirable to study the titration curves of sulphonic acids of known constitution, i.e. containing $-SO_3H$, COOH and -OH (phenolic) groups orientated in various positions. Since the sulphonated coals may have one, some or all of these groups, comparison of its titration curves with those of some of the known sulphonic acids might lead to some useful information. Following acids were selected as they provided a variety of orientation of different groups:-

No.	Acid	Description of the groups present.	
1.	Naphthalene sulphonic acid		One $- SO_3H$
2.	Flavianic Acid (2:4 dinitro-1-naphthol 7-sulphonic acid)		One $- SO_3H$ and one $-$ OH (Phenolic)
3.	m-sulpho benzoic acid		One $- SO_3H$ and One $-$ COOH
4.	Salicyl-sulphonic acid		One $- SO_3H$, One $-$ COOH and One $-$ OH (Phenolic)

5/

5. Naphthol-Disulphonic acid



Two – SO_3H and One – OH

Titration curves for the above acids were obtained in the manner given below:-

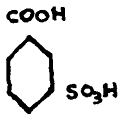
It was not essential to take an exact quantity of the known acid as it was the shape of titration curve rather than the quantitative estimation of the acid which was required. A known and roughly weighed quantity of the pure acid was introduced in 100 ml. beaker. 50 ml. of distilled water were added and the contents were stirred with a small glass stirrer to dissolve the acid. The pH of the acid solution was determined by means of a glass-electrode pH meter. Standard alkali was run from a microburette in small increments, the solution thoroughly stirred, and the pH value was again determined. In this way pH was determined after successive additions of alkali care being taken to add alkali in smaller increments near the point of inflection which was indicated by sudden rises in pH for addition of small amount of alkali.

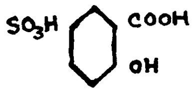
The results have been presented in Table XX and in figures 17 and 18 & 18A on pages 160 - 164.

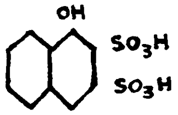
TABLE XX (CONTD).

Titration of known acids.

Alkali used = 0·1N Sodium Hydroxide.

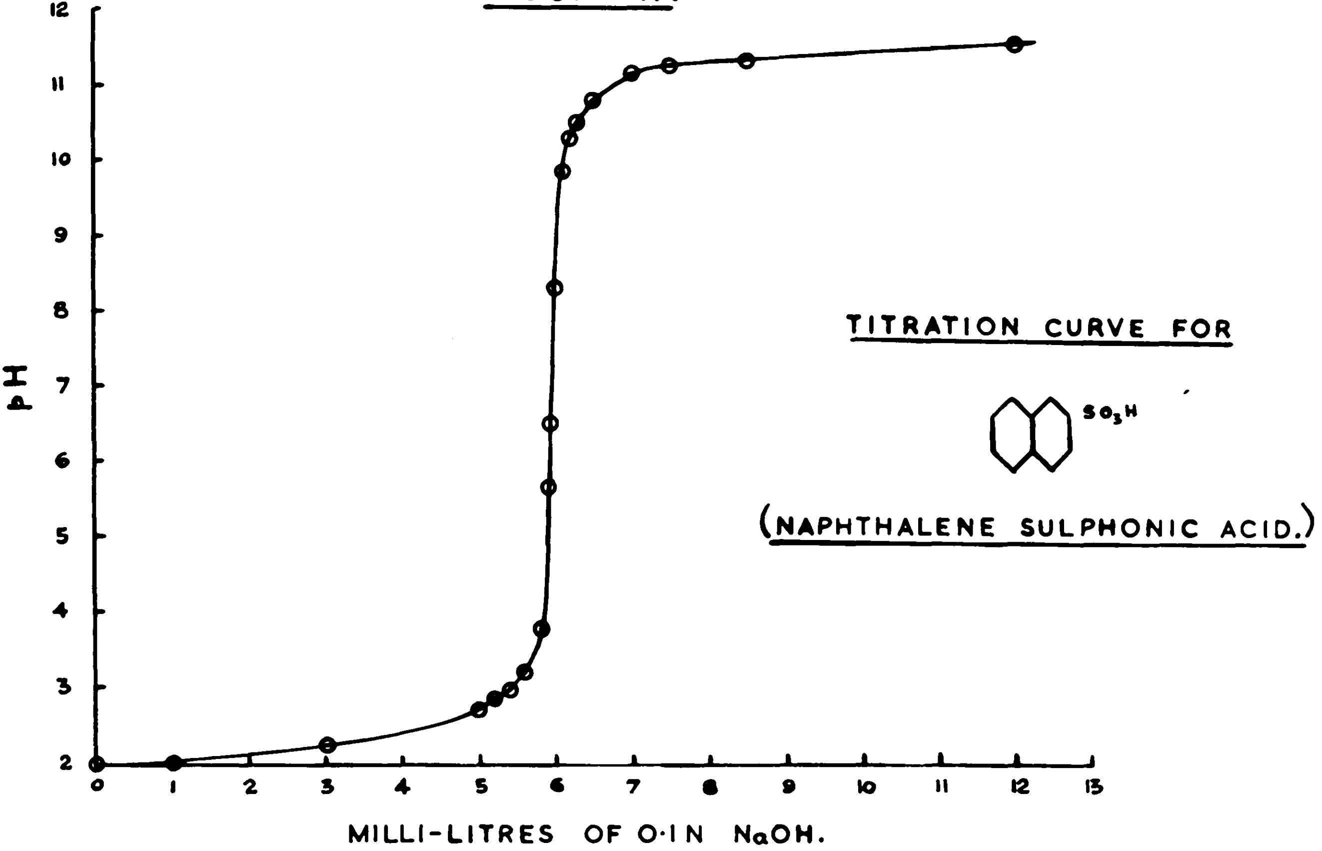




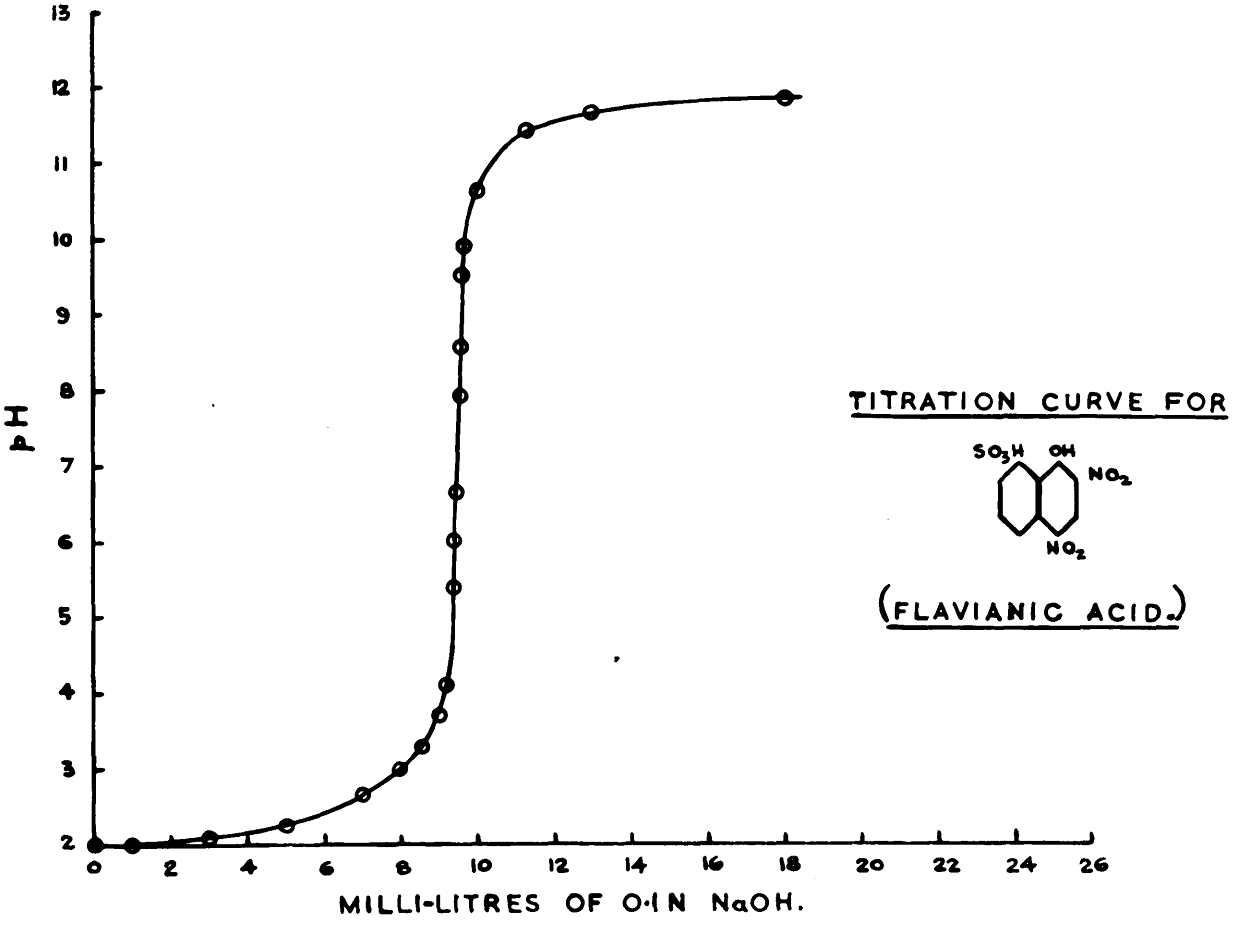


Ml.alkali added	pH	Ml.of alkali added	pH	Ml of alkali added	pH
0·00	2·20	0·00	2·20	0·0	2·68
1·00	2·34	1·00	2·34	1·0	3·45
2·00	2·58	3·00	2·62	1·1	3·86
3·00	3·06	4·00	2·90	1·2	5·65
3·60	3·46	4·50	3·10	1·3	8·48
4·00	3·68	5·00	3·38	1·4	8·98
4·40	3·87	5·40	3·70	1·5	9·25
4·80	4·08	5·60	4·05	1·6	9·42
5·40	4·54	5·80	5·38	1·8	9·79
5·80	5·04	5·90	8·74	2·0	10·11
6·00	6·01	6·00	9·86	3·0	11·38
6·10	7·90	6·20	10·54	4·0	11·85
6·20	9·64	6·4	10·84		
6·40	10·56	6·6	11·00		
6·70	10·96	7·0	11·22		
8·00	11·46	8·0	11·44		
10·00	11·60	10·0	11·60		
13·00	11·68				

FIGURE 17.

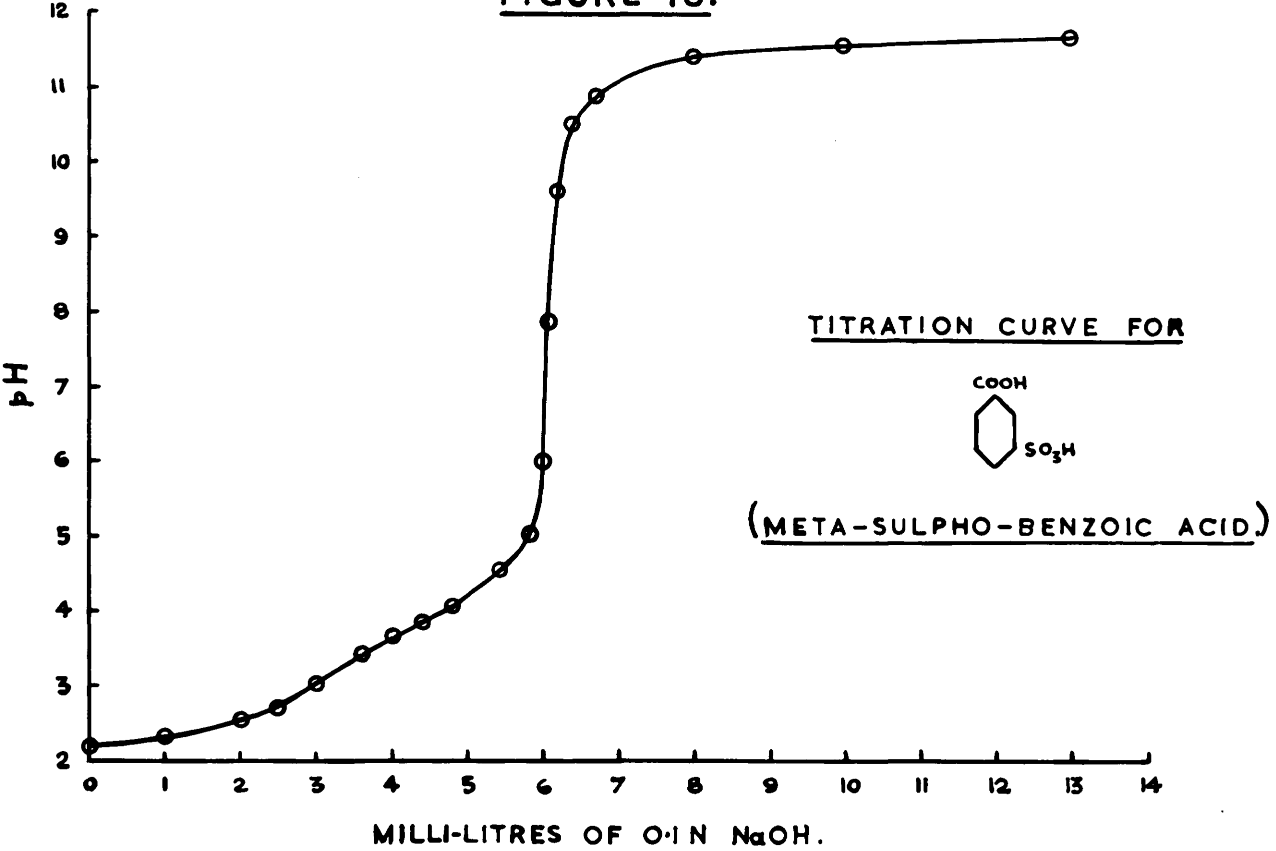

TITRATION CURVE FOR

(NAPHTHALENE SULPHONIC ACID.)


TITRATION CURVE FOR

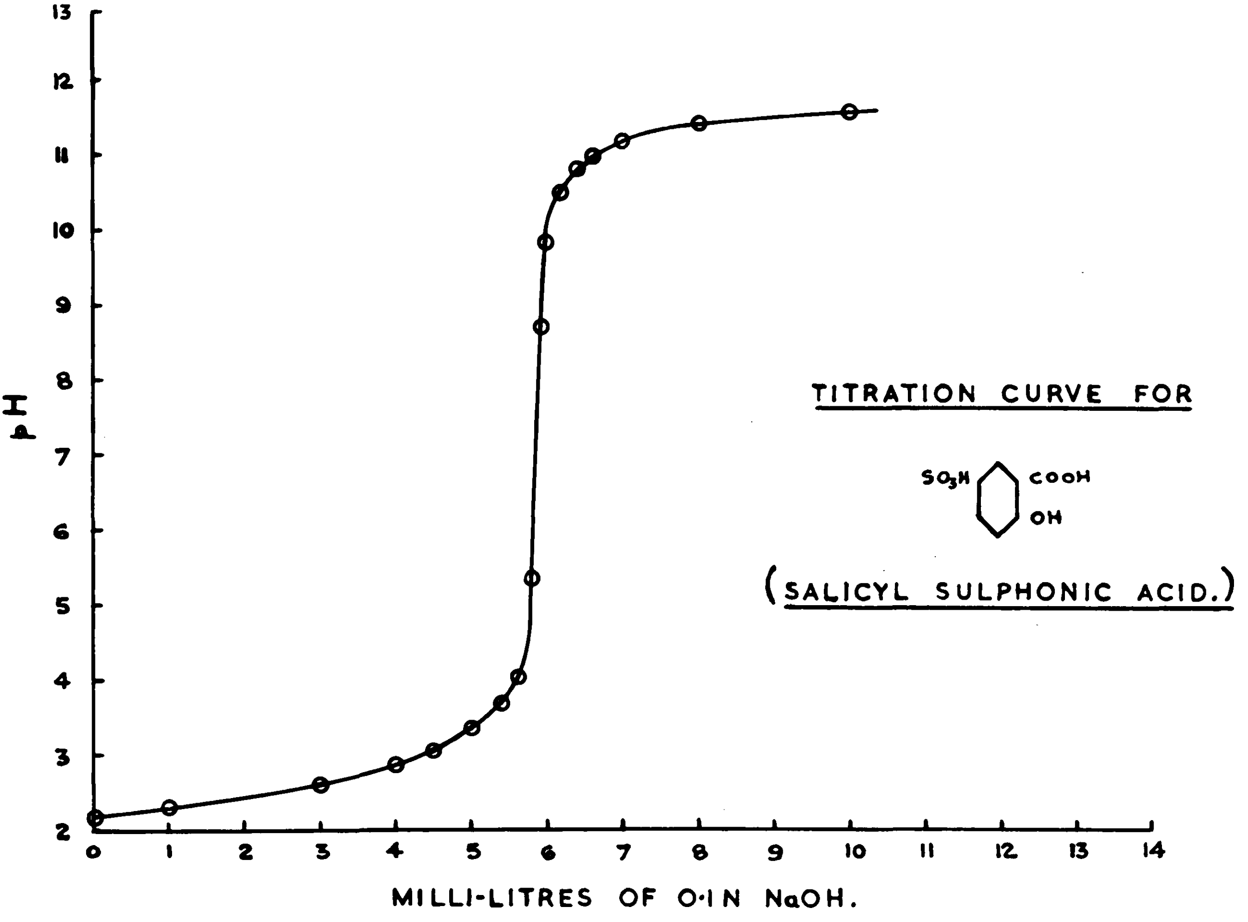
(FLAVIANIC ACID.)

FIGURE 18.



TITRATION CURVE FOR

(META-SULPHO-BENZOIC ACID.)



TITRATION CURVE FOR

(SALICYL SULPHONIC ACID.)

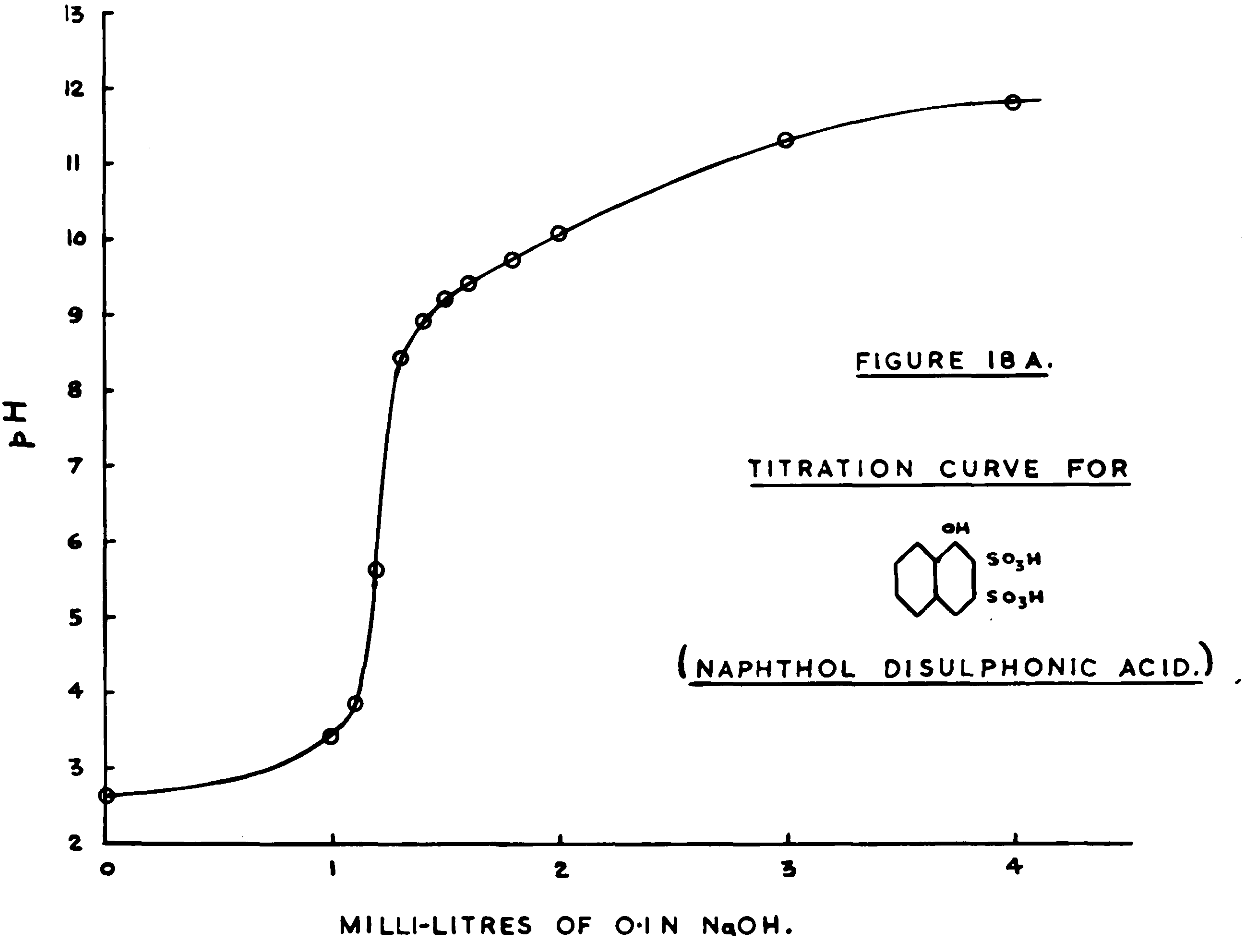


FIGURE 18 A.

TITRATION CURVE FOR

(NAPHTHOL DISULPHONIC ACID.)

(v) Study of the effect of the ionic strength of the solution on the pH - neutralization curves of Zeo-Karb H.I.

From the previous experiments it was obvious that although the pH neutralization curves of sulphonated coals in aqueous solution showed some similarity to the pH-neutralization curves of sulphonic acids, it did not provide any scope for characterizing the material by definite constants. It was thought desirable, therefore, to study the pH neutralisation curves of Zeo-Karb H.I. in presence of salt solution on somewhat similar lines to that of Griessbach (loc.cit.) and also to study variations in the pH neutralization curves as the ionic strength of the solution is changed, since like the base-binding capacity of wool (69), base-binding capacity of hydrogen-ion-exchanger should also be a function of this variable.

Material:-

It was essential in this study to use a rather large quantity of hydrogen ion-exchanger of a constant exchange capacity. Therefore, Zeo-Karb H.I., made by The Permutit Company Ltd., was used throughout in this investigation. The material had the exchange capacity of one milliequivalent per gram of air-dried material. Zeo-Karb H.I. was regenerated and dried in the manner described on page 151 and it was this fully regenerated material which was used in all the experiments which follow.

Procedure:-

Twelve 5 gram portions of the air dried Zeo- Karb H.I. (hitherto referred as H-ion-exchanger), prepared in the manner described above, were taken in twelve numbered bottles. 20 ml. of distilled water were introduced into each bottle to allow the material to swell. The requisite quantity of sodium chloride solution was added to all the bottles so that when the volume of the solution in each case was made to 50 ml. the desired ionic strength of the solution was obtained. Increasing quantities of the standard N/1 sodium hydroxide were then added in bottle No.2 to bottle No.12. The bottle No.1 was left as a blank. Distilled water was then added to all the bottles to bring the final volume in each case to 50 ml. The contents of each bottle, after corking, were thoroughly shaken and allowed to stand overnight. Next morning when the equilibrium had been obtained, the pH value of the suspension, in each bottle, was determined by the glass electrode.

Following this procedure six experiments were performed using zero, ·01N, ·05N, ·1N, ·5N and 1N sodium chloride concentration of the solution.

Results.

Results of these titration experiments

have/

have been tabulated in Table XXI and figure 19 on page 169 and 170 respectively. From the experimental results in this table, the loading ratios of the exchanger (i.e. the ratio of equivalents exchanged by the exchanger to the total exchange capacity of the ion-exchanger) at various instants in the course of neutralization were calculated in the following manner:-

When a H-ion-exchanger, HA, is neutralised with an amount, say X equivalents of alkali, and if the neutralization is carried in an electrolyte solution containing from the outset a constant amount, C equivalents, of sodium chloride, then at equilibrium the various concentrations can be represented as:-

$$\begin{array}{ccccccc} HA & + & Na & \rightleftharpoons & NaA & + & H \\ Y - Y_2 & & X + C - Y_2 & & Y_2 & & Y_2 - X \\ (= Y_1 \text{ suppose}) & & & & & & \end{array}$$

where Y = The total H-ion exchange capacity of the exchanger, HA, in equivalents hydrogen at the start of the reaction.

Y_2 = Total number of equivalents exchanged by the exchanger at the equilibrium.

Y_1 = $Y - Y_2$ = Un-exchanged hydrogen in equivalents of the exchanger at the equilibrium.

If the volume of the solution were one litre, then $\log \dfrac{1}{Y_2 - X} = \log \dfrac{1}{(H)} = pH$

Thus/

Thus knowing pH on addition of X equivalents of alkali and the volume of the solution (50 ml. in these titration experiments), it is possible to calculate the value of Y_2. Knowing the value of Y, i.e. 5 milliequivalents (as 5 gms. of exchanger of exchange capacity 1 m.e./gram were taken) in this case, the values of Y_2/Y (loading ratio), Y_1 and Y_2/Y_1 could be calculated.

In the manner stated in the foregoing lines, the values of loading ratios, i.e. Y_2/Y at various instants during the course of neutralization were calculated for all the titration experiments using different ionic strengths of NaCl and have been presented in Tables XXII to XXVII on pages 171 - 176. The results of loading ratios against pH for the different ionic strengths have been plotted in figure 20 on page 177.

