THE ADSORPTION OF PHOSPHATE ON MICA SURFACES

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ABSTRACT

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The surface chemistry of the 001 face of cleaved mica sheets was studied with a view to understanding some of the fundamental processes underlying the phenomenon of fixation of phosphate by soils.

Radiochemical techniques were developed to make quantitative studies of the adsorption, an important part of these being practical procedures for obtaining sufficient cleanliness and freedeom from airborne contamination. Lack of uniformity of adsorption, as shown by autoradiography, was taken to indicate contamination, and techniques were developed to avoid this. Other techniques enabled the continuous monitoring of the sample during adsorption or desorption kinetic experiments.

It was shown that adsorption of phosphate on the untreated mica sheets was low, but the adsorption was greatly enhanced if the mica had been treated with aqueous solutions of certain cations such as gallium, aluminium and iron.

From the measurement of the amount of phosphate adsorbed, as a function of the conditions of aluminium treatment, it was concluded

that the phosphate could be adsorbed by at least three different processes, all of which could be of importance in phosphate fixation by soils. As well as these processes, which occurred on clean, flat, mica surfaces, there were others, involving the edges of mica sheets, and unknown, but probably organic, films on both mica and air-water surfaces. These could all be of comparable importance in soils.

The kinetic measurements of phosphate adsorption and desorption on aluminium-treated mica indicated that many hours were required for attainment of equilibrium, and were quantitatively consistent with the hypothesis that in some cases the adsorption and desorption kinetics were controlled by diffusion of phosphate into particles of some material, possibly a hydrous oxide, adsorbed on the mica. The existence of such particles was supported by the fact that up to one phosphate molecule per two square Angstrom units of mica surface was adsorbed, (and this did not appear to be a value at which the surface was saturated.)

Kinetic measurements of ^{67}Ga sorption processes were consistent with diffusion of gallium through a thin water film, with a diffusion coefficient several orders of magnitude lower than that of single ions in free solution. This may indicate that the gallium was adsorbing as particles, in agreement with the requirements of the phosphate experiments.

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CHAPTER 1

INTRODUCTION

Background to the Project

Agricultural production is limited by a number of factors, one of which is the lack of available plant nutrients in the soil. This can be due to a complete lack of nutrient in the soil, but often there is ample nutrient present, in a form which is apparently unavailable to the plant. This form is known as "fixed" nutrient. In many places, and particularly in New Zealand, it is found that the fixation of phosphate by soil is of great economic importance, because it leads to the use of only a small proportion of the superphosphate applied as fertiliser. It is found by soil chemists that strongly fixing soil will remove added phosphate from soil solution within a few hours, (so-called phosphate "retention"), but that the same soil will take many months to "fix" the phosphate so that agricultural production falls. This time delay means that by annual top-dressing satisfactory growth can be achieved, but only by wasting much phosphate.

The chemical form of this fixed phosphate is not well understood, and it might be that knowledge of the processes involved would suggest alterations to current agricultural practice which could result in the use by plants of a greater fraction of the applied superphosphate, or the use of phosphate already present in the soil.

At least some of the fixed phosphate is associated with adsorption by the clay mineral fraction of the soil, (Black (1943), Stout (1939)). This fraction of soil can contain several kinds of surfaces on which adsorption of anions could be postulated, among them being those of the hydrous oxides, and the edges of the mica-type minerals such as montmorillonite or kaolinite. A major disadvantage of studying these clay minerals directly is the problem of obtaining them in a pure form, and because of the variety of surfaces present, and lack of detailed knowledge of their structure, the interpretation of results obtained is difficult.

The present experiments concern the adsorption of phosphate on the 001 surface of muscovite mica crystals. This surface is similar to some of the surfaces occurring in soils, on, for example, montmorillonite, kaolinite and halloysite, so that the information on its properties may be of relevance to the studies of clay minerals.

Quite apart from this possible application to soil chemistry, the results will be directly useful as a contribution to surface chemistry, one of the greatest problems in which is that of knowing the nature of the surface. At least at the instant of preparing the surface by cleaving the mica, the nature of the surface is known, and it will not be affected by any previous treatments as will all surfaces other than those of freshly cleaved crystals.

SOME PROPERTIES OF MICA

Muscovite is an alumino-silicate mineral which can be very easily cleaved along the 001 crystal plane. This property arises from the structure, in which two layers of silicate tetrahedra, with their bases forming two parallel planes of oxygen atoms and their vertices pointing towards each other, are strongly bonded together by aluminium atoms coordinated to the oxygen atoms at the vertices. (Each tetrahedron has its corners defined by the four oxygen atoms of the SiO_4 group.) Hydroxyl groups are also bonded to these aluminium atoms, (Jackson & West (1930, 1933)). Some of the silicon atoms (up to 25%) are replaced by aluminium, and some of the aluminium atoms are replaced by divalent atoms, particularly magnesium. When this replacement occurs there is an unbalance of charge within the layer, and this is balanced externally by the presence of potassium or other monovalent ions. These monovalent ions serve to bind successive layers together, but this binding is comparatively weak, so that cleavage between the layers occurs readily. The monovalent ions exposed by cleavage are readily replaced by other cations in solutions in contact with the mica, so that the surface acts as a cation-exchanger, with one negative site per 47 square Angstrom units (Grim (1953)).

If the monovalent cation can be replaced by one of higher valency, the question arises of whether these extra valencies can be satisfied by the mica, in which the charge sites are 7 Angstroms apart. This has not been, to the author's knowledge, satisfactorily answered.

An important consequence of the structure, as far as the present work is concerned, is that the cleavage is sometimes so perfect that up to several square centimetres of a single crystal cleavage plane can be obtained (Tolansky (1948)). While it is not expected that the mica used in the present work was so perfect, it would be expected that the total area of any edges caused by imperfect cleavage would be very small indeed, in comparison with the total 001 face area. Thus the mica surface is well characterised, with only a few types of adsorption site. It has convenient physical properties, being obtainable in large, uniform pieces, which are strong and gas-tight, even in sheets thin enough to allow the passage of soft β-particles.

Anion Adsorption by Mica

It has been stated above that the surface of mica is predominantly a cation-exchange material, (although some anion-exchange capacity would be expected from imperfect cleavage), so it would seem an odd choice for phosphate adsorption experiments. It is concluded in this thesis that the samples used had a small, but significant, anion-adsorption capacity when freshly cleaved, but most of the work was directed towards studying the much greater adsorption of phosphate on mica which had been previously treated with solutions containing molar concentrations of certain cations. A cation particularly efficient at enhancing the adsorption is aluminium.

An immediate, plausible explanation for this enhanced adsorption is clear from the previous discussion of the cations on the mica surface. One could suppose that the aluminium replaces the potassium in the cation-exchange position, and that only one valency bond of the aluminium is satisfied by the surface, leaving two to be satisfied by exchangeable anions. The author is wary of this approach, for he has shown that there are other possible explanations for the phenomenon, and certain aspects of the adsorption are difficult to explain on this model.

A REVIEW OF SOME ASPECTS OF PHOSPHATE SORPTION

This section is devoted to describing phenomena in various fields more or less remote from the study of mica, in order to show that the behaviour of phosphate on aluminium-treated mica is qualitatively similar to adsorption phenomena in many other systems. It is the author's view that the explanation for adsorption on mica ought not to rely on the peculiarities of the mica surface, but should be guided by the more general properties of surfaces.

Phosphate Retention by Soils

It has been suspected for a hundred years that the retention of phosphate by soil is in some way related to the presence of iron and aluminium. For example, Warington, (1868) proposed that iron and aluminium oxides are responsible. (He also referred to the view of Liebig that the retention is due to surface attraction by all the components of the soil). Many attempts have been made since then to correlate the phosphate fixing ability of soils with thier chemistry, some of the more recent ones being Coleman et al (1960), Saunders (1965), Saini and McLean (1965), and Bromfield (1965). These authors, after somewhat more sophisticated comparisons of many soils, came to the conclusion that phosphate retention is stronglycorrelated with the presence of aluminium in the soil, two of them (Saunders, and Bromfield), finding a correlation also with iron, one of which (Bromfield's)appeared to be due to an iron-aluminium correlation. Saini and McLean, and Saunders, found correlations between the amount of aluminium in the soil and the amount of organic matter present.

The mechanisms for phosphate retention in soils have been reviewed by Hemwall (1957). He stated that most workers agree that the simple iron or aluminium phosphates, such as $AlPO_4$, are unimportant in soils, and that if any compound were formed it would be of the form $M(H_2O)_3(OH)_2H_2PO_4$. Such compounds have solubility products which are compatible with the known ionic concentrations in some soils, and there is some evidence that a constant solubility product of iron or aluminium and phosphate does exist in soils. (See also Wright & Peech (1960)).

Hemwall reviewed a considerable amount of evidence that the ability of clays to fix phosphate is related to aluminium derived from the clays by decomposition. That such a source of aluminium is possible is shown by the fact that any attempt to replace all exchangeable cations by hydrogen ions results in the formation of a mixed hydrogen-aluminium clay, the aluminium ions coming from the clay lattice. If aluminium is removed from the clay particles they no longer fix phosphate.

Hemwall's own work has shown that a constant solubility product is found between aluminium and phosphate in equilibrium with various clay minerals. He therefore concluded that the fixation of phosphate by soils is due to the formation of hydrous phosphates of definite composition. These phosphates may be either precipitated, or sorbed on to the surfaces of clay minerals.

Bache (1963), has considered the possibility that solubility product principles apply in soils, and decided from measurements of solubility products that this is not likely. In a later paper (Bache 1964), he showed that at low phosphate concentrations, phosphate is adsorbed on to hydrous aluminium or iron oxides, while at higher concentrations precipitation occurs. If there is no aluminium or iron left adsorption occurs on the precipitate.

In the last few years increasing attention has been paid by soil chemists to the rate at which the phosphate in the soil can reach the growing plant. Several workers (Barber (1966), Nye (1966), Lewis and Quirk (1962, 1965), Olsen (1965)), have considered diffusion of phosphate through the soil solution, and have decided that this is important to the plant, either by showing that other transport processes are insufficient, or that the rate and amount of uptake agrees with diffusion calculations. Such calculations are difficult because the soil solution concentration can be maintained by desorption of phosphate from the soil particles.

Olsen and Watanabe (1966) have performed experiments on the rate of release of phosphate from soil particles, using ion-exchange resin, and have found that some of the adsorbed phosphate (in a particular soil) is released at a rate comparable with the diffusion process, and some much more slowly. Cooke and Larsen (1966), from somewhat limited data, decidedthat the desorption of phosphate from soil particles is diffusion controlled, and deriveda rate parameter that correlated with pot experiments on phosphate availability.

Thus it appears that some of the phosphate retention in soils is probably due to adsorption, associated with aluminium, and that the kinetics of desorption are slow, on the laboratory time-scale. Both these qualitative features are found in the mica-aluminium-phosphate system.

Inorganic Phosphate Complexes

One could hypothesise that there is a complex iron or aluminium phosphate adsorbed on the surface. Birisov et al (1966) have found evidence for complexes of the form $MH_2PO_4^{2+}$ in dilute solutions containing phosphate at pH 2 to 4 where M is Am^{3+}, Ce^{3+}, Pm^{3+} and Y^{3+}. Van Wager and Callis (1962) mentioned the formation of polymers when Al_2O_3 is dissolved in H_3PO_4, and Jameson and Salmon (1954a, b) have shown the existence of $M(HPO_4)_3^{3-}$ in solutions of M_2O_3 in phosphoric acid, where M is Al or Fe. None of these cases is directly related to the problem in hand, but they do point to the possibility of as yet unknown polymers or cationic complexes.

Inorganic Ion-Exchangers

Perhaps more directly relevant to the present problem is the extensive literature on inorganic ion exchangers, especially in the field of radioactive waste decontamination. Most of this work is concerned with cation exchange, as, for example, is that of Hure et al (1958), who used montmorillonite as a cation exchanger to decontaminate reactor waters. These authors found that the hydrogen and zirconium form of montmorillonite adsorbed phosphate efficiently. Amphlett (1964) has discussed inorganic ion exchangers from the practical point of view, and Kraus et al (1958) have discussed the ion-exchange properties of hydrous oxides. Under appropriate conditions gels of these oxides can be precipitated so that they retain an appreciable anion-exchange capacity. Although zirconium oxide is usually used, because of its very low solubility, similar effects can be observed with aluminium oxide. A very common inorganic anion exchanger is zirconium phosphate, as a non-stoichiometric gel, and it would be expected that the corresponding aluminium compound would have similar properties. An important point which arises from the work on these inorganic ion-exchangers is that the reaction kinetics are always diffusion limited (Amphlett (1964)). Huffman et al (1960), working on the dissolution of various ferric phosphates, found a low activation energy for dissolution, which could imply a diffusion limitation in that case too. In view of this it would seem unwise to postulate that slow reaction rates limit the overall kinetics of other systems involving iron or aluminium and phosphate, unless the kinetics are much faster than those of the ion-exchange experiments, or direct evidence is obtained.

Kepak (1965) worked with precipitated aluminium and iron oxides, from the viewpoint of radioactive waste decontamination. He investigated the sorption of $^{35}SO_4$ and $^{32}PO_4$ on these materials as a function of pH (at constant ionic strength), concentration of carrier, and time.

The sorption increased with decreasing pH, after allowing for partial dissolution of the sample at the lowest pH's (pH 2), although this effect was much more prominent at 10^{-6}M concentrations than 10^{-1}M concentrations. A simple ion-exchange model presented postulated the equilibrium,

$$\text{M-OH} + \text{A}^- \rightleftharpoons \text{M-A} + \text{OH}^-$$

with equilibrium constant,

$$K = \frac{[\text{M-A}][\text{OH}^-]}{[\text{M-OH}][\text{A}^-]}$$

so that

$$\log([\text{M-A}]/[\text{A}^-]) = \log(k) + \log[\text{M-OH}] - \log[\text{OH}^-].$$

[M-A] was found from the decrease in solution concentration, and the left-hand side was called the "distribution coefficient", k_d.

Thus $\log(k_d) = B + p(OH) = C - pH$,

where B and C are constants, if only small amounts are adsorbed. The slope of the graph of $\log(k_d)$ versus pH approached -1 only for the adsorption of 10^{-6}M phosphate between pH 4 and 8, being much smaller in all other cases. Allowing for multiply charged anions or changes in [M-OH] did not give better agreement, so there must be some less obvious explanation for the sorption.

The sorption isotherms (plots of amount adsorbed against equilibrium concentration) for both anions on both the oxides were given as log-log plots, which were almost linear between 10^{-2} and 10^{-8} M/1, with a slope of $\frac{1}{2}$, indicating a dependence on the square root of the concentration.

The sorption showed a rapid increase during the first two hours, followed by a much slower increase.

These results are similar to the results described in this thesis, for the adsorption of phosphate on aluminium-treated mica.

Anion Adsorption by Cation Exchangers

It appears that treatment of the surface of mica with aluminium changes it in some way from a cation adsorber to an anion adsorber. This has been known for some time to occur in ion-exchange resins (Helferrich (1962)), and Spedding (1964) carried out roughly quantitative measurements on the effect, using many cations and anions on various cation exchange resins. Helferrich favoured the explanation that the regions of charge in the resin are localised, so that not all the bonds the aluminium can make can be satisfied by the resin, and these extra ones involve ionic bonds to anions in the solvent penetrating the resin. Spedding claimed that ion-pair formation is responsible.

A similar effect was reported by Blaker (1953) who was able to use anionic dyes on an anionic fibre, by performing a preliminary adsorption of copper ions.

Another observation possibly of relevance is that Holland (1964, p. 436) reported that soaking glass in $SnCl_2$ or $AlCl_3$ improves the adhesion of adhesives. He believed that this treatment leaves some metal oxide on the surface.

Metallic Surface Chemistry

There are many widely-scattered papers on the adsorption of cations and anions by metal oxide, or metallic surfaces, (which are usually covered with their oxides).

An interesting point for the interpretation of this field is that the "roughness factor" of a polished aluminium or glass surface is in the range 1½ to 2 (Shepard and Ryan (1956) and Cosgrove (1956)) so that the actual surface area is no more than twice the geometric area.

A series of papers of interest to the present work has been published by Herczynska and coworkers (1959-66). She has studied the adsorption of numerous radioactive cations and anions, mostly on metal surfaces, but also on glass and plastic. She is particularly concerned with the variation in adsorption as a function of pH, and has a rather unusual approach to the theory of the problem. Some people, (for example, Kepak) assume that the pH effect is due to displacement of the equilibrium

$$M\text{-}OH \rightleftharpoons M^{+} + OH^{-}$$

or

$$M\text{-}OH \rightleftharpoons M\text{-}O^{-} + H^{+}.$$

Excess hydrogen ions will neutralise the OH^{-} ions in the first case, so that the positively charged surface becomes an anion exchanger, and, similarly, in the second case the surface becomes a cation exchanger. Herczynska prefers to assume that the surface adsorbs H^{+} or OH^{-} ions from the solution, and that these then act as anion or cation exchange sites.

Herczynska (1965) described some experiments in which tritium uptake by aluminium and copper discs was compared for different pH solutions, using autoradiography, with a scintillating liquid between sample and film. Extreme non-uniformity of adsorption on each disc is prominent in the published autoradiographs, and it was stated that these were selected to show the best results. The author suspects from this, that in these experiments, and therefore probably in her other work, she was using insufficiently clean techniques. It appears from her results that a roughly constant amount of tritium is adsorbed at acid pH's, this amount being considerably more than that adsorbed at alkaline pH's. She ascribed this to adsorption of tritium ions, but it seems equally possible that it could be hydrogen ion exchange with the hydrogen in OH groups on the surface.

Whatever the mechanism involved, the results in a set of papers published in and before 1961 are of interest, for they show that adsorption from tracer concentrations of radioactive materials can occur on to a wide variety of surfaces. Anions used were $^{131}I^{-}$ (on gold and platinum), $^{35}SO_4^{2-}$ (on gold, platinum and perspex), and $^{32}PO_4^{3-}$ (on gold, platinum, stainless steel, tin, copper, aluminium, perspex, and glass). In most cases there is one maximum in the adsorption at about pH 2 - 4, and another at about 7 - 10. Similar experiments were performed with $^{137}Cs^+$, $^{65}Zn^{2+}$, and $^{60}Co^{2+}$, with the general conclusion that a maximum in adsorption occurs at pH 9 - 11.

It is unfortunate that in all these experiments the measure of the activity adsorbed was the percentage of the activity adsorbed relative to the total amount in the drop of solution originally placed on the surface. This is not a very useful measure of the adsorbing properties of the surface, and no quantitative comparison with the present work is possible, although it is of interest to note that the values obtained varied from 1 to 100%.

Measurements on the kinetics of adsorption showed a rapid rise at first, followed by slower changes, and sometimes a decrease in the amount adsorbed.

Herczynska's earlier work was performed with no attempt at constant ionic strength. In the work described in the 1961a paper she controlled the ionic strength (with $NaNO_3$) as well as the pH, with the surprising result that a maximum adsorption occurred at a certain ionic strength about 0.05. The exact strength and amount adsorbed depended on the pH. (This was found for $^{32}PO_4$ on copper and tin, and ^{65}Zn on tin and glass). It seems that the interaction of the ions and surfaces is not to be described in terms of a simple ion-exchange theory, but must take into account secondary effects such as sorption of anions on to cations.

Kinetics of Surface Chemical Reactions

It seems to be characteristic of reactions of liquid-solid surface chemistry that the kinetics are a combination of fast and slow changes. Imré (1931) must have been one of the earliest workers to study desorption kinetics with radio-isotope experiments. He used thorium B and mesothorium II (lead -212 and actinium -228 respectively, adsorbed on to crystalline precipitates of barium sulphate, and found that his kinetic data could be described by a constant plus two exponential terms.

Bourne (1965) studied the removal of ^{14}C- tristearin from stainless steel with NaOH, and found that the desorption curve could be expressed as a sum of two exponential terms, one being much slower than the other. However, in this case the abscissa was not time, but number of washes of a certain duration in the NaOH. The amount removed was nearly independent of the duration of each wash. He could find no evidence for more than one kind of radioactive compound, and was convinced he had a pure system. He took the data of many other workers in the field of cleaning technology, and found that they all can be described in the same way, despite great differences between the systems.

Dlouhy and Maly (1958) have investigated in detail the adsorption and desorption kinetics of radioactive cations on stainless steel. They referred to two other workers in the field of radioactive decontamination who analysed the kinetics of adsorption into two exponential terms, and analysed their own data into three terms, saying that they had previously missed one term through not studying adsorption at very short times or desorption at very long times. (This is very similar to a conclusion of Furkert (1965)).

They showed that repeated desorptions of ^{65}Zn from stainless steel, under (unspecified) varying initial conditions, gave good reproducibility of time constants for the exponential terms, the scatter being less than 10% of the mean values over four experiments. They found that the same time constants (which corresponded to half-lives from 2 minutes to four hours) were obtained from the analysis of either adsorption or desorption experiments. Similar analyses were made of adsorption experiments of ^{45}Ca and ^{210}Po on stainless steel, and ^{91}Y on aluminium.

The values of some of the rate constants for desorption of ^{65}Zn were affected by stirring rate, the slowest one becoming 30% faster and more predominant with increased stirring. Differences of the same order of magnitude were found on adding 10^{-3}M Fe^{2+} solutions, and the fastest desorption rate constant was doubled by changing the pH from 9.0 to 5.0. The slowest adsorption rate constant depended on the concentration of the adsorbing solution, doubling as the concentration increased from 1 to 25 μC/ml.

They developed a quite general theory of adsorption, the detailed mathematical results of which they admitted are probably too complicated to be useful. This theory predicts that the time variation of adsorption of one component of a mixture of M components competing for the same sites, should be expressable in terms of a sum of M exponentials, whose time constants depend in a complicated way on the relative probabilities of interaction with the surface. It was found to be impractical to perform a quantitative comparison between experiments and theory, and although some qualitative comparisons were made, the authors do not appear to have shown any strong links between their theory and experiments.

Amer et al (1955) found that the kinetics of extraction of phosphate from soil by anion-exchange resin (under "infinite load" conditions) could be described as a sum of three exponential terms, which they regarded as quite empirical functions. Olsen and Watanabe (1966) followed their approach and obtained similar results.

Shao (1965) found that the results of isotope exchange kinetic experiments with $^{32}PO_4$ on soils could be analysed into four or five exponentials, each of which he attributed to a different chemical species.

The above experiments show that the data from a wide variety of kinetic experiments may be resolved into exponential terms. Most of the papers avoid trying to attribute the exponentials to individual species, and the author is inclined to agree with this approach.

THE RESULTS OF PREVIOUS WORK AT VICTORIA UNIVERSITY OF WELLINGTON

For the past few years a group of workers in the Chemistry Department of Victoria University of Wellington has been studying various aspects of the problem of phosphate fixation. Some of the work has been devoted to the study of phosphate exchange kinetics on soils (e.g. Shao (1963, 1965) and Watkinson (1967)), and some to the study of adsorption and desorption kinetics on mica. The remainder of this introduction is devoted to a critical summary of the main experimental techniques and results described in those theses dealing with the sorption on mica, together with a brief indication of the theoretical concepts used. This material formed the framework within which the present project was started, although most of it is superseded by the results presented later.

The general procedure was to take a piece of mica and treat one side with a solution containing about one molar concentration of a salt, and after rinsing off the excess salt, to treat that side of the mica with a solution containing a radioactive anion. The activity adsorbed on the mica was measured by the count rate of an end window geiger counter placed near that side of the surface not used for the adsorption. The amount on the surface was studied as a function of several parameters, the one of most concern being the time of desorption into deionized water.

Development of Sample Holders

This work was started by Furkert (1965), who studied the adsorption of $^{32}PO_4$, using 20th Century Electronics Ltd type EW3H Geiger counters as his samples. The aluminium clamping ring round the edge of the mica was protected from the solutions used by coating it with paraffin wax, which was also coated on the sides of the counter and the edge of the window. Furkert also developed a brass holder, to which mica split from a block could be stuck, the counter being protected from the solution by the holder, and detecting the radioactivity which passed through the back of the sample (see fig.1.1). The use of end windows was continued by Rankin (1964) who used $^{35}SO_4$. For his work with cations other than aluminium he waxed a clean window over the top of the original window, and used that. It was found simultaneously by Morris (1964) and Burns (1966) that the paraffin wax was a good adsorber of phosphate after it had been treated with iron or calcium ions. Furkert had tested wax for phosphate adsorption and found none, but he had not treated the wax with a cation first.

The sample holder was redesigned by Morris and Burns, in such a way that radiation from phosphate on the wax was prevented by the holder and desorbing solution from reaching the counter. This design, (fig.1.1) was the one used in the first experiments of the present thesis.

Preparation of Mica for Phosphate Adsorption

In Furkert's experiments aluminium-treated mica was prepared by soaking the mica in a 1M solution of an aluminium salt (chloride, nitrate or sulphate), using several immersions for at least half an hour in separate samples of solution. No attempt was made to clean the end windows before use.

Morris appears to have taken care to start with a clean surface by cleaving the mica before waxing it to the holder. He also introduced the practice of treating the mica for a week with a 0.1M solution of HCl containing strong-acid cation-exchange resin, before a further treatment for one day with a molar solution of the desired salt. The purpose of the acid soak was to replace the cations on the surface with H^+ ions, which he assumed will be readily replaceable with other cations.

The excess iron solution was rinsed off with 0.1M HCl., and the sample was soaked in several changes of deionized water for a day. Furkert soaked his samples similarly after the cation treatment, the solution being adjusted to the pH of the solution in which desorption kinetics were to be followed. This process of "equilibration" was introduced to ensure that all the aluminium on the surface was in the form appropriate to the pH to be used, it being supposed that changes in these forms might be slow. No way of testing whether this procedure was either necessary or sufficient was suggested by either author.

Contamination Problems

Furkert found that it was difficult to get desorption kinetics different from those found for aluminium-treated mica, unless strict precautions were taken to eliminate aluminium contamination. These precautions included the use of polythene containers for all solutions and polythene adsorption and desorption vessels. However, Rees (1962) has shown that for the purposes of analytical chemistry polythene gives no less aluminium contamination than glass. Polythene has the disadvantage that scratches are very difficult to clean, and Eicholz et al. (1965) have shown that hard glass gives less adsorption of many radioactive cations from dilute solution, than does polypropylene. In the present thesis no evidence has been found for significant aluminium contamination from Pyrex glass, in situations where it would be expected to be important.

No discussion of techniques used to clean the vessels has been given in other theses, and from current practice at the start of this work it would seem to consist of merely rinsing, or the use of detergent and scouring powder.

The use of deionized water was introduced by Morris, in order to reduce the concentration of aluminium ions in the solutions. The resin used contained quaternary ammonium compounds, which are well known to be unstable, so that they introduce polymeric amines into the water. The use of this water was discontinued part way through the present thesis after reading the paper by Shenkel & Kitchener (1958), who specifically warn against the use of present-day anion-exchange resins in low-area surface chemistry.

Adsorption at Constant Time

All the above authors, and also Hendy (1965) and Perrott (1965), found that the amount of phosphate adsorbed on similarly-prepared micas was subject to large fluctuations. Morris ascribed this to variable "wettability" of the surface, the non-wetting regions presumably adsorbing a different amount from the rest. Despite these variations of a factor of two or more in the amount adsorbed, some general points emerge from the work. Furkert showed that the adsorption of phosphate in half an hour on to $Al(NO_3)_3$-treated mica was about ten times more than that on to NaCl-treated mica, equal to that on $Al(Cl_3)$-treated mica, and a third of that on $Al_2(SO_4)_3$-treated mica. The adsorption on to NH_4Cl-treated mica and KCl-treated mica approximately equalled that on NaCl-treated mica. These conclusions were reached in experiments where adsorption on wax could have been important. Morris found that $FeCl_3$-treated mica took up about ten times as much phosphate as NaCl-treated mica or HCl-treated mica. Rankin found that $AlCl_3$-treated mica took up about twenty times as much sulphate as NaCl- or HCl-treated mica, and that the desorption kinetics for the NaCl and HCl cases were faster than the $AlCl_3$ case. He stated, however, that the monovalent-ion-treated micas take up <u>no</u> sulphate.

Some information on the effect of pH of the phosphate adsorption solution on the amount adsorbed was obtained by Furkert, who found that, of the four pH's studied, most went on at pH 5.5, about 15% of this at pH 3.5, 1% at pH 1 and less than 1% at pH 0.

By a rather complicated dilution measurement, Furkert established that the adsorption of phosphate on to the Geiger counter end window was proportional to the phosphate concentration, from carrier-free concentrations up to at least 10^{-7}M/l. At 10^{-6}M/l a deviation of one point from proportionality occurred, which Furkert attributed to saturation of the adsorption sites.

Adsorption Kinetics

Rankin was able to follow the adsorption of sulphate on to mica by counting the activity of the surface while it was in contact with the adsorption solution. The low energy β particle from ^{35}S will only penetrate 20 mg/cm^2 of solution, so that only a small volume of solution near the surface is "seen" by the counter. It turns out that the amount of sulphate adsorbed on aluminium-treated mica surfaces is much greater than the amount in this volume of solution, so that in an adsorption measurement the solution background requires only a small correction to be made to the count rate. In the case of $^{32}PO_4$, the background is comparable with the increase, so that Furkert, Morris and Hendy concluded that this technique was unsuitable for $^{32}PO_4$.

Rankin did not do quantitative adsorption kinetic studies, but showed clearly an effect due to aluminium ions in solution. He added some $AlCl_3$ to a radioactive sulphate solution in which a counter had been previously placed, and observed a ten-fold increase in the (background-corrected) count rate, over a time interval of half an hour.

Quantitative experiments on phosphate adsorption kinetics of phosphate on iron-treated mica were attempted by Morris, who developed a technique for soaking the sample for successive short periods, removing and rinsing the sample in order to count the uptake. He showed that although the shapes of the curves were similar, the amount adsorbed at equilibrium varied. He also found that drying the surface during an experiment greatly increased the adsorption rate. About 20 hours were required for the system to come to equilibrium, and about 50% was adsorbed after one hour.

Similar results were obtained by Hendy, who studied the variations in adsorption kinetics of phosphate on aluminium-treated mica using similar techniques to Morris. He varied the anion associated with the aluminium, and also the ionic strength of the solution, and found many differences in adsorption rates. Only one of the experiments was duplicated (successfully), and it is the author's opinion that in the light of current knowledge the variations observed cannot be attributed to the controlled variables until further work has confirmed the results.

Desorption Kinetics

All the workers whose theses are being reviewed here described their desorption kinetics results by resolving them into a sum of several exponential terms. The method used to find these terms is as follows.

The logarithm of the count rate is plotted against time, and it is usually found that at low count rates, that is, after a long time, the graph becomes linear. The extrapolation to zero time, and the slope of this linear region are considered to give the initial amount and time constant of the slowest exponential term, and the contribution of this term to the count rate at shorter times is calculated and subtracted from all points not on the linear region. This leaves a new set of numbers, which are treated in the same way. Up to 6 terms can be found in this way from the data obtained. It has been found that extending the time range of an experiment usually requires the introduction (or "discovery") of another term. A justification for obtaining so many terms from one experiment has been that each term has been found to describe the kinetics over a time of the order of several times the half-life of the term. Looking at the other axis of the graph, as it were, one could equally well say that the exponential fits the data well only over the last ten percent (or whatever it is) of the total change.

It was found by these workers that the half-lives of the terms obtained by this process were reproducible, with a spread of results equal to 10% to 30% of the mean. The half-lives were found to differ by factors of ten, so that identification of the same process in different experiments was easily possible. The relative amounts of each term at t = 0, found by extrapolation, were found to vary widely, even when the conditions of preparation were similar. Superimposed on this random variation were systematic variations due to different conditions of the experiment.

The desorption rate constants found by these workers seem to be remarkably constant. Thus, neither Furkert nor Morris could find any recognisable trends as the pH was changed from pH 3 to pH 9, the phosphate being adsorbed on to aluminium- or iron-treated micas respectively. As the time of adsorption of phosphate on to the mica was increased, the relative amounts of each term changed, but the same rate constants could be found, (Burns, Morris).

Burns found the same rate constants for desorption of phosphate from mica treated with K^+, Na^+, Mg^{2+}, Ba^{2+}, Sr^{2+}, Ni^{2+}, Ca^{2+} and Al^{3+} ions. Micas treated with H^+ or NH_4^+ ions were very similar to these, except for the lack of the fastest term. However Ni^{2+} and Co^{2+} were also used by Perrott, and his results conflict with those of Burns, as follows -

System	Half-lives (hours)
Burns Ni^{2+}	4800, 210, 22, 1.1, 0.11
Perrott Ni^{2+}	5100, 39, 3.3, 0.4, 0.07
Burns Co^{2+}	4600, 160, 23, 1.4, 0.14
Perrott Co^{2+}	1300, 107, 8.1, 1.13, 0.56, 0.05

The author has also repeated much of the work of Burns, and finds no agreement between his results and those of Burns, and very little between his own results. It appears that Burns and Morris used exactly the same procedure in each experiment, including the step of a day's soak in water before the phosphate adsorption, whereas the author and Perrott were more inclined to vary the procedure in ways which current thinking indicated should not alter the results. The variability probably indicates that these minor variations were important, and that the working hypotheses were either a gross oversimplification or totally wrong.

Perrott investigated the effect on desorption kinetics of using complex cations, in which most of the metal coordination positions were occupied by strongly bonded chelates, so that the stereochemistry of phosphate adsorption would be greatly restricted. It was thought that these cations might have a reduced number of exponential terms, but this was not found, and the results were similar to those found with other cations.

The amount of each exponential term has been found to vary with the time of adsorption of the phosphate, relatively more of the shorter half-life terms being found if the adsorption is short than if it is long. No variations with pH of the amounts have been found. Similar conclusions about amounts and half-lives were reached by Rankin, for the desorption of sulphate from aluminium-treated mica.

Removal of Adsorbed Anions by Chemical Reagents

Because of the interest of the system to soil chemists, experiments have been performed by most authors in order to see the effect on the adsorbed anions of reagents used in soil extraction procedures. These experiments were usually performed after about 5 days of desorption, so that the fast changes were all over.

Furkert found that citrates and carbonic acid had no effect on the desorption rate of phosphate, from aluminium-treated mica, while 0.5N hydrochloric or sulphuric acids caused rapid desorption of most, but not all, of the phosphate. 0.1N sodium hydroxide removed all the phosphate rapidly, and 0.5M ammonium fluoride at pH8.5 removed nearly all the phosphate within one hour.

Morris showed that 4M sodium chloride and 0.5M sodium bicarbonate had no observable effect on the desorption rate of phosphate from iron-treated mica. 0.1M sodium hydroxide caused very rapid desorption of phosphate from both iron-treated wax and iron-treated mica, and ammonium fluoride caused fast desorption of phosphate from iron-treated mica, the rate increasing as the pH of the solution decreased.

Rankin showed that ammonium hydroxide at pH 11, sodium hydroxide at pH 8, hydrochloric acid at pH 1, and an unspecified concentration of phosphate ions quickly removed most of the sulphate from aluminium-treated mica.

Effect of Drying on Desorption

These drying experiments were usually performed by desorbing a sample for a short time, removing it from the solution and then storing it in a dry atmosphere or vacuum for the desired time. The sample was then replaced in a desorbing solution, and the slope of the resulting desorption graph was compared with the slope of the graph obtained before drying the sample.

Furkert found that no change occurred in the desorption of phosphate from aluminium-treated mica after 3 weeks drying over silica gel.

Morris found that drying for 100 hours in vacuum over phosphorous pentoxide before desorbing phosphate from iron-treated mica resulted in a considerable increase in the amount of short half-life terms, and also led to decreases in the half-lives of two of the terms.

Perrott extended these measurements to phosphate on many other cation-treated micas, and some soils, and showed that the effect was a generally occurring one.

Theories

Several different theories have been advanced to explain the above phenomena. Because of the relative ease of acquiring kinetic data, most of the theories have been attempts to explain the kinetics, with no account being taken of other information, except the greater uptake on mica treated with aluminium and iron solutions. All have assumed that the exponential terms found by resolving the kinetic data may be assigned to first- or pseudo-first-order reactions. Furkert and Morris appeared to favour some model like that described earlier in the introduction, in the section on anion adsorption by mica, where anions are attached by those bonds of the cations which are not satisfied by the surface. On this model one would expect no adsorption by monovalent cations. The different reactions could possibly be assigned to the different forms of phosphate and iron found at various pH's, but since no correlation between variations in pH and the desorption kinetics was found, this hypothesis is unlikely to be true. The reactions could correspond to differences in stereochemistry of the adsorption compound, but Perrott appeared to eliminate this possibility.

Perrott, on the basis of his drying experiments, postulated that water is somehow responsible for the retention of orthophosphate. He reviewed the evidence in the literature for the presence of an ordered water structure near the surface, which might form a matrix in which phosphate could become imbedded. He decided that this is a possibility, although he did not refer to a major review article by Graham (1964), who concluded that ordering in the structure cannot persist more than a few Angstrom units from the surface. Perrott did not explain how this system could give rise to the observed very slow processes.

Adsorption kinetics have received somewhat more detailed theoretical attention than desorption kinetics. Morris considered that the observed increase was controlled by the sum of an adsorption reaction, which was first order in solution phosphate concentration, and a desorption reaction, which was first order in the amount of phosphate on the surface. He derived a relationship between the amount on the surface and the time, but could have saved a lot of data processing and gained much more accuracy by integrating his equation 8, p. 113, with respect to time. His method involved a graphical determination of the slope of the adsorption curve, the variations with time of this gradient being then resolved into a sum of exponentials, as predicted by his theory.

Hendy assumed that in a process similar to that postulated by Morris, the availability of adsorption sites for phosphate was controlled by the desorption from these sites of previously adsorbed anions. He made a serious mathematical error, which led to erroneous conclusions about the effect of certain parameters. His experimental results were inconsistent with either his version or the corrected version, but the author feels that the theory is worth testing again, under the conditions he has found to be necessary, and so presents his correction of the theory as an appendix.

CONCLUSIONS

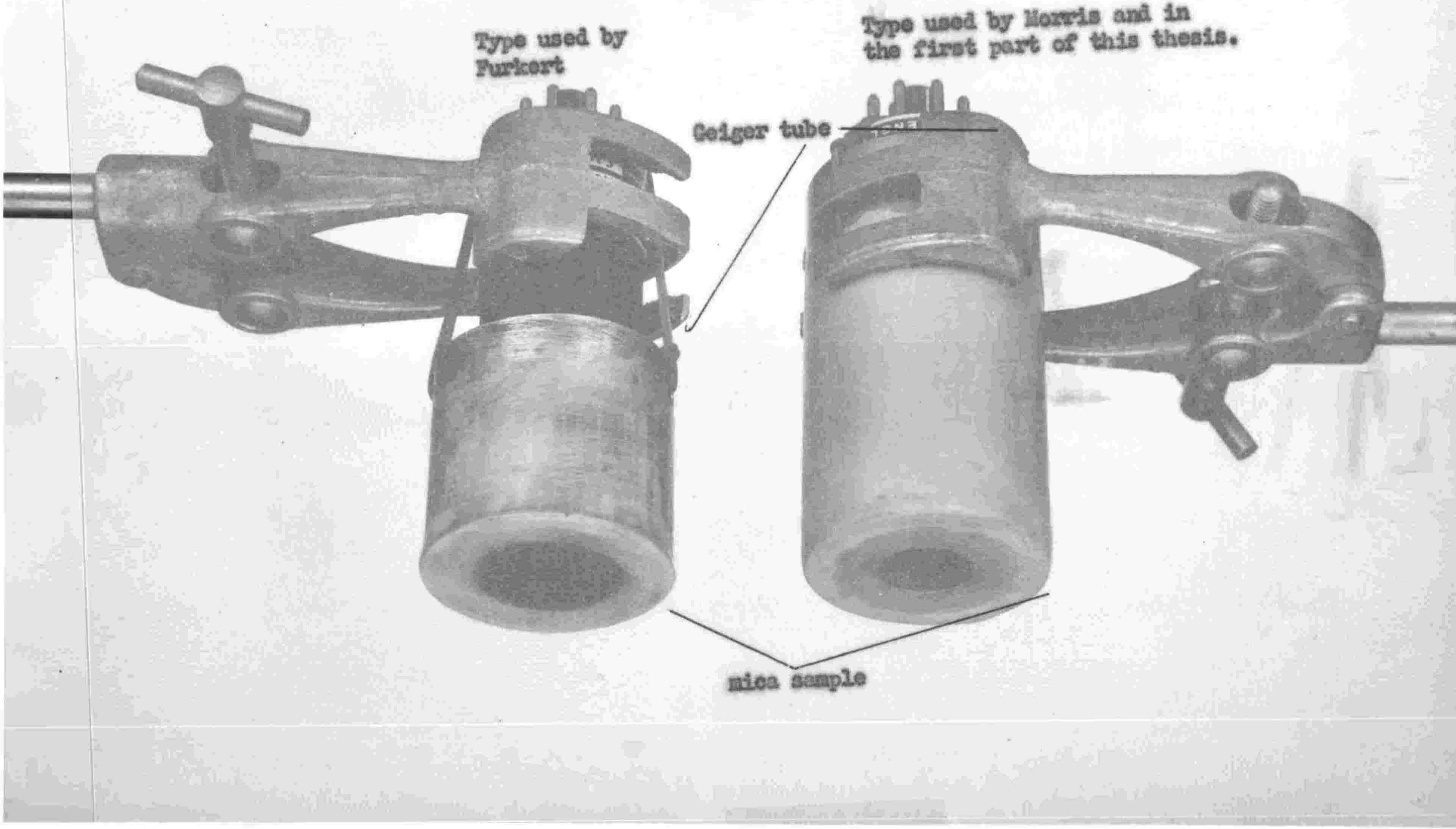
Phosphate adsorption is often found in situations where exchangeable aluminium or aluminium oxides are present. The mechanism is sometimes not describable by conventional ion-exchange models, being influenced in unexpected ways by the presence in solution of other ions.

The kinetics of adsorption and desorption are slow, and can, in common with many other surface reactions, be described as a sum of exponential terms. No consistent explanation for either the adsorption or kinetics is available.

The work described in the following chapters is an attempt to characterise and explain the phosphate adsorption on mica surfaces, in the hope that some points of interest to soil chemistry and other fields might become clear. It started with a continuation of the line developed by Morris and Furkert, in which kinetic studies were made with various cations used for pre-treatment of the mica, and developed into experiments on the details of amounts and kinetics of adsorption on aluminium-treated mica, which led eventually to an understanding of some of the processes involved.

Fig. 1.1

Sample Holders for Desorption Experiments



CHAPTER 2

BASIC TECHNIQUES AND INSTRUMENTATION OF THE KINETIC EXPERIMENTS

This chapter describes techniques used in several sections of the thesis. Those aspects peculiar to each section are elaborated further in the appropriate places.

APPARATUS

Detection of Activity

The apparatus used in the preliminary kinetic experiments was much the same as that used by previous workers. The mica was stuck to the brass holder designed by Morris and Burns (fig. 1.1), and a type EW3H end window geiger counter was held inside the holder with three wedges of cork.

An octal socket was used to connect the coaxial signal lead to the counter to reduce electrical noise problems below those obtained with the crocodile clips used previously. This probably accounts for the lack, in the present work, of problems reported by others when certain types of stirrers were used, and when several experiments were desorbed in to the same vessel.

Electronic Quench Units

An electronic quenching device was used (Crotty 1962), its main advantage being a constant dead time. It has been claimed that the use of the quenching unit increases the life and plateau length of the tube, but it does seem possible that by considerably increasing the capacitive load on the tube it may actually degrade the long-term performance. Since many of the tubes had a life relatively short compared with quoted lives of $10^9 - 10^{10}$ counts, advice was sought from the makers of these tubes (20th Century Electronics Limited, England). They had no adverse criticism of this quench circuit, but enclosed a leaflet (No. GC10) in which it was stressed that the capacitance across the EW3H must be less than 20 picofarads. The value of the coupling capacitor used was 2000 picofarads, so this may be the source of trouble. Other points made in the leaflet were that halogen-quenched tubes must not be operated at more than 60v. above their starting voltage, and should be shielded from light whenever a voltage is applied. These precautions were not previously known to be necessary. It was also said that when quenching an EW3H the dead time may be taken equal to the quench time (at least when this is longer than 300 μSec). This confirmed the practice introduced by the author, which was to set the quench time equal to the convenient value of 600 μSec. (= 10^{-5} min.), using a calibrated "Tectronix" oscilloscope, and to take this quench time as the dead time of the tube. When using a quench on the EW3H the makers recommend using the lowest possible voltage consistent with the stability of the power supply and sensitivity of the quench to triggering.

Counting and Recording Electronics

Power to operate the quench unit, and the E.H.T. voltage, was obtained from a Philips power supply module, type PW4022. This unit also contains an amplifier, through which pulses were sent to the pulse counting electronics, which was either a Philips scaling module, type PW4032, or a ratemeter module, type PW4042. The ratemeter was usually connected to a Honeywell-Brown chart recorder, to enable a continuous measurement of count rate versus time. The chart speed could be varied between 24" per hour and ¼" per hour by using appropriate drive motors and gears, but because of the complexity of changing speeds, it was usual to use two separate recorders, one running at 1" per hour used for the entire experiment, and another at 24" per hour for the sometimes rapidly changing start of an experiment.

The time taken for the chart recorder to travel from 0 to 100 percent of full scale was about 1 second, so the major limit in the response time of the system was the necessity to have an integration time in the ratemeter long enough to obtain statistically significant results. This in the best cases was about 3 seconds, but was more often 10 seconds. At this value, it is not possible to follow changes in count rate reliably if they have a half-life of less than, say, 30 seconds. This rate is the maximum it seems worth trying to obtain with the present techniques of applying and removing the phosphate solution.

For some of the work a six-channel point-plotting version of the recorders was used, connected in such a way that two of the recorder channels were used for each of three working channels. One possible trouble when doing this could arise from the fact that the output of the ratemeters used was at 80 volts above ground potential. It was necessary to avoid connecting an instrument to a channel adjacent to a channel connected to a ratemeter, if that instrument could be damaged by being connected, by the make-before-break selector switch on the recorder, to the ratemeter. When several ratemeters were being used no trouble could arise from this cause. It would be serious if the ratemeters were to be used in conjunction with transistorised equipment of any kind.

The recorders used were basically of 5 mV full scale sensitivity, whereas the ratemeter range was from 80 to 80.5 volts. It was therefore necessary to reduce the sensitivity of the recorder, and this was done by connecting a potential divider of 47 ohms and 4700 ohms across the output from the ratemeter, and taking the recorder signal from across the 47 ohm resistor. The exact value of the dividing resistors is not critical, as the ratemeter-recorder combination is calibrated against the 50 cycle mains frequency, but the resistors must be stable. (It is as well to remember that the mains frequency is controlled to give an accurate average of 50 c/s, and that at times of peak load the frequency may fall slightly.)

It was found useful to note the identification numbers on the electronic units used for a particular experiment, for over the long duration of an experiment failure was quite common, and if a fault was recognised in a module it was possible to trace back through previous experiments to examine them for effects of the fault.

Geiger Counter Selector Switch

Because of the long duration of experiments the number of experiments performed was limited to some extent by the amount of electronics available. A switch was developed which enabled one power supply module and one scaler module to be used to follow the progress of up to six experiments at once. This was done by counting on a Sodeco printing impulse counter, the scaled pulses from the geiger counter over a half-hour period. Every 10th, 100th or 1000th pulse could be caused to operate the Sodeco counter, and at the end of the half-hour period the total number of impulses into the Sodeco counter were printed on a paper tape, the register was reset to zero, and the E.H.T. supply was switched on to the next geiger counter.

The full description of this instrument is given as an appendix. This device is useful after the first rapid part of a run is over, and only small changes are occurring between each ½ hour period. Then it becomes very convenient, for the digital representation is a much more convenient description of the data than the analogue one.

DATA PROCESSING

Manual Methods

It is essential to the success of the exponential analysis of the data, which was the basis of all previous interpretation, that a large amount of information on the curve shape be available. This requires a large amount of effort on the part of the experimenter, in order to perform the various calculations involved in proceeding from the recorder chart to the final graph. The author has developed computer techniques which reduce this work to a minimum, but since computers are not convenient for short calculations, and become unavailable for one reason or another, and often at critical times, he has developed some short cuts appropriate to manual calculation.

Previous workers have developed a nomogram for calculation of dead time corrections. In the present work the dead time of the counter was fixed by the quench at 0.6 milliseconds, so that a table was prepared which enabled direct reading off of the correction to within 1% (table 2.1). The value of $\triangle$ corresponding to the tabulated number nearest the apparent count rate is found, and added to the apparent count rate to get the dead-time corrected count rate, to within 1%. For large rates add or subtract δ for each 1000 c/min. difference between the apparent rate and the nearest value in the table.

A short table to convert days to hours was found convenient, but is not reproduced because of its simplicity.

The chart paper used in most of the work was graduated lengthwise in inches and thirds of an inch. It was often found convenient to read off at fifths and tenths, and a useful guide for this was a sheet of translucent paper ruled in fifths of an inch. This was placed over the chart and moved along as required.

The records showed some statistical scatter, in some cases amounting to an inch or so. It was found to be reliable to estimate the mean of such a line to within 2%, by using a transparent straight-edge placed so that one edge was judged to lie along the mean. The curve was approximated by a series of straight lines drawn this way, and then the values of the lines were taken as the data.

The chart paper is calibrated across its width with 200 divisions. It was found possible to read directly from these the number of counts per minute being recorded, without having to perform any multiplication, by using four moveable scales as a guide. Four scales were necessary because the ratemeters used gave powers of ten times 300 c/min., 1000 c/min., 3 c/sec. or 10 c/sec. for full scale deflection, depending on the model of ratemeter and the range in use. Two strips of chart paper about one inch wide were cut from a roll of chart paper and stuck to thin cards. One was used for meters calibrated in counts/minute and the other for those in counts/second. The 1000 c/min. scale was marked 0, 50, 100, etc. from left to right, at each ten divisions along one edge. Along the opposite edge every second division was marked 0, 3, 6, 9, etc. up to 300, the numbers being alternately in each of two rows parallel to the edge, to improve legibility. The strip used for meters calibrated in counts per second was marked every tenth division with 0, 9, 18, etc. up to 180 for the scales which were multiples of 3 c/sec., and interpolation was done by adding or subtracting 0.9 counts/minute/division. For the scales which were multiples of 10 c/sec. every second division was marked 0, 6, 12, 18, etc. up to 600. With a little practise it is almost as quick to read off directly in counts/minute using the scales as it is to read in percent of full scale deflection without the scale.

For decay corrections of ^{32}P the tables prepared by Morris were used. Other isotopes used were all processed by computer.

Computer Methods

Because of the large number of experiments performed by the author, not to mention those done by others or proposed for future workers, it appeared worth while to make the effort required to develop a computer programme to process the data.

The work can be divided into two parts. One is the processing of raw data (coordinates on a chart) into a table or graph of count rate versus time. This involves allowing for rate-meter range, chart speed, small errors when ranges are changed, attenuating filters introduced to extend the range of radioactivity measurable, dead time of counters, background activity, and decay. This data processing is independent of the type of experiment or the particular theory it is desired to test. The second type of processing involves taking the above processed data and fitting it to some sort of theory. This is the more complicated sort of programme, and one which is likely to be discarded or modified as theories come and go. For this reason the programme, which was originally developed as one which both processed the data, and then allowed the analysis into exponential terms to be performed, was modified into other versions which merely processed the data. Copies of the programmes are bound in as appendices.

The computer for which the programmes were written was an Elliott 503 owned by the Applied Mathematics Division of the Department of Scientific and Industrial Research. The Algol programming language was used to write the programme. The programme is input on paper tape, and the data is output on a lineprinter and a graphical plotter, using the standard procedures. A full description of the preparation of data for processing is included as an appendix.

The aim of the programmeswas to reduce the effort required by the user to a minimum, so that the data is read off the chart in terms of percentage of full scale at points which are either entered as data, or, being regularly spaced, can be calculated by the computer. It is simple to switch from one method of specifying the time coordinate to the other, and to allow for changes in any of the correction factors which are applied. The numbers are entered on a standard form as they are taken off the chart, and are then punched on tape by the University's flexowriter operator. After checking (by the user) of the typewritten copy for punching errors, the data and programme tapes are left with the computer staff. If a plain data processing programme is used a printed copy of the results of processing, plus a graph, is returned in a few days, depending on the computer load.

If it is desired to use programme UCHH04 to analyse the curve into exponentials a special arrangement must be made with the computer staff, for the decision on what part of the curve is to be considered exponential has been left to the user's discretion, and not made a part of the computing. To make this part automatic would require a considerable degree of sophistication, which is probably not justifiable until the theoretical reasons for the analysis are much more firmly established than at present. The user must arrange to be present when his programme is running, and he supplies data manually, from the information on the graphs produced during the running of the programme. An average time of ten minutes calculation per experiment is required for this method, whereas for a manual calculation a long experiment would take from one half to one day.

TABLE 2.1

DEAD TIME CORRECTION FOR $\tau = 0.60$mS

Rate(c/m)	Δ	δ
20,000	5000	50
19,000	4500	50
18,000	4000	50
17,000	3500	50
16,000	3100	40
15,000	2700	40
14,000	2300	40
13,000	2000	40
12,000	1700	30
11,000	1400	30
10,000	1100	30
Rate	**Δ**	**δ**
9500	1000	20
9000	900	20
8500	800	20
8000	700	20
7500	600	20
7000	530	15
6500	450	15
6000	380	15
5500	320	10
5000	270	10
Rate	**Δ**	**δ**
4500	210	10
4000	170	10
3500	130	10
3000	100	
2500	60	
2000	40	
1500	25	
1000	10	

Find rate in table nearest to apparent rate. Add Δ, then add or subtract δ for every 100 c/min difference between apparent rate and nearest value in table.

CHAPTER 3

COMPARISON OF PHOSPHATE DESORPTION KINETICS EXPERIMENTS ON MICA TREATED WITH VARIOUS CATIONS

INTRODUCTION

This work was started against the background of the work of Furkert, Morris and Rankin. These workers had apparently established that carrier-free phosphate, when adsorbed on to mica treated with various salt solutions, could be desorbed into deionized water, the kinetics of the desorption being characteristic of the cation in the salt solution. This conclusion was firmly established for aluminium and ferric salts, and more tentatively so for certain monovalent-cation salt solutions, such as potassium. The aim of the present thesis at that stage was therefore to study phosphate linkage to mica surfaces by cations of the alkali metals and alkaline earths, in the hope that systematic variations would give a clue to the mechanisms involved. It was also proposed to attempt to find the source of the variations observed in the percentage of phosphate adsorbed, in experiments performed under apparently identical conditions.

It became apparent after a few experiments had been completed (a process which took up to several months), that consistency of results obtained in different experiments was not easily achieved in the systems being studied, so that the objectives were temporarily narrowed, to attempting to obtain the same results twice in two identical experiments. The salt chosen to soak the mica in was potassium chloride, because it was readily available, and of relevance to soil systems. The techniques and results will be described in terms of the twenty-five experiments performed with potassium-treated mica, and the results obtained with mica treated with other cations will be presented in the light of the conclusions drawn from that work.

TECHNIQUES

The technique inherited from previous workers, mainly Morris, was to split a piece of mica, wax a brass holder, (fig. 1.1), place that side of the mica which was not freshly cleaved on to the molten wax on the holder, and, after cooling, to put more wax over the edges of the mica. The mica and holder were then soaked for several days in dilute HCl containing hydrogen-form ion-exchange resin, then in the salt solution, and finally in the phosphate solution.

In the course of the first few experiments alterations to this technique were made. The mica was first stuck to the holder, then trimmed to the same size as the holder, and then split. The thickness of the piece of mica remaining on the holder was measured approximately in the first few experiments (until it was established that absorption of radiation in this mica was quite insignificant compared to other variations between experiments) by the difference between the weight per square centimeter of the piece of mica put on, and the weight per square centimeter of that taken off.

After some trouble with sample holders leaking when made this way, the mica was stuck to the brass with "Araldite" epoxy-resin adhesive, type AV100 and HV100 (made by C.I.B.A. Limited). It was found undesirable to use heat to cure the resin in this work, because of the difference between the coefficients of thermal expansion of brass and mica, which sometimes resulted in a strain sufficient to break the mica. Under appropriately controlled conditions, though, the compressional strain on the mica when cooled can be used to produce a circular depression in the mica, and this was later used by A. Langdon to contain small quantities of solution on clean mica.

In order to increase the activity per unit volume of the solutions used, without becoming involved with excessive total amounts of radioactive materials, the volume of phosphate solution used was reduced to less than a millilitre by placing drops of it on the upward facing sheet of mica. The solution was confined by the wax border around the mica, or in some cases, by the surface tension of drops which did not wet the mica, and was removed by soaking most of it up with filter paper, the rest being rinsed off with a wash bottle. Concentrations used were typically in the range 1 to 10μC/ml.

A method was devised which enabled an approximate estimate of the ratio of the phosphate concentration in the solution to the total amount adsorbed. During the adsorption a screen with a hole approximately 1/16" diameter in it was placed in the holder between the geiger counter and mica surface, and the count rate measured. This depended on the thickness of the phosphate solution, but since about the same volume was used each time, and since the solution was usually confined by the wax, which was approximately constant in its position, this count rate should provide, within a factor of two or so, a guide to the solution activity. An estimate of the adsorption power of the mica is therefore the ratio of the initial count rate (I.C.R.) to this solution count rate (S.C.R.) of the run. It was found that the screen used transmitted about 0.2% of the counts which would be obtained inside the holder from a uniform source without the screen.

It was necessary to change the desorbing solution occasionally, especially at the start of a run where the amount of activity lost by the surface could be large compared with the amount remaining. It was found necessary when doing this to ensure that the geiger counter did not change its position relative to the magnetic stirrer, for the magnetic field could significantly alter the count rate. This was most easily shown by shielding the counter with a sheet of iron over the stirrer, and far enough away that back-scatter would be unimportant. A five percent change was observed in one case upon doing this.

PRESENTATION OF RESULTS

It was expected at the start of the work that when the data was analysed into exponential terms in the way used by previous workers, clear correlations between the half-lives of these exponentials and the experimental conditions would be observed. It was found to be possible to obtain values for these half-lives in most cases, but when different experiments on potassium-treated mica were compared there appeared to be no common values.

Twelve parameters are required to specify a curve in this way, if there are 6 exponential terms, and it is difficult to use the numbers to compare two curves qualitatively, so that the numbers are not an empirically useful description of the data, when great variations are occurring. The method adopted here to show the variation in kinetics is to graph the count rate, (normalised to 100% at zero time) against the logarithm of the time in hours. This distorts the slope of curves, since $\frac{dc}{dt} = \frac{dc}{d(\log t)} \cdot \frac{1}{t}$.

This means that if two lines have the same slope on the log plot, but one is at short times and the other at longer, than the one at short times has a much greater rate of change of count rate with time than the other. However, it means that the data from the whole of an experiment running from a few seconds to thousands of hours can be presented on one graph.

A computer programme was developed to plot data from all experiments on the same-sized graph, so that comparisons were easily made by superimposing the relevant graphs.

RESULTS OF EXPERIMENTS ON POTASSIUM-TREATED MICA

Some Problems

The time over which results were obtainable from an experiment depended greatly on the initial count rate. If this were too low then a long instrumental time constant was required, so that very fast processes at the start of the experiment were missed. The count rate would also approach the background in a comparatively short time, due to decay if not desorption, thus ending the experiment before long-lived processes could be found. It was found with potassium-treated micas that the I.C.R./S.C.R. defined previously varied from 30 down to 0.03, this factor of 1000 difference being practically uncontrollable, so that very often only limited information could be obtained.

Occasionally most surprising things occurred, such as a count rate increasing during a desorption experiment. In one experiment the count rate rose continuously from the start of the desorption up to a constant maximum value. The difference between this maximum and the count rate at any time was found to be exponentially dependent on the time, with a half life of 26 minutes. The holder was later found to have leaked, and so presumably the increase was due to phosphate diffusing from the side of the holder into the field of view of the counter. It is mentioned to illustrate the way a spurious effect can give an exponentially varying count rate, and as an example of a reason for which experiments have to be abandoned.

Comparison of KOH and KCl Treatment

The first successful experiments on potassium-treated mica were performed using mica which had been soaked in dilute HCl plus cation exchange resin for a week, and then soaked in a potassium salt solution. This soaking in acid had been used by previous workers to convert the mica to a "hydrogen form", which supposedly was easy to convert to any other form. Two samples were used, one soaked in 1M KOH for four hours (sample 19), the other in 1M KCl for four hours (sample 20). They were rinsed and a few drops of carrier-free $^{32}PO_4$ solution were placed on their surfaces for 10 minutes, after which they were desorbed into deionized water at pH 5.5. The results of the two experiments are compared in graph 3.1 and table 3.1.

It is clear that the two are extremely different from each other, so that something other than the cation was affecting the adsorption. The one in which KCl was used showed scarcely any decrease in count rate for the first few hours, so that some spurious effect was probably present.

Duplicates Treated with KOH, and then KCl

Two samples were prepared by cleaving the mica in deionized water (from a wash bottle), soaking it in KOH, (to remove aluminium as aluminate), and then in KCl. The samples (numbers 22 and 23) produced this way and soaked for 10 minutes in carrier-free phosphate, both leaked after a few hours, but the data obtained is also shown in graph 3.1, and the desorption rates are clearly different from each other and the previous results.

Potassium ^{32}P-Phosphate

To eliminate a possible source of aluminium contamination, and to ensure that the pH of the phosphate solution was around 5.5, a quantity of potassium form ion-exchange resin, more than sufficient to remove the hydrogen ions from the HCl in the radioactive phosphate solution, was added in all subsequent potassium mica experiments.

Duplicates Split in KCl Solution, then Soaked in KCl

The next samples (numbers 24, 25 and 27) were prepared by splitting them in a jet of 0.1M KCl, and keeping the surface covered with KCl except when it was necessary to dry it in order to put wax around the edges.

After a 10 minute soak in the active potassium phosphate solution a very small fraction of the activity was found to have been adsorbed. Samples 28 and 32 were prepared similarly to samples 24 to 27, but the phosphate was adsorbed in the presence of 0.5M KCl. It is clear from graph 3.2, which presents the results of these experiments, that duplicate runs were far from identical, but in this kind of experiment such conclusions are not aways obvious from looking at the raw data.

Effect of Ion-exchange Resin

Rather than wait the several weeks for these experiments to finish it was decided to press on with another set of experiments to investigate the effect of different ways of treating the mica with potassium solutions.