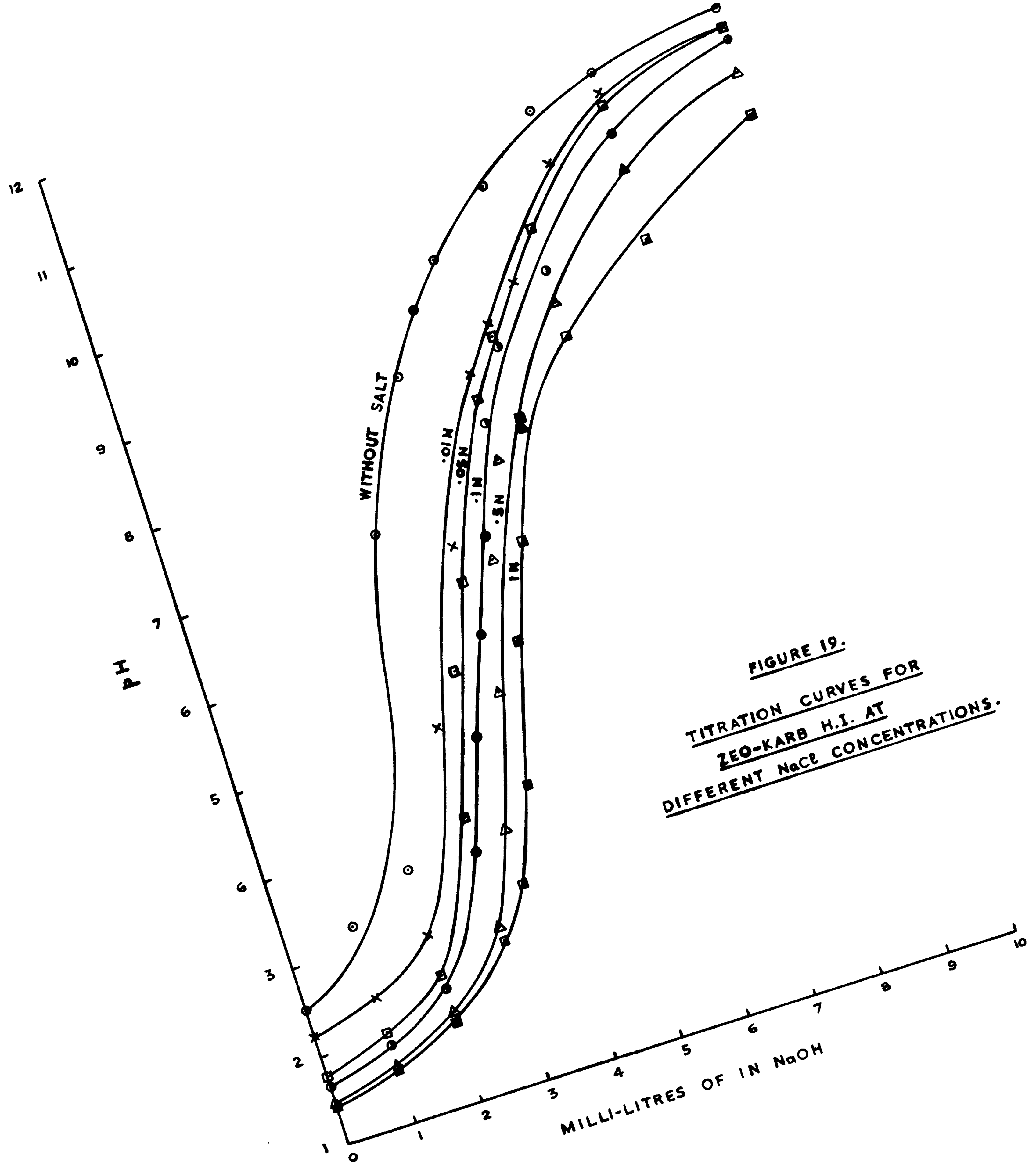


FIGURE 19.

TITRATION CURVES FOR ZEO-KARB H.I. AT DIFFERENT NaCl CONCENTRATIONS.

TABLE XXII

pH - Neutralization results of Zeo-Karb H.I. (without NaCl)

Sample take in each bottle = 5 grams.
Maximum exchange capacity of sample = 5 milliequivalents = Y
Total final volume of contents in each bottle = 50 ml.
Alkali used = N/1
So one ml. of N/1 alkali ≡ 1 m.e. of NaOH

Ml.of N/1 NaOH added ≡ X milliequivalents	pH	$Y_2 - X$ (milliequivalents)	Milliequivalents exchanged by the exchanger at equilibrium Y_2	Loading Ratio Y_2/Y (percentage)
1·0	3·25	0·0	1·0	20
2·0	3·65	0·0	2·0	40
3·0	7·23	0·0	3·0	60
4·0	8·80	0·0	4·0	80
4·5	9·45	0·0	4·5	90
5·0	9·90	0·0	5·0	100

TABLE XXIV.

pH - Neutralization results of Zeo-Karb H.I. in ·05N NaCl solution.

Sample taken in each bottle = 5 grams.
Maximum exchange capacity of sample = 5 milliequivalents=Y
Total final volume of contents in each bottle = 50 ml.
Alkali used = N/1 NaOH
1 ml. of alkali = 1 milliquivalent of NaOH

Ml.of N/1 NaOH added = X milliequivalents	pH	Y_2 - X (milliequivalents)	Milliequivalents exchanged by the exchanger at equilibrium Y_2	Loading ratio Y_2/Y (percentage)
0·0	1·78	0·85	0·85	17·0
1·0	2·04	0·45	1·45	29·1
2·0	2·44	0·18	2·18	43·6
3·0	4·01	0·00	3·00	60·0
3·5	5·55	0·00	3·5	70·0
4·0	6·45	0·00	4·0	80·0
5·0	8·30	0·00	5·0	100·0

T A B L E XXV

pH - Neutralization results/of Zeo-Karb H.I. in ·1N NaCl solution.

Sample taken in each bottle = 5 grams.
Maximum exchange capacity of sample = 5 milliequivalents = Y
Total final volume of contents in each bottle = 50 ml.
Alkali used = $N/_1$ NaOH
1 ml. of alkali = 1 milliequivalent of NaOH

Ml of $N/_1$ NaOH added = X milliequivalents	pH	Y_2 - X (milliequivalents)	Milliequivalents exchanged by the exchanger at equilibrium Y_2	Loading ratio Y_2/Y (percentage)
0·0	1·66	1·1	1·10	22·0
1·0	1·89	0·65	1·65	33·0
2·0	2·28	0·27	2·27	45·4
3·0	3·60	0·01	3·01	60·2
3·5	4·80	0·00	3·5	70·0
4·0	5·85	0·00	4·0	80·0
4·5	6·85	0·00	4·5	90·0
5·0	8·01	0·00	5·0	100·0

T A B L E XXVI

pH - Neutralization results of Zeo-Karb H.I. in ·5N NaCl solution.

Sample taken in each bottle = 5 grams.
Maximum exchange capacity of sample = 5 milliequivalent = Y
Total final volume of contents in each bottle = 50 ml.
Alkali used = $N/_1$ NaOH
1 ml. of alkali = 1 milliequivalent of NaOH

Ml.of $N/_1$ NaOH added = X milliequivalents	pH	$Y_2 - X$ (milliequivalents)	Milliequivalents exchanged by the exchanger at equilibrium Y_2	Loading ratio Y_2/Y (percentage)
0·0	1·46	1·75	1·75	35·0
1·0	1·65	1·10	2·10	42·0
2·0	2·02	0·48	2·48	49·6
3·0	2·74	0·09	3·09	61·8
3·5	3·76	0·00	3·5	70·0
4·0	5·18	0·00	4·0	80·0
4·5	6·58	0·00	4·5	90·0
5·0	7·60	0·00	5·0	100·0

T A B L E XXVII

pH - Neutralization results/of Zeo-Karb H.I. in 1N NaCl solution.

Sample taken in each bottle = 5 grams
Maximum exchange capacity of sample = 5 milliequivalents = Y
Total final volume of contents in each bottle = 50 ml.
Alkali used = $N/_1$ NaOH
1 Ml. of alkali = 1 milliequivalent of NaOH

Ml. of $N/_1$ NaOH added ≡ X milliequivalents	pH	Y_2 - X (milliequivalents)	Milliequivalents exchanged by the exchanger at equilibrium Y_2	Loading ratio Y_2/Y (percentage)
0·0	1·43	1·85	1·85	37·0
1·0	1·60	1·25	2·25	45·0
2·0	1·90	0·65	2·65	53·0
3·0	2·60	0·13	3·13	62·6
3·5	3·14	0·04	3·54	70·8
4·0	4·12	0·00	4·00	80·0
4·5	5·66	0·00	4·50	90·0
5·0	6·68	0·00	5·00	100·0

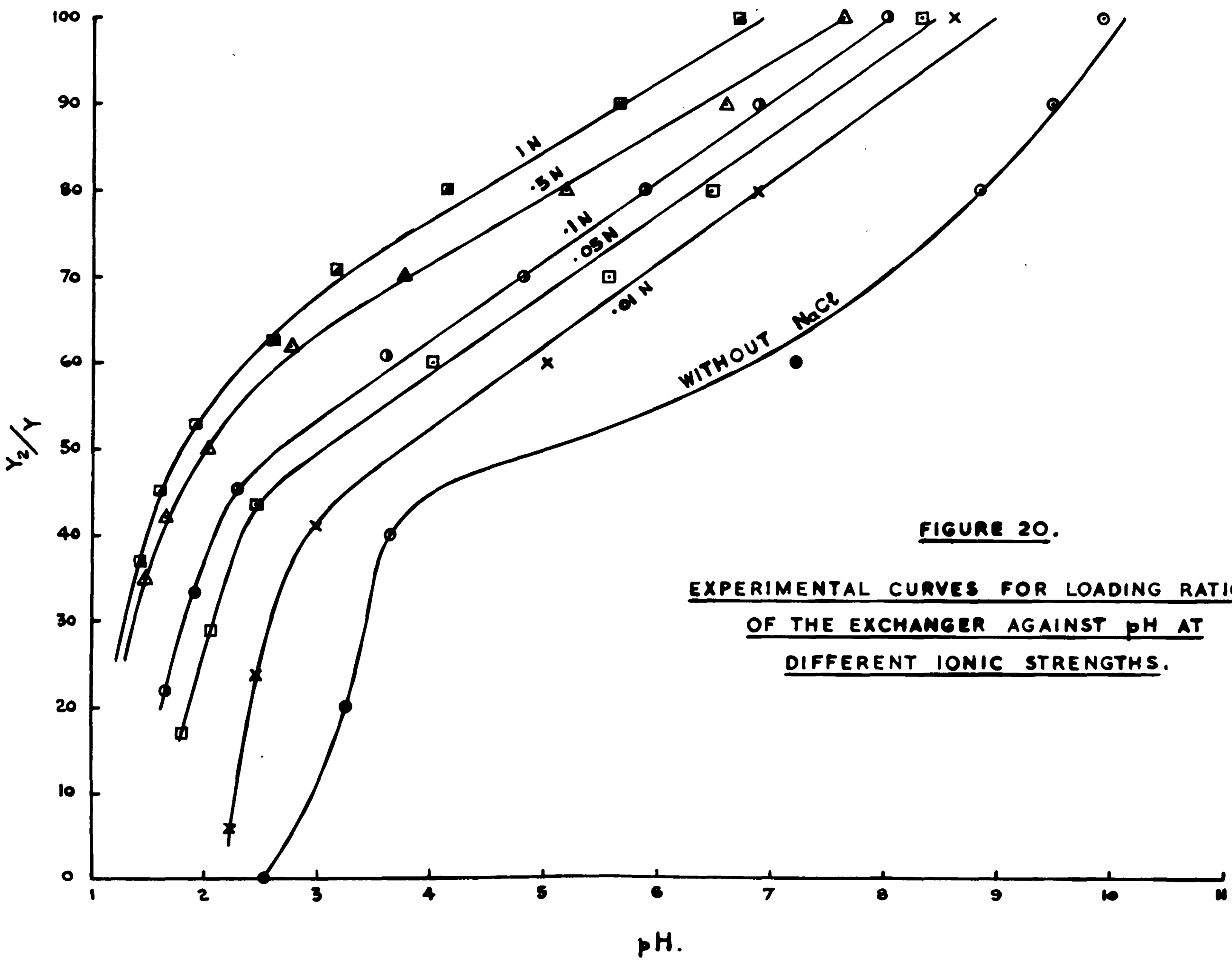


FIGURE 20.

EXPERIMENTAL CURVES FOR LOADING RATIOS OF THE EXCHANGER AGAINST pH AT DIFFERENT IONIC STRENGTHS.

VI Study of the application of Sulphonated Coals to the Anodizing of Aluminium.

By virtue of their behaviour as insoluble acids hydrogen exchangers have been used to catalyse the reactions which are normally catalysed by the hydrogen ion, e.g. hydrolysis of starch to glucose (70) etc. etc. A rather interesting study has been made in the application of this property of sulphonated coals to give H-ions, to catalyse the "anodising of aluminium".

Anodic oxidation or anodizing (72) is an electrolytic process for thickening the oxide film present on all aluminium surfaces. This process may be applied for various reasons e.g. to provide a key for painting, to provide an insulating coating for an electrical conductor, for decorative purposes or to increase the naturally high resistance of an aluminium surface to corrosion. The film so formed may also be dyed in a wide range of colours (73).

Commercial processes for anodic oxidation of aluminium and its alloys are based on the use of either chromic (72), sulphuric (74) or oxalic (75) acid as electrolyte. Since H-ion-exchangers (sulphonated coals) are quite strong acids and are capable of ionizing in contact with water, it was thought/

thought it might provide a useful study by using aqueous suspension of sulphonated coal either alone or in conjunction with sulphuric acid as electrolyte and to study its effect on anodizing process with respect to quantity and quality of the oxide film formed.

(i) Experimental:-

Apparatus:- The apparatus used is shown in fig. 21 (page 180) It consisted of a large glass beaker, A, surrounded by a water-bath, B, to control the temperature of the electrolyte because the process was exothermic and formation of the anodic film is very sensitive to change of temperature (81). The beaker, A, had a lead plate, P, as cathode and the the aluminium foil, F, as anode. A stirrer, S, was used to keep the electrolyte of the beaker, A, of uniform temperature. The cell was connected in an electrical circuit, shown in fig.22 (page 181) which was fed by D.C. mains through a fixed resistance consisting of electrical bulbs. An ammeter and a volt meter were connected appropriately to indicate the current and the voltage at which the anodizing was being carried out.

Procedure:-

The aluminium foil was cut into suitable strips of 2" x 7" size so that at least five strips (2 inches x 1 inch/

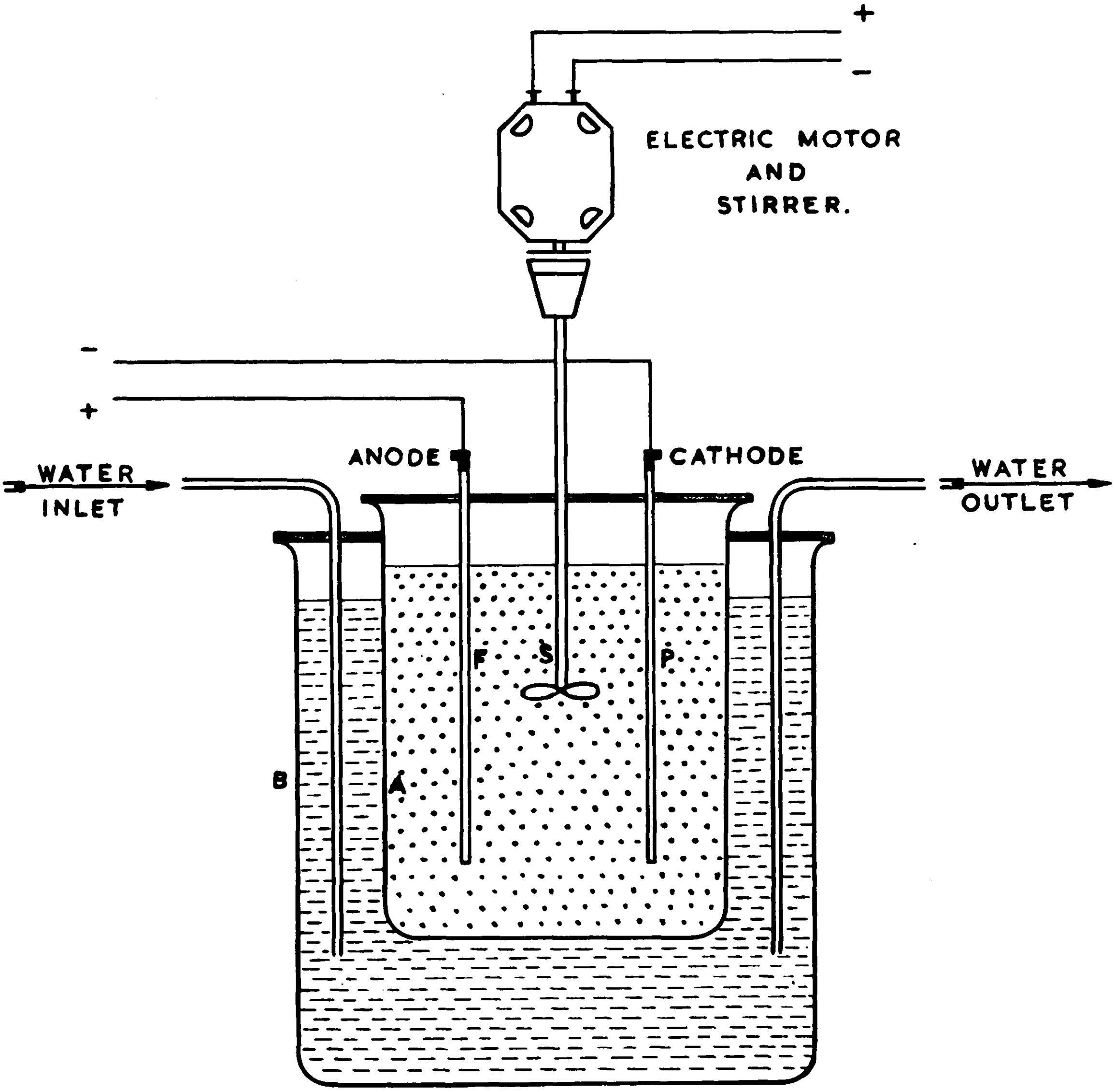


FIGURE 21.

ANODIZATION CELL.

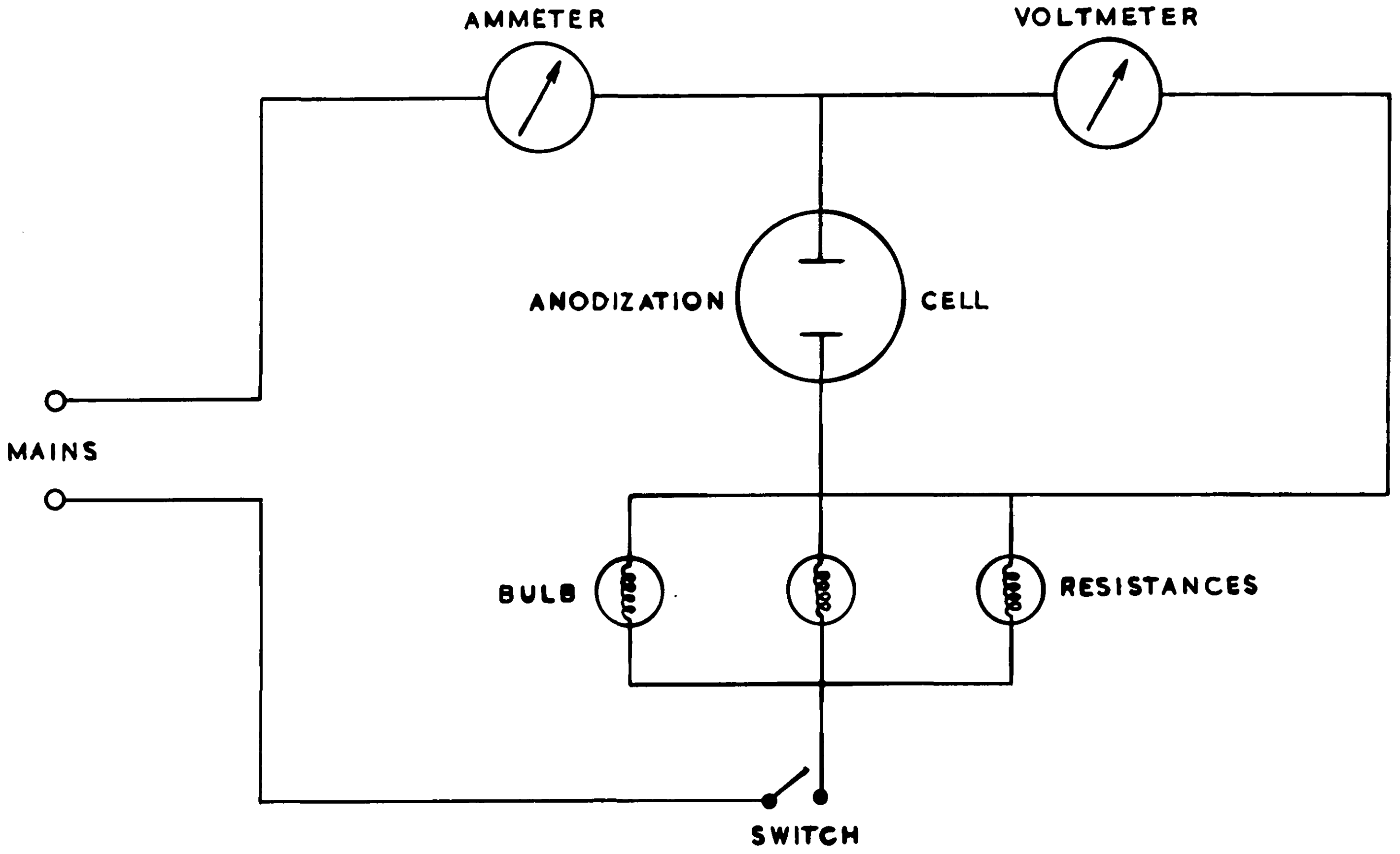


FIGURE 22

ELECTRICAL CIRCUIT FOR ANODIZATION.

x 1 inch) of anodized aluminium were obtained each time. This was degreased by dipping in carbon tetrachloride and wiping it dry with a clean cotton wool swab. After washing with distilled water it was suitably placed as an anode in the electrolyte the temperature of which had been brought to 25°C previously. The current was then switched on. After the foil had been anodized for the required time, it was taken out of the cell after switching the current off, washed with distilled water and dried.

The dry anodized aluminium foil was cut into five pieces (2" x 1") and two of these were accurately weighed. These two were then boiled in the stipping solution (a mixture of phosphoric acid (35 ml. of 85% acid), chromic acid (20 grams of $Cr\ O_3$) made to one litre with water) which dissolved away the oxide. These were then washed, dried and reweighed. The loss in weight was due to the dissolving away of oxide and gave a measure of the anodizing.

Experiments using sulphonated coal.

Use of sulphonated coal suspension alone was not a success as it was not conducting enough to give the required current density at low voltage. Thelatter was essential as high voltage tended to spoil the aluminium foil. So it was thought to use it in conjunction with different concentrations/

concentrations of sulphuric acid.

(ia) Effect of different concentrations of sulphuric acid on anodizing ... with and without sulphonated coal.

50 grams of the active sulphonated coal (prepared in the laboratory) were suspended in 2 litre of water in the beaker, A, in figure 21 (page 180) and 25 ml. of concentrated sulphuric acid (sp.gr.1·84) were added to it. The aluminium foil of the standard size, as already stated, was taken and anodized for one hour at 25°C in the standard way described on page 179. More concentrated sulphuric acid was then added to make the total quantity of acid in the beaker, A, 50 ml and again a standard aluminium foil was anodized for one hour at 25°C. In this way the anodizing of different aluminium foils was done for total amount of acid being 100, 150 and 215 ml.

All these experiments at various concentrations of sulphuric acid were carried without using the sulphonated coal to compare with the corresponding results obtained with the exchanger.

All the anodized pieces were cut into pieces 2" x 1" and the amount of the oxide formed was determined in duplicate in each case in the standard manner described on page 182. The results obtained have been tabulated in

Table/

Table XXVIII and presented in figure 23 on pages 185 - 186.

(ii) Study of the effect of time on anodizing with and without sulphonated coal.

Beaker, A, containing 215 ml. of concentrated sulphuric acid, 50 grams of sulphonated coal in 2 litre of water, was used to study the effect of time of anodizing on the amount of oxide film formed. Thus the other conditions were kept same and different aluminium foils were anodized for 1/4, 1/2, 2 and 4 hours. Same number of aluminium foils were anodized under the same conditions for similar variations in time without using any sulphonated coal. The oxide formed on 2" x 1" strips was estimated in the standard way.

The results obtained have been tabulated in Table XXIX on page 187 and presented in figure 24 on page 188.

(iii) Effect of concentration of sulphonated coal.

As it became clear from the previous two sets of experiments that exchanger does catalyse the anodizing process quite appreciably from the commercial point of view, it was thought desirable to determine the effect of different concentrations of H-ion-exchanger on the anodizing process keeping all the other condition of the experiment constant./

TABLE XXVIII

Effect of different concentrations of sulphuric acid on anodizing with and without sulphonated coal.

Time of anodizing = 1 hour
Temperature of anodizing = 25°C

ml. of concentrated sulphuric acid per 2 litre of electrolyte.	oxide in milligrams/2"x1" strip of anodized aluminium.		Increase in milligrams	Percentag increas
	without sulphonated coal	with sulphonated coal		
25·0	51·1	62·2	11·1	21·7
50·0	47·6	58·1	10·5	22·1
100·0	41·8	48·7	6·9	16·5
150·0	35·5	40·3	4·8	13·5
215·0	29·0	33·2	4·2	14·5

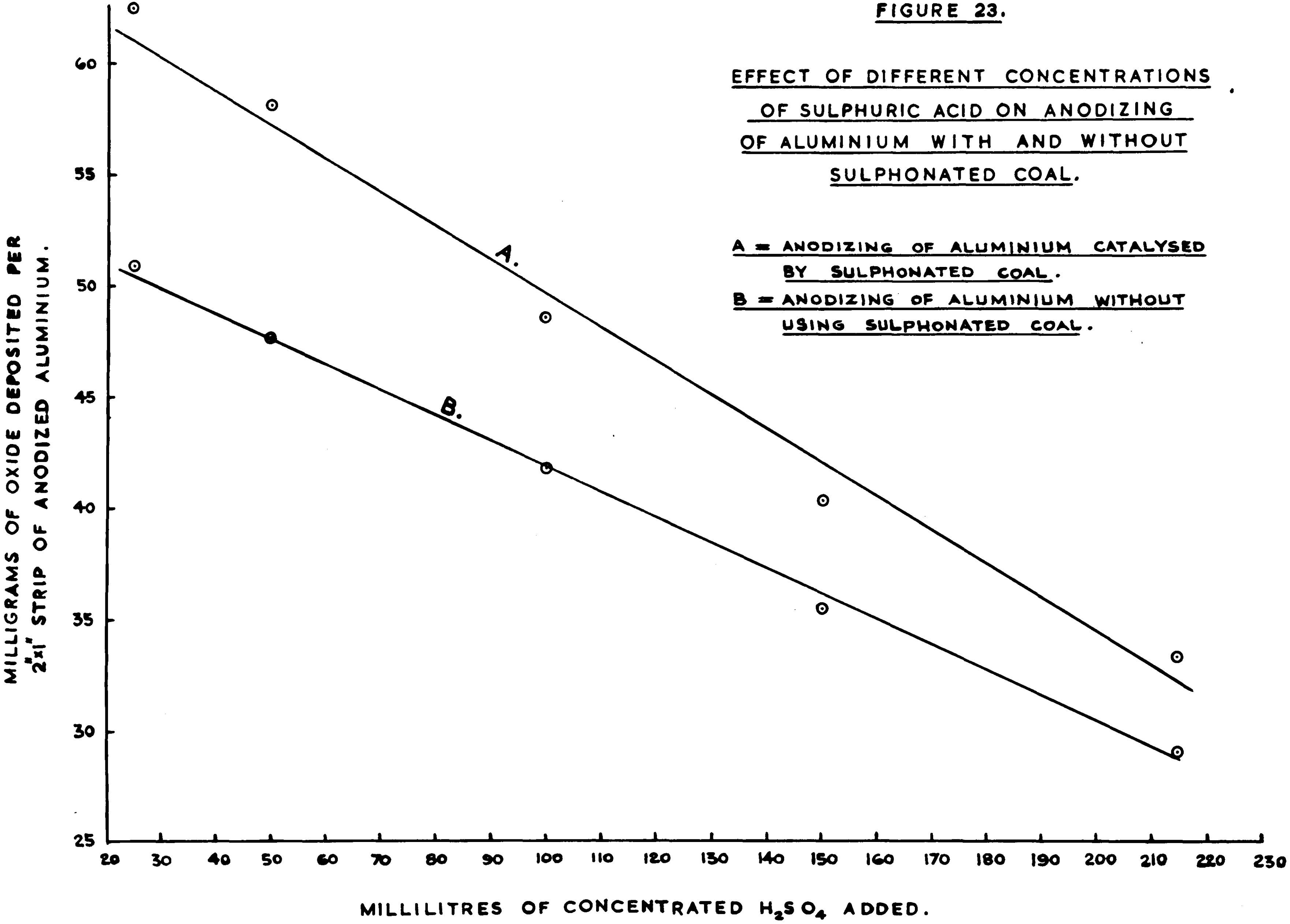


FIGURE 23.

EFFECT OF DIFFERENT CONCENTRATIONS OF SULPHURIC ACID ON ANODIZING OF ALUMINIUM WITH AND WITHOUT SULPHONATED COAL.

A = ANODIZING OF ALUMINIUM CATALYSED BY SULPHONATED COAL.

B = ANODIZING OF ALUMINIUM WITHOUT USING SULPHONATED COAL.

TABLE XXIX

Effect of Time on anodizing as catalysed by sulphonated coal.

Voltage = 9·5 volts
Current = 0·65 amperes
Temperature of anodizing = 25°C

Time in Hours	oxide in milligrams/2"x1" strip of anodized aluminium. without sulphonated coal	with sulphonated coal	Increase in milligrams	Percentage increase.
0·25	8·4	11·5	3·1	36·9
0·5	18·6	22·7	4·1	22·1
1·0	35·3	40·3	5·0	14·2
2·0	49·6	57·0	7·4	14·9
4·0	50·8	57·0	6·2	12·2

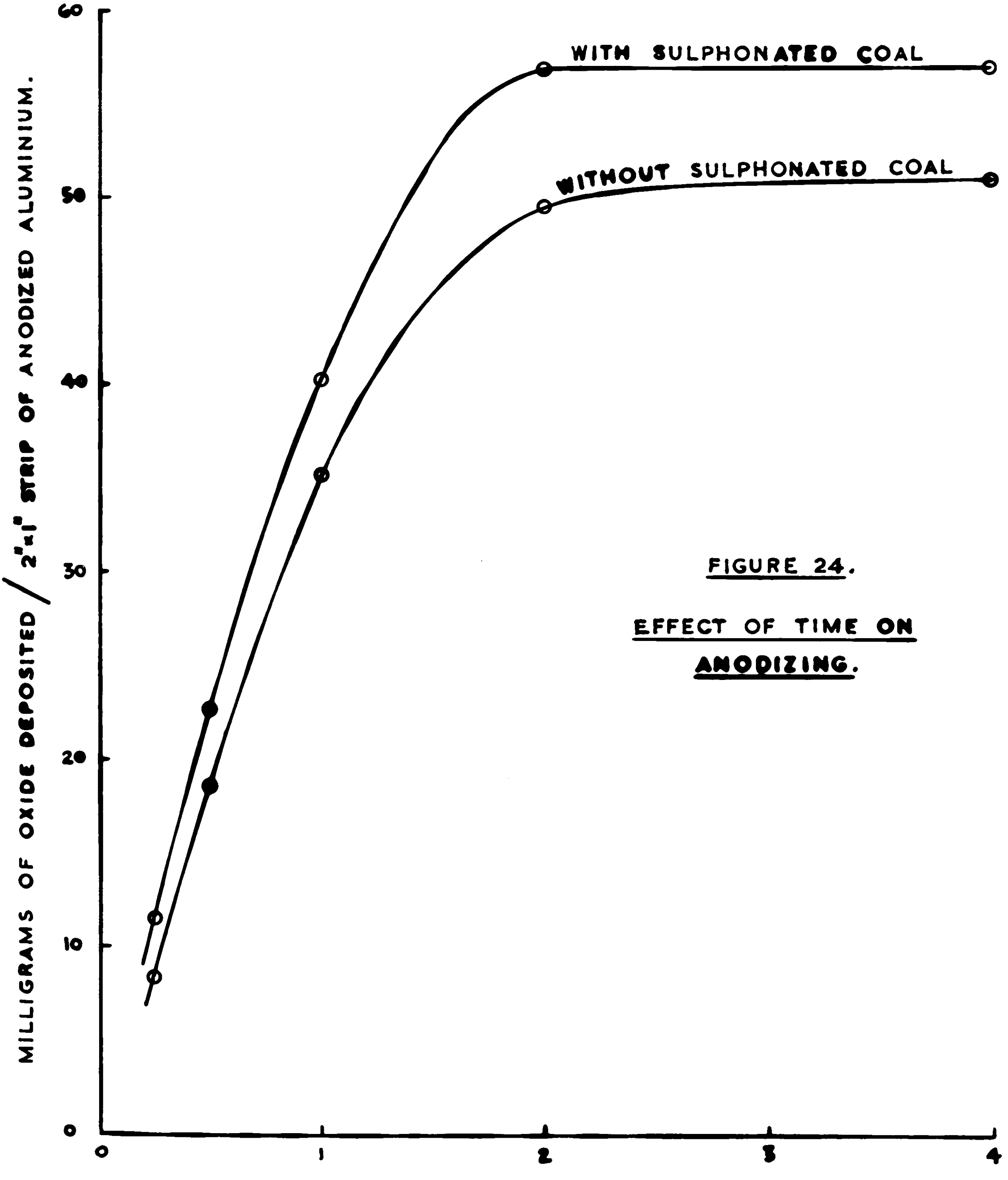


FIGURE 24.

EFFECT OF TIME ON ANODIZING.

constant. Consequently 5, 20 and 50 grams of the exchanger were used to anodize aluminium foils of standard size for one hour at 25°C, using an electrolytic bath containing 215 ml. of concentrated sulphuric acid diluted to 2 litres with distilled water. The amount of oxide formed on 2" x 1" strips was estimated in the usual way.

The results have been tabulated in Table XXX given below:-

TABLE XXX

Effect of Sulphonated Coal concentration on anodizing of aluminium.

Temperature of anodizing = 25°C
Time of anodizing = 1 hour
Current = 0·65 Amps.
Voltage = 9·5 Volts

Amount in grams of sulphonated coal/2 litre of electrolyte.	oxide in milligrams/ 2" x 1" strip of anodized aluminium.
5	41·0
20	43·0
50	40·0

(iv) Study of the effect of sulphonated coal on the quality of anodizing:-

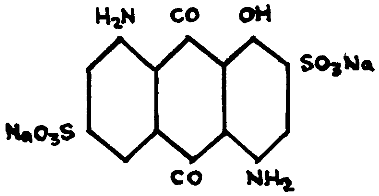
The quantity of oxide film, although is

a/

a measure of the anodization but does not indicate the quality of the oxide film with respect to the commercial use the particular anodizing is being done for. Thus for dyeing purpose, for example, the oxide film should be rigid and porous, and at the same time in sufficient thickness, to absorb the maximum of dye. It was decided, therfore, to compare the quality of the oxide film produced by sulphuric acid-exchanger mixture with that produced by sulphuric acid alone under the same conditions, by studying the dyeing qualities of the aluminium foils anodized by these two methods. Dyeing with two dyes only was studied and is given below:-

(i) Dyeing with solway blue BNS (Colour Index No.1054)

This is an anthraquinone acid dye of the following constitution



2" x 1" strips of the aluminium foil anodized for one hour at 25°C using electrolyte containing 215 ml. concentrated sulphuric dissolved in 2 litre of distilled water with and without 50 gms. sulphonated coal were used for dyeing. Each strip was dyed in 50 ml. of ·02% solution of the dye in water at 40°C for a certain duration of time.

At/

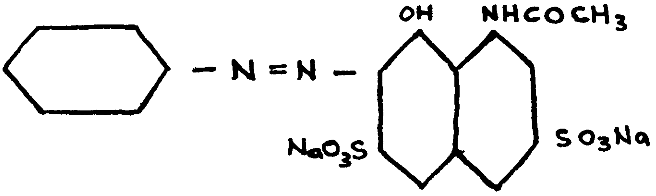
At the end of the required absorption time, the concentration of the dye left in the dye bath after absorption was estimated colorimetrically on Hilger Spekker Absorptiometer. Thus the dye absorbed by the anodized aluminium strip was obtained by deducting this from the initial concentration.

The absorption of dye by each type of strip was studied for different times of absorption viz. 4, 16, 24, 48 hours and 4 days. This was done to find out the time required for maximum absorption of dye in both the cases.

The results obtained are given in Table XXXI on page 193 and presented in figure 25A on page 194

(ii) Dyeing with Azo-Geranine 2 GS (colour index No.31)

This is an acid azo dye of the following constitution:-



The dyeing of the strips (2" x 1"), anodized under the same conditions as in the previous experiment, was done by using 51 ml. of aqueous ·01% solution of the dye at 40°C. The estimation of the dye absorbed and the study of the effect of time on dyeing was done on the same lines as stated in the previous experiment.

The/

The results obtained have been tabulated in table XXXI on page 193 and presented in figure 25B on page 194.

TABLE XXXI

Results of Dyeing of aluminium anodized with and without sulphonated coal.

Concentration of Solway Blue BNS used = ·02%
Concentration of Azo-Geranine 2GS used = ·01%
Size of anodized strip taken for dyeing = 2"x 1"
Temperature of dyeing = 40°C

	Solway Blue BNS dye absorbed by aluminium 2"x1" strip anodized.		Azo-Geranine 2GS dye absorbed by aluminium 2"x1" strip anodized.	
Time of dyeing	without sulphonated coal m.gms.	with sulphonated coal m.gms.	without sulphonated coal m.gms	with sulphonated coal m.gms.
4	3·2	4·6	0·5	1·1
16	5·0	6·9	0·7	2·3
24	6·5	5·1	0·9	1·9
48	6·5	5·1	1·3	0·7
96	-	4·5	-	0·7
112	5·3	-	1·0	-

FIGURE 25A.

SOLWAY BLUE BNS
DYE ABSORPTION CURVES.

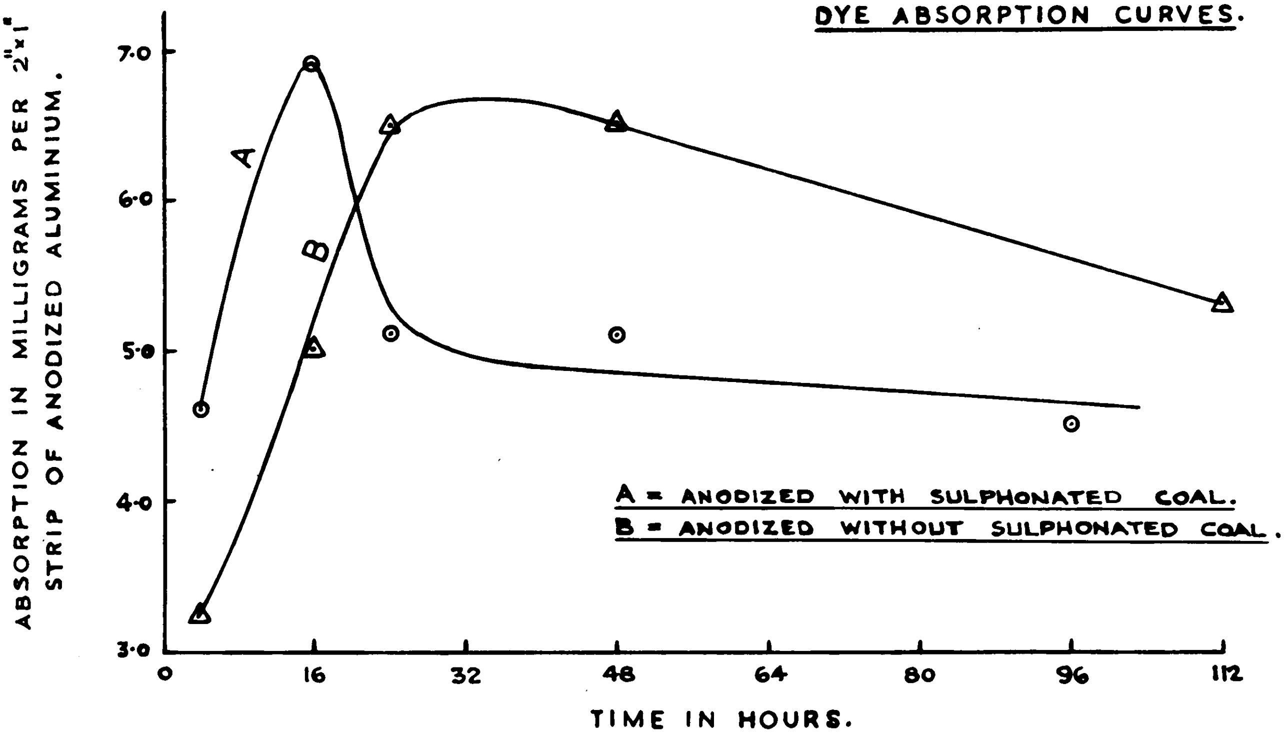
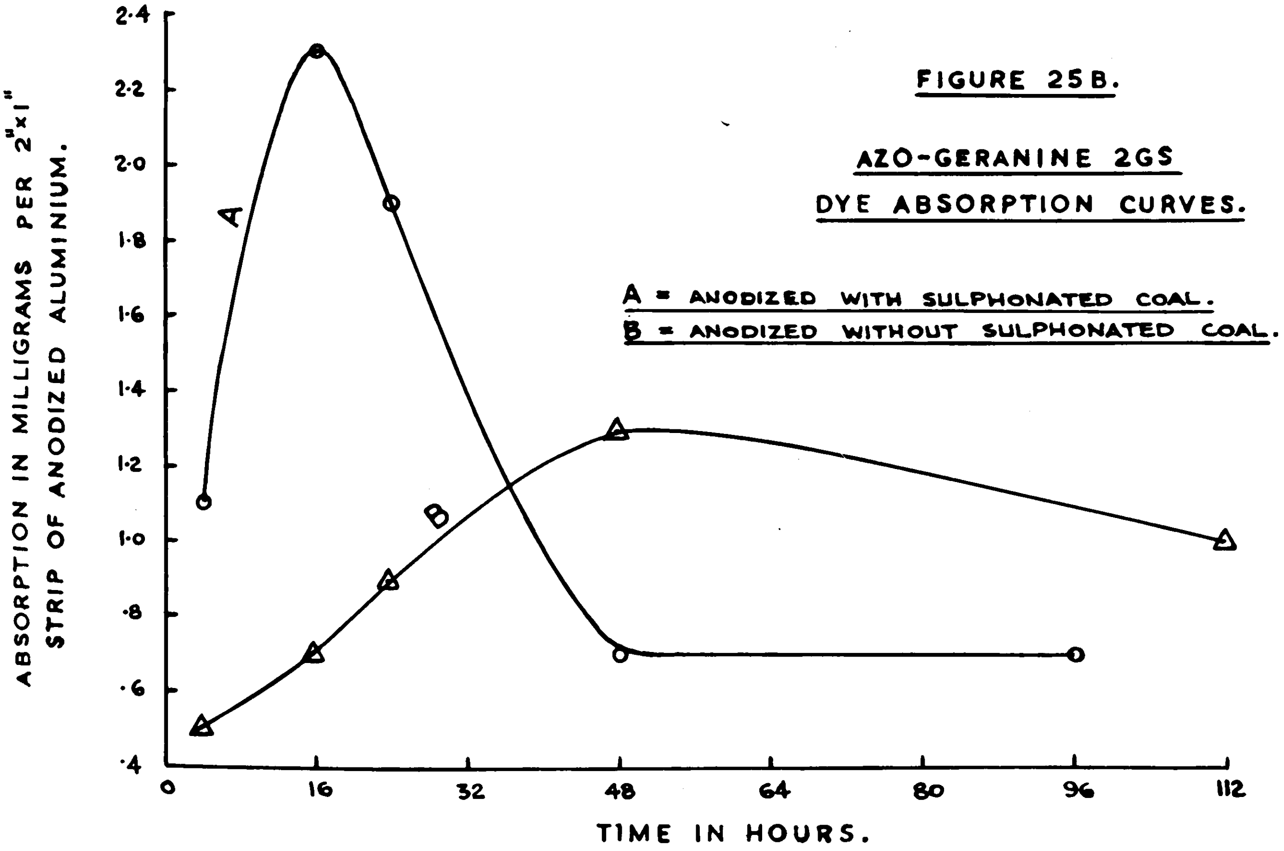


FIGURE 25B.

AZO-GERANINE 2GS
DYE ABSORPTION CURVES.



SECTION 3.

DISCUSSION OF RESULTS.

I. Study of Physical and Chemical factors in sulphonation of coal.

It is known that the base-exchange properties of the sulphonated coal depend upon a number of factors under which the sulphonation was carried. Some of these factors, as mentioned in the experimental section (page 137) were studied and the results obtained are discussed in the pages to follow.

(i) Effect of Temperature.

An increase in the sulphonation temperature is known, in general to accelerate both the rate and degree of reaction. This fact is borne out by a consideration of the figure 10 (page 140) where in the initial stages the base-exchange capacity, which in turn is a function of the degree of sulphonation, rises rapidly with the increase in the reaction temperature. After about 100°C, the curve begins to become less steep, probably due to simultaneous sulphonation and oxidation, the latter probably at the cost of the former. This is because oleum exercises an oxidizing action - a characteristic which is accentuated at higher temperatures. In fact oxidation also contributes to a rise in the exchange properties/

properties but the exchange phenomenon with a sulphonic group, which is probably introduced in coal by this reaction, is much pronounced. That is why the curve is steep but not as steep as in the initial stages. Besides it may also be due to the process being near completeness as after this, the curve, at 110 - 120°C, tends to become much flatter. Although by raising the reaction temperature further, from 120 to 150°C, a slight increase in the exchange capacity is recorded but/is it rather small - Besides the resulting product has low attrition value, as could be seen by its visual examination.

At 110 - 120°C (and up to 150°C) when the curve tends to become flatter, probably either the saturation stage is reached or it may be some such groups are being introduced which do not materially contribute to the base-exchange capacity; or else it may be the sulphonation of inner-removed parts of coal particles taking place which ordinarily do not or cannot take an active part in the base-exchange phenomenen since it is a surface phenomenen.

(ii) Effect of Time.

Like the temperature, the time of reaction also appears to affect the rate of reaction which increases quite steeply in the initial stages (refer fig 11 on page 142) but begins to become less and less steep from one/

one hour to three hours after which the curve tends to become flattened when, as in the case of temperature, a saturation stage is reached. Similar arguments as put forward in the "study of effect of temperature" apply here also for the possible explanation of the shape of the curve. It may be observed from the figure that 3 - 4 hours seems to be the best time for carrying on the sulphonation (the other factors being unchanged) to yield a material of optimum exchange capacity.

(iii) Effect of concentration:-

Experience has shown that the activity of sulphuric acid as a sulphonating agent is directly related to its sulphur trioxide concentration. From our present knowledge of the sulphonation reaction, it appears that aqueous sulphuric acid may be conceived as a solvent for the active sulphonating agent, viz., free or combined sulphur trioxide. Water does, of course, ameliorate the intensity of the reaction and also is known to inhibit the formation of oxidation products. Thus if the curve, showing the relation between the increase in the concentration of SO_3 in oleum and the base exchange capacity of the resulting product, in figure 12 (page 145) is studied, it will be noticed that the product of only 65·2 m.e./100 gm. is produced by concentrated sulphuric acid. The increase in the SO_3 content of oleum for the reaction/

reaction gives a rise in the exchange capacity of the resulting material. The rise, however, is not as steep as it becomes from 8 to 16%. It is probably due to the fact that in the initial stages viz. from zero to 8%, quite a portion of this extra concentration of SO_3 is used up in obviating the decelerating influence of water produced during the reaction which, of course, results in an indirect increase in the rate of sulphonation. At concentrations above eight per cent, probably the amount of SO_3 is enough not only to absorb the water produced during the reaction but also for active sulphonation of the material. Increase in SO_3 beyond 16% results in a comparitively smaller increase in the exchange capacity, and the curve tends to flatten, indicating probably the approach of the saturation stage as explained "on the study of effect of temperature" on pages 195-96.

(iv) Effect of Temperature, Time and Concentration of Oleum on sulphonation.

From the study of these three variables in sulphonation, it can be concluded that, to prepare a base-exchange material with optimum capacity from this coal, oleum (20% SO_3) must be used and the reaction should be carried on for three to four hours at 110 - 120°C. It may be added, however, that these limits are not strictly to be observed as small/

small changes in temperature, time and concentration do not have a great effect on the exchange capacity of the resulting product. Any undue increase in any of these variables does not yield a corresponding increase in the exchange capacity of the resulting material. Besides any small increases obtained are at the cost of loss of some of the physical characteristics e.g. gain of about 4 m.e./100 gm. in the exchange capacity by raising the temperature (refer Table XIV on page 139) of reaction from 120 to 150° was accompanied with corresponding loss in its attrition value.

(v) Effect of approximately 100% nitric acid - oleum mixture on sulphonation of coal.

Due to industrial utility of these carbonaceous exchangers, much attention has been paid to produce material of higher exchange capacity which has resulted in a growing number of patented processes for sulphonation of coal (52, 53, 54, 55, 56, 57, 58). In most of these processes use is made of oxidants which probably introduce carboxyl groups along with the usual sulphonic group. Since it was possible to have approximately 100% nitric acid which is a very strong oxidizing agent, the effect of nitric acid - oleum mixture on sulphonation was studied. It may be noted from figures 13 and 14 (pages 149 - 150) where the results have been/

been presented that the exchange capacity of the resulting material increases very steeply with the increasing percentage of nitric acid in the sulphonating acid mixture. Probably all the side chains, available in a coal molecule which cannot take any part in sulphonation, get oxidized to the -COOH groups which are responsible for this steep rise in the exchange capacity. It may be observed, here, that the argument is supported by the fact that so far as sulphonation is concerned, a stage of saturation is already obtained in the previous experiments, (Effect of Temperature etc. pages 195-199), the maximum exchange capacity of the resulting product being 150·3 m.e./100 grams. It may be further noted from the figure that the curve reaches a maxima corresponding to an exchange capacity of 213 m.e./100 gms and about 7·3% nitric acid in the sulphonation mixture. After this, very curiously, the exchange capacity begins to fall and tends to become constant. Probably this is due to the start of decarboxylation along with oxidation and also the start of degradation of coal. (Cf. stages of oxidation of coal on pages 8 - 11). At the flat portion of the curve probably the oxidation of coal is being nearly balanced by the decarboxylation of -COOH groups and degradation of coal.

It will be noted, therefore, that

addition/

addition of nitric acid increases the base-exchange capacity of the resulting material, the optimum being obtained by a mixture of 7·3% nitric acid with oleum (20% SO_3). In this particular case a maximum increase of about 41% in the exchange capacity (Table XVII on page 148) (using the value obtained by oleum (20% SO_3) alone,as standard) was obtained by using 7% nitric acid in the oleum-nitric acid mixture.

II. Study of Titration Curves of Sulphonated coals.

The base-exchange properties exhibited by sulphonated coal are due to the possible introduction of sulphonic acid group or groups in the coal molecule. Since oxidation along with sulphonation increases the exchange capacity of the resulting material (78,79) it is thought that possibly the introduction of carboxyl groups is responsible for this. That the exchange phenomenen may be due to sulphonic acid and carboxyl groups in sulphonated coal is further sustained by the discovery by Adams and Holmes (loc.cit.) of synthetic exchange resins, as the use of sulphonated organic compounds in the manufacture of ion-exchange resins give a higher exchange-capacity material. It may be observed, therefore, that a H-ion-exchanger is an insoluble acid and has ions of its own to exchange for others. It may have a single type of ionic bond (mono functional) or have a number of types of exchange groups attached to the same molecule or matrix (polyfunctional). So it was thought that a study of the titration curves of these"insoluble acidoids" might prove a valuable aid in characterizing the H-ion-exchangers, since the titration curve will depend upon the degree of ionization of the various groups in an exchanger.

(i) Preparation of material for titration.

All the material used for the study of the titration curves was regenerated fully by leaching with excess of 0·5N Hcl so that all the exchangeable bases were removed and the regenerated substance had maximum exchange capacity.

(ii) Time required for equilibrium between acidoid and alkali.

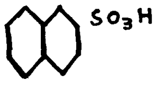
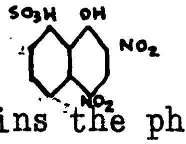
As the equilibrium between a hydrogen ion exchanger and alkali added to it was not established quickly, therefore it was essential to determine the most suitable conditions under which titration could be done and reproduced. Thus some experiments were done, as given on pages 152 - 154, to determine the time required for attainment of equilibrium between sulphonated coal and alkali added to it. It may be noted from figure 15 on page 154 that the change in pH with time is quite marked in the first two hours, specially so in case of those mixtures where the final pH is in the acidic range. This is probably because exchanger particles exist in aggregates and when alkali is added, the bulk of it goes to neutralize the outer surfaces of the particles with which it first comes in contact. The remaining portion of the exchanger takes up the alkali gradually from the over neutralized portions until the equilibrium/

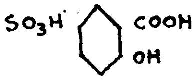
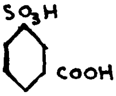
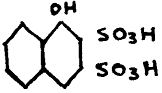
equilibrium is established. The pH just after addition of alkali is, therefore, much higher than the final pH when the equilibrium had been attained. However, from the figure 15 (on page 154) it is obvious that the equilibrium is established after about 12 hours after which the pH becomes independent of time. So in all the titration experiments the pH of the exchanger-alkali suspension was taken after keeping the contents overnight to ensure the attainment of equilibrium and hence the reproducibility of results.