These experiments were guided by a rather curious observation, that the exponential analysis of four quite different experiments gave very similar numbers. These experiments involved desorption of phosphate from mica treated with $FeCl_3$ by Morris, with a nickel amine complex by Perrott, with HCl and with KOH by the present author. The actual values of the half-lives found were (in hours) -

KOH	HCl	$FeCl_3$	Ni Complex
1760	2500	4300	6780
100	120	80	93
7.5	8.2	12	6.3
1.1	1.5	1.5	1.25
0.17	0.17	0.15	0.15
0.033	0.026	0.023	0.03

The experiments by Morris had been repeated several times, but the other results had been found only once each. That such a diverse range of treatments should produce such similar results was most surprising, especially in view of the great dissimilarity between these experiments and all the others. The only factor common to these experiments as far as the author could see was the use of mica, which had of course been used before, and the treatment of the mica with HCl containing cation exchange resin before the cation treatment. This latter treatment had also been used before with no corresponding similarities in the half-lives, but it was decided to perform several experiments with different treatments of the mica involving the use or lack of use of deionized water, distilled water, and cation exchange resins. There was a general suspicion about the use of ion-exchange resins, particularly the quaternary ammonium anion exchangers, because of the discolouration of water shaken with the fresh resin, and the obvious surface active potentialities of their decomposition products. They had been originally used in this work to remove aluminium ions, but it was quite possible they could be doing as much harm as good.

Samples 36 and 38 were treated in 0.1M HCl plus cation exchanger for two days, and then with 1M KCl for three days. Sample 34 was soaked in deionized water plus hydrogen-form cation exchanger for two days and KCl for two days. Sample 35 was as sample 34 except that no resin was in the deionized water. Samples 33 and 37 were prepared using distilled water and KCl and it was hoped to compare them with the others. The results are shown in graph 3.3.

Conclusions

It is clear from the duplicated runs that uncontrolled variations are as great as any differences between different treatments, so the only conclusion to be drawn was that some dominating factor was being ignored. The four similar runs recognised may have accidentally obtained the same conditions. Other cations were being studied concurrently with potassium, and since it appeared from previous work that for aluminium and iron, at least, the techniques were satisfactory, these others were investigated to see if reproducibility was any better with them.

RESULTS OF EXPERIMENTS ON LITHIUM-TREATED MICA

The first few experiments failed because of leaks or unexplained rises or falls in surface activity. Sample 9 was desorbed for 45 hours, and then more phosphate was adsorbed on to the surface. This resulted in a very large uptake from the solution (ICR/SCR = 40, compared to 1 for the initial adsorption), which suggests that the surface had been drastically altered by the first desorption, but the desorptions were similar. A third adsorption gave ICR/SCR = 1, but much slower desorption kinetics. The kinetic data is shown in graph 3.4. Sample 29 showed a large uptake (ICR/SCR = 4), whereas samples 42 and 43 took up very little (ICR/SCR about 0.05). The comparative kinetics of these experiments are also shown in graph 3.4, and they appear to be no more reproducible than potassium, except that samples 9 and 29 seem quite similar. Sample 9 was prepared by soaking in acid plus resin, and then in Li_2SO_4, while samples 29, 42 and 43 were split in a jet of Li_2SO_4 and soaked in Li_2SO_4. These differences seem not to matter.

Readsorption of phosphate gives quite different kinetics each time, so that the concept of a surface which remains the same through several cycles of adsorption and desorption is clearly inapplicable for lithium-treated surfaces under these conditions, although it seemed to work for Furkert with aluminium-treated mica.

RESULTS OF EXPERIMENTS ON SODIUM- AND CAESIUM-TREATED MICAS

Similar results to the above were obtained with mica treated with sodium and caesium chloride solutions. Sample 13 had been treated with deionized water containing hydrogen form resin before soaking in 1 M. NaCl for several days, while the other samples were all split in the appropriate salt solution and left to soak in that solution for several days. The phosphate solutions used had all been treated with cation-exchange resin to make the cation in the phosphate solution the same as that used to treat the mica.

The sodium results, including two readsorptions on to the same samples are given in graph 3.5, and the caesium ones in graph 3.6. Great differences between supposedly similar experiments are clear.

RESULTS OF EXPERIMENTS ON DIVALENT-ION-TREATED MICAS

The situation was no better for duplicate experiments using the alkaline earth cations. The results for calcium are shown in graph 3.7. It was estimated that 90% of the activity in the original phosphate solution was initially adsorbed on sample 84, while about 1% was adsorbed in the other cases. This strong adsorption contrasts greatly with Burns's result that no detectable adsorption occurred on a calcium-treated mica.

Results for magnesium-, strontium-, and barium-treated micas are shown in graph 3.8. Some similarity between duplicates is apparent for the case of strontium, but not the others.

RESULTS OF EXPERIMENTS ON ALUMINIUM-TREATED MICA

Results from two experiments on aluminium mica are shown in graph 3.9, and they can fairly be described as similar. A fast recorder was not used for sample 40, so that the fast process at the start was missed, and this similarity is not at all obvious from the exponential parameters, which are presented in table 3.3.

EXPONENTIAL TERMS FOUND FROM THE PRECEDING EXPERIMENTS

The preceding experiments were all analysed into exponential terms, using the programme UCHH04 on the 503 computer. A few experiments were analysed both manually and with computer assistance, and, as expected from the fact that the decision-making was done in the same way in both methods, the results were comparable.

The graphs already presented show that similarity of shape was not noticeable, but it is conceivable that this is due merely to varying proportions of the various species represented by a limited set of half-lives. The low probability of this possibility is most easily shown from table 3.2, which lists in numerical order all the half-lives found in the experiments with potassium-treated mica. If these half-lives were due to a few species, this should be immediately apparent in the distribution in values about certain numbers. The author does not know of any statistical technique for searching for such preferred values, but visual inspection suggests that the spread around such numbers would be so great that little chemical significance could be attached to them.

The results found for cations used by Burns (1966) are compared with his results in table 3.3. The percentages would be expected to differ, because Burns used a time of 30 minutes in phosphate, while the author used a time of 10 minutes. The author's results differ so much among themselves, that agreement with Burns would be surprising, and is not apparent.

CONCLUSIONS

The experimental techniques described by previous workers in the group must have been such that some or many important factors had been ignored, and only by strictly following a "recipe", which led to these factors remaining constant, and therefore concealed, could reproducible results be obtained. Apparently minor or unimportant variations, as attempted in this work, led to great changes in these unrecognised factors, and consequent variations in adsorption properties.

Several of these factors are described in succeeding chapters, which discuss other kinds of surface adsorption experiments, and a return to kinetic measurements is made in Chapter 7.

TABLE 3.1

TABLE OF I.C.R./S.C.R. FOR PHOSPHATE DESORPTION EXPERIMENTS

Sample Number	I.C.R./S.C.R.	Nature of Surface
19	30	Mica treated with HCl, KOH
20	4	" " " " KCl
22	0.5	" " " KOH, KCl
23	2.7	" " " " "
24	0.06	Mica split in KCl, soaked in KCl
25	0.1	" " " " " " "
27	0.2	" " " " " " "
28	0.2	" " " " " " ", KCl in $^{32}PO_4$
32	0.4	" " " " " " " " " "
33	0.07	Mica soaked in DW then KCl
34	0.09	" " " DDW/resin " "
35	0.53	" " " DDW " "
36	0.16	" " " HCl/resin " "
37	0.5	" " " DW " "

TABLE 3.2

HALF-LIVES (IN HOURS) FOR DESORPTION OF PHOSPHATE FROM POTASSIUM-CHLORIDE-TREATED MICA SURFACES.

2580	186	32	8.3	1.7	0.5	0.03
1850	130	27	5	1.2	0.3	0.02
1480	127	22	3.5	1.2	0.2	0.02
1300	100	15	3.1	1.1	0.2	
827	100	15	3	0.75	0.07	
661	61	14	2.7	0.5	0.06	
600	49	19.6	2.3	0.5	0.04	

TABLE 3.3

COMPARISON OF DESORPTION KINETICS WITH THOSE FOUND BY BURNS (1966)

	Burns (30 min)		Hoare (10 min)			
Cation	$t_{\frac{1}{2}}$	%	$t_{\frac{1}{2}}$	%	$t_{\frac{1}{2}}$	%
Magnesium	4100	31	612	31	670	4
	190	17			52	3
	18	10	13	12	10	7
	1.7	19	2	15	2.2	25
	0.11	23	0.27	42	0.25	31
					0.03	30
Barium	4200	29			1830	2
	150	15	340	4		
	27	12	32	1		
	0.9	22	2.8	95	2.9	1
	0.19	22			0.3	13
					0.02	84
Strontium	4000	35	3000	1.5		
	170	19	68	1.5		
	18	11	6.9	2.6		
	1.3	13	1.1	5.4		
	0.21	22	0.17	11		
			.007	78		
Aluminium	4500	24	2870	20	4730	35
	350	19	101	10		
	24	6	8.1	33	9.9	15
	2.1	22	0.9	33	0.6	33
	0.13	29			0.02	16

Fig. 3.1 - Potassium-Treated Mica

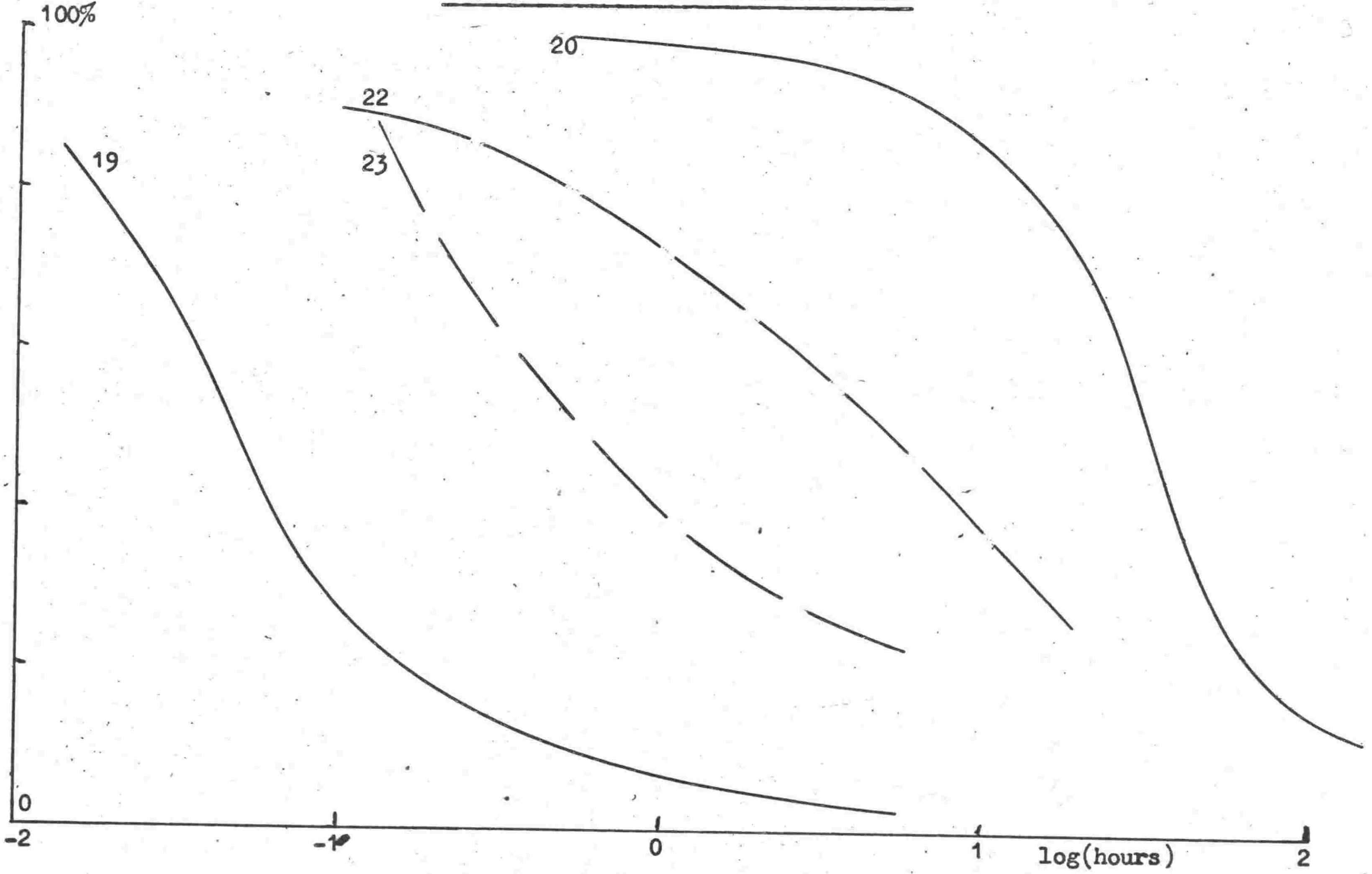


Fig. 3.2 - Potassium-Treated Mica

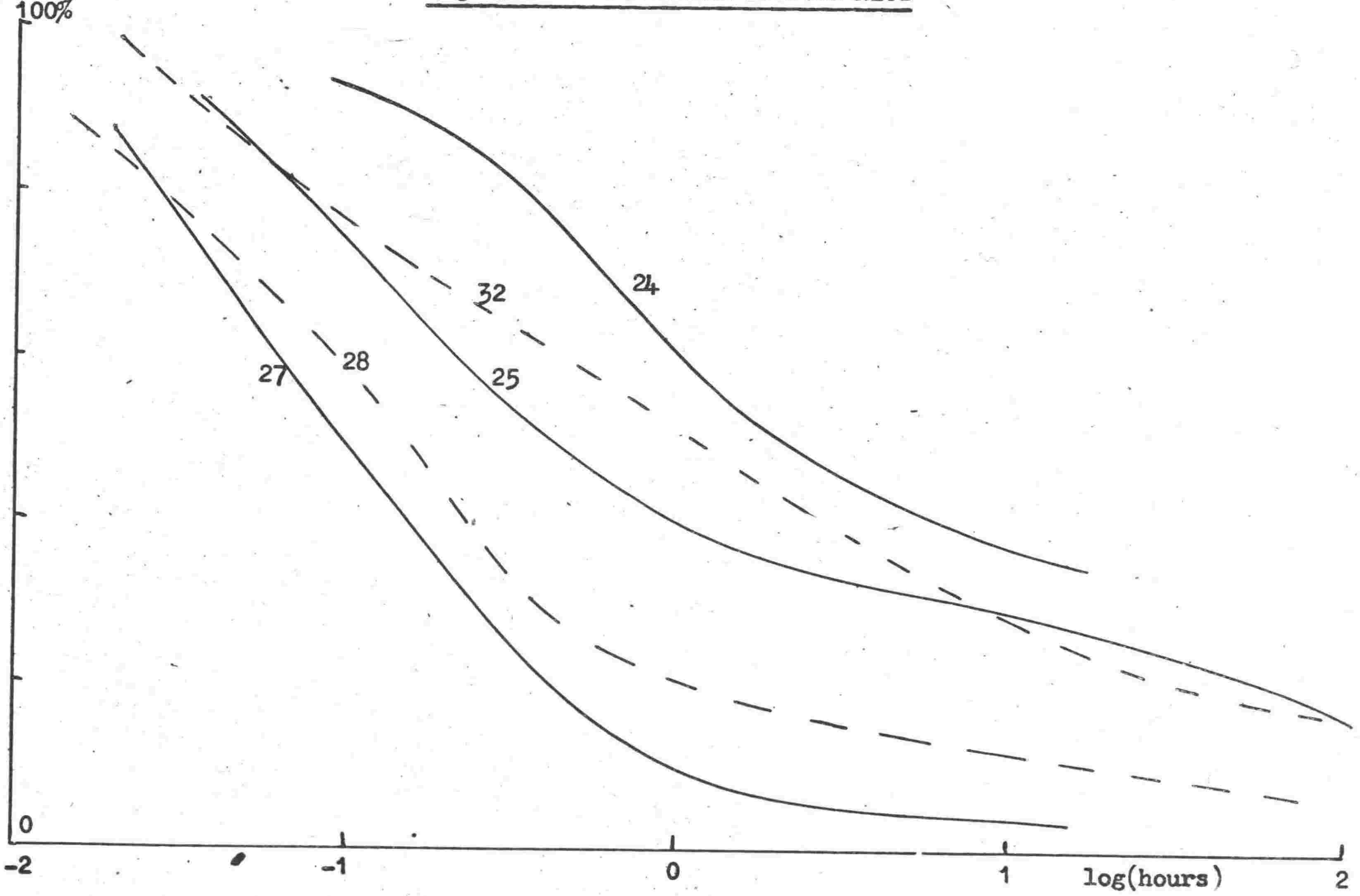


Fig 3.3 - Potassium-Treated Mica

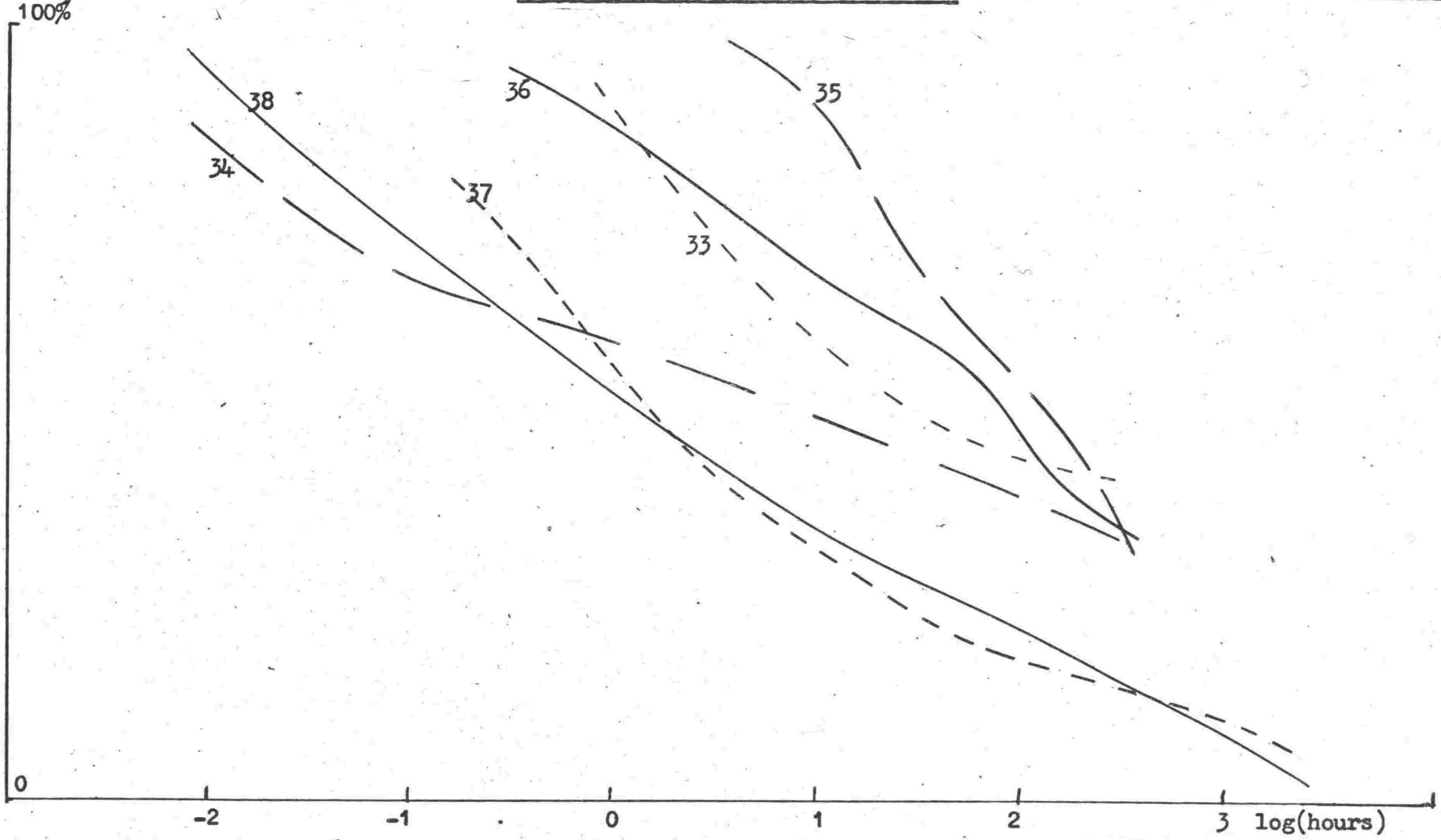


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Fig 3.4 - Lithium-Treated Mica

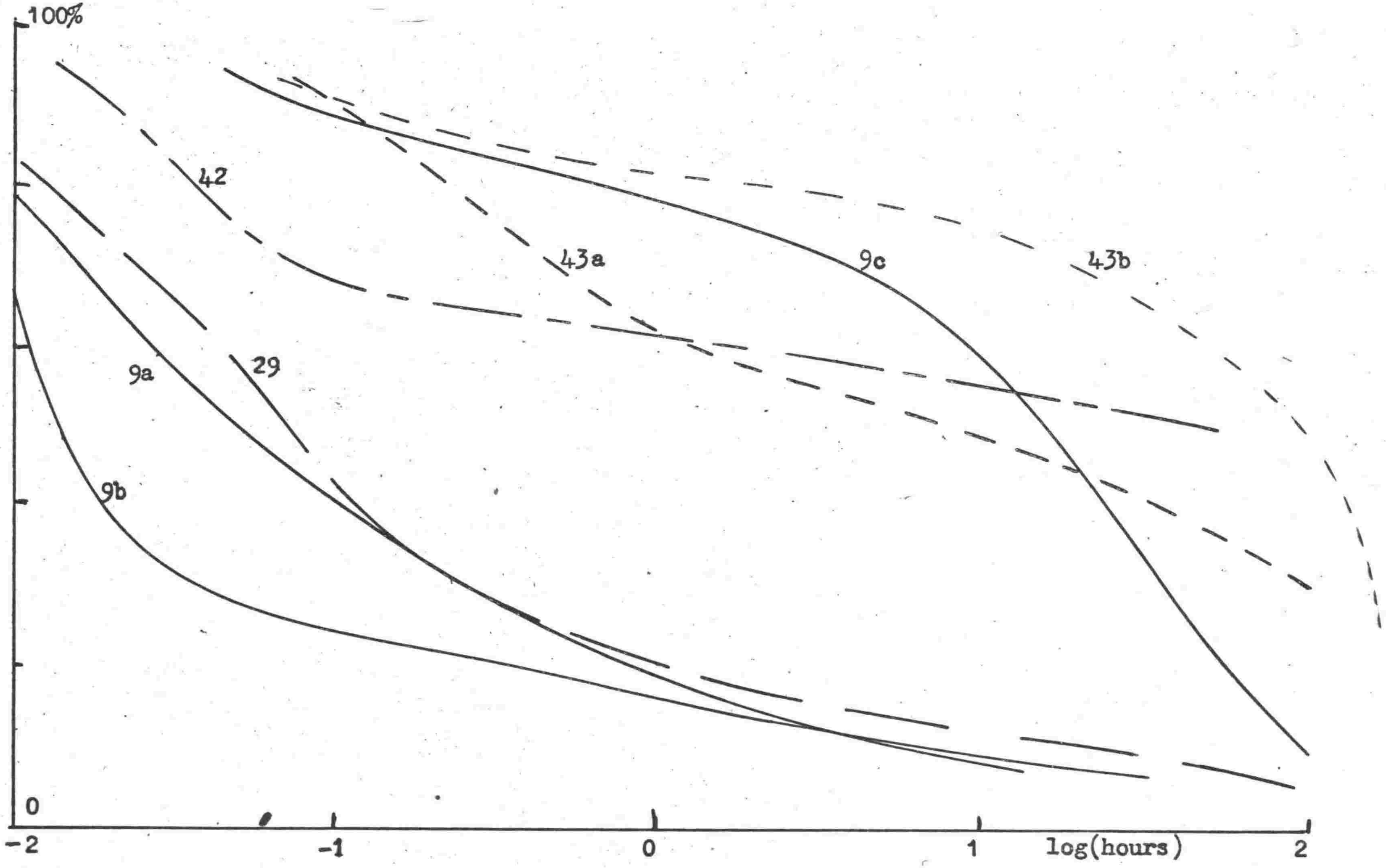


Fig. 3.5 - Sodium-Treated Mica

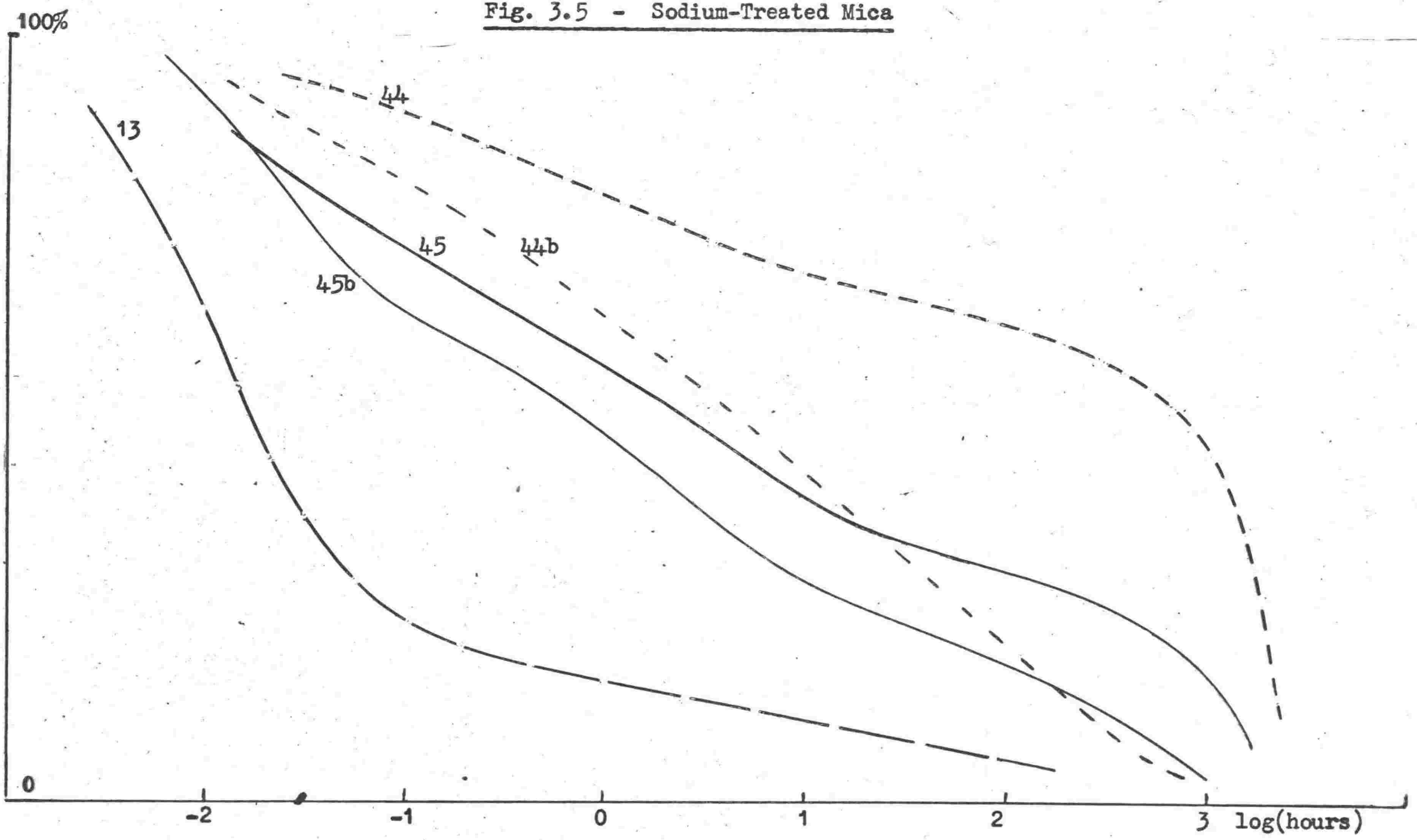
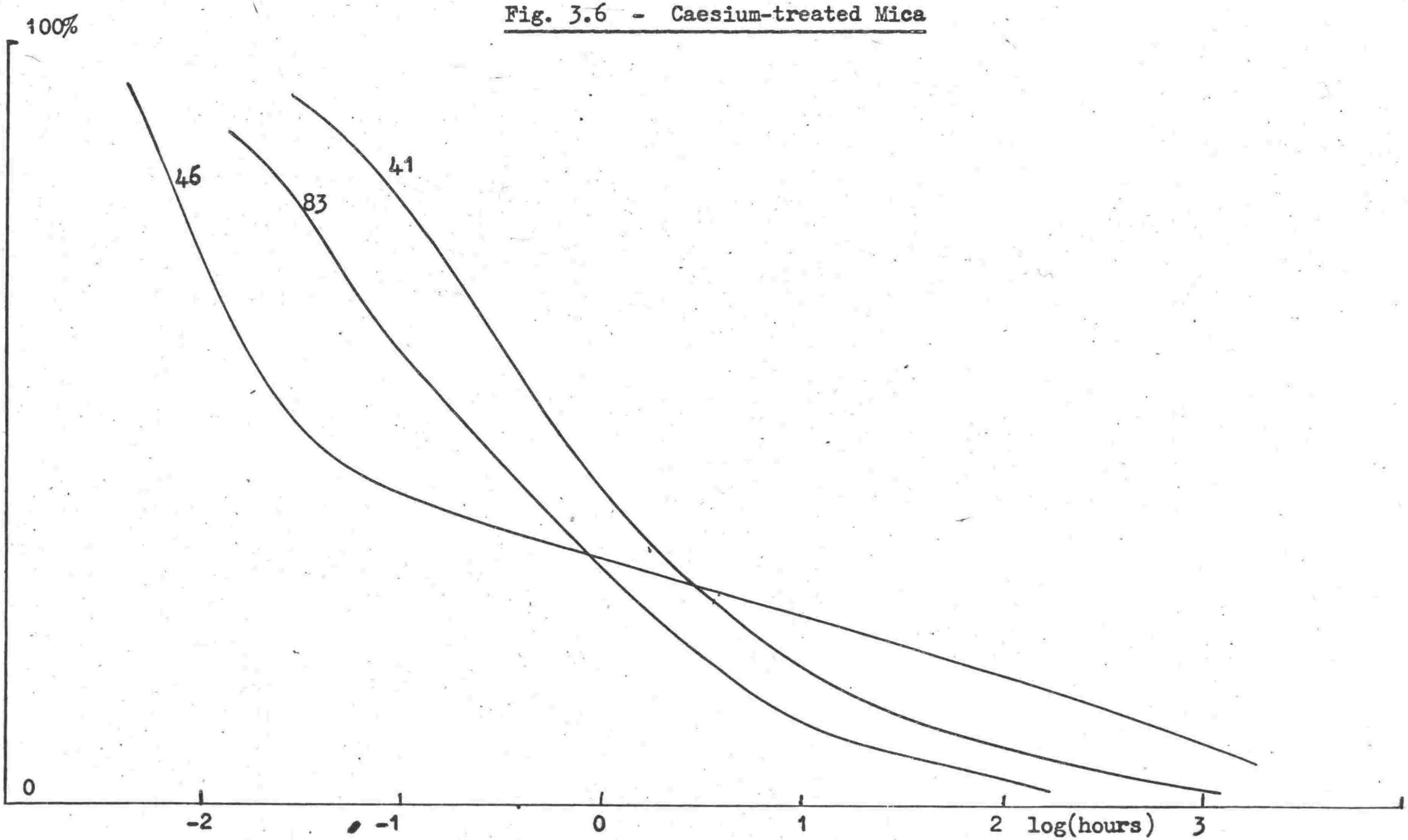


Fig. 3.6 - Caesium-treated Mica



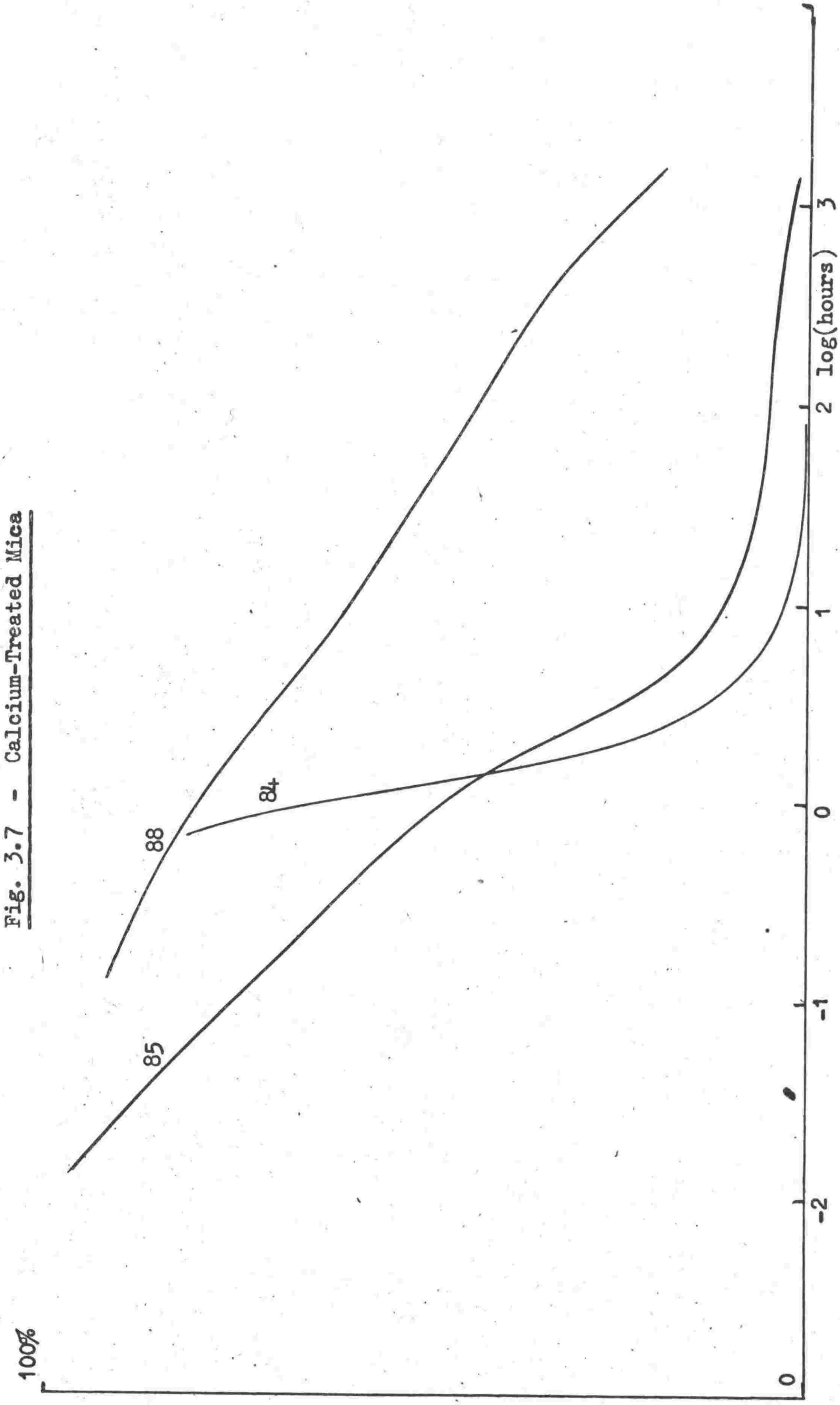


Fig. 3.7 - Calcium-Treated Mica

Fig. 3.8

Magnesium-, Strontium-, and Barium-Treated Mica

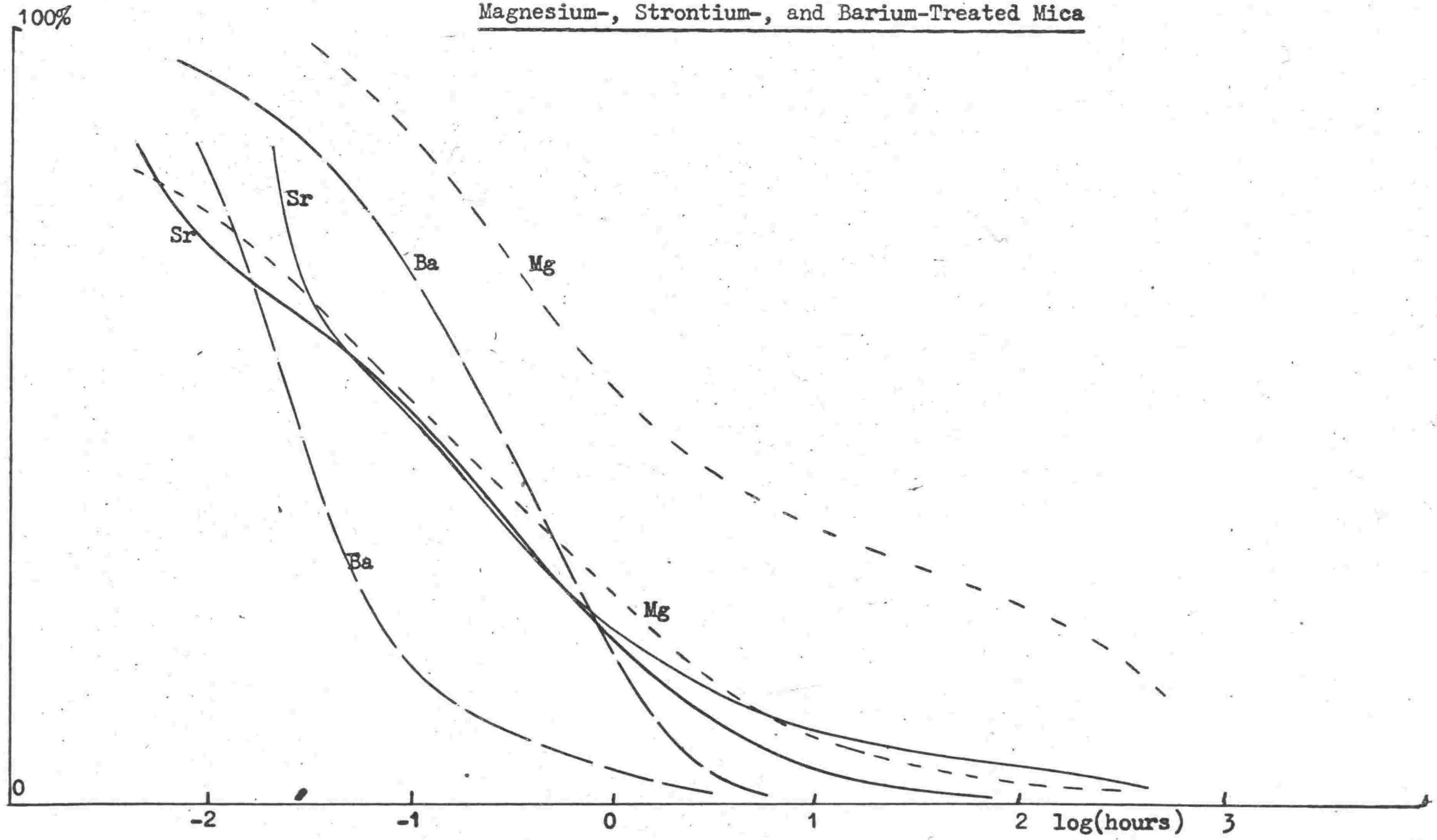
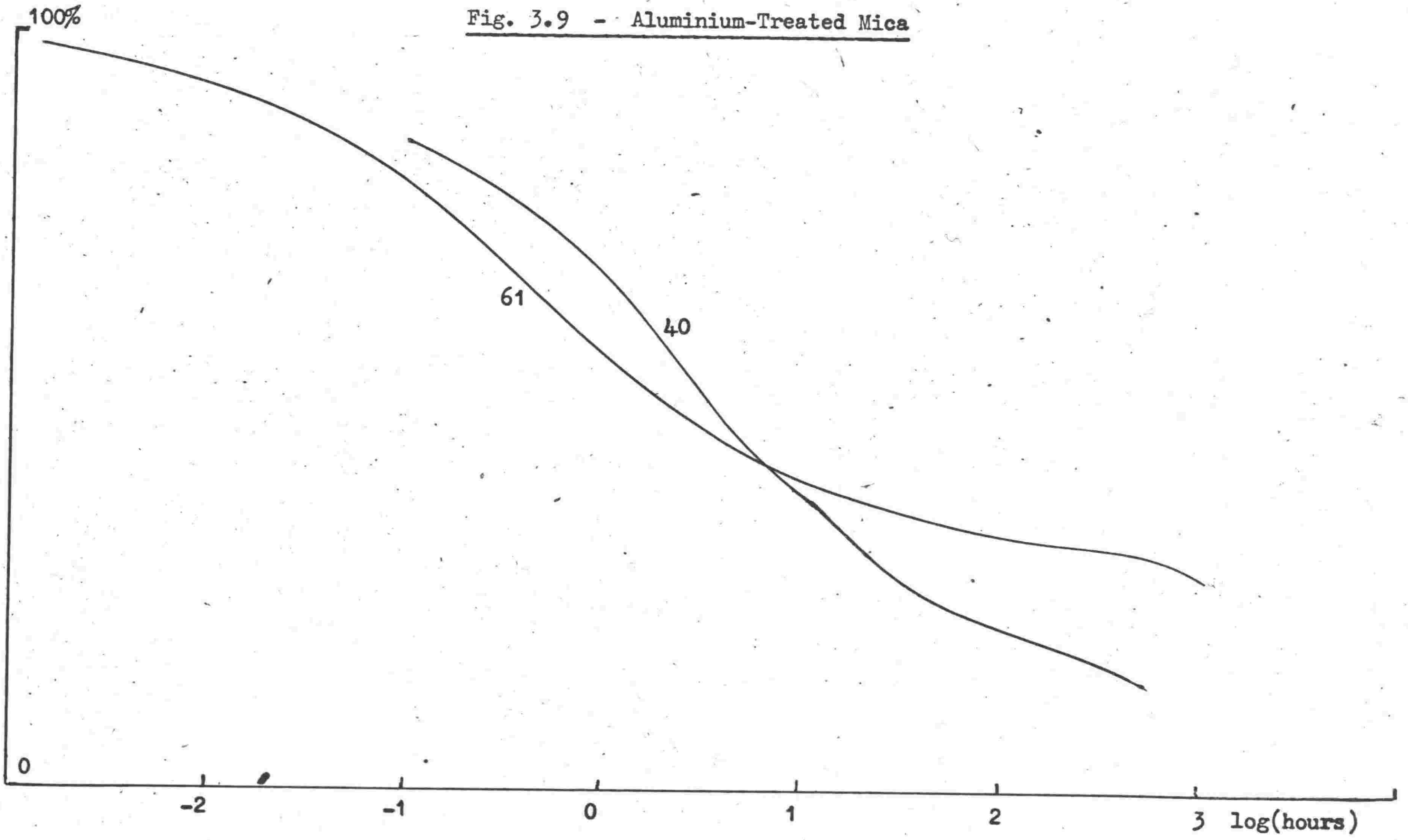


Fig. 3.9 - Aluminium-Treated Mica



CHAPTER 4

SEARCH FOR ALTERNATIVE MEASUREMENT TECHNIQUES

INTRODUCTION

One of the greatest difficulties in surface chemistry is finding a measurement technique suitable to the problem in hand. This chapter collects together descriptions of the techniques which preceded, and led to the development of, the methods used to obtain the desired information on phosphate sorption.

The experiments described in the first four sections of this chapter were designed to test various consequences of the hypothesis that the mica surface was covered by a layer of water up to several hundred Angstrom units thick. The possibility of coherent water films several layers of molecules thick has been reviewed by Low (1961) who was in favour of such a possibility, and Graham (1964) who was not. Perrott (1965) extensively reviewed the evidence that such a layer might affect phosphate adsorption. It seemed possible that such a layer could exist, and that it might be thicker and more stable if aluminium ions were incorporated in it. Phosphate ions could also be incorporated in this layer, and diffuse out when the mica was placed in water, so that the existence of such a layer was of relevance to the present project.

The last two sections describe measurements related to the problem of contamination.

ELECTRICAL CONDUCTIVITY OF SURFACE FILMS ON MICA

Preparation of the Sample

Mica is a very good electrical insulator, and it is well known that thin water films on such materials can greatly increase their apparent electrical conductivity. It seems probable that if a water film is present on the mica, and is made much thicker or more coherent by treatment of the mica with aluminium salt solutions, then this should be detectable by means of an alteration in the impedance between two electrodes on the mica surface.

The electrode system used involved the vacuum evaporation of two gold films on to the surface, with a gap between them about $\frac{1}{2}$ mm wide and up to 3 cm long. This was performed by the author in the apparatus used by the Physics Department for the construction of silicon radiation detectors. Electrical contact was made to the films by attaching copper wires with electrically conducting silver cement.

Measurement Technique

The measurements were made using a 90v. battery as a source of voltage, and a Pye galvanometer, driven by a galvanometer amplifier designed and built in the Physics Department, to measure the current which flowed. The maximum overall sensitivity of this arrangement was 5×10^{-11} amps/division. Preliminary measurements with a Radiometer (Copenhagen) Megohm-meter showed that the dry impedances of the samples were about 10^{12} ohms, which was just measurable with the galvanometer system. It was found necessary to check for leakage currents very carefully, by setting up the measuring system without the sample connected and checking that no current flowed. Perspex sheet was found to be satisfactory for mounting components on.

It was found that samples which had been wet (or even breathed upon) took several minutes to come to equilibrium, so it was found convenient to connect the galvanometer amplifier output to a recorder.

Conclusions

The results showed that the conductivity of the sample was not significantly changed, at the present level of accuracy, by treatment with either distilled water, or aluminium chloride followed by washing in distilled water. It appeared that the resistance could not have decreased to, say less than 10^{11} ohms. If the resistivity of the water is assumed equal to that of pure water in equilibrium with the atmospheric carbon dioxide, which is about 10^6 ohm-cm, and the width and length of the gap between the electrodes were 0.1 cm and 1.0 cm, respectively, then these figures imply a thickness of the water layer of no more than 100 Angstrom units.

However, there is some work in the literature on similar studies to the above, made on glass surfaces. (Ida and Kawada (1963), and Ida, Hirata and Kawada (1964)). Glass will adsorb a monomolecular water layer at 50% relative humidity, and 100 layers at 97% humidity. The D.C. conductivity of the water film at 93% humidity is very voltage dependent, with a large change of slope at 6 volts. If the sample is vacuum dried, and then the relative humidity is allowed to rise, then at some low but unknown water adsorption a high maximum in the conductivity is found. These facts indicate that the electrical properties of thin water films are far different from bulk water, and although interesting in themselves (and quite widely studied), mean that the conductivity is probably of little use at this stage for defining the dimensions or chemical properties of the surface layer.

To enable more accurate measurements of the high resistances found, a sample holder was designed to allow a Cary Model 32 vibrating-reed electrometer to be used for resistance measurements. In view of the above comments, and the development of other, more direct techniques, this work was discontinued before construction of the sample holder was completed.

NUCLEAR RESONANCE ABSORPTION OF PROTONS

Theory

If a beam of protons is fired at a target, then it is found that when the incident protons have certain kinetic energies there is a much greater probability of certain nuclear reactions occurring than if the protons have greater or lesser energies. If the target contains fluorine such a reaction occurs at 340.5 ± 1 KeV. The reaction is easily detected by means of the very high energy (about 20 MeV) gamma ray emitted by the sample. The reaction was of particular interest from the viewpoint of surface chemistry because of its very small energy range. Protons in water can be expected to lose, on average, about 200 eV of energy per Angstrom unit of path. Thus in 10 Angstrom units the proton would lose 2 KeV of energy.

Consider an experiment where a beam of protons of variable energy is fired at a target, and the products of the (p, γ) reaction are detected. If the target contains a layer 10A. thick of fluorine, then no reaction will be detected while the energy is below 340.5 KeV, a high count will be obtained when the energy is right on that energy, and no reaction will be detected with higher energies. If the target contains a much thicker layer containing fluorine, then, as before, no counts will be obtained below the reaction threshold, but above the threshold reactions will occur for a much greater energy range, for protons having initially too much energy will slow down in the first few Angstrom units, and then, having the critical energy, will be absorbed. The variation in count rate with energy above the threshold will give information on the distribution of the fluorine in the layer.

Results

This experiment was attempted, using the Physics Department Van der Graff accelerator and associated equipment. (The idea of using the resonance to detect elements was suggested to the author by Dr P. B. Johnson of that Department, and he kindly devoted a very late evening's work to the experiment). It was proposed to examine mica treated with sodium fluoride, mica treated with lithium chloride, and a blank of untreated mica. (Lithium shows a similar resonance within the energy range available on the accelerator.)

The samples were mounted on a cooled copper backing plate, and inserted in the target chamber, which was then evacuated. The first one, treated with NaF, showed a very clear increase in detector count rate at precisely the right energy, but this count rate remained constant as the energy was increased upwards to the limit available. The sample was replaced by the blank, which showed the same behaviour.

Conclusions

It appeared that the mica used contained an appreciable fraction of fluorine, and this is consistent with published analyses of various micas (e.g., Mauguin, 1913) in which fluorine can comprise up to about 0.1% of the total weight.

The method might be thought capable of variation, by measuring the effect of a non-fluorine-containing layer over the mica, on the proton energy. However, the bombardment by protons destroys the surface, and in about ½ hour in the present experiments the mica (about 2 x 10^{-3}cm thick) was completely punctured. This destruction of the surface is likely to occur with all particle bombardment techniques, such as α-particle scattering or neutron diffraction, unless the mass and energy of the particles are low. This eliminates most methods except perhaps low energy electron diffraction, for which no apparatus was available.

During the final search of the literature for this thesis the author came across an abstract of an article by Moeller & Starfelt (1966) in which the above technique was used to find the depth distribution of fluorine contamination in zircalloy, so the idea appears sound in principle. The sample used in this case would have had a high thermal conductivity, so that destruction by overheating would have been less important.

OPTICAL OBSERVATIONS OF THE SURFACE

Infra-red Absorption

This work started from the point of view that in the absence of any information to the contrary, there might be sufficient material adsorbed on the surface to produce a significant absorption of infra-red radiation. Accordingly, measurements were made of both powdered mica* and single sheets of mica, using a Perkin-Elmer 221 recording

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* The powder was prepared by rubbing a sheet of clean mica with a clean single-edge razor blade, held perpendicular to the mica surface. This is a simple way of producing a very fine powder, which is otherwise quite difficult with mica.

infra-red spectrophotometer. The mica was found to have an intense absorption at a frequency which indicated the presence of O-H bonds, but no change in the spectrum was detectable on treating the mica with either water or aluminium chloride solution, then rinsing and air-drying it.

Interference

The measurements on single sheets of mica were complicated by the occurrence of interference between light which passed straight through the mica, and that which was internally reflected twice within the mica. This interference varies with wavelength, λ, maxima of intensity occurring when $2\mu t = n\lambda$ where is the refractive index of the mica sheet of thickness t, and n is any integer. Maxima occur when $\frac{1}{\lambda} = \frac{n}{2\mu t}$, so that on a scale linear in wavenumber ($= \frac{1}{\lambda}$) the maxima are evenly spaced, with a wavenumber separation of $\frac{1}{2\mu t}$. The interferences can therefore be used to measure the mica thickness. The fact that they occur at all indicates that the thickness must be relatively constant over the area of the light beam.

An experiment was carried out to see if any appreciable increase in thickness occurred when the mica was soaked in aluminium chloride. The wavenumber change was estimated by a procedure which averaged the value over eight maxima, giving an accuracy of 1% in thickness. The thickness was found to be 2.67×10^{-3}cm at one place, but investigation showed that this could change by up to 5% with position on the mica. At some positions "beats" in the graph of intensity versus wavenumber were visible, showing that a sharp small change in thickness occurred in that part of the mica covered by the light beam. This variation of 5% corresponds to a 1 micron change in thickness, or 10^4 Angstrom units. As would be expected it was much greater than any changes occurring when the sample was treated with aluminium chloride. That it occurs shows that the assumption that the surface is a single crystal cleavage plane is untrue, but the changes are clear-cut, so that probably areas of a few square millimeters (comparable with the beam dimensions) are flat. No evidence for intense anion or cation adsorption along the edges of these small steps was ever found, which indicates that the area of these steps and their adsorbing power per unit area is low enough that they do not become more important than the faces in the experiments of this thesis.

SENSITIVE WEIGHING MEASUREMENTS

Balance Used

If an adsorbed layer is supposed to have the density of water, and if the area of the sample is 10cm^2, it is easily seen that every 10 Angstrom units thickness will increase the weight by a microgram. This is small but within the range of the Cahn electrobalance.

This balance is a device which counteracts torque developed by the gravitational force on the mass acting at the end of a beam, by the torque produced by an electric current flowing in a small coil mounted in a radial magnetic field at the centre of the beam. It is very like a moving coil meter, with the needle horizontal and the sample pan suspended at one end, and an extension of the beam to enable counterweights to be attached. The current in the coil is adjusted manually until the end of the beam is brought back to a reference mark. Various circuits are provided for adjusting and calibrating the sensitivity of the balance, and measuring accurately the current flow. It will read weights to 1 in 10^4, or 0.1 microgram, whichever is larger, and will accept loads of up to 2.5 grams.

Measurement Procedure

The samples used had a weight of about 25 milligrams, which could be, according to the specifications, weighed to within 2.5 μgrams. Since only small weight changes were of interest, the following procedure was developed. A standard of aluminium foil was made having a weight within 1 mg of the sample, and lighter than it. This was put on the sample side of the balance beam, and counterweights, which included a 1 mg calibrated weight, were added to the other until balance was almost achieved, when the final adjustments were made with the electrical zero adjust control. The 1 mg weight was then removed from the counterbalance side, which was very nearly the same as adding a milligram to the sample side. The calibrate control was then adjusted for 100% reading. The 1 mg weight was then replaced, and the sample put on instead of the standard. Its weight could then be found, relative to the standard. This procedure enabled the balance to be used at any time for the measurement, without fear of drift in zero or calibration.

Measurement of the samples was not completely straight-forward because of an unexpected source of variation in apparent weight, which was apparent upon rotation about a vertical axis of the sample when hooked on to the beam. This must change slightly the effective point of suspension on the beam. By carefully controlling this orientation, and the position, in the loop on the beam, of the hook which held the sample, it was possible to get reproducibility between weighings of ± 2 μg.

Sample Preparation

It was soon clear that if the mica were to be dipped in solutions both it and the solutions must be very clean, for otherwise drops of water on the mica took a long time to dry, and dust particles could be seen. This led to the development of techniques for keeping the mica clean, such as the use of solvent-cleaned tweezers, of chromic-acid cleaned glassware, and of gloves. These techniques were successful in this context, and led on to the following two sections, to the eventual success of the autoradiographic work, which had for some time been notably unsuccessful, and to a complete reorganisation of the approach to the overall aims of this and concurrent theses.

It might be wondered why such a point as strict cleanliness took a long while to be recognised, both by the author, and by his predecessors and colleagues. There is no excuse or single explanation. It was probably a combination of the original approach to the problem, which was centred on processes occurring in soils, where "cleanliness" can hardly be defined, and the lack of any criterion for cleanliness. The early workers found reproducibility of results, and this was a good ground for supposing that no serious mistakes were being made in techniques. The only explanation offered by the author for their reproducibility, which contrasts so greatly with his own results using their techniques, is that in making no attempt at all to obtain clean samples, they ensured that they were all similarly contaminated. The author varied the techniques in minor ways, some of which were designed to improve the cleanliness, and thus varied the nature or degree of contamination.

Results

It was found that by using the final techniques developed for weighing, the mica samples could be washed in distilled water, dried, and weighed several times without altering the weight significantly. They could also be treated with 1 M. $AlCl_3$ for an hour, rinsed and dried without altering the weight. If the sample were soaked for a week in 1 M. $AlCl_3$ the weight was found to decrease by about 20 μg, which indicated that the solution was removing or dissolving flakes of mica.

It can be said that a one hour soak in aluminium chloride does not cause the permanent adhesion of more than 2 μg of material to 10cm^2 of mica. The possibility exists that sufficient aluminium remains on the surface to swell and affect a greater thickness of solution than estimated from the dry weight.

ORGANIC LIQUID FILMS ON WATER

Soap Films

Experiments with phosphate adsorption on to clean surfaces, which followed the work recorded in the previous section, suggested that in some cases phosphate is adsorbed on to organic material, and in other cases not. To study such organic systems it would be necessary to be able to prepare reproducibly a surface covered with known organic material. The work described by Blodgett (1935) suggested a way of producing well characterised surfaces of either a hydrophobic or hydrophilic nature. She described ways of producing multiple layers of stearic acid soaps on glass substrates, in such a way that each layer is an almost perfect monolayer. It is possible to choose whether the methyl end or the acid end of the molecules is outwards, by adjusting the conditions of the experiment.

The technique involved producing a monolayer film of the stearic acid on water of suitable pH and containing divalent cations, in a region bounded by a floating waxed silk thread. A constant compression of the film was obtained by putting a drop of oleic acid outside the thread. When a glass slide was passed through the surface the monolayer adhered to the glass, on either the downward or upward passage, depending on the conditions.

The author carried out some preliminary experiments in this field, but was frustrated by wetting of the waxed silk thread by the oleic acid, and its subsequent sinking. This may well have been caused by impure reagents.

Benzene Films

A point which arose in the above experiments, and which proved of great interest, was that it was found that a small drop of benzene on clean water would spread out to form a very thin even film, rapid evaporation of which was seen by variations in the interference colours. On the other hand, if the water surface was not clean the benzene would form a thick lens-shaped drop on the surface, no interference would be visible, and evaporation would be much slower. This difference was used as a criterion for cleanliness of solution surfaces, and techniques were developed which enabled "clean" surfaces to be obtained reproducibly. An easy way to view these surface effects was to have the solutions in a petrie dish (without a cover), which was sitting in the object position of an overhead projector used for lecture demonstrations. Light passed through the water and surface, into an optical system which projected a focussed image of the surface on to a screen.

Cleaning Techniques

It was found that some drastic measures were necessary to clean the glassware used, and that chromic acid was satisfactory. Vapour degreasing of metals in trichlorethylene was satisfactory, but cumbersome with the improvised apparatus used. (An aluminium pot with a metal gauze stand inside, and a large evaporating dish of cold water on top, was heated on a hotplate.) A very serious source of contamination was found to be grease from fingers. If tweezers happened to touch a hand, and the touched part was put in the water, the spreading was stopped. Repeated dipping in water appeared to clean the tweezers. Paraffin wax on the water was found not to affect the spreading, and this was consistent with the use of it in Blodgett's work.

It was found that an uncovered solution in the laboratory did not remain clean by this test for more than an hour.

The above conclusions were not of as much significance in themselves, as they were in giving the author a feeling for the problems of surface chemistry. The field is one in which future workers might find some valuable experimental background.

ADSORPTION OF RADIO-ISOTOPES ON LIQUID-AIR INTERFACES

Introduction

This section presents results which provide evidence for the importance of thin films of contaminants in adsorption phenomena. The conclusions drawn explain the results of Chapter 3, and guided the development of techniques used in later chapters.

Adsorption on Oleic Acid Films

Oleic acid had been found, in the work described in the previous section, to spread over a surface and prevent the spreading of benzene. An experiment was performed to see whether this layer of oleic acid would adsorb anions. An EW3H end-window Geiger counter was held $\frac{1}{2}$" above a solution of carrier -free $^{35}SO_4$, $\frac{1}{2}$" deep. The soft β-ray from ^{35}S has a small range in water, so that only that sulphate near the surface is detected. A count rate of about 1000 counts per minute was obtained. A very small drop of oleic acid (carried on a fine, clean nichrome wire) was added to the surface, and this produced a decrease in the count rate to about 750 c/min. Upon adding a drop of 1M. $AlCl_3$ the count rate rose slowly, to a maximum of 2100 c/min. after eight minutes, and then fell to a stable value of 1300 c/min after a total of 14 minutes. Addition of further $AlCl_3$ made no change. The count rate was thus nearly doubled by adding $AlCl_3$.

Contamination of Adsorption Apparatus

An accidental demonstration of a similar phenomenon with $^{32}PO_4$ occurred when some attempts were being made to use the circulating apparatus, designed for the clean desorption experiments described in Chapter 7, for some adsorption experiments. In this apparatus an end-window counter (Philips 18505) is mounted inside a thin-windowed glass tube, which is immersed in the desorbing or adsorbing solution. With the tube held just above the active solution the count rate was found to be 1000 c/min. On immersing it in the solution the rate dropped to 200 c/min. Removing the tube away from the solution showed about 50 c/min. were adsorbed to the glass, and when the tube was held above the solution again the rate rose to 400 c/min. When the tube was re-immersed the rate was still 200 c/min. The change from 400 to 200 c/min. is explicable in terms of the amount of solution visible to the counter, but much of the initial 1000 c/min. must have been adsorbed on the solution surface. The counter was used to explore the variation in count rate with position outside the apparatus, and it was found that there was a very great increase in count rate near the liquid-air boundary of the main chamber of the apparatus. This place remained active when the solution was removed, and it was clear that some surface-active material had also been adsorbed because this same region was hydrophobic, in contrast to the hydrophilic nature of the rest of the apparatus.

Solution Contamination from the Air

An experiment was prepared to show the effect on phosphate adsorption of leaving solutions exposed to the air. 150 ml. of distilled water was placed in a clean 150 ml. beaker, and a Philips 18505 end-window Geiger tube was held about $\frac{1}{2}$ cm. above the surface. A magnetic stirrer with a glass-coated follower was used to mix the solution. $^{32}PO_4$ was added, and the count rate quickly came to a constant value of 2270 c/min. After about 5 minutes the stirrer was turned off in case the surface was being mixed. The count rate remained the same for the next 20 minutes, but then started to rise, quickly at first, and then more slowly, until about $2\frac{1}{2}$ hours after the start, at which time the count rate was 2700 c/min. This rate was maintained for the next 18 hours, at which time the stirrer was turned on. This caused a further rise in count rate to 3500 c/min. after another 2 hours. After three hours at this level the stirrer was turned off, with no change occurring in the count rate. Without shifting the counter the surface was penetrated by a clean glass rod about 1 mm. diameter, which was used to lightly agitate the surface. The count rate fell to 3200 c/min. 6 minutes after this. The counter was then removed, in order to test that no splashing on to it had occurred, and it was found that the insignificant amount of about 50 c/min. was present. The counter was then replaced, and a few drops of 1M. $AlCl_3$ were added. No immediate change occurred, but after about 4 hours the rate of increase of count rate started to increase steadily, until 24 hours after adding the $AlCl_3$, the count rate had reached 15,000 c/min. During this rise the surface was agitated several times, but this resulted merely in a small decrease in the count rate, without altering the rate of increase. The addition of distilled water to the solution, so that the walls of the beaker were shielded by water from the counter, merely caused a slight rise in count rate, showing that the walls were not involved in the observed effect.

A similar experiment was carried out with the beaker and counter in a large plastic-covered box (the "clean box" of the quantitative adsorption work), with a similar result to the first part of the above experiment.

Conclusion

It is clear that accidentally occurring surface films may greatly affect adsorption phenomena, and suitable precautions must be taken against them.

CHAPTER 5

AUTORADIOGRAPHY

INTRODUCTION

Hendy (1965) pointed out the usefulness of autoradiography as a technique for comparing the adsorption of radioisotopes on to variously-treated mica surfaces. It is possible that not all mica surfaces are the same, but Hendy's technique, at least in principle, enabled different parts of the same cleavage plane to be treated with different cations, so that direct comparison between the cations should be possible. Adsorption of anions is thought by some to occur mainly on edges, and if this effect is at all important, the adsorption sites should be visible as lines across the autoradiograph.