(iii) Study of pH-Neutralization Curves of H-ion-exchanger in the absence of salt in the solution:-

The results of titration of two different sulphonated coals have been shown in Table XIX on page 156 and in figure 16 on page 157. It may be observed from the curves that both the materials behave like moderately strong acids. The points of inflection are not very well defined, and specially trail off near the end in the alkaline region - probably due to the buffering action of phenolic groups which may be present in the material. It may further be noted that although the exchange capacity of exchanger No.1 is 100 m.e./100 gms and of the exchanger No.2 126·7 me./100 gms (requiring 10·0 ml. and 12·67 ml. of 0·1N sodium hydroxide respectively for complete neutralization of one gram - amount taken for each experiment), only/

only 6·0 ml. and 7·6 ml. of 0·1N NaOH had been added at pH =7 to the respective exchangers. It is obvious, therefore, that in straight neutralization in aqueous solution (in the absence of any salt) the exchange goes on even in the alkaline region.

These titration curves give the impression that these sulphonated coals are monobasic acids with some phenolic groups which are responsible for the trailing off of the curves in the alkaline region. It was thought that a study of the titration curves of organic acids of known constitution i.e. containing $-SO_3H$, $-COOH$ and $-OH$ (phenolic) groups orientated in different positions and in different numbers, might provide a useful parallel to the titration curves of the two exchangers in fig. 16 (on page 157). The results of titration of the different acids, which were studied, are given in Table XX, on pages 160 and 161, and figure 17, 18 and 18A on pages 162, 163, and 164. It may be noted from these figures that whereas naphthalene sulphonic acid () gives an inflection corresponding to a monobasic acid, the neutralization curve of the flavianic acid () is not much different although it contains the pheolic (-OH) in addition to a $-SO_3H$ group. Similarly neutralization curves of salicyl sulphonic/

sulphonic acid () appears as if it were a monobasic acid although it contains a $-SO_3H$, a $-COOH$ and a $-OH$ group. On the other hand the titration curve of m-sulphobenzoic acid () shows points of inflection corresponding to a diabasic acid. Naphthol sulphonic acid () which contains two $-SO_3H$ groups and one $-OH$ group curiously enough gives a single inflection in its titration curve thus behaving as a monobasic acid, although in the alkaline reigon the curve trails off instead of being flat - probably due to the buffering action of phenolic group. It may be noted, therefore, that whereas numbers of points of inflection in the titration curve of an acid, corresponding to its basicity should be obtained, it is not always true e.g. as in the case of the organic acids taken above. So the titration curves of the two sulphonated coals, (figure 16 on page 157), do not bring out the exact basicity of the material which, however, behaves like an acid.

(iv) Study of the effect of ionic strength of the solution on the pH-neutralization curves of Zeo-Karb. H.I.

Although the titration curves of sulphonated coals, in the absence of any salt in the solution, bring out the fact that the exchanger is a strong insoluble acidoid they do not offer data for characterizing the exchanger/

exchanger by definite constants. It was decided, therefore, to study the effect of the presence of a neutral salt, sodium chloride, in the solution on the pH-neutralization curves and also to study the variations in pH-neutralization curves as the ionic strength of the solution is changed, since like the base-binding capacity of wool(69), the base-bind capacity of the H-ion-exchanger should also be a function of this variable.

Zeo-Karb H.I. (supplied by Permutit Co. Ltd) was used throughout this investigation as it was essential to have a large quantity of material of constant base-exchange capacity. The material had an exchange capacity of one mill-equivalent per gram of the air dried material.

The results of the titration of Zeo-Karb H.I. in presence of different ionic concentrations are given in Tables XXI to XXVII on pages 169 - 176 and figures 19 and 20 on pages 170 and 177 respectively. It may be noted from figure 20 (on page 177) in which loading ratio, which is, of course, a measure of the base bound, is plotted against pH, that simple regularity exists between the different curves obtained using different sodium chloride concentrations, except the "without NaCl" curve (at the extreme right of the figure 20). It will be noted that 0·01N curve has slight resemblence to "without NaCl" curve. In general all the curves/

curves except the "without Nacl" curve have nearly the same slope specially at the mid-point i.e. the point at which half the maximum base-binding capacity is found. It is interesting to note that addition of a small amount of salt tends to increase tremendously the quantity of the base-bound at the same pH, at lower pH values, e.g. at pH 2•8, in the absence of salt only about 7% of the base is bound; the addition of NaCl, sufficient to bring concentration to 0•01N, increases this figure to about 38% i.e. nearly five fold. As the ionic concentration is further increased from •01N to 1N the base bound also increases e.g. 48% at •05N, 51% at •1N, 61% at 0•5N and 65% at 1N (at pH 2•8). Thus addition of salt to bring concentration to 1N increases the base bound about nine fold at pH 2•8 as compared to amount of base bound in the absence of salt at the same pH. It may be noted, however, that this factor becomes less as the pH increases. Thus at pH 3•6, in the absence of salt the base bound is about 39% against 48% for •01N NaCl and 74% for 1N - the latter being not even twice the amount of base bound at "no salt" concentration. Therefore it appears that the base-binding capacity is a function of the ionic concentration of the solution.

Another interesting fact which may be noted/

noted from the fig. 20 is the simple regularity that relates the curves obtained with different ionic strengths. Thus each time the concentration is doubled the mid point of the curve is shifted to a pH value, lower by nearly 0·3 units, and when the concentration is made five times, the pH of the mid point of the curve is shifted to a lower value by about 0·7 units. Thus the number of units, in terms of pH, by which the mid points of any two adjacent curves are separated, is nearly equal to the logarithm of the ratio of the ionic concentrations which the curves represent. This relation holds good between concentrations of 0·01N to 1 N NaCl and is shown in figure 26 on page 211 where a straight line is obtained by plotting the pH of the mid points against logarithms of the ionic concentrations. (The values of pH for mid-points of the titration curves for different ionic strengths have been got from figure 20 (page 177) and are given in Table XXXII on next page.) It may be noted, however, that pH value of the mid-point of "without salt" curve is shifted from 5·0 to 3·75 i.e. by 1·25 units by addition of sufficient sodium chloride to bring the concentration to ·01N.

TABLE XXXII

pH for mid-points of titration curves for Zeo Karb H.I. for different ionic strengths.

Ionic strength (normality of NaCl)	Logarithm of ionic concentration.	pH of mid-point.
0·0	-	5·00
0·01	-2·0	3·75
0·05	-1·3	3·00
0·10	-1·0	2·70
0·50	-0·3	2·00
1·00	0·0	1·75

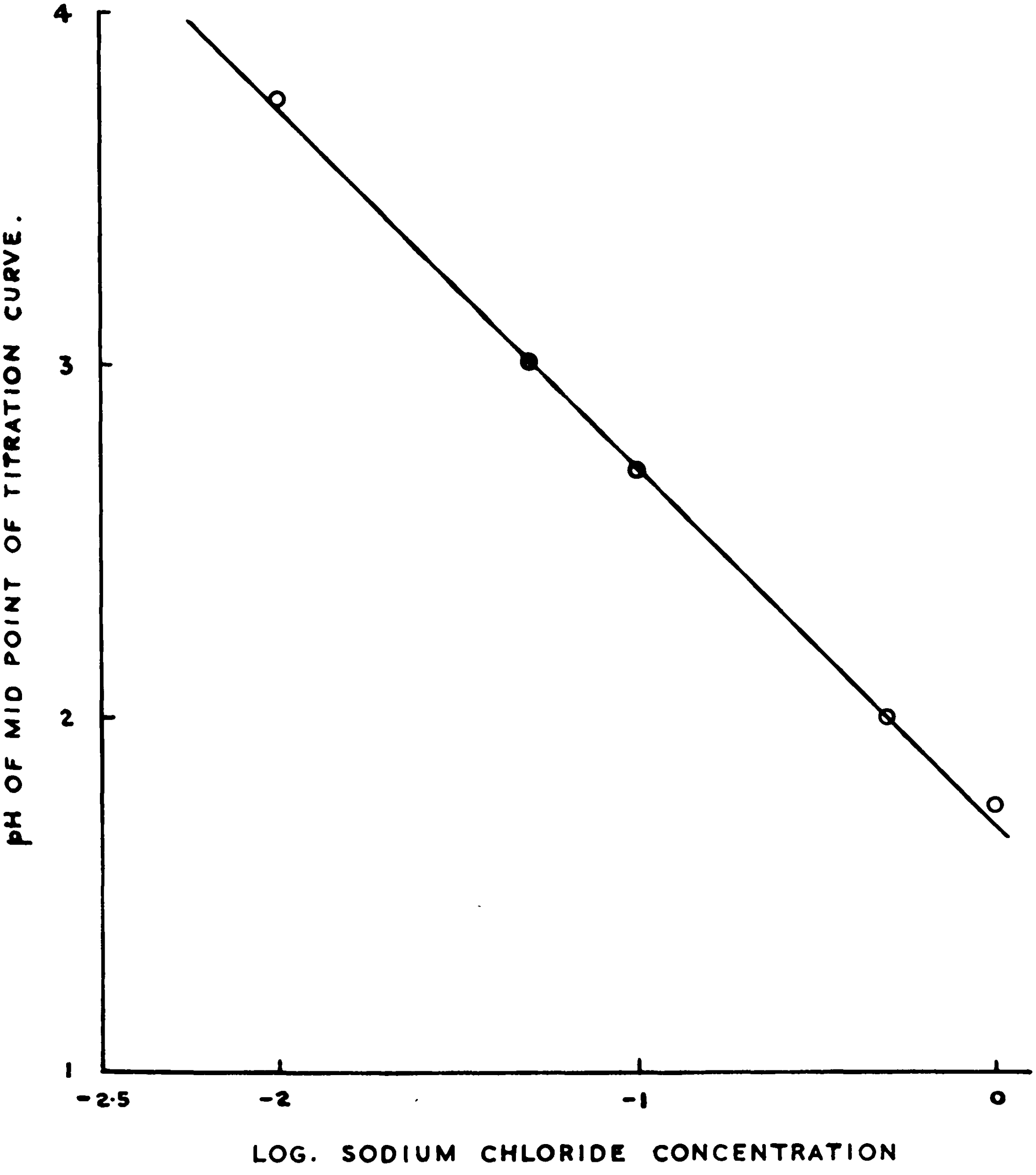
It may, therefore, be noted from the foregoing discussion that the base-binding capacity of the H-ion-exchanger is a function both of pH and the ionic strength of the solution.

Correlation of Experimental data with Griessbach's equation.

Griessbach (loc.cit.) formulated an equation, similar to the Jenny and Wiegner equation (loc.cit.), for the exchange equilibria of a hydrogen exchanger. According to him, if a hydrogen exchanger is gradually neutralized, as shown in equation I on page 212, in the presence of a small amount/

FIGURE 26.

GRAPH SHOWING RELATION BETWEEN pH OF MID-POINT AND LOG OF NaCl CONCENTRATION.



amount of a neutral salt, the pH of the resulting mixture at any instant of measurement, provided the equilibrium had been obtained, is given by the equation II:-

$$\underset{Y_1}{HA} + Na \rightleftharpoons \underset{Y_2}{NaA} + H \quad \ldots\ldots\ldots\ldots\ldots \text{I}$$

$$(Y_1 = Y - Y_2)$$

$$pH = \log\frac{1}{C} + \log\left(1 + \frac{k_2}{k_1}\left(\frac{Y_2}{Y_1}\right)^p\right) \ldots\ldots\ldots \text{II}$$

where Y = maximum exchange capacity, in equivalents hydrogen, of the exchanger, HA, at the start.

Y_2 = total number of equivalents exchanged by the exchanger at the instant of measurement

Y_1 = Un-exchanged equivalents hydrogen of the exchanger, HA, at equilibrium.

$\frac{k_2}{k_1}$ = Ratio of the apparent dissociation constants of the ion-exchanger salt, NaA, and the ion exchanger acid, HA.

p = constant (exponent)

C = concentration of the neutral salt present.

Theoretical values for pH calculated from the equation II with various values of exponent p, for various ratios of $\frac{k_2}{k_1}$ and for various loading ratios i.e. $\frac{Y_2}{Y}$ for 0·01N sodium chloride concentration are tabulated in

Table/

Table XXXIII on page 214/5 and presented in the form of theoretical curves for pH against loading ratio in figure 27 on page 216.

It may be noted from the figure 27 that the pH of the mid-point of a titration curve is independent of the exponent p. This fact can also be derived from the equation II mathematically as:- At mid-point $\frac{Y_2}{Y}$ is one half and hence $\frac{Y_2}{Y_1}$ equals unity. Thus substitution of value of unity for $\frac{Y_2}{Y_1}$ in the equation II shows that pH will be independent of value of p since unity raised to any power is unity.

As the values of pH for the mid-points of pH loading ratio-curves are independent of the values of p, so the theoretical values for pH for various loading ratios, $\frac{Y_2}{Y}$, and for various ratios of $\frac{k_2}{k_1}$ are calculated from the equation II for ·05, ·1, ·5 and 1N concentration of sodium chloride using the value of exponent, p, equal to 4 only (value of p equal to 4 is chosen because, as is shown later, the experimental pH-neutralization curves show a similarity in shape to the corresponding theoretical curves obtained with p equal to 4). These theoretical results have been tabulated in Tables XXXIV to XXXVII on pages 218 - 224 and presented in/

T A B L E XXXIII

Theoretical values of pH for different loading ratios in ·01N ionic strength of solution.

(calculated from Griessbach's equation on page 212)

Loading Ratio $\frac{Y_2}{Y}$ (percentage)	$\frac{Y_2}{Y_1}$	pH when p = 0·5 and $\frac{K_2}{K_1}$ is				pH when p=1 and $\frac{K_2}{K_1}$ is			
		·1	1	10	100	·1	1	10	100
10	0·111	2·01	2·12	2·64	3·53	2·00	2·05	2·32	3·08
20	0·25	2·02	2·18	2·78	3·71	2·01	2·10	2·54	3·42
30	0·43	2·03	2·20	2·88	3·82	2·02	2·16	2·72	3·63
40	0·666	2·03	2·26	2·96	3·92	2·03	2·22	2·88	3·83
50	1·00	2·04	2·30	3·04	4·00	2·04	2·30	3·04	4·00
60	1·50	2·05	2·35	3·12	4·10	2·06	2·40	3·20	4·18
70	2·333	2·06	2·40	3·21	4·19	2·09	2·52	3·39	4·37
80	4·0	2·08	2·48	3·32	4·30	2·15	2·70	3·61	4·60
90	9·0	2·11	2·60	3·49	4·48	2·28	3·00	3·96	4·95

(continued on next page)

TABLE XXXIII (CONTD.)

Theoretical values of pH for different ratios in ·01N ionic strength of solution.

(Calculated from Griessbach's equation on page 212)

Loading Ration $\frac{Y_2}{Y}$ (percentage)	$\frac{Y_2}{Y_1}$	pH when p= 2 and $\frac{K_2}{K_1}$ is				pH when p=4 and $\frac{K_2}{K_1}$			
		·1	1	10	100	·1	1	10	100
10	0·111	2·00	2·00	2·05	2·35	2·00	2·00	2·00	2·01
20	0·25	2·00	2·03	2·21	2·86	2·00	2·00	2·02	2·14
30	0·43	2·01	2·07	2·45	3·29	2·00	2·02	2·13	2·64
40	0·666	2·02	2·16	2·73	3·66	2·01	2·08	2·47	3·32
50	1·00	2·04	2·30	3·04	4·00	2·04	2·30	3·04	4·00
60	1·50	2·09	2·51	3·37	4·35	2·18	2·78	3·71	4·70
70	2·333	2·19	2·81	3·74	4·74	2·60	3·49	4·47	5·47
80	4·00	2·41	3·23	4·21	5·20	3·42	4·41	5·41	6·41
90	9·00	2·96	3·91	4·91	5·91	4·82	5·82	6·82	7·82

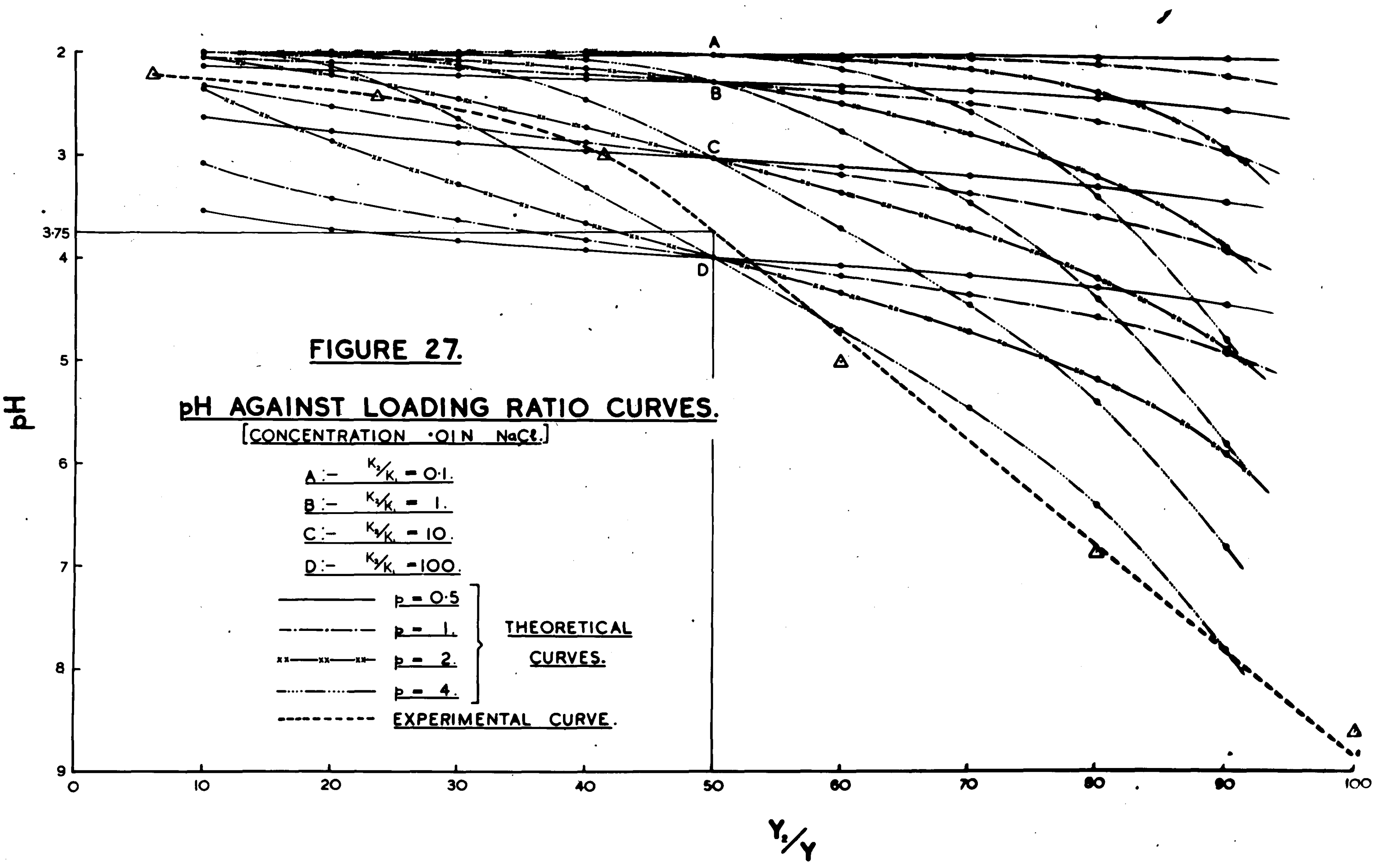


FIGURE 27.

pH AGAINST LOADING RATIO CURVES.

[CONCENTRATION ·01 N NaCl.]

in the form of theoretical curves for pH against loading ratio, $\frac{Y_2}{Y}$, in figures 28 to 31 on pages 219,221,223 & 225 respectively.

The experimental curves for the pH against loading ratio of the exchanger, for individual ionic strengths i.e. ·01, ·05, ·1, ·5 and 1N (constructed from the experimental data corresponding to each ionic strength in Tables XXII to XXVII on pages 171 - 176), have also been plotted in the respective figures along with the corresponding theoretical curves for comparison.

It may be noted from figure 27 (page 216 that the experimental curve for Zeo- Karb H.I. (in ·01N ionic strength) seems to be between the theoretical curves for value of $\frac{k_2}{k_1}$ between 10 and 100. It has very little similarity in shape to any of the curves with p=1. This is probably indicative of the fact that in Zeo- Karb H.I. exchange the simple Law of Mass action does not hold. The value of p seems to be about 4 as the experimental curve seems to be more like the theoretical curves with value of exponent, p, being 4.

Calculation of value of $\frac{k_2}{k_1}$

As the pH of the mid point of a pH - loading ratio curve is independent of the exponent, p, the numerical value of $\frac{k_2}{k_1}$ of an exchanger can be calculated by substituting the experimental value of pH for the mid-point in equation/

T A B L E XXXIV

Theoretical values of pH for different loading ratios in ·05N ionic strength of the solution.

(Calculated from Griessbach's equation : page 212)

Loading Ratio $\frac{Y_2}{Y}$ (percentage)	$\frac{Y_2}{Y_1}$	pH when p = 4 and $\frac{K_2}{K_1}$ is			
		·1	1	10	100
10	0·11	1·30	1·30	1·30	1·31
20	0·25	1·30	1·30	1·32	1·44
30	0·43	1·30	1·32	1·43	1·95
40	0·67	1·31	1·38	1·77	2·62
50	1·00	1·34	1·60	2·34	3·30
60	1·50	1·48	2·08	3·01	4·01
70	2·33	1·90	2·79	3·77	4·77
80	4·00	2·73	3·71	4·71	5·71
90	9·00	4·12	5·12	6·12	7·12

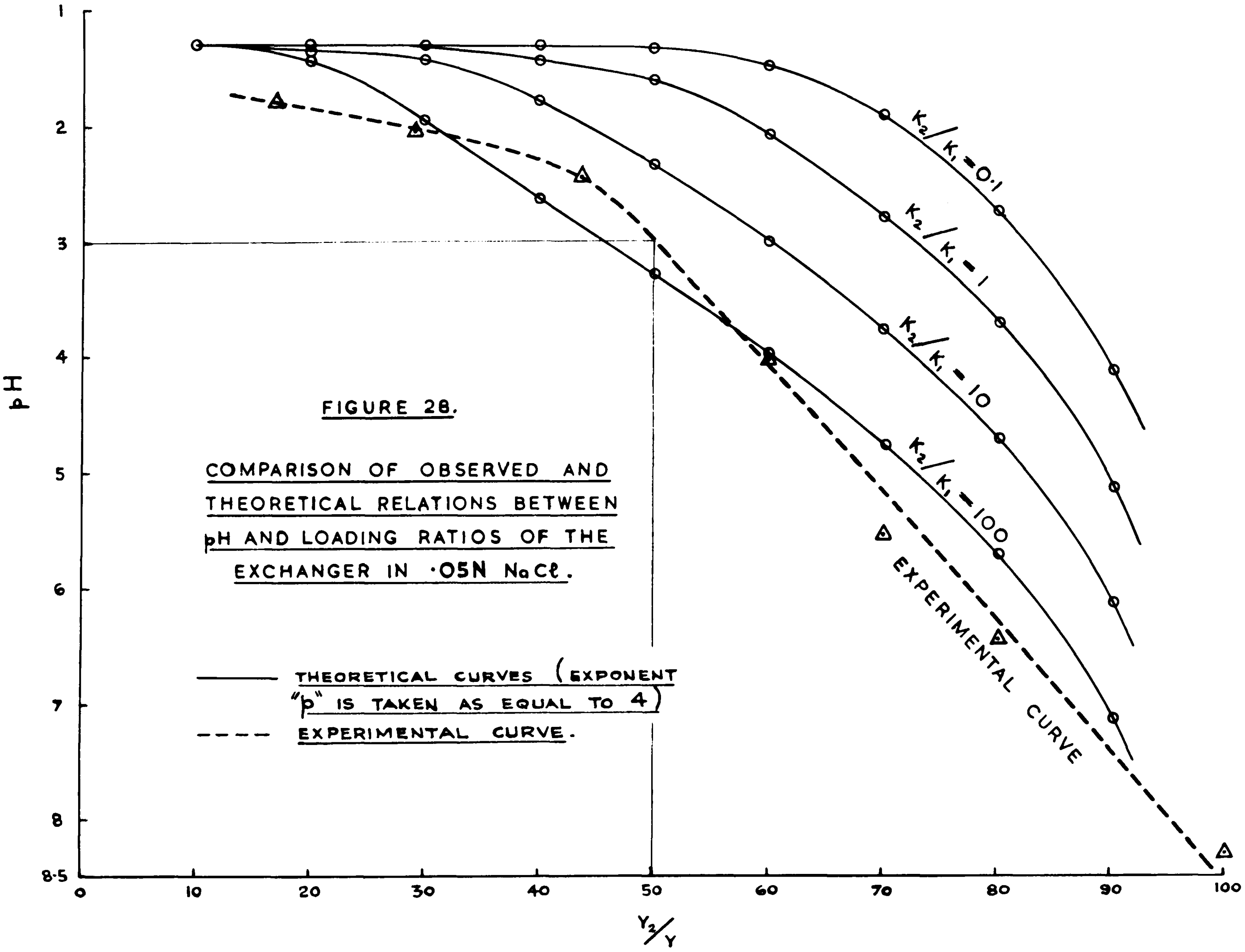


FIGURE 28.

COMPARISON OF OBSERVED AND THEORETICAL RELATIONS BETWEEN pH AND LOADING RATIOS OF THE EXCHANGER IN ·05N NaCl.

TABLE XXXV.

Theoretical values of pH for different loading ratios in •1N ionic strength of the solutio

(Calculated from Griessbach's equation : page 212)

Loading Ratio $\frac{Y_2}{Y}$ (percentage)	$\frac{Y_2}{Y_1}$	pH when p = 4 and $\frac{K_2}{K_1}$ is			
		•1	1	10	100
10	0•11	1•00	1•00	1•00	1•01
20	0•25	1•00	1•00	1•02	1•14
30	0•43	1•00	1•01	1•13	1•65
40	0•67	1•01	1•08	1•47	2•32
50	1•00	1•04	1•30	2•04	3•00
60	1•50	1•18	1•78	2•71	3•71
70	2•33	1•60	2•49	3•47	4•47
80	4•00	2•43	3•41	4•41	5•41
90	9•00	3•82	4•82	5•82	6•82

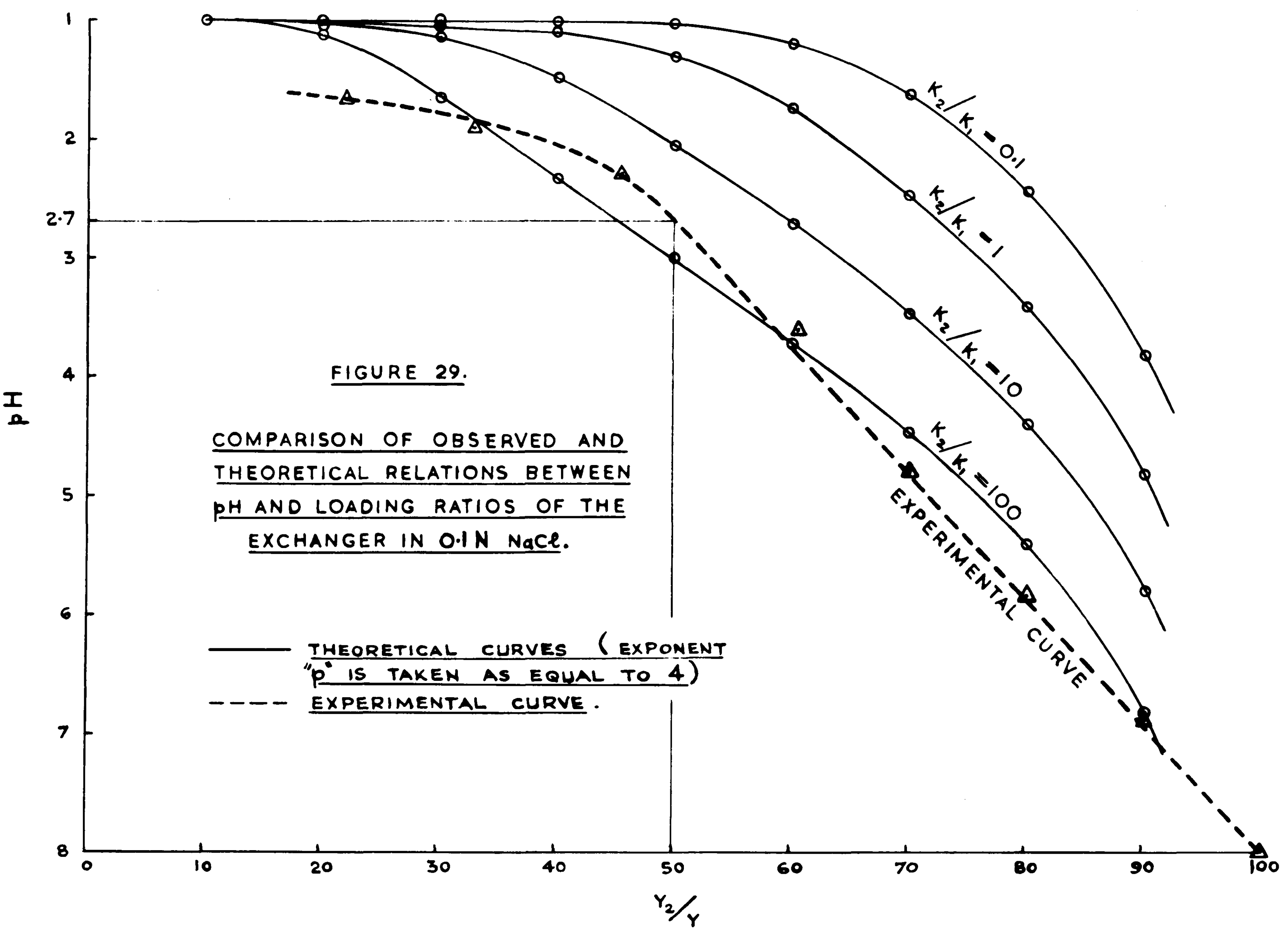


FIGURE 29.

COMPARISON OF OBSERVED AND THEORETICAL RELATIONS BETWEEN pH AND LOADING RATIOS OF THE EXCHANGER IN 0·1 N NaCl.

TABLE XXXVI

Theoretical values of pH for different loading ratios in ·5N ionic strength of the soluti

(Calculated from Griessbach's equation : page 212)

Loading Ratio $\frac{Y_2}{Y}$ (percentage)	$\frac{Y_2}{Y_1}$	pH when p = 4 and $\frac{K_2}{K_1}$ is			
		·1	1	10	100
10	0·11	0·30	0·30	0·30	0·31
20	0·25	0·30	0·30	0·32	0·44
30	0·43	0·30	0·32	0·43	0·95
40	0·67	0·31	0·38	0·77	1·62
50	1·00	0·34	0·60	1·34	2·31
60	1·50	0·48	1·08	2·01	3·01
70	2·33	0·90	1·79	2·77	3·77
80	4·00	1·73	2·71	3·71	4·71
90	9·00	3·12	4·12	5·12	6·12

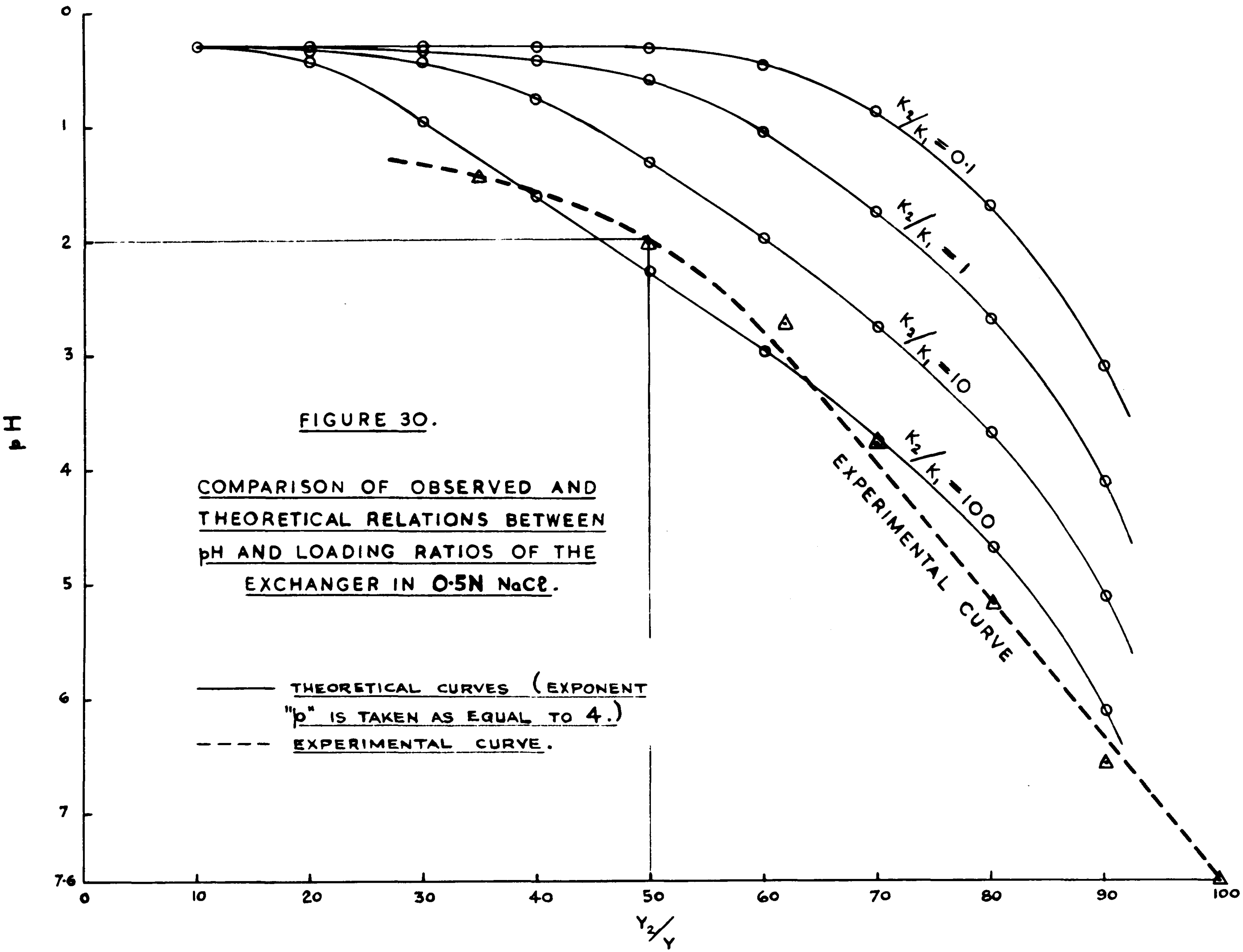


FIGURE 30.

COMPARISON OF OBSERVED AND THEORETICAL RELATIONS BETWEEN pH AND LOADING RATIOS OF THE EXCHANGER IN 0·5N NaCl.

TABLE XXXVII

Theoretical values of pH for different loading ratios in 1N ionic strength of the solution

(Calculated from Griessbach's equation : page 212)

Loading Ratio $\frac{Y_2}{Y}$ (percentage)	$\frac{Y_2}{Y_1}$	pH when p = 4 and $\frac{K_2}{K_1}$ is			
		·1	1	10	100
10	0·11	0·00	0·00	0·00	0·01
20	0·25	0·00	0·00	0·02	0·14
30	0·43	0·00	0·02	0·13	0·65
40	0·67	0·01	0·08	0·47	1·32
50	1·00	0·04	0·30	1·04	2·00
60	1·50	0·18	0·78	1·71	2·71
70	2·33	0·60	1·49	2·47	3·47
80	4·0	1·43	2·41	3·41	4·41
90	9·0	2·82	3·82	4·82	5·82

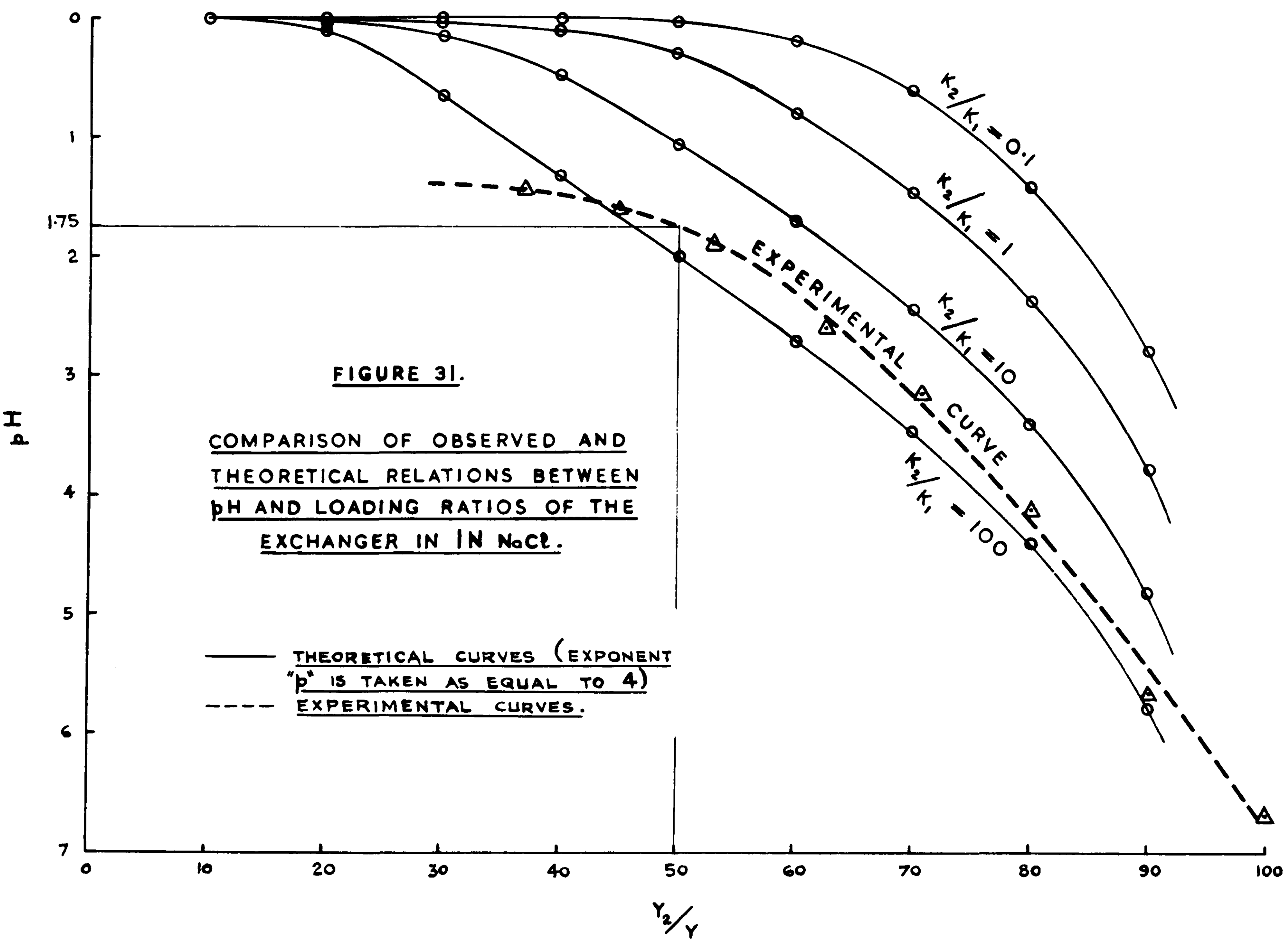


FIGURE 31.

COMPARISON OF OBSERVED AND THEORETICAL RELATIONS BETWEEN pH AND LOADING RATIOS OF THE EXCHANGER IN 1N NaCl.

equation II (page 212). Thus in this way the value of $\frac{k_2}{k_1}$ for Zeo-Karb H.I., when the neutralization is done in presence of ·01N sodium chloride solution, is calculated and is included in Table XXXVIII on page 228. The experimental value of pH for mid-point was obtained from the corresponding experimental curve in figure 27 (page 216)

Effect of ionic strength.

A study of the experimental pH-loading ratio curves of the exchanger for ·05, ·1, ·5 and 1N ionic strengths along with the corresponding theoretical curves (which have incidentally been drawn only for value of p = 4) in figures 28 to 31 on pages 219, 221, 223, 225, suffices to show that the foregoing observations in the study of the experimental curve for ·01N ionic strength and corresponding theoretical curves, hold good in all these cases also viz. the experimental curves lie between the theoretical curves for values of $\frac{k_2}{k_1}$ between 10 and 100. In all these figures it is obvious that the experimental titration curves for different ionic strengths also show a similarity (like the experimental curve for 0·01 N) to the theoretical curves with p = 4. It may be noted, however, that with increase in ionic strength, the value of p decreases, though, slightly. It will be noted that change in the value of p is more perceptible in/

in the case of the experimental curve for 1N ionic strength.

As in the case of ·01N ionic strength, the values of $\frac{k_2}{k_1}$ for Zeo-Karb H.I. have been calculated from the pH for mid-points of the corresponding experimental titration curves when the neutralisation was done in different ionic strengths i.e. ·05, ·1, ·5 and 1N. The results, tabulated in Table XXXVIII on page 228, show that the value of $\frac{k_2}{k_1}$, within limits of experimental error, does not change when the ionic strength of the solution, in which the neutralization is carried, is changed from ·01 to 1N. The value of $\frac{k_2}{k_1}$ for Zeo-Karb H.I. as found by this method, is of the order of 50.

Effect of ionic strength on pH of the mid-point.

It has been discussed on pages 208 - 210 and shown in figure 26 on page 211 that the pH at which half of the maximum combination occurs, i.e. the mid point systematically becomes lower with increase in the ionic strength, the distance (with respect to pH) between any two adjacent mid points being nearly equal to the logarithm of the ratio of the ionic concentration which the two mid-points represent. This fact is also brought out from Griessbach's equation mathematically as shown:-

pH value/

TABLE XXXVIII

Effect of ionic concentrations on value of $\frac{K_2}{K_1}$ for Zeo-Karb H.I.

Ionic Strength (normality of NaCl)	pH of mid-point	$\frac{K_2}{K_1}$
0·01	3·75	55·2
0·05	3·00	49·0
0·10	2·70	49·1
0·50	2·00	49·0
1·00	1·75	55·2

pH value of the mid point at two ionic strengths C_1 and C_2 will be given as

$$pH = A = \log \frac{1}{C_1} + \log \left(1 + \frac{k_2}{k_1}\right)$$

$$pH = B = \log \frac{1}{C_2} + \log \left(1 + \frac{k_2}{k_1}\right)$$

If $\frac{K_2}{K_1}$ is same in both the cases; this is the case with Zeo-Karb. H.I. from .01N - 1N NaCl strength (Refer page 228)

(at mid point $\frac{Y_2}{Y_1} = 1$ hence $\left(\frac{Y_2}{Y_1}\right)^p = 1$)

so the difference in pH at two concentrations is

$$A - B = \log \frac{1}{C_1} - \log \frac{1}{C_2}$$

$$= \log \frac{C_2}{C_1}$$

The experiment results in figure 26 seem, therefore, to fairly fit the Griessbach's equation.

III Anodizing of aluminium as catalysed by sulphonated coal.

During the electrolytic process of anodizing of aluminium, as described on page 179, the oxygen produced at the anode by the passage of the current through the solution, being in the nascent form, attacks the metal surface and begins to give a coating of aluminium oxide. This oxide film becomes a part of the circuit and allows the electrolyte and hence the anodizing current and oxygen ions to flow through it because of its porous nature. It may be observed, however, that as the process continues, the film goes on becoming thicker and thicker and does increase the resistance thus decreasing the current flowing through it. This, in turn, decreases the rate of film growth as the current is rather an important factor in anodizing of aluminium.(80) While this anodic oxidation is proceeding, the outer films of the oxide are being dissolved by the sulphuric acid. Therefore as the rate of the film growth decreases as the current decreases due to increase in the resistance because of growth of oxide film, a point may be reached at which the growth of the film is exactly balanced by solution of the film at the surface. This point, probably, establishes the maximum thickness of oxide which may be produced in a particular bath for a specific set of conditions. This fact is very obvious if figure 24 (page 186) is/

is considered where amount of oxide film formed is plotted against the time of anodizing under the two conditions, i.e. with and without the exchanger. It may be noted from this figure that in both the cases the amount of oxide film increases quite steeply at first but after about one hour tends to become constant, becoming completely so after about 2 hours.

Catalysing effect of sulphonated coal.

A significant point is brought out by the consideration of the figure 24 (page 188) that at any instant of measurement, the amount of oxide film formed, in the presence of sulphonated coal is more than formed without it. This is probably due to the fact that the conductance of the electrolytic bath is increased because of contribution of H-ions by the sulphonated coal thus increasing the current which is an important factor in the amount of oxide film formed.(80). Besides, this increased conductance is obtained with no dissolving action on oxide film by the sulphonated coal. Similarly a consideration of the figure 23 (page 186) where the effect of concentration of sulphuric acid with and without sulphonated coal is plotted against the oxide-film formed, also shows that at any concentration of sulphuric acid, the amount of oxide formed with the sulphonated coal is more than without it and may be explained in the same way. It may be noted/

noted, however, that as the concentration of the sulphuric acid increases, the amount of oxide formed, in both cases, decreases probably due to the fact that amount of oxide dissolved is more. But it is believed that the quality of the oxide film, obtained at higher concentrations of sulphuric acid, is better for dyeing purposes. It will be noted, however, that the catalytic effect becomes comparatively less in higher concentrations of sulphuric acid probably due to progressive suppression of ionization of this insoluble acidoid by increasing concentrations of sulphuric acid.

It may be mentioned at this stage that the oxide deposited on the two square inch piece of aluminium foil was done in duplicate in all cases and was found to be easily reproduceable. Consequently it has been assumed in all these determinations that active surface area on these anodized strips was fairly constant.

Thus it is obvious that the presence of sulphonated coal catalyses the anodizing of aluminium. This effect is quite significant as may be noticed from Table XXXIX given on page 233. These values have been calculated from figure 24 on page 188.

It/

TABLE XXXIX

Amount of oxide formed. m.gms/ 2"x1" strip of anodized aluminium.	Time in minutes required to form this amount of oxide on 2"x1" strip of anodized aluminium.		Percentage time saved.
	without sulphonated coal.	with sulphonated coal.	
10	18	16	22·2
20	35	27	22·9
30	51	42	17·6
40	75	58	22·7
50	135	84	37·8

It may be noticed from Table XXXIX that a saving of man hour from about 20% to about 40% could be affected depending upon the amount of oxide (the total amount of oxide required to be formed is governed by the subsequent use for which the anodized metal is intended) to be deposited on the metal. And although the amount of oxide formed is not always a criteria for good dyeing properties it is a good index for anti-corrosive properties of aluminium. This fact of the saving of man-hour becomes all the more important because, as is obvious from table XXX on page 189, where the effect of different concentration of sulphonated coal on anodizing is shown, even a very small amount of sulphonated coal, in fact practically in traces, i.e. 0·25% (5 grams in 2 litre) yields the same catalysed effect as 2·5%. So the cost incurred by way of addition of sulphonated coal is negligibly small compared to saving in time.

Quality of anodized film as produced by sulphonated coal.

As already stated the quantity of oxide-film produced by anodizing in presence of sulphonated coal is significantly more, so next step was to determine its quality as applied to dyeing. Since dyeing of anodized aluminium is a function of the absorption power of the film besides the quantity, it was expected to get a higher absorption of dyes by the anodized aluminium which were prepared by using carbonaceous exchanger if the film was of required quality. This expectation is completely borne out by the experimental results, given in table XXXI on page 193 and figures 25A and 25B (page 194) It may be noted, thus, that the maximum absorption of dye is about 4% higher in case of Solway Blue BNS and about 77% higher in case of Azo-Geranine 2 GS compared to 14% increase (refer Table XXIX on page 187) in the oxide film obtained by anodizing at one hour at 25°C - since these strips were used for dyeing. Whereas it establishes the good quality of the film, such a great difference in the increase in the dyeing with Solway Blue BNS and Azo-Geranin 2GS may be due to difference in the mechanism of dyeing of the two dyes. It may, however, be also due to the difference in particle size of the two dyes. Thus it may be the size of Azo-Geranin 2GS molecules is big for the size of the pores of the film produced without sulphonated coal and it has hindrance in getting through these pores which might have now been removed due to, possibly increased porosity caused by the catalytic effect of sulphonated coal; while small increase in the absorption of Solway Blue BNS may be due to small increase in the quantity of oxide-film only, as its molecules might be small enough to pass through the pores in the previous film.

An/

An interesting fact that may be noted from the figures 25A and 25B (page 194) is that in the case of both the dyes the time required for maximum absorption (after this the desorption begins as is obvious from the figure), is cut down to 16 hours compared to 32 hours required in case of Solway BNS and 48 hours in case of Azo-Geranine 2GS. Since it is well-known that the process of dyeing is a function of particle size of the dye, more porous is the anodic film (as probably it is when sulphonated coal is used), easier it is for the dye molecules to move freely into the film and get fixed quickly, thus reducing the time required for maximum absorption.

Thus it may be mentioned here that the use of sulphonated coal as a catalyst in the manufacture of anodized aluminium for dyeing purposes offers not only the advantage of more maximum dye absorption but also a saving in time of the order of 33% to attain the same. In practice, however, the material is never dyed to a stage of maximum dye absorption, yet it will be noted from the curves in figures 25A and 25B that whatever duration of time may be used to dye the material to a particular shade, the one prepared with the use of sulphonated coal gives a significant saving in time which may also be of the same order.

SECTION 4.

SUMMARY and CONCLUSIONS.

A study of the action of sulphuric acid of oleum strength on coal has been made with respect to the ion-exchange properties introduced in this so called sulphonated coal. An apparatus and procedure for sulphonating the coal under any desired conditions and the subsequent isolation of the sulphonated coal has been described. Ensminger's method (loc.cit.) of determining the base-exchange capacity of the soils was adopted with minor modifications for the determination of the base-exchange capacity of the products prepared during this investigation.

Some of the factors which affect both the rate and the degree of the sulphonation re-action, which in turn affect the ion exchange properties of the resulting product, have been studied. It has been shown, thus, that an increase in the temperature and time of reaction results in a steep rise in the ion-exchange capacity of the resulting product up to 100°C and 1 hour respectively. From 100-120°C and 1-3 hour the rise in the exchange capacity tends to become less and less steep and ultimately becomes nearly constant at about 120°C and 3-4 hours respectively. A saturation stage of sulphonation of coal is reached at which stage either such groups are being introduced which do not manifest/

manifest themselves in the ion-exchange phenomenon or the innermost regions of the coal particles are being sulphonated which do not or cannot contribute to the ion-exchange properties - this being essentially a surface phenomenon. It has also been shown that an increase in the concentration of SO_3 in oleum results in gradual rise in the exchange capacity of the corresponding product up to about 8% of SO_3, probably due to its acting mainly as a dehydrating agent. Oleum of strength between 8-16% SO_3 gives a steeper rise in the exchange properties of the resulting product at which strength it is not only obviating the decelerating action of water but also takes an active part in the sulphonation. Again a saturation stage is reached at about 20% SO_3 oleum. It has been found that to get a material of optimum exchange capacity with the coal being used, sulphonation must be carried with 20% SO_3 oleum at 110-120°C for 3-4 hours.

A study of the effect of approximately hundred per cent nitric acid - oleum (20% SO_3) mixture on the exchange properties of the resulting sulphonated coal is described. It shows that 7% nitric acid gives the product of optimum exchange capacity of 212·4 m.e./100 gms which represents an increase of about 41% on the exchange capacity of the product prepared with oleum (20% SO_3) alone. This is probably/

probably due to introduction of -COOH groups along with usual sulphonic acid groups which are believed to be introduced by sulphonation. Use of more than 7% HNO3 results in a decrease in the exchange capacity of the product - probably due to degradation of coal structure.

Study of the Titration Curves of H-ion-exchangers.

This was undertaken with a view to characterizing the H-ion-exchangers. In the method of studying the pH neutralization curves which is described on page 152, it is shown that it took 12 hours for equilibrium to be reached between exchanger and alkali. The titration curves of two samples of sulphonated coals have been studied (in the absence of any salt in solution) and it has been shown that although this showed that H-ion-exchanger behave like soluble acids, ~~but~~ the study did not offer sufficient data for charasterization.