Hendy's experiments showed not only that there were differences between those areas of the mica treated with different cations, but also that there were gross irregularities within these areas, which made interpretation difficult. Hendy's technique involved the use of petroleum jelly to divide the mica up into regions which could be treated independently, and this was the technique used in the preliminary experiments.

DEVELOPMENT OF TECHNIQUES

Preliminary Experiment

The first experiment was an investigation of the variation in the amount of P-32 phosphate adsorbed as a function of the time for which the mica was soaked in 1M. $Al_2(SO_4)_3$.

A sheet of mica about 3" in diameter was cleaved in a stream of deionized water, dried, and a circular rim of petroleum jelly applied. Drops of aluminium sulphate (1M.) solution were applied at various times such that when they were all rinsed off together, one part of the mica had soaked for 22 hours, another for 3½ hours, and two others for 34 and 5 minutes. These aluminium solutions all failed to spread on the mica, so that the edges of the drops were well defined. After rinsing the mica a carrier-free P-32 phosphate solution was placed inside the circle of petroleum jelly for 10 minutes, and then rinsed off. The subsequent autoradiograph is shown (fig. 5.a) and although the circular dark spot corresponded to the area soaked in aluminium sulphate for the longest period, a similar amount was then taken up by an area of mica outside the ring of petroleum jelly, which had not been soaked at all in aluminium sulphate.

The technique clearly needed improvement, so a number of experiments were carried out to try and obtain the same adsorption of phosphate on all parts of a sheet of mica treated uniformly.

Attempts to Obtain Uniform Adsorption

A piece of mica about 3 inches in diameter, which had been soaking for several days in 1M. $Al_2(SO_4)_3$ solution, was rinsed with deionized water and dried, and a rim of petroleum jelly put around its edge. It was soaked in deionized water for 10 seconds, drained, and then carrier-free phosphate solution was placed within the circle of jelly for 10 minutes, after which the mica was rinsed again. The spectacularly unsuccessful result is shown (fig. 5.b).

Several reasons for this effect were considered and investigated.

a) It was thought that the phosphate solution might become depleted in activity by adsorption on some parts of the mica before reaching others.

b) It was observed that water collected in drops on the surface. These could dilute the solution, or the adsorption on those areas which dried first might be affected in the way described by Morris (1964) and Hendy (1965). Also if these drops contained dissolved aluminium this might precipitate at the drop edge.

c) The mica surface might have different adsorption properties at different places.

Phosphate Concentration Changes

There appeared to be no correlation between the position of irregularities and points of application of solution, except when drops of concentrated carrier-free phosphate solution were placed on the mica and then diluted with water.

Drying Effects

The position of drops were observed while the mica dried, but no correlation between these and the autoradiographs were recognisable.

An experiment was performed in which part of the mica was allowed to dry and part prevented from drying. This was done by putting a small circle of petroleum jelly on a mica sheet before putting it in an aluminium solution for several days. The sheet was withdrawn, rinsed by immersion in several changes of water, and the inner circle was filled with water while allowing the rest to dry in air for 30 minutes. A further circle of petroleum jelly was put around the edge of the mica sheet, and the whole covered with a carrier-free phosphate solution for 10 minutes. The resulting autoradiograph is shown (fig. 5.c) and proves that drying was not the problem.

Structure of Mica Surface

If the unevenness were related to the structure of the mica, it would be expected that two faces which were adjoining before cleavage would be mirror images of each other, or, at least, show changes along boundaries which were originally together.

An autoradiograph from an attempt to show this, using the previous techniques, is reproduced in fig. 5.2 , and several other similar attempts were made. It is clear that the patterns of adsorption are not related to the mica structure. It was noted during the experiment that these two surfaces were hydrophilic, and that the autoradiographs were relatively uniform.

Other kinds of experiments were devised to show the effect of mica structure. One of these involving rubbing the mica with cotton wool, a process which produced fine scratches visible by optical interference effects. A sheet of mica which had soaked in 1 M. $AlCl_3$ for 4 weeks was rubbed with $AlCl_3$ soaked cotton wool along a recognisable line and returned to the aluminium solution for 2 hours. It was then rinsed, dried, and rubbed again along a parallel line with dry cotton wool. After putting jelly around the edge, the surface was soaked in carrier-free phosphate for 10 minutes, rinsed and autoradiographed. The result (fig. 5.2c) showed that the wet wipe caused no changes in the amount of phosphate adsorbed, whereas the dry one, which presumably removed the aluminium, caused phosphate to be not adsorbed. The mica was replaced in $AlCl_3$ for 9 hours, and then more phosphate was added. The autoradiograph (fig. 5.2d) shows that the uptake by the mica after this second aluminium treatment was not much affected by the dry rub.

Cleanliness

From the preceding work it appeared that the desired uniformity was not to be forthcoming from existing techniques. Experiments in autoradiography were therefore discontinued, until in the course of the experiments described in Chapter 4, it was found that even films of water could only be obtained on the mica by ensuring that all equipment used was scrupulously clean. A piece of mica soaked in $AlCl_3$ under these conditions (for an infra-red absorption experiment) was soaked in carrier-free phosphate solution, and the resulting autoradiograph is shown in fig. 5.3a.

There were two notable features in this result : the uniformity of the adsorption, and the lack of any extra adsorption at the edges of the mica. In previous work the edges had been carefully protected from active solutions, but in these experiments they were in direct contact with the solution. Both these features were consistently found in the many experiments which followed.

Conclusions

The non-uniformity must have been due to the presence, on the mica or on the surface of the phosphate solution, of films of materials, some of which adsorbed phosphate, and others of which prevented the adsorption of phosphate. Similar effects were probably present in the kinetic experiments of Chapter 3, and the experiments of the author's predecessors in this group.

The problem of phosphate adsorption on mica was therefore treated as one about which nothing was reliably known, and attempts were made to build up a new set of facts about adsorption under clean conditions.

CLEAN AUTORADIOGRAPHIC TECHNIQUES

The preceding work suggested that consistent results could only be obtained if attention were paid to keeping solutions and samples clean, and this was amply borne out by further work. It seems from subsequent experience that providing sufficient care is taken about cleanliness, consistent results can be obtained from a variety of experiments on the adsorption of anions and cations on mica surfaces.

Methods Used for Cleaning

Holland (1964) has compared the efficiency of various methods of cleaning glassware, and comes to the conclusion that a short treatment with hot chromic acid is second only to heavy ion bombardment as a way of cleaning glass. Acid treatment is a convenient way of cleaning apparatus of the kind used here so it was adopted as the usual technique.

It is frequently suggested, mainly because of biological work, that this cleaning technique results in chromium contamination of solutions. Butler & Johnstone (1954) have shown, using ^{51}Cr, that adsorption of chromium on Pyrex glass does occur (probably as Cr^{3+}) but after an initial wash of one minute in running water, no further removal occurs, and even rubbing with a paper tissue fails to remove any more. The amount adsorbed in their experiments from a radioactive cleaning solution in 24 hours was 0.01 $\mu g/cm^2$, equivalent to about 3% of a monolayer coverage of the glass. Because of the slow rate of desorption this level of contamination would not be expected to be important in the present work.

In the present work the chromic acid was heated in a two litre beaker in an aluminium pot, with a layer of sand between the pot and beaker to distribute the heat evenly. The pot was to contain the acid in the event of breakage of the beaker, and was heated on a "simmerstat"-controlled hot plate. The chromic acid was made by adding technical sodium dichromate to technical concentrated sulphuric acid until saturation.

At the temperature of about 110°C. used for the chromic acid bath, it was found that the acid rapidly (within three days) changed from a yellow-brown colour to green. This indicated decomposition of the acid with formation of chromic salts, but the hot mixture still remained a more potent cleaning agent than the cold fresh acid, or hot H_2SO_4.

Metal tools were initially cleaned by vapour degreasing with trichlorethylene, but it was later found to be simpler and more satisfactory to use chromic acid. Metals, including stainless steel, were found to be rapidly attacked by the hot acid but not the cold, so these were cleaned in the cold acid for several hours. Some stainless steels, after being attacked by the hot acid, and then by hot concentrated nitric acid, acquired a very corrosive-resistant matte-white finish.

Vessels Used for "Clean" Experiments

Previous workers in this group had refrained from using glassware in situations where it was felt that small quantities of aluminium might affect the results, and instead used plastic (polyethylene or polyvinylchloride) vessels. Rees (1962) has shown in work on low level aluminium analyses that plastic vessels cannot be freed from aluminium contamination, and it seems likely that chromic acid would damage their surfaces, so such vessels were not used.

The qualitative experiments were generally performed in beakers having a capacity between 10 ml.and 100 ml. These beakers were kept before and during use in either one pint screw top preserving jars or dessicators.

Stock radioactive solutions were kept in 5 ml Pyrex glass conical flasks, with plastic stoppers, (fig. 6.1).

Tools

Tools were classified as "clean" and "ordinary". The ordinary tools (a pair of scissors and a pair of 6" fine tipped tweezers) were used to handle the mica before it had been split.

The clean tools were two pair of 6" fine tipped stainless steel tweezers (two were available in case one was dirtied at a delicate stage of an experiment), a pair of stainless steel scissors with blades about 3" long, a pair of 6" locking forceps, two 3" sewing needles, and a single-edge razor blade.

Also used were stainless steel clips, which were mounted on a stand (fig. 5.6a), in order to provide a place to hang mica after it had been split and before use.

In some experiments fine (s.w.g. 30) nichrome wire was used to make hooks, from which the mica was hung via a small hole made by a needle. The tools were kept in chromic-acid-cleaned beakers.

Preparation of Mica

The mica (Muscovite) was cleaved dry in all these experiments, by lifting the sheets apart with a needle, which was inserted in the edge of the mica after exposing the cleavage planes by a low angle cut along one edge with a razor blade. During this operation and all subsequent ones, the mica and tools were handled only with light elastic gloves on, these gloves being cleaned occasionally with cotton wool soaked in alcohol. This precaution was taken because of the serious effects of the grease deposited on tools by fingers, as observed in the experiments with benzene films on water. It was thought that this grease might ultimately find its way down the tools to the parts touching the mica, by contact with other objects.

The outside sheet of a cleaved piece of mica was discarded, and then another sheet with two fresh faces was cleaved off. This sheet was held with tweezers while the edges, which were probably dirty or scratched by the needle, were cut off with clean scissors. The mica was then considered ready for use, and was either used immediately or stored while hanging from a clip, under an inverted 2 litre beaker.

Cleanliness Criterion

It was found to be essential to keep covered any part of the equipment or solutions used, for after more than a few minutes exposure to the laboratory atmosphere, effects attributed to dirt could be detected. A useful guide to whether a surface was clean was to note whether it was wetted by the solutions in contact with it. It was always found that a surface (glass, metal or mica) which did not wet was dirty. Unfortunately the converse is not true, and a surface which does wet well can show, by a subsequent autoradiograph, to have the uneven or unexpected adsorption characteristic of dirty surfaces.

An extreme example was a sheet of mica which had been left overnight under an inverted beaker after cleaving. It showed perfect wetting, but after soaking the lower half in a ^{32}P-phosphate solution under conditions which should have produced adsorption it was found that this lower part had adsorbed none, while the upper part, which had merely been in contact with the washings, had adsorbed much phosphate evenly. There was no possibility of confusion of the ends because tweezer marks were clearly visible in the mica at the active end.

Such anomalies do not appear to occur when the mica is used within an hour after splitting, and all vessels and tools are cleaned just before use.

Exposure and Development

After the phosphate had been adsorbed the mica was rinsed for 10-30 seconds with water and allowed to dry, either naturally, or, in the later experiments, under an infra-red lamp. The mica was supported, while drying by the sides of a rectangular card with two edges folded up ¼".

When dry the mica was placed on one half of a sheet of lightweight quarto typing paper, the other half folded over it, and both halves were stapled together. The mica was placed on a sheet of Kodak Royal Blue X-ray film in a dark-room and the two placed between the pages of a book, which was closed and pressed flat with a lead weight. The film was left in the dark-room to expose for a time which varied from 10 minutes to several weeks, depending on the activity, but which was generally about 16 hours (i.e., overnight).

A discussion of the details of exposure of the film by isotopes which decay by electron capture is included as an appendix.

The film was fully developed (about 3 - 5 minutes) in Kodak D-19 developer, rinsed, fixed for twice the time taken for the film to clear, and washed for from ½ hour to 24 hours.

The dried film was protected by stapling it within a folded sheet of quarto typing paper.

LIMITATIONS OF AUTORADIOGRAPHY

Autoradiography is a simple way of obtaining qualitative information on the distribution of radioactivity on a surface, and is capable of very high resolution of differences in activity at different places. It is not an easy way of obtaining quantitative information on the relative amounts of activity on different parts of the surface, and even if photometers are employed the range of measurement on any one film is only over one order of magnitude, whereas pulse counters will work with the same accuracy over many orders of magnitude. However, in the absence of any information at the start of the work, the qualitative results were most useful.

INTENSITY STANDARD

It was considered desirable to be able to compare the activity per unit area on different pieces of mica, and different autoradiographs, and a way of doing this would be to include with every autoradiograph a sample which had several areas of different activity per unit area. The blackening produced by any sample could then be compared with the blackening produced by the standard, and hence with the blackening produced by any other sample.

Since ^{32}P has an inconveniently short half-life for such a standard, some other isotope would have to be used. Suitable isotopes, which are pure beta emitters of long half-life, are ^{45}Ca, ^{63}Ni, ^{185}W and ^{35}S. The calcium is not desirable for health reasons, the nickel has rather too low an energy, and the tungsten is not much different in its radiation properties from sulphur. A supply of $^{35}SO_4$ was available and was used in attempts to make a standard.

A series of 10^{-4}M. Na_2SO_4 solutions were produced with total $^{35}SO_4$ activities varying by a factor of ten between each solution and the next. A drop of each solution was put on a strip of filter paper which was then dried, glued to a piece of cardboard, and sprayed with a clear plastic varnish. An autoradiograph of the strip is shown in fig. 5.3c. Much of the activity in each drop appeared in a ring around the outside of the drop, so that this method was unsatisfactory. A similar attempt with sulphate on mica showed the same effect even more strikingly (fig. 5.3b). This work was not followed up, and the counting techniques described later would have superseded it, even had the standards been successful.

PARAMETERS INVOLVED IN PHOSPHATE ADSORPTION

The amount of phosphate adsorbed in the experiments performed here could be affected by a large number of the conditions of the experiment. The basic experiment consists of splitting a sheet of mica, putting it in a solution of a salt, rinsing it, placing it in a phosphate solution, and rinsing it again. Variable factors, some of which have been investigated, and others of which were held constant, include -

Splitting the mica in air or water
Nature of the cation and anion of the salt solution
Concentration of the salt solution
Time spent in the salt solution
pH of the salt solution
Time of both rinses
pH of rinsing solutions
Nature of cations in phosphate solution
pH of phosphate solution
Concentration of phosphate solution
Time spent in phosphate solution.

A complete study of all the factors affecting phosphate adsorption would clearly be very extensive, so in this work the following parameters were held constant -

The mica was always split in air.
The salts used were all chlorides
Except in one experiment, the salts were all at one molar concentration
The pH of salt solutions was that of the salt dissolved in water
The phosphates were all potassium salts (but contamination by other cations was observed).

ALUMINIUM CONTAMINATION OF PHOSPHATE SOLUTIONS

First Indications of this Possibility

The first experiment planned was to test the effect of treating the mica with cations. It was expected that aluminium-treated mica would adsorb more phosphate than untreated mica, so an experiment was designed to compare other salts with aluminium ones. As a preliminary test the experiment was performed with aluminium on each piece of mica to check that the results were reproducible. A piece of mica was cut with three slots in it as visible in the autoradiograph shown in fig. 5.3d. The four "legs" of the mica were dipped into separate 10 ml. beakers of aluminium chloride for 17 hours, then the entire strip was rinsed successively in pH 3 HCl, and two changes of distilled water. The whole strip was then soaked in carrier-free ^{32}P phosphate solution for 10 minutes, after which it was rinsed with distilled water.

The uptake of phosphate can be seen to be the same on each "leg", but what is more surprising is the uptake on that part not treated with aluminium. This could have been due to aluminium adsorbed on the mica while rinsing it. Alternatively, the mica might not need the aluminium treatment in order to adsorb phosphate.

Comparison of Fresh and Used Phosphate Solution

In order to test whether the aluminium treatment was a necessary step, pieces of freshly-cleaved mica were placed in P-32 phosphate solutions. One solution had previously been used for experiments with aluminium-treated mica, and another was freshly prepared, and of approximately the same activity. A third piece of mica was placed in the first solution again after leaving hydrogen form AG50W cation exchange resin in the solution for two hours. The autoradiographs, (fig. 5.4a) show that the mica in fresh phosphate did not take up phosphate in the way expected of aluminium mica, whereas that in phosphate previously used with aluminium mica did, even though the mica had not been treated with aluminium solutions.

It appears that the phosphate solution which had been used with aluminium-treated mica had become contaminated with some material which caused freshly-cleaved mica to adsorb much more phosphate than it would from an uncontaminated solution.

An experiment which showed the aluminium contamination affect most clearly is shown in fig. 5.4 b and c. In this experiment mica sheet 1 was placed in fresh phosphate solution for 10 minutes, then sheet 2, which had been treated for 18 hours with 1M. $AlCl_3$, and rinsed, was placed in the solution for 10 minutes, and finally a fresh sheet 3 of mica was placed in the phosphate for 10 minutes. The solution has clearly been altered by adding the aluminium treated mica.

This aluminium contamination effect was investigated in more datail at a later stage in the experimental work, after developing the quantitative techniques described in the next chapter. Since the results are essentially qualitative, and directly relevant to the present discussion, they are presented here, even though the lessons learned are not applied until later.

Successive-Rinse Washing Techniques

These experiments all involved the use of "mini-beakers", which are rectangular glass containers of inside dimension about .3 cm by 1 cm by 3 cm, constructed by the glassblower to the author's specification (fig. 6.1). These enabled a smaller volume of solution to be used with a given piece of mica, and thus used less P-32 phosphate, or enabled much higher concentrations to be safely used, than when 100 ml beakers were used. These experiments were performed with 10^{-5} molar phosphate solutions, in order to be consistent with the adsorption experiments with carrier.

The experiments were designed to show the effect of different degrees of washing the mica after soaking it for one minute in a 1M. $AlCl_3$ solution. In the first experiment four samples were used, so that four similar phosphate solutions were prepared. Pieces of freshly cleaved mica were first placed in each solution for 10 minutes to check that no adsorption occurred on the face of untreated mica. The samples were all soaked in 1M. $AlCl_3$ for one minute, then rinsed for $\frac{1}{2}$ minute with pH 5.5 deionized water, from a wash bottle. The first one was rinsed for one minute in each of three 100 ml beakers of deionized water, the second was rinsed similarly in two beakers of water, the third in one, and the fourth not at all, and after the rinsing the samples were put in the separate phosphate solutions for 10 minutes. A further set of blanks was put in the phosphate solutions after the samples. The autoradiograph (fig. 5.3e) shows that this washing technique led to aluminium contamination of the phosphate. It can be seen also that the amount of phosphate adsorbed away from the edges of the two most thoroughly washed samples had been reduced considerably. There was, in fact, more phosphate on this part of the blanks than on the sample. An explanation for this might be that aluminium was coming off the edges of the sample, but since the phosphate solution was not agitated, the aluminium could not, in 10 minutes, move far from the edge. When the sample was removed and the blank inserted, the solution became mixed, so adsorption on the blank was uniform.

The Effect of Removing the Edges from the Mica

To check that the aluminium was coming from the edges of the sheet of mica, a piece of mica was soaked for one minute in $AlCl_3$ and washed with a wash bottle for ½ minute and in 100 ml deionized water for 1 minute. The edges were then cut off and the mica was washed in two more 100 ml beakers of deionized water, before soaking in phosphate for 10 minutes. The experiment was performed in duplicate with blanks before and after. The autoradiograph (fig. 5.5a) shows that adsorption on the faces of both the samples and second blanks had been greatly reduced by this treatment. The intense adsorption apparent on the edges of the second blanks was possibly due to aluminium contamination of the scissors, which were not washed between cutting the edges off the samples, and cutting the blanks off the stock sheet of mica.

Continuous-Flow Washing Techniques

It appeared from the above work that a convenient but thorough method for washing the mica should be devised. Photographs of the final version of a continuous flow washing device designed in conjunction with A.G. Langdon are shown in fig. 5.6b and 5.7. An experiment which compared the phosphate uptake after washing the aluminium-treated mica for 20 minutes, 10 minutes and 4 minutes at a flow rate which replaced the water in the washing device every 2½ minutes, is shown in fig. 5.5b. The uptake on both the samples and blanks clearly decreased with increase of the washing time, although the decrease in the amount on the sample was not great for times greater than 10 minutes.

Conclusions

These washing experiments show that the results obtained in an adsorption experiment may greatly depend on the degree of contamination of the phosphate solution by the cation previously adsorbed on the surface. This will in turn depend on the washing technique used, the length and amount of fracture of the edges of the mica, and the volume of solution used. Some of the quantitative experiments in the next chapter were carried out before the importance of the aluminium contamination problem was fully realised, but the above factors were approximately constant, so that the conclusions are still valid, so long as this limitation is borne in mind.

ADSORPTION OF PHOSPHATE ON MICA TREATED WITH VARIOUS CATIONS

Choice of Cations Used

A wide variety of cations had been used by previous workers in the group, but the author had found that only aluminium was at all satisfactory in his kinetic experiments. It was therefore decided to compare the adsorption of phosphate on mica treated with aluminium under clean conditions, with the adsorption occurring on mica treated with other cations, in order to see whether any of the adsorption in the kinetic experiments was likely to be due to the cations used.

The adsorption of mica treated with hydrogen, potassium or calcium ions is particularly interesting, because these ions would be likely to be present on the surfaces in soils.

It had already been noted that aluminium and iron cations were particularly good at enhancing adsorption, and that these cations hydrolysed readily, and had very insoluble phosphates. Other cations which might be expected to have such properties were therefore also tried.

Phosphate Solutions Used

Having shown that aluminium-treated mica would contaminate the phosphate solutions it became clear that when comparing different cations it would be necessary to use separate P-32 phosphate solutions. Because the work at this stage was all with carrier-free radioactive solutions, it could not be guaranteed that the solutions were identical, but this objection was overcome by making up a bulk solution from which the individual ones were obtained. Later work showed that small amounts of carrier in experiments with aluminium-treated mica did not make a significant difference to the adsorption of the radioactive fraction.

Comparison of Al^{3+}, Ca^{2+}, K^+ and H^+

An experiment was performed to compare the adsorption of mica treated with $AlCl_3$, $CaCl_2$, KCl and HCl one molar solutions for two days. Separate phosphate solutions and rinsing solutions were used for each mica strip, and a freshly-cleaved piece of mica was placed in each phosphate solution for 10 minutes just before putting the cation-treated mica in. All phosphate soaking times were 10 minutes. The autoradiograph reproduced in fig. 5.8c shows that the phosphate uptake by calcium-, potassium- and hydrogen-treated micas is indistinguishable from untreated mica, and very much less than that adsorbed by aluminium-treated mica.

An additional experiment was performed, where a piece of aluminium-treated mica was soaked in a calcium solution, and a piece of potassium-treated mica and a piece of calcium-treated mica were soaked in an aluminium solution. These three pieces were then soaked in similar phosphate solutions, along with a piece of mica which had only been soaked in aluminium solution. These four all showed approximately the same degree of blackening on the film, so that the treatment with calcium or potassium had no discernable effect on the mica surface.

It therefore seems that the adsorption of phosphate on to the mica-type surfaces of soil minerals saturated with potassium, calcium or hydrogen ions is likely to be unimportant as a mechanism of phosphate fixation.

Comparison of Al^{3+}, Fe^{3+}, Cr^{3+}, Co^{2+}

Other cations studied included cobalt (II), chromium (III) and iron (III), which are compared with aluminium in fig. 5.8a. Iron-treated mica adsorbed an amount slightly greater than aluminium, and chromium-treated mica an amount slightly less than aluminium, while cobalt-treated mica adsorbed very little, even on its edges.

Cu^{2+}, Ni^{2+} and Mn^{2+}

Copper (II)- Nickel (II)- and manganese (II)- treated micas all were indistinguishable from blanks.

Ga^{3+}

Gallium-treated mica took up at least as much phosphate as aluminium-treated mica. It was also found that soaking the mica in an .01M. $GaCl_3$ solution resulted in only slightly less uptake of phosphate than soaking it in a 0.2M. $GaCl_3$ solution. Also, there appeared to be no contamination of the phosphate solution by gallium, after the .01M treated mica had been soaked in it, although there was after the .2M treated one (fig. 5.8b).

Summary of Cation Effects

To summarise the effect of cations, then, we may say that mica which has not been treated with any solution other than the carrier-free phosphate takes up phosphate only on the edges. Treatment with potassium, calcium, hydrogen, cobalt, copper, nickel and manganese solutions does not increase the amount adsorbed on the face, as far as this method of measurement is concerned. Treatment with aluminium, gallium, iron, or chromium solutions produces extensive uptake of phosphate on the face.

A Possible Explanation for Differences between Cations

The four ions which produce extensive phosphate sorption all undergo extensive hydrolysis in water, and it is conceivable that the process of washing them results in the formation of hydroxides, which then act as anion exchangers. To test this hypothesis two samples soaked in the same $AlCl_3$ solution were used, one being washed with deionized water at pH 5.5 and the other with .1M. HCl, followed by deionized water. These were found to absorb the same amount of phosphate in 10 minutes from a carrier-free phosphate solution, so that hydrolysis in the wash solution seems unlikely to be a major effect.

SURFACES OTHER THAN MICA

Brief studies were made on the relative adsorption of phosphate by glass microscope slides, polythene sheet, aluminium foil, and aluminium-treated mica.

Comparison of Aluminium Metal, and Aluminium-Treated Mica

The aluminium metal used in this experiment was B.D.H. laboratory reagent grade aluminium foil about .002" thick. It was cleaned by dissolving the outer surface with 1M. KOH for twenty minutes, and then thoroughly washing in deionized water. One sample of it was treated with $AlCl_3$ for an hour, and another was treated with $CaCl_2$ for an hour. These two are compared with untreated aluminium metal, and aluminium-treated mica in fig. 5.9 a and b. The same phosphate solution was used for all the samples, and although it appears from the autoradiograph to have become progressively dirtier, there seems to be no significant difference between any of the samples. This could be interpreted to mean either that the adsorbing material on aluminium-treated mica is similar to that on aluminium metal, or, bearing in mind the experiments which showed aluminium contamination of the solution to be important, that the nature of the adsorbing surface is unimportant. If the surfaces are the same, they could be either aluminium hydroxide or some unknown external contaminant.

Comparison of Aluminium-Treated Glass, Polythene and Mica with Untreated Glass and Polythene

Containers of solution had frequently been found to adsorb phosphate from carrier-free solutions. With Pyrex glass beakers it had been noticed that solutions in which only potassium- or calcium-treated micas had been placed did not loose much activity to the walls of the beaker, whereas ones in which aluminium-treated mica had been placed lost much on the walls. (This was measured by monitoring the beakers after rinsing them). This effect was investigated by autoradiography. Two microscope slides and two pieces of polythene were treated 24 hours with cold chromic acid, rinsed, soaked four days in deionized water, and then another day in fresh deionized water. One piece of polythene and one glass slide were then soaked for several hours in aluminium chloride. Each piece of material, and one sheet of aluminium-treated mica, was then soaked in a carrier-free phosphate solution for 10 minutes. The resulting autoradiograph is shown in fig. 5.9c and d. It appears that adsorption is the same for polythene as aluminium-treated mica and glass, and that clean glass not treated with aluminium does not take up phosphate. (The last conclusion is not entirely supported by the adsorption on the edges of the sheet shown, and some other experiments.)

Conclusion

It appears that the possibility of adsorption on a material in this kind of experiment cannot be reliably predicted from its bulk composition, and that there seems to be a curiously constant amount per unit area adsorbed. The remaining experiments will deal only with mica surfaces.

EFFECT OF CARRIER PHOSPHATE

Most previous workers in this group had used carrier-free phosphate solutions exclusively. Furkert (1965) had performed one set of experiments to see the effect of carrier on P-32 phosphate uptake, and decided that up to at least 10^{-6}M concentration the phosphate uptake is proportional to the concentration in the solution. Under these conditions adding carrier to the solution does not affect the uptake of P-32 phosphate by the surface. A comparison between solutions containing the same (unknown) concentration of P-32 phosphate, and 10^{-2}, 10^{-4}, 10^{-6} and no moles/litre of added inactive phosphate, is shown in fig. 5.10 d and e, for times in the phosphate of 10 minutes and 2 hours. (Each time is a separate autoradiograph, so comparison of the effect of time is not possible.) The higher concentration ones are somewhat uneven, due to the imperfect cleanliness of techniques in use at this stage, but it appears that up to 10^{-6} molar concentration, the adsorption is proportional to concentration, while at greater concentrations than 10^{-4} molar, adsorption increases less rapidly, confirming Furkert's results, which were not obtained on clean surfaces. This effect is investigated quantitatively in the next chapter.

EFFECT OF PHOSPHATE pH

Experiments were carried out at pH 5.5, pH 4 and pH 2, using aluminium-treated mica, and HCl to adjust the pH. The first experiment, fig. 5.5c, was performed in solutions containing only HCl and carrier-free phosphate, a 10 minute soak-time beingused, and showed adsorption decreasing with pH. Because of the changing anion concentration in this experiment the corresponding experiment was performed using solutions which were also .01M. in sodium chloride (while still carrier-free in phosphate). This showed (fig. 5.10a) that adsorption at pH 4 was the same as at pH 5.5, while that at pH 2 was considerably less. This experiment was later repeated quantitatively.

KINETICS OF UPTAKE OF PHOSPHATE

The kinetics of uptake from carrier-free phosphate solution were investigated in conjunction with the effect of the time of soaking the mica in aluminium chloride. A sheet of clean mica about 2" square was prepared. It was hung from the device shown in fig. 5.11, which allowed it to be lowered in $\frac{1}{4}$" steps into a 250 ml beaker of solution. It was first lowered from one side into an aluminium chloride solution in such a way that successive strips were soaked for 23 hours, $2\frac{1}{4}$ hours, $11\frac{1}{2}$ minutes, $1\frac{1}{2}$ minutes and not at all. The mica was then removed, and rinsed in pH 3 HCl and two changes of distilled water. It was then suspended from a side adjacent to the previous one and lowered in a similar way into a carrier-free P-32 phosphate solution for 24 hours, 2¼ hours, 10 minutes and 1 minute. It was then rinsed and autoradiographed.

The result is shown in fig. 5.10b. The variation visible is due to the time spent in the phosphate solution, the time in aluminium having no effect, except that there was slightly more phosphate on the strip soaked in aluminium chloride for the longest time, for a phosphate adsorption time of 10 minutes or 2¼ hours. This autoradiograph also shows up the difficulty of comparing areas of greatly differing intensity, although the detail within each area separately can be brought up by a suitable exposure. (The black spots visible were not present on other exposures of this sample and must have been due to chemical or radioactive contamination of the film or sample.)

This experiment suffered from aluminium contamination, which explains the lack of effect of the time in aluminium. It shows that under these conditions some phosphate is rapidly sorbed, but much of it takes a long time.

The kinetics of uptake under other conditions were investigated similarly, by lowering a strip of mica for successively decreasing times into a phosphate solution. The results of soaking a piece of mica for 120, 27, 7 and 2 minutes in 10^{-4} M. KH_2PO_4 with P-32 phosphate added is shown in fig. 5.10c. Although not very clean, it shows that much of the activity goes on in the first two minutes, but that some still takes a long time to go on.

Another experiment investigated the kinetics in the presence of 0.01 molar sodium chloride. The aluminium-treated mica was soaked in the carrier-free phosphate/sodium chloride solution for 158, 30, 7 and 2 minutes, and again some phosphate took several hours to be adsorbed.

HIGH RESOLUTION AUTORADIOGRAPHY

It should be clear from the preceding work that the major advantage of autoradiography is that it enables the distribution of the radioactivity on a surface to be seen. This distribution is often expected to be uniform, but many of the factors which may upset an experiment act non-uniformly, so that taking an autoradiograph is a useful precautionary check in any low-area surface chemistry experiment. Any autoradiograph has a finite resolution, though, and it is quite possible that a distribution which is uniform on an X-ray film might be shown to be decidely non-uniform on an emulsion which has a much higher resolution. Accordingly, a few experiments were designed to go to the limit of resolution of this technique.

Technique

Ilford G5 stripping film was used. This has a gelatin base on which is deposited the emulsion, 5 μ thick. The base is attached to a glass plate from which it can be peeled by scoring around the edges with a sharp razor blade. A piece of film is cut to the required shape (while still on the glass), removed and inverted (using two pairs of tweezers), and placed emulsion side downwards on the surface of a beaker of distilled water. The mica is put into the beaker, and brought up underneath the film, lifting the film from the water in such a way that the film drapes itself around the mica. The combination is then laid on another sheet of mica (larger than the first) to dry and expose. After explosure the film is developed, fixed and washed while still on the mica. These solutions may be contaminated by radioactivity from the mica so should be discarded appropriately after use.

While the film is still damp after washing, a small rectangle of film should be cut out, placed on a clean microscope slide, and protected with a cover slip.

Samples

The radioactive samples chosen were of two types. The first was a mica sample which had adsorbed phosphate from a solution containing 3×10^{-7} moles/litre of $AlCl_3$ and 5×10^{-5} moles/litre KH_2PO_4 with $^{32}PO_4$ added. It might be expected that this solution would contain colloidal aluminium phosphate particles which would stick to the mica, and be small enough that the X-ray film would not resolve them. The other was a piece of mica which had been soaked in $^{67}GaCl_3$ solution with 10^{-6} moles/litre $GaCl_3$ carrier at pH 2-3. There could be some colloidal particles of gallium hydroxide in this solution. Both strips of mica were about 1½" by ¼".

Results

Photomicrographs from these specimens are shown in fig. 5.12. From these there is no clear evidence that the phosphate is distributed non-uniformly, for the spots visible are the same size as the fog grains visible when a piece of unexposed film is developed. The size of these grains is about one micron.

It is possible that there is some tendency for the grains to be clustered, but this could only be shown by a statistical analysis, of a degree of sophistication beyond the author's knowledge. It will, however, be useful to consider the upper limits to the degree of non-uniformity consistent with the results.

The range of the radiation exposing the film is in both cases much greater than the emulsion thickness, so that the density of exposure from a point source will be approximately uniform over an area of diameter equal to the emulsion thickness, and decrease rapidly outside this area. Because of the comparable values of grain size and emulsion thickness, this means that any source less than a micron in diameter would expose a cluster of about 10-100 grains. Such clusters can be found in the examples shown, but some would be expected in any random array of grains.

From the average value of the space between exposed grains can be estimated the minimum number of particles containing radioactivity. The spacing is probably less than 10 microns, so that at least 10^6 particles per square centimeter must be present. (If the spacing is due to statistical fluctuations, then there could be a very much larger number, up to the infinite limit of a uniform layer.)

The implications of these results are discussed in later chapters, in conjunction with other experimental results.

CONCLUSIONS

Mica treated with certain cations adsorbs phosphate from dilute solutions.

The adsorption occurs evenly, (even on a microscopic scale), and reproducibly, provided care is taken to prevent contamination of the solutions and mica by the unknown substances present on them under ordinary laboratory conditions. The adsorption of phosphate by the edges of the mica sheets is not much greater than that of the 001 faces of the sheets, under some conditions of treatment, although in the absence of cation treatment the edges adsorb much phosphate and the faces little. This point is treated in more detail in the next chapter.

The cations which have been found to particularly enhance the adsorption on the 001 faces are those of aluminium, iron, gallium, and to a slightly lesser extent, chromium. Those which have been tried and found not to alter the adsorption properties are calcium, potassium, hydrogen, cobalt, copper, nickel and manganese. It may be concluded that this adsorption is associated with cations of elements which are extensively hydrolysed in aqueous solution.

Small amounts of these cations accidentally introduced into the radioactive phosphate solution greatly enhance the adsorption of phosphate by the mica, but there appears to be some adsorption which is independent of these cations in the phosphate solution.

Many different kinds of surfaces adsorb phosphate to about the same extent, from carrier-free solutions. This would suggest either that the uptake is not limited by the number or nature of adsorption sites on the surfaces, or that these sites are similar, and therefore probably controlled by some factor other than the bulk nature of the material.

The adsorption of phosphate is proportional to concentration at concentrations less than 10^{-6}M., but at higher concentrations the adsorption increases less rapidly than the concentration.

The adsorption (at constant ionic strength) decreases as the pH decreases below pH 4. This is the opposite behaviour from that expected from ion-exchange models of anion adsorption.

The kinetics of phosphate adsorption are slow, taking many hours to come to equilibrium. This is consistent with much other work on the kinetics of surface reactions. No evidence was found for the dependence of the phosphate uptake on the time the mica was soaked in aluminium, because the phosphate solution used was contaminated with aluminium.

The conclusion regarding the lack of adsorption of phosphate by calcium-treated mica is of interest to soil chemistry. It is clear that the presence of aluminium on the soil mineral surfaces would enhance phosphate fixation. It is well known that some clay minerals, for example montmorillonite, are unstable in the hydrogen form, and decompose to release aluminium from the lattice. If the montmorillonite were in the Ca form, this decomposition would be hindered, so that aluminium would not be released into the soil. The above experiment shows that the calcium on mica-type surfaces does not itself cause phosphate fixation.

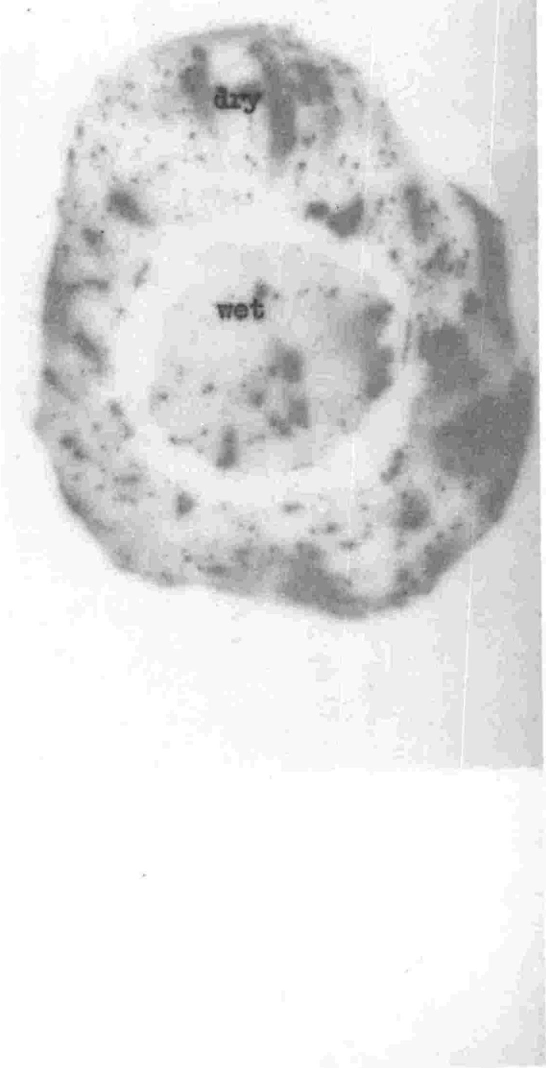
This is a possible explanation for the smaller importance of phosphate fixation on the alkaline limestone soils than on acid soils. It was shown that treatment of the mica (or aluminium metal) with calcium as well as aluminium did not reduce the adsorption, but in agriculture this result might not be found, so that liming a soil might lead to less fixation, and perhaps even to release of previously-fixed phosphate.

It is generally believed that the response to liming a soil is due to pH changes, but it is possible that calcium may also play a part. Field work should be carried out with, for example, KOH and $CaCl_2$, to separate out pH and calcium effects.

Fig. 5.1

B. Uniform Treatment

C. Effect of Drying



A. Aluminium time of soak

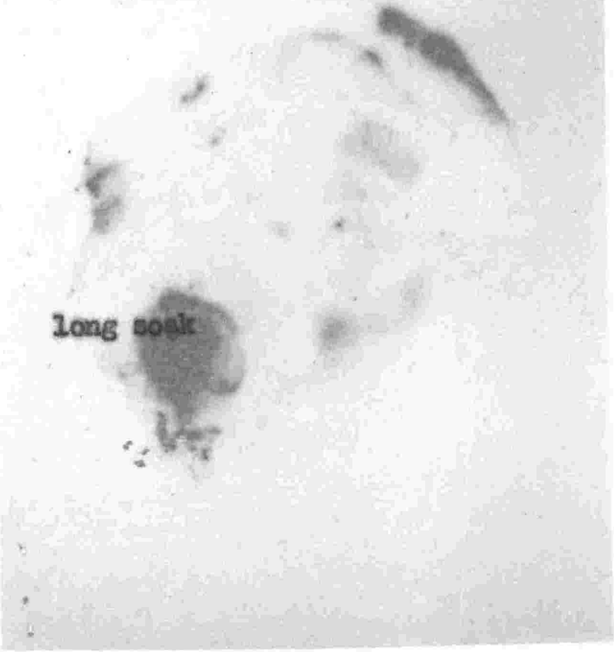
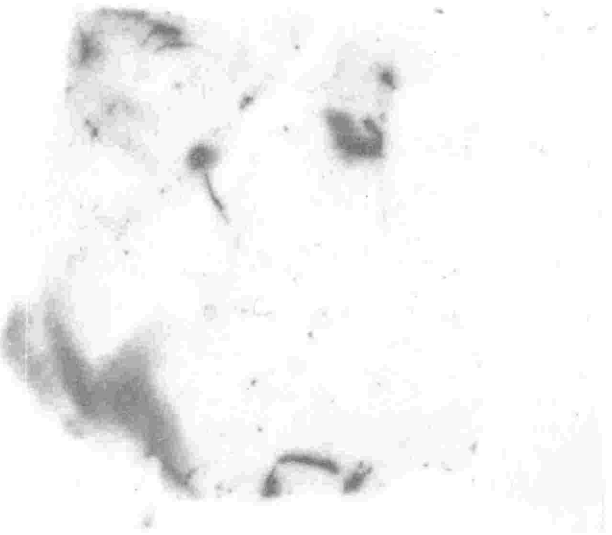


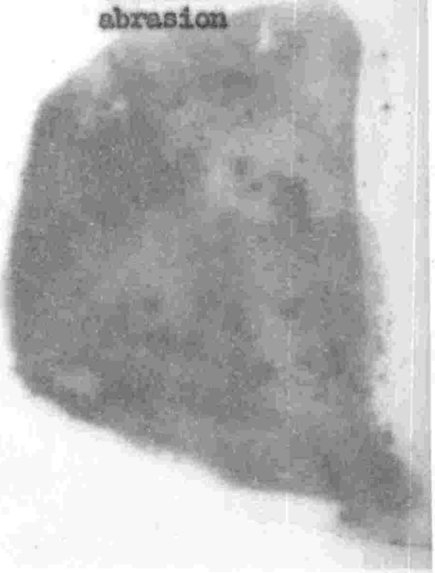
Fig. 5.2

A and B were opposite faces

B



D. Aluminium treatment after abrasion



A

24/10

C Abrasion of Mica

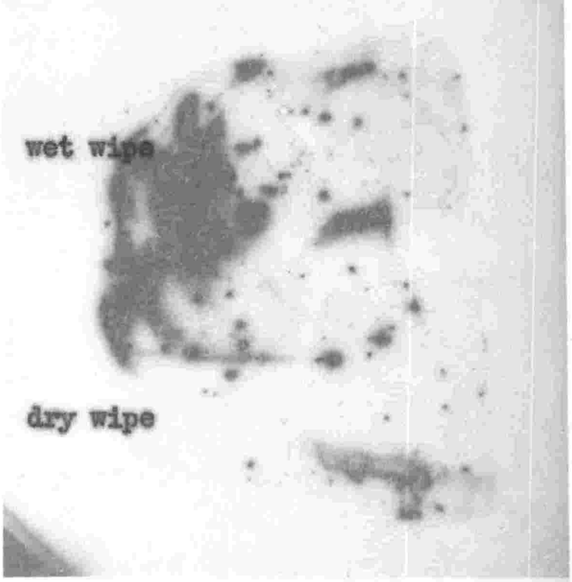
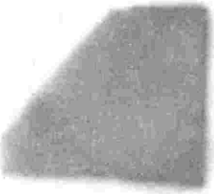


Fig. 5.3

A.
Clean Mica



B.
"Standard" spots on mica.

C.
"Standard" spots on paper.

D.
Reproducibility of Aluminium Treatment.

E. Washing of mica

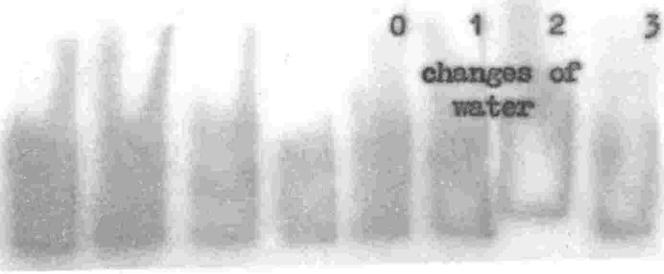
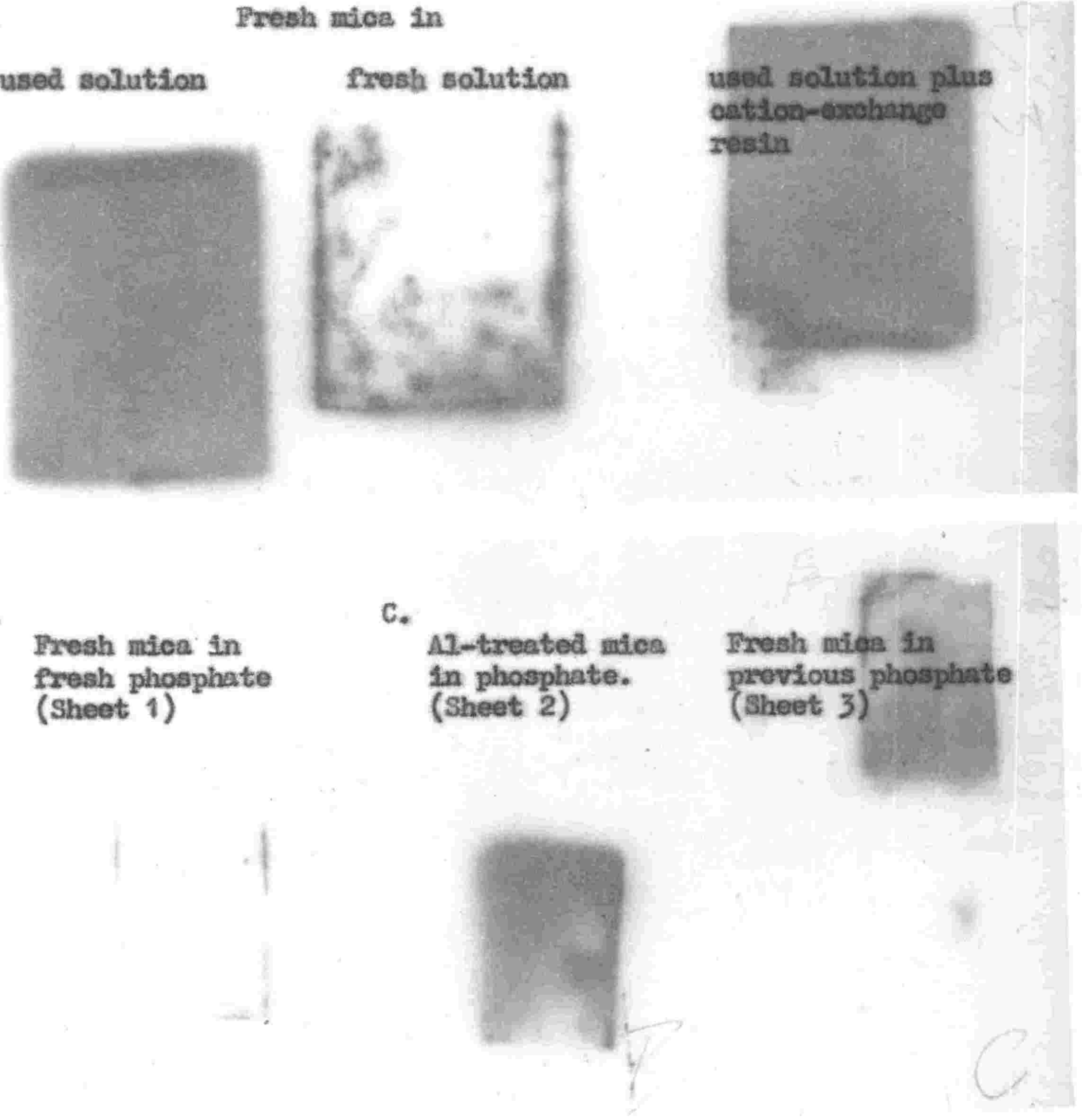


Fig. 5.4

Aluminium Contamination



A. Fresh mica in

used solution

fresh solution

used solution plus cation-exchange resin

B. Fresh mica in fresh phosphate (Sheet 1)

C. Al-treated mica in phosphate. (Sheet 2)

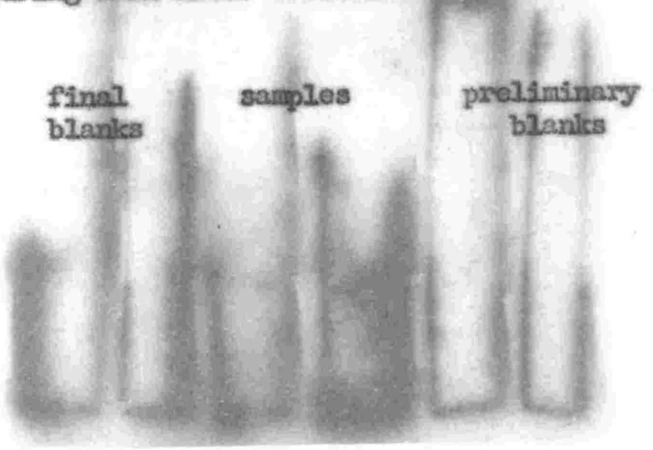
Fresh mica in previous phosphate (Sheet 3)

Fig. 5.5

2 OS B1

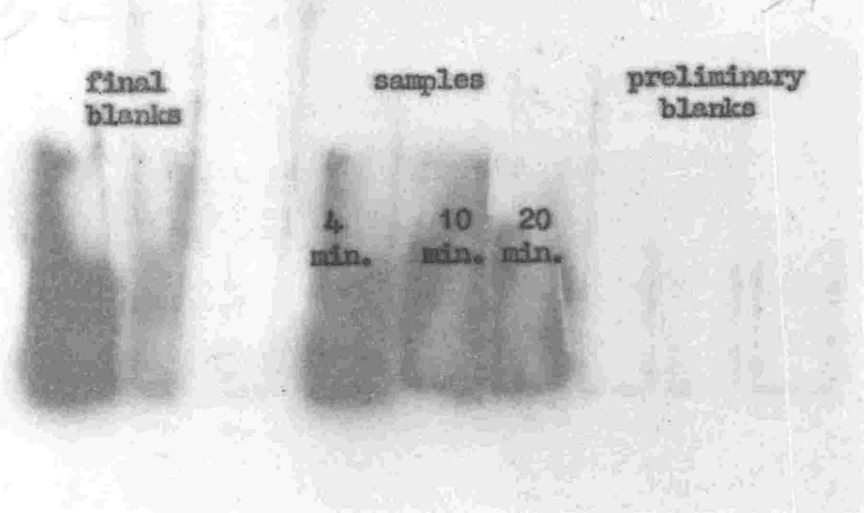
A.

Edges cut off during wash after aluminium treatment.



B. Time in washing device

B1



C Effect of pH (varying ionic strength)

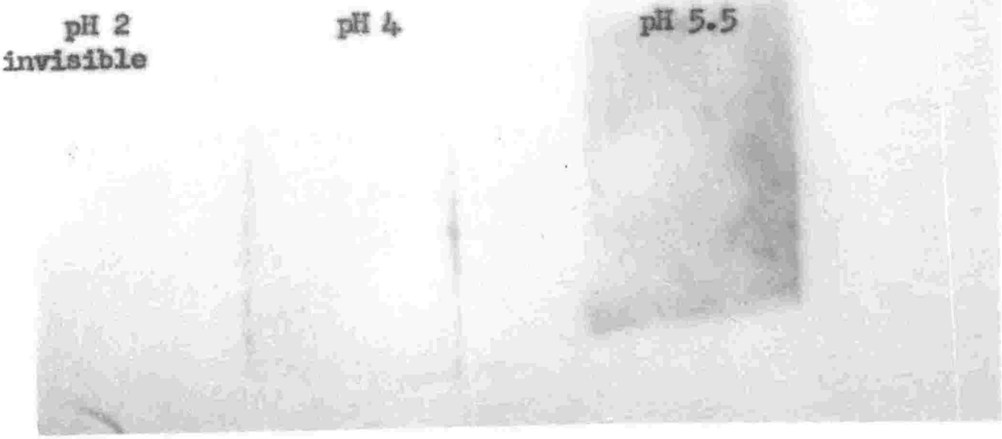


Fig. 5.6

Fig. 5.6a

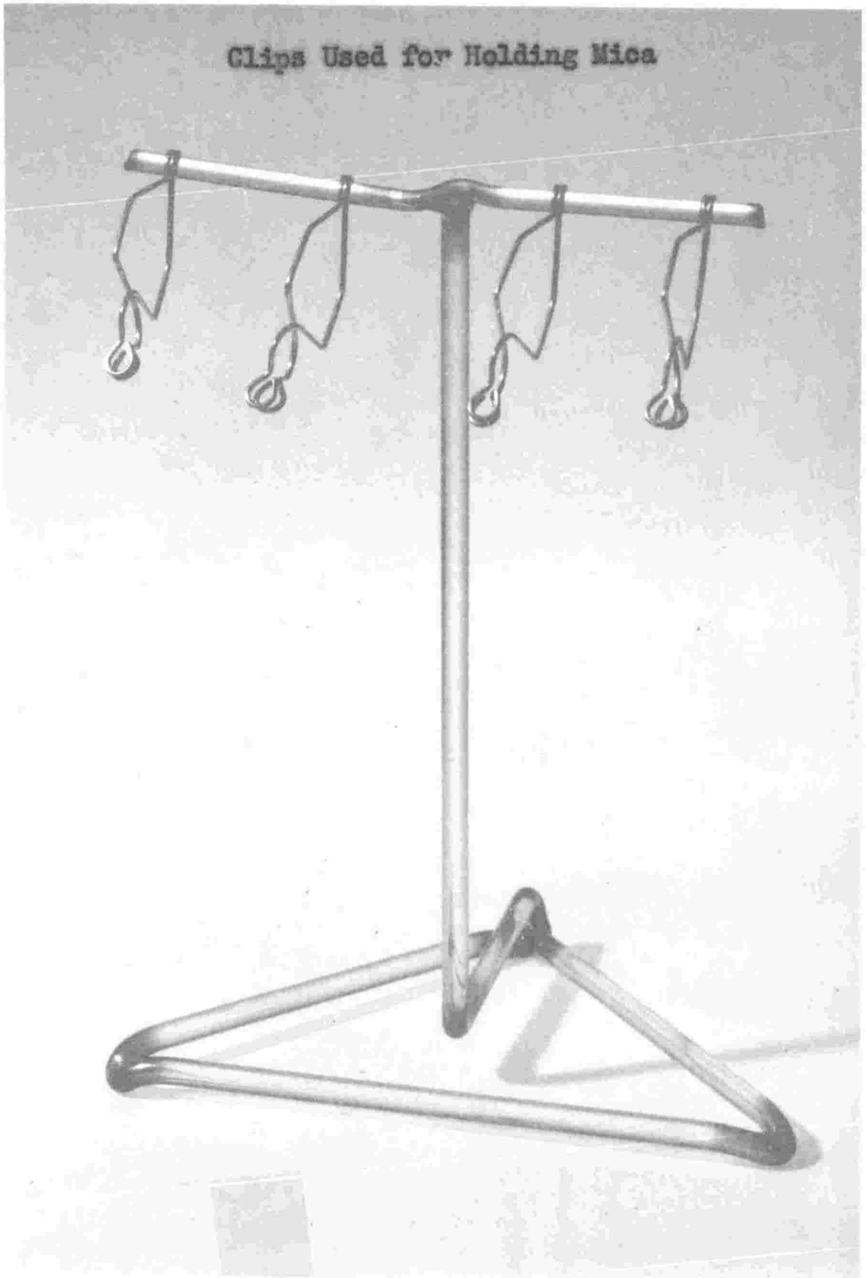

Clips Used for Holding Mica

Fig. 5.6b

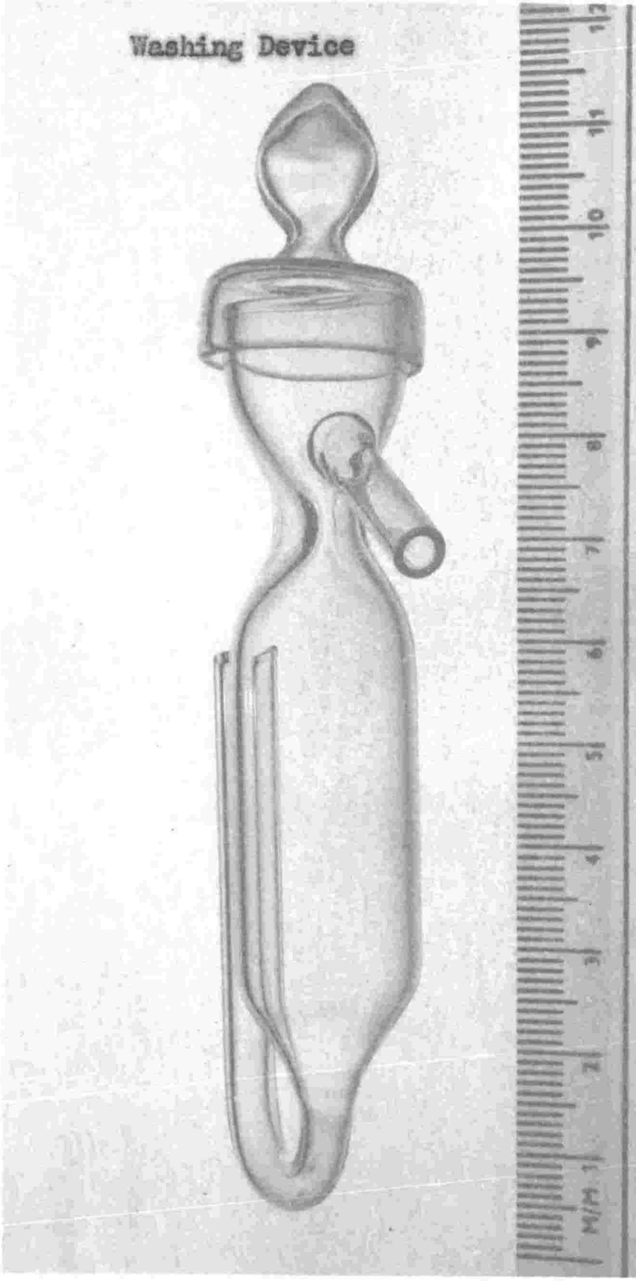

Washing Device

Fig. 5.7

Washing Device in its Covered Stand

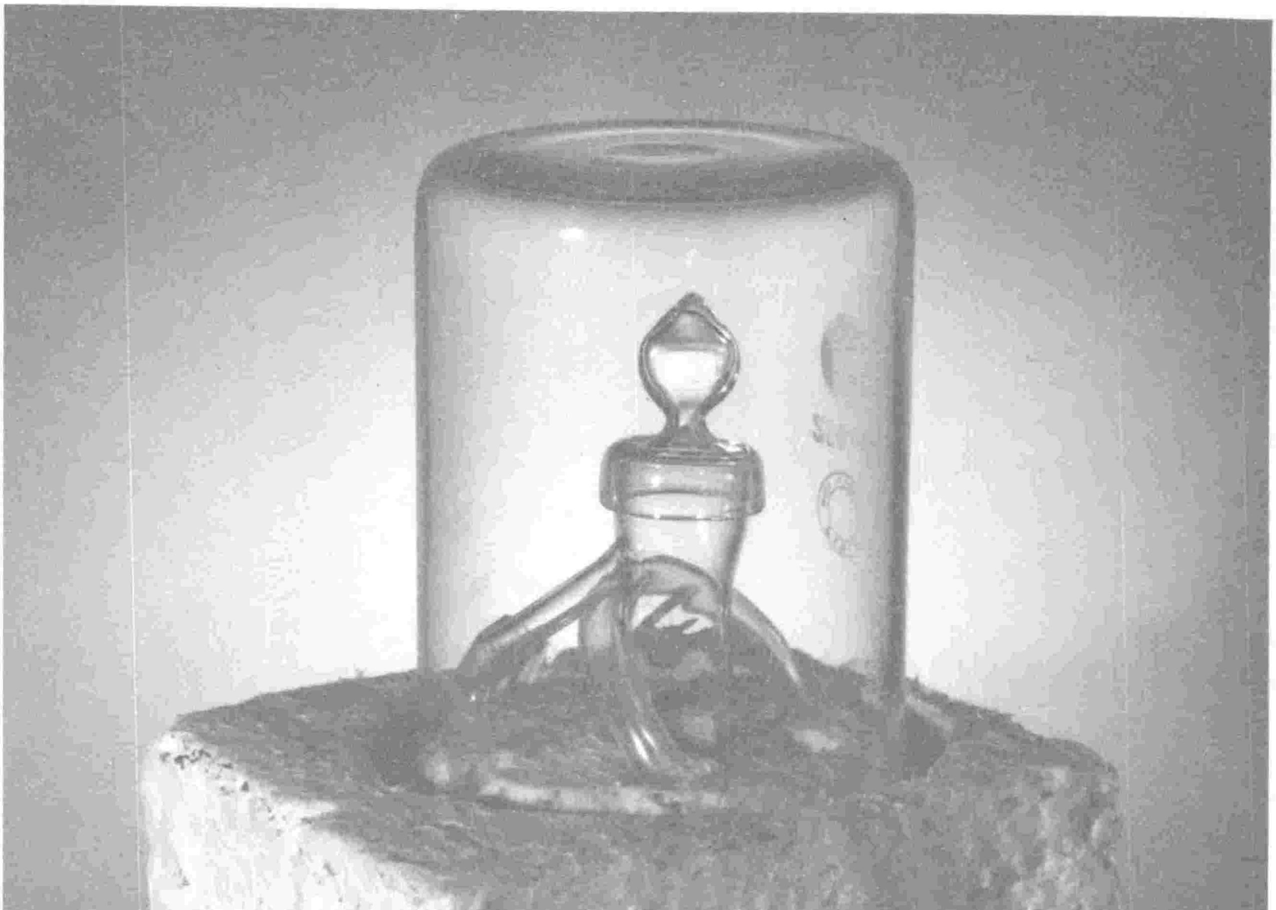


Fig. 5.8

Comparison of Various Cation Treatments

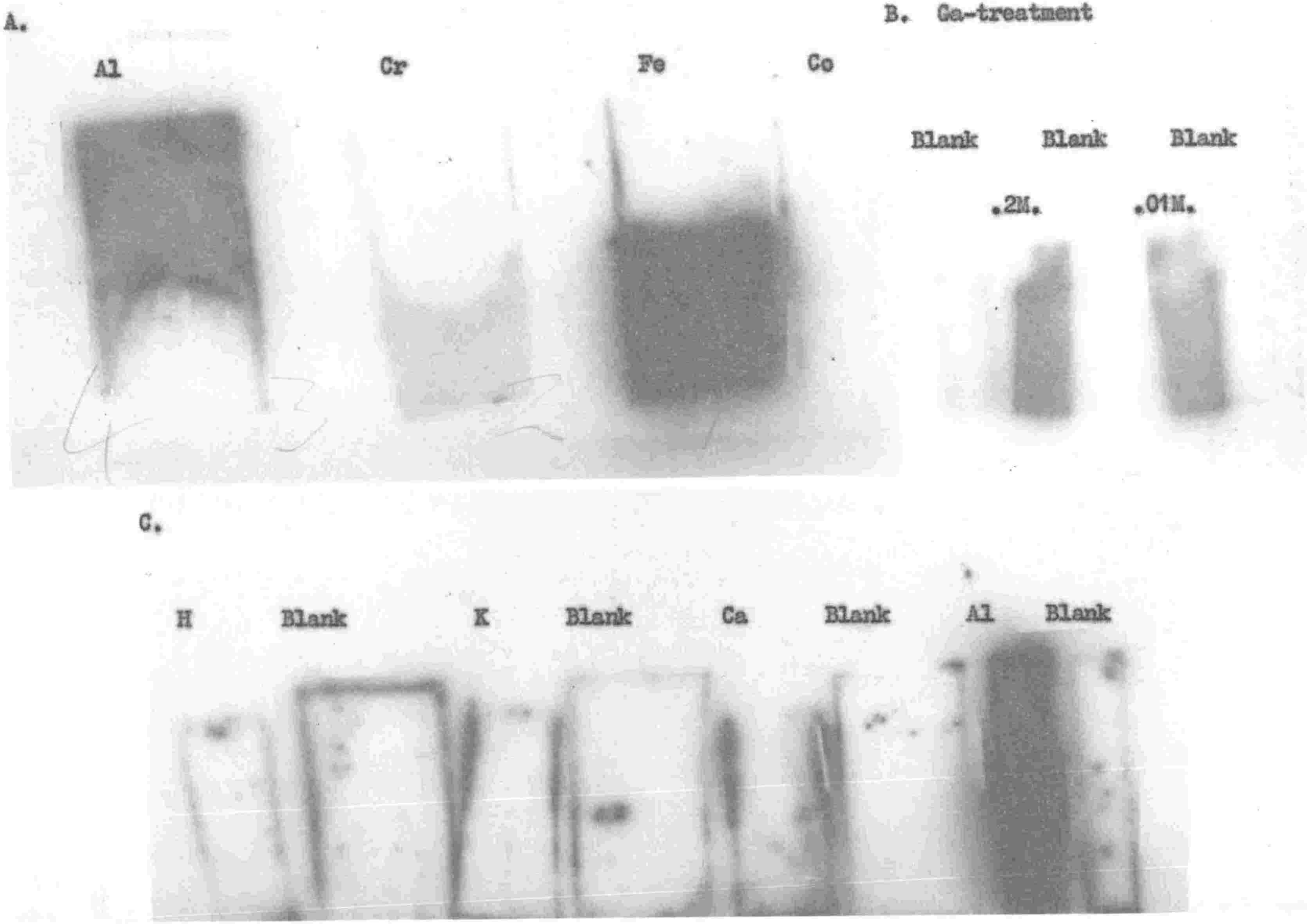


Fig. 5.9

Phosphate Sorption on Various Surfaces

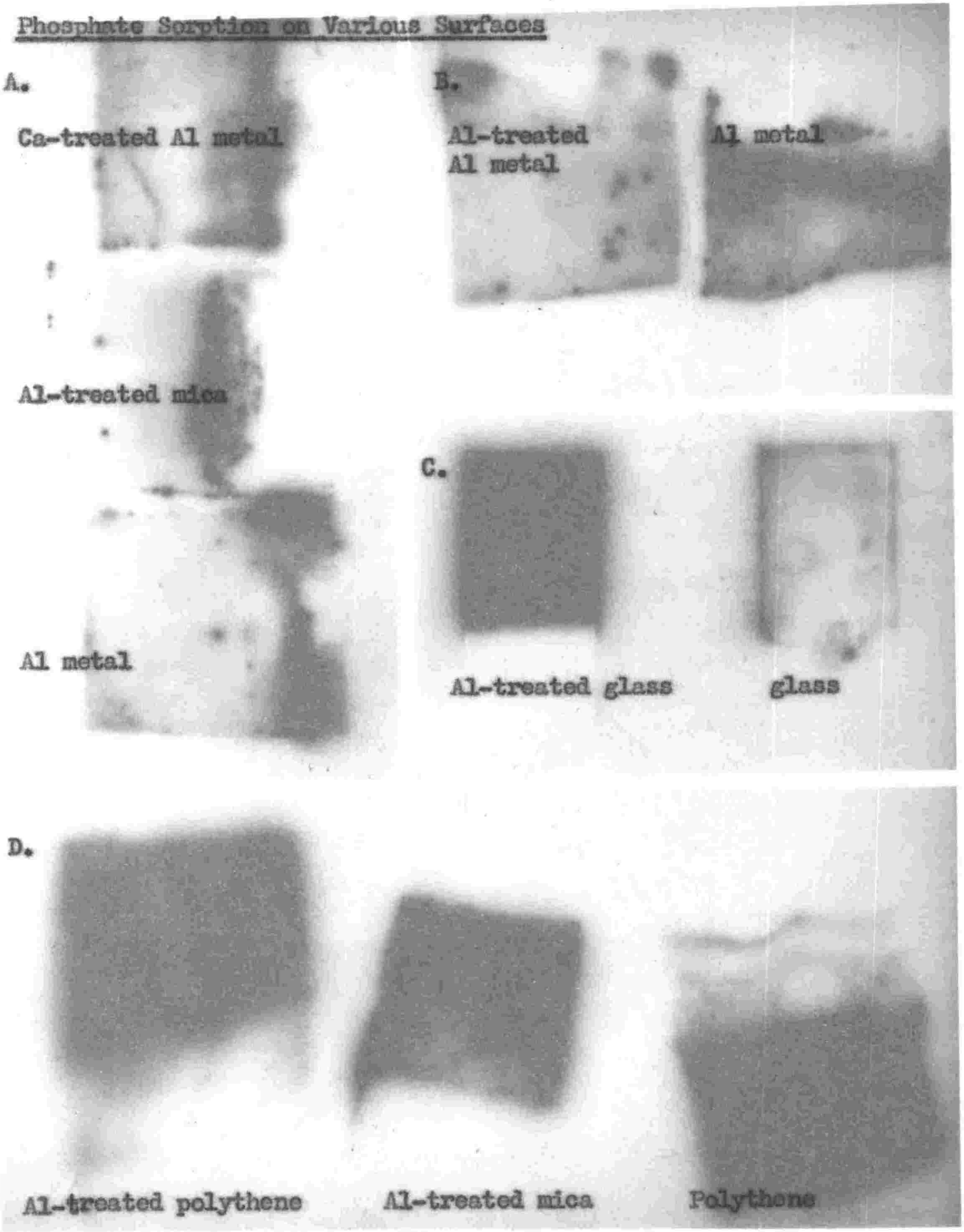
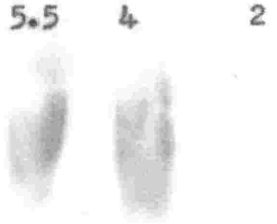
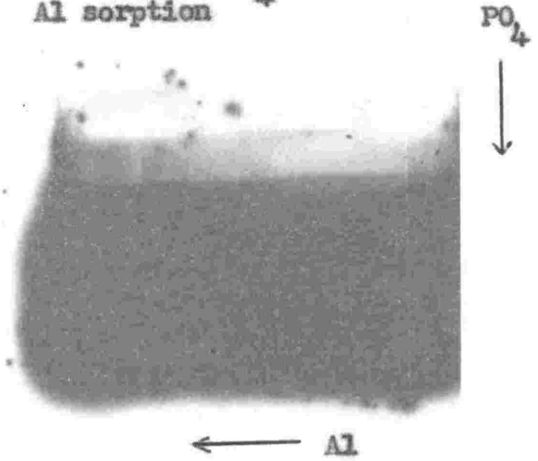


Fig. 5.10

A. pH of Phosphate
.01M. NaCl

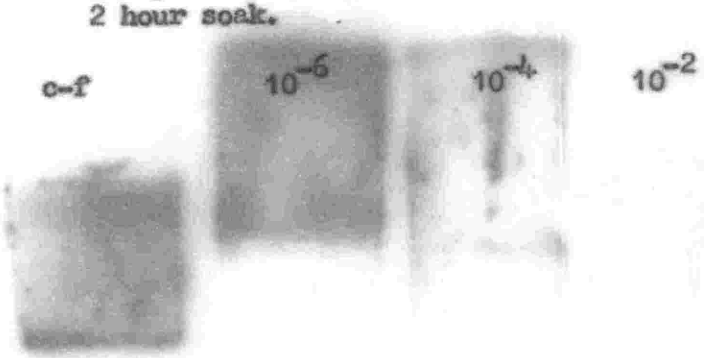


B. Kinetics of PO_4 and
Al sorption



C. Kinetics of PO_4
sorption at
10^{-4}M.

D. Phosphate concentration
2 hour soak.



E. Phosphate concentration - 10 min. soak

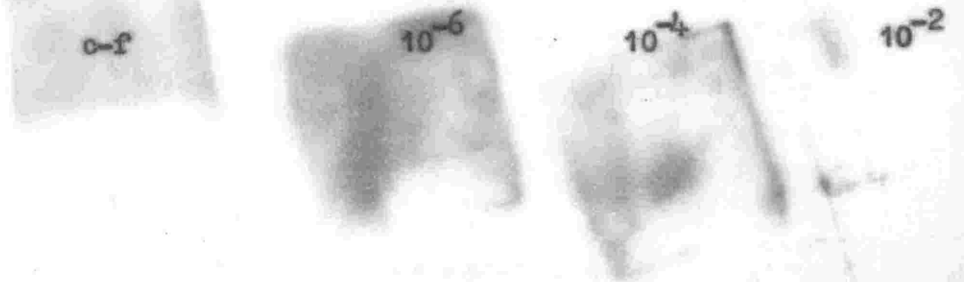


Fig. 5.11

Apparatus for Adsorption Kinetics by Autoradiography

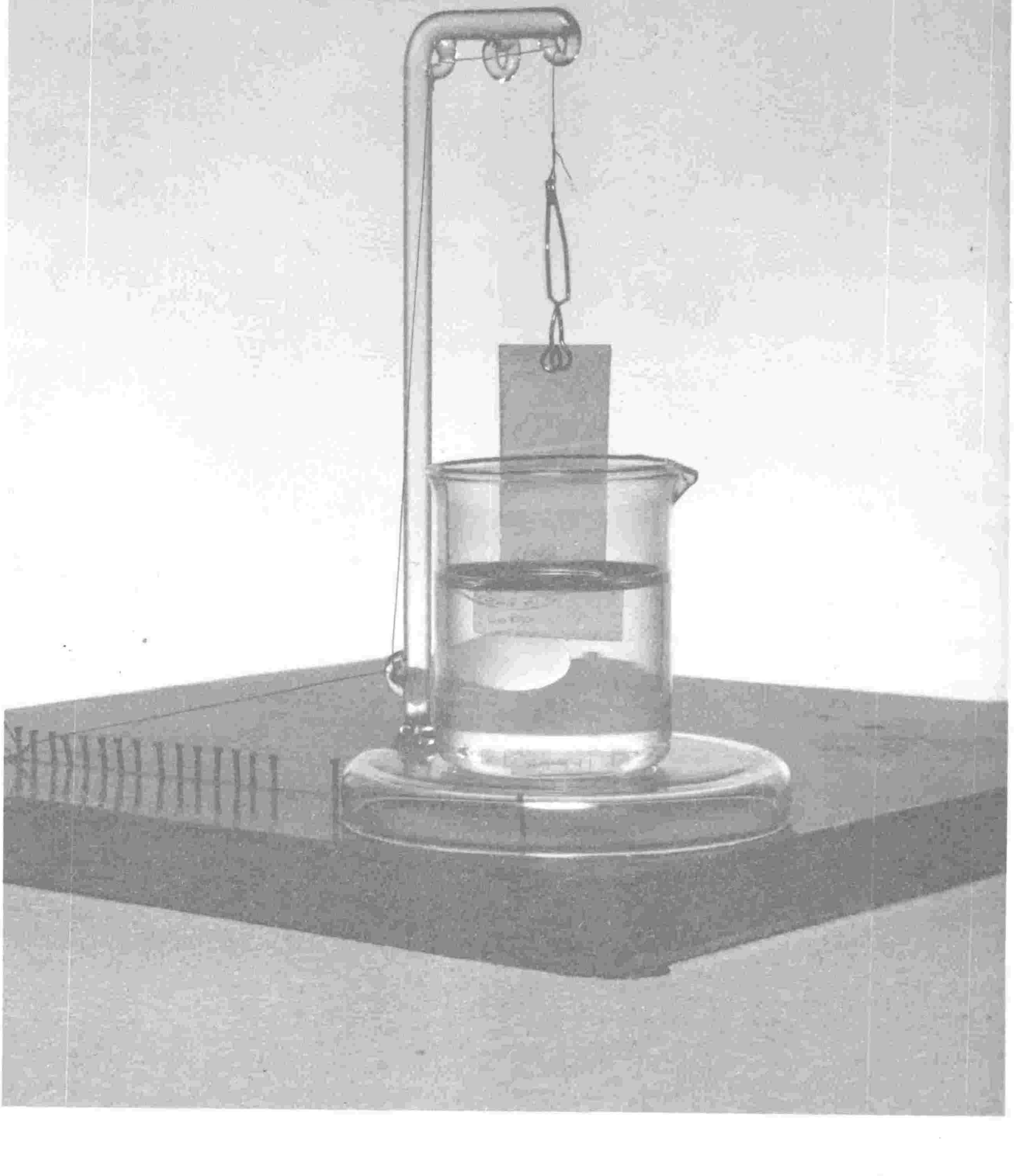
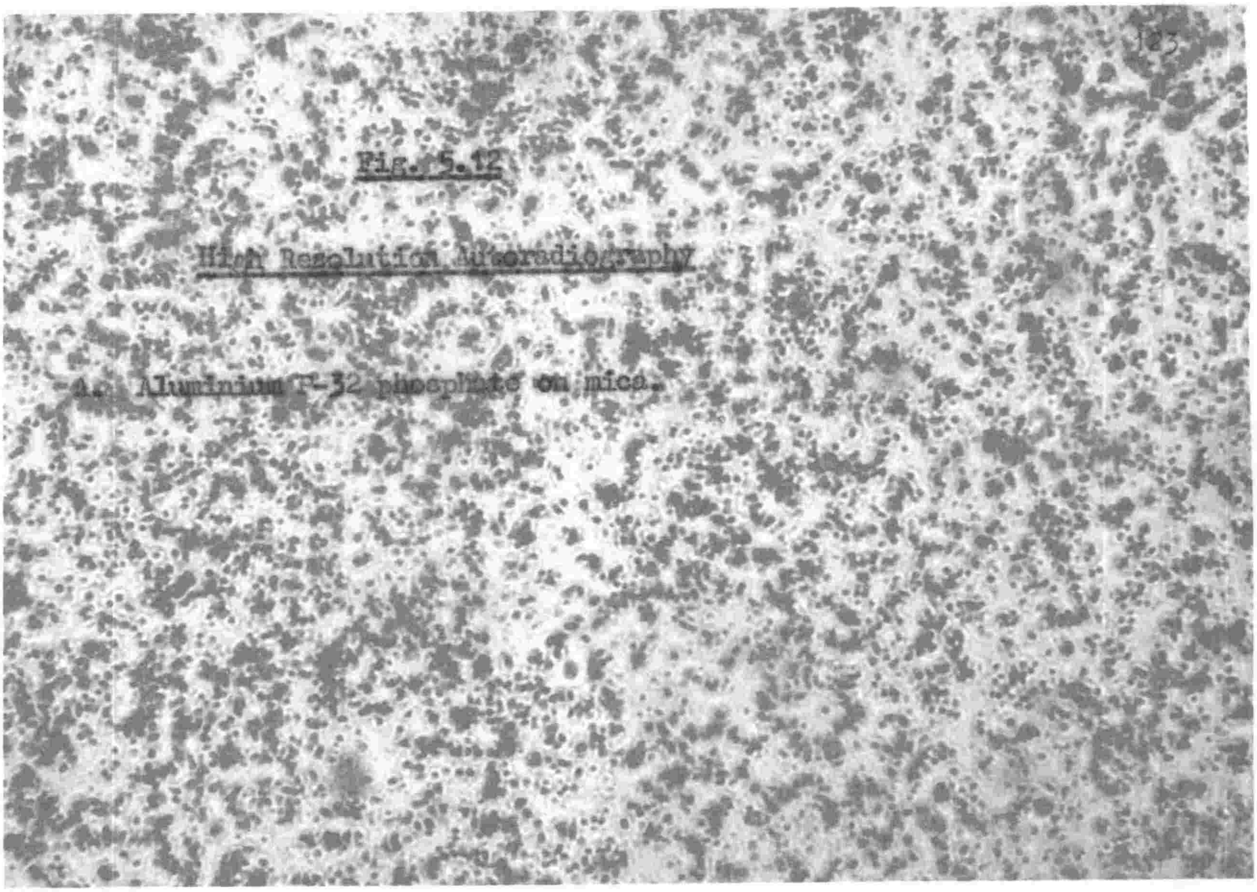
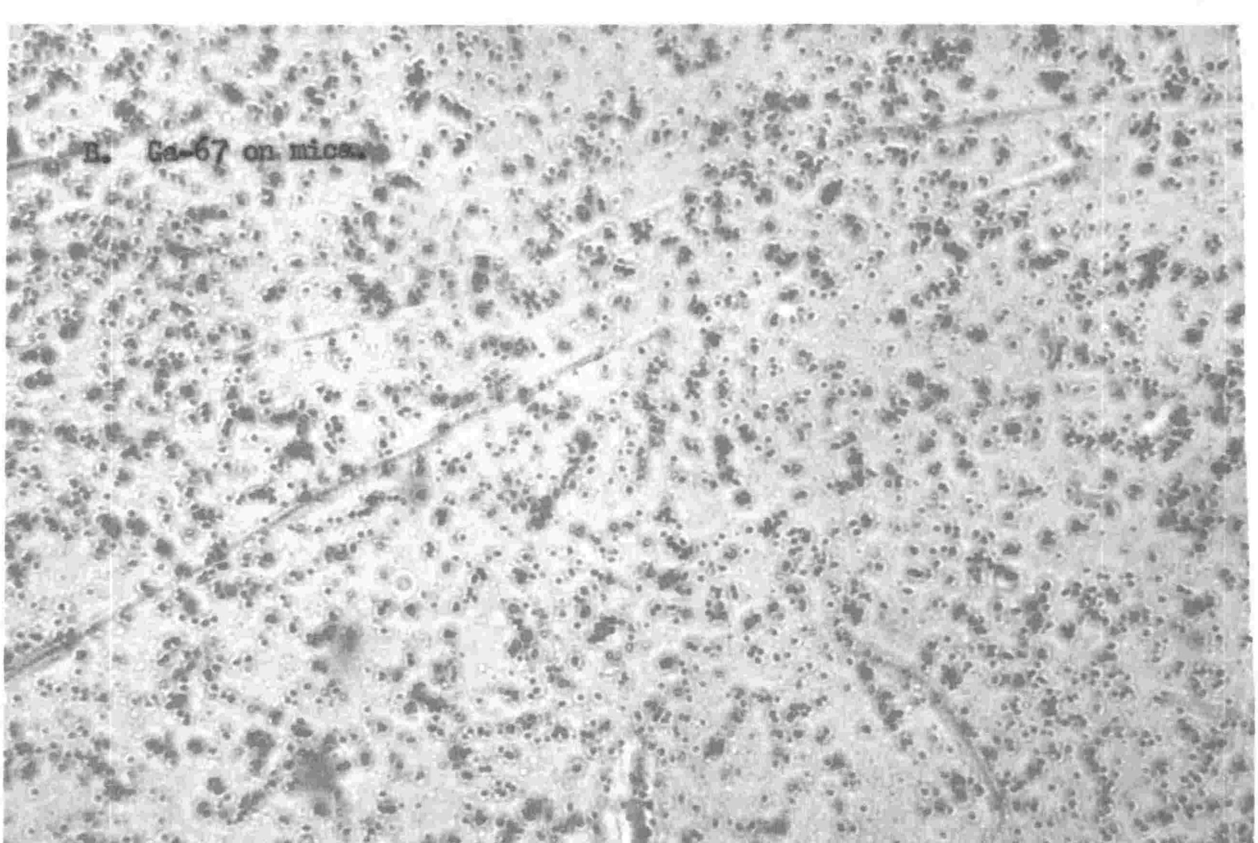


Fig. 5.12

High Resolution Autoradiography



A. Aluminium P-32 phosphate on mica.



B. Ga-67 on mica.

RADIOCHEMICAL TECHNIQUES USED TO MEASURE PHOSPHATE ADSORPTION

Principle of Measurements

The term "specific activity" of a phosphate solution is used in this thesis to refer to the disintegration rate per gram of phosphorous. The actual radioactive measurements are given in terms of count rate on a particular counting instrument, but provided all measurements are made on the same counter, under similar conditions, then the ratios of measured count rates can be used in place of the ratios of absolute activities.

Provided that the radioactive and inactive phosphate are in the same chemical form, and that the specific activity of the solution is constant during an adsorption, the specific activity of the solution and the adsorbed material will be equal.

A number which is proportional to the specific activity is found by dividing the count rate of any aliquot of the solution by the amount of phosphate in that aliquot. Because of the equal specific activities, this number will also equal the count rate of the surface divided by the amount of phosphate on the surface.

We may therefore find the total amount of phosphate on the surface from its count rate, the phosphate concentration of the solution, and the count rate of an aliquot of the solution.

Counting Planchettes

Disposable counting planchettes were made by punching them from sheet aluminium .002" to .004" thick, using for a punch a $\frac{7}{8}$" diameter steel cork borer held in a stationary drill press, with a sheet of $\frac{1}{4}$" thick

CHAPTER 6

QUANTITATIVE MEASUREMENTS ON THE ADSORPTION OF PHOSPHATE BY MICA

INTRODUCTION

In the previous chapter qualitative experiments were described in which P-32 phosphate was adsorbed on to mica surfaces. In this chapter the same system is studied quantitatively.

Since the time necessary for the adsorption process to go to completion was long on the laboratory time scale, it was necessary, when studying the effect of variations in concentration parameters, to make a compromise between performing all the desired experiments in a limited time, and making measurements of true equilibrium values. The work described in the present chapter leans heavily towards the first alternative. In Chapter 8 the kinetics of attainment of equilibrium are described, under a limited set of concentration conditions.

Because of the very small area of the mica surfaces used, very little material is adsorbed, so the only way to obtain sufficient sensitivity is to use radioactive tracer techniques. Standard radiochemical methods were modified to enable the total amount of phosphate adsorbed from a mixture of active and inactive phosphate to be estimated from the activity of the mica.

rubber beneath the aluminium. This gave a smoothly drawn shallow dish, in the centre of which a depression was made, using the rounded end of a ¼" diameter test tube to press the aluminium into a 3/16" diameter hole in a brass disc, (fig. 6.1).

Measurement of Solution Activity

A sample of the solution was placed in the depression in the planchette, and since the aluminium surface was hydrophobic if not cleaned, the solution formed a small drop. The volume of the drop was known, either by using a micro-pipette of some kind, or by weighing. From the volume, and the known concentration of phosphate, the amount of phosphate in the drop was known. The drop was evaporated under an infra-red lamp, leaving the phosphate sample as a thin film on the planchette. (Spitting of the solution while it was being dried was tested for with very active drops, but not found). The activity corresponding to the known amount of phosphate was measured by placing the planchette beneath an end window (EW3H) Geiger counter in a lead castle.

Measurement of Mica Activity

The method used to obtain a known area of the mica sample was to use a slightly modified ticket clip to produce a circular punch about 0.2" in diameter. The area of this was found to be 0.20 cm^2, by weighing several punches of a sheet of paper of measured weight per square centimeter. The pieces of mica produced in this way were about the same size as the evaporated drops of solution, so that the efficiency of counting such a piece of mica on a planchette in the same counting arrangement was equal to that of counting the solution aliquot.

There is one complicating factor, if the radioactivity is on both sides of a sheet of mica, and that is that there is some attenuation of the radiation from the bottom side of the mica. For ^{32}P this effect was not very serious, since it was found that the count rate decreased by about .4% for every 1 mg/cm^2 thickness of mica. The overall error in the average count rate of a piece of mica 15 mg/cm^2 thick, was about 3%. This error, if significant, could be determined in any particular case by weighing the sample, but at the level of accuracy reached in the present work, this was not necessary.

Measurement of the Volume of the Sample of Solution

Several alternative methods of finding the volume of the sample of solution were tried. The one finally adopted was to weigh the sample, but because the sample must be weighed immediately it is taken, this is sometimes inconvenient. Weighing would be inconvenient when work is being done in a glove box, so two kinds of micropipettes which deliver a constant volume were investigated.

One was a capillary tube with a constriction, and the other was a short capillary tube inserted inside a larger tube. It was found to be difficult to rinse the first kind, and both suffered from the disadvantage that they had to be touched on to a hydrophilic surface to empty them and remove the drop from the end. If the planchettes were cleaned in chromic acid they became hydrophilic, but the solution then spread all over them, thus giving an unknown and variable counting geometry.

A small disc of filter paper could be used to take up the solution, but this meant that the pipette became dirty, and had to be cleaned before being re-used. This was an important disadvantage, so for all the present work the solutions were dropped from a fine dropper made from drawn "Pyrex" tubing, which was not allowed to touch the planchette, or the solution on the planchette. The planchettes were weighed on a "Mettler" balance, each weighing being ± .2 mg, and typical drop weights being in the range 10 to 50 mg.

Definition of a Useful Adsorption Parameter

It was found useful to have a parameter relating the amount adsorbed to the amount in solution. This parameter has been called the "adsorption ratio", and is defined as the ratio of the number of counts/min/cm^2 of mica to the number of counts/min/cm^3 of solution. In a "mini-beaker" (see Chapter 5 and fig. 6.1), the shape of the solution approximates a rectangular prism of side area equal to that of the sample. In this case the adsorption ratio, which has the dimensions of centimeters, is the thickness of solution containing an amount of phosphate equal to that adsorbed. If the adsorption is proportional to concentration then this ratio should be constant for various concentrations. It has usually been represented by the symbol "q" in this thesis.

EVALUATION OF REPRODUCIBILITY AND ACCURACY OF THE TECHNIQUES

Weighing

A planchette with a drop of water on it was weighed four times over a period of five minutes, and found to weigh 0.6230, 0.6233, 0.6229 and 0.6229 grams. This showed that evaporation was unimportant. The weight of the planchette was 0.6005 ± 0.0002 grams, so the drop weighed 22.4 ± .4 mg, which is a 2% accuracy.

Counting

A piece of mica punched from a sample was counted five times, being removed from the counter each time. The count rates found, with standard deviation of the counting on each count being about 1.5%, were 2100, 2122, 2060, 2120 and 2130 counts/minute, which are well within 2σ of mean value.

Solution Activity

The accuracy of this was found to be significantly less than that of the combined weighing and counting errors, and was greater for solutions containing carrier than carrier-free solutions. For a carrier-free solution values of 5.85, 6.39, 6.22, 5.04, 5.03 and 5.69×10^4 counts/minute/ml. were found, which gives a mean value of $(5.7 \pm .7) \times 10^4$, an error of ± 12%. For a 10^{-2} molar KH_2PO_4 solution values of 4.79, 5.60, 4.76, 4.80, 4.77 and 5.08×10^4 counts/minute/ml were found. These numbers have a somewhat skew distribution, for which a spread of ± 8% could be quoted, but it seems that most of the samples are much closer to a low value, while occasionally a sample has a spuriously high value. This might be due to the presence of P-32 phosphate adsorbed on to particles of dirt in some samples. Surface films have been found in this work (Chapter 4) to adsorb phosphate strongly, and these could well be picked up by the dropper and transferred to the solution sample, giving a spuriously high count rate. Strict cleanliness of solutions and droppers is clearly essential if reliable results are to be obtained.

Overall Reproducibility of Adsorption of Mica

For these experiments the strips of mica were cut off a large sheet split at the start of the experiment. They were soaked in 1M $AlCl_3$

for five minutes and washed in the continuous washer (see Chapter 5) for ½ hour. The strips were then soaked in a carrier-free phosphate solution for 10 minutes, rinsed with distilled water and dried. The samples were autoradiographed to check their uniformity, and then counted. The solution activities were measured before and after soaking the samples in the phosphate, freshly cleaved samples were placed in each solution after the aluminium mica, and another solution sample was taken after these blanks. Autoradiographs of four of the five samples, and of the five blanks are shown in fig. 6.2. It can be seen that although two of the blanks were contaminated with aluminium and three were not, there was little difference in the amounts adsorbed by the samples. Adsorption was also approximately uniform all over the surfaces.

The data obtained from counting the activity is shown in table 6.1, and it is clear that the aluminium-contaminated blanks adsorbed much less phosphate than the corresponding samples. It would therefore be expected that the contamination would not seriously affect the adsorption on the aluminium-treated samples.

Sample number 3 was made the day before the other four, and this accounts for its absence in the autoradiograph. (Samples 1, 2 and 4 were used in unrelated experiments.) Its adsorption is decay corrected so that it is comparable to the others. The figures for the activity on the mica have been converted to counts/minute/cm^2, neglecting the attenuation of the β-rays by the mica.

The main aim of the experiment was to study the range of the adsorption ratio in a set of similar experiments, and the variation found is about ± 20% from the mean. Compared with ordinary chemical measurements this is poor, yet as an advance from the qualitative techniques previously used it is quite good, especially when the minute quantities involved in this carrier-free measurement are considered. The accuracy at higher concentrations should be expected to be better than this.

The adsorption ratio on the untreated "blank" micas is seen to vary by a factor of 500, while that on the aluminium-treated samples varies only by a factor of 1.4, and is not correlated with that on the blanks. This confirms that aluminium contamination is unimportant on these samples, as stated before on the basis of the relative amounts adsorbed by the samples and blanks. It is worth noting that from the results of this experiment it can be said that from carrier-free phosphate solution aluminium-treated mica adsorbs several hundred to a thousand times as much phosphate as does untreated mica.

This work shows that the techniques outlined will give, with carrier-free phosphate, results with a reproducibility of about 20%, the errors being due mostly to problems associated with the small amounts of material involved.

THE EFFECT OF ALUMINIUM ON LOSSES TO THE GLASS

In the preceding experiment, the blank experiments were performed the day after those on the samples, except for sample 3, where two days elapsed, and it is of interest to note the change in solution concentration over this time. Out of the four left for one day, the two which were aluminium contaminated had lost nearly half their activity, while the others had lost much less. The total amount lost to the mica was much less than the change observed, so that the aluminium must have been causing losses in other ways, probably to the glass surface.

PRECAUTIONS AGAINST AIR-BORNE CONTAMINATION

At about the time these quantitative techniques were being developed it was decided that it was unsatisfactory to attempt to work on benches open to all the air-borne contamination of the laboratory. This dust is a problem in analytical chemistry at the milli-microgram level for metals (Thiers (1955)) and it would be expected to be much more serious if the organic materials in the dust were important.

A possible way of avoiding this problem would be to use a glove box with a filtered air supply, but working with gloves can be inconvenient, a balance would be needed inside the box, and only one person can conveniently use a glove box. The method adopted in the present work is a compromise between cleanliness, convenience and cost.

A four-sided wooden box was made, and lined with clear polyvinylchloride sheet. The plastic also covered the top and front (fig. 6.3). The front lifted up for use, allowing some contamination to enter, but the level still remained much lower than that prevailing outside the box, as shown by the layer of dust which soon accumulated on the top.

Inside this box were kept all the tools in common use, those which were to remain clean being covered by inverted test tubes or beakers. Water was led in through one hole to the continuous flow washer, and out through another.

The standard of cleanliness, as judged by uniformity of autoradiographs, was markedly improved by this arrangement.

CALCULATION OF THE NUMBER OF ADSORBED MOLECULES PER SQUARE ANGSTROM UNIT

It has been found convenient when using carrier solutions to express the amount of phosphate adsorbed on the surface in terms of the number of molecules per square Angstrom unit. This is then easily compared with the order of magnitude expected on the basis of the various theories. A monolayer coverage of hydrated ions would require about one ion per 30 sq. A., although the formation of hydrated oxides could greatly decrease the amount per unit area. The number of negative charge sites formed by isomorphous replacement within the mica is about one per 50 sq. A.

If the solution has a concentration of C moles of KH_2PO_4 per litre, and a count rate on the planchette of S counts/minute/ml, then 1 count/minute means that C/1000S moles are present, so that

$$x \text{ counts/minute/cm}^2 = \frac{xC}{1000S} \text{ moles/cm}^2$$

$$= 6qC \times 10^4 \text{ ions/sq.A.}$$

where q = x/S is the adsorption ratio previously defined. Similar considerations (with possible complications from the number of ions per molecule) apply with other adsorbing species.

CONCENTRATION OF "CARRIER-FREE" P-32 PHOSPHATE

The phosphate solutions obtained from the Radiochemical Centre, Amersham, had a specific activity of from 20 to 50 curies per milligram of P, and a concentration of about 1 mc/ml. This implies that the concentration of phosphate in the original solution was about 10^{-6} M. The solutions in which the samples were soaked had activities about 10^{-2} μc/ml, when carrier-free solutions were being used, so that if these were made by dilution of a fresh stock solution the nominal carrier concentration would have been 10^{-11} M. Even after six half-lives had elapsed (3 months) the concentration of phosphate from the stock solution was below 10^{-9} M.

ADSORPTION ON UNTREATED MICA

It was known that some phosphate was adsorbed by untreated mica, but in the light of the experiments in the previous chapter, it seemed possible that this might be due to the presence of certain cations in the water used.

J. Watkinson (personal communication) has found that the upper limit to the amount of aluminium in the distilled water used was less than 10^{-9} moles/litre, so this seems to be an unlikely source of significant amounts of aluminium.

The adsorption might have been affected by the desorption of chromium ions from the walls of the chromic-acid-cleaned beaker into the solution. To test this possibility an experiment was carried out on the adsorption on mica from 5×10^{-5}M. KH_2PO_4 + $^{32}PO_4$, in such a way that a comparison could be made between each member of a set of mini-beakers treated overnight with 1M. KOH, concentrated HCl and concentrated HNO_3, after an initial cleaning in chromic acid. Two beakers were treated in each reagent, after first being cleaned with chromic acid and rinsed thoroughly. The values obtained for the number of phosphate molecules adsorbed per 1000 square Angstrom were -

Chromic acid only	0.65,	0.82
Chromic acid and KOH	0.39,	0.17
Chromic acid and HCl	1.13,	0.55
Chromic acid and HNO_3	0.64,	0.52.

The slight reduction observed with KOH is probably not significant, since adsorbed cations are more readily removed with acid than alkali (see work with ^{67}Ga - Chapter 10). The adsorption is probably not related to chromium contamination.

The adsorption ratio on these blanks from 5×10^{-5}M. KH_2PO_4 was about 2×10^{-4}cm, and is comparable with the values of 3×10^{-5} to 3×10^{-4}cm found in carrier-free experiments. This indicates that the adsorption on untreated mica is proportional to concentration, up to 5×10^{-5}M. KH_2PO_4.

THE EFFECT OF ALUMINIUM CONCENTRATION

The Time Spent in $AlCl_3$

It was known from the autoradiograph experiments that when the mica was soaked in 1M. $AlCl_3$ the time of soaking made no difference to the amount of phosphate adsorbed. Since it was not known whether this applied at lower aluminium concentrations, the experiments were carried out over a range of times in $AlCl_3$.

The Procedure Used

The concentrations of $AlCl_3$ used were 1, 10^{-2}, 10^{-4}, and 10^{-6} molar, all adjusted to pH 2 with HCl. After soaking the mica for the desired time in the aluminium solution, it was rinsed briefly with deionized water, and then soaked for one hour in 10^{-4}M. KH_2PO_4 solution containing about 1 μC/ml of $^{32}PO_4$. It was then rinsed again and dried. Separate phosphate solutions were used for each concentration of aluminium, but the same one was used for each extension of the time of soaking.

Results

The results are tabulated below as the number of molecules per 1000 square Angstrom units -

Concentration moles/l	Time 2 min.	10 min.	1 hr	5 hrs	25 hrs	Blank
1	18	15	10	10	8.3	11.5
10^{-2}	1.7	3.1	4.8	3.8	3.8	0.9
10^{-4}	0.11	0.11	0.08	0.21	0.11	0.24
10^{-6}	0.05	0.14	0.22	0.16	0.11	0.05

It is clear from this table that the amount adsorbed was independent of the time. The amount of phosphate adsorbed by untreated mica from the badly aluminium-contaminated phosphate solution used for the 1M. aluminium-treated samples was the same as that adsorbed by treated mica. Also, the amount adsorbed by mica treated with 10^{-4} or 10^{-6} molar solutions was less than that adsorbed by untreated mica in the previously described experiments, and no more than that adsorbed by untreated micas in the experiments on aluminium contamination described later, so that these results are inconclusive. The phosphate used for the 10^{-2} M. aluminium-treated samples appears not to have been aluminium contaminated, but the phosphate adsorption was still independent of time, after a 10 minute adsorption. The aluminium must therefore have been rapidly adsorbed.

THE EFFECT OF PHOSPHATE CONCENTRATION

Aims

It was expected from Furkert's work that as the phosphate carrier concentration was increased, the total amount of phosphate adsorbed would increase, linearly at first, and then flattening off to some maximum value. It was hoped to find this value and use it as evidence for or against the theories which had been proposed to explain the adsorption phenomenon.

Little was known about the kinetics of phosphate adsorption at low phosphate concentration, and nothing at all at higher concentrations. Experiments were therefore designed to find the variation with concentration of the amount adsorbed at a set of different times.

Techniques

Each sample was washed for 30 minutes after a 5 minute soak in aluminium chloride. A separate phosphate solution was used for each measurement, and its activity was determined before and after the measurement. Stock phosphate solutions of the concentrations used were made and stored in clean volumetric flasks, and extracted with clean pipettes. (If a solution is poured from a flask it is contaminated with dirt from the lip of the flask.) The 10^{-6}M. solution was analysed for the author by J. H. Watkinson and found not to change significantly in concentration over several months.

To reduce the changes in concentration during the experiments with dilute phosphate solutions, a volume of 50 ml. was used at 10^{-5}M. and 10^{-6}M. concentrations. The mica strips were held in these solutions with the stand shown in fig. 6.1. "Mini-beakers" of volume 1 ml.

were used at higher phosphate concentrations, to provide more concentrated P-32 phosphate where changes in the phosphate concentration were small.

Results

The results are shown in table 6.2 and fig. 6.4. The points above 10^{-6}M. on the log-log graph for a 10 minute soak in phosphate all lie near a straight line of slope 0.50, even at the highest concentrations used. This can be described by saying the points lie on a Freundlich isotherm, in contrast to a Langmuir isotherm, which would require one straight line of slope 1.0 at low concentrations, and another line parallel to the concentration axis, at high concentrations. The value obtained for the slope indicates that the amount adsorbed is proportional to the square root of the concentration. Although this is in the range expected for Freundlich isotherms, (Glasstone, (1955)) there is no obvious reason for this value.

The corresponding experiments with a time of soaking in phosphate of 100 and 1000 minutes were also performed, and the results are shown in the same table and graph as the previous results. It can be seen that while the values for 100 minutes are very similar to those for 10 minutes, those for 1000 minutes are somewhat greater at low concentrations and become approximately equal at high concentrations. In general, the longer solutions are kept the harder it is to keep them clean, and it has been found difficult to get consistent results when long soaking times have been employed. For this reason not too much emphasis should be placed on the 1000 minute curve.

The value of q for carrier-free phosphate in this experiment was greater than that obtained previously for carrier-free phosphate, which was (within expected errors) the same as that obtained in this experiment for 10^{-6}M., but the difference is probably not significant.

Conclusions

Below 10^{-6}M. phosphate concentration the amount of phosphate adsorbed is proportional to concentration, whereas above this concentration the adsorption is proportional to the square root of concentration. It appears that a change in the sorption mechanism occurs at about 10^{-6}M.

THE EFFECT OF THE TIME SPENT IN THE PHOSPHATE SOLUTION

Aim

The previous set of experiments gave a reasonable indication of the effect of varying the concentration of the phosphate solution, but left some doubt as to the effect of varying the time spent in the solution. Experiments were therefore performed with the time variation as the main object, the difference from the previous experiment being that all the experiments were performed simultaneously, using similar pieces of mica, and more values of the time of soaking were used to enable accidental variations to be detected.

Results

The experiments were performed at two concentrations, 10^{-6}M and 10^{-3}M, but at the lower concentration 100 ml beakers of solution were used, covered by inverted beakers, and it was found that solutions in these beakers could not be relied on to remain clean for more than an hour. The results presented are only those for the 10^{-3}M. solution, the kinetics of uptake at 10^{-6}M. being studied by the direct technique described in Chapter 8. The results, tabulated below, show that the amount adsorbed increased with time until a maximum was reached at about 100 minutes.

Time (min.)	Molecules/sq.A.
1	.014
3	.028
10	.040
30	.060
100	.103
300	.103
1000	.045

The result for 1000 minutes is much lower than expected, and since the phosphate solution concentration used in the calculations was that after the adsorption, so that a decrease in concentration with time would give too high a value for the adsorption, it seems probable that this value must be affected by some error of the kind previously found.

Conclusion

It seems from this that the previous 100 min. adsorption isotherm is probably similar to that which would be found in an experiment carried to equilibrium.

ADSORPTION ON UNTREATED MICA FROM SOLUTIONS CONTAINING BOTH ALUMINIUM AND PHOSPHATE IONS

Aim

It has already been shown that mica treated with a phosphate solution containing a small amount of aluminium adsorbs much phosphate, whereas mica treated with dilute aluminium solutions adsorbs very little. In order to find out how this occurs, some experiments were carried out in which various amounts of aluminium chloride were added to a 5×10^{-5} molar KH_2PO_4 solution containing P-32 phosphate.

Technique

The solutions were prepared by adding to ½ ml of 10^{-4}M. phosphate solution ½ ml of an aluminium chloride solution of twice the desired final concentration of aluminium (assuming no precipitation of aluminium). These volumes were dispensed using fine-pointed droppers connected by ½" of rubber tube to a 1 ml syringe graduated in .01 ml, care being taken not to draw any solution into the syringe. (This would have contaminated both the solution and the syringe.) This method of measurement was checked by weighing 0.50 ml of solution and was found to be accurate to 2%.

The pH of the mixed solutions was found to be 5.5 - 5.3.

Results

Several experiments were performed, and it was found that the results within each experiment were consistent, but the amount adsorbed was not always the same in different experiments. The data is set out in table 6.3., for four experiments, the aluminium concentration increasing down the page. It may be seen that up to aluminium concentrations of about one micro-mole per litre, no effect due to the added aluminium can be seen, but above this there is a sharp increase to about twenty times the amount adsorbed on the blanks, the actual values depending on the experiment, but remaining constant with further increase in concentration.

The Effect of Time Elapsed after Mixing the Solutions

Several explanations, including dirty mica and adsorption of P-32 phosphate on suspended dust particles, were advanced to explain the above inconsistencies, but no way to test these hypotheses was found. However a further experiment showed that the time elapsed between mixing the solutions and putting in the mica sample was directly related to the uptake of phosphate.

In this experiment six solutions were made by mixing ½ ml of 4 x 10^{-6}M. $AlCl_3$ and ½ ml 10^{-4}M. KH_2PO_4 + $^{32}PO_4$. A piece of mica was added to each one at some known time after first mixing the solutions, and was left there for 10 minutes. From the plot of the amount adsorbed against time elapsed between mixing the solutions and inserting the mica (fig. 6.5), the possible source of variation can be seen. The results are reasonably consistent with the time intervals between mixing and using the solutions in the original experiments.

The Amount of Aluminium Adsorbed by the Mica

There are several points which arise in connection with the relationship between the amount of phosphate adsorbed and the amount of aluminium added to the solution. In the last part of experiment U2 19 molecules/1000 sq.A. were adsorbed from a solution containing 2.6 x 10^{-9} moles of aluminium in 1 ml. The autoradiograph showed that the phosphate was evenly distributed over a total area of 3.8 cm^2 of mica, which gives an amount of phosphate on the mica of 1.2 x 10^{-9} moles. Because of hydrolysis each aluminium atom will be associated with between one and three $H_2PO_4^-$ ions, but it is seen that, assuming the phosphate uptake is accompanied by aluminium uptake, a considerable fraction of the aluminium was adsorbed on to the mica, and one would expect more to be adsorbed on to the glass beaker.

A Comparison Between the Amount of Aluminium Added and the Amount of Phosphate Lost from the Solution.

After the results listed under U4 were obtained the solutions were left overnight and a new mica strip put in four of them. It was found from the solution activity after this second strip had been soaked that about half the phosphate had been lost from the solution in each case where aluminium had been added, while less than 10% was lost from the solution used for the blank. The amount of phosphate involved was about 2.5×10^{-8} moles $H_2PO_4^-$. The amount of aluminium added was about 0.3 to 0.6×10^{-8} moles Al^{3+}. This seems to be not enough to react with all the phosphate lost, and yet it seems to have been associated with the loss. The amount of phosphate adsorbed by the mica was found to be about half that adsorbed the first time.

The only explanation for these results, other than supposing that each aluminium ion removes from solution eight or more phosphate ions, seems to be that there were several phosphate containing species present, some of which had a higher specific activity than others, and were preferentially removed in the presence of aluminium. Such a situation could arise if "radiocolloids" were present in the stock carrier-free radioactive solution, and if phosphate on these colloids exchanged only slowly with external carrier. Unsuccessful attempts to find such species are described in an appendix.

Separate Treatment with the Aluminium and Phosphate

It is of interest to show whether the phosphate would go on equally well if it were first treated with the aluminium solution and then with the phosphate. From the results previously reported on the effect of time and concentration of the aluminium solution this would not be expected, but to test this directly two pieces of mica were placed respectively in 2.6×10^{-6}M. and 8.5×10^{-7}M. $AlCl_3$ for 10 minutes, briefly rinsed, and then placed in 5×10^{-5}M. KH_2PO_4 + $^{32}PO_4$ for 10 minutes. They adsorbed .57 and .69 molecules/1000 sq. A. respectively, which is indistinguishable from the blank, so that at this level the aluminium in the phosphate solution is much more effective at causing phosphate sorption than is aluminium of the same concentration applied separately to the mica.

Conclusions

The above evidence all points towards adsorption of a precipitated aluminium phosphate on to the mica. High resolution autoradiographs were taken (see previous chapter) to try and see the particles, without success, but this merely implies that the particles were less than a few microns apart. If all the phosphate in every square micron were collected in one particle, then this particle would be about the largest size allowed on this information. Since there were about 10 molecules adsorbed per 1000 sq.A. in this experiment, and 1 sq. micron = 10^8 sq. A., there would have been at the most 10^6 molecules in a particle. This could have been a sphere about 100 molecules in diameter. The diameter of the hydrated aluminium phosphate molecule which would have been formed would be about 10A., so that the particles would have been about 0.1 μ in diameter. This seems reasonable for colloidal material.

THE EFFECT OF THE pH OF THE ADSORBING SOLUTION

Techniques

Qualitative experiments with carrier-free phosphate were used in the previous chapter to show that the amount of phosphate adsorbed was the same at pH 4 as at pH 5.5, and at lower pH's decreased.

A similar experiment was carried out using the quantitative techniques described here. The solutions from which the phosphate was adsorbed were 10^{-1}M. in NaCl, 10^{-4}M. in KH_2PO_4, and contained HCl to adjust the pH to the desired value. The mica was soaked in $AlCl_3$ for 21 hours, and then rinsed with a wash bottle, which probably means that the solutions were aluminium-contaminated. (This experiment was performed before most of those which defined the nature of aluminium contamination.) The samples were soaked for 1 hour in the phosphate solution.

Results

The following results were obtained -

pH	Molecules/1000 sq.A.	log (molecules/1000 sq.A.)
2.2	0.05	- 1.3
3.2	0.12	- 0.92
4.3	2.0	0.30
5.5	23	1.36

The results are plotted in graph 6.6, which shows that the logarithm of the amount adsorbed is proportional to pH, with a slope of 0.9. If the point corresponding to pH 2.2 is neglected, and because of its low count rate this is probably justifiable, the slope of the line through the three points left is very close to 1.0.

Conclusions

It seems that, under aluminium-contaminated conditions with constant ionic strength and varying pH, the amount of phosphate adsorbed is inversely proportional to the hydrogen in concentration in the phosphate solution. As noted before, this is the variation with pH expected for cation adsorption, and not anion adsorption.

CHECKS ON CONSISTENCY OF RESULTS

In the course of this work there may be found several results, in different experiments, which one would expect to be comparable. A phosphate concentration of about 10^{-4} occurs frequently, and one should be able to make small corrections for concentration by assuming a square root dependence.

Aluminium contaminated phosphate solutions at pH 5.5 occur in the time experiments involving the time of aluminium soaking, the pH, and deliberate aluminium contamination. The amounts of phosphate adsorbed, in molecules per 1000 sq.A., were 10, 20 and 30. (This last figure is corrected to 10^{-4}M.) Thoroughly washed mica in 10^{-3}M. KH_2PO_4 occurs in the phosphate adsorption kinetics experiment, and if the adsorption is corrected to 10^{-4} molar one obtains an adsorption of about 30 molecules per 1000 sq.A.

The phosphate isotherm experiment showed an adsorption of about 70 molecules per 1000 sq.A. at 10^{-4}M.

There is thus a considerable spread in these values, but considering the wide range of conditions and the variations in technique due to improvements with experience, it is considered that the factor of two separating the greatest and least from the median is an acceptable variation in these pioneering experiments.

ADSORPTION OF PHOSPHATE ON GALLIUM-TREATED MICA

Aims

This work was performed to enable a comparison to be made between the amount of gallium adsorbed, as determined by ^{67}Ga measurements, and the amount of phosphate adsorbed by gallium-treated mica.

There were two main points of interest. One was the maximum amount of phosphate adsorbed by mica treated with a gallium solution which was known to give a certain amount of sorbed gallium. The other was the amount of phosphate adsorbed by mica treated with gallium solutions of various strengths. The variations in amount of phosphate adsorbed could be compared with the amount of gallium adsorbed.

Variation in Phosphate Sorption with Gallium Concentration

Strips of freshly-cleaved mica were soaked in pH 3 gallium solution of concentration 10^{-6}, 10^{-4}, 10^{-3}, 10^{-2} or 0.2 moles/litre for ten minutes, rinsed with a wash bottle, and soaked in carrier-free phosphate solutions for ten minutes. They were then rinsed, dried and autoradiographed. Further strips of untreated mica were soaked in each of the phosphate solutions as a check on gallium contamination of the solutions.

The adsorption ratios found were as follows -

	Adsorption Ratio	
Gallium Concentration	Sample ($\times10^{-3}$cm)	Blank ($\times10^{-3}$cm)
10^{-6}	1.5	0.1
10^{-4}	1.0	.03
10^{-3}	24	-
10^{-2}	54	.05
0.2	85	5

The 0.2M. solution led to contamination of the phosphate solution, but the more dilute ones did not. All the gallium-treated samples adsorbed at least ten times more phosphate than the uncontaminated blanks, but there seems to be a sudden jump in the amount adsorbed, at 10^{-3}M. concentration of gallium, above which the adsorption is approximately constant.

In Chapter 9 it is shown that the amount of gallium adsorbed increases linearly with concentration, up to about 10^{-5}M. above which the amount increases very slowly with concentration. The sudden increase in the amount of phosphate adsorbed might be related to this saturation of the surface with gallium, although the correlation between the experiments is not exact.

Amount of Phosphate Adsorbed on Gallium-Treated Mica at High Phosphate Concentrations

The mica samples in these experiments were all treated with 0.01 M. $GaCl_3$ at pH 3 for 10 minutes, and then put in a phosphate solution, of carrier-free, 10^{-4}, or 10^{-6}M. concentration, for 10 minutes.

The amounts adsorbed were as follows -

Phosphate Concentration	Adsorption Ratio	PO_4 Molecules per 1000 sq.A.
Carrier-free	5×10^{-2}	-
10^{-4}	3×10^{-3}	18
10^{-2}	7×10^{-5}	42

It appears that above 10^{-4}M. not much more phosphate is adsorbed with increasing concentration. The amount adsorbed is comparable with the amount adsorbed at the end of the linear part of the isotherm of phosphate adsorption on 1M.-aluminium-treated mica, and could correspond to a monolayer.

Relationship Between the Amounts of Gallium and Phosphate Adsorbed

In Chapter 9 it is shown that in 10 minutes 14 ± 4 molecules of gallium per 1000 sq.A. are adsorbed from a 0.01 M. $GaCl_3$ solution.

It therefore appears that the amount of phosphate sorbed under these conditions is approximately equivalent to the amount of gallium sorbed.

CONCLUSIONS

Techniques

Techniques have been developed which enable quantitative measurements of the amount of a chemical species adsorbed on the crystal cleavage planes of mica. The reproducibility is sufficiently good for preliminary investigations, and will probably improve as the techniques are practised. Inherent in the radio-chemical methods used is a high sensitivity and a wide concentration range.

Adsorption Isotherms

The adsorption of phosphate by thoroughly-washed aluminium-treated mica has been found to be proportional to the phosphate concentration, from carrier-free concentration levels up to about 10^{-6}M. $H_2PO_4^-$.

At higher concentrations, up to 10^{-2}M., the adsorption is proportional to the square root of the concentration.

The amount of phosphate adsorbed at the change from linear to square root dependence on concentration is about one phosphate ion per 100 square Angstrom units. At this concentration the ions are about 10 Angstrom units apart, and if the adsorbed species is a hydrated aluminium phosphate, this could be near to saturation of a monolayer cover.

However, the phosphate which adsorbs at higher concentrations must require the establishment of a thick layer, especially at the highest concentration used, where there is one phosphate ion for every two square Angstrom units. This phosphate must be associated with aluminium, and since the solutions used appeared not to be aluminium contaminated, the aluminium must have been present at greater than a monolayer thickness, even in the low concentration experiments. The phosphate would have to penetrate into this aluminium layer at high concentrations, and there seems to be no reason why it should not do so at low concentrations. Thus the change is probably not due to saturation of sites on a flat surface.

It is shown that the adsorption on to mica treated with .01M. $GaCl_3$ does not rise as far as that of mica treated with 1M. $AlCl_3$, and does not vary with the square root of the phosphate concentration. This could be due to the different cations, but an alternative explanation, which the author was unable to test fully because of lack of time, would be that formation of the thick layer of cations necessary to accommodate the extra phosphate occurs only when the mica has been treated with very concentrated cation solutions. This hypothesis is supported by the equivalence between the quantities of phosphate and gallium adsorbed.

A limited amount of data suggests that the adsorption on to untreated mica may be proportional to concentration, up to 10^{-4}M. Under these conditions the amount adsorbed is only about one phosphate ion per 1000 square Angstrom units, so that a monolayer coverage would not have been reached.

Controlled Aluminium Contamination

The addition of aluminium to a 5×10^{-5}M. KH_2PO_4 solution results in a great increase in the phosphate adsorption on untreated mica if the concentration of aluminium is greater than about 10^{-6}M. There is a decrease in the amount of phosphate adsorbed, with the increase of time between the mixing of the aluminium and phosphate solutions, and the addition of the mica. These two results suggest that a precipitate of aluminium phosphate can form at these concentrations, and adsorb to the mica surface. The amount of phosphate adsorbed under these conditions is independent of the amount of aluminium added above the critical concentration, even though the aluminium does not exceed the amount of phosphate present. The amount adsorbed is equal to about one phosphate ion per 50 or 100 square Angstrom units, which is similar to the amount adsorbed at the slope change in the adsorption isotherm.

pH Variation of Adsorption

It was found that the amount of phosphate adsorbed from a 10^{-4}M. PO_4 solution at an approximately constant ionic strength maintained by 0.1M. NaCl., decreased with decreasing pH from pH 5.5 to pH 2. The amount adsorbed was inversely proportional to the hydrogen ion concentration between pH 3 and pH 5.5.

The fact that the hydrogen ion concentration is important suggests that an equilibrium which involves hydrogen ions is important at some stage in the adsorption. This equilibrium would presumably involve the dissociation of hydrogen from some site, possibly an O-H group, and the consequent production of a negative site. The number of these sites would be reduced by the common-ion effect as the pH was lowered, so that the adsorption of cations would be reduced. The experimental evidence suggests that this leads to a reduction in the amount of phosphate adsorbed, so that the adsorption of phosphate is dependent on the adsorption of cations on the surface.

If it is supposed that the aluminium is adsorbed before the phosphate, then there cannot be a great excess of cations on the surface, for it seems that any reduction in their number is directly related to a reduction in the amount of phosphate adsorbed. However, it is known that by increasing the phosphate concentration, more phosphate is adsorbed, at least ten times as much as in the present experiments being adsorbed, so that on this hypothesis excess aluminium must be present. The hypothesis is therefore untenable.

The phosphate must be adsorbing as a part of a positive ion, and when it is considered that the solutions used were probably contaminated with aluminium, due to insufficient washing, this seems reasonable. The phosphate may have been sorbed on to particles of colloidal aluminium hydroxide, or have formed aluminium phosphate colloid or ions.

Kinetics of Phosphate Adsorption

These experiments were difficult to perform because of dirt contamination problems, but with 10^{-3}M. KH_2PO_4 the adsorption is 40% complete after 10 minutes, and at equilibrium after 100 minutes.

TABLE 6.1

REPRODUCIBILITY OF ADSORPTION ON ALUMINIUM-TREATED MICA FROM CARRIER-FREE PHOSPHATE.

Sample No.	Sorbed Activity $(c/min/cm^2)$		Solution Activity $(x10^5$ c/min/ml)			Adsorption Ratio $(x10^{-2}$ cm)		
	Sample	Blank	After Sample	After Blank	Ratio	Sample	Blank	Ratio
3	6,300	2.5	1.16	0.70	1.7	5.4	.0036	1500
5	6,100	20	0.79	0.64	1.2	7:7	.031	250
6	10,800	1150	1.76	0.92	1.9	6.1	1.2	5
7	8,600	75	1.41	1.4	1.0	6.1	.054	110
8	5,700	750	0.68	0.37	1.8	8.4	2.0	4.2

TABLE 6.2

RESULTS OF PHOSPHATE ISOTHERM EXPERIMENT

10 MINUTE ADSORPTION

Concentration (M.)	Adsorption Ratio (cm)	Ions per 1000 sq.A.
Carrier-free	0.22	-
10^{-6}	9×10^{-2}	5.4
10^{-5}	2.8×10^{-2}	17
10^{-4}	1.2×10^{-2}	72
10^{-3}	3.4×10^{-3}	200
10^{-2}	1.4×10^{-3}	840

100 MINUTE ADSORPTION

Conc. (M.)	Ions/1000 sq.A.
10^{-6}	3.7
10^{-5}	14
10^{-4}	66
10^{-3}	100
10^{-2}	280

1000 MINUTE ADSORPTION

Conc. (M.)	Ions/1000 sq.A.
10^{-6}	20
10^{-5}	45
10^{-4}	170
10^{-3}	280
10^{-2}	475

TABLE 6.3

ALUMINIUM CONTAMINATION OF 5×10^{-5}M. KH_2PO_4 SOLUTIONS

Concentrations in millimicromoles/litre. (Conc.)
Adsorption in molecules/1000 sq.A. (Ads.)