In view of the fact that the base binding capacity of wool is a function of the pH and the ionic strength in which its neutralization is carried (69), the pH neutralization curves of Zeo-Karb H.I. were studied in the presence of different concentrations of NaCl. It has been shown there that the base bound at pH/2·8 increases 5 fold and 9 fold the amount bound in the absence of salt, when sufficient NaCl/

NaCl is added to bring the ionic strength to ·01N and 1 N respectively. This factor becomes smaller as the pH is increased. It is further shown that distance (with respect to pH) between any two mid-points (i.e. point at which 50% base is bound) is nearly equal to the logarithm of the ratio of the ionic concentration which the mid-points represent. Thus the base-binding capacity of the exchanger is a function of pH and the ionic strength of the solution in which the neutralization is carried.

Correlation of the experimental data with Griessbach's equation (loc.cit.) shows that these observations can be explained on this theoretical equation and that the base-binding capacity should be a function of the ionic strength and pH. It has been further shown that the value of $\frac{K_2}{K_1}$ for the exchanger Zeo-Karb H.I.

$$HA + Na \rightleftharpoons NaA + H$$

i.e. ratio of apparent dissociation constants of the ion-exchanger salt, NaA, and the ion-exchanger acid, H A, is of the order of 50 and is not affected by change of the ionic strength of the solution, in which titration is done, from ·01 to 1N. The value of p, the adsorption exponent (refer page 226) is shown to be nearer 4 as found by comparing the experimental/

experimental titration curves with the theoretical curves as obtained from Griessbach's equation. This is slightly affected by change in ionic strength as can be judged by the graphical representation of these curves (pages 216-225). The decrease in the value is more perceptible in the case of titration curve for 1N ionic strength.

Application of H-ion-exchangers to the anodizing of aluminium.

A possible application of the H-ion-exchanger - the insoluble acidoids - to the anodizing of aluminium has been studied. A method of anodizing in the presence of H-ion-exchangers has been described. It has been shown therein that the quantity of the Al_2O_3 formed under any conditions of anodizing is more when H-ion-exchanger is used than without it - probably due to the fact that the conductance of the electrolytic bath is increased because of the contribution of H-ions by the sulphonated coal, thus increasing the current which is a vital factor in the amount of oxide film formed. Besides this increased conductance is obtained with no dissolving action on oxide film by sulphonated coal.

It is seen that a saving of time from 20 - 40% could be affected by using sulphonated coal depending upon the amount of oxide to be deposited. This saving in time/

time is very significant as the presence in the electrolyte of 0·25% of the exchanger, the cost of which is very small, is sufficient to show above effects. Since the quantity required is so small, it need not be regenerated when the electrolyte is replenished but fresh exchanger my be economically added.

It has been further shown that the quality of the oxide film as applied to dyeing of anodized aluminium is even better than one obtained without use of H-ion-exchanger, because the maximum absorption of dye in the case of azo-Geranine 2 GS increased by 77% over that obtained without the use of exchanger. Another interesting fact is shown that whatever duration of time is used to dye an anodized aluminium to a particular shade, a saving in the time of dyeing of the order of 33% is affected, in case of the one anodized in the presence of sulphonated coal. The results obtained, therefore, are very encouraging.

* 1

APPENDIX I

Description of Thermistor[2] and experimental procedure of its application to the determination of the molecular weight of the substance (isolated by action of nitric acid on coal).

The Thermistor.

The thermistor is a resistance body with a large negative temperature coefficient of resistance and is made of complex oxides by firing at high temperature. Due to its method of production and firing at high temperature it remains unaffected in service up to temperatures up to 500°C. The resistance R of the element at any temperature T (°K) is governed by the following equation

$$R = a e^{\frac{b}{T}}$$

where/

---

* Refer page 49.

[1] A paper with the title "The Application of a Thermistor to the determination of the molecular weight of Humic Acids" has since been accepted for publication in the Journal of the Royal Technical College - still in press.

[2] This instrument has recently been developed by Standard Telephones and Cables Ltd., Footscray, Kent.

where a and b are constants. This shows that conductance of the material increases rapidly with increasing temperature. The thermistor element is free from polarisation and other disturbing factors since conduction in the materials used in its making is purely electronic. The fact that each element is claimed to have stable and reproduceable characteristics render it eminently suitable for the accurate measurement of small temperature changes over a wide temperature range.

Several forms of the resistance elements with different characteristics are available. Type F was chosen for this investigation as it had a safe maximum operating temperature of 300°C and its resistance varied from about 2000 ohms at 20°C to approximately 10 ohms at 300°C. Its general arrangement is shown in fig. 32 on page 245. It consists of a small oxide bead incorporated in the seal-off tip of a glass tube; the resistance element is therefore protected against the chemical action of gases or liquids while in use. The bead is about 0·02 inches in diameter and is integrally formed on two parallel platinum wires which, in turn, are welded to two cunife leads and the whole sealed in a thin glass tube after evacuation. The weight of the whole assembly is less than two grams.

The circuit used is shown in fig. 33

on/

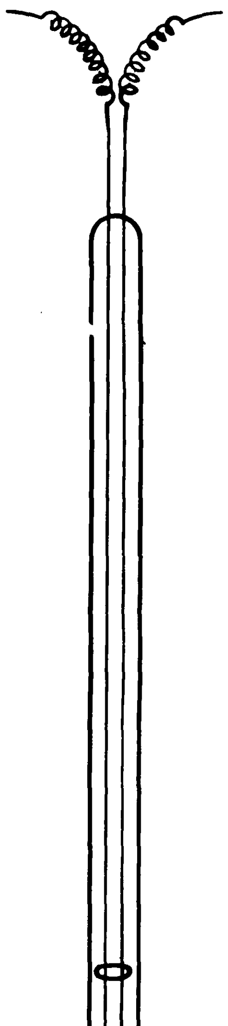


FIGURE 32.

THERMISTOR.

on page 247. The thermistor was mounted in one arm of a bridge network, the out of balance voltage of which was fed into a D.C. amplifier recommended by the makers. A moving coil instrument was used to indicate the out-put of the amplifier. The operating conditions and the zero of the meter were adjusted by (a) a variable resistance R_1 in the bridge circuit and (b) a variable potentiometer R_2 connected across the H.T. voltage supply.

Calibration of the Thermistor.

As is obvious, the instrument had to be calibrated and it was done by measuring its resistance at a number of temperatures ranging from -40°C to 90°C using a lo power Wheatstone bridge. The results obtained are presented in fig. 34 on page 248 in which $\log_{10} R$ is plotted against $\frac{1}{T} \times 10^3$, R being the resistance of the Thermistor in ohms at any temperature $T^{\circ}K$. Evidently the relation between R and T is a linear one and may be expressed by the following equatio

$$R = a\, e^{\frac{b}{T}} \quad .... \quad I$$

From the experimental graph (fig.34), the values of constants were found to be $a = 0{\cdot}026$ and $b = 3340$. By differentiation, the rate of change of resistance with temperature may be found to be:-

$\frac{dR}{dT}$ /

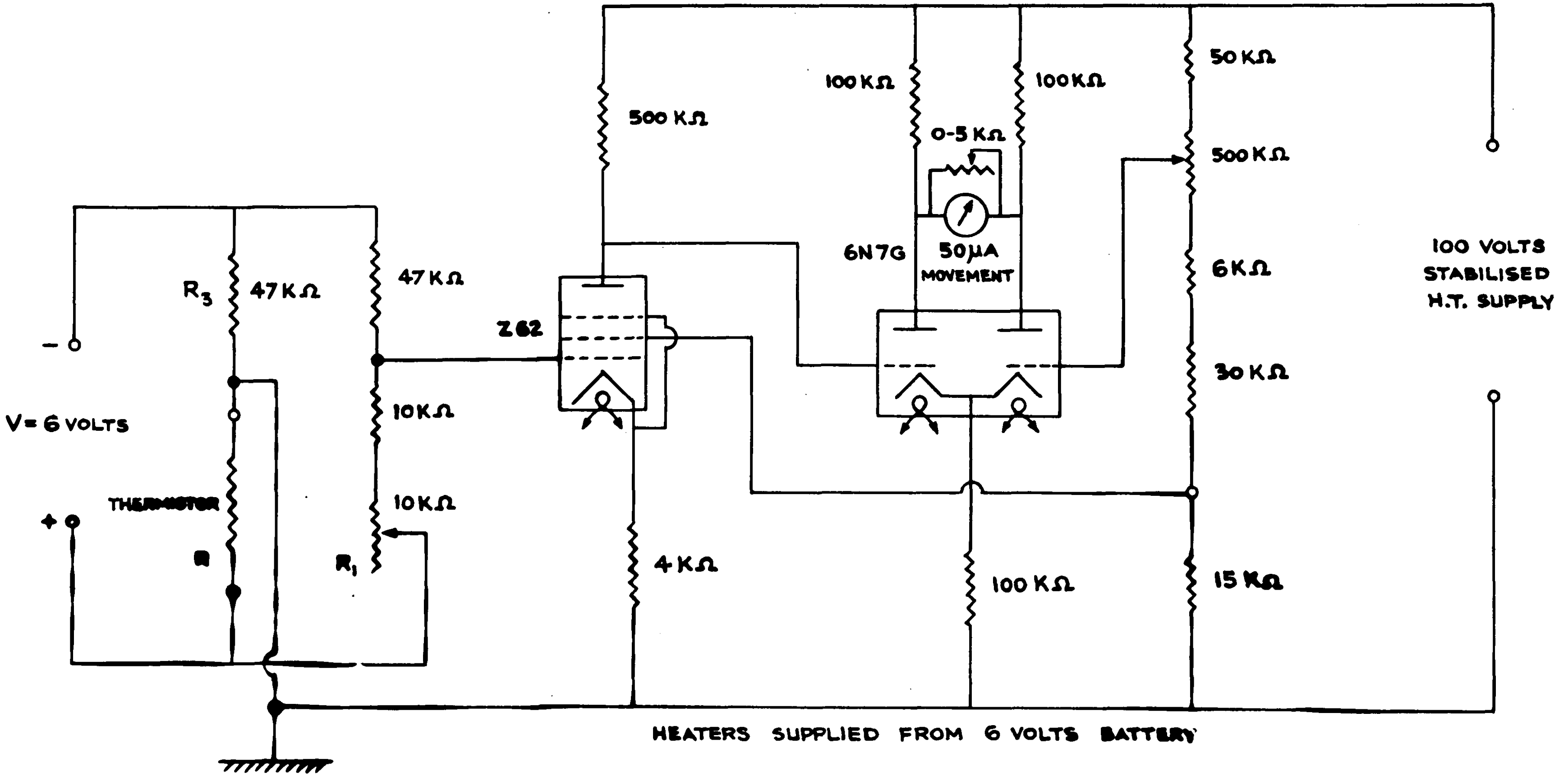


FIGURE 33.

ELECTRICAL CIRCUIT FOR USE WITH THERMISTOR.

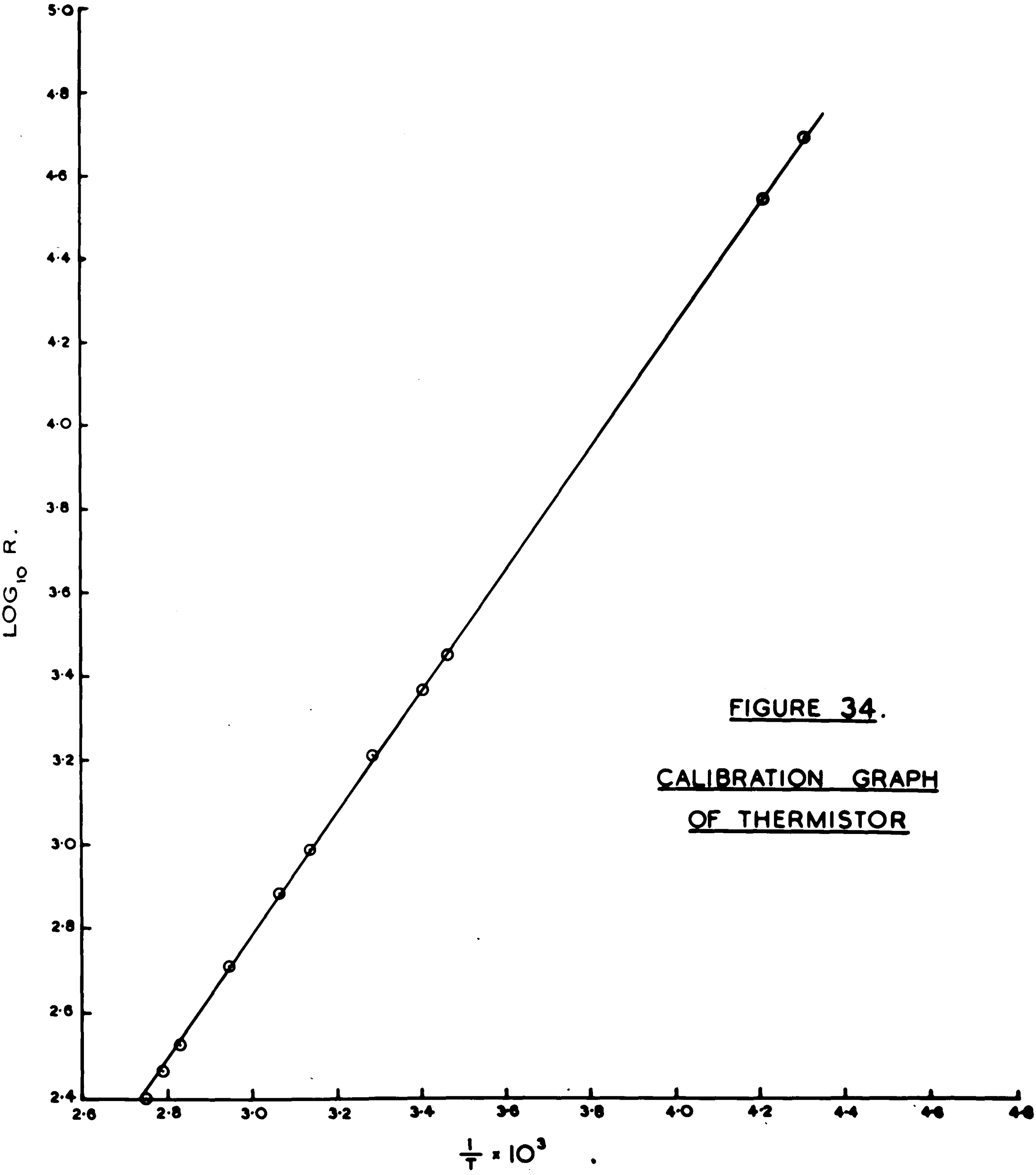


FIGURE 34.

CALIBRATION GRAPH OF THERMISTOR

$$\frac{dR}{dT} = - a \frac{b}{T^2} e^{b/T}$$

$$= - \frac{b}{T^2} R \qquad \ldots\ldots\ldots\ldots \quad \text{II}$$

The rate of change of the out of balance voltage, v, with R can also be determined since

$$v = \frac{V R_3}{R + R_3} + K$$

where V is the supply voltage to the bridge, R_3 is fixed resistance in the bridge circuit and K is a constant. Then

$$\frac{dv}{dR} = \frac{- V R_3}{(R + R_3)^2} \qquad \ldots\ldots\ldots\ldots \quad \text{III}$$

and $$\frac{dv}{dT} = \frac{dR}{dT} \times \frac{dv}{dR}$$

$$= \frac{b}{T^2} \times R \times \frac{V R_3}{(R + R_3)^2} \qquad \ldots\ldots\ldots\ldots \quad \text{IV}$$

$\frac{dv}{dT}$ can therefore be evaluated at any temperature T.

The relationship between the input voltage to the amplifier and the indication on the meter connected to the output was determined as follows:-

Scale readings corresponding to the

freezing/

freezing points of the pure solvent and solvent with the solute were determined during the preliminary stages of an experiment in a manner described later. The difference between these two scale readings then corresponded to the depression in the freezing point of the solvent caused by the presence of solute. The thermistor was then disconnected from the circuit and a calibrating voltage was applied which gave nearly the original deflection. The deflection previously obtained was reproduced by altering the voltage, and the difference in applied voltage necessary to accomplish this was recorded. The relationship between the deflection and the voltage necessary to produce it under the conditions of the experiment was then easily obtained. The amplifier was calibrated before and after each experiment in order to reduce or eliminate the effect of drift and non-linearity.

Experimental Procedure:-

Cryoscopic measurements were made in the apparatus shown in figure 35 on page 251. A wide-mouthed test-tube (diameter 2·5"), A, was supported in a 2 litre tall pyrex beaker through an aluminium lid. The annular space was filled with powdered solid carbon dioxide to form a cooling bath. This whole freezing point assembly was lagged with powdered cork. A large cork fitted in the mouth of the test-tube, carried/

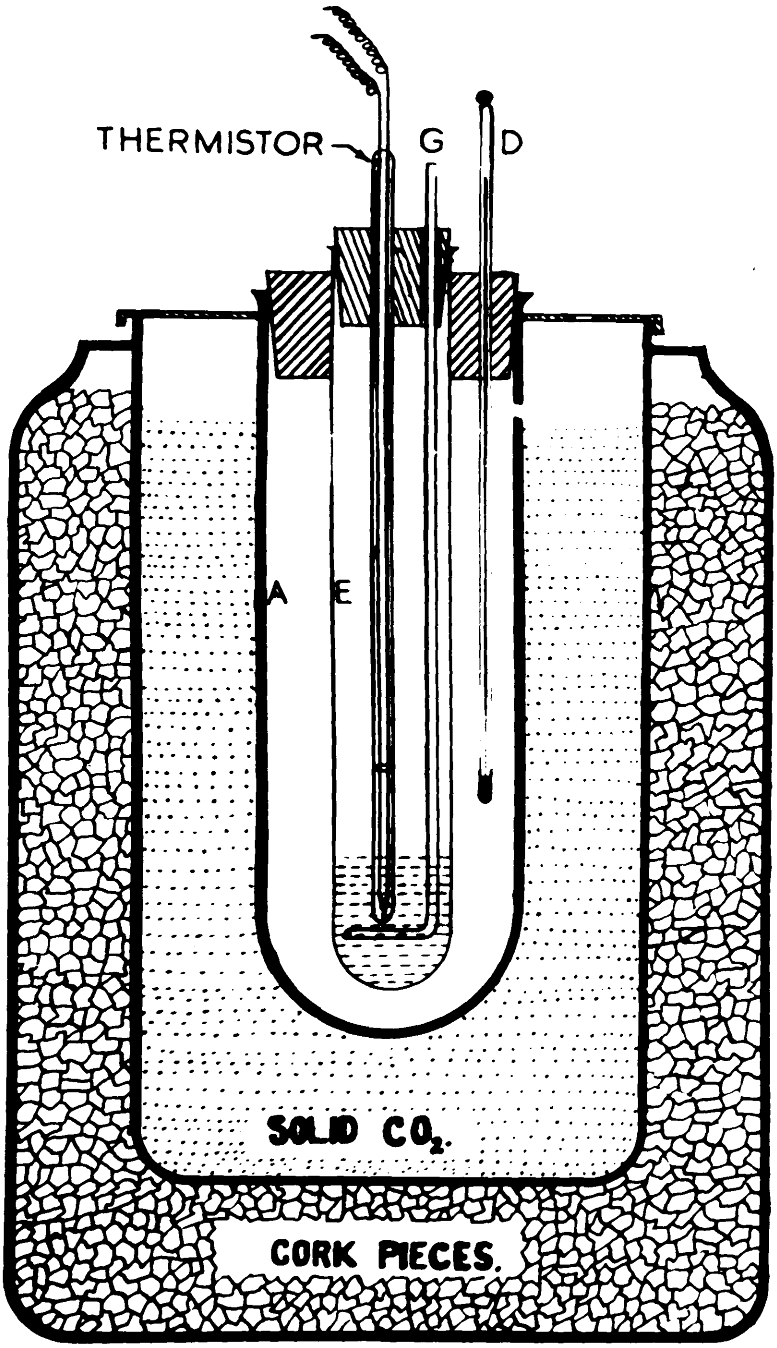


FIGURE 35.

MOLECULAR WEIGHT DETERMINATION APPARATUS USING THERMISTOR.

carried an alcohol thermometer, D, to indicate the temperature of the air-bath, A, and the standard 15 m.m, test-tube, E, which contained the cryoscopic solvent. The thermistor and a stirrer, G, were fitted through a rubber stopper in the mouth of the smaller test tube, E.

Analar solvent, in suitable quantity was introduced into the bottom of the smaller test-tube, care being taken that none adhered to the sides of the tube. Stirrer, G, and the thermistor were then fixed in position. In the meantime a standard resistance approximately equal to that of the thermistor element at the freezing point of the solvent replaced the thermistor in the electrical circuit; the resistance of the element at any temperature was obtained from the temperature - resistance characteristics of the thermistor, shown in fig. 34. The needle of the microammeter was brought on the scale by adjusting the variable resistance R_1, so that when the thermistor was introduced in place of the standard resistance, the needle would indicate a deflection within the scale at the freezing point of the solvent. At the freezing when the conditions became steady, the thermistor being in the circuit, final adjustments were made to the controlling resistance R_2 to maintain the needle reading at 45 divisions (± 1 division) at the freezing point.

After the initial conditions had been satisfactorily maintained, the solvent was warmed by exposure to room temperature. The test-tube, containing the solvent was then fitted into the air-bath, A, the temperature of which was a few degrees below the freezing point of solvent. The needle of the microammeter moved below the zero of the scale, as the solvent supercooled but immediately returned when the solvent solidified. This reading was taken as corresponding to the freezing point of the solvent. Determinations, which were carried in duplicate, were reproduceable to one scale division.

In the meantime another 15 mm. diameter test-tube containing a weighed quantity of the solvent had been made ready and a weighed amount of the substance under investigation introduced. In order to counteract any effect of re-melting on the freezing point of solvent, the contents of this test-tube were subjected to the same number of cycles of melting and freezing as the solvent alone.

After removing the thermistor and stirrer from the freezing point tube, washing with acetone and drying (this required about two minutes only), these were introduced into the other test-tube containing the solvent-solute mixture. The freezing point of the mixture was determined in exactly the/

the same manner as stated above and the relevant scale reading noted. Results of the duplicate experiments agreed within one division on the scale.

The freezing point of the pure solvent was again made in duplicate and mean of the readings were taken to be representing the true freezing point. This was done to compensate for the slight drift in the needle of the microammeter. The difference in the scale readings for the freezing point with and without the solute then corresponded to the depression in the freezing point of the solvent caused by the presence of the substance under investigation. After converting this difference in the two readings into centigrade degrees, the molecular weight of the substance under investigation was calculated by using the standard cryoscopic formula.

Results:-

Method of calculation of the depression in freezing point.

The method of calculation of the freezing point depression from the above two scale readings is illustrated by taking the results of one of the experiments as:-

Solvent used = Pyridine

Melting Point = - 42°C (231°K)

R = /

$$R = a\,e^{b/T}$$ (equation I on page 246)

$$= 0{\cdot}026e^{3340/231}$$ (a = ·026, b = 3340)
(refer page 246)

$$= 49550\ \Omega$$ IV

also $$\frac{dR}{dT} = -\frac{bR}{T^2}$$ (equation II on page 249)

Substituting the value of b, R and T in the above equation

$$\frac{dR}{dT} = \frac{-3340 \times 49550}{(231)^2}$$

$$= -\ 3100\ \Omega\ /^{\circ}C$$ V

Also $$\frac{dv}{dR} = \frac{-\ V\ R_3}{(R + R_3)^2}$$ (equation III on page 249).

Substituting in the above equation value of

$V = 6$ volts

$R_3 = 47000$

$R = 49550$ (calculated above in IV)

$$\frac{dv}{dR} = -\frac{6 \times 47000}{(49550 + 47000)^2}$$

$$= -\ 0{\cdot}302 \times 10^{-4}\ \text{v}/\Omega$$ VI

Hence $$\frac{dv}{dT} = \frac{dR}{dT} \times \frac{dv}{dR}$$

$$= -\ 3100 \times -0{\cdot}302 \times 10^{-4}$$ (from V and VI)

$$-=\ 0{\cdot}0935\ \text{v}/^{\circ}C$$

As/

As the change in input millivolts to the amplifier required to give the same change in deflection was 3·5

Hence the change in temperature $\Delta T = \frac{3{\cdot}5 \times 10^{-3}}{0{\cdot}0935}$

$$= 0{\cdot}0375^{\circ}C$$

The molecular weight was then calculated by applying the standard cryoscopic formula.

The above experiment was carried out using two cryoscopic solvents viz. pyridine and furfural. The results obtained which have been tabulated in tables III and IX on pages 50 and 62 confirmed the low molecular weight obtained by other methods employing standard procedures.

APENDIX II *

Experimental description of the determination of the molecular weight of the substance (isolated by action of nitric acid on coal) by Barger's Osmosis method.

(i) Measuring Capillary Tubes:-

Quill tube with a uniform diameter of 1·5 m.m. was employed. The diameter of all the tubes was checked by a travelling microscope. The tubes were of thin walls which helped in focussing the menisci under the microscope. Small lengths of 2.1/2" size were employed during all the measurements.

(ii) Preparation of Solutions:-

(i) Substance under investigation:- one per cent solution of the substance was prepared in three different solvents viz. acetone, furfural and pyridine. The idea was to check the molecular weight in all the three solvents.

(ii) Comparison solutions:- Azobenzene was selected as the comparison substance because of its solubility in various organic solvents, the degree of purity in which it was available and the fact that it did not contain any group which/

---

* Refer page 54.

which might have reacted with the product under investigation. A 0·2M solution of azobenzene was kept as a stock solution and comparison solutions of different molality were prepared by dilution of this solution with the solvent from a micro-burette.

(iii) Procedure:-

After some preliminary practice the capillary tubes could be fitted with little difficulty. The measuring capillary, as it is called, was taken between the middle finger and thumb, and its upper end, which was rounded, was closed with the index finger. The other end was then dipped below the surface of the comparison solution so that only a small amount of the solution entered. The tube was then raised, turned horizontally, the finger was removed and by tilting, the droplet was moved about 3 m.m. in the capillary. The tube was once more held vertically, the upper end being again closed with the index finger and its open end was made to touch the second solution i.e. solution of the substance, and the droplet was taken exactly in a manner described above. This was repeated until seven droplets, of the two solutions alternately, were in the capillary; they were allowed to enter it until the last was about one centimeter from the opening. Finally, with the capillary tube kept/

kept horizontal, both ends were sealed with plasticine. In this way several capillaries were filled with seven droplets with the same standard solution droplets and different comparison solutions, placed alternately in the tube.

The prepared measuring capillaries were mounted at each end on a microscope slide, by means of plasticine; the slides were then labelled. When sealed and mounted, the tubes had the appearance as shown in figure 36A (page 260) In the diagram the drops are numbered in the order in which they entered the tube, and the drops of the comparison solution are shaded black. The first and the last drops are about 5 m.m. long and were not measured, for they decrease generally by evaporation into the air-spaces near the end. The drops 2, 4, and 6 contained the substance the molecular weight of which was being determined.