U1		U2		U3		U4	
Conc.	Ads.	Conc.	Ads.	Conc.	Ads.	Conc.	Ads.
		0	0.66	0	0.65	0	1.0
		0	0.51	0	0.82		
27	.66	50	1.4				
81	.62	140	0.78				
270	2.1	360	1.1				
270	1.9	400	0.96				
810	3.6	850	2.5				
				1200	12		
				1640	16		
				2120	17	2000	9.6
2700	27	2600	19			3000	9.2
						3500	9.5
						4000	9.5
						5000	11.2
						6000	10.6
						8000	9.6

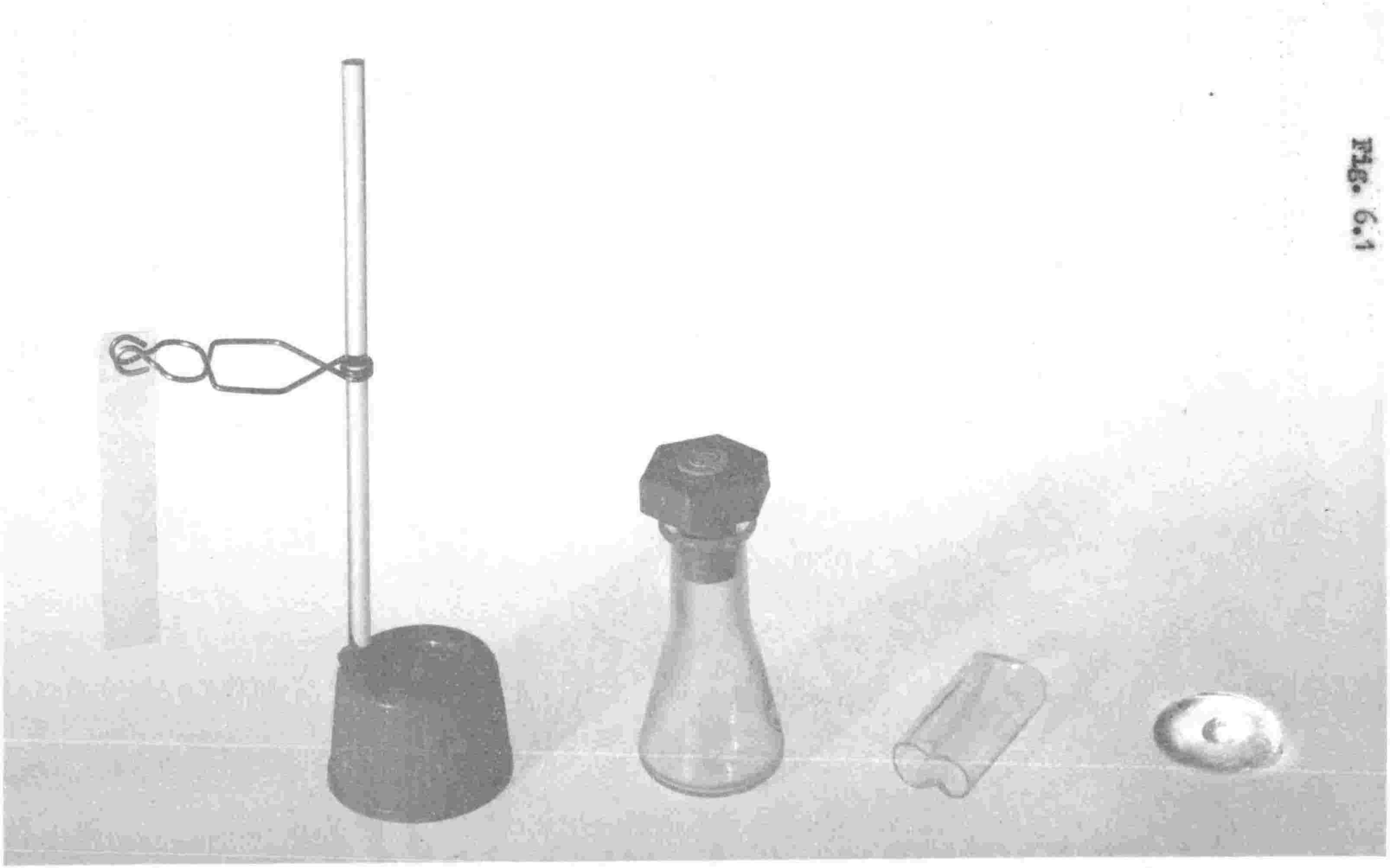
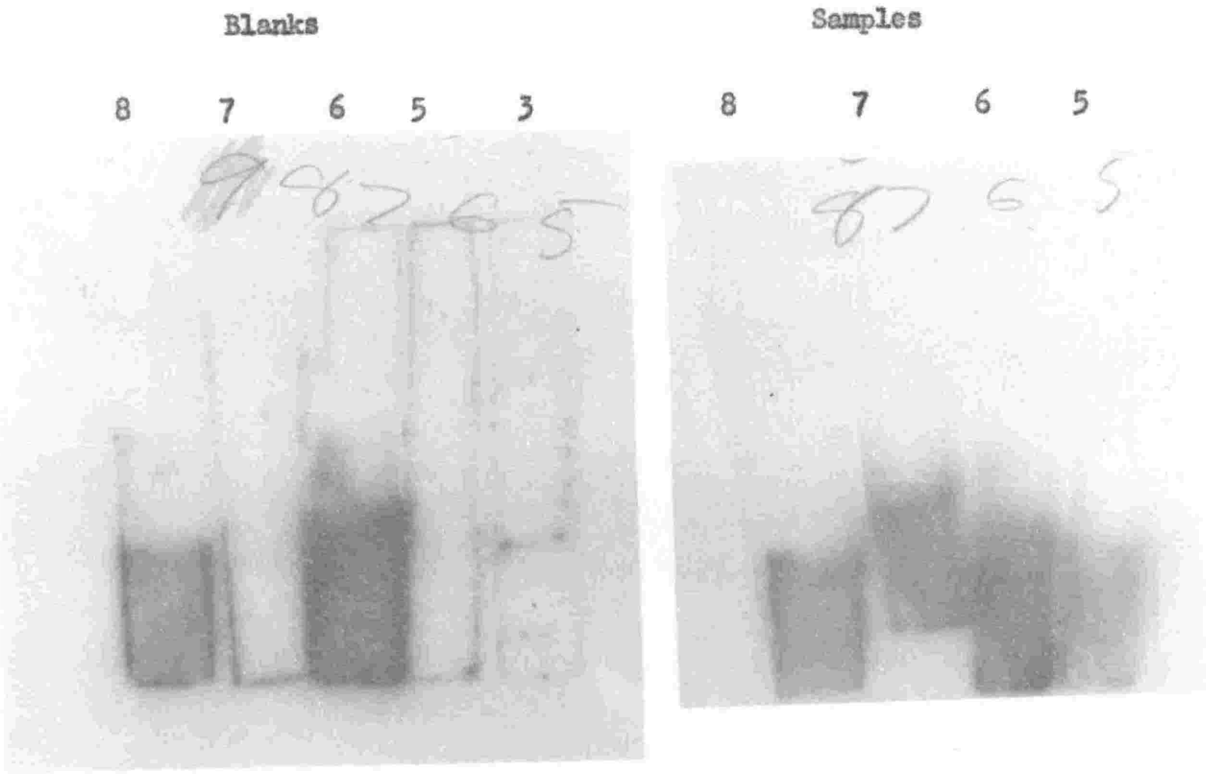

Stand for holding a mica strip in a 50 ml. beaker
Flask used for radioactive stock solutions
A mini-beaker
A counting planchette

Fig. 6.1

Fig. 6.2



Reproducibility of Adsorption on Aluminium-Treated Mica

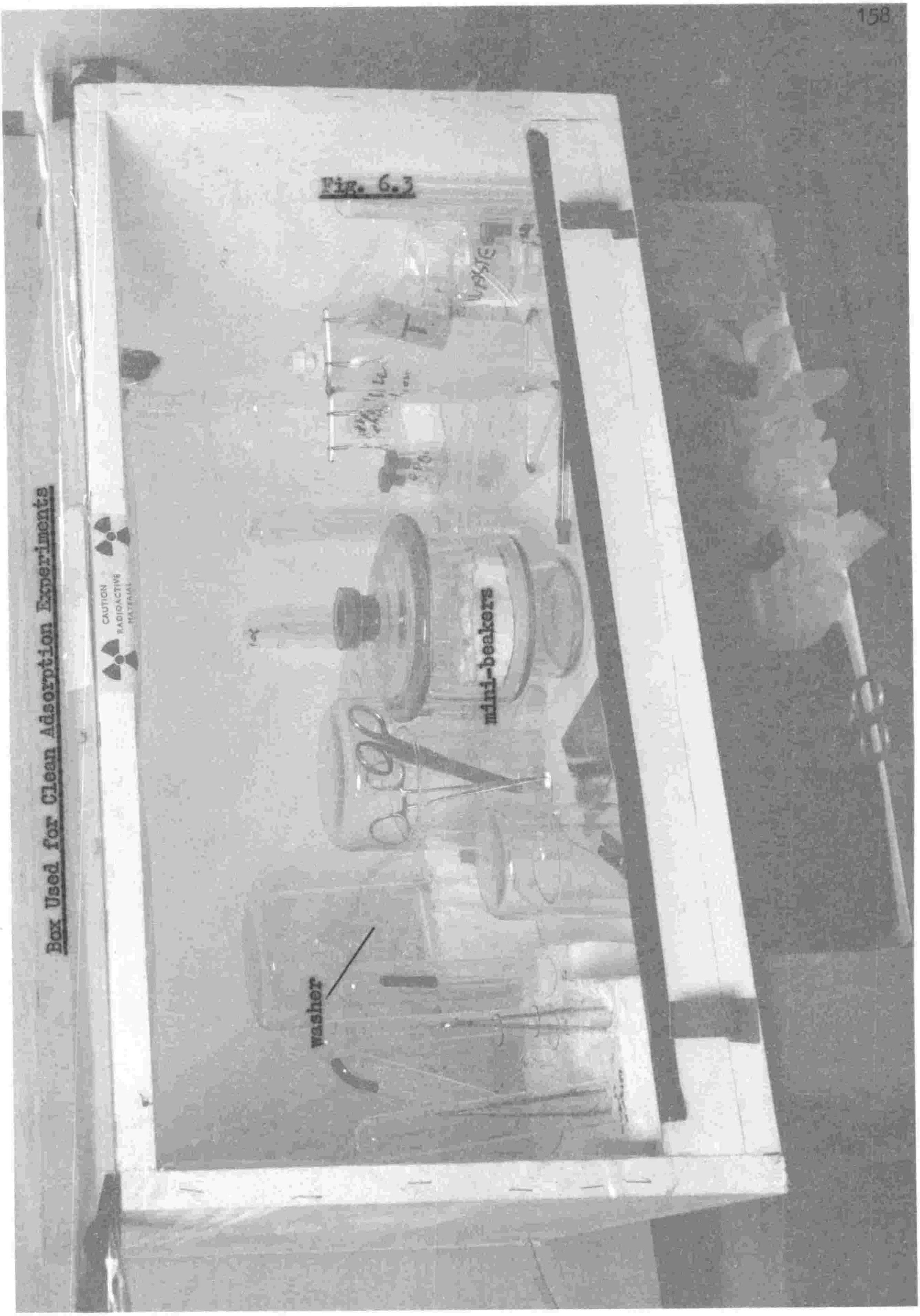


Fig. 6.3

Box Used for Clean Adsorption Experiments

Fig 6.4 - Phosphate Adsorption Isotherms

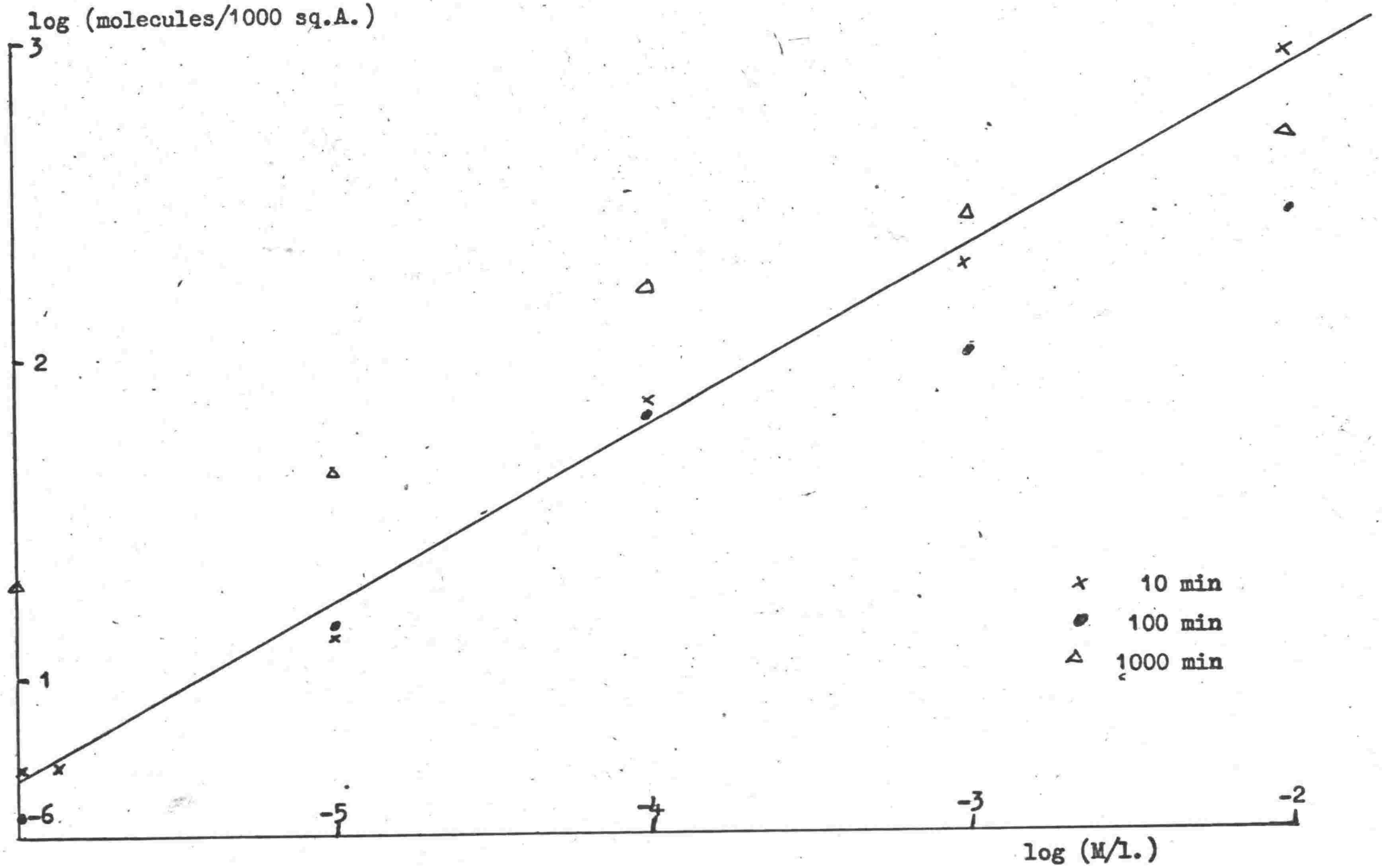


Fig. 6.5

Aluminium Phosphate Adsorption as a Function of Time Delay Between Mixing and Adsorption.

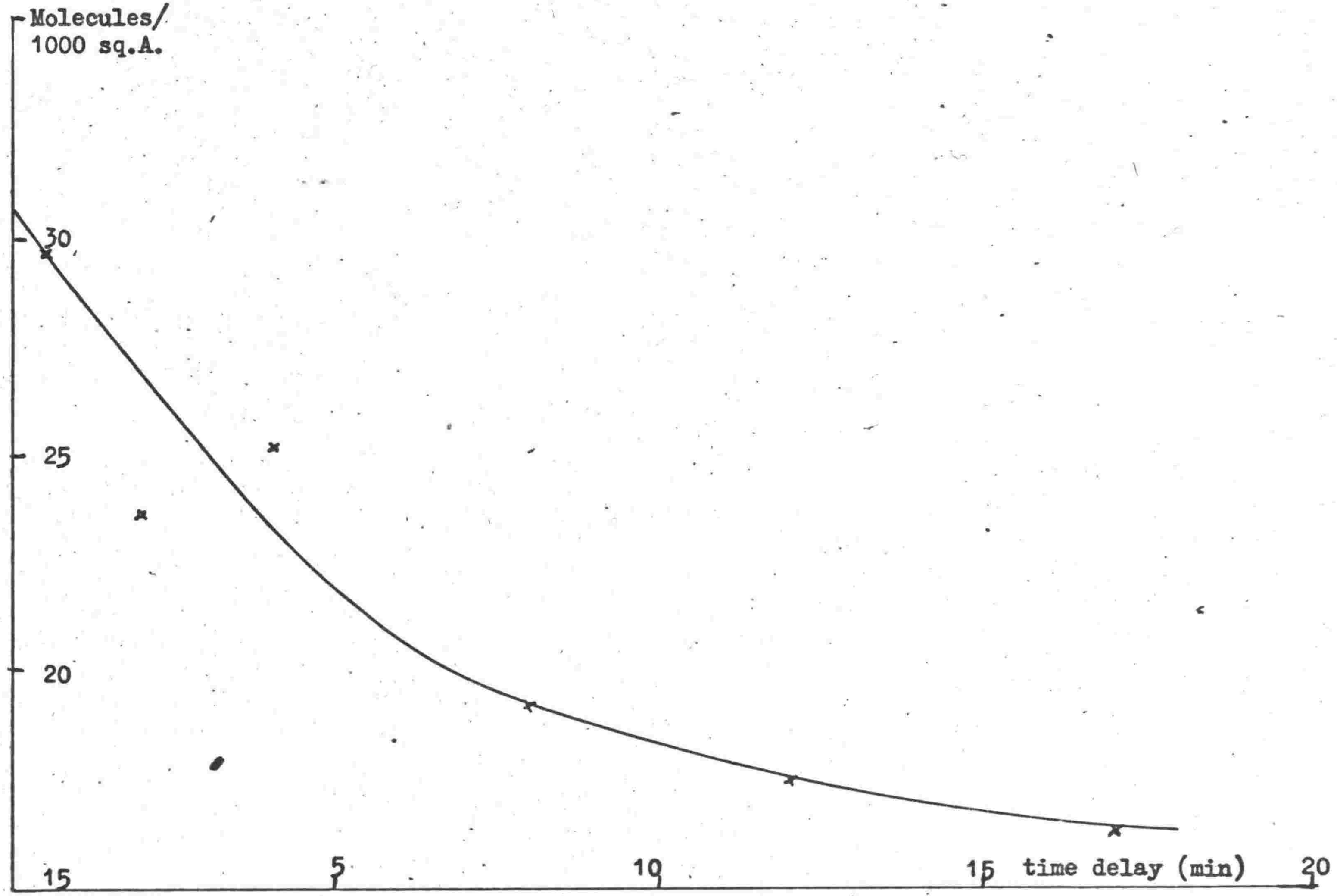
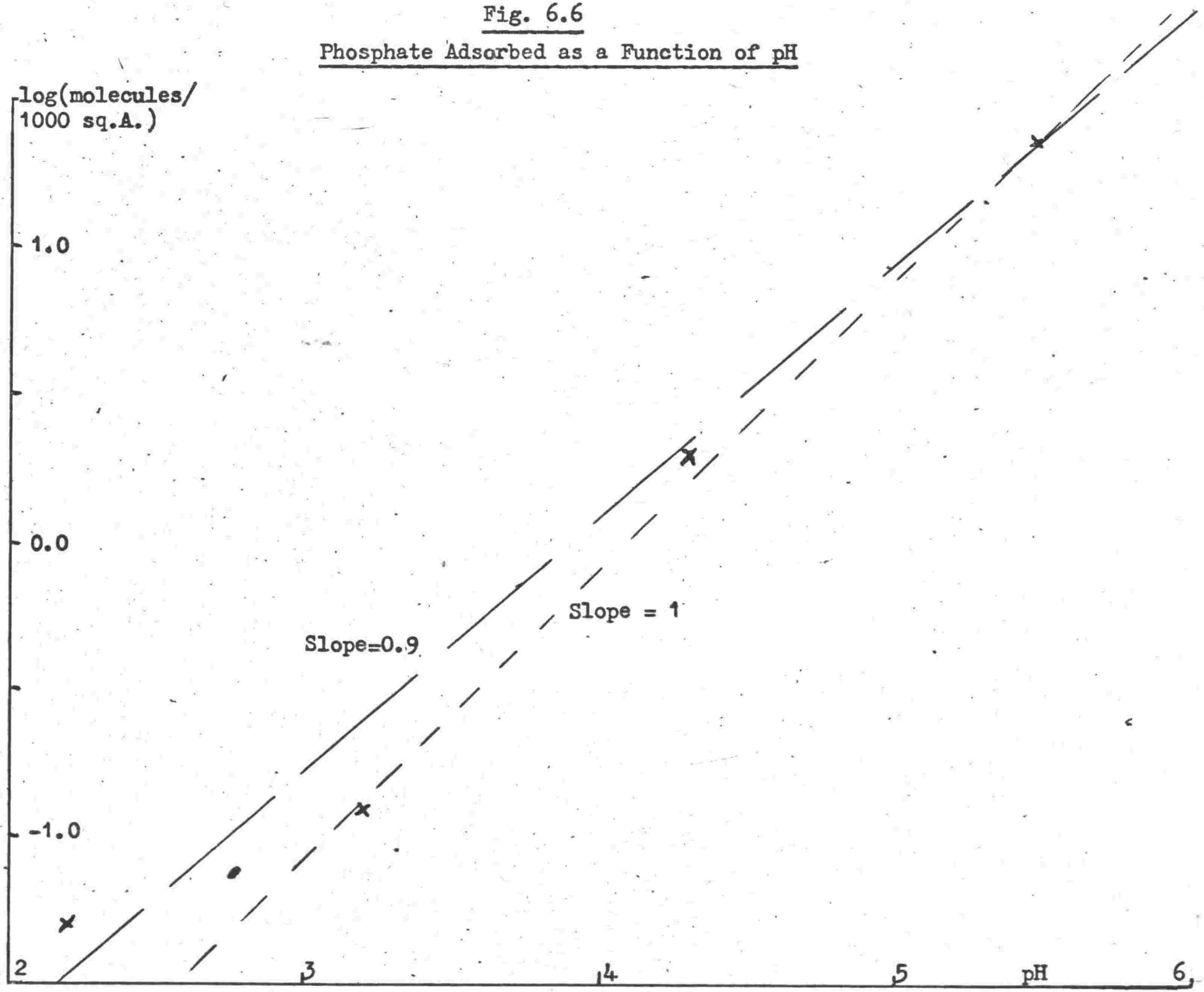


Fig. 6.6

Phosphate Adsorbed as a Function of pH



CHAPTER 7

THEORY AND DESIGN OF ADSORPTION AND DESORPTION EXPERIMENTS

INTRODUCTION

Previous Theories

In Chapter 1 it was shown that previous workers in this group, and several workers on other aspects of surface chemistry, have found that the results of sorption kinetics experiments can be expressed as a sum of several terms which vary exponentially with time. The half-lives of the terms vary in length from a few minutes to several months.

Any first-order reaction gives rise to an exponential variation with time of the concentration of that component whose concentration determines the rate. An obvious step to take, therefore, is to advance the hypothesis that each of the observed exponential terms corresponds to a particular first-order reaction. If this were to be a good description of the experimental system, one would expect that one could obtain the same half-lives, and therefore the same reactions, in several similar kinds of experiment. Furkert (1965), Morris (1964) and Burns (1966) found that this did happen, and that by varying the length of the adsorption time before a desorption experiment, the shape of the desorption graph was greatly altered, but the same half-lives could be found. The variations were present only as changes in the initial amount of each term.

Theories were advanced in the above theses to explain the possible kinds of reactions occurring at the surface, and these were mostly consistent with the evidence available.

There are several unsatisfactory features of this kind of approach. One is that the time scale of the reactions is so very much longer than the usual kind of chemical reaction. For example, ion-pairs, to which the surface complexes were likened by Spedding (1964), have a life of the order of 10^{-10} seconds. Many chemical reactions are slow, of course, but this is often due to the low probability of collision of the reacting species. If the present examples are first-order reactions with the rate determined by the concentration of surface species, then there is only one reacting species, so that this factor cannot be involved. not likely to be pseudo 1st order

In order to reconcile the difference between the rates in these experiments and those of ordinary chemistry, it has been postulated that the surface in some unknown way modifies the environment so that the rates become very slow. This still leaves the problem of how several species, whose compositions cannot be very different, can have half-lives of desorption several orders of magnitude different from each other.

The Possibility of Diffusion Limitation of Reaction Rate

An area of chemistry closely related to surface chemistry is that which deals with ion-exchange. A great deal of work has been performed on the kinetics of ion-exchange reactions, on both organic and inorganic materials. Helferrich (1962) concludes that in nearly every case the exchange rate has been limited by diffusion, either in the film of unstirred solution around the particles of ion-exchanger, or within the particles themselves. He says that some authors have ascribed reaction rate parameters to the process, but that such parameters are only valid over a limited range of conditions. It therefore seems that some confusion between diffusion and reaction rate is possible.

The major difficulty of applying a diffusion theory to the present system is that there does not appear to be an appropriate absorbing medium present. There is always an unstirred film of water near any surface, being not less than 10^{-3} cm thick, and often about 10^{-2} cm. depending on the stirring rate (Helferrich (1962)). This will provide one diffusion step, but it is easily shown that it leads to a simple exponential variation with time, and that, using the known values of diffusion coefficients in water, the changes would be expected to be more rapid than actually found. (Complete reaction should occur within a few minutes.)

It was therefore necessary to postulate some material into which the phosphate could diffuse and be absorbed. From the detailed theory which was developed, several necessary properties of this material could be determined, and compared with other chemical knowledge.

A characteristic of the two versions of the diffusion theory which were developed is that only two parameters can be independently varied in order to adjust the theory to fit the data. This is in contrast with the six parameters needed to describe the three exponential terms required to fit the same data on the alternative theories.

Nomenclature

A difficulty arises from the use of the use of the words "adsorption" and "absorption". The present interpretation is that the "adsorption" is due to "absorption" within a thin layer on the surface. The word "adsorption" will be used when the general phenomenon is being considered, and "absorption" when the details of processes within the hypothetical surface film are under discussion.

THE DIFFUSION MODEL FOR A UNIFORM LAYER

The Absorbing Layer

The materials used as inorganic ion-exchangers are often hydrous oxides or phosphates. The cations which are particularly good at enhancing phosphate fixation on mica surfaces (i.e., Al, Ga, Fe), also hydrolyse readily to give gelatinous hydrous oxides. Although this may not be a highly significant correlation, it was thought to be worth postulating that there could be a coherent film of hydrous oxide on the surface, into which the phosphate anions diffused, and in which they exchanged with hydroxyl groups or other adsorbed anions.

A theory was proposed in which phosphate was supposed to diffuse, with constant diffusion coefficient, from the solution into a thin planar layer of absorbing material over the surface. After a time which could be short compared with the time to come to equilibrium, the solution concentration was reduced to zero, so that the phosphate diffused out again. The layer was supposed to be uniformly composed of a porous material which absorbed phosphate reversibly and rapidly, in such a way that the total concentration in any small volume within the layer was directly proportional to the concentration of the solution in that volume. The kinetics of diffusion in the solution in such a system is shown by Crank (1957), p. 122, to behave as if the absorption did not occur, and the diffusion coefficient, k', in free solution is replaced by $k = k'/(p + 1)$, where the total amount in the solution plus absorbing medium is found by multiplying the amount in solution by p.

The Solution of the Diffusion Problem for Desorption Experiments

The necessary solution of the diffusion equation may be found in Carslaw & Jaegar (1947), where the concentration profile in the layer is given for a constant solution concentration and an arbitrary initial concentration profile. The initial profile used was that which would be found after diffusing into a medium, initially at zero concentration, for a time, θ, with constant solution concentration, V. The concentration profile at time, t, after changing the concentration of the solution to zero, was thus found, and then an integration was performed over the film thickness in order to find the total amount in the layer at time, t.

The result of the somewhat involved algebraic manipulations performed is given here, and the mathematical details are given in an appendix.

The amount of phosphate absorbed per unit area of the surface, x, is given by

$$x = A \sum_{n=0}^{\infty} \frac{1 - e^{-(2n + 1)^2 B\theta}}{(2n + 1)^2} e^{-(2n + 1)^2 Bt}$$

where $A = 8lpV/\pi^2$

l is the layer thickness

$B = k\pi^2/4l^2$

and the other quantities are as previously defined.

It is of interest to note that this expression is a sum of exponentials, and that the proportion of the longer half-life terms increases as θ increases. However, the variation between the half-lives of successive terms is not as great as expected from the results of the graphical analysis. This could be a consequence of the graphical method used to find the exponentials, since several terms with similar half-lives mightapproximate to one with some sort of average half-life.

It is convenient to define a function $F(Bt) = \frac{8}{\pi^2} \quad \frac{e^{-(2n+1)^2 Bt}}{(2n+1)^2}$.

Then, $$x = \frac{\pi^2 A}{8} (F(Bt) - F(B(t+\theta))).$$

For t = 0, $$x_0 = \frac{\pi^2 A}{8} (1 - F(B\theta)), \quad \left[\sum_0^\infty \frac{1}{(2n+1)^2} = \frac{\pi^2}{8}\right]$$

so that $$x/x_0 = \frac{F(Bt) - F(B(t+\theta))}{1 - F(B\theta)}.$$

<u>Useful Approximation - Short Adsorption Time</u>

The above expression for F converges only slowly for small Bt, but it is shown in the appendix that

$$\sum_0^\infty e^{-(2n+1)^2 B} = \tfrac{1}{2}\sqrt{\frac{\pi}{B}}\left[\tfrac{1}{2} + \sum_1^\infty (-1)^n e^{-(n\pi)^2/(4B)}\right].$$

The right-hand side of this expression is rapidly converging for small B, and by integrating both sides it is shown that

$$\frac{\pi^2}{8} F(Bt) = \frac{\pi^2}{8} - \tfrac{1}{2}\sqrt{Bt} \qquad \text{for } \underline{Bt < 0.4.}$$

By substituting in the above expression for x/x_0 it is easily shown that

$$x/x_0 = \sqrt{t/\theta + 1} - \sqrt{t/\theta} \qquad \text{for } \underline{B\theta \text{ and } Bt < 0.4}.$$

To simplify comparison of the theory with experiment the function $\sqrt{t+1} - \sqrt{t}$ was tabulated for $0.01 < t < 100$, using the Elliott 503 computer. The original tabulation was for t accurate to three significant figures, but one percent accuracy in the function is easily obtained from a tabulation to two significant figures, and an approximate interpolation for some parts of the table, which is given in the appendix.

For $Bt > 0.3$, the original expression for $F(Bt)$ is highly convergent, so that only the first term need be taken. That is, $F(Bt) = \frac{8}{\pi^2} e^{-Bt}$. This gives

$$x/x_o = \frac{1 - e^{-B\theta}}{\sqrt{B\theta\pi}} \; e^{-Bt} \text{ for } \underline{B\theta < 0.4 \text{ and } Bt > 0.3}.$$

That is, if the adsorption time is short, then at short times x/x_o varies as the tabulated function $\sqrt{t/\theta + 1} - \sqrt{t/\theta}$, while at longer times x/x_o is proportional to e^{-Bt}.

Useful Approximation - Long Adsorption Times

For long adsorption times different approximations are needed. Using the first exponential term approximation for large $B\theta$,

$$x/x_o = \frac{\pi^2/8 - e^{-B(t+\theta)} - \frac{1}{2}\sqrt{Bt\pi}}{\pi^2/8 - e^{-B\theta}} \; .$$

By expanding the denominator of this expression by the binomial theorem, it may easily be shown that within 1% accuracy the first two terms of the expression have the total value 1 for $Bt < 0.1$ and $B\theta > 2.3$. The larger the value of θ then the larger t may be.

For large Bt, the first exponential term approximation may be used for both series.

Thus, for long adsorption times,

$$x/x_o = 1 - \frac{\sqrt{\pi B}}{2(\pi^2/8 - e^{-B\theta})} \cdot \sqrt{t} \quad \text{at short times and}$$

$$x/x_o = \frac{(1 - e^{-B\theta})}{(\pi^2/8 - e^{-B\theta})} \, e^{-Bt} \quad \text{at long times.}$$

It is a common misconception that diffusion processes give variations as the square root of the time. The above results show that in this case it is to be expected only for the initial part of a desorption from near-equilibrium conditions.

Expression for Adsorption Kinetics

The variation in the adsorption with time may be found by substituting t = 0 in the original series expansion for x. This leads to

$$x = \tfrac{1}{2}A\sqrt{\pi Bt} = \frac{2pV}{\sqrt{\pi}} \cdot \sqrt{kt} \qquad \text{for } Bt < 0.2$$

and

$$x = A(\pi^2/8 - e^{-Bt}) \qquad \text{for } Bt > 0.3.$$

These two expressions are explicit functions of Bt. If we write $x_\infty = A\pi^2/8$, then x/x_∞ is a function only of Bt. In the similar case of adsorption into spherical particles Reichenberg (1953) has shown that it is useful to prepare a table of values of Bt corresponding to values of x/x_∞. The data from an experiment is then tested for agreement with the theory by finding, from the table, the expected value of Bt for various values of x/x_∞, where x_∞ is the equilibrium amount adsorbed. These values are plotted against the actual time at each point, and if the data fits the theory a straight line, of slope B, should result.

The above expressions were used to compile a table of values, using the Elliott 503 computer, and this table was used in the attempts to fit the adsorption data to the theory. An abbreviated version is included as an appendix.

DIFFUSION INTO SPHERICAL PARTICLES

Desorption After a Short Adsorption

The above results apply to diffusion where the medium has planar geometry. It is possible that the true situation involves diffusion of phosphate into roughly spherical particles adhering to the surface. If it is assumed that the adsorption properties are similar to those postulated for the planar layer, that the presence of the surface does not affect the spherical geometry (i.e., the particles do not have a flat side, and no concentration changes occur in the solution near them), and that the spheres are all the same size, it is shown in the appendix, in a similar way to the previous case, that

$$x/x_o = \frac{G(Dt) - G(D(t+\theta))}{1 - G(D\theta)},$$

where $$G(Dt) = \frac{6}{\pi^2}\sum_1^\infty \frac{1}{n^2} e^{-n^2 Dt} \qquad (D = k\pi^2/a^2).$$

$$= 1 - \frac{6}{\pi^{3/2}}\sqrt{Dt} + \frac{3}{\pi^2}Dt \qquad \text{for } \underline{Dt < 1}.$$

(Reichenberg (1953)).

For small $D\theta$ and Dt this gives

$$x/x_o\left(1 - \sqrt{\frac{D\theta}{4\pi}}\right) = \sqrt{1 + t/\theta} - \sqrt{t/\theta} - \sqrt{\frac{D\theta}{4\pi}}.$$

Thus a plot of $\sqrt{t/\theta + 1} - \sqrt{t/\theta}$ versus x should give a straight line, just as in the case of the planar model, but the value of x should be negative instead of zero when $\sqrt{t/\theta + 1} - \sqrt{t/\theta} = 0$. From this intercept and the slope, D can be calculated.

For large Dt, the series for G(Dt) is rapidly convergent, although not as fast as F(Dt), so that for $Dt > 1$ and $D\theta < 1$,

$$x/x_0 = \frac{2e^{-Dt}(1-e^{-D\theta})}{2\sqrt{\pi D\theta} - D} .$$

Thus the variation with t is similar to the planar case.

Desorption After a Long Adsorption

For the case of $D\theta > 2.3$ and Dt small, it is found that

$$x/x_0 = 1 - \frac{2\sqrt{\pi Dt} - Dt}{\pi^2/3 - 2e^{-D\theta}} .$$

For $Dt < 0.01$ this approximates a variation with $\sqrt{t}$, but not very well. A table of values of $2\sqrt{\pi x} - x$ for various x has been computed, and may be used to show the fit at short times, after D has been calculated from the results at large Dt.

For $D\theta > 1$ and $Dt > 1$, it is easily shown that

$$x/x_0 = \frac{(1 - e^{-D\theta})}{(\pi^2/6 - e^{-D\theta})} e^{-Dt},$$

which is very similar to the planar case.

Adsorption Kinetics

The adsorption kinetics are described by

$$x = \frac{8Na^3pV}{\pi}\sum_1^\infty \frac{1}{n^2}\left(1 - e^{-n^2Dt}\right)$$

$$= C\sum_1^\infty \frac{1}{n^2}\left(1 - e^{-n^2Dt}\right)$$

where $C = \frac{8Na^3pV}{\pi}$, and there are N spheres, each of radius a.

$$x = \frac{\pi^2C}{6} - C\sum_1^\infty \frac{e^{-n^2Dt}}{n^2}$$

so if Dt is small

$$x = C\sqrt{\pi Dt} - \tfrac{1}{2}CDt$$

and if Dt is large $x = C\left(\frac{\pi^2}{6} - e^{-Dt}\right)$.

If x_∞ represents the equilibrium amount absorbed, then

$$x/x_\infty = 1 - \frac{6}{\pi^2}\sum_1^\infty \frac{e^{-n^2Bt}}{n^2} = S.$$

Reichenberg (1953) has tabulated S as a function of Bt, so that for any value of x/x_∞, a value of Bt can be found. A plot of t versus Bt should give a straight line through the origin, of slope, B.

CONSEQUENCES OF THE DIFFUSION THEORY

Number of Parameters

The diffusion theory predicts that the entire kinetic behaviour of both adsorption and desorption experiments should be describable in terms of the two parameters A and B (or C and D). The methods of finding the values of these parameters vary with the values of t and θ, but the same numbers should be derived from all cases. This is a far more rigid theory than the many-complex one, where new complexes are postulated once the results are found to differ from those expected from the initial assumptions.

Cleanliness

It is clear that extreme difficulty would be experienced trying to sort out more than one such diffusion process in an experiment, so that conditions must be as clean as possible.

Constancy of the Diffusion Coefficient

A major assumption made in the diffusion theory is that of constant diffusion coefficient. This can be ensured by performing the experiments by isotopic exchange at chemical equilibrium, but this suffers from the disadvantage that with present techniques the solution surfaces cannot be kept clean long enough for the initial equilibration to be performed. The other serious disadvantage is that the activity adsorbed would be greatly reduced, unless the phosphate concentrations were below about 10^{-5}M. This would not matter as much in desorption experiments as in the adsorption experiments.

The present experiments had developed from adsorption experiments, and were performed as such, rather than as isotope exchange experiments. Because the phosphate concentrations used were very low, it was hoped that no important variations in diffusion constant with concentration would be present.

Design of Desorption Experiments

Some thought was given to the changes occurring when the sample is removed from the adsorbing solution and rinsed. Immediately after rinsing the sample, and before putting it in the desorbing solution, the concentration at the outer face is zero, so that diffusion within the film will occur in much the same way as when the surface is in the solution; but since no flow away from the face is possible until it is in the solution, the concentration will build up and transfer will slow down. Drying of the layer would also be expected to alter its properties. These considerations suggest that as little time as possible should be spent in transferring the sample from the adsorption to desorption solutions, and that the desorption time should be measured from the instant of first rinsing the surface.

With these points in mind a new set of apparatus was designed for adsorption and desorption measurements.

MODIFICATIONS TO THE DESORPTION TECHNIQUES

Cleaved-Sample Method

Before the diffusion theory had been developed, and the conclusion reached that no time should be wasted between adsorbing and desorbing, a method was developed to enable a relatively clean sample to be desorbed. This involved preparing a sheet of radioactive mica about 2" square, by dipping a piece of clean, freshly-cleaved mica into first a 1M $AlCl_3$ solution, and then, after a brief rinse, into a radioactive phosphate solution. This mica was radioactive on both sides, so it was then laid on the suction plate shown in fig. 7.1, with wet filter paper between it and the plastic surface. A water driven suction pump caused the mica to be held firmly to the plate, so that it was a simple matter to cleave the sheet into two. The top sheet had one clean radioactive face and one non-active one. This non-active face was placed against a sheet of clean mica of similar size glued to a conventional brass sample holder, which had been cleaned by vapour degreasing. The two pieces of mica were held together by clean stainless steel chromatography clips, and then placed in 2 litres of clean distilled water in a chromic-acid-cleaned glass beaker. The desorption kinetics were followed in the usual way. The desorbing solution was not changed during the experiment, in order to avoid having to pass the sample through a probably dirt-contaminated air-liquid surface, and at the end of the experiment it was shown that an insignificant amount of radioactive phosphate remained in the solution. (Most of it was probably absorbed by the walls.)

This technique appeared to solve the cleanliness problem, but it generally took about 10 minutes to cleave the mica and get it into the desorbing solution. The analysis of some results according to the diffusion model suggested that this delay was affecting the results obtained at the start of the experiment, so that an alternative method which required no splitting of the mica was sought.

Circulating Apparatus

It appeared that the only satisfactory way to work with clean mica was to immerse the whole sheet in the solutions, since any way of attaching anything to protect one side would involve the use of some form of adhesive. This would undoubtedly contain surface-active materials, which would probably contaminate the solutions. Having put phosphate on both sides it is necessary to desorb it from both sides, so the apparatus shown in fig. 7.3 was designed. In this apparatus the desorbing solution is caused, by a glass centrifugal pump, to circulate past the sample, which is held about 1 mm away from a thin glass wall by a set of glass hooks and a central glass rod opposing the hooks. The sample is positioned so that it is in the centre of the stream of water through the sample chamber, and it is found that fast, even flow past both faces occurs. The total volume of the apparatus is about 1100 ml, and if the concentration of activity in the solution rises appreciably, the solution can be replaced while the apparatus is going by flowing fresh solution into the bottom of the spherical chamber, and collecting the overflow from the top. The activity on the sample can be measured with either a Philips 18505 geiger tube above the sample, next to the thin window, or with a scintillation counter below the sample, with appropriate screening from the bulk of the desorbing solution. (Both counters are shown together in the photograph.) The former is appropriate for strong beta emitters, such as ^{32}P, and the latter for isotopes (e.g. ^{67}Ga), which emit γ-rays strong enough to allow a reasonable proportion to penetrate the solution and glass.

The sample is prepared by cleaving it in the normal way, and cutting it a little larger than the size required when it is to be inserted in the glass hooks. It is soaked in the adsorption solution for the required time, removed and rinsed. Narrow strips are then cut off both edges and the bottom, it is slipped between the hooks (fig. 7.2), and the end used for holding the mica is cut off. The holder is then inserted in the apparatus.

This apparatus has several disadvantages, but these are in practice minor. They are, that any activity adsorbed on the glass is counted more efficiently than that on the mica, that the activity in solution is counted, and that with ^{32}P an attenuation of about 75% occurs in the water, and 85% in the glass, so that overall about 4% of the activity on the mica is counted, compared with counting the mica next to the end window.

The first two effects are small (if the glassware is clean, in the case of the adsorbed phosphate), and the third can usually be compensated for by using sufficient activity on the sample. In response to the demand for a thinner window the glassblower developed a technique for making windows which would produce less than 20% attenuation of ^{32}P radiation, but these were not available until after the experiments described in this thesis had been performed.

The centre rod which holds the mica against the hooks would have been replaced by two such rods on the circumference of the circle on which the hooks are, in further sample holders.

ADSORPTION TECHNIQUES

Previous Work

A large part of the work of Hendy (1965) consisted of adsorption studies. He used the technique suggested by Morris (1964), in which the sample was placed in the radioactive solution for a short time, removed, rinsed, counted in air, and replaced in the solution for a further period. The experience of this thesis suggests that it would be extremely difficult, if not impossible, to perform the experiment this way without getting solution surfaces thoroughly dirty.

The most satisfactory method, from the point of view of cleanliness, is to count the sample while it is still in the adsorbing solution. This leads to the presence of a strong background from the solution, which means low accuracy at the start of the adsorption, due to the small difference between total count and background count. There is also a possible systematic error near the end, due to changes in solution concentration. However, since even qualitative information on adsorption was likely to prove valuable, techniques were developed for this kind of experiment.

Use of the Circulating Apparatus

Some attempts were made to use the circulating apparatus, which had been designed for desorption experiments, for adsorption studies, but these generally failed because the glass adsorbed an amount of activity comparable with that on the surface. This made it clear that the counter must not be able to "see" any phosphate adsorbed on glass surfaces near the mica. This rules out the possibility of reducing the amount of solution contributing to the background count by restricting the volume of solution with a glass wall. The mica should preferably be the only barrier between the counter and an "infinite thickness" of solution.

Mica Window Apparatus for ^{32}P

The mica could be glued to a sample holder which keeps the solution away from the counter, but this leads to the possibility of contamination.

The method which was decided to be most suitable avoided the use of glues, by using the surface tension forces of water on clean glass and mica. The first model, designed for use with ^{32}P solutions, is shown in fig. 7.4.

The clean mica sample, after treatment with cation solution and washing, is placed on the ground-flat top of the chromic-acid-cleaned apparatus, after filling the apparatus very nearly to the top with the desired solution. This leaves an air bubble between the mica and solution, but this is then expelled by compressing the rubber bulb on one side-arm, while lifting the mica up on one side. After a little practise this can be done very quickly. On releasing the bulb, the pressure in the water next to the mica becomes less than atmospheric. No air can enter because of surface tension, so that no water can escape. A Geiger tube is placed above the mica and the adsorption measurements commence, either immediately, if the solution was radioactive before adding the mica, or when the active solution is added through the side arm.

In the quest for cleanliness it was decided to avoid, where possible, the use of polythene-coated magnetic stirrers. When a clean glass one was used the very high coefficient of friction between clean glass surfaces caused rapid wear of the surfaces, and the accumulation in the solution of suspended glass fragments. When this occurred changes in the solution activity were noted, which made it appear that the glass fragments were adsorbing much phosphate. The magnetic stirrer was therefore replaced by a propeller-type stirrer on a side arm.

Mica Window Apparatus with Small Volume

The above apparatus, which had a volume of about 100 ml., was too large for the experiments with ^{67}Ga, so after experience with a modification due to A. G. Langdon, (which was similar to the top one in fig. 7.5, except for an additional side-arm), a further modification was made which avoided the one remaining problem. (The stirring was done with a polythene coated magnetic follower made from a section of steel needle and some drawn-out polythene tubing). This problem was that evaporation occurred around the boundary between the mica and the glass, reducing the solution volume, until eventually air entered from the side-arm. By putting an extra rim around the edge, as in the lower model in fig. 7.5, this evaporation was almost completely prevented, so that the experiments could run for several days.

COLLIMATION OF ACTIVITY

The Geiger counters in the adsorption and desorption experiments were used in conjunction with a collimator, which in the adsorption case was a 3 mm thick brass disc with a hole in the centre, placed as close to the sample as possible. This was used so that phosphate near the glass-mica boundary, or on the edges of the desorption sample, would not be "seen" by the counter. Its effectiveness was shown by plotting the variation in count rate from a small source, as a function of distance from the centre, and in all cases the count rate from a point source of ^{32}P at the extremity of the sample was less than 3% of its count rate at the centre.

Autoradiographs showed no evidence for extra adsorption on the mica at the glass-air boundary of adsorption experiments, and little for edge adsorption in desorption experiments, so that the effect of sorption near the boundaries would probably be negligible.

STIRRER MOTORS

With one of the adsorbing vessels described above, and with the desorbing vessel, a motor is used to drive a stirrer or pump. It was found that the conventional laboratory stirrers were unsuitable for this work because their speed is regulated by a balance between power input and load. In the present applications most of the load is bearing friction, which decreases as the motor warms up and speeds up, with the result that if the motor starts to run faster, the load decreases, making it run even faster. It was generally found that the motors would either run too fast, or stop. The practice was therefore adopted of using A.C. induction motors, whose maximum speed is regulated by the supply frequency, this speed being chosen to be convenient for the present use, (about 1000 - 1500 r.p.m.).

The most suitable motors available were those manufactured for driving electric fans. It is convenient if they are the "shaded pole" type, which require no external condenser. The motors tried all suffered from overheating when run normally, since they were designed for use in a forced draught of air, but it was found that the overheating problem was eliminated, and the power not significantly affected, by operating them at about 100 v. A.C.

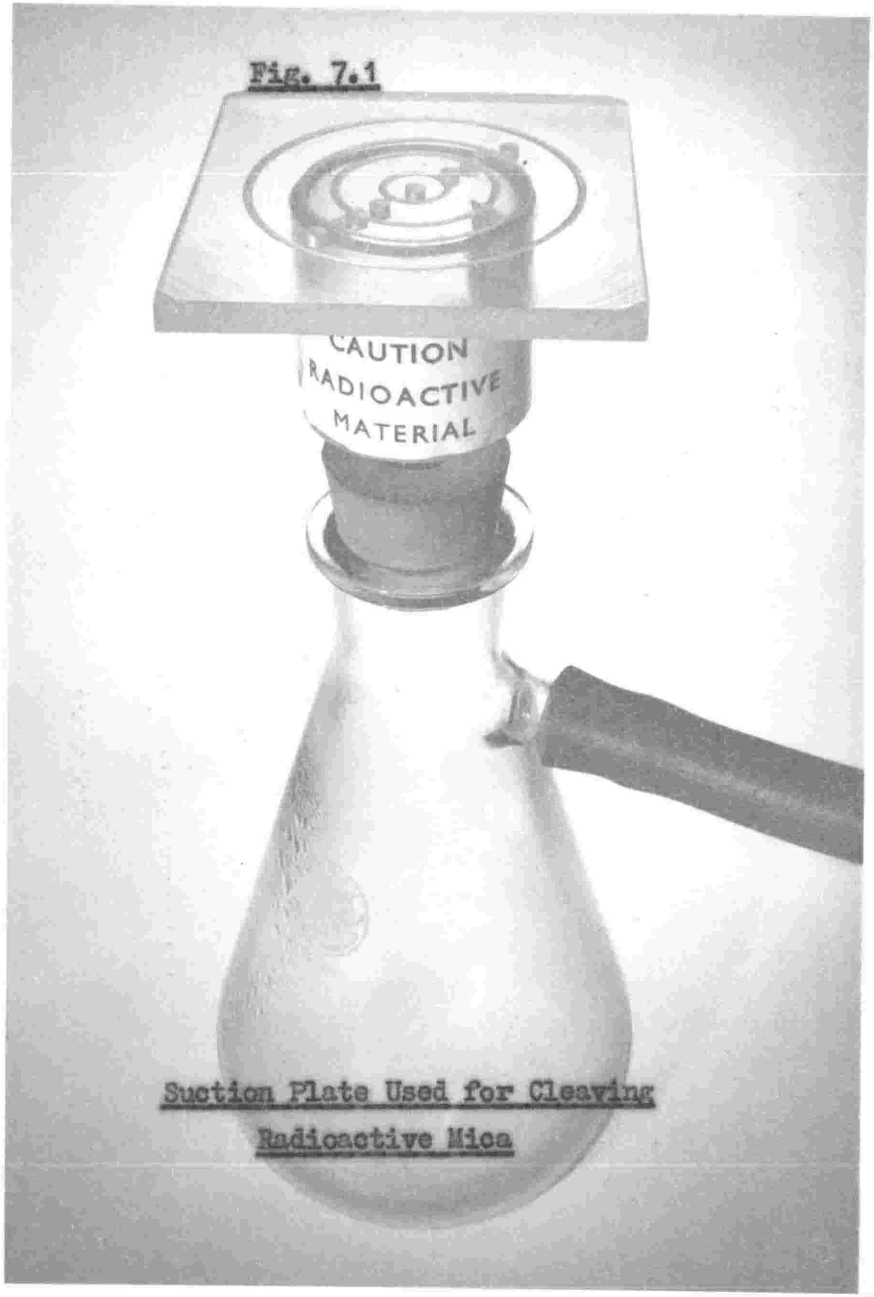
A light motor which is better protected from water splashes, fumes, etc, than most is that used in the 6" G.E.C. "Expelair" fan, and several of these were used.

A chuck from a conventional stirrer was mounted on one of the induction motors, but a better chuck is that used for hand drills, the chucks being available separately, at a reasonable cost.

CONTAINERS FOR THE ADSORPTION SOLUTIONS USED IN DESORPTION EXPERIMENTS

Because of the low efficiency with which the activity is counted, a very large amount needs to be adsorbed by the samples, so that the solutions need to contain a high concentration of activity. To avoid using a large total amount of activity, glass containers were developed which were of approximately rectangular shape, about 8 mm thick by 2.5 cm wide by 5 mm tall. They are shown mounted in polystyrene in fig. 7.6.

Fig. 7.1



Suction Plate Used for Cleaving Radioactive Mica

Fig. 7.2

Sample Holder for Desorption Apparatus

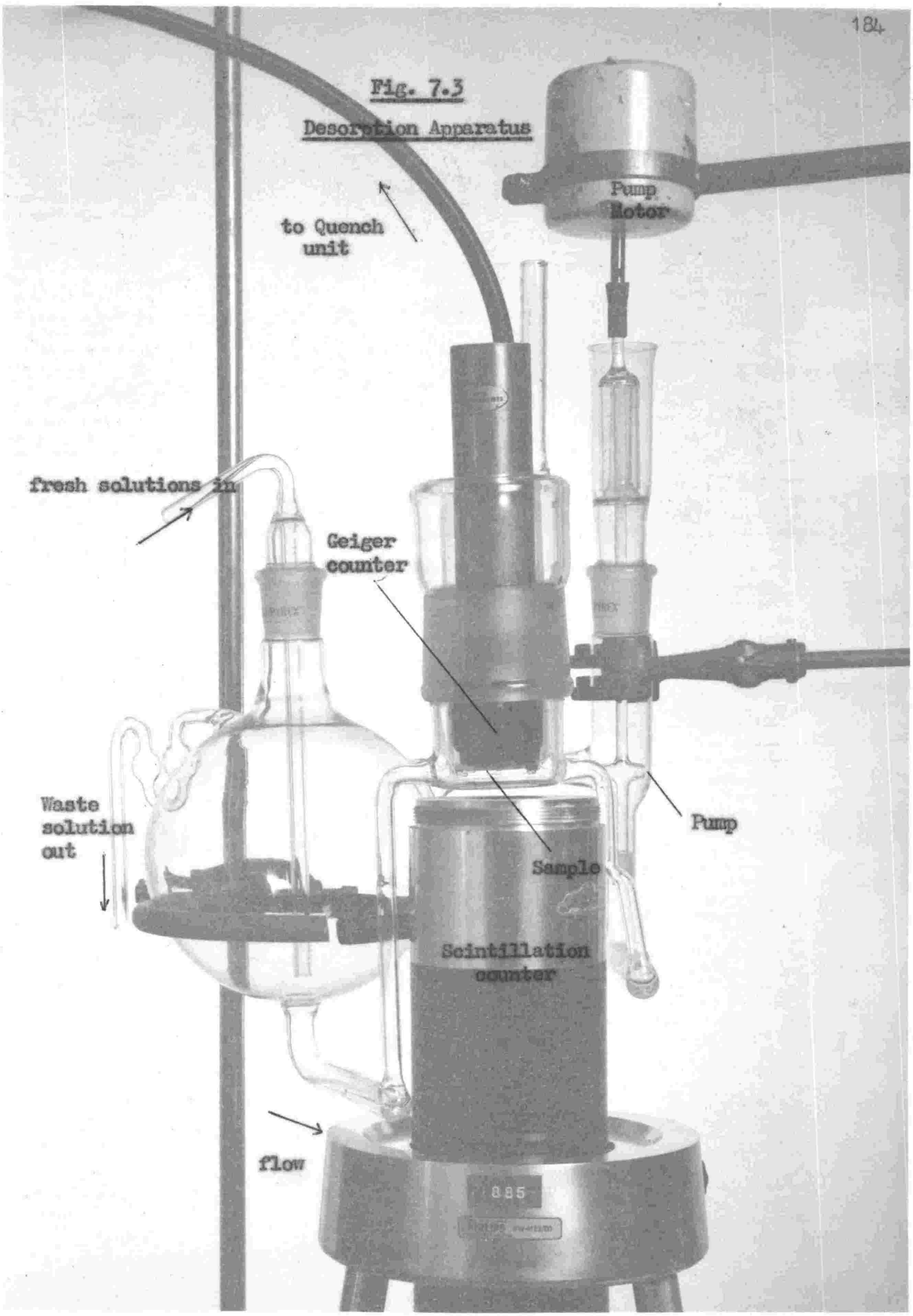
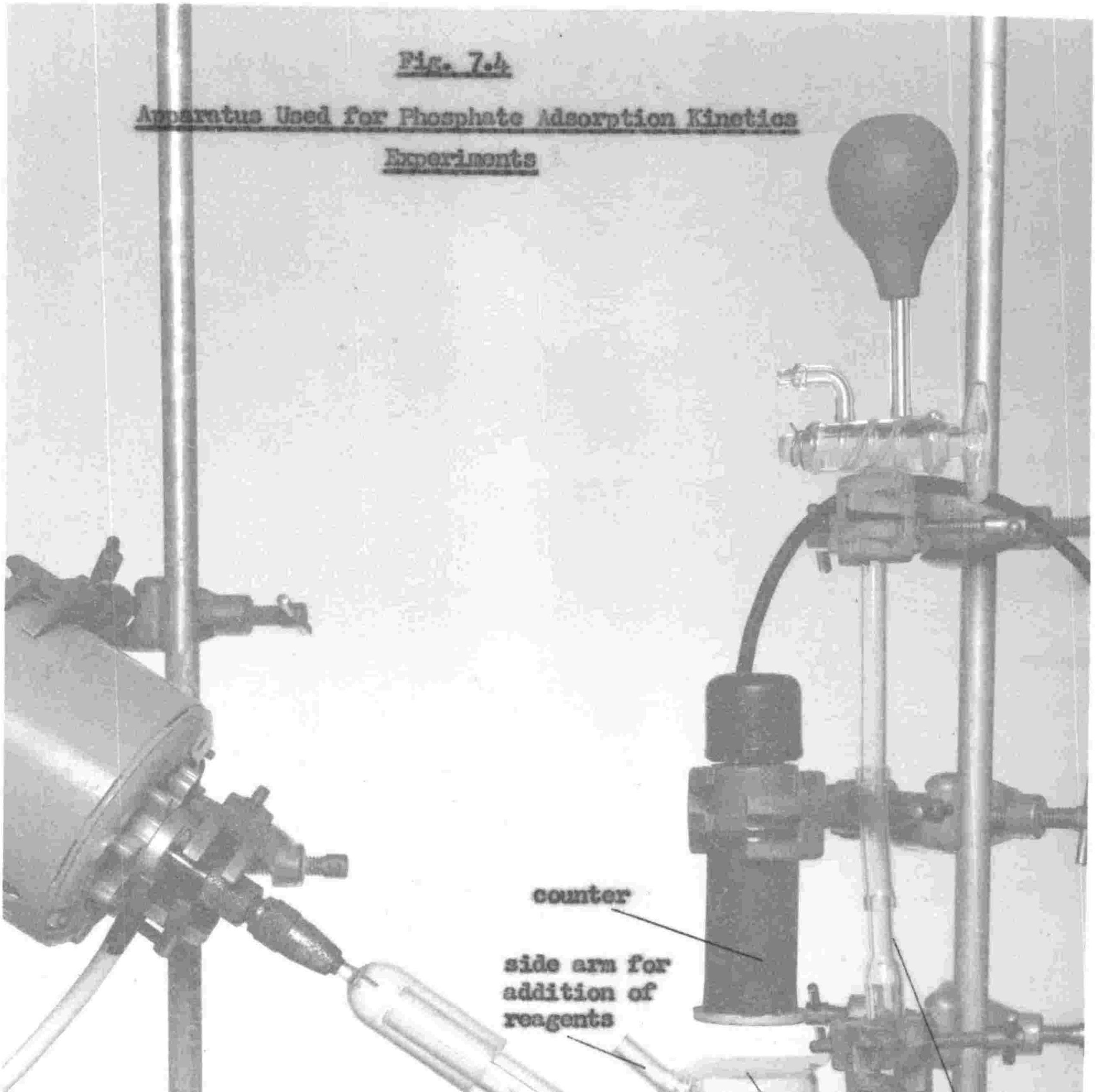


Fig. 7.3

Desorption Apparatus

Fig. 7.4

Apparatus Used for Phosphate Adsorption Kinetics Experiments



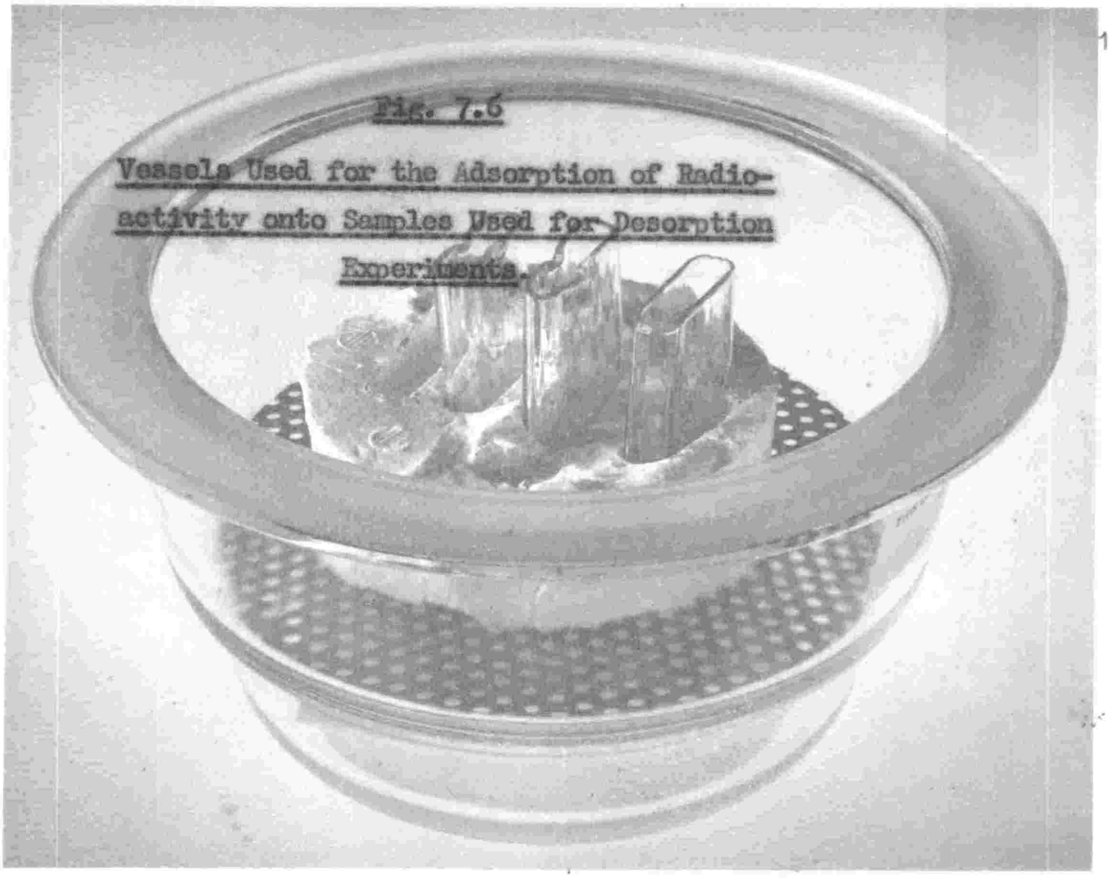


Fig. 7.6

Vessels Used for the Adsorption of Radioactivity onto Samples Used for Desorption Experiments.

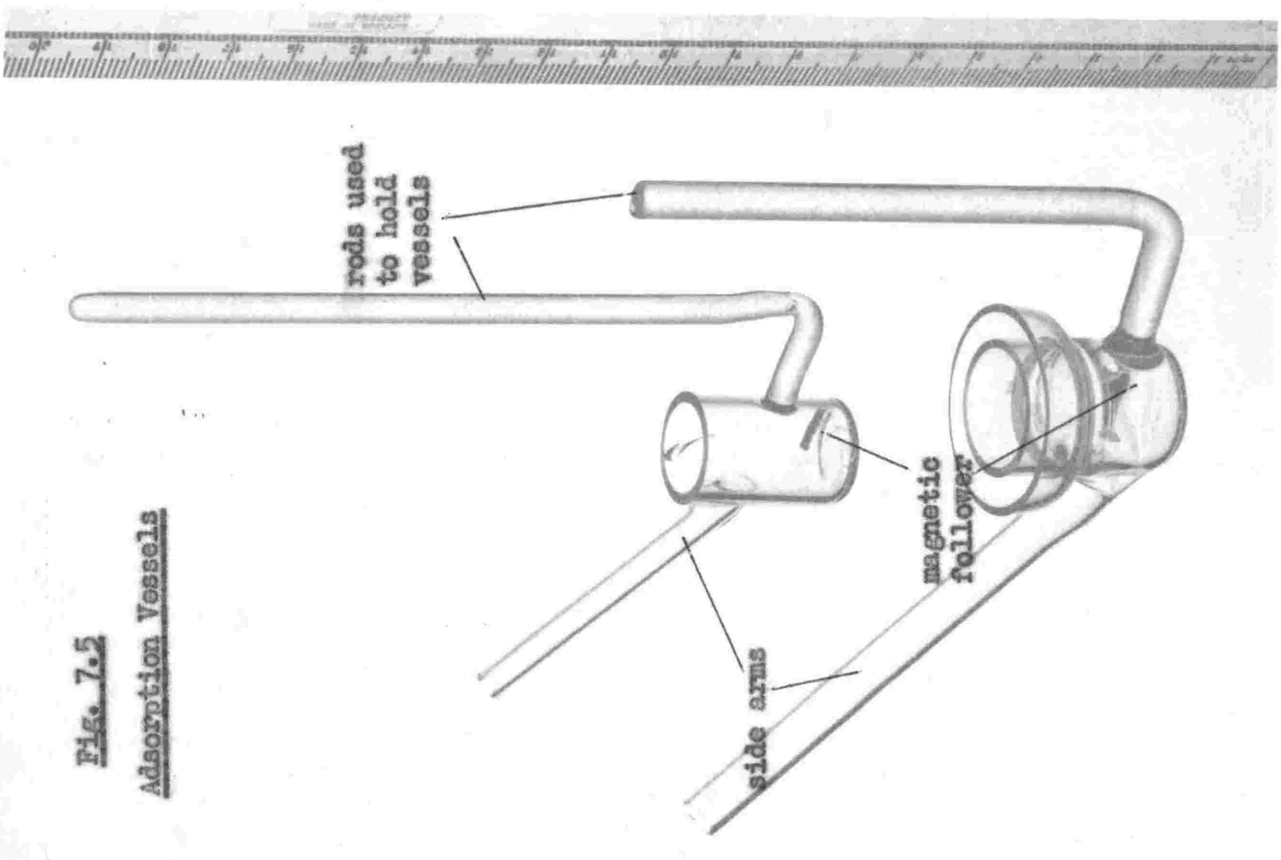


Fig. 7.5

Adsorption Vessels

CHAPTER 8

PHOSPHATE SORPTION KINETICS ON ALUMINIUM-TREATED MICA

AIMS

The main aim of the experiments described in this chapter was to establish whether the kinetics of adsorption and desorption could be described on the basis of a diffusion model. It was hoped to show that all the data from an experiment performed under clean conditions could be fitted to a two-parameter equation derived from a simple diffusion model.

The predicted variation is sufficiently complicated that it is unlikely that any other equation would lead to a good fit with as few a number of parameters, so that the achievement of a good fit can be taken as an indication that the equation is of the correct form. This leaves the possibility that the same equation could be derived on different assumptions.

Various diffusion models could be invented, and it would be expected that the form of the variation would be similar in all cases. The two cases considered in the previous chapter, where the phosphate diffuses in an adsorbing medium in the shape of a thin layer or spherical particles, are two examples of a single type of diffusion model. Although very similar in their qualitative predictions, these two are sufficiently different in their quantitative aspects that it is worthwhile trying to distinguish them. Other kinds of diffusion model, such as diffusion through an unstirred film to an impenetrable surface, would give even more different variations with time. (See Chapter 10).

The author feels that if one or other of the theories can be fitted to the data, then this is good evidence for the validity of the underlying assumptions.

The main assumptions in both models, apart from Fick's second law, are the constancy of the diffusion coefficient, and the geometrical conditions. If a good fit is obtained, then the diffusion coefficient must be at least approximately constant. A good fit would also give some information on the shape of the medium in which diffusion occurs, and this would be a major advance in the description of the process.

The geometrical conditions chosen for the theories are the two extremes possible under the circumstances. The actual situation could be some intermediate case, such as squat cylinders, but the theory which fits best should give a general indication of the shape.

CONDITIONS OF THE EXPERIMENTS

Aluminium Treatment

All the experiments were performed on mica which had been handled under the clean conditions used in Chapter 6. The mica was soaked in a 1M. aluminium chloride solution for five minutes, rinsed with distilled water, and washed in flowing distilled water for thirty minutes.

Hydrogen-Ion Concentration

The aluminium chloride used was at the pH of the dissolved salt (about 2.5). All other solutions were at pH 5.5, controlled by atmospheric carbon dioxide.

Concentration of Phosphate

The solutions used for phosphate adsorption in both adsorption and desorption kinetics experiments were 10^{-6}M. KH_2PO_4, plus an amount of "carrier-free" $^{32}PO_4$ small enough that the total phosphate concentration was not affected by it. This concentration was chosen because it is small enough that the adsorption should be on the linear part of the adsorption isotherm, so that not much reduction in the P-32 phosphate adsorption would occur, compared with the adsorption from carrier-free material. It is large enough that it may be reliably obtained by dilution from a higher concentration.

There was an implicit assumption in the diffusion theory, that the adsorption should be proportional to concentration. This is true at 10^{-6}M. concentration and below. The desorptions were all into distilled water.

Time of Initial Phosphate Adsorption

In one desorption experiment the sample was soaked for five minutes in the active phosphate solution, before rinsing it and inserting it in the holder of the apparatus. In all other desorption experiments a time of ten minutes was used. A short time was used partly for consistency with earlier work, and partly in the hope that the short time approximation of the theories would be clearly applicable. At longer adsorption times it could happen that neither approximation would be good, unless the adsorption were so prolonged that contamination and solution concentration changes could become important.

Apparatus

The devices described in Chapter 7, and shown in figs 7.3 and 7.4 were used for adsorption and desorption.

RESULTS OF ADSORPTION MEASUREMENTS

Method of Presentation

The measured count rates are the sum of the count rate from the adsorbed radioactive material, the count rate from the material in the solution near the surface, and the background. These last two may be regarded as constant and equal to a count rate, b. The actual count rates will be designated by primed symbols, x', while those due to the adsorbed activity will be designated by unprimed symbols, x.

Both the planar and spherical theories predict that at very short times the count rate should be proportional to $\sqrt{t}$, so that b can be found by extrapolating the graph of x' versus $\sqrt{t}$ to zero time.

Both theories also predict that at long times the value of log $(x_\infty - x) = \log (x'_\infty - x')$ should be proportional to time. By estimating x'_∞ and plotting this graph, small errors in x'_∞ appear as a deviation in the points from a straight line, at small values of $x'_\infty - x'$. A value of x'_∞ can be found (by trial) which fits the last few points, and since the possible range is no more than a few percent this cannot be regarded as forcing the data to fit the theory.

Having found the value of b and x'_∞, it is possible to estimate the fractional change in count rate, $\frac{x}{x_\infty} = \frac{x' - b}{x'_\infty - b}$, which has occurred by time, t. This can be used to estimate a value for Bt (or Dt), using the tables of Reichenberg (1953) for the spherical case, or the corresponding table produced by the author for the planar case. If the shape of the experimental curve is the same as that of the theoretical one, then the plot of the values of Bt (or Dt) versus t should be a straight line through the origin.

Results

Graphs of the results from the five experiments completed are shown in figs. 8.1 to 8.5. The results of runs 202 and 205 give good straight lines up to Bt = 2, which corresponds to 92% completion of the adsorption. The graphs of runs 204 and 206, while curved, are not in great disagreement with the diffusion hypothesis. The graph of run 203 is straight, but has an intercept of about 1½ hours on the t axis. This run started with a linear change in count rate with time.

In order to plot the above graphs it was necessary to plot the graphs of $\sqrt{t}$ versus x and log $(x'_\infty - x')$ versus t. From these values of the parameters A, B, C and D have been estimated, for runs 202, 204, 205 and 206, in order to obtain another check on the measure of agreement between theory and experiment. The results and estimates are presented in tables 8.1 and 8.2.

Interpretation

Except for runs 202 and 205 (in which the spherical theory is better), there seems to be no great advantage of one theory over the other. The Bt - t plots are reasonably consistent with diffusion theory, but a better judgement on the measure of agreement can perhaps be made from the results in table 8.2. These show that although neither the $\sqrt{t}$ or log approximations describe the whole of the results, the parameters from one approximation are similar to those of the other. Also, the fraction of the change described by an exponential term (determined from the intercept of the log plot at $t = 0$), is about that predicted from the theory. (This statement is justified by the correspondence between the values of A or C derived from $x'_\infty - b$ and the log plot intercept.)

It may therefore be said that over 90% of the adsorption process can be described by a process of diffusion of ions into an absorbing medium, whose shape is unknown, but possibly a layer of equal sized spheres.

RESULTS OF DESORPTION MEASUREMENTS

Presentation of Results

A plot of count rate versus $\sqrt{t/\theta + 1} - \sqrt{t/\theta}$ should give a straight line for short times, on either theory, but on the planar theory this line must pass through the origin, whereas on spherical theory this line should have a negative intercept on the count rate axis. The desorption experiments performed under clean conditions with the circulating apparatus did, in fact, lead to negative intercepts.

It is most unlikely that imperfect experimental conditions could lead to this result, for all one could expect would be a positive intercept, due to the presence of some activity not changing with time. Discussion of the results therefore proceeds in terms of spherical theory only.

Results

The graphs of count rate versus $\sqrt{t/\theta + 1} - \sqrt{t/\theta}$ and log (count rate) versus time are shown, for each of the experiments completed, in graphs 8.6 to 8.9. Run 303 is omitted because the first part of the experiment was lost due to instrumental troubles, but otherwise there has been no selection of data.

The slopes and intercepts of the graphs are shown in table 8.3.

It appears from the graphs that not all the slowest desorption can be accounted for by the simple logarithmic term chosen. This is not surprising, in view of the high probability of contamination with dirt, adsorption on the edges, and non-uniformity in particle size distribution. In run 302 this has been allowed for by subtraction of 210 c/min from the data, but in others the logarithmic term appears to account for most of the change not described by the $\sqrt{t/\theta + 1} - \sqrt{t/\theta}$ expression, and this correction has not been made.

From each of the two approximations the values of D and x_o were independently calculated, and the results are shown and compared in table 8.4.

Interpretation

The agreement between the two extreme ends of the change is good when the difficulties of the experiment are considered, and must indicate that the original series expression is a good description of the results. The author believes that this expression is sufficiently unique that the agreement between the theory and experiment is good evidence for proposing that the kinetics are diffusion-controlled, and that the medium in which the diffusion is occurring is well approximated by a set of spheres of uniform size.

CONCLUSIONS

Nature of the Rate-Limiting Step

The data from both adsorption and desorption kinetics measurements can be represented by a two-parameter equation derived from a diffusion model. For the reasons previously stated, this is regarded as sufficient evidence for diffusion control of the rates.

Nature of the Material on Which Sorption Occurs

Of the two geometrical conditions tried, only that corresponding to a set of equal-sized spheres fits the data well in both kinds of experiment.

It may therefore be said that in these experiments the phosphate is being absorbed by particles adhering to the mica surface.

This conclusion is radical from two points of view. The first is that it suggests that the mica itself acts merely as a supporting medium, and does not play an active role in the adsorption process, except, perhaps, that it might actively attract the particles. The second is that the sorption of the particles is not confined to their outside surface.

It seems that the only material one could reasonably postulate for the absorbing material is a hydrous aluminium oxide, and there are three pieces of supporting evidence available.

Churms (1966) has investigated the kinetics of sodium, potassium and chloride sorption on hydrated alumina, and concludes that diffusion into the particles accounts for the slow kinetics found.

A. Langdon (personal communication), working in the author's group, has found that ^{35}S-sulphate is not strongly sorbed on to a mica surface in contact with a 10^{-4}M. $AlCl_3$ solution at pH 3, containing ^{35}S-sulphate. If a 10^{-4}M. $AlCl_3$ solution is made slightly alkaline with ammonium hydroxide, and then made up to about pH 3 - 4, and a little of this solution is added to the previous one, so that the pH is not significantly increased, then the amount of ^{35}S on the surface rapidly increases. This shows that it is not aluminium ions which are responsible for sulphate sorption at 10^{-4}M. aluminium concentration, but the particles of hydroxide. In the one molar solution there could well be sufficient hydroxide particles to have similar effects even at low pH's, for even if they were not in equilibrium with the solution, it is well known that they would take a long time to dissolve.

It has been shown by Follett (1965), using electron microscopy, that kaolinite treated with colloidal ferric hydroxide suspensions becomes coated on its silicate face with the colloidal particles. In his case the particles were 30 - 100 Angstrom units in diameter, and uniformly distributed over the surface, so that such particles are possible. A diffusion process into a medium only tens of atoms in diameter is probably not statistically reasonable, but the difference between the direct evidence and the present case is a question of degree, rather than kind.

Variations in Numerical Values of the Diffusion Parameters

The values of the parameters C and D obtained for the spherical diffusion model are presented in table 8.5.

The values of C should be proportional to the solution activity, and the values are shown of the ratio of C to S, the number of counts per minute per millilitre on a planchette in a particular lead castle. This count rate is not directly comparable with that in the adsorption and desorption measurement, but the ratio of C to S in each set should be constant. It is not, which indicates that the amounts adsorbed are not as reproducible in these experiments as in those of Chapter 6. Some of the variation could be due to variations in counting geometry and Geiger counter efficiency.

The values of D (in hours^{-1}) vary from .05 to 1.3, but five of the eight results lie in the range 0.2 to 0.7.

Since $D = k\pi^2/a^2$, where k is the diffusion coefficient and a is the particle radius, these variations can be explained by relatively small differences in particle size in the various experiments. This can be attributed to variations with time of standing after mixing or stirring the aluminium solutions.

Conclusions from Numerical Values of the Diffusion Parameters

We have $D = k\pi^2/a^2$. For simplicity the value of 0.36 hours^{-1} or 10^{-4} secs^{-1} is chosen as a representative value, so that $k/a^2 = 10^{-5}$ sec^{-1}.

The high-resolution autoradiographs of Chapter 5 suggest that a is less than 1 micron, $= 10^{-4}$ cm, so that $k < 10^{-13}$ cm^2/sec. Values of k in other systems range from 10^{-5} for ions in solution to 10^{-20} for ions in crystals, so that this certainly falls within the very wide limits possible.

Since $C = 8Na^3pV/\pi$, it is necessary to compare C and V. This was done approximately for the adsorption experiments, and led to a value of a^3Np of about 0.1 cm. Assuming that the mica is nearly completely covered with these particles, then we can say that each particle occupies $(2a)^2 = 4a^2$ cm^2, so that $N = 1/(4a^2)$ and $a^3N = a/4$. Thus $p = 0.4/a$.

For $a = 10^{-4}$, $p = 4000$. Since the concentration in the solution used was 10^{-6}M. the phosphate concentration in the particles on this model would be greater than 4×10^{-3}M. This is not unreasonable, but it is not surprising that at greater concentrations the adsorption should fail to be proportional to concentration. Note that on this model the phosphate molecules are spread at a low concentration through a considerable thickness (1 micron), of material, in contrast to the monolayer suggested by the isotherm experiments.

The most valuable conclusion is that it appears that the observed variations in adsorption with time can be explained by diffusion into small particles with a diffusion coefficient very much less than that obtained in the usual kind of diffusion experiments. The boundary between solid and solution cannot be taken as completely impermeable, and adsorption cannot be assumed to be confined to the surface of the particles.

TABLE 8.1

RESULTS OF PHOSPHATE ADSORPTION EXPERIMENTS

Graph	Property	Run 202	Run 204	Run 205	Run 206
$\sqrt{t}$	intercept	660	1000	970	820
	slope	280	2000	150	405
$\log(x'_\infty - x')$	x'_∞	2060	5350	1315	1330
	intercept	2.94	3.58	2.36	2.32
	slope	.020	0.30	0.095	0.27
counts/min/ml		1.8×10^4	3.3×10^4	2.7×10^4	2.2×10^4

(Note - units of B are hours^{-1})

TABLE 8.2

VALUES OF PHOSPHATE DIFFUSION PARAMETERS FROM ADSORPTION EXPERIMENTS

		Run 202		Run 204	
Parameter	Source	Planar	Spherical	Planar	Spherical
A or C	$x'_\infty - b$	1130	850	3530	2650
A or C	log-intercept	870	870	3800	3800
$A\sqrt{B}$ or $C\sqrt{D}$	$\sqrt{t}$	316	158	2300	1130
$A\sqrt{B}$ or $C\sqrt{D}$	log	248 or 187	183 or 187	3150 or 2930	2200 or 3150
B or D	log slope	0.046	0.046	0.690	0.690

		Run 205		Run 206	
Parameter	Source	Planar	Spherical	Planar	Spherical
A or C	$x'_\infty - b$	280	210	415	310
A or C	log intercept	230	230	210	210
$A\sqrt{B}$ or $C\sqrt{D}$	$\sqrt{t}$	170	85	460	230
$A\sqrt{B}$ or $C\sqrt{D}$	log	131 or 109	98 or 109	330 or 165	246 or 165
B or D	log slope	.219	.219	.625	.625

TABLE 8.3

RESULTS FROM PHOSPHATE DESORPTION EXPERIMENTS

Graph	Property	Run 301	Run 302	Run 304	Run 305
$\sqrt{t/\theta+1} - \sqrt{t/\theta}$	slope	7100	2400	323	1030
	intercept	-320	-360	-34	-90
$\log_{10}x$	slope	0.133	0.45	0.55	0.27
	intercept	2.84	2.70	2.06	2.34
	θ	0.0834	0.167	0.167	0.167

Note - times are in hours.

TABLE 8.4

DIFFUSION PARAMETERS FROM PHOSPHATE DESORPTION EXPERIMENTS

	D		x_o		C	
	f(t)	log(x)	f(t)	log(x)	f(t)	log(x)
Run 301	.304	.307	7100	8150	26,000	30,000
Run 302	1.6	1.0	2040	2660	2,600	4,200
Run 304	.83	1.27	320	440	540	620
Run 305	.62	.63	1020	980	2,020	2,800

The columns labelled f(t) are derived from the graph of x versus $\sqrt{t/\theta+1} - \sqrt{t/\theta}$, and those labelled log(x) from the graph of log(x) versus t.

$$C = \frac{2x_o}{2\sqrt{\pi D\theta} - D\theta}.$$

TABLE 8.5

COMPARISON OF THE DIFFUSION PARAMETERS OBTAINED FROM THE PHOSPHATE KINETICS EXPERIMENTS

Adsorption	C	C/S	D (hours^{-1})
Run 202	860	.047	.046
Run 204	3000	.091	.690
Run 205	220	.0081	.22
Run 206	260	.012	.63
Desorption			
Run 301	28,000	.063	.31
Run 302	3,400	.012	1.3
Run 304	580	.0028	1
Run 305	1,900	.011	.62

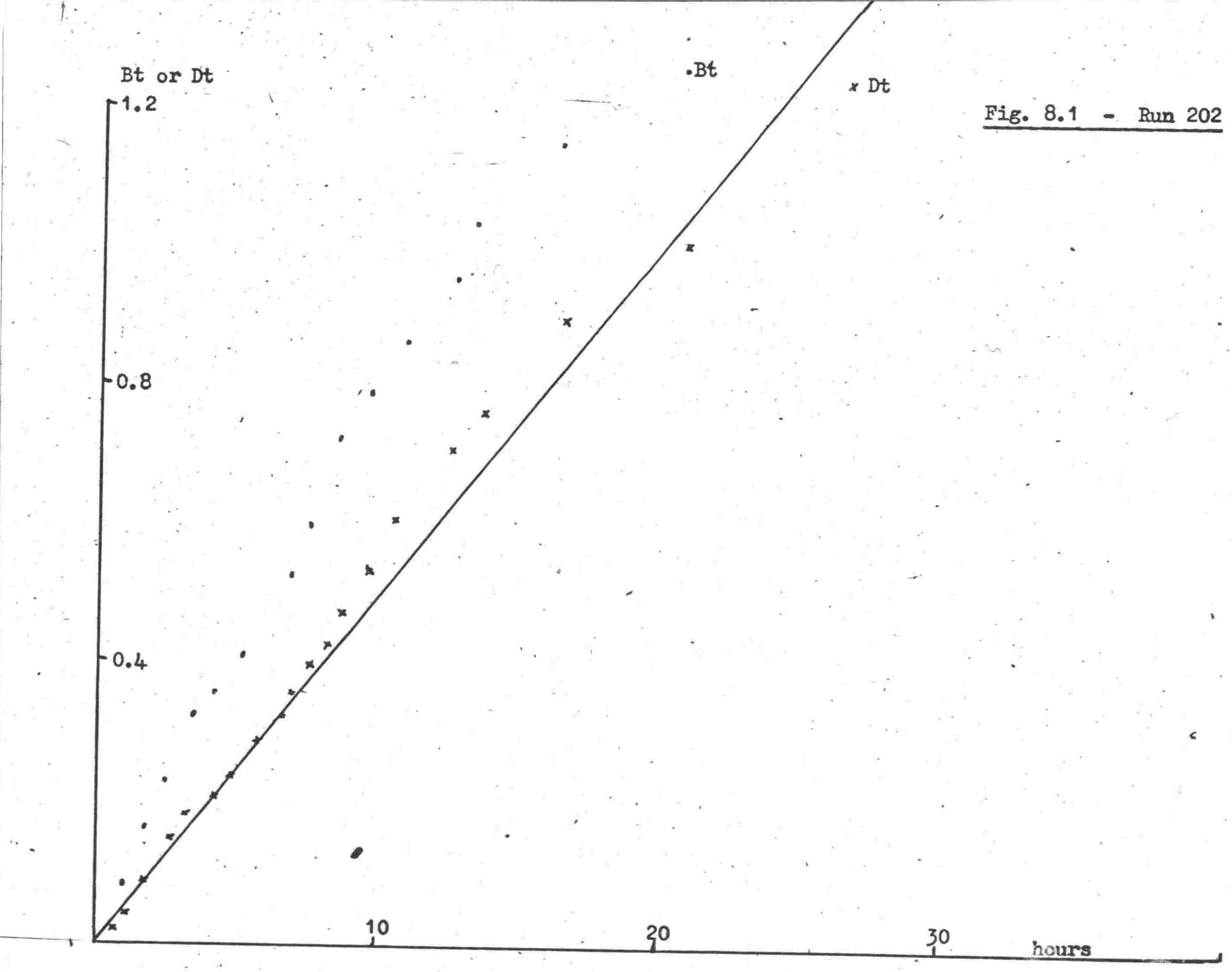
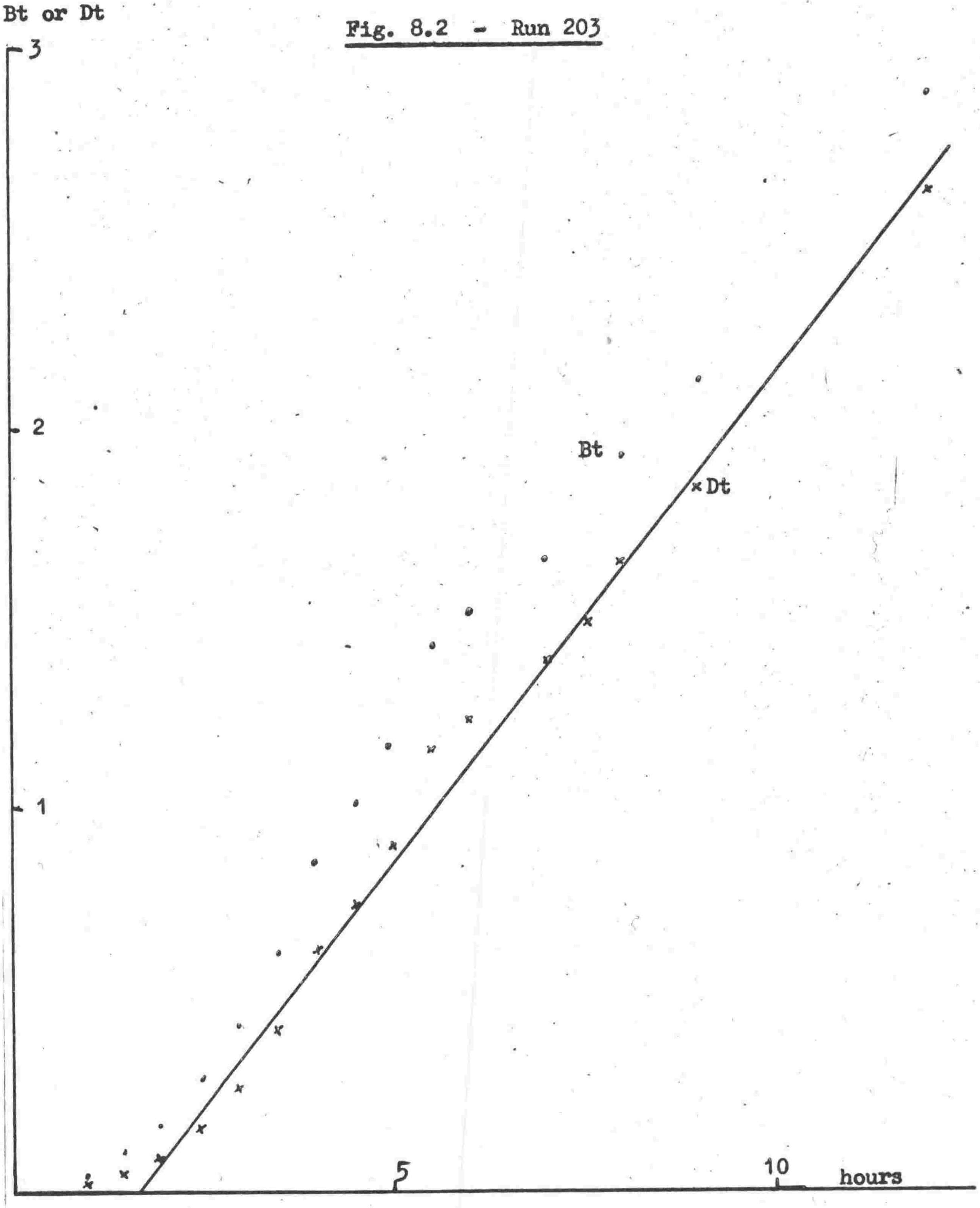


Fig. 8.1 - Run 202

Fig. 8.2 - Run 203



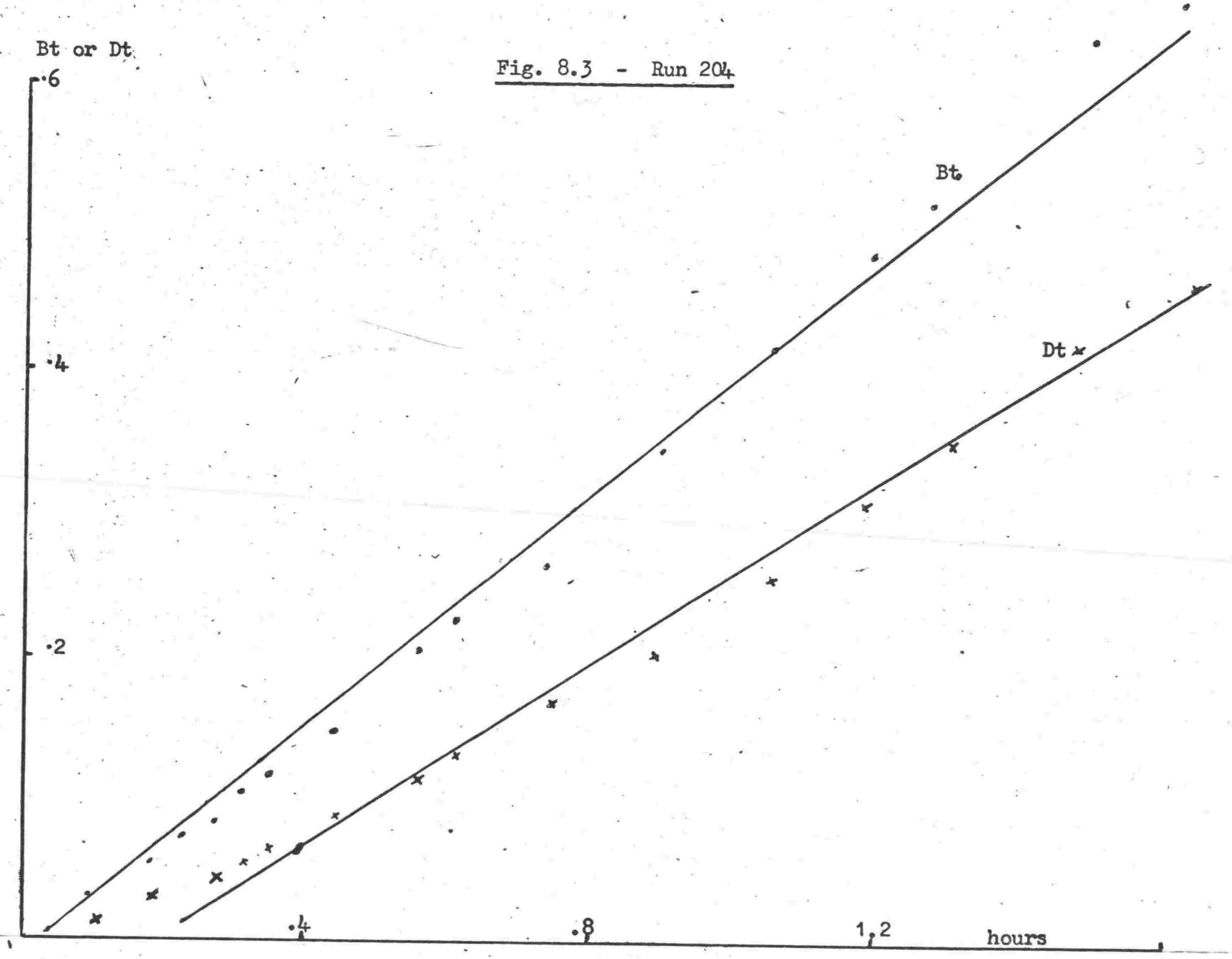


Fig. 8.3 - Run 204

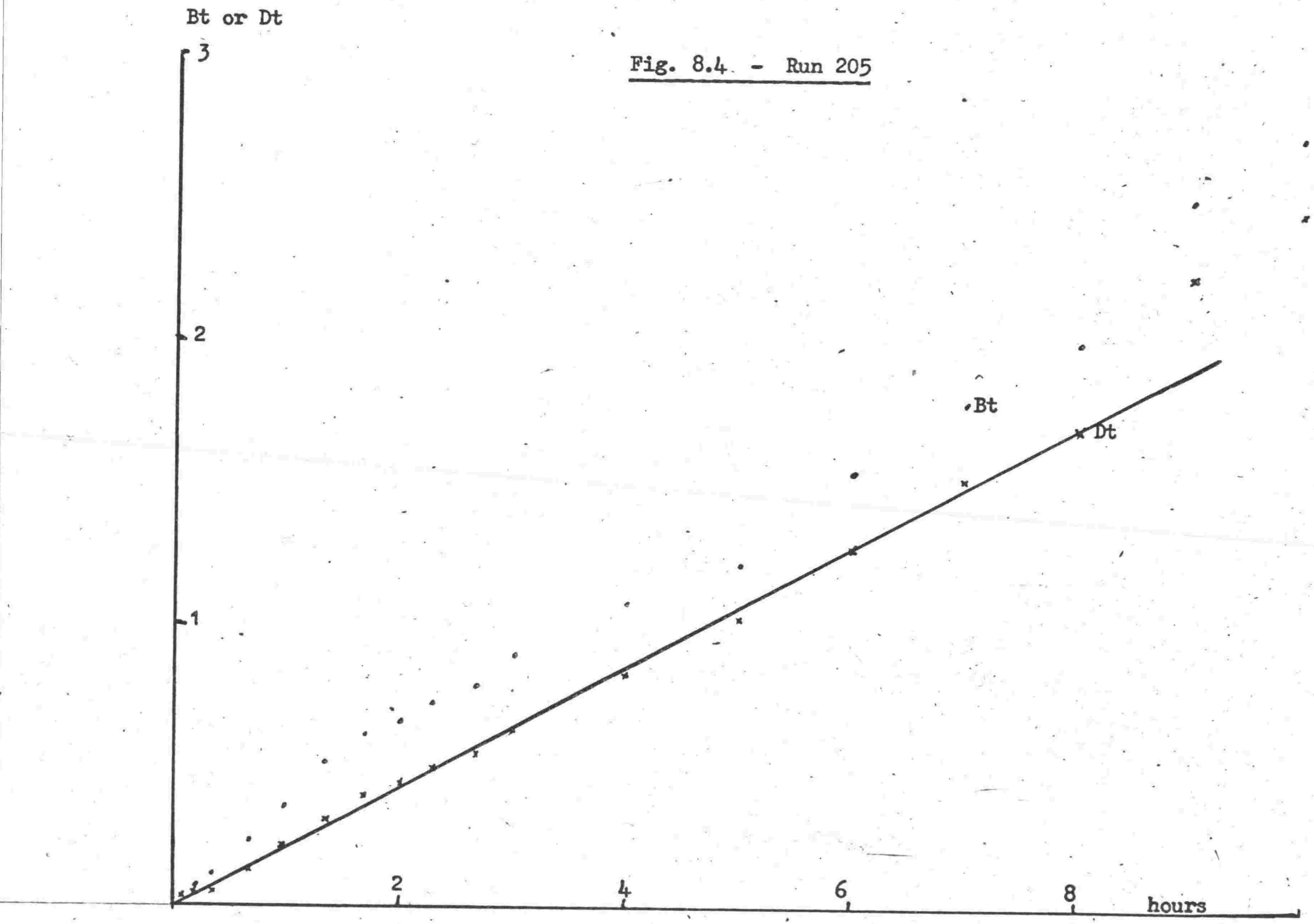


Fig. 8.4 - Run 205

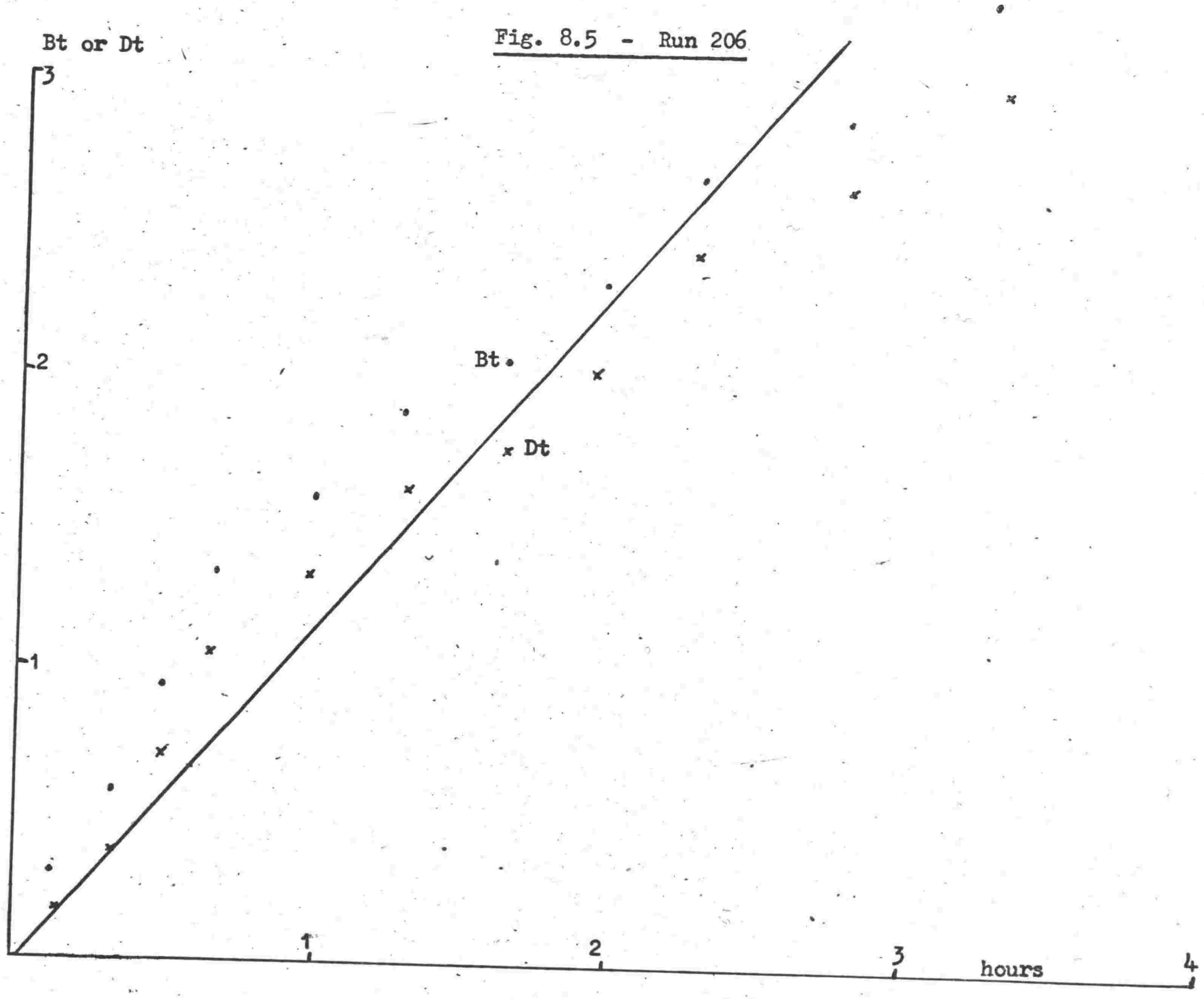


Fig. 8.5 - Run 206

Fig. 8.6 - Run 301

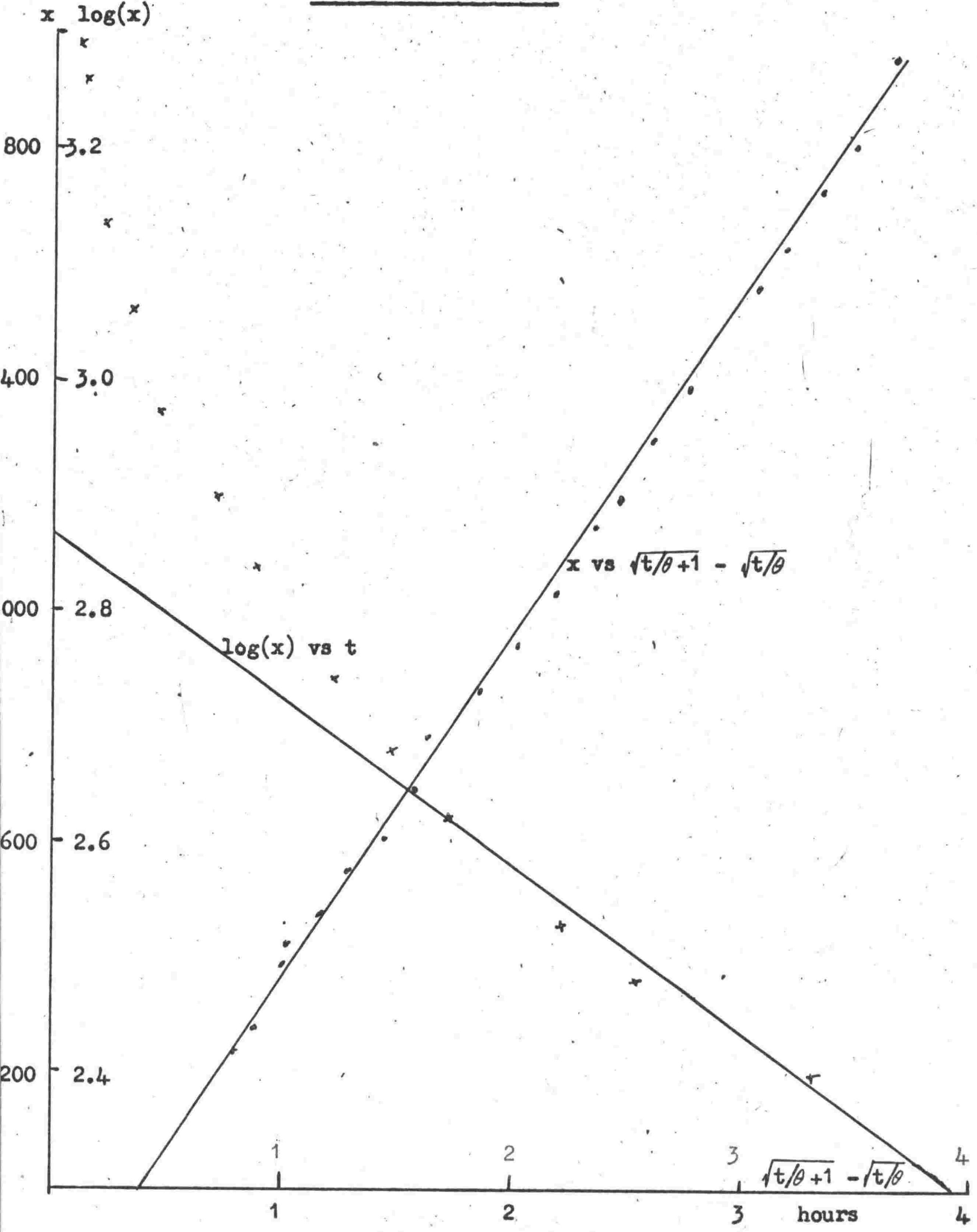


Fig. 8.7 - Run 302

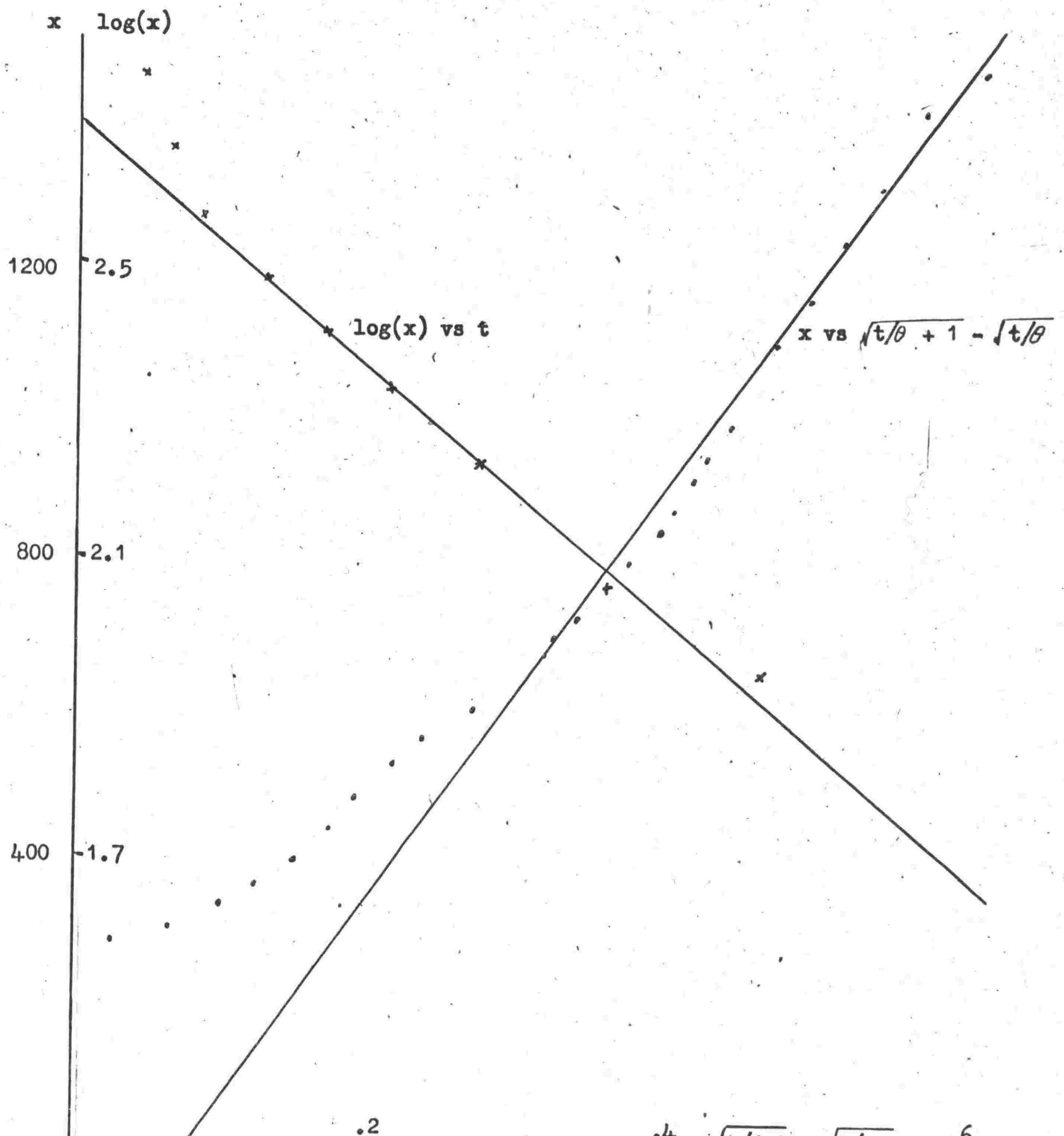


Fig. 8.8 - Run 304

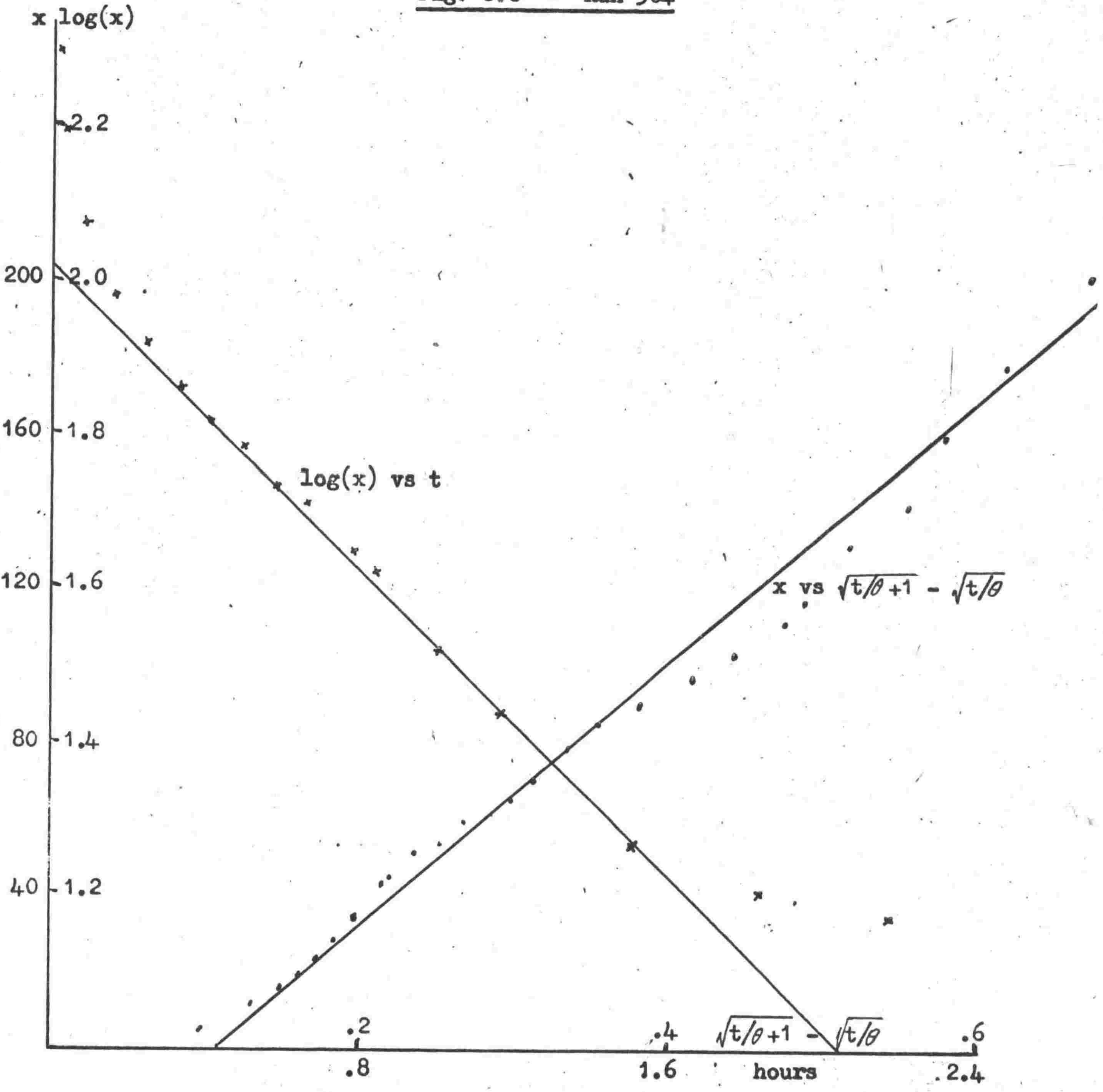
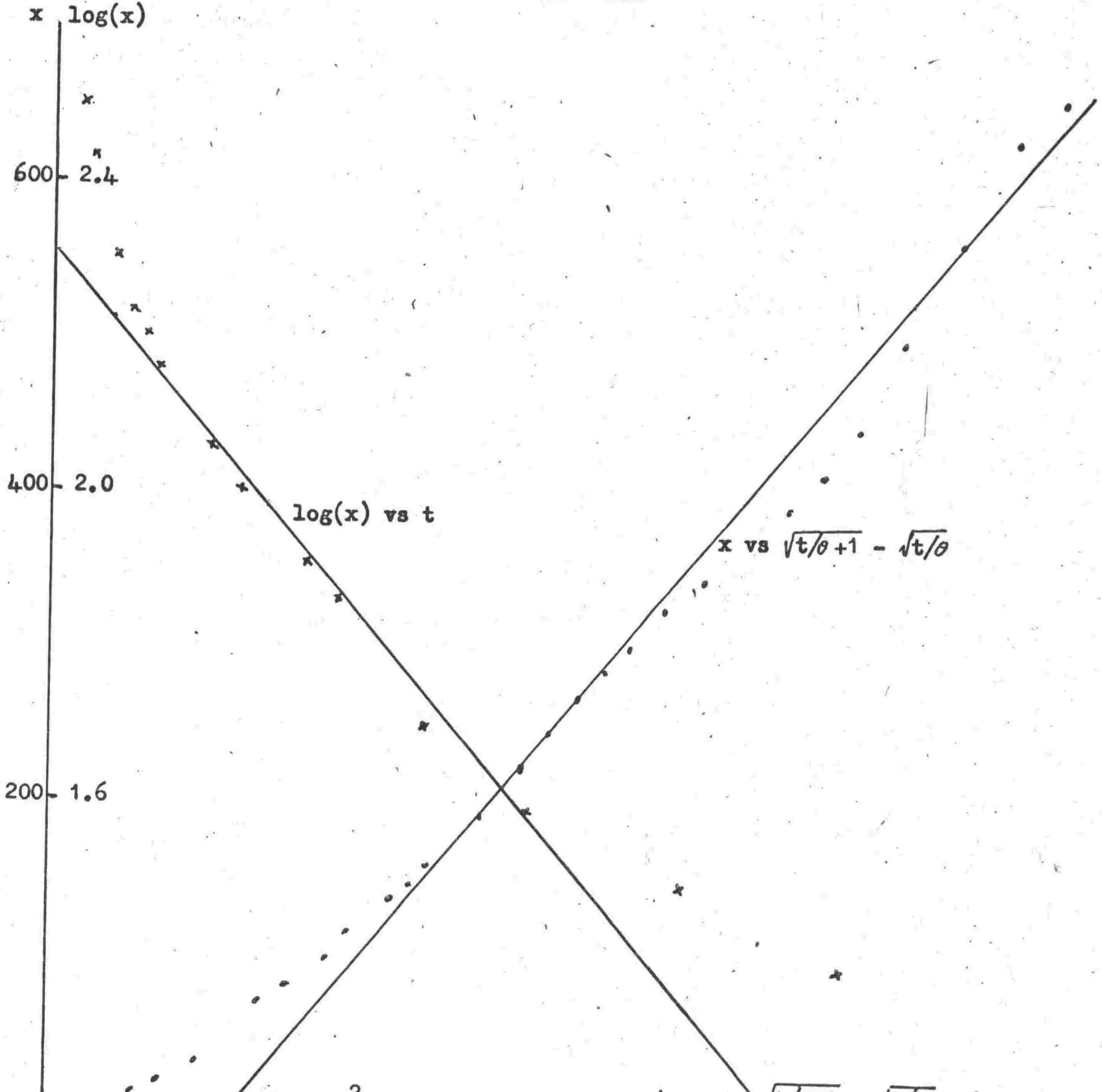


Fig. 8.9 - Run 305



CHAPTER 9

PRELIMINARY SURVEY OF THE ADSORPTION OF RADIOACTIVE CATIONS ON TO MICA SURFACES

INTRODUCTION

It was clear from the work of Morris and Furkert that adsorption of phosphate was greatly dependent on the previous treatment of the mica with a salt solution, this being particularly noticeable with aluminium and iron salts. The effect of other cations was not so clear-cut, but at the start of the work (before Burns' thesis was available) it was expected that the monovalent and divalent ions would also influence the phosphate adsorption. Since the role of the cation was not clear, it was considered that valuable information could come from studies on the adsorption by mica of various cations. It was hoped that it would be possible to relate the phenomena observed with phosphate to the behaviour of the cations.

ISOTOPES USED

Specific Activity

It was decided to work with carrier-free or very high specific activity isotopes in order to ensure maximum sensitivity. If adsorption proved to be sufficiently great, then material of lower specific activity could be used later.

Monovalent Cations

Of the alkali metals the only ones with useful isotopes are potassium, rubidium and caesium. Inactive rubidium is expensive and was not used in this work. ^{131}Cs decays by electron capture, with a 9.6 day half life, and is available at a reasonable price from the Radiochemical Centre, Amersham, England. The X-rays emitted from this isotope were expected to be counted reasonably efficiently with an end-window Geiger couter (but see appendix on nuclear radiations), so it was well suited to the present techniques. About 1½ millicuries of ^{131}Cs were used early in this thesis.

A co-worker in the group, J. H. Watkinson, obtained some high specific activity ^{42}K from the Australian Atomic Energy Commission at a later stage in the work, so the opportunity was taken to perform a few adsorption experiments with this isotope on mica. K-42 emits a 3.5 MeV β^- which is easy to detect, but its short (12.5 hour) half-life, and its specific activity (1 curie/ gram K at the start of the experiments, compared with up to 5 x 10^4 curies/gram P for "carrier-free" ^{32}P) limited the range of experiments which could be performed.

Cobalt

There was a Moessbauer spectrometer available in the department, and some work on the assymetry of the environment of ions adsorbed on alumina has been reported by Flinn et al (1964) using this technique. It was hoped that if sufficient ^{57}Co could be adsorbed direct information on the nature of surface complexes could be obtained. The internal conversion electrons from ^{57}Co could easily be detected (see appendix), the half-life of 270 days is not too long, and the material was available carrier-free from the Radiochemical Centre, although at a rather high price if more than a millicurie or so was required.

Trivalent Cations

The cations of greatest interest are aluminium and iron, for these appear to be the most relevant to phosphate adsorption in soils. Aluminium has no isotope with a half-life between those of 6.6 min ^{29}Al and 10^6 year ^{26}Al, so is not suitable. A. G. Langdon was working with high specific activity ^{55}Fe, and apart from comparing the adsorption of the other isotopes with it on two occasions, work with this isotope was left to him.

Gallium is known to behave in soil in a manner very similar to aluminium (N. Wells, personal communication), and was shown earlier in this work to greatly enhance the adsorption of phosphate on mica surfaces. It has an isotope, ^{67}Ga, which decays by electron capture with a 78 hour half-life, and is available carrier-free from the Radiochemical Centre at a reasonable price. (It is about ten times more expensive from Nuclear Science & Engineering, U.S.A.). The half-life is inconveniently short, but long enough to enable an extensive set of results to be obtained, if the work is carefully planned.

Chromium also has been found to enhance phosphate adsorption, so ^{51}Cr (E.C., 28 days) carrier-free solution was ordered. It was unavailable because the suppliers (The Radiochemical Centre, Amersham) were unable to obtain vanadium target material sufficiently free from chromium.

^{131}Cs EXPERIMENTS

Amount Adsorbed

This isotope was obtained at an early stage of the work, when many of the pitfalls had not been seen. Consequently, it is difficult to say anything very conclusive about the adsorption of this isotope on to mica. The surfaces used were almost certainly contaminated by dirt similar to that observed in the section on the preliminary autoradiograph experiments. The amount adsorbed was found to vary more or less randomly with various treatments of the mica, which included soaking it in acid, water, $AlCl_3$, CsCl or no solutions before putting a few drops of stock ^{131}CsCl (0.5mC/ml pH 5.5) on to the surface. The highest amount adsorbed was 1000 counts/minute on a desorption sample, and the lowest less than 10 counts/minute. The count rate from the solution while the ^{131}Cs was adsorbing was about 30,000 counts/minute. If it were the Xe K X-ray being counted, then the attenuation in the mica and solution would be small, and since the solution would be in a layer about 0.1 cm. thick the adsorption ratio would be about 1% of 0.1 cm or 10^{-3} cm. If it were the L X-ray, as seems more likely, the radiation detected would be attenuated much more rapidly than this, and the adsorption ratio would be lower, by perhaps a factor of 10. Thus the adsorption ratio was probably about 10^{-4}cm.

The relative adsorption of ^{131}Cs and ^{55}Fe by a mica surface was found by an autoradiograph experiment. ^{55}Fe was found to be adsorbed (uniformly) but no ^{131}Cs could be found. The relative activities per millilitre were not known for the two isotopes, but later work on the iron suggested that its activity was probably less than that of the caesium, so that adsorption of caesium on to this surface was much less than the adsorption of iron.

Kinetics of Desorption

Some kinetic experiments were performed, but their results are not presented, since they are similar to the early phosphate kinetic experiments, in their variability and uncertainty of interpretation.

^{42}K EXPERIMENTS

The ^{42}K Solution

These experiments were performed when the need for cleanliness had been realised, and some progress had been made towards that end, but the quantitative and "mini-beaker" techniques had not been developed. The activity of the solution was probably about 100 μC/ml, when being used, at a specific activity of about 1 curie/gram K. The concentration of K in the working solution was therefore about 10^{-4} grams/ml or about 2×10^{-3} moles/litre. This was much higher than had been used previously in any experiments, but it was considered to be worthwhile to try the experiment while the material was available.

The Amount Adsorbed

An autoradiograph experiment at pH 3, 5.5 and 10 was first performed. Three sheets of mica about 2 inches square were cleaved and their edges trimmed with clean scissors. One drop of the potassium solution adjusted to pH 3 with HCl was placed on one sheet with a chromic-acid-cleaned dropper, a drop of the untreated stock solution was placed on another, and a drop of a solution left for an hour in contact with OH^- form ion-exchange resin was placed on a third. The sheets of mica were placed as nearly horizontal as possible, but since the surface was very hydrophilic, the solutions ran towards the edges. After half an hour the surfaces were rinsed, and autoradiographs taken. The result (fig. 9.1a) shows that the potassium was adsorbed, but in a far from uniform manner.

Another autoradiograph experiment was designed to show the effect of adsorption time on the amount of ^{42}K adsorbed. A strip of freshly cleaved mica about 1½" by 6" was prepared and held horizontally. Drops of the neutral KCl solution were placed on the surface for 30 minutes, 8 minutes, 3 minutes, 1 minute and 20 seconds, and then washed off simultaneously. The autoradiograph (fig. 9.1b) suggests that the adsorption is not related to the time of contact between mica and solution, and is probably entirely on edges or dirty areas.

These results do not in themselves tell much about the amount of potassium adsorbed by the mica surface, especially because of the high concentration of inactive potassium, but the author feels that these results conflict so greatly with those found with ^{67}Ga under similar conditions that the mica must have had a much lower capacity for potassium than gallium. This conclusion, although important, would need to be substantiated by further quantitative work before being used. It raises interesting questions concerning the actual ion-exchange capacity of a mica surface, in comparison with its theoretical capacity, and the techniques developed here are most suitable for investigating this problem.

Desorption Kinetics

Several desorption kinetics experiments were performed, using the brass sample holders used in the preliminary phosphate experiments, after cleaning them in a vapour degreasing bath before use. Sheets of mica 2" square were glued to the holders with "Araldite" adhesive, and cleaved just before using them. The edges of the sheets were left unprotected, but were far enough away from the used portion that they should have had no effect. The ^{42}K solution was placed on the inverted sample for the required time, rinsed off, and the sample placed in the desorbing solution. The solution on the surface was counted through an attenuating filter during the adsorption in some cases, so that an estimate of the percentage adsorbed was possible. This was usually about 0.2% but did vary greatly on occasion. If it is assumed that the thickness of the solution was $\frac{1}{2}$ mm, then it can be said that the adsorption ratio was about 10^{-4} cm, provided adsorption was uniform (which was seldom the case).

The desorption kinetics in eight out of the ten experiments performed were very fast, about 80% coming off in the first five minutes, and 95% in the first hour. However, two samples which were supposedly prepared in the same way as the others desorbed much slower than them (one scarcely at all when decay had been allowed for). After the initial very rapid change of count rate had slowed down, the desorption of one run was greatly speeded up by reducing the pH to about 2. On the other hand, one of the slow ones was not affected by pH 1.3 HCl.

Most of the samples were autoradiographed after desorbing them, and it was found in all these that the activity was present as small spots.

Conclusion

It is concluded that the potassium was probably being adsorbed by something other than the 001 cleavage plane exchange sites, and that desorption from the surface was generally much more rapid than that found for phosphate or ^{67}Ga (see Chapter 10).

^{57}Co EXPERIMENTS

Techniques

These experiments were performed after most of the techniques described in this thesis had been thought of, if not fully developed. They were made difficult because of the very small amount found to be adsorbed. No desorption experiments were attempted, because of the low activity, and the uncertainty of interpretation of such experiments.

The active solution was ^{57}Co carrier-free, 1.0 mC in 1 ml 1.1N HCl. 0.1 ml. of this solution was diluted to 1 ml. for the experiments. Some of the experiments were performed by placing a drop of this active solution near the end of a mica strip of dimensions about 1½" by ¼", held horizontally by a stainless steel clip on a stand like the one in fig. 5.6a. The drop was then confined by the edges of the strip. Other experiments were performed with diluted solutions in the mini-beakers.

The samples were counted using the EW3H Geiger counters.

pH Adjustment

The working stock solution was at pH 1 initially, and at this pH it was expected that cation adsorption would be much less than at higher pH's.

It was not thought advisable to remove hydrogen ions by neutralisation with alkali, because the cations introduced might strongly compete with the cobalt ions, which were present at very low concentrations. The pH was therefore increased by other methods.

The first method used was to add OH^- form anion exchange resin (analytical grade) to the cobalt solution. This increased the pH to about 5 - 6. The second was to evaporate the solution to dryness with an infra-red lamp, and redissolve the $^{57}CoCl_2$ in distilled water.

Impurities in the "Carrier-free" Solution

A yellow non-crystalline deposit was found on the Pyrex mini-beaker when the solution had dried. This experiment was repeated with some fresh solutions in very carefully cleaned glassware with the same result. The deposit dissolved in water. On evaporating again and heating gently on a flame the deposit turned black, and only partly dissolved in pH 1 HCl. That which remained would not dissolve in 10 minutes in 35% HCl at 100°C. A sample of the redissolved material was dried again and gave another yellow-green deposit which went brown on gentle heating, and dissolved in HCl.

The amount of radioactive material present in these operations was not more than a microcurie. This corresponds to about 10^{-10} grams, which should be quite invisible. The observed properties were consistent with the evaporated deposit being cobalt chloride, but this would require a far lower specific activity than the specification. It is of interest to note that the Radiochemical Centre say in "The Radiochemical Handbook" that their carrier-free ^{57}Co solution will pass the "Analar" test for distilled water. This standard will allow up to 5 p.p.m. of impurities, but the solution used was not even up to this standard.

Adsorption Experiments

A set of experiments was performed with ^{57}Co solution which had been treated with ion-exchange resin. Some of the solution was put on untreated mica and some on mica treated with $AlCl_3$ or KH_2PO_4.

Strong adsorption on the edges was found in all cases, except where the surface had been treated with 1M. $AlCl_3$ and washed with a wash bottle, in which case no adsorption occurred anywhere. This shows that aluminium solutions can cause "blocking" of the adsorption sites on the edges, whereas potassium solutions cannot, and this effect must be another manifestation of the strongly adsorbing behaviour of aluminium ions.