For the measurement, the slide with the capillary tubes was placed in a Petri dish and water at room temperature was added until the capillaries were just dipping. These were thus protected from air currents while the image was made clearer under the microscope which was focused on the axis of the capillary because here both menisci of a drop were most sharply defined. The smallest interval between the menisci in the axis of the capillary was measured to within

2-3 /

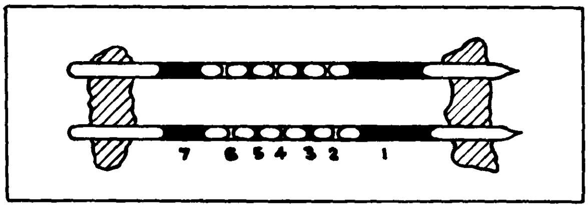


FIGURE 36A.

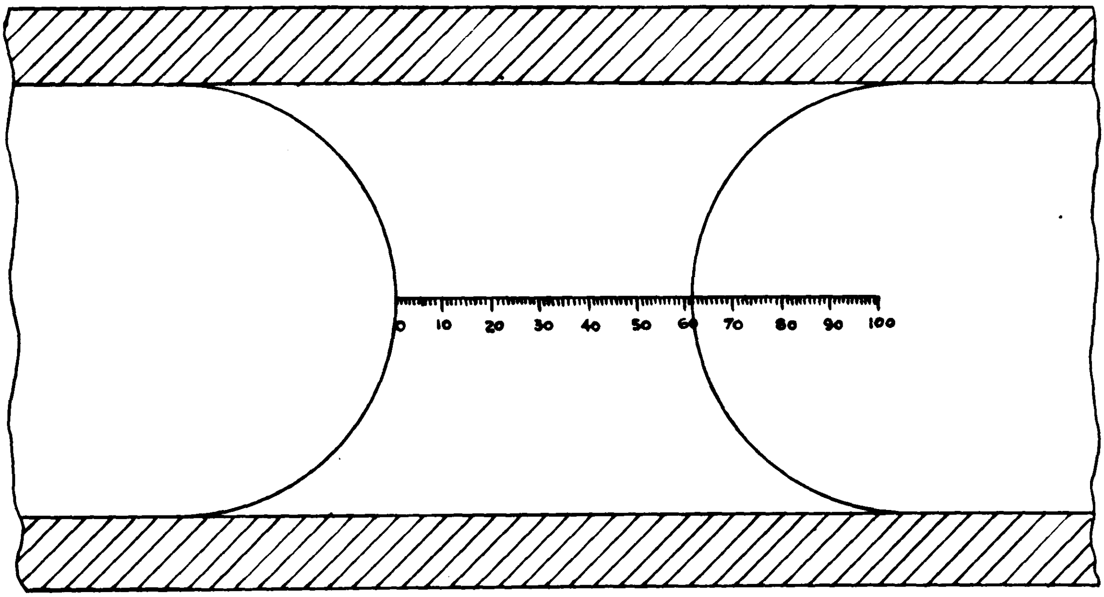


FIGURE 36B.

2-3μ by bringing one meniscus exactly to the zero of the micrometer by moving the Petri dish which was fixed on the mechanical stage of the microscope. The exact coincidence of the meniscus with zero was obtained by moving the eyepiece (with the scale in it) transversely in the tube of the microscope, in which it had a little play. Under the microscope, the drops and scale present the appearance shown in fig. 36B. The interval between the two menisci was reported in terms of the micrometer scale as it was the direction of the change rather than the magnitude which was required.

The readings which then followed were taken after time intervals varying from one solvent to another depending upon how much time it takes with the particular solvent to attain the osmotic equilibrium; e.g. with acetone equilibrium is attained in about 12 - 24 hours whereas with pyridine it takes several days, about 120 hours in this case. So the readings were taken after appropriate intervals till the osmotic equilibrium was obtained. This was when no further change in the size of the drops took place.

Preliminary experiments were performed to get an idea to choose a series of comparison solutions so that some produced an increase and the others a decrease in the distance between the menisci concerned. In the case where/

where smallest change occured showed the smallest isothermal distillation that might have taken place. This showed that the two solutions were nearly isotonic. Only in exceptional cases is no change observed. Thus the molecular weight was calculated by the following formula:-

$$\text{Molecular weight} = \frac{\text{concentration of sample} \times 10}{\text{Molecular concentration of comparison solution.}}$$

Results:- Results have been tabulated in Table V, VI, VII and VIII on pages 58 - 61.

REFERENCES.

1. E.S. Moore, "Coal - its properties, analysis, classification, geology, extraction, uses and distribution". John Wiley and Sons, New York, 1940, page 3.

2. M.C.Stopes and R.V. Wheeler, "Constitution of Coal", Dept.Sci.Ind.Research (Brit.), Monograph 1918, pp 58.

3. C.S. Fox, Fuel, 1930,LIX, 548.

4. C. Harries, "Unter Suchungen uber die naturlichen und Kunstlichen Kantschukarten," Berlin,1919,p.17

R. Hill, J.R.Lewis,and J.L. Simonson, Trans. Faraday Soc., 1939, XXXV, 1067.

5. W. Francis, Fuel, 1938,XVII, 363.

6. Mahler, Ann. Mines., 1913, IV, 163.

7. M.P.E.Berthelot, Ber., 1869, II, 57.

8. E. Donath and F. Braunlich, Chem.-Ztg., 1904, XXVIII, 180, 953.

9. O. Dimroth and B. Kerkovius, Ann., 1913, CCCXCIX, 120.

10. H. Meyer, and K. Steiner, Monatsh, 1914, XXXV, 391.

11. H. Meyer, and K. Steiner, Monatsh, 1914, XXXV, 475.

12. W. Francis,and R.V. Wheeler, J.C.S., 1925, CXXVII, 2236.

12a. J. Marcusson, Z.Angew. Chem., 1921, XXXIV, 521.

13. W. Fuchs, and W. Stengel, Ann., 1930, CCCCLXXVIII, 267.

14. B. Juettner, R.C. Smith, and H. Howard. J. Amer. Chem. Soc., 1937, LIX, 236.

15. Fischer, Franz, and H. Schrader, Ges. Abh. Kennt. Kohle., 1920, V, 307.

15a. "International Critical Tables". McGraw Hill Book Co. Inc., New York, 1926, Vol.IV, p.183.

16. R.C. Smith, and H.C. Howard, J. Amer. Chem. Soc., 1935, LVII, 512.

17. Cottrell, J. Amer. Chem. Soc., 1919, XLI, 721.

18. G. Barger, J.C.S., 1904, LXXXV, 286.

19. C.F. Brown, and A.R. Collet. Fuel, 1938, CCCLIX.

20. I. Ubaldini, and C. Siniramed, Studi Ricerche Combustibili, 1932-33, IV, 333; Ann. Chim. Applicata, 1932, XXII, 340, 1933, XXIII, 585.

20a. I. Ubaldini. Brenstoff. Chem., 1930, XVIII, 273; (as reported in J. Indian Chem. Soc., 1942, XIX, 294-5)

21. H.B. Charmbury, J.W. Eckerd, J.S. Latoree, and C.R. Kinney, J.Amer.Chem.Soc., 1945, LXVII, 625.

22. W. Fuchs, and A.G. Sandhoff, Fuel, 1940, XIX, 45, 69.

23. Oden, and Sven, "Die Huminsauren, Theodor Steinkopff", Dresden, 1922, pp. 84-92.

24. W. Fuchs, Brenstoff-Chem., 1887, I, 97.

25. G. Thiessen, and C.J. Engelder, Ind. Eng. Chem., 1930, XXII, 1131.

26.	M. Samec, and B. Pirkamier,	Kolloid-Z., 1930, LI, 96.
27.	Fuch and Horn,	Brennstoff-Chem., 1931, XII, 60.
28.	"Decomposition of Picric Acid".	"A text book of Organic Chemistry" by Schmidt, 1936, p. 425.
29.	R.F. Marchard,	J.Prakt, Chem., 1845, XXXV, 228.
30.	V. Giraud,	Bull. Soc.Chim., 1894, III, 11, 389.
31.	E. Phillippi, and R.Thelen,	Ann., 1922, CCCCXXVIII, 296.
32.	A.E. Beet,	Fuel, 1940, XIX, 108.
33.	H. Strache, and R. Lant,	"Kohlenchemie, Akademische Verlagsgesellschaft," Leipzig, 1924, p.305.
34.	L.J. Simon,	Compt. rend., 1924, CLXXVIII, 495.
35.	D. Florentin,	Bull. Soc. Chim., 1924, XXXV, 228.
36.	J.F. Durand,	Compt. rend, 1924, CLXXVIII, 1822
37.	A.J. Petrick, and P. Groenewond,	J.Chem.Met. Mining Soc., S.Africa 1938, XXXVIII, 370.
38.	D.J.W. Kreulen,	Brennstoff-Chem., 1929, X, 397.
39.	J.T. Way,	J.Roy. Agr. Soc. Engl., 1850, XI, 313.
40.	E. Eichorn,	Landw. Jahrb., 1875, IV, 1; Pogg. Ann., 1858, CV, 126.
41.	E. Lamberg,	Z.deut. geol. ges., 1870, XXII, 335.

42. R. Gans, Jahrb. Kgl. preuss. geolog. Landesanstadt, 1905, XXVI, 179; 1906, XXVII, 63.

43. R. Gans, G.P. 197, 111, (1906); U.S.P. 914, 405, (1909), 943, 535, (1909), 1,131,503, (1915).

44. F.Fischer and W. Fuchs, Brennstoff-Chem., 1927, VIII, 291.

45. G. Borrowman, U.S.P. 1,793,670 (1931).

46. W. Vaughn, U.S.P. 2,190,853 (1940).

47. Ellis, Carleton, U.S.P. 2,198,379 (1940).

48. O. Liebknecht, U.S.P. 2,206,007 (1940).

49. E.B.Higgins, U.S.P. 2,163,167 (1938).

50. P. Smit, U.S.P. 2,171,408 (1939), 2,191,063, (1940), 2,205,635, (1940), 2,198,393 (1940); Arch. Suikerind. Ned.-Indie, 1,143 (1940).

51. H.F. Walton, J. Physical Chem.1943, XLVII, 371.

52. R. Riley and F.C. Nachod, U.S.P. 2,382,334 (1945) Chem. Abstracts., 1945, XXXIX, 4709.

53. A.S. Behrman, U.S.P. 2,376,896 (1945)

54. R. Furness, and J.Crossfield & Sons Ltd. B.P. 455,374, (1936)

55. United Water Softeners Ltd. B.P. 450,574 (1936)

56. I.G. Farbenindustrie, A.G. F.P. 823,808 (1938)

57. R.Furness, and J.Crossfield & Sons Ltd. B.P. 486,471 (1938).

58. I.G. Farbendustrie, A.G. B.P. 492,316 (1938).

59. B.A. Adams and E.G. Holmes, J.S.C.I., 1935, LIV, 1-6T; B.P. 450,308-9 (1936), 474,361 (1937); F.P.796,796-7 (1936); U.S.P. 2,104,501 (1938), 215,883 (1938), 2,191,853 (1940).

60. H.F.Walton, J.Chem. Educ., Sept.1946, 454.

61. H. Jenny, Kolloid-Beih., 1927, XXIII, 428.

62. H.F. Walton, J. Frankalin Inst., 1941, CCXXXII, 318.

63. J.B. Ferguson, J.R. Musgrave, and J.R. Patton. Can.J. of Research B, 1936, XIV, 243.

64. J. Schubert, G.E. Boyd and A.W. Adamson, J.Amer.Chem. Soc., 1947, LXIX, 2818.

65. A.P. Vaneslow, Soil. Sci., 1932, XXXIII, 95.

66. J. Kielland, J.S.C.I., 1935, LIV, 232T.

67. R. Griessbach, "Uber die Herstellung und Anwendung neuer Austanschadsorbienten, inbesonders auf Harzbasis," Verlag Chemie, Berlin, 1939.

68. H. Jenny and G. Wiegner, Kolloid-Z, 1927, XLII, 268.

69. J.Steinhardt, and M.Harris. J.Res.Nat.Bur.Stand., 1940, XXIV, 335.

70. British Patent, B.P. 509,710.

71. S. Sussman, Ind.Eng.Chem., 1946, XXXVIII, 1228. Idem, Ind.Chem., 1947, XXIII, 188.

72. G.D. Bengough, J.M. Stuart, B.P. 223,994 (1923).

73. G.D. Bengough, J.M. Stuart, B.P. 223,995 (1923).

74. C.H.R. Gower and Atafford O'Brien & Partners Ltd. B.P. 290,901 (1927).

75. Hosin Zaidan, Rikagaku, and Kenkyugo, B.P. 226,536 (1924).

76. L.E. Ensminger, Soil Sci., 1944, LVIII, 425.

77. L.B. Golden, "A comparison of methods of determining the exchangeable cations and exchange capacity of Maryland soils." Soil Sci. Soc. Amer. Proc. 7: 1942, 154-161.

78. British Patent. B.P. 492,316, (1938).

79. Paul C. Goetz. U.S.P. 2260,971 (1941).

80. Aluminium Development Association. "Anodic oxidation of Aluminium and its Alloys", A.D.A. Information Bulletin No.14, p.6.

81. Aluminium Development Association. "Anodic oxidation of Aluminium and its Alloys", A.D.A. Information Bulletin No.14, p.21.

ADDITIONAL PAPERS

1. "Physical Characteristics of Soils: IX. Relation Between Ultraclay and Volume of Floc."

   By Amar Nath Puri, Balwant Rai, and Rajindra Pal.

   Reference: Soil Science, Vol. 58, No. 2, August, 1944.

* 2. "Coagulation Values of Calcium Ions for Dilute Clay Suspensions."

   By Amar Nath Puri, Balwant Rai, and Rajindra Pal.

   Reference: Proceedings of the Lahore Philosophical Society, Vol. VI, No. 2, December, 1944.

* 3. "The Application of a Thermistor to the Determination of the Molecular Weights of Humic Acids."

   By J.R. Campbell, J.T. Pender and R.P. Puri.

   Reference: Journal of the Royal Technical College, 1949 (in press).

* As the reprint copies of these are not available at this time, the author regrets his inability to submit same.

R. P. Puri.

Department of Technical Chemistry,
Royal Technical College,
GLASGOW.

Reprinted from Soil Science
Vol. 58, No. 2, August, 1944

PHYSICAL CHARACTERISTICS OF SOILS: IX. RELATION BETWEEN ULTRACLAY AND VOLUME OF FLOC

AMAR NATH PURI, BALWANT RAI, AND RAJINDRA PAL
Panjab University Institute of Chemistry, Lahore, India

Received for publication March 6, 1944

The flocculation of soil colloids has been studied by several workers from time to time. Russel (12) and Weigner (13) have tried to bring the flocculation of soil colloids in line with the coagulation and flocculation of soils in general.

Puri (5) directed attention toward the influence of the nature of exchangeable bases present in a soil on the flocculation values for different ions and showed that the higher the valency of the exchangeable base, the smaller the flocculation value for a given electrolyte. Almost at the same time, Anderson (1) and Mattson (2) independently came to a similar conclusion regarding the influence of exchangeable ions.

Müller (3), on a purely theoretical basis, calculated that the smaller the radius of the particle, the higher must be the concentration of a given electrolyte to reduce its electrokinetic potential by a given amount. In other words, the smaller the size of particles in suspension, the greater will be the concentration of the electrolyte required for coagulating the suspension.

It will be seen, however, that one particular aspect of the problem has not been studied so far. No attention seems to have been paid to the *volume* of the flocculated mass after it has completely settled. Soil is a polydisperse system. It consists of particles of all sizes. Even the conventional clay fraction (<0.002 mm.) is not homogeneous but consists of particles of various sizes, starting from 0.002 mm. and ending at a much finer size in the truly colloidal region. The contributions of the particles of the various sizes to the volume of the floc must vary with the size. The smaller particles in suspension, which contribute largely to the total surface presented by the dispersed phase, would probably also contribute largely to the volume of the floc.

In the present paper attention is directed toward this problem in particular. The volume of the flocculated mass of clay suspensions, the contribution made toward this value by the particles of various sizes usually present in soils, and the variations produced by altering such factors as pH value, concentration, and time of aging are studied in detail.

DEVELOPMENT OF THE TECHNIQUE

In order to standardize the technique of determining floc volume of soils, preliminary studies were made of the effect of various factors, such as concentration of clay suspension used, nature and concentration of flocculants employed, and time and speed of centrifuging required to produce a compact mass of the flocs.

Clay (<0.002 mm.) was separated from 1 per cent soil suspensions dispersed by the HCl-NaOH method. For determining the floc volume, 4 cc. of the clay suspension was always used. The chlorides of Ca, Ba, and Al were found to be about equally effective as flocculants, and 1 cc. of 0.25 *N* solution was found to be enough even in the case of highly clayey suspensions. The chlorides of alkali metals, as expected, did not cause flocculation unless much higher concentrations were employed, and even then the effect was rather slow. The centrifugal machine used consisted of an ordinary ceiling fan having necessary attachments for holding three centrifugal tubes at a time and could be worked at the rate of 620 revolutions per minute. The time of centrifuging was found to affect the values considerably at first, but after about half an hour no further decrease in volume took place, as maximum compaction and settling of flocs had occurred by then. The procedure adopted for determining the floc volumes of soils was, therefore, as follows: A 1 per cent suspension was prepared, after maximum dispersion by the HCl-NaOH method, and clay was pipetted off in the usual way. Four cubic centimeters of the clay were put in the measuring tube, 1 cc. of 0.25 *N* $CaCl_2$ solution was added, and the suspension was centrifuged for half an hour. The volume of the settled mass was read directly from the measuring tube, which was calibrated accurately up to 0.01 cc.

TABLE 1

Mechanical analysis of soils P. C. 13 A. T. and P. C. 245 A. T.

SOIL NUMBER	SUMMATION PERCENTAGE UP TO DIAMETER										
	0.00004 *mm.*	0.000063 *mm.*	0.0001 *mm.*	0.00025 *mm.*	0.0006 *mm.*	0.001 *mm.*	0.002 *mm.*	0.005 *mm.*	0.01 *mm.*	0.02 *mm.*	0.06 *mm.*
P. C. 13 A. T.	27.2	30.7	41.0	49.2	54.5	57.7	62.8	75.7	78.2	82.9	89.5
P. C. 245 A. T.	9.8	10.2	12.6	20.5	28.6	30.1	46.0	61.2	74.1	84.4	93.7

The reliability of the values obtained by following the procedure outlined was tested on 12 soils by taking each soil in three separate lots and determining the volume of the floc in each case. The values obtained in all cases were almost identical.

EFFECT OF pH ON FLOC VOLUME

Two soils, P. C. 13 and P. C. 245, both acid-treated and free from exchangeable bases, were studied to determine the effect of the pH value on the floc volume. Mechanical and ultramechanical analyses of these soils were determined by the chainohydrometer (9) and the micropipette (10) methods respectively. The results are given in table 1.

To 5-gm. portions of the acid-treated soils varying quantities of NaOH were added and the suspensions allowed to stand 24 hours, after which their pH values were determined. The suspensions thus obtained at different pH values were diluted to give a 1 per cent concentration, and their floc volumes were determined. The clay content was also determined in each case. The results are plotted in figures 1 and 2. Both the floc volume and the clay content increase with the pH value, but whereas the clay content reaches its maximum

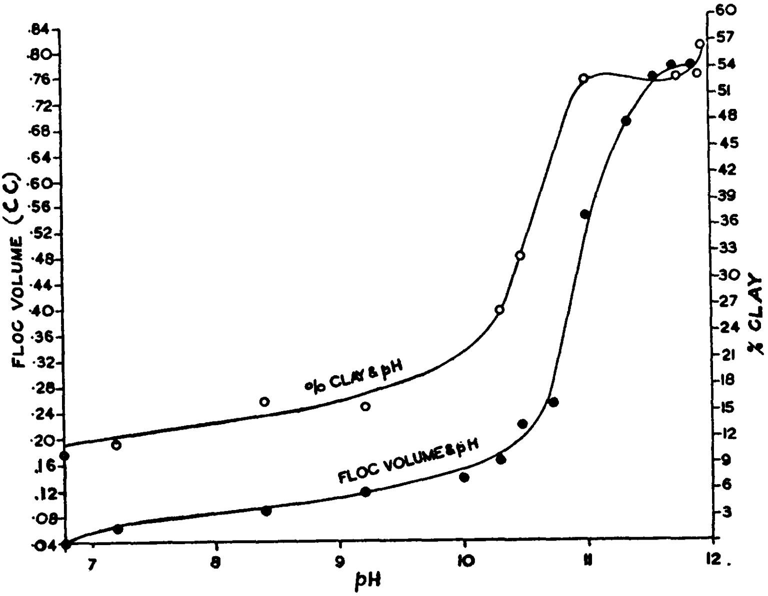


FIG. 1. EFFECT OF pH VALUE ON CLAY CONTENT AND FLOC VOLUME OF SOIL P. C. 13, ACID-TREATED

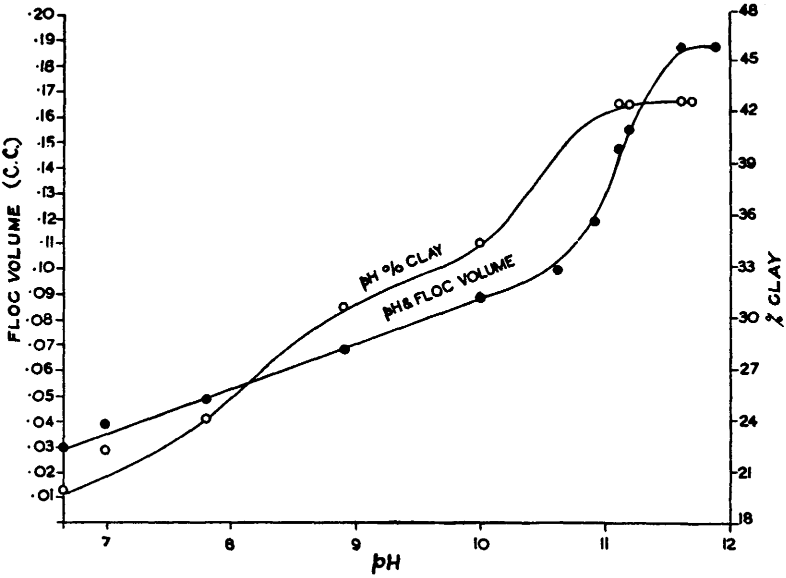


FIG. 2. EFFECT OF pH VALUE ON CLAY CONTENT AND FLOC VOLUME OF SOIL P. C. 245, ACID-TREATED

value at about pH 10.8 the floc at this point attains only a fraction of its maximum value. In fact, the pH-floc-volume curve becomes very steep at this pH and the increase in floc volume is continued to pH 11.6, after which it becomes constant.

Puri and Lal (7) have shown that maximum dispersion in soils, as reckoned on the basis of conventional clay (<0.002 mm.), takes place at pH 10.8. The abrupt increase in the floc volume beyond this pH and its continued increase thereafter show that beyond this point further dispersion takes place. But as the clay content remains virtually constant at pH values higher than 10.8, it appears that it is the clay that is further subdivided into ultraclay particles at these high pH values. This second dispersion—that of clay into ultraclay—is completed at about pH 11.6, as beyond this value no increase in floc volume is noticed. It is only at this stage that soil is completely dispersed into its ultimate primary units. Further evidence on this point is offered in the succeeding part of this paper.

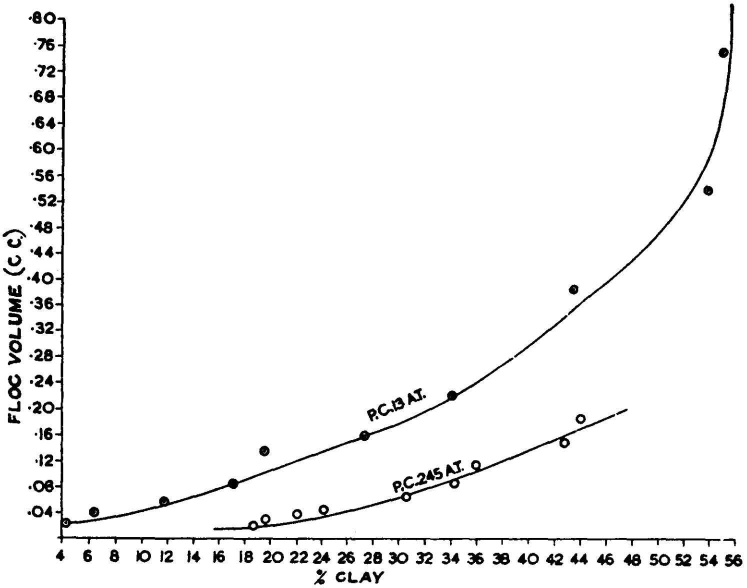


FIG. 3. RELATION BETWEEN CLAY PERCENTAGE AND FLOC VOLUME OF SOILS

The relation between floc volume and clay content is plotted in figure 3. For the same clay content, P. C. 13 soil gives a greater floc volume than does P. C. 245. The reason for this lies in the fact that P. C. 13 is much richer in ultraclay than P. C. 245 (table 1) and therefore a given amount of clay in P. C. 13 contains a larger number of finer particles than does the same amount of clay in the other soil. This obviously leads to the conclusion that size distribution in the ultraclay region, rather than the clay itself, is mainly responsible in determining the floc volume.

For further evidence on this point, another set of experiments was undertaken. It has been shown (8) that a soil dispersed by different methods, though giving almost equal values for clay content, gives entirely different values for various sizes of ultraclay. For instance, the methods involving acid treatment yield much higher values for ultraclay than the other methods. In order, therefore, to decide conclusively whether it is conventional clay (<0.002 mm.) as a whole or the so-called ultraclay particles which are primarily responsible for the floc volume, three soils were dispersed by the HCl-NaOH method (4), the Na_2CO_3-NaOH method (6), and the sand method—in which the soil is shaken 24 hours with five times its weight of 1-mm. sand particles—a mechanical method of dispersion which has been shown to give maximum clay content (11). The values for clay (<0.002 mm.), ultraclay (<0.0001 mm.), and the flocculated volumes are given in table 2.

Although clay content is almost the same in every soil, irrespective of the method of dispersion, floc volume is different and so is ultraclay. As ultraclay increases when the soil is dispersed by the acid treatment, so does the floc volume. The discrepancy in the values of floc volume for the same values of clay content is so great that it is absolutely useless to attempt any correlation between conventional clay and floc volume. The correlation, if any, must be looked for in the percentages of particles of various sizes in the ultraclay region. It is not unlikely that the correlation will not depend on particles of any particular size but will rest with the whole size distribution in the region of ultraclay.

TABLE 2

Floc volume of soils when dispersed by different methods

SOIL NUMBER	CLAY BY DIFFERENT METHODS			PARTICLES <0.0001 MM. BY DIFFERENT METHODS			FLOC VOLUME BY DIFFERENT METHODS		
	Sand method	Na_2CO_3 method	HCl-NaOH method	Sand method	Na_2CO_3 method	HCl-NaOH method	Sand method	Na_2CO_3 method	HCl-NaOH method
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*cc.*	*cc.*	*cc.*
P. C. 13 A. T.	53.9	55.0	57.5	3.1	8.1	35.3	0.06	0.16	0.42
P. C. 123 A. T.	72.1	76.0	77.5	2.0	7.2	11.2	0.02	0.12	0.22
P. C. 245 A. T.	37.8	39.0	42.7	1.3	5.7	6.2	0.01	0.10	0.11

In this connection, table 2 shows also that although P. C. 123 contains much more clay than P. C. 13, it gives a lower value for the floc volume. This is because P. C. 13 is richer in the ultraclay fractions.

EFFECT OF AGING

During the course of these studies, it was discovered that the floc volumes of suspensions increased on standing. As the floc volume and ultraclay have already been shown to increase together, it is very likely that increase in floc volume with time is due to corresponding increase in the ultraclay content. Dispersion of clay into ultraclay in that case would be a rather slow process.

The effect of aging was studied further on two soils, P. C. 13 and P. C. 142.

To 5-gm. portions of acid-treated soils, varying quantities of NaOH were added and the suspensions were shaken for 24 hours in the mechanical shaker. They were then diluted to 500 cc. in order to give a 1 per cent suspension, and their pH values were determined by means of the glass electrode. Thereafter the floc volume, clay content (<0.002 mm.), and percentage of ultraclay particles (<0.0001 mm.) were obtained. The determination of these values and of the pH values of all the suspensions was repeated after varying intervals of time. The results are given in table 3.

TABLE 3

*Effect of aging of soil suspension**

SUSPENSION NUMBER	0.1*N* NaOH added	pH					FLOC VOLUME					CLAY CONTENT					PARTICLES UP TO 0.0001 MM.†			
		2 hours	26 hours	65 hours	90 hours	7 days	2 hours	26 hours	65 hours	90 hours	7 days	2 hours	26 hours	65 hours	90 hours	7 days	26 hours	65 hours	90 hours	7 days
	cc.						*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	%	%	%	%	%	%	%	%	%
Soil P. C. 13 A. T.																				
1	0.5	7.1	7.05	6.95	6.95	6.95	0.05	0.07	0.08	0.08	0.08	9.8	10.5	11.2	11.4	11.4	3.4	4.7	5.3	5.4
2	1.5	7.3	7.10	7.10	7.1	7.1	0.08	0.09	0.12	0.12	0.12	30.1	32.2	33.0	33.0	33.1	5.6	8.6	9.7	9.8
3	2.0	9.0	8.40	8.3	8.3	8.3	0.20	0.30	0.41	0.43	0.43	40.2	43.2	43.1	44.0	44.2	17.1	26.3	27.2	27.3
4	3.0	10.3	9.40	9.3	9.3	9.3	0.30	0.42	0.49	0.50	0.50	58.8	59.0	60.1	60.2	60.2	25.1	29.8	30.1	30.1
5	4.0	10.7	9.7	9.6	9.5	9.5	0.48	0.65	0.70	0.70	0.70	64.0	63.5	63.6	63.8	64.0	32.1	36.5	36.5	36.6
6	5.0	11.0	10.0	9.9	9.8	9.8	0.55	0.70	0.72	0.73	0.73	64.0	64.0	64.2	64.2	64.3	34.1	38.2	38.5	38.7
7	6.0	11.4	10.35	10.2	10.2	10.2	0.65	0.73	0.73	0.74	0.74	64.0	64.8	65.0	65.1	65.1	36.1	38.3	38.8	38.8
8	7.0	11.5	10.35	10.2	10.2	10.2	0.70	0.76	0.76	0.76	0.76	64.8	64.8	65.1	65.2	65.2	37.1	39.1	39.2	39.8
9	8.0	11.6	10.35	10.3	10.2	10.2	0.71	0.76	0.76	0.76	0.76	64.6	65.0	64.8	65.2	64.8	37.2	39.3	40.0	40.1
Soil P. C. 142 A. T.																				
1	0.5	7.0	6.90	6.85	6.80	6.80	0.05	0.07	0.08	0.08	0.08	12.1	12.3	12.5	12.7	13.0	4.1	5.0	5.1	5.1
2	1.5	7.6	7.5	8.4	7.3	7.3	0.09	0.12	0.13	0.13	0.13	25.7	26.1	26.7	26.8	26.8	6.8	8.2	8.8	9.6
3	2.0	8.8	8.3	8.2	8.1	8.1	0.20	0.32	0.39	0.41	0.41	40.2	40.3	40.2	40.3	40.3	16.1	17.1	25.1	25.5
4	3.0	9.2	9.0	8.9	8.8	8.8	0.28	0.38	0.46	0.48	0.48	50.1	51.1	51.3	52.0	52.0	20.1	23.1	28.1	28.1
5	4.0	10.8	9.9	9.7	9.7	9.7	0.57	0.62	0.63	0.63	0.63	62.0	62.1	61.9	62.3	62.5	28.1	30.1	31.1	31.2
6	5.0	11.0	10.1	10.0	9.55	9.55	0.61	0.65	0.65	0.66	0.66	62.8	62.4	62.5	63.0	63.0	30.0	31.2	31.2	31.2
7	6.0	11.2	11.1	10.0	9.55	9.55	0.65	0.68	0.69	0.69	0.69	63.2	63.5	63.5	63.6	63.6	32.0	33.0	33.0	33.1
8	7.0	11.4	10.3	10.2	10.1	10.1	0.65	0.69	0.70	0.70	0.70	63.2	63.1	63.2	63.2	63.1	33.2	33.9	34.0	34.1
9	8.0	11.5	10.5	10.2	10.1	10.1	0.66	0.69	0.70	0.70	0.70	63.0	63.0	63.1	63.1	63.2	34.1	34.6	34.2	34.2

* The time of shaking, 24 hours, is not included.

† As 24 hours' settling time is required to allow pipetting from the minimum depth of 1 mm., the value for 2 hours could not be obtained.

The following conclusions may be drawn:

As far as conventional clay is concerned, the various suspensions at different pH values acquire stable structure soon after 24 hours' mechanical shaking, for no appreciable increase in clay content is noticed up to 7 days' standing. Furthermore, the maximum dispersion on the basis of conventional clay is attained at pH 10.8–11.0.

The ultraclay (<0.0001 mm.), however, continues to increase in all cases up to 65 hours' standing reckoned from the end of the 24 hours' mechanical shaking. This happens even in suspensions at pH values higher than 11, though the effect is less pronounced. This shows that ultraclay requires not only higher pH values than 10.8 but also a longer time than the usual 24 hours' shaking for complete dispersion. This will be readily understood if we assume that dispersion of soil takes place gradually, the coarser particles being resolved first, followed by the particles in the clay region, and then by those in the ultraclay region. After about 90 hours (including 24 hours of shaking), complete dispersion has taken place on the basis not only of conventional clay but also of ultimate primary particles in the truly colloidal region. Keeping the suspensions for a longer time than this does not produce any further change in ultraclay, and the suspensions acquire a comparatively permanent stable state.

The floc volume, like ultraclay content, increases with time of standing. The increase continues for as long as 65 hours in suspensions at lower pH values, but for only 26 hours in more alkaline suspensions, although ultraclay in the latter case increases to a small degree up to 65 hours. This apparent discrepancy will be readily resolved by reference to figure 5, in which the effect of concentration of ultraclay on floc volume is plotted. It will be seen that beyond a certain limit of ultraclay, the floc volume tends to become constant. This aspect is discussed in a subsequent section of this paper.

The pH value continues to decrease with time in all cases until it also becomes constant. This usually happens after 65 hours of standing, though the rate of fall gradually slows down. The explanation for the fall of pH value with time lies in the fact that the reaction between alkali and the acidoid takes place very slowly, as the soil particles exist in aggregates and the reactions involved take place only at the surface. When these aggregates, on contact with alkali, are gradually resolved, first, into smaller aggregates and then into ultimate primary units, fresh surfaces become exposed and the reaction continues if enough alkali is present. This will continue until hydrogen in the exchange complex is completely replaced by sodium. No further fall in pH value will then take place. As the maximum dispersion can take place only when the acidoid is completely converted into sodium saloid, the ultraclay particles continue to increase with the progressive increase of sodium in the exchange complex and attain constant value only when sufficient alkali is kept in contact with the acidoid long enough to complete this reaction.

CONTRIBUTION OF PARTICLES OF VARIOUS SIZES TO FLOC VOLUME

Although it appears that ultraclay particles determine to a large extent the volume of the flocculated mass, it is of interest to find out whether coarser particles also make a contribution toward this value and, if so, what is the magnitude of this contribution and at what particle size does it begin.

Two H-soils, with differently shaped size-distribution curves, were selected and dispersed by the addition of NaOH to raise their pH value to 11.0 and by shaking mechanically for 48 hours. Particles of various sizes were pipetted after appropriate times of settling and their floc volumes as well as their summation percentages were determined in the usual way. The results are given in table 4. It will be seen that particles coarser than 0.0001 mm. (10^{-5} cm.) do not make any material contribution to the floc volume. Particles finer than this, however, begin to affect this value to an increasing degree. It is interesting to note that although P. C. 13 contains only 27 per cent of particles below 0.00004 mm., these particles contribute 90 per cent toward the floc volume.

In order to determine the floc volume of any silica that might have gone into solution as a result of alkalinity of the medium, the two suspensions were filtered by means of Houston's pump and the floc volumes measured in the usual way by the addition of 1 cc. of 0.25 *N* $CaCl_2$ to 4 cc. of the filtrates. The flocculated

TABLE 4

Ultraclay as determined by the pipette method and by the flocculated volume method

SOIL NUMBER	FLOC VOLUME	ULTRACLAY					
		$<10^{-5}$ cm. (0.0001 mm.)		$<10^{-5.2}$ cm. (0.000063 mm.)		$<10^{-5.4}$ cm. (0.00004 mm.)	
		Pipette method	Flocculated volume method	Pipette method	Flocculated volume method	Pipette method	Flocculated volume method
	cc.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
116	0.11	6.9	6.0	4.0	4.35	3.1	3.5
117	0.04	3.2	2.37	1.7	1.50	1.2	1.30
118	0.15	8.3	7.87	5.2	5.60	4.5	4.27
119	0.38	20.2	16.3	11.4	11.0	9.1	8.8
120	0.06	4.0	3.25	2.5	2.15	2.0	1.80
121	0.05	3.6	2.80	2.5	1.80	1.7	1.50
122	0.04	3.0	2.37	1.6	1.50	1.3	1.30
124	0.04	2.9	2.37	1.5	1.50	1.4	1.30
125	0.06	4.5	3.25	2.5	2.15	1.8	1.80
126	0.22	11.3	11.00	7.4	7.10	6.1	5.75
127	0.18	10.0	9.12	6.0	6.32	4.9	5.25
128	0.08	6.2	4.06	2.5	2.80	2.2	2.20
129	0.26	13.3	12.5	8.7	8.12	6.8	6.50
130	0.23	10.8	11.50	7.5	7.36	6.0	5.92
132	0.22	9.7	11.00	7.2	7.10	5.6	5.75
133	0.18	7.8	9.12	5.8	6.32	5.0	5.25
134	0.04	2.5	2.37	1.4	1.50	1.2	1.30
135	0.05	2.60	2.80	1.5	1.80	1.2	1.5
136	0.10	6.0	5.50	3.3	4.0	2.8	3.0
137	0.10	5.8	5.50	3.2	4.0	2.65	3.0
138	0.20	9.1	10.0	6.1	6.72	5.7	5.5
139	0.08	5.1	4.06	3.0	2.8	2.4	2.2
141	0.42	19.8	18.00	13.5	12.7	9.9	9.7
142	0.55	31.1	30.50	22.1	20.2	15.8	16.3
144	0.13	6.7	7.0	4.3	5.0	3.75	4.2
149	0.27	12.4	12.8	9.01	8.40	6.83	6.66
152	0.06	4.1	3.25	1.5	2.15	1.36	1.80
153	0.14	6.6	7.50	4.5	5.30	3.72	4.50
159	0.13	6.2	7.0	4.5	5.0	3.4	4.20
160	0.10	5.1	5.50	3.9	4.0	2.5	3.00
163	0.11	5.2	6.00	4.0	4.35	2.9	3.69
165	0.30	14.0	13.75	9.4	9.00	7.1	7.30
166	0.19	9.8	9.56	6.3	6.52	5.2	5.37
167	0.06	3.0	3.25	2.1	2.15	1.6	1.8
168	0.08	3.3	4.06	2.6	2.80	2.0	2.20
169	0.06	2.9	3.25	2.2	2.15	1.8	1.80
172	0.33	15.0	14.65	9.8	9.66	7.7	7.81
173	0.08	3.2	4.06	2.6	2.80	2.13	2.2
175	0.11	5.3	6.00	4.1	4.35	3.0	3.65
177	0.04	2.5	2.37	1.8	1.50	1.51	1.30
181	0.20	9.7	10.00	6.8	6.72	5.6	5.75
182	0.04	2.5	2.37	1.7	1.50	1.5	1.30
183	0.08	3.5	4.06	2.5	2.80	2.3	2.20

TABLE 4—*Concluded*

SOIL NUMBER	FLOC VOLUME	ULTRACLAY					
		$<10^{-5}$ cm. (0.0001 mm.)		$<10^{-5.2}$ cm. (0.000063 mm.)		$<10^{-5.4}$ cm. (0.00004 mm.)	
		Pipette method	Flocculated volume method	Pipette method	Flocculated volume method	Pipette method	Flocculated volume method
	cc.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
184	0.13	6.3	7.00	4.5	5.00	3.5	4.20
221	0.07	4.6	3.65	2.5	2.47	1.7	2.00
222	0.18	9.5	9.12	6.0	6.32	5.1	5.25
223	0.11	6.6	5.20	4.2	4.00	3.1	2.90
224	0.16	10.0	8.25	5.7	5.90	4.7	5.0
226	0.13	6.2	7.00	4.8	5.00	3.2	4.20
227	0.11	7.0	5.20	4.4	4.00	2.9	2.90
229	0.20	11.0	10.00	7.2	6.72	5.2	5.50
230	0.15	8.2	7.87	5.1	5.60	4.5	4.77
231	0.17	12.0	8.68	10.4	6.11	6.9	5.12
232	0.17	12.4	8.68	10.2	6.11	6.0	5.12
233	0.25	12.0	12.25	8.2	7.87	6.5	6.30
234	0.20	16.6	10.00	7.5	6.72	5.9	5.50
245	0.16	9.2	8.25	5.4	5.90	4.7	5.0
246	0.32	14.8	14.35	9.2	9.40	8.0	7.64
249	0.20	9.7	10.00	6.8	6.72	5.6	5.50
291	0.11	9.5	5.20	3.7	4.00	3.00	2.90
Rawalpindi clay	0.07	3.1	3.65	2.6	2.47	3.6	2.00
13	0.58	41.0	40.0	30.7	27.0	27.0	22.0
15	0.10	7.0	5.5	5.1	4.0	3.2	3.0

mass was found to be absent altogether in P. C. 149. It had a negligibly small volume in P. C. 13, because of the presence of humus.

EFFECT OF CONCENTRATION OF SUSPENSION ON FLOC VOLUME

In order to study the effect of concentration on floc volume, four typical acid-treated soils were fully dispersed and clay was pipetted off in the usual way from 1 per cent suspensions. Different dilutions of each clay were prepared by taking 0.25, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4 cc. of the suspension and making to a volume of 4 cc. in each case with water. The floc volumes were determined as usual. The results are plotted in figure 4: 100 per cent concentration represents original clay without any dilution, 50 per cent represents the original clay diluted half and half with water, and so on. It will be seen from the results that floc volume does not increase in the same proportion as the concentration and that at a certain stage it becomes constant and quite independent of the concentration. This fact may be attributed to the mutual compression caused by the particles. As the concentration of the suspension increases, the force of compression also increases because of the increase in number of particles occupying the same space.

In figures 5, 6, and 7, the same results are plotted on the basis of the three ultraclay sizes (<0.0001, <0.000064, and <0.00004 mm.). The values plotted along the abscissas were obtained by dividing the percentages of various sizes

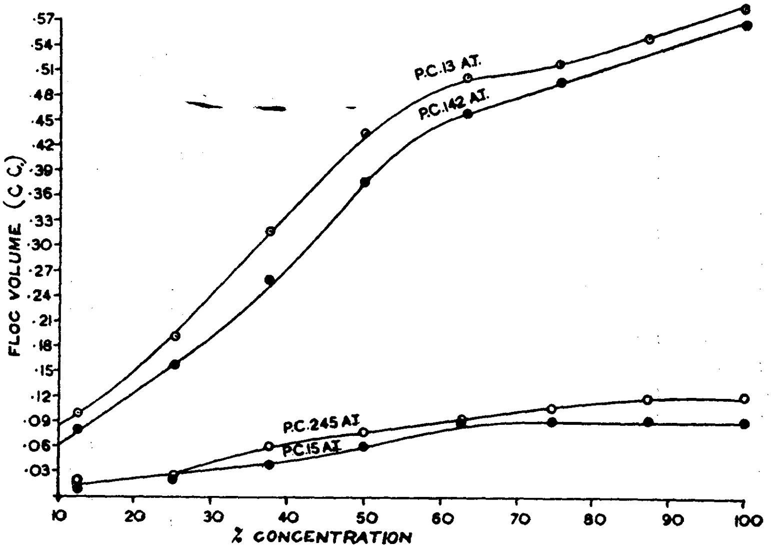


Fig. 4. Effect of Concentration of Clay on Floc Volume of Soils

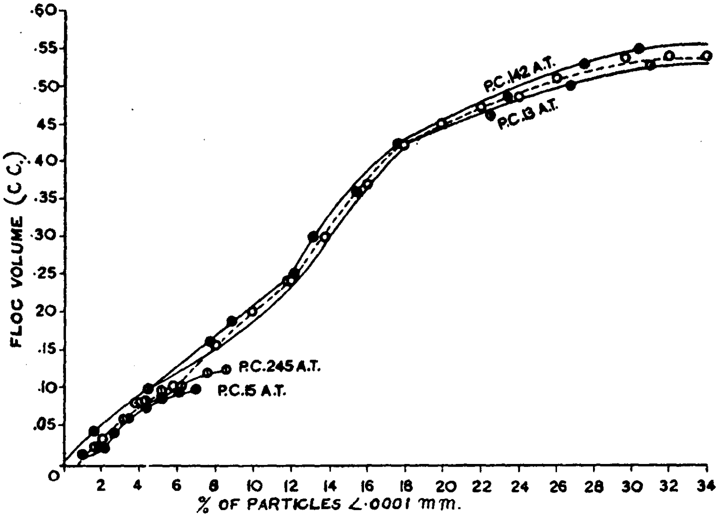


Fig. 5. Relation Between Floc Volume of Soils and Percentage of Particles <0.0001 mm.

actually present in the soil by the number of times the clay was diluted. It will be seen that after a certain concentration of ultraclay particles is reached, the floc volume becomes constant.

Furthermore, all four curves for each of the three particle sizes (figs. 5, 6, and 7) have similar shapes. That all four curves for any particle size are not superimposed is to be expected, as it has already been shown that particles <0.0001

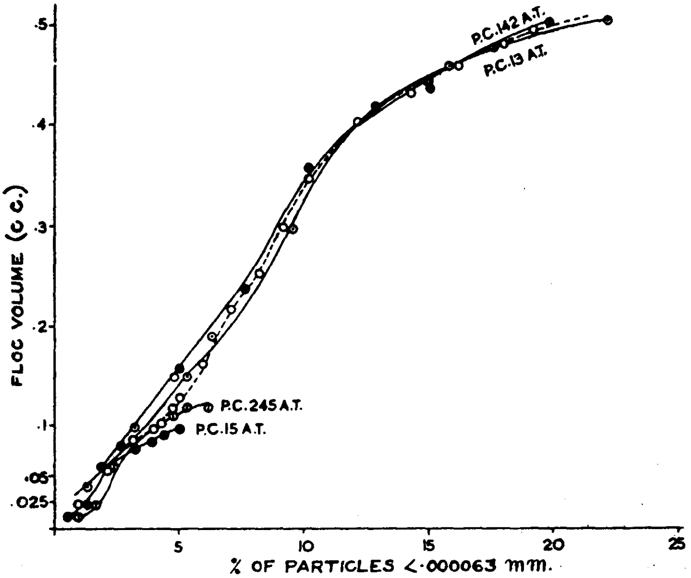


FIG. 6. RELATION BETWEEN FLOC VOLUME OF SOILS AND PERCENTAGE OF PARTICLES <0.000063 MM.

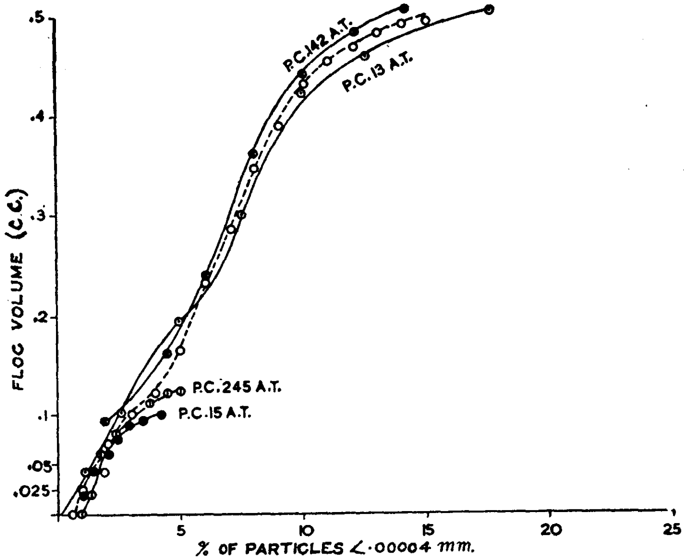


FIG. 7. RELATION BETWEEN FLOC VOLUME OF SOILS AND PERCENTAGE OF PARTICLES <0.00004 MM.

mm. do contribute to the floc volume, and when any two soils contain the same summation percentage of particles <0.0001 mm. diameter, it does not necessarily imply that their size distribution curves for various fractions below this size will be alike. The dotted curve in each figure was obtained by plotting mean values of ultraclay particles corresponding to various floc volumes. The mean curves may be used in calculating the percentages of various ultraclay particle sizes present in a suspension, as discussed in the following section.

ULTRACLAY PARTICLES AS DETERMINED FROM FLOC VOLUMES OF SOILS

Although it is not possible to determine with absolute accuracy, from knowledge of floc volume, the percentages of various fractions in the ultraclay region, a number of soils were studied to find out the degree of accuracy that can be attained. A method that would give readily within a few hours a fairly, if not absolutely, accurate measure of the percentages of particles of such fine dimensions as <0.000063 mm. obviously would be very helpful.

For this study, mean values of percentages of particles of various sizes (<0.0001, <0.000063, and <0.00004 mm.) corresponding to different values of flocculated volume were obtained from the mean curves plotted in figures 5, 6, and 7. All that need be done then is to find out the floc volume of a soil by the method outlined at the beginning of this paper, i.e., take 4 cc. of clay separated from 1 per cent fully dispersed soil suspension and determine its floc volume on the addition of 1 cc. of 0.25 *N* $CaCl_2$ followed by centrifuging for half an hour. The percentages of particles of various sizes can then be read on reference to the mean values.

This method was tested on 63 soils. The percentages of particles of all three sizes as determined by the micropipette technique and by the proposed method are given in table 4. The agreement is fairly close.

Thus the ultraclay fractions can be determined with a fair degree of accuracy by the proposed method. As no particular skill on the part of the observer is involved and determinations of such fine particles in a number of soils can be taken down within a few hours, the method has much to be said in its favor.

SUMMARY

A simple and rapid method of determining the floc volume of soils is described. It is shown to depend on the particle size in the ultraclay range.

The percentages of various ultraclay fractions present in a soil can be determined by measuring the floc volume of the soil.

Variations in pH value and in time of aging are shown to affect the floc volume as well as the ultraclay.

REFERENCES

(1) ANDERSON, M. S. 1929 The influence of substituted cations on the properties of soil colloids. *Jour. Agr. Res.* 38: 565.

(2) MATTSON, S. 1929 The laws of soil colloidal behavior: II. *Soil Sci.* 28: 373–409.

(3) MÜLLER, H. 1928 Zur Theorie der elektrischen Ladung und der Koagulation der Kolloide. *Kolloidchem. Beihefte* 26: 257–311.

(4) Puri, A. N., and Amin, B. M. 1928 A comparative study of the methods of preparation of soil for mechanical analysis with a note on the pipette method. Agr. Res. Inst. Pusa Bul. 175.

(5) Puri, A. N. 1930 Studies in soil colloids: III. Flocculation of soil colloids. India Dept. Agr. Mem. Chem. Ser. 11 (6).

(6) Puri, A. N. 1936 Dispersion of soils for mechanical analysis by sodium carbonate or sodium oxalate treatment. *Soil Sci.* 42: 267–272.

(7) Puri, A. N., and Lal, M. 1938 Dispersion and stability of soil colloids in water: I. Auto-disintegration. Punjab Irrig. Res. Inst. Res. Pub. 4 (10).

(8) Puri, A. N., and Puri, B. R. 1938 Dispersion and stability of soil colloids in water: II. Ultraclay and the efficiency of dispersion methods. Punjab Irrig. Res. Inst. Res. Pub. 4 (11).

(9) Puri, A. N., and Puri, B. R. 1939 Physical characteristics of soils: IV. Density gradients in sedimenting columns and a chainohydrometer for mechanical analysis of soils. *Soil Sci.* 48: 149–160.

(10) Puri, A. N., and Puri, B. R. 1941 Ultramechanical analysis of soils. *Jour. Agr. Sci.* 31: 171.

(11) Puri, A. N., Dyal, P., and Rai, B. Studies in soil dispersion: I. (To be published *Indian Jour. Agr. Sci.*).

(12) Russel, E. W. 1932 The present position of the theory of coagulation of dilute clay suspensions. *Jour. Agr. Sci.* 22: 165.

(13) Weigner, G. 1931 Coagulation. *Jour. Soc. Chem. Indus.* 50: 55.