The mica treated with KH_2PO_4 behaved no differently from untreated mica, and neither did mica which had a drop of 10^{-4}M. KH_2PO_4 on the surface before adding the ^{57}Co.

The adsorption ratio was found to be only about 10^{-4} cm. in most cases, which was too low to allow the measurement of an adsorption isotherm. The amounts adsorbed were far too small for Moessbauer work, which it was estimated would require a minimum rate of about 10,000 counts/minute, allowing for the fact that only 10% of disintegrations give the 14 KeV γ-ray used. (It was also likely that the ^{57}Co would not give a Moessbauer effect, since it would have to be in a strong crystal structure in order to do this.)

More experiments were carried out with the ^{57}Co which had been dried to increase the pH, with similar results to the above.

Conclusions

The amount of ^{57}Co adsorbed on mica surfaces is too small to allow useful experiments to be performed. The adsorption on the edges seems to be much greater than that on the 001 face, so that these may possess a greater cation exchange capacity than the faces.

^{67}Ga EXPERIMENTS

Counting Techniques

The ^{67}Ga atom decays by electron capture, with a 78 hour half-life. (The decay rate was determined and shown to agree with this figure.) The solution obtained from the Radiochemical Centre, was 10 ml. of carrier-free solution in 0.1 M. HCl, of activity about 500 μC per ml. on the day experiments began. Because of the short half-life much thought went into the planning of the experiments, in order to ensure that those experiments requiring the highest activity could be performed first.

The first experiment involved testing the efficiency of counting the radiation. It was found that the end window Geiger counter was almost as efficient as the scintillation counter, and because of the low background of the Geiger counter it was more suitable for these experiments.

In the light of previous experience with electron-capture isotopes an experiment was performed to measure the attenuation by the mica sample of the radiation from the lower face of the sample. A piece of radioactive mica from one of the early experiments was cleaved into a sheet 6 mg/cm^2 thick, and from the ratio of the count rate when the active side was up and when it was down, the half-thickness for adsorption of the radiation (assumed exponentially attenuated) was 2.6 mg/cm^2. This indicates that most of the counts being recorded were due to the soft radiation and not the K X-Rays. (See appendix on detection of radiation). Because of this, the contribution of the lower surface to the total count rate varied with the mica thickness. Rather than weigh the mica in each experiment to determine its thickness, and allow the application of a correction factor, it was decided to use thick pieces of mica so that the contribution of the lower surface would be small (less than 20%).

If a set of samples were to be compared, then strips of equal thickness cut from the same sheet of mica were used, and it was assumed that only one side of the mica was counted. The error of a few percent which this simplification introduces into the absolute measurements is quite insignificant at the present level of reproducibility.

Preliminary Adsorption Experiments

The first adsorption experiments used the stock solution diluted with pH 3 HCl. The count rate per millilitre was measured twice within 10 minutes to check that no rapid adsorption was occurring on the glass, and the two determinations agreed to 3%. Three samples of freshly-cleaved mica were soaked in this solution for 1 minute, 10 minutes and 100 minutes respectively, and then rinsed with distilled water. The solution activity was measured again after these samples had been in the solution. Autoradiographs showed that activity was adsorbed evenly, and no extra adsorption on the edges was observable in these experiments, so the total activity was calculated from the activity/cm^2.

The amounts of activity adsorbed are listed in the following table -

Time	Counts/min/cm^2	Total Activity	Solution Activity
1 min.	130	0.10×10^4	3.5×10^4
10 min.	270	0.22×10^4	
100 min.	950	0.76×10^4	0.8×10^4

It is clear that ^{67}Ga is being lost to the glass from the carrier-free solution, in the four hours between taking the two solution activities. Despite this reduction in solution concentration the amount of ^{67}Ga adsorbed increased with the increasing time in the solution.

Elimination of the Precipitation Hypothesis

It had been previously postulated that the cations adsorbed because of precipitation occurring when the surface was washed with the pH 5.5 wash solution. The results showing that the adsorption depends on time in the solution were evidence against this, but the following experiment was performed to eliminate this possibility.

X concentration not the same.

Two samples were soaked in the same ^{67}Ga carrier-free solution for 1 minute. Then one was washed with pH 5.5 distilled water from a wash bottle, and the other with pH 3 HCl. in the same way, and for the same time (20 seconds). This was repeated with a 10 minute soak in the gallium solution. The results were -

Time	pH Wash	Adsorption Ratio (cm)
1 min	5.5	1×10^{-2}
1 min	3.0	2×10^{-2}
10 min	5.5	2.8×10^{-2}
10 min	3.0	10.8×10^{-2}

The adsorption is clearly not due to precipitation in the wash solutions. It was noticed that autoradiographs of all these carrier-free experiments showed no excess adsorption on the mica edges over that adsorbed by the face.

Rinsing Conditions

It was important to have an approximate idea of how rapidly the activity was washed off the surface, in order to choose suitable conditions for rinsing off excess solution. If this loss is not too rapid, the washing conditions do not have to be strictly standardised.

An experiment with varying washing times in pH 3 HCl was performed, using the continuous-flow washer described previously. After a 10 minute soak in carrier-free ^{67}Ga the samples were rinsed for a few seconds with distilled water, and then placed in the washer for varying times, rinsed briefly with distilled water again, and dried. The flow rate of solution in the washer was approximately constant at about one complete change per minute. The same ^{67}Ga solution was used throughout, and the activity was found to have decreased by a factor of three from start to finish. Results are shown below -

Time	Activity/cm^2	Total Solution Activity
$\frac{1}{2}$ min.	2.4×10^3 c/min.	4.5×10^4 c/min.
1 min.	2.0 "	
2 min.	1.5 "	
4 min.	0.53 "	
8 min.	0.95 "	
16 min.	0.35 "	1.3×10^4 c/min.

If it is assumed that all the samples started off with 2.5×10^3 c/min/cm^2, and each sample was of area 2 cm^2, then the total activity removed by the mica would be $12 \times 2.5 \times 10^3 = 3 \times 10^4$ c/min., which approximately equals the observed decrease in solution activity. This is a great over-simplification because of the reduction in adsorption as the solution becomes more dilute, but it does show that there is not a very large amount of activity removed from the solution by the mica and then washed off in the first half minute. On the basis of this experiment subsequent samples were all washed for about $\frac{1}{2}$ minute with a wash bottle.

Carrier Gallium Chloride

A 0.2M. $GaCl_3$ solution was prepared by dissolving gallium metal in hot concentrated HCl containing a little HNO_3, in a silica crucible. The gallium solution was evaporated almost to dryness, to remove HCl, but avoid hydrolysis. It was then made up to 10 ml. with pH 3 HCl, filtered, and stored in a glass flask. The concentration was shown by gravimetric analysis (as oxinate) to be 0.18 M. Solutions from 10^{-2} to 10^{-6}M. were prepared by successive dilution.

pH Variation of Adsorption

It was clear from the preliminary experiments that experiments needed to be performed at high ^{67}Ga concentrations, so that not very much dilution of the stock solution would be permissible. Since the stock was at pH 1 this meant that a fairly acid pH would result. These experiments were carried out to find out what was the lowest pH which could reasonably be used. Because of this practical orientation of the experiment no attempt was made to work at constant ionic strength. The experiments were performed in the presence of 10^{-6}M. gallium chloride, in order to be comparable with the isotherm experiments which follow.

The solutions used were made as follows. 0.1 ml. of 10^{-5}M. $GaCl_3$ at pH 4 was added to each of five clean mini-beakers. To the first was added 0.9 ml 1 M. HCl and 0.02 ml ^{67}Ga solution (pH 1). This solution was assumed to have a pH of 0. To the second was added 0.9 ml 0.1 M. HCl and 0.02 ml of ^{67}Ga. This was assumed to have a pH of 1. To the third was added 0.1 ml. of 0.1 M. HCl and .8 ml. distilled water, and .04 ml. of ^{65}Ga solution. 0.1 ml. of this third solution was added to the fourth beaker and diluted with 0.8 ml. distilled water, and 0.1 ml. of this fourth solution was added to the fifth beaker and diluted similarly. The pH of the last three solutions was measured after the experiment was complete. The activity per ml. of all the solutions was found after each of the two experiments performed with this set of solutions. All the above volume measurements except those of the radioactive solutions were made using a 1 ml. syringe calibrated in 0.01 ml, attached to a 1.5 ml capacity pyrex glass dropper. The stock radioactive solution was dispensed with a dropper whose drop size had been measured.

Two sets of samples were used, one of which was soaked for ten minutes, and the other for 1000 minutes. The amount adsorbed at each pH is shown in the table, along with the ratio of the activities of the solution (after correction for decay) before and after the 1000 minute experiment.

pH	Molecules per 10^5 sq.A. 10 Minute	Molecules per 10^5 sq.A. 1000 Minute	Solution Ratio
0	6.2	5.2	0.92
1	22	55	1.0
2.1	74	174	1.8
2.9	58	128	3.5
3.9	56	940	3.4

The autoradiograph of the pH 3.9 1000 minute sample showed an unique, mottled appearance, so it was felt it should be disregarded. It seems that at pH's lower than 2 the adsorption starts to fall off seriously, with about a four-fold decrease in adsorption for a ten-fold increase in hydrogen ion concentration. This result meant that unless the pH of the stock radioactive solution was increased in some way, the concentrations of ^{67}Ga had to be limited to no more than about a tenth of that of the stock. This provided a serious limitation in some of the isotherm experiments. No attempt was made to increase the pH of the stock solution, because of the high probability of going too far and precipitating gallium hydroxide if a base were used, of hydrolysis if the solution were evaporated to dryness, and of introducing impurities if anion exchange resin were used. It is of interest to note that the solution concentration changed markedly with time at pH 3 and 4. This illustrates the reason for keeping the stock in a highly acid solution.

Adsorption Isotherms - Time of Adsorption

The above experiments provided sufficient background to proceed with further work, in which the amount of gallium adsorbed was found, as a function of the gallium concentration. Ideally, the experiments would have been carried out in such a way that the equilibrium amount of gallium was adsorbed at each concentration. However, it was known that at the lower concentrations of carrier the concentration in solution would decrease considerably over a long period of adsorption.

It was suspected that the adsorption process might not be rapidly reversible, so that it was not necessarily valid to assume that the final solution concentration was the concentration in equilibrium with the amount adsorbed. The experiments were therefore carried out with a short (10 minute) adsorption time, as well as a long one (800 minutes).

Adsorption Isotherms - Solutions Used

The experiments were performed in mini-beakers, using about 1 ml. of solution each time. The solutions were all at pH 2.2, the reason for this comparatively low pH being that about 0.05 ml. of ^{67}Ga solution had to be added to obtain sufficient activity on the sample immersed in the most concentrated solution used. The solutions of gallium chloride had all been made to pH 3 originally, but the addition of the pH 1 ^{67}Ga stock solution brought the pH down.

Solutions having gallium concentrations from 10^{-2} to 10^{-6}M. were prepared by adding the active gallium to samples of the stock solutions. Two further dilutions were made from the 10^{-6} solution, immediately before using the solutions. These were performed by diluting drops of a portion of the 10^{-6}M. solution which had been "spiked" with a little ^{67}Ga. The concentration of ^{67}Ga in the solutions was measured, and this allowed calculation of the total gallium concentration. Further ^{67}Ga was then added to bring the concentration up to the desired level. The tabulated data below includes the final concentration of the gallium solutions, calculated from the activity of the solutions before and after the experiments. Both experiments at each concentration used the same gallium solution.

Adsorption Isotherms - Results

The results are presented in the table below, and also as a graph of the logarithm of concentration, versus the logarithmof the number of atoms of gallium adsorbed per square Angstrom unit (fig. 9.2).

10 Minute Immersion		800 Minute Immersion	
Concentration (moles/litre)	Atoms/ 1000 sq.A.	Final Concentration	Atoms/ 1000 sq.A.
10^{-2}	14 ± 4	5.7×10^{-3}	32 ± 10
10^{-3}	7.0*	6.3×10^{-4}	12*
10^{-4}	3.0	7.8×10^{-5}	4
10^{-5}	5.0	5.1×10^{-6}	5.4
10^{-6}	1.2	3.3×10^{-7}	1.4
1.1×10^{-7}	0.098	2.9×10^{-8}	0.24
3.0×10^{-8}	0.034	6.5×10^{-9}	0.15
Carrier-free	$1.1 \times 10^{6}x$**	Carrier-free	$4.4 \times 10^{6}x$**

* The precision of the amount adsorbed is ± 10% except for the 10^{-2}M. experiments.

** x is concentration in moles/litre.

The graph shows that there are two distinct regions in the adsorption isotherm. At concentrations of 10^{-6}M. and below the adsorption is proportional to concentration, since on the log-log plot the points lie on a line of slope = 1. Above 10^{-6}M. the variation with concentration is much slower, and is probably not significantly different from zero for the 10 minute curve. It is much slower than the square root dependence found for phosphate on aluminium-treated mica. Thus it appears that adsorption is proportional to concentration up to a certain limit, after which adsorption is constant. This is characteristic of systems where adsorption is occurring on a limited number of sites.

The number of atoms per 1000 square Angstrom units at saturation appears to be between 5 and 20. That is, there is one gallium atom per 50 to 200 square Angstrom units. From the crystal structure of mica, it is calculated that there should be one cation exchange site every 50 square Angstrom units. This is certainly of the right order of magnitude, so that it seems possible that the gallium adsorption is occurring at the ion-exchange sites. On the other hand, a monolayer of hydrous oxide might have a comparable number of gallium atoms per square Angstrom unit.

Adsorption Isotherms - Edge Adsorption

It has previously been noted, with carrier-free solutions and up to 100 min. immersion time, that no more gallium was adsorbed on the edges than the face. It was found in the set of experiments with a 10 minute immersion that this was true up to 10^{-6}M. At higher carrier concentrations (and constant ^{67}Ga concentration) the amount of radioactive gallium on the edges decreased less rapidly than the amount on the faces, as the concentration of carrier increased. (This was clear from the appearance of the autoradiographs at higher concentrations.) It appears that saturation of the edges does occur, but at a higher concentration than that at which it occurs on the faces.

It was also found that when the mica was soaked for 800 minutes in the dilute solutions edge adsorption was considerably greater than face adsorption.

It appears that some of the factors governing uptake by the edges are different from those operating on the faces. The fact that the edge adsorption eventually decreases with increasing carrier concentration indicates that a definite adsorption process is occurring, and it is not due merely to inclusion of solution in holes. A study of the edge adsorption could be made in a way similar to the present study of face adsorption, by cutting edges off and counting them, but it was expected that these experiments would be complicated by the difficulty of cutting an edge cleanly and reproducibly, and by the time for diffusion into cracks along the edge.

Changes in Solution Concentration

One curious point not explained by the present work was how the solution concentration changed so much during the 800 minute adsorption. The changes observed at the higher concentrations were far greater than the amounts adsorbed on to the mica. It might be possible that the ^{67}Ga was not in isotopic equilibrium with the inactive gallium, and in a form such as a colloid, which adsorbs more strongly than the inactive form. This would be consistent with the observed variation of adsorption with concentration, if it is supposed that the two different gallium species compete for the same sites on the mica, but not on the glass beaker. ^{67}Ga could then be adsorbing on the glass at 10^{-2}M. This assumption seems very doubtful, but no better one is known to the author.

CONCLUSIONS

Comparison of Cations

The only cationic isotope adsorbing in usefully large amounts was ^{67}Ga. Adsorption of ^{57}Co was certainly much less than that of gallium, and of such a low amount that detailed experiments were impossible with the present techniques. It is not known for certain whether the more advanced of the techniques developed would have been successful for ^{131}Cs or ^{42}K, but adsorption of ^{42}K would probably be low.

These differences could be explained in terms of an ion-exchange process, at the sites derived from isomorphous substitution in the mica, if it were assumed that the equilibrium constants of exchange are such that more gallium is sorbed, at a given low concentration, than any of the other ions. The number of moles adsorbed at saturation will be the same for all ions, though. Since so little of the other ions was adsorbed, it was impossible to determine the maximum uptake, and the hypothesis of ion-exchange can be neither proved nor disproved.

Mechanism of Gallium Sorption

The evidence in the next chapter on kinetics of gallium sorption suggests that the gallium may be in the form of colloid-sized particles, which are adsorbed by the surface. This would be more likely for easily hydrolysed ions like gallium and iron, than cobalt, caesium and potassium, and this could explain the great differences in sorption properties.

The maximum amount of gallium adsorbed corresponds to about one gallium atom per 100 square Angstrom units. This is consistent with either sorption on to the exchange sites, or the formation of a monolayer of hydrous gallium hydroxide.

It is not consistent with adsorption of the gallium as colloidal particles, because a monolayer of such particles would contain much more gallium than a monolayer of ions, and it is difficult to see why adsorption should stop at less than a monolayer.

Edge Adsorption

From the results of the cobalt and gallium experiments it appears that the edges of the mica sheets have a definite adsorption capacity for cations.

In the case of cobalt the capacity per unit area is very much greater than the capacity of the face per unit area at low concentrations. For gallium, the edge capacity is equal to or less than that of the face at low concentrations, but adsorption on the edges saturates at a much higher concentration than that at which the face saturates, so that above about 10^{-4}M. the edge adsorption per unit area is greater than that of the face.

This conclusion conflicts with much of the interpretation of measurements on the cation adsorption and anion exclusion of clay minerals. It seems possible that the faces of clay minerals are not clean crystal cleavage planes as expected here, but are damaged or coated with impurities, in such a way as to give rise to a cation exchange capacity similar to the theoretically expected one. Alternatively, the 001 face in the present experiment may have been coated with some material which reduced the cation exchange capacity.

Fig. 9.1

Adsorption of ^{42}K on Mica

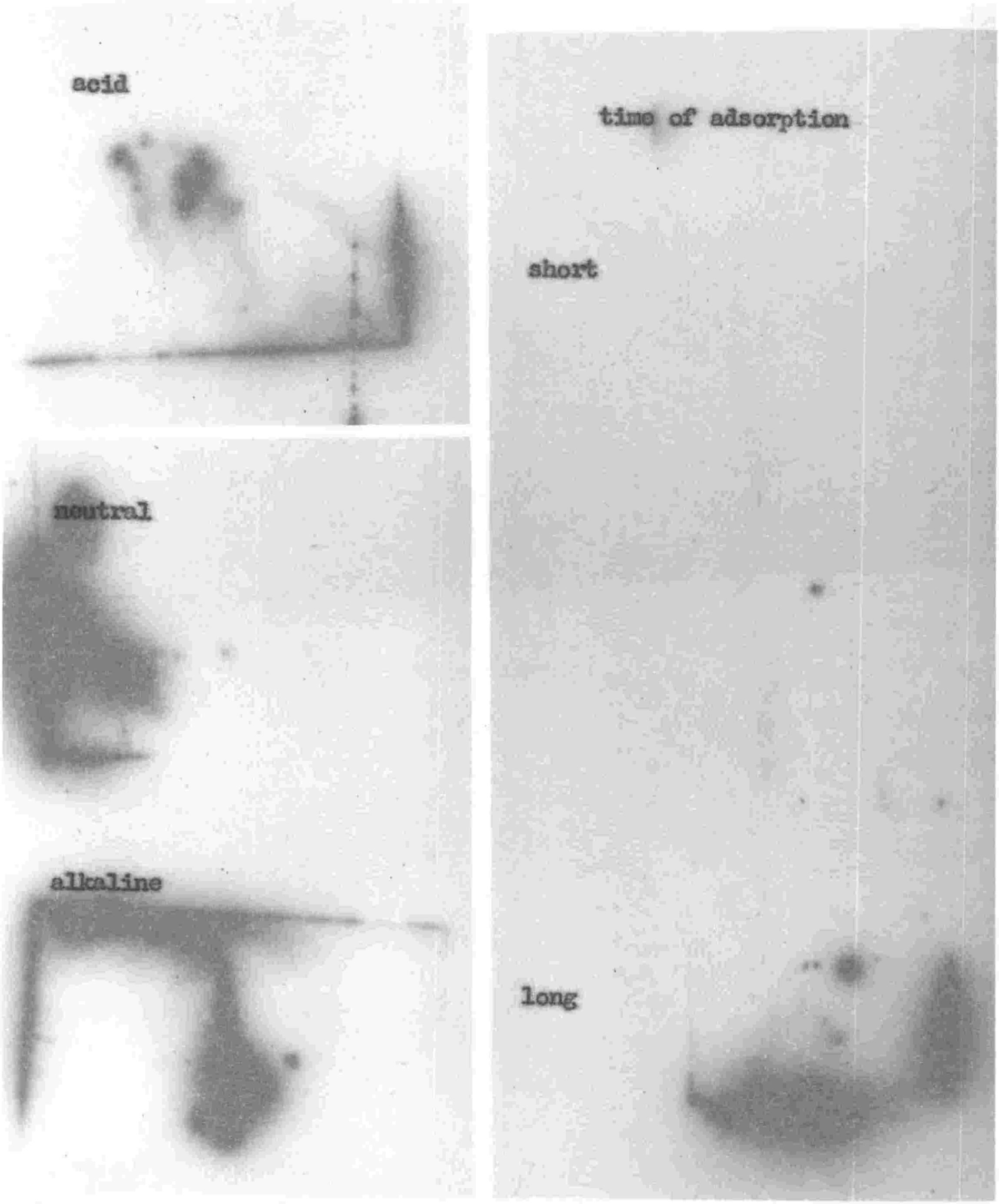
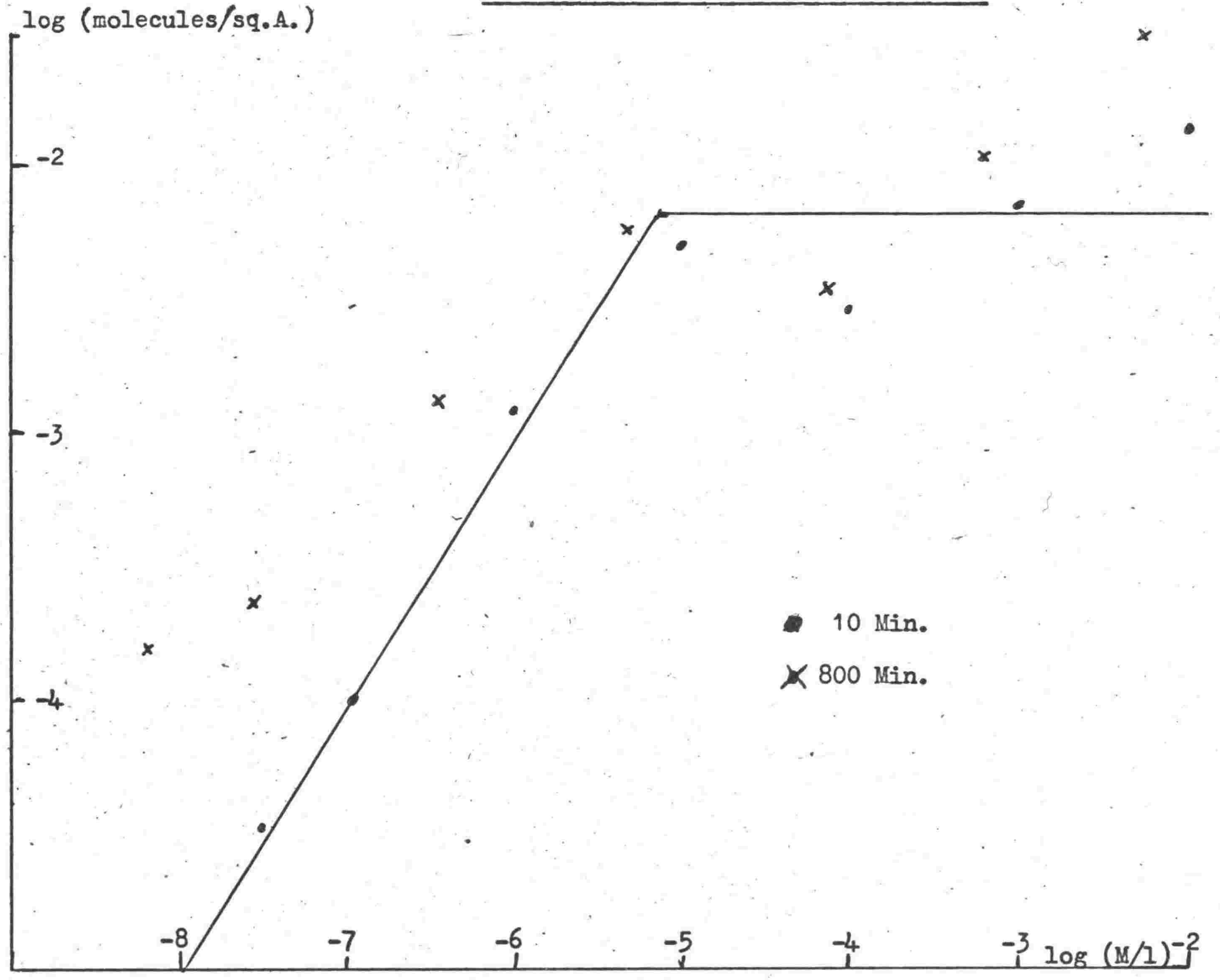


Fig 9.2 - ^{67}Ga Adsorption Isotherm



CHAPTER 10

KINETICS OF ^{67}Ga SORPTION

REASONS FOR PERFORMING THE EXPERIMENTS

A major reason for studying the kinetics of a surface reaction is to enable the proper planning of equilibrium experiments, so that adsorption can be carried to equilibrium, and the effect of losses in rinsing solutions can be estimated. This was not the main aim of the present experiments, for the "equilibrium" experiments were performed first, while the activity of the solutions was sufficiently high. The results will, however, enable such planning in future experiments, and aid in the interpretation of the previous ones.

The quantitative description of the changes with time could be expected to throw some light on the processes controlling the adsorption, and thus supplement the information obtained from the equilibrium studies. In has previously been found in this work that, by studying another aspect of the problem, one may gain information about factors which influence the results found from other experiments, but which cannot be separately recognised in them. This means that any new kind of experiment is well worth performing.

There are many variations possible in the experiments, and because of the short half-life and low pH of the gallium solution, only some of the most important factors were investigated. The author regards these experiments as exploratory, and considers that much work remains to be done.

CONDITIONS OF ADSORPTION EXPERIMENTS

Apparatus

Several small versions of the continuous adsorption apparatus described in Chapter 7 were used in these experiments. In most cases the count rate rose to several times the count rate from the solution alone, so that reasonable accuracy was obtained.

Adsorption Solutions

In order to get reasonable statistical significance for the ratemeter reading it was found necessary to use about 0.1 ml of pH 1 ^{67}Ga solution, diluted to the 5 to 10 ml volume of the adsorption vessels. This fixed the maximum pH at about pH 3, and the minimum would have been about 2.5.

Apart from fluctuations in pH due to variations in the dilution of the stock ^{67}Ga, the only controlled variable in the adsorption experiments was the concentration of carrier gallium added to the solution before putting the mica in contact with it. The amount of carrier ranged from none to 10^{-6} moles/litre.

PRESENTATION OF ADSORPTION DATA

Correction for Variations in the Maximum Amount Adsorbed

To compare the adsorption kinetics of various experiments the results should be expressed in terms of the count rate, corrected for the background, the count rate from the solution near the window, and the concentration of radioactive gallium in the solution. It was found that solutions with equal concentrations of ^{67}Ga gave rise to adsorption of greatly differing amounts of ^{67}Ga, so it was considered more useful to divide the count rates by the equilibrium count rate, instead of correcting for the solution concentration. (Autoradiographs showed that the adsorption was evenly distributed over the mica, so the variations were probably not due to unclean conditions.)

Decay Correction

The data have all been corrected for decay of the gallium, by multiplying the count rate by a factor derived from the decay of the ^{67}Ga in the time since the start of the experiment. This gave a constant equilibrium count rate, whereas the uncorrected count rate showed a maximum, so that this procedure gave the right kind of result. It may be argued that not all the gallium has been on the surface for the full time of the experiment, and should therefore not be corrected for, but the use of the correction allows for the lower probability of adsorption of a ^{67}Ga atom, because of the decay in the solution activity.

The Function Used

The adsorption data are plotted as $\log_{10} \frac{100(x'_\infty - x')}{x'_\infty - b}$ versus t, where x'_∞ is the measured equilibrium count rate, b is the initial count rate and x' is the measured count rate at time t. This function was chosen because the results looked as though they could be represented by an exponential approach to an equilibrium value, and this would be consistent with either an ion-exchange or diffusion model. The function is chosen to give a straight line graph if this is so, and to normalise all graphs to the same ordinate scale.

RESULTS OF ADSORPTION EXPERIMENTS

Comparison of Adsorption Kinetics at Different Gallium Concentrations

The results of the eight experiments completed are shown in figs. 10.1 and 10.2, each graph being drawn as described in the previous paragraph. There appear to be two kinds of graphs - those that are straight and those that are not. Two of the graphs shown in fig. 10.1 have values at the start of the run which do not fall on the later straight region, but this fast change is only a few percent.

Table 10.1 presents information about the different experiments, separated according to the group to which the experiment belongs. The author can see no correlation between the results and the techniques used. In the same table is presented information about the straight graphs which is used later in an attempt to explain the differences in the slopes.

It appears that there are as many points of difference between experiments performed at the same concentration as there are between experiments at different concentrations, so that concentration does not markedly affect the adsorption rate, below 10^{-6}M.

The Effect of pH on the Kinetics and Amount Adsorbed

After run 501 had come to an equilibrium, about .02 ml of 1M. HCl was added, which would have brought the pH down to about 2. This resulted in a rapid decrease in count rate, to a new equilibrium value.

Several hours later a few drops of 1M KOH were added, which shifted the pH to about 4. The count rate rose once more, but much more slowly than the previous fall.

The results of these experiments are plotted in fig. 10.3, as $\log(|x'_\infty - x'|)$ versus time, and it is seen that each change was exponential.

The Effect of Large Amounts of Gallium Added at Equilibrium

After four of the carrier-free experiments had come to equilibrium, or nearly to equilibrium, sufficient 0.2M. gallium chloride was added to bring the gallium concentration up to about 5×10^{-3}M. at which level the surface should have been saturated with gallium, according to the previous experiments. In each case there followed an almost immediate decrease of between 5% and 20% of the amount adsorbed, after which the decay-corrected count rate remained constant.

Addition of a similar quantity of pH 3 HCl made no change in the rate, so that it was not a pH or dilution effect.

This result poses some interesting questions, discussion of which will be given in the theoretical sections of this chapter.

pH Effects After Adding Gallium to the Solution at Equilibrium

After the count rate had come to a new constant value after adding $GaCl_3$, HCl was added to the solution. Decreasing the pH to about 2 made no difference to the count rate, in great contrast with the carrier-free situation. In two experiments 0.1 ml of 10M. HCl was added, to decrease the pH to about 1. This produced a decrease in the count rate, with about a third of the total change being over in the first half hour, with a rate which decreased with time. The remainder of the change, in both cases, was with a constant rate of change (fig. 10.4).

This constant rate of change is difficult to explain. It is unlikely to be due to an accidental combination of changes, because the two cases in which it occurred were not identical. It could be due to diffusion across a film, with a constant concentration on both sides, but this would require the concentration of active gallium near the surface to be independent of the amount on the surface. This could be so if the material on the surface had a constant solubility product, which is a quite different assumption from that used later to explain the kinetics at low concentrations.

This effect, and the lack of exchange between gallium in solution and surface adsorbed active gallium, may indicate that the nature of the adsorbed material has been drastically altered by the addition of the gallium.

CONDITIONS OF DESORPTION EXPERIMENTS

Apparatus

The circulating apparatus described in Chapter 7 was used for all these experiments, with a scintillation counter being used to detect the γ-rays from the sample. The counter detected the activity in that part of the solution which was in the sample chamber, as well as that on the sample. It was found that because of this effect the scintillation counter detected about 1% of the activity removed from the sample, if the solution was not changed, and this could lead to significant errors when less than 10% of the original amount remained on the sample. The solutions were changed whenever 50% or less of the activity present at the previous change remained on the surface.

Preparation of Samples

The mica samples were freshly-split, and immersed in solution containing ^{67}Ga, and, sometimes, carrier to 10^{-6}M., for 10 minutes. These solutions were contained in specially made beakers with flat sides (fig. 7.6) so that a small amount of solution (about 7 ml.) could be used to treat the samples.

After this treatment the sample was briefly rinsed with distilled water, three edges were cut off, and it was inserted in the sample holder. The last edge was cut off and the holder inserted into the apparatus.

RESULTS OF DESORPTION EXPERIMENTS

The Effect of Various Reagents on the Desorption Rate

A sample was prepared as above with a 10^{-6} M. gallium solution, and desorbed into pH 5.5 distilled water. A small change occurred rapidly at first, but after the first few minutes changes were very slow, being mostly, but not entirely, due to decay. Reagents were added to the desorbing solution, and flushed out with distilled water after observing their effect.

Adding potassium chloride to 0.1 M. concentration did not affect the desorption rate, and neither did 0.01 M. $CaCl_2$, 0.01 M. ammonium oxalate at pH 4, potassium hydroxide at pH 12, or 0.01 M. $AlCl_3$ at pH 3.5.

Adding HCl had no effect until the pH was near pH 3, below which a rapid increase in the rate of desorption was found. (It should be noted that this was the pH of the adsorption solution.)

The lack of effect of most of these reagents suggests that the desorption rate was not being controlled by the probability of ion-exchange with components of the solution. The effect of pH below pH 3 probably indicates that some new mechanism was coming into action.

Comparison of Desorption Experiments at Various pH's

Desorption experiments were performed in which the pH of the desorbing solution was held constant, at pH 5.5, 3 or 2. The adsorption solution was at pH 3 and either carrier-free or 10^{-6} M. In all cases except one the acid was HCl, the exception being H_3PO_4 at pH 2.

The results are presented in fig. 10.5, in which the percentage of the initial count rate is plotted as the logarithm of the time. Bearing in mind that $\frac{dx}{dt} = \frac{1}{t} \cdot \frac{dx}{d(\log(t))}$, the rate of desorption is seen to increase very much as the pH is lowered.

It is apparent that using H_3PO_4 instead of HCl does not decrease the rate of desorption. One would expect phosphate to be adsorbing on to the surface under these conditions, and it seemed possible that the phosphate would prevent the gallium desorption. This does not happen.

INTERPRETATION OF GALLIUM SORPTION KINETICS

Results to be Explained by Theory

It is clear from the data in figs. 10.1 and 10.2 that different processes are occurring in different adsorption experiments performed under supposedly similar conditions. It must therefore be concluded that the conditions of adsorption were insufficiently well controlled. The Bt/t plots for spherical particles are shown in fig. 10.2 for those experiments not giving an exponential change, and they are sufficiently non-linear that it can be said that diffusion into a set of similar spheres is not occurring. From the similarity previously found between plots for this model and the thin planar sheet model, it can be said that the latter model is also inapplicable.

No satisfactory explanation for these results was found, and it seems likely that they indicate the existence of unknown phenomena. The discovery of an explanation for them might well throw a new light on the whole process.

It seems reasonable to regard the results in fig. 10.1 to be the ones which the theory should describe. The theory should, if possible, take into account the effect of the solution pH on both the desorption rate, and the equilibrium amount adsorbed. Other points to be explained are the lack of effect on the desorption kinetics of cations other than hydrogen, and the lack of effect of extra gallium on the amount adsorbed at equilibrium in adsorption experiments.

A Reaction-Rate Theory for the Kinetics

Let us assume that the amount of gallium on the surface is the result of an equilibrium, in which the probability of forming a surface complex, S-Ga, in a short time, dt, is proportional to the concentration of Ga in the solution, and the probability of the reverse reaction in the same time is proportional to the amount of S-Ga. The first assumption agrees with the observation that the rate of adsorption of ^{67}Ga is independent of the amount of carrier present, at concentrations less than 10^{-6}M., and the second will ensure that exponential variations are obtained. We may write:

$$\frac{d[S\text{-}Ga]}{dt} = L[Ga] - M[S\text{-}Ga]$$

where L and M are the proportionality constants for the forward and back reactions. Solving this equation gives

$$[S\text{-}Ga] = \frac{1}{M}\left(L[Ga] - Ne^{-Mt}\right)$$

where N is a constant to be fitted to the boundary conditions. This leads to the conclusion that the equilibrium amount adsorbed equals $L[Ga]/M$.

Writing R for the count rate due to [S-Ga], and R_∞ for R at $t = \infty$, we get

$$\log (R_\infty - R) = \log (N/M) - 0.4343\ Mt \qquad \underline{\text{if } R_\infty > R}$$

or

$$\log (R - R_\infty) = \log (-N/M) - 0.4343\ Mt \qquad \underline{\text{if } R_\infty < R.}$$

This agrees with the results in fig. 10.1, and predicts that the desorption results should show an exponential variation with time.

Also, R_∞ is proportional to L[Ga]/M, so that MR_∞ is a constant, if L and [Ga] are constant. The half-life of the process is inversely proportional to M, so that with decreasing pH M must increase. The theory predicts that if M increases, the equilibrium amount adsorbed decreases, in such a way that the product MR_∞ is constant, provided that L has not been altered by the change in pH.

This theory is consistent with the lack of effect of adding cations to the desorption solution, for in that case only the first order desorption process is occurring.

The only major difficulty is found when considering the effect of adding more than sufficient gallium to saturate the surface. We shall consider the equilibrium amounts of active and inactive species adsorbed at total concentrations greater than those required to saturate the surface. Writing the amounts per unit area of active and inactive species on the surface as c^* and c respectively, we can say that

$$c + c^* = s \qquad \text{(s is a constant).}$$

At equilibrium the specific activity of the gallium on the surface must equal that of the gallium in solution. Writing V and V^* for the concentrations of inactive and active gallium in the solution, we have

$$c/c^* = V/V^*.$$

Therefore, $c^* = S/(1 + \frac{V}{V^*}) \doteqdot \frac{sV^*}{V}$.

Regarding this as a relation between c^* and V, at constant V^*, and writing c^*_{sat} for the value of c^* at a solution concentration of V_{sat}, at which the surface is just saturated, we have

$$c^* = c^*_{sat} \frac{V_{sat}}{V}.$$

Thus the amount of activity on the surface after adding carrier should be less than that before, by a factor equal to the ratio of the concentration required to saturate the surface to the new concentration (c^*_{sat} equals the constant amount adsorbed at $V < V_{sat}$.) In the present experiments this ratio was about 0.01, so that nearly all the activity should have been removed.

The rate of the change should be equal to the rate of decrease in a desorption experiment, and so should be easily detectable.

The lack of effect of carrier can only be explained on this model by supposing that once the surface concentration reaches a certain level, exchange between the surface and solution is no longer possible. This might occur if many gallium atoms became joined together in a polymeric hydroxide or hydrous oxide.

A Diffusion Theory for the Kinetics

It is assumed in this theory that the rate-limiting process is the diffusion which occurs through a non-absorbing medium, of thickness l, between the stirred solution and the mica surface. There are R counts/minute/cm^2 adsorbed, and the adsorbed material is concentrated in a planar layer near the surface.

It is assumed that R is proportional to the concentration C_s in the solution immediately adjacent to the surface. This could be due to an equilibrium similar to that postulated in the previous sub-section, but could also be a result of electrostatic forces in a double layer. Thus it is assumed that

$$R = qC_s$$

where q is a constant which may vary with conditions other than C_s, for example, pH.

It will also be assumed that the concentration gradient within the diffusion layer does not change with distance from the mica. This is equivalent to supposing that there are large reservoirs for the diffusing material at both boundaries.

The bulk solution concentration is V counts/minute/ml, and the concentration at distance x from the mica is C.

From Fick's first law we have

$$\frac{dR}{dt} = k\frac{dC}{dx},$$

so that

$$\frac{dC_s}{dt} = \frac{k}{ql}(V - C_s) = B(V - C_s)$$

where

$$B = \frac{k}{ql}.$$

This equation is very similar to the equation obtained in the previous sub-section, and its solution may be written as

$$C_s = V - \frac{N}{B} e^{-Bt}$$

and thus $R = q(V - \frac{N}{B} e^{-Bt})$

where N is a constant fixed by the boundary conditions.

For adsorption, $R = 0$ at $t = 0$, so $N = B$, and

$$R = qV\ (1 - e^{-Bt}).$$

For desorption, $R = R_o$ at $t = 0$ and $V = 0$, so

$$R = R_o e^{-Bt}.$$

When the pH is changed, without altering V, one can suppose that the hydrogen ions diffuse into the surface layer much faster than the gallium diffuses out. This changes q from q_1 to q_2, and thus alters the value of C_s. If R_o is the equilibrium amount adsorbed before the pH change,

$$R_o = q_1 V.$$

The pH change results in an instantaneous change in C_s, without altering R.

Thus, at $t = 0$, $q_1 V = q_2(V - \frac{N}{B})$

so that $\frac{N}{B} = V(q_2 - q_1)/q_2$.

This leads to $R = q_2 V(1 - \dfrac{q_2 - q_1}{q_2}\ e^{-Bt})$, which can be re-written as

$$R_\infty - R = (1 - \frac{q_1}{q_2}) R_\infty e^{-Bt},$$

where $B = k/lq_2$.

Since $R_\infty = q_2V$, $BR_\infty = kV/l$, and is constant. Thus the product of the slope of the logarithm plot and the equilibrium amount adsorbed is constant.

This same conclusion has already been derived from the reaction rate theory. In fact, the forms of the equations from both theories are so similar that experimental evidence cannot be used to distinguish them. Even the assumption that q decreases with decreasing pH may be regarded as a consequence of an increase in the desorption part of an equilibrium at the surface.

Which theory is preferable depends mainly on the assumptions one is prepared to make. One can choose to accept either a very small diffusion coefficient or a very slow rate.

Application of Theory to the Results of Run 501

In this experiment , described in the section on the results of adsorption experiments, the pH was varied when equilibrium had been reached. The kinetics of the changes are presented in fig. 10.3, and the changes were all exponential functions of time as predicted on either theory.

For all these changes the concentration of the solution was approximately constant, and it seems reasonable that k and l might be constant. It is less clear whether L in the reaction-rate theory should be independent of pH. The values of BR_∞ from the three parts of this experiment were as follows -

	R_∞	B	BR_∞
First adsorption	2460	0.34	840
Second adsorption	1320	0.74	970
Desorption	360	3.4	1230

The desorption values are the least accurate, because of the small difference between the equilibrium count rate and that of the solution, and it would be reasonable to expect a possible error in this case of 20% in the value of R_∞. The three values of BR_∞ are probably not significantly different from each other.

Both theories are therefore in agreement with the results of this experiment. However, it seems likely that the effect of low pH would be to decrease the negative charge of the surface, and therefore slow down the adsorption. This is equivalent to saying that L should decrease, and therefore decrease the product MR_∞ at low pH. This was not found, so the diffusion theory is preferred.

Use of the Theories to Compare the Adsorption Experiments

The theories predict that the produce BR_∞ should be proportional to either LV or kV/l, where L is the adsorption rate constant in the reaction-rate theory. In either case the product is expected to be proportional to V, and substantially independent of other factors, such as the value of q. The count rate of the solution, R_s, could be assumed proportional to V, the solution concentration of radioactive material. However, a correction needs to be made for the attenuation of the radiation in the mica.

Since with ^{67}Ga it is mainly the initially mono-energetic internal conversion electrons which are being detected, it is a reasonable approximation to assume that there is a distance, r mg/cm^2, which equals an effective range of all the electrons. If the amount of material between an atom and the Geiger counter is less than r then its internal conversion electron will be detected, but if it is greater than r the electron will be stopped before reaching the counter. This is an over-simplification, but the measurements of attenuation of ^{57}Co internal conversion electrons, reported in the appendix on nuclear radiation detection, suggest that it is sufficiently good for a qualitative description.

Thus, we may assume that the count rate, R_s, due to the solution, is proportional to $V(r - a)$ where a is the mica thickness in mg/cm^2.

The constant of proportionality is the same as that relating the activity adsorbed and R_∞, so that

$$\frac{BR_\infty}{R_s}(r - a) \text{ is constant.}$$

Thus we have $\dfrac{BR_\infty}{R_s} = K(r - a)$. (K is a constant.)

In table 10.1 the values of $\dfrac{BR_\infty}{R_s}$ and a for each of the exponential adsorption experiments are shown. There is clearly no correlation between these two quantities, so that some uncontrolled variation in the adsorption conditions must have been present in these experiments, also.

Comparison of Desorption Kinetic Data with Theory

The desorption data is presented as graphs of log (% count rate) versus time in figs 10.6 and 10.7. It is clear that the graphs are far from linear, so that the theory is inapplicable. Attempts to derive straight lines by subtraction of constant or varying terms failed.

Autoradiographs were made of the samples after desorption, and there was no evenness, the presence of which would have suggested contamination.

CONCLUSIONS REGARDING THE KINETICS OF GALLIUM SORPTION

Adsorption Results

The reproducibility of the adsorption experiments was not as good as could be expected from the work in Chapter 9. Most of the results fit a simple theory, though, and some of the implications are discussed here.

The half-lives of the adsorption processes range from 2 to 10 hours. The author feels this is too slow to be reasonably attributable to an ion-exchange reaction limited by an exchange-rate step. His reason is that such rates are not normally found in ion-exchange reactions unless diffusion is important, but it is, of course, possible that reactions on mica surfaces could be unique. An ion-exchange reaction should also be affected by the presence of other ions, but this was found not to happen.

If a diffusion hypothesis is put forward, then one has that $\frac{k}{l}$ = BR_{∞}/V. This ratio will be equal to about .02 times the value of

R_∞ slope/$(0.434R_s)$, since R_s would be the count rate from about 20 mg/cm^2 of solution, instead of 1 cm^3 of solution. This gives $\frac{k}{l} \doteq 0.1$ cm/hr $\doteq 3 \times 10^{-5}$ cm/sec.

It seems unreasonable that l should be much greater than 10^{-3}, so that $k < 3 \times 10^{-8}$ cm/sec, which is considerably smaller than diffusion coefficients for single ions. Mysels (1959) shows that the diffusion coefficient of a particle of radius a is $2.15 \times 10^{-13}/a$. Substituting $k = 3 \times 10^{-8}$ gives $a \doteq 10^{-5}$ cm = 1000 Angstrom units.

This is a reasonable diameter for particles in a gallium solution at 10^{-6}M., but it would be surprising if the same sized gallium particles were present in a carrier-free solution. Mellish et al (1964) have shown that the particle size in dilute yttrium solutions at pH 11 decreases rapidly with concentration, being about 3000 Angstrom units at 10^{-5}M., 2000 Angstrom units at 10^{-6}M., and less than 50 Angstrom units in carrier-free solution. However, all these results were obtained in solutions where very great care had been taken to remove all extraneous particles from solutions, whereas in the present experiments these precautions had not been taken. The results of Mellish et al. suggest that in experiments such as the present ones the carrier-free solutions may consist of suspensions of very small colloidal particles of inactive material, on to which the ions are adsorbed. This might explain why the particle size appears to be similar to that at greater concentrations, despite the much smaller amounts of gallium adsorbed.

The results obtained for the kinetics at 10^{-6}M. are consistent with the high-resolution autoradiograph experiment. If the radius of a particle is 1000 Angstrom units, then it will contain about 2×10^7

gallium atoms, assuming that there are about six water molecules per gallium atom. The autoradiographs required that there be more than 10^6 particles per square centimeter, so this means there are at least 2×10^{-3} gallium atoms per square Angstrom unit, which is about the value found from the isotherm experiment, at 10^{-6}M.

Additional evidence that colloidal particles with positive charges will be adsorbed if they are present is provided in a paper by Follett (1965). This author studied the adsorption of colloidal "ferric hydroxide" by kaolinite particles at pH 2 - 4.4, using electron microscopy. He found that the particles, of diameter 30 - 100 Angstrom units, were adsorbed uniformly over the silicate surface of the kaolinite particles, and that they were not able to be displaced by pH 1 HCl. In this case the particles were found to adsorb very quickly, as would be expected from their small radius, but it is conceivable that the gallium might be larger, and therefore slower.

Desorption Results

No satisfactory explanation of the gallium desorption kinetics has been developed. It is possible that the apparatus used gave a greater flow rate over some parts of the sample than others, and thus a variation in the thickness of the layer through which the diffusion occurred. This would be expected to lead to non-uniformity of the activity remaining on partially desorbed samples, but autoradiographs were made, and this was not found.

Another explanation might be that although the particle size range for adsorbing particles was narrow, after adsorption some change in the size distribution might have occurred, thus giving a wide range of diffusion coefficients.

Effect of pH

The amount of gallium adsorbed by the surface is strongly dependent on pH, below pH 3. This could be due to several reasons. One is competition for a limited number of cation exchange sites. Another is that hydrogen ions could adsorb on the surface and electrostatically repel the positively charged gallium ions or particles.

Another possibility is that the sites on which the gallium is adsorbed are formed by dissociation of an O-H group. This will be repressed by a common-ion effect at low pH.

Yet another is that the gallium is present as gallium hydroxide (solid) at pH 3, and that these particles dissolve in the more acid solution. Much more work remains to be done before this is fully explained.

Exchange of Gallium

This phenomenon does not appear to occur. The replacement of gallium by other cations in a desorption experiment also does not occur, so that the desorption is not a simple cation exchange between the surface and the solution.

One automatically assumes that an exchange process limits the equilibrium amount adsorbed in an adsorption experiment, at concentrations less than those required for saturation, but adding a large amount of carrier does not lead to desorption of most of the adsorbed gallium. The author postulates that when the surface is saturated with gallium, the atoms become linked into a polymeric sheet, attached to the mica at many places. There is then a very low probability that an isolated group of atoms will lose contact with the sheet and the mica simultaneously.

That this kind of effect is not an isolated case is shown by an experiment of A. G. Langdon (personal communication). He found that the rate of desorption of ^{55}Fe adsorbed on to a surface in the presence of sufficient carrier to saturate the surface, was very much slower than the desorption rate from surfaces with less carrier.

TABLE 10.1

DATA FROM ^{67}Ga ADSORPTION KINETICS EXPERIMENTS

Run No.	Carrier Concentration	Volume Vessel	Volume Acid	$\frac{\text{Volume Acid}}{\text{Volume Vessel}}$	Slope	R_∞	R_s	$\frac{.434\ R_s}{R_\infty \cdot \text{slope}}$	$a(mg/cm^2)$
504		5.0	.05	.010					
510	10^{-7}	9.0	.10	.011					
505		6.8	.05	.0074					
501		5.0	-	-	0.15	3000	1350	1.3	8.5
506	10^{-6}	6.8	.10	.015	0.12	400	620	5.6	8.8
509		6.8	.06	.0088	0.15	830	400	1.3	7.6
511	10^{-8}	9.0	.10	.011	0.035	2240	1360	7.5	5.8
512		6.8	.07	.010	0.075	760	300	2.3	5.5

Fig 10.1 - ^{67}Ga Adsorption Kinetics

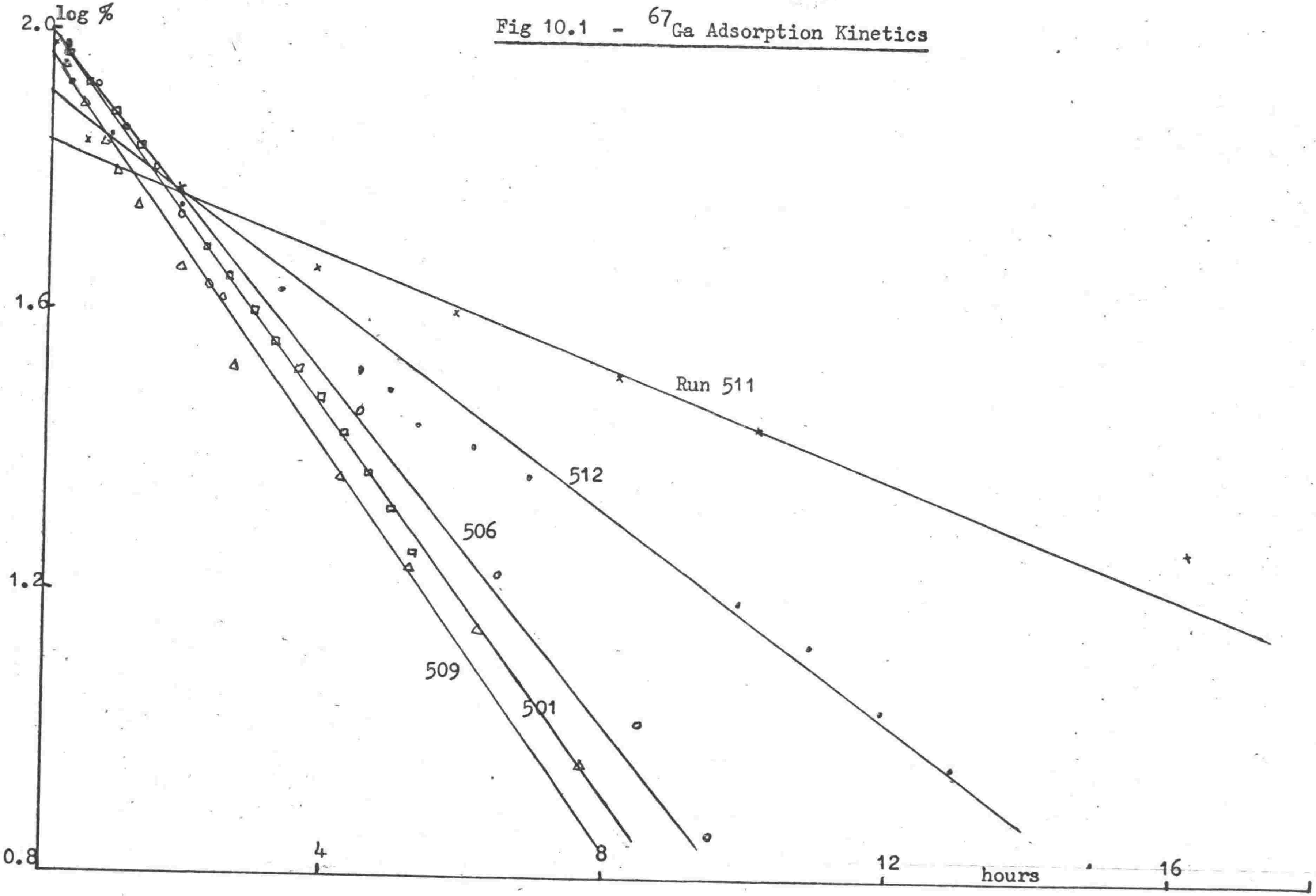
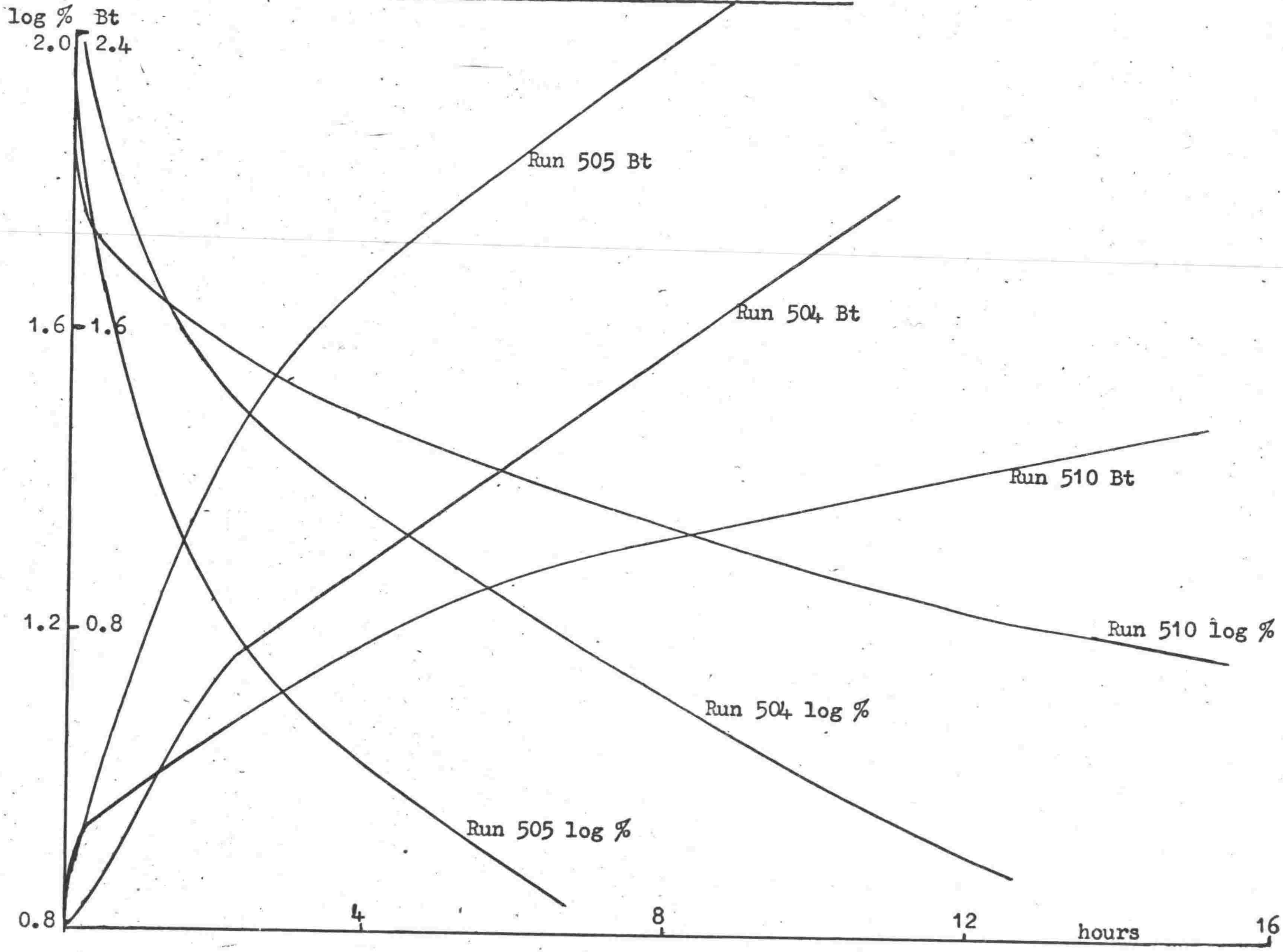


Fig 10.2 - ^{67}Ga Adsorption Kinetics



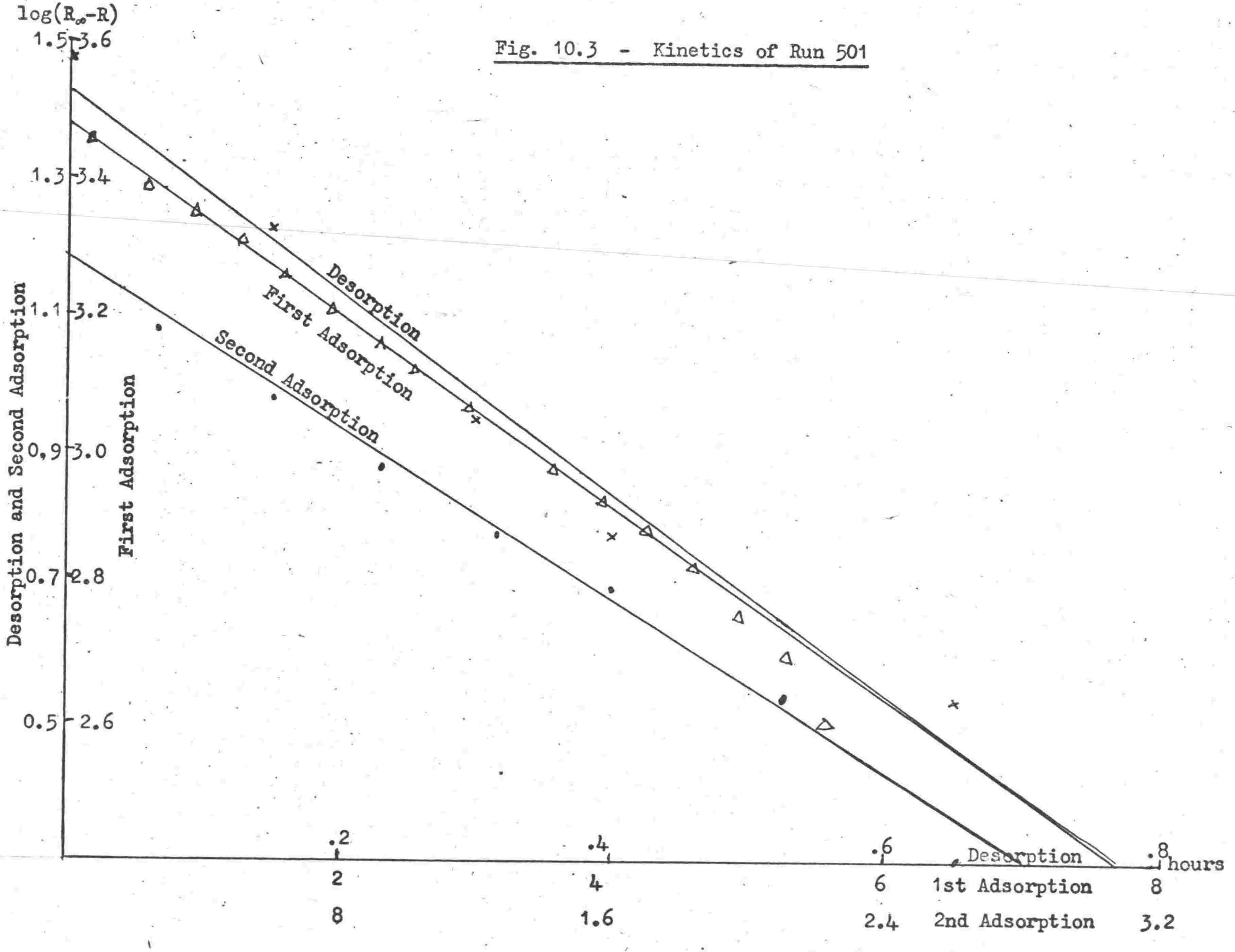


Fig. 10.3 - Kinetics of Run 501

Fig. 10.4

Desorption of ^{67}Ga at Low pH After Adding Carrier

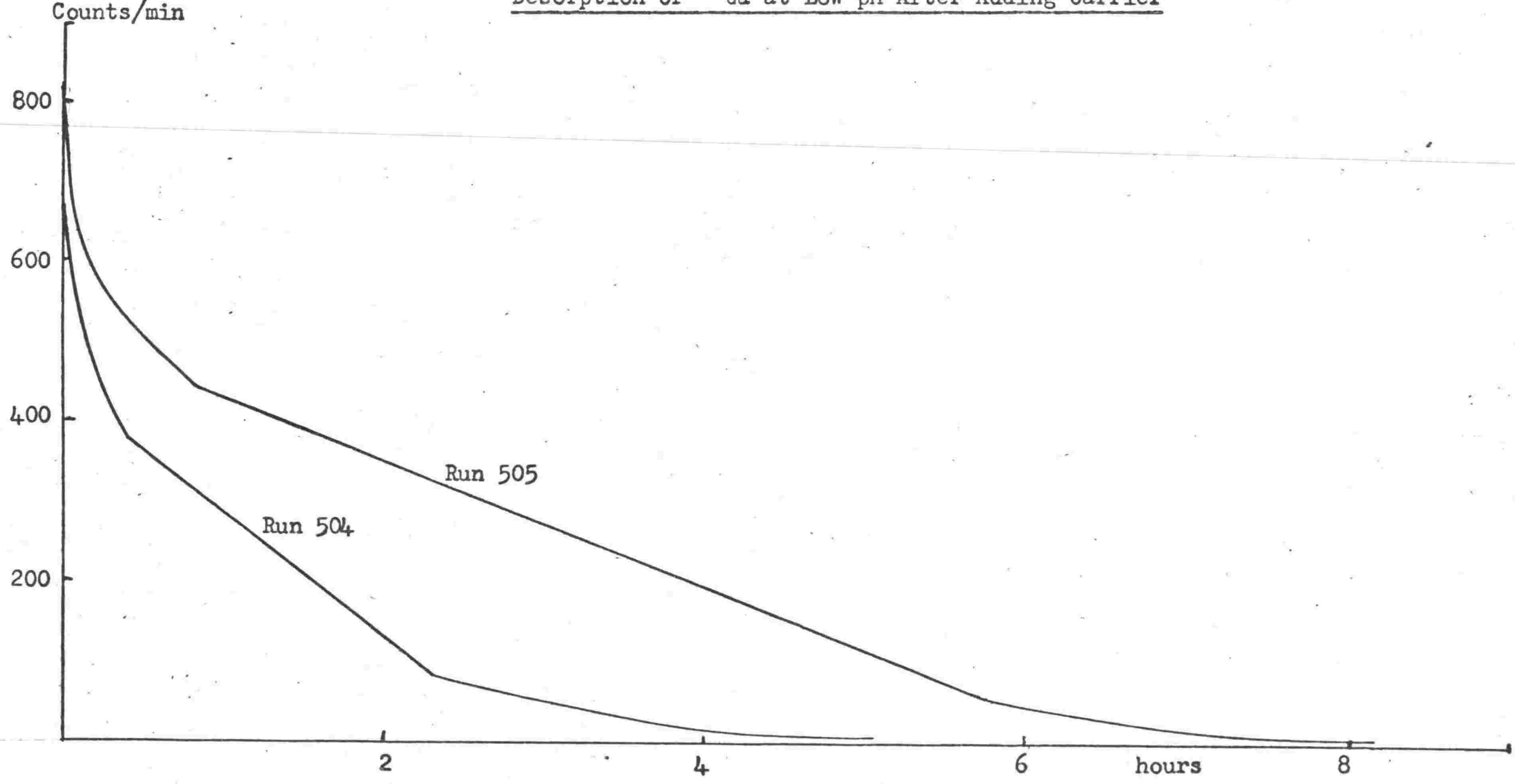


Fig. 10.5 - Desorption of ^{67}Ga

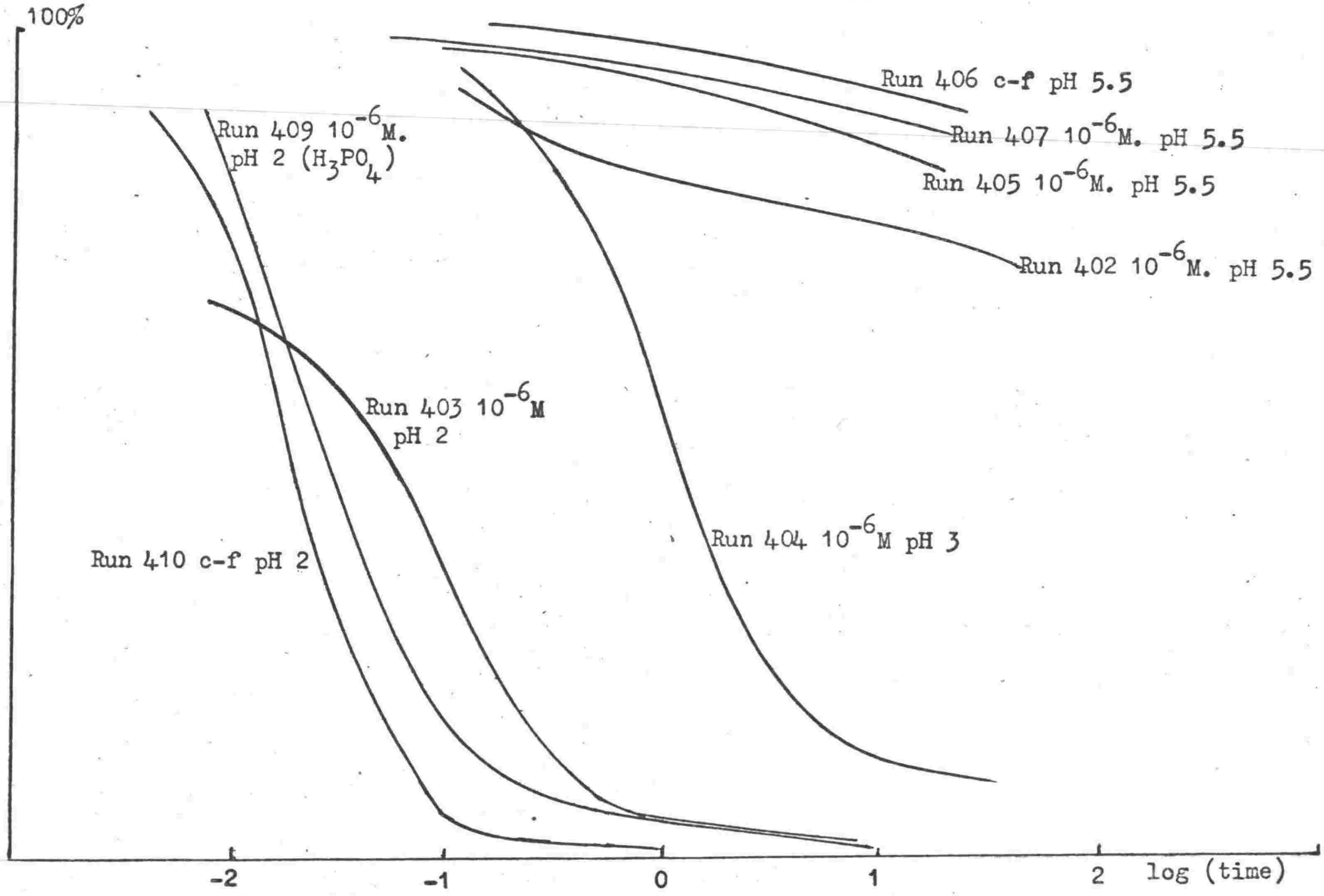


Fig 10.6 - ^{67}Ga Desorption Kinetics pH 2

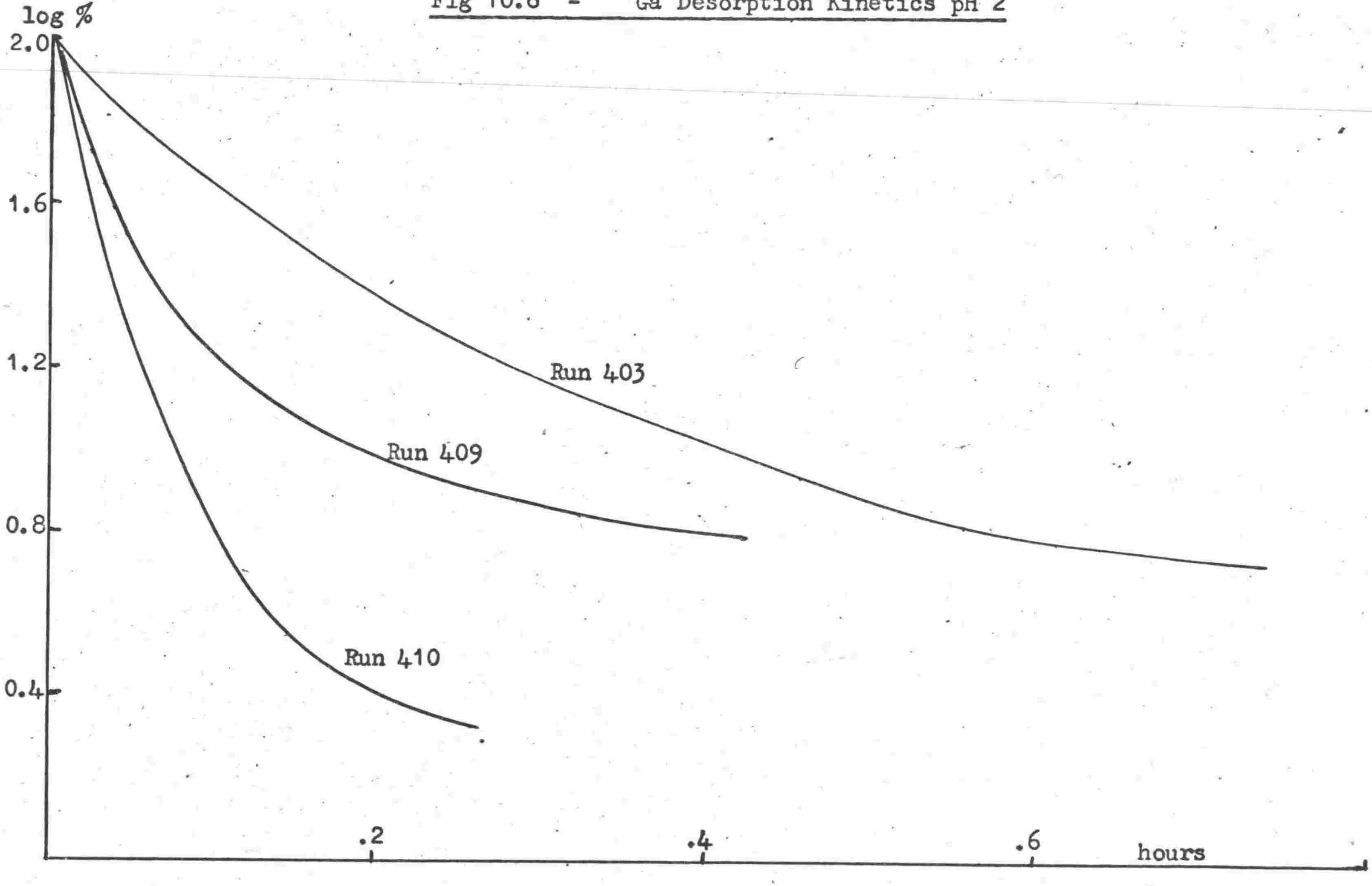
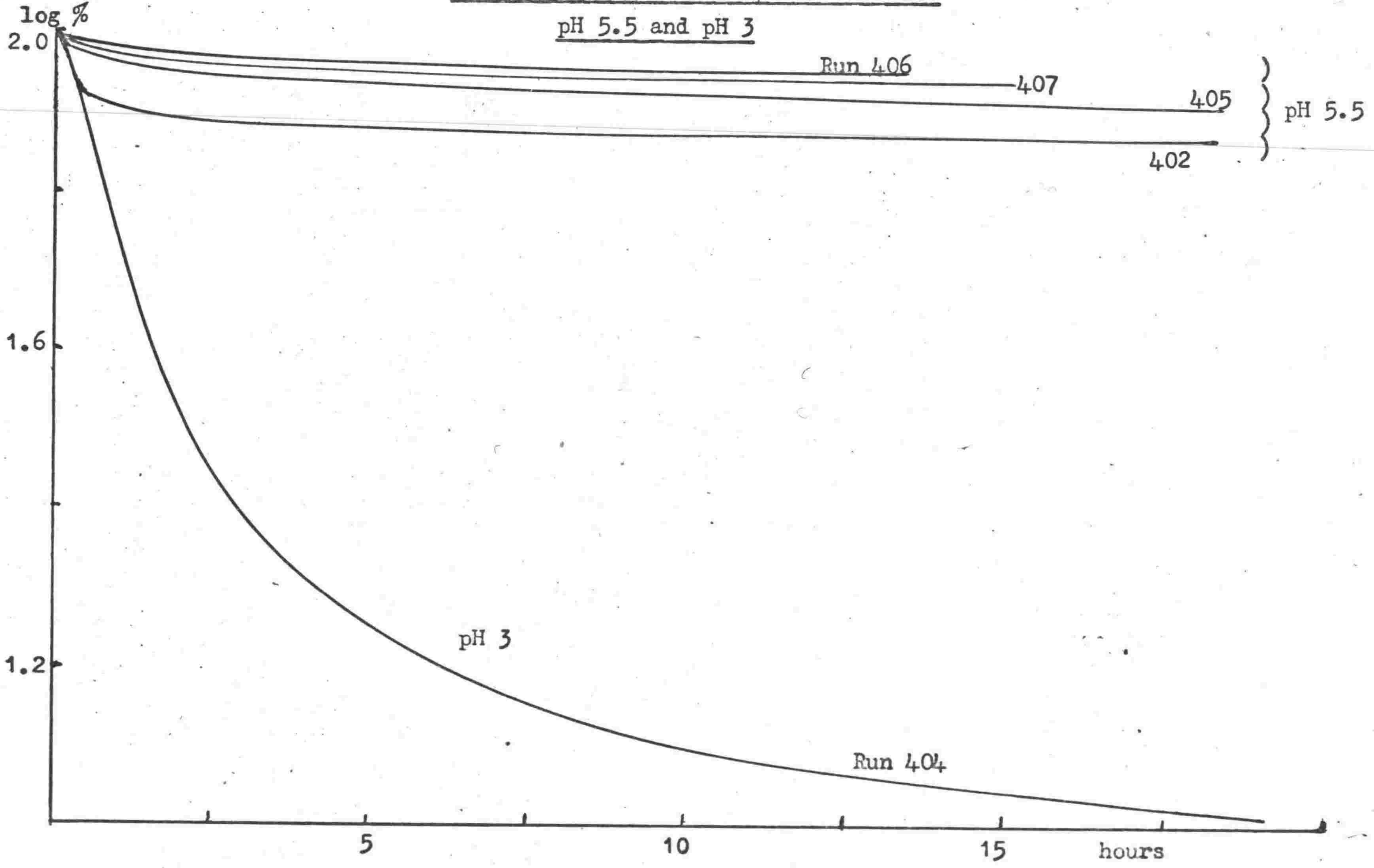


Fig 10.7 - ^{67}Ga Desorption Kinetics

pH 5.5 and pH 3



CHAPTER 11

EXTENSIONS OF THE TECHNIQUES WHICH ENABLE THE MEASUREMENT OF ADSORPTION ON SURFACES

INTRODUCTION

A major difficulty in the study of the surface chemistry of soil minerals is that several different kinds of adsorption site are possible on each mineral, so that it is difficult to decide which of several alternative sorption mechanisms are operating in a particular experiment. In the present thesis this difficulty has been largely avoided by using as a sample a large single crystal of mica, in such a way that only the sorption which occurs on the 001 cleavage plane is measured. This technique could clearly be immediately extended to the study of any other crystals which may be cleaved to produce areas greater than a few square millimeters of single cleavage planes. Such crystals are unfortunately few in number.

An alternative approach, presented here, is to measure the adsorption of a system in which two kinds of surfaces occur, and correct, if necessary, for the known adsorption of one of them.

The system used for the experiments was the fracture zone produced at the edge of the sheet of mica when cutting it with scissors. The adsorption on this edge varied considerably, even along one edge, and this was probably due to variations in the shattering of the edges caused by the scissors used to cut the mica. It is, however, possible and useful to make approximate measurements.

The edge adsorption was low on mica which had been treated with aluminium, so the measurements were made on the untreated mica.

TECHNIQUE USED

A sheet of clean mica 12 mg/cm^2 thick was prepared in the usual way, and cut into ¼" wide strips with stainless steel scissors cleaned in a hot sulphuric acid/nitric acid cleaning bath. The strips were placed respectively into carrier-free, 10^{-6}, 10^{-4}, or 10^{-2} molar phosphate solutions at pH 5.5, each solution containing 10^4 counts per minute per ml. of P-32 phosphate. After 10 minutes the strips were removed, rinsed with distilled water from a wash bottle, dried and autoradiographed.

The adsorbed radioactivity was nearly all on the edges, as expected. Strips 1 mm. wide were cut off around the edges, cut into short sections, and counted in the same counting arrangement used for the solution activity determination.

RESULTS

The adsorption was determined for each of the three edges of the strips, the values found being shown below -

Solution Concentration (Moles/litre)	Solution Activity (Counts/min/ml.)	Counts/min/cm L.H.S.	Bottom	R.H.S.
Carrier-free	1.4×10^4	100	400	400
10^{-6}	0.9×10^4	30	200	60
10^{-4}	0.9×10^4	10	-	10
10^{-2}	0.7×10^4	-	-	-

The fact that the adsorption of activity decreased with increasing carrier concentration shows that the activity was not due to the material left behind when the solution trapped in the cracks in the edges dried.

The activity of 100 c/min/cm corresponds to the amount of activity in .01 cm^3 of solution per cm of edge. Therefore, this figure corresponds to the adsorption on one edge of all the phosphate from a volume of solution equal to the entire volume of the mica. This volume is clearly too large to be trapped in the cracks of the edge, and this confirms the previous conclusion.

The thickness of the edge was of the order of 10^{-2} cm. Microscopic examination of mica edges showed that the shattered zone extends from the edge to a distance approximately equal to the mica thickness, so that for comparison with the activity adsorbed by aluminium-treated mica, the 100 c/min/cm can be assumed to be spread over an area of 0.01 cm^2. The activity per unit area was therefore 10^4 c/min/cm^2, so that the adsorption ratio of the untreated edges was about 1 cm.

The adsorption ratio of the untreated 001 face was previously found to be of the order of 10^{-4}cm, so that the edges adsorb about 10,000 times as much phosphate per unit area as the face, from carrier-free solution. This adsorption could be due to the adsorption on a large 001 face area exposed by the separation of the cleavage planes which might have occurred during cutting, but this would require the presence of 10,000 such planes. Since the thickness of the mica was of the order of .01 cm, this would require that 20% of the theoretically possible cleavage planes were exposed. This seems unreasonably high, when it is considered that the mica is difficult to cleave.

Thus some sorption must be occurring on the broken edges exposed by cutting the mica.

The autoradiographs of the aluminium-treated mica showed no extra adsorption on the edges when the phosphate solutions were aluminium-contaminated, and seldom showed edge adsorption when the mica was washed for 30 minutes. This implies that the adsorption ratio on the aluminium-treated mica edges was no greater than that on the face. Thus the adsorption ratio on the aluminium-treated edges was less than 0.1 cm, whereas the adsorption ratio on to the untreated edges was greater than 1 cm.

Treatment of the edges with aluminium solutions therefore reduces the amount of phosphate adsorbed by the edges. This could be explained in two ways. The aluminium may be adsorbed by the edges to such an extent that it (and its associated water molecules) fills the spaces between the shattered layers. The phosphate then sees a relatively flat surface of aluminium hydroxide, rather than the very great area of shattered mica. On the other hand, the phosphate may be adsorbed on to particles of aluminium hydroxide in solution, and these may be too large, or of the wrong charge, to be adsorbed by the edge.

CONCLUSIONS

The above experiments show that the broken edges of freshly cleaved mica crystals absorb up to 10,000 times more phosphate per unit area than the 001 cleavage plane. This enhanced adsorption of the broken edges is almost completely suppressed when aluminium ions are adsorbed on the mica crystals.

This result confirms the widely held belief that broken edges of mica-type minerals may have anion-adsorption sites.

It would be possible to extend the measurements to examine the kinetics of phosphate uptake by edges, and to study the effect of treating the edges with reagents which might enhance or reduce the adsorption.

CHAPTER 12

CONCLUSIONS

TECHNIQUES

The earlier experiments showed that the kind of cleanliness common in ordinary chemical experiments is quite inadequate for experiments of the kind performed here. Techniques were therefore developed which gave a standard of cleanliness which was shown to lead to reproducible and self-consistent results.

Radiochemical methods were developed which enabled the total amount of anions or cations adsorbed on mica surfaces to be measured. Techniques were developed which enabled the continuous measurement of the amount of radioisotope on a mica surface, during either adsorption or desorption experiments.

THE ADSORPTION OF PHOSPHATE BY MICA

Untreated Mica

It was found that freshly-cleaved mica adsorbed much phosphate on its edges, and a little on its 001 cleavage plane. The existence of anion adsorption sites on the edges is consistent with the usual concepts of adsorption by clay minerals, but the adsorption of anions by the 001 face is surprising. It is not known what this is due to, but the amount adsorbed seems to be much lower than that adsorbed by other processes examined in this thesis.

The Effect of Cation Treatment

It was found that treating the mica with concentrated aluminium, gallium, chromium or iron solutions greatly enhanced the adsorption of phosphate, while many other salts did not affect the amount adsorbed. Similar effects of cations were noted if very low (10^{-6}M.) concentrations of them were present in the phosphate solutions, but it seems that these two kinds of adsorption process are different.

Measurements of the adsorption of phosphate from an aluminium-contaminated solution, as a function of pH, suggest that in this case the phosphate forms a positively charged complex ion or colloid, which is then deposited on the surface.

Measurements of a phosphate adsorption isotherm on mica treated with 1M. $AlCl_3$ solution suggest that the phosphate is being adsorbed by a deposit of some aluminium compound (probably a hydrated oxide or hydroxide), which is many atoms thick. On the other hand, measurements of an isotherm on mica treated with 0.01M. $GaCl_3$ solution suggest that only a very thin layer might be formed. This difference may reflect the difference in concentrations, rather than the cation.

Kinetics of Sorption Processes

The kinetics of phosphate adsorption and desorption are consistent with a description of the process in terms of diffusion into spherical adsorbing particles of diameter less than one micron. This conclusion is one which is probably of general validity in many experiments on surface chemistry, although only one other author, (apart from the workers with ion-exchangers) appears to have proposed that the slow kinetics frequently found are due to diffusion into the adsorbing material.

THE ADSORPTION OF CATIONS BY MICA

Of the radioactive cations used only gallium was found to be strongly adsorbed on to the 001 face of mica crystals, although potassium and cobalt were found to be strongly adsorbed by the broken edges of the mica. Gallium was also found to be adsorbed by the edges, so that it appears that much of the cation-adsorbing power of mica-type minerals might occur at the edges.

The kinetics of gallium adsorption were consistent with the diffusion controlled adsorption of particles having a diameter of 0.1 microns. These particles could have been formed from a gallium hydroxide or hydrous oxide at the 10^{-6}M. concentration of $GaCl_3$, but must have been dust particles at the carrier-free concentrations.

A POSSIBLE MECHANISM FOR PHOSPHATE SORPTION ON ALUMINIUM-TREATED MICA

It has been shown that much more than a monolayer of phosphate can be adsorbed by aluminium-treated mica, and that the kinetics of phosphate adsorption and desorption on aluminium-treated mica are consistent with diffusion of phosphate ions into spherical particles of absorbing material situated on the mica surface.

It is therefore postulated that treatment of the mica with a 1M. aluminium chloride solution at pH 3 leads to the deposition on the mica of a large number of approximately spherical particles of a hydrated aluminium oxide or hydroxide, these particles having a diameter between 100 and 10,000 Angstrom units. These particles are postulated to absorb phosphate, either by ion exchange or by some other sorption process, which occurs not only on the outside of the particles, but also internally. The sorption process therefore proceeds at a rate controlled by diffusion into the particles.

There is no direct evidence for the presence on the surface of the aluminium "hydroxide" particles, but indirect evidence is available from the radioactive gallium adsorption experiments, and from the work of Follett (1965) on the adsorption of ferric hydroxide by kaolinite.

It might be wondered why the particles should be adsorbed to the mica surface. Follett's work showed that the iron hydroxide particles did adsorb on to the mica-like surface of kaolinite, and the analogy with the present case is fairly direct. Particles of the "hydroxide" in solution would be expected to be positively charged, and since the mica has a cation-exchange capacity due to isomorphous substitution within its lattice, one would expect there to be strong attraction between the particles and the mica, despite the neutralisation of the charges by ions in solution. The charges of the particle and mica are completely neutralised if they are isolated and an average is taken over a long time, but when the particles and mica are near each other, random thermal fluctuations in the number of ions near the surfaces will mean that there will be, on the average, an attractive force between them. When a particle is very close to the mica, there is no room between them for ions, and the particle becomes electrostatically held to the surface.

The remaining question is how do the particles form in the aluminium chloride solution? It has been shown (Davies & Rideal (1961)) that the pH near a positively-charged surface would be higher than that in the bulk solution. It could therefore be postulated that the mica surface is saturated with Al^{3+} ions, which over-compensate for the original negative charge. This would result in a high pH near the surface, so that the aluminium ions on the surface would hydrolyse. It is difficult to see how this could lead to formation of a thick layer of "hydroxide" or to formation of particles, since any further sorption of cations would be strongly hindered by the positive charge. The surface is therefore unlikely to be responsible for the formation of the particles.

It is well known that aluminium "hydroxide" particles, once formed, are only very slowly redissolved, even at a pH much lower than that required to cause precipitation. It is therefore possible that at some stage (either when making the solution or when putting it into a wet beaker), these particles were formed in the solution, and remained there until the mica was inserted into it. When it is recalled how very small the amounts involved are, it seems also possible that the concentration needed might be present even in an equilibrium solution, and that this amount might be too small to be detected by any other method.

RELEVANCE TO SOIL CHEMISTRY

It was shown in the introduction that there is much evidence associating the fixation of phosphate by soil with the presence in the soil of aluminium or iron. The present thesis suggests that this correlation might be due to the ability of aluminium and iron hydroxides to sorb phosphate.

The phosphate fixation process in soils is slow, and it is possible that the slowness is related to a diffusion process similar to the one described here. This statement is supported by measurements of another worker in this group (J. H. Watkinson), who has shown that the kinetics of phosphate exchange on soils in laboratory experiments can be described by a diffusion model.

SUGGESTIONS FOR FURTHER WORK

Techniques

It appears that in some of the present experiments unexplained large changes in solution concentrations have occurred. An attempt to show that changes in specific activity occurred was unsuccessful, but chromatography revealed the presence of at least two phosphate-containing species (Appendix IV). These results, and the difficulty found when attempting to perform adsorption experiments at long times of treatment, suggest that there could be some benefit from investigations of possible sources of contamination.

Amounts Adsorbed

It is still not clear what is the nature of the "bond" between the phosphate and the previously sorbed aluminium compound. Further work could be devoted to finding out whether the phosphate is held by ion-exchange or some other sorption process.

There is still scope for measurements on the phosphate sorption as a function of cation concentration, at high anion concentrations. More experiments relating anion and cation adsorption would also be useful.

Kinetics of Sorption

There is some evidence that the phosphate adsorbed on to .01M. gallium-treated mica might be adsorbing on to a thin layer of a gallium compound, whereas the phosphate adsorption kinetics experiments performed were all on mica which was probably covered with a thick layer of aluminium oxide or hydroxide. It therefore seems possible that the kinetics of phosphate adsorption on the mica treated with dilute gallium (and perhaps aluminium) solutions might be considerably faster than the kinetics of the present experiments. If this were found it would be strong evidence for the diffusion theory presented here.

From the lack of reproducibility of the gallium kinetics experiment it seems that there is some important factor yet to be defined in that kind of experiment.

Cation Exchange Experiments

It appears that adsorbed gallium does not exchange with high concentrations of gallium in solution. This effect might indicate a change in form of the adsorbed layer at different concentrations, and could give useful information if investigated further.

GEIGER TUBE SELECTOR SWITCH

This switch was developed because of the need, in the first kinetic experiments performed in this thesis, to make measurements of radioactive count rate over periods of time lasting up to several months. During most of this time the count rate would be changing only very slowly, so that a measurement over a fairly long period a few times a day would be adequate. It was found that manually counting the samples was a rather more time-consuming task than it would appear from the simplicity of the job, mainly because of the interuption to other work which occurred. It was also useful to have a frequent record in order to follow and recognise anomalies in the change in count rate.

Crotty (1962) has described a device designed with the same problem in mind, in which scaled pulses from several experiments could be fed into a device which allowed pulses from one experiment to be fed into a counter for a prescribed time, and then be printed on paper tape at the end of that time, after which pulses from the next experiment were fed in, and so on. This device worked well, but was inefficient, in that a separate power supply and scaling unit, together costing more than £100, were required for each experiment, and were for most of the time idle.

The present switch uses only one power supply and scaler, and relays are used to switch the power supply to the separate Geiger tubes used in the experiments. This requires that all the tubes have similar characteristics, but with tubes such as the 20th Century Electronics EW3H, and Philips 18505, this is not difficult to ensure.

Crotty's switch used a Post Office type uniselector to switch channels, but it was found impossible to obtain one which could be relied on to have good enough insulation for the 500 - 1000 volts used by the Geiger tubes, so it became necessary to introduce relays. Relays were obtainable to handle this voltage, at the very low power levels used, and it was found possible to dispense with the uniselector by using a few condensers and extra relay contacts.

The switch is connected to a Philips type PW4022 power supply via a quench unit which plugs on to the back of the switch. The power supply is connected in the usual way to a Philips type PW4032 scaler, the sockets in the rear of which are connected to two sockets at the rear left of the switch. After turning on, the unit is ready to use. A push switch is provided on the front panel to change channels manually.

Block Diagram

This indicates broadly the relationship of the component units, which are described now.

E.H.T. Supply and Amplifier are one composite unit made by Philips, The Netherlands.

Scaler Philips, Netherlands, type PW4032.

Quench Unit is one of a large number built in the department to a design described by Crotty (1962)

Printer/Counter is manufactured by Sodeco of Geneva, Switzerland. Type ITPb3.

The remaining units are individual sections within the switch.

Starter This is a relay which ensures that the unit starts in the event of a power failure, and that it starts on channel 1.(Relay L7).

Timer This is a motor-driven arm which interrupts a light beam, changing the resistance of a light dependant resistor (L.D.R.), so that a transistor drives a relay which operates the printer drive unit.

Printer Drive This is a relay pair which causes printing of the accumulated count, reset of the printer, and change of the channel selector. (Relays L8 and L10).

Channel Selector Contains 6 relays, one for each channel. It connects the E.H.T. to a Geiger tube, operates an indicator light, and selects the scaling factor appropriate for each channel.

Scaling Factor One of six three-position switches is connected via the channel selector to the scaler, in such a way that the scaling factor can be set at 10, 100 or 1,000.

Cycle Mark causes an extra zero print at the end of each cycle.(L12).

Pulse Shape is a relay used to couple the scaler and printer. (L9)

All the units except the scaler and E.H.T. units are contained on the one chassis, and all fit in a standard 19" rack. (see photo, figL1).

Switches are provided to enable E.H.T. sockets to be connected in parallel if less than 6 counters are to be used simultaneously.

Description of Block Diagram (Fig. I.2)

At intervals determined by the rotation speed of the motor in the timing unit (usually 30 minutes), a pulse is fed (via relay L11) into the printer drive (relay L10). This first causes the printer to record the counts accumulated since the previous print operation, then resets the counter to zero, and causes the channel selector to change to the next channel. When this occurs the appropriate indicator light comes on, the quench unit is connected to the appropriate E.H.T. socket, and the appropriate scaling factor selector switch is connected to the scaler. When the change from channel 6 to channel 1 occurs, an additional print operation is made (without changing channels again, of course), in order that the line of zeros printed can be used to identify the start of the cycle.

Description of Circuit Diagram (Fig. I.3)

The details of connections between the channel relays, L1 to L6, and the E.H.T. sockets, indicator lights and scaling factor selector switches have been omitted for clarity, and are quite straightforward.

Suppose the power supply is turned on after being off for more than a few seconds. Current from the 50v. supply flows through contact 1 of L12 (abbreviated to L12/1) to L7, which switches on as C7 charges, and then off once C7 is fully charged. (Note: relay contacts drawn  are closed only when no current is flowing in the coil, and those drawn  are closed only when current is flowing). While L7/1 is closed, L1 is energised, and L1 is held on by current through the holding contact L1/1, even after L7 turns off.

L1 remains on until the light path from the lamp to the light dependant resistor is interrupted by the arm mounted on the motor shaft, or the push button switch S1 is depressed. When this occurs the base-emitter voltage of the transistor, which was otherwise enough to cause bottoming, becomes very small, so that the transistor cuts off. Relay L11, which was previously on, turns off, (the diode short circuiting the back-E.M.F.), allowing C11, which charged while L11 was on, to discharge through L10, causing L10 to switch on, then off. Contact 3 on L10 closes and opens, providing a pulse to cause the printer to operate. Contact 4 on L10 opens, and this disconnects the holding contacts on the channel relays from the power supply. This causes the "on" relay out of L1 to L6 to turn off, but only after a delay, caused by, in this case, the discharge of C6 through L6/3 and L1. However, the time constants are set so that L10 stays on long enough that L1 turns off. When this occurs, C1 discharges through L1/3 and L2, causing L2 to turn on. Times are adjusted so that before C1 is discharged, giving L2 a chance to turn off again, L10 has turned off, closing the relay holding circuit contacts, L10/4, and ensuring that L2 stays on.

While L10 was on condenser C10 rapidly charged through a 1k-ohm resistor, so that when it turns off C10 turns L8 on and off. This causes the printer to reset to zero.

Nothing further happens, except for the accumulation of counts through relay L9 until the light beam is interrupted again, when the analogous set of events causing change to channel 3 occurs.

When the change from channel 6 to channel 1 occurs, the operation is a little more complicated. Operation of the relays L11, L10 and L8 occurs as before, and in addition L12 operates. Consider condenser

C12. When L1 is off, L6 is on and L7 is off, then C12 is connected on one side through L12, 27k-ohm and L1 to ground, while the other is at 50v. It is therefore charged to 50v. When L1 turns on, the previously grounded side of the condenser C12 is connected through L12 and, because of the polarity change, the diode, to 50v. The condenser therefore discharges and turns L12 on. At this stage L11 is normally off because the shutter has not passed the lamp completely. When L12 closes L11 is turned on again, via L12/2, and initiates another print operation. This would normally cause a further change of channels, but this is forestalled because when L12/1 opened as L12 turned on, condenser C7 discharged through L7, which causes L1 to stay on while the usual relay hold circuit breaks in the course of the printing operation.

Adjustment of Delay Times

It is necessary that L10 remain on for a time greater than the time required to turn one of L1 - L6 off, but less than twice this time (assuming that this time is the same for all of L1 - L6). The switching times for L1 - L6 may be varied in several ways, for example by adjusting the contact pressure, the capacitances or the locking screws on the armature. This last adjustment is used to set all the switching times approximately equal, and the time is best measured by removing the printer from its case, holding L10 on manually, and looking with an oscilloscope at the voltage on the relay hold line. When L10 is held on in this way, the relays cycle continuously, enabling a rapid check on all the times.

The time for which L10 remains on is measured by looking at the voltage of C10 with the oscilloscope, and is adjusted by changing C11.

Electrical Noise

Many problems were experienced at first with the occurrence of spurious pulses, due to triggering of the quench unit by pulses from the printer.

The combination of smoothing circuits, short-circuiting diodes, and neon tubes shown in the circuit was used to cure this problem.

Scaling Errors

A random error is introduced into the count registered by the counter owing to the fact that the scaler does not start at zero at the start of each cycle, and does not finish on zero at the end. The first of these could give a maximum error of +1 in the scaled count, and the second a maximum error of -1. This means that the average error will be zero, and the maximum error is ±1.

Dead Time of Printer

This was estimated, by using uniformly spaced pulses of varying rates, to be about 0.5 seconds. The input pulses to the printer have a random scatter in their time distribution, but the process of scaling reduces greatly the variation in time between pulses occurring at the printer, compared to the variations in the time between the original pulses. Evans (1955) discusses the time distribution of pulses from an s-fold scaler, and shows that the probability, P_T, that the interval between pulses, after scaling by a factor s, will be less than or equal to T is

$$P_T = 1 - e^{-aT} \sum_{0}^{s-1} \frac{(aT)^n}{n!}$$

where a is the average rate before scaling.

Thus if T is the dead time of the printer

$$R_{obs}/R = 1 - P_T$$

where R_{obs} is the observed number of counts in a certain time, and R is the true number. Pearson and Hartley (1958) have tabulated

$$\sum_{j=0}^{c-1} e^{-m} \frac{(m^j)}{j!} = 1 - P_T \quad (\text{if } m = aT \text{ and } c = s),$$

and from this the following table of aT against P_T has been prepared for s = 10 and s = 100.

P_T	aT (s = 10)	aT (s = 100)
.001	3.0	72
.005	3.7	76
.01	4.1	79
.02	4.6	81
.05	5.5	84

It appears from this that losses are very small, provided the rate remains below a certain value, and then rapidly increase at rates above this value. This is a consequence of the regularity of scaled pulses. For the present scaler, the dead-time is unimportant at rates less than 360 counts per minute with 10-fold scaling, and 8,600 counts per minute with 100-fold scaling. These rates correspond to 1000 counts and 2600 counts respectively, on the printer in a 30 minute period. It should therefore be possible to obtain three-figure accuracy for the count rates, in all cases, except those of less than 30 counts/minute unscaled count rate.

Geiger Counter Selector Switch

Fig. I.1

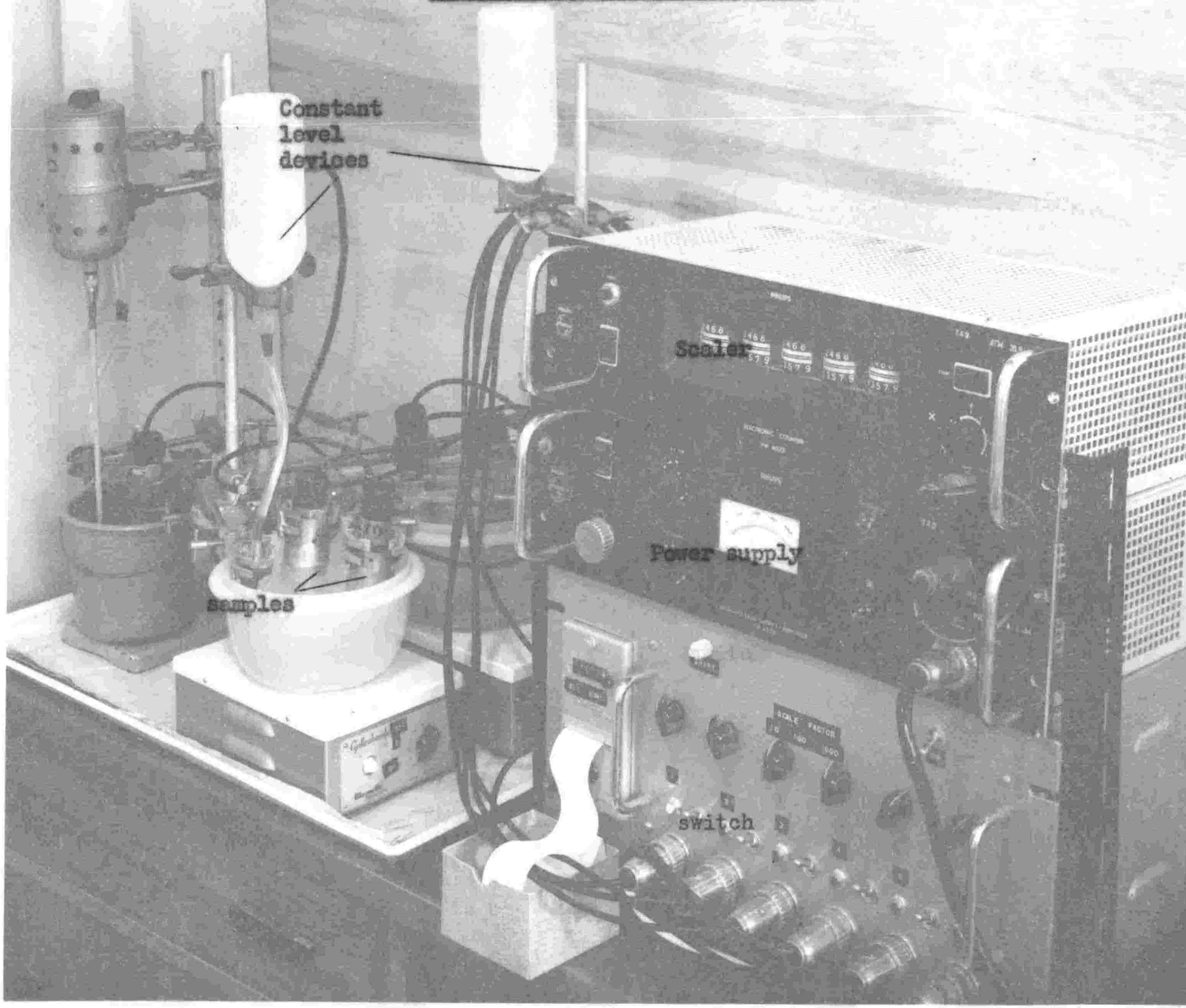


Fig. I.2

SELECTOR SWITCH BLOCK DIAGRAM

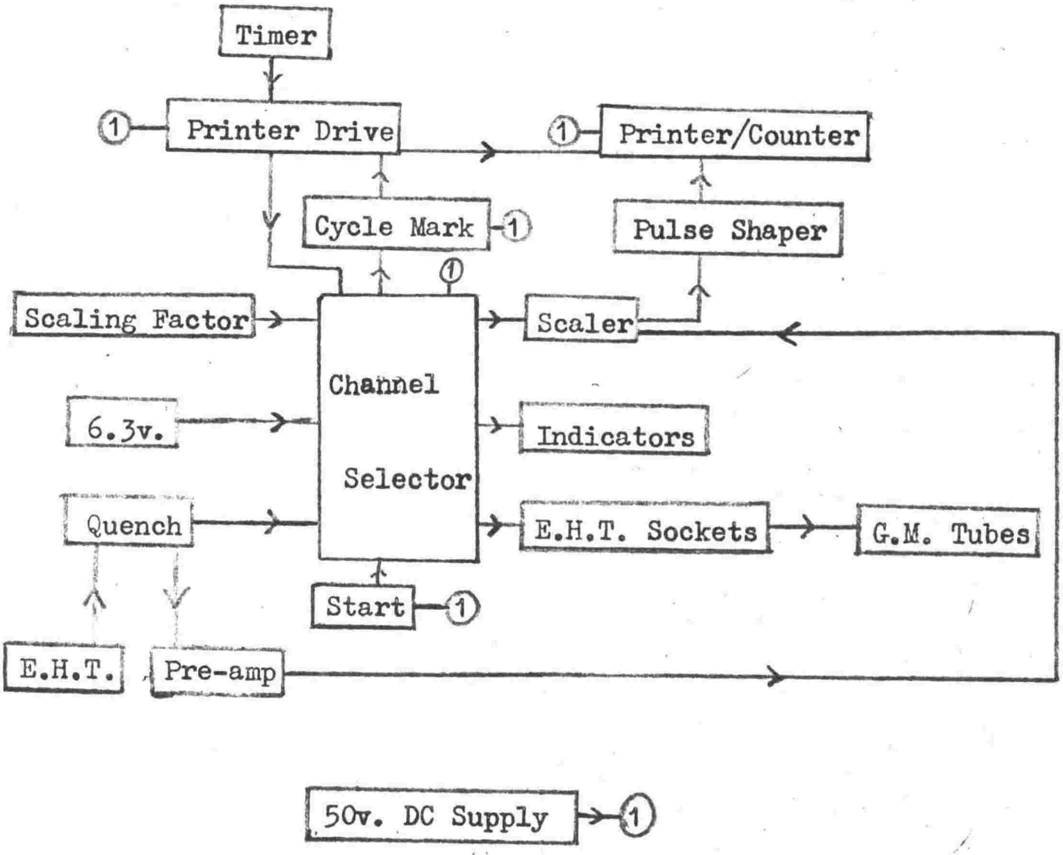
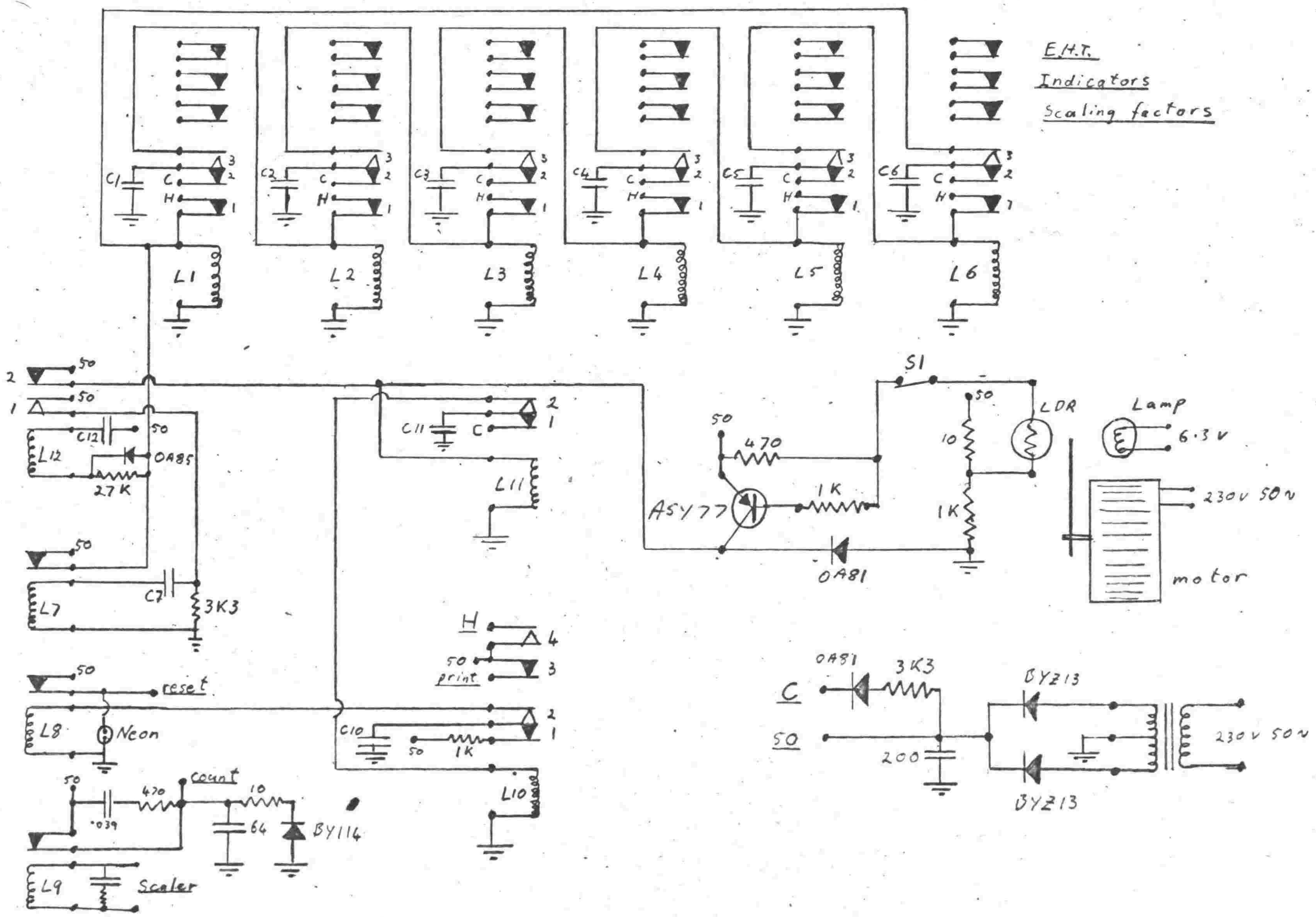


Fig. I.3 - Circuit of Selector Switch



APPENDIX II

EXCHANGE-RATE THEORY OF ADSORPTION KINETICS

This is an extension of a theory originally presented by Hendy (1965), in which some mathematical errors led to wrong conclusions. Hendy was concerned with the adsorption of phosphate on to what he thought were sodium ions on the mica surface, and the notation he uses is influenced by this belief. The notation used here is simplified, so that S represents the adsorption site on the surface, whatever it might be. It is assumed that S is most of the time combined with an anion, but that an equilibrium does exist between the ionic species and the combination, and that the rates of reaction can be calculated from a simple model. It is supposed that radioactive phosphate, represented as P, is being adsorbed from carrier-free solution containing chloride ions, represented as Cl. The reactions occurring are represented as

$$\text{S-Cl} \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \text{S} + \text{Cl}$$

and

$$\text{S-P} \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} \text{S} + \text{P}$$

P and Cl are aqueous species, and S-Cl, S-P, and S are surface-bound species. Since S is ionic, and we are not considering OH^- as a significant species, the concentration of S in forms other than S-Cl and S-P must be very low. Thus we can write

$$\{S\text{-}Cl\} + \{S\text{-}P\} = B, \text{ a constant.} \qquad (1)$$

The constants, k, in the above equations are defined on the assumption that we can write

$$\frac{d\{S\text{-}P\}}{dt} = k_2' \{S\}\{P\} - k_2\{S\text{-}P\} \qquad (2)$$

and
$$\frac{d\{S\text{-}Cl\}}{dt} = k_1' \{S\}\{Cl\} - k_1 \{S\text{-}Cl\} \qquad (3)$$

Since P is radioactive, we can assume the count rate measured is proportional to $\{S\text{-}P\}$. We therefore want an expression for $\{S\text{-}P\}$ as a function of time.

Substituting from (1) into (3) we find

$$-\frac{d\{S\text{-}P\}}{dt} = k_1' \{S\}\{Cl\} - k_1\{B + k_1 \{S\text{-}P\} \qquad (4)$$

(2) and (4) give

$$\frac{1}{k_2'\{P\}} \left(\frac{d\{S\text{-}P\}}{dt} + k_2\{S\text{-}P\}\right) = \frac{1}{k_1'\{Cl\}} \left(k_1B - k_1\{S\text{-}P\} - \frac{d\{S\text{-}P\}}{dt}\right)$$

$$\frac{d\{S\text{-}P\}}{dt}\left(1 + \frac{k_1'\{Cl\}}{k_2'\{P\}}\right) = -\{S\text{-}P\}\left(k_1 + \frac{k_2k_1'\{Cl\}}{k_2'\{P\}}\right) + Bk_1$$

So
$$\frac{d\{S\text{-}P\}}{dt} = D - E\{S\text{-}P\}, \text{ where} \qquad (5)$$

$$D = \frac{Bk_1}{1 + \dfrac{k_1'\{Cl\}}{k_2'\{P\}}} \quad \text{and } E = \frac{k_1 + \dfrac{k_2k_1'\{Cl\}}{k_2'\{P\}}}{1 + \dfrac{k_1'\{Cl\}}{k_2'\{P\}}}$$

This differs from Hendy's expression, in that E in his expression has dimension of $[Cl]^{-1}$, instead of those of k, which it clearly ought to have, on general dimensional considerations. The above expression for E depends on the ratio of $[Cl]/[P]$, and this is an important experimental variable, in that the rate-constant in the integrated form of (5) depends on the concentration of phosphate, under some conditions.

Integration of (5) is performed readily, by the substitution of $y = D - E[S-P]$, and on substituting back again it is found that

$$[S-P] = D/E + ([S-P]_o - D/E)e^{-Et}$$

For an adsorption experiment, $[S-P] = 0$ at $t = 0$ so $[S-P]_o = 0$. D/E is the value of $[S-P]$ at infinite time, so that

$$\frac{[S-P]}{[S-P]_\infty} = (1 - e^{-Et}) \qquad (6)$$

or

$$[S-P]_\infty - [S-P] = [S-P]_\infty e^{-Et}$$

Thus the adsorption on to this site, S, in the case where phosphate is added at zero time to the solution containing chloride ions at equilibrium, has an exponential approach to the equilibrium count rate.

Suppose there are n such sites, S_1, S_2 ------ S_n, for each of which equation (6) holds, separately. Then the total count rate is proportional to $\sum_n [S_nP]$.

$$[S_1-P] + [S_2-P] + \text{------} = [S_1-P]_\infty (1-e^{-E_1t}) + [S_2-P]_\infty (1-e^{-E_2t}) + \text{---}$$

so that $\sum_n [S_n-P] = \sum_n [S_n-P]_\infty - ([S_1-P]_\infty e^{-E_1t} + [S_2-P]_\infty e^{-E_2t} + \text{---})$.

Thus the total count rate at infinite time, minus the total count rate at time t, is a sum of exponential terms, and so would be resolvable in the same way (and subject to the same conditions and comments) as the desorption experiments of Furkert and Morris.

For this theory to hold, the half-lives must be related to the solution composition.

We can write $$E = \frac{k_1 + k_2 R}{1 + R}$$

where $$R = \frac{k_1' [Cl]}{k_2' [P]} .$$

If $R \ll 1$ then $E = k_1 + k_2 R$, but it cannot be said that because R is small, E is independent of R, because the relative magnitude of k_1 and k_2 are not known.

If $R \gg 1$, then $E = k_2 + \frac{k_1}{R}$. Thus in one or other of these two cases E should be independent of R, since it is not possible to have an ambiguous situation in both. It is possible to have independence of R in both cases, if k_1 and k_2 are comparable in size, but in this case there is some dependence at $R \doteqdot 1$. Because it is possible to vary $[Cl]$ and $[P]$ independently over a range of about 10^6, it should be possible to obtain the desired values of R. By a suitable choice of experiments it should be possible to obtain k_1, k_2 and $\frac{k_1'}{k_2'}$.

If this predicted variation could be found, then it would be convincing evidence for the complex dissociation theory, as opposed to the diffusion-controlled-kinetics theory, since the latter would predict only minor effects on the rate due to chloride, although the total amount might be affected. The difficulty of performing such experiments, especially if more than one such complex is formed, is formidable, and no attempt was made here to test the conclusions.

An experiment useful in testing the diffusion theory is to vary the adsorption time in a set of desorption experiments. Morris found that the shorter the adsorption time, the more rapidly the phosphate desorbed, and that the results could all be analysed into the same half-life species, the changes observed being merely in the amounts present at the start. This is consistent with the present theory, because for large R, that is low phosphate concentration, the rate of adsorption is largely controlled by the desorption rate constant. This means that the fastest desorbing species also adsorb fastest, so there will be relatively more of them, at short adsorption times, than the slower ones, which will, however, eventually catch up the faster ones.

This treatment of the exchange-rate theory does not avoid the basic difficulty that it is necessary to assume several simultaneous processes. Once one starts doing this one rapidly gets to the point where one is merely fitting the data to an empirical formula, which gives no information as to the validity of the postulates made. It would be of value, if at some stage it is possible to reduce the kinetics to a single exponential variation with time.

APPENDIX III

Mathematics of the Diffusion Model

The model used is that of an infinite plane sheet, thickness l, in which the diffusion coefficient is k. One boundary is impermeable, the other is held at a concentration pV for a total time θ, and then reduced at time $t = 0$ to zero concentration. The concentration at distance x from the impermeable face is v.

A relevant solution to the diffusion equation is given by Carslaw & Jaeger (1959) (p. 104). If the initial variation of v with x is $v = f(x)$, and $v = \phi(t)$ at $x = l$, then

$$v = \frac{2}{l}\sum_{n=0}^{\infty} e^{-k(2n+1)^2\pi^2 t/(4l^2)} \cos((2n+1)\pi x/(2l)).$$

$$\cdot\left[(2n+1)\pi k(-1)^n/(2l)\int_0^t e^{k(2n+1)^2\pi^2\lambda/(4l^2)}\phi(\lambda)d\lambda + \right.$$
$$\left. + \int_0^l f(x')\cos((2n+1)\pi x'/(2l))dx'\right].$$

For desorption, $\phi(t) = 0$, so

$$v = \frac{2}{l}\sum_0^{\infty} e^{-k(2n+1)^2\pi^2 t/(4l^2)} \cos((2n+1)\pi x/(2l)) \cdot$$
$$\cdot\int_0^l f(x')\cos((2n+1)\pi x'/(2l))dx'.$$

The amount of absorbed material per unit area is

$$\int_0^l v\,dx = \sum_{n=0}^{\infty} A_n \int_0^l \cos\frac{(2n+1)\pi x}{2l}\,dx,$$

where the x-independent terms are included in A_n,

$$= \sum_0^{\infty} \frac{2lA_n}{(2n+1)\pi} \left.\sin\frac{(2n+1)\pi x}{2l}\right]_0^l$$

$$= \sum_0^{\infty} (-1)^n \frac{2lA_n}{(2n+1)\pi}$$

The initial distribution is a result of diffusion with $v = 0$ at $x < l$ and $t = 0$, and $v = pV$ at $x = l$, all t. From Carslaw & Jaegar's equation 5, p. 101,

$$f(x) = pV + \frac{2}{l}\sum_{m=0}^{\infty} e^{-k(2m+1)^2\pi^2\theta/(4l^2)} \cos((2m+1)\pi x/(2l))\, \frac{2lV(-1)^{m+1}}{(2m+1)}$$

$$= pV + \sum_{0}^{\infty} B_m \cos((2m+1)\pi x/(2l))$$

where B_m is independent of x.

A_n includes $\int_0^{\ell} f(x') \cos((2n+1)\pi x'/(2l))dx'$

$$= \int_0^{\ell} (pV + \sum_{m=0}^{\infty} B_m \cos((2m+1)\pi x/(2l)) \cos((2n+1)\pi x/(2l))dx$$

$$= (-1)^n \frac{2lpV}{(2n+1)\pi} + \sum_{m=0}^{\infty} B_m \cos\frac{(2m+1)\pi x}{2l} \cos\frac{(2n+1)\pi x}{2l}\, dx\,.$$

Now $\int \cos mx \cos nx dx = \frac{\sin(m-n)x}{2(m-n)} + \frac{\sin(m+n)x}{2(m+n)}$ if $m^2 \neq n^2$

(see Chemical Rubber Co. handbook, 46th ed., p. A135), and this leads to

$$\int_0^{\ell} \cos\frac{(2m+1)\pi x}{2l} \cos\frac{(2n+1)\pi x}{2l}\, dx = 0, \text{ for } m^2 \neq n^2.$$ For $m = n$

we have $\int_0^{\ell} \cos^2 \frac{(2m+1)\pi x}{2l}\, dx = \frac{1}{2}l$

Thus $\int_0^{\ell} f(x) \cos((2n+1)\pi x/(2l))\, dx$

$$= (-1)^n \frac{2lpV}{(2n+1)\pi} + \frac{1}{2}l\, B_n$$

$$= (-1)^n \frac{2lpV}{(2n+1)\pi} + \frac{1}{2}l \cdot \frac{2}{l} \cdot \frac{2l(-1)^{n+1}pV}{(2n+1)\pi}\, e^{-k(2n+1)^2\pi^2\theta/(4l^2)}$$

$$= (-1)^n \frac{2lpV}{(2n+1)\pi} (1 - e^{-k(2n+1)^2\pi^2\theta/(4l^2)})$$

This means that

$$\int_0^{\ell} v dx = \sum_0^{\infty} (-1)^n \frac{2l}{(2n+1)\pi} \cdot \frac{2}{l} \cdot e^{-k(2n+1)^2\pi^2 t/(4l^2)} \;\cdot$$

$$\cdot\, (-1)^n \frac{2lpV}{(2n+1)\pi} (1 - e^{-k(2n+1)^2\pi^2\theta/(4l^2)})$$

$$= A\sum_{0}^{\infty}\frac{1-e^{-(2n+1)^2B\theta}}{(2n+1)^2}\cdot e^{-(2n+1)^2Bt}$$

where $A = \frac{81pV}{\pi^2}$ and $B = \frac{k\pi^2}{4l^2}$.

Derivation of an Equivalent Series

It is shown in chapter 7 that the count rate can be expressed in terms of a function $F(B) = \frac{8}{\pi^2}\sum_{0}^{\infty}\frac{e^{-(2n+1)^2B}}{(2n+1)^2}$, which converges only slowly when B is small.

Titchmarsh (1937) has shown that if $F_c(x)$ is the Fourier cosine transform of a function $f(x)$, that is,

$$F_c(x) = \sqrt{\frac{2}{\pi}}\int_0^{\infty} f(t)\cos(xt)dt,$$

then

$$\sqrt{\pi}\Big[\tfrac{1}{2}F_c(0) + \sum_{1}^{\infty}F_c(n\pi) = \sqrt{2}\Big[\tfrac{1}{2}f(0) + \sum_{1}^{\infty}f(2n)\Big]. \qquad (1)$$

If we define $f(x) = e^{-B(x+1)^2}$, so that $f(2n) = e^{-B(2n+1)^2}$, we find

$$F_c(n\pi) = \sqrt{\frac{2}{\pi}}\int_0^{\infty}e^{-B(t+1)^2}\cos(n\pi t)dt.$$

Substituting $y = t+1$, this becomes

$$F_c(n\pi) = \sqrt{\frac{2}{\pi}}\int_1^{\infty}e^{-By^2}\cos(n\pi(y-1))dy$$

$$= \sqrt{\frac{2}{\pi}}\Big[\int_1^{\infty}e^{-By^2}\cos(n\pi y)\cos(n\pi)dy + \int_1^{\infty}e^{-By^2}\sin(n\pi y)\sin(n\pi)dy$$

$$= \sqrt{\frac{2}{\pi}}(-1)^n\int_1^{\infty}e^{-By^2}\cos(n\pi y)dy$$

$$= (-1)^n\sqrt{\frac{2}{\pi}}\Big[\int_0^\infty e^{-By^2}\cos(n\pi y)dy - \int_0^1 e^{-By^2}\cos(n\pi y)dy\Big]$$

$$= (-1)^n\sqrt{\frac{2}{\pi}}\Big[\sqrt{\frac{\pi}{4B}}\,e^{-(n\pi)^2/(4B)} - \int_0^1 e^{-By^2}\cos(n\pi y)dy\,.$$

(Integral found in C.R.C. handbook 46th ed. p. A173.)

Substituting in line (1), we find

$$\tfrac{1}{2}\Big[\tfrac{1}{2}\sqrt{\frac{\pi}{B}} - \int_0^1 e^{-By^2}dy\Big] + \sum_1^\infty \tfrac{1}{2}\sqrt{\frac{\pi}{B}}(-1)^n e^{-(n\pi)^2/(4B)} - \sum_1^\infty(-1)^n\int_0^1 e^{-By^2}\cos(n\pi y)dy$$

$$= \tfrac{1}{2}e^{-B} + \sum_1^\infty e^{-(2n+1)^2}. \qquad (2)$$

Write $\sum_1^\infty(-1)^n\int_0^1 e^{-By^2}\cos(n\pi y)dy = S.$

$$\int_0^1 e^{-By^2}\cos(n\pi y)dy = \int_0^1 \frac{1}{n\pi}e^{-By^2}d(\sin(n\pi y))$$

$$= \frac{1}{n\pi}e^{-By^2}\sin(n\pi y)\Big]^0 - \frac{1}{n\pi}\int_0^1 \sin(n\pi y)e^{-By^2}(-2By)dy$$

$$= \frac{2B}{n\pi}\int_0^1 y\sin(n\pi y)e^{-By^2}dy$$

$$\text{so } S = \frac{2B}{\pi}\sum_1^\infty\frac{(-1)^n}{n}\int_0^1 ye^{-By^2}\sin(n\pi y)dy$$

$$= \frac{2B}{\pi}\int_0^1 ye^{-By^2}\Big(\sum_1^\infty\frac{(-1)^n\sin(n\pi y)}{n}\Big)dy.$$

It can be shown that $\sum_1^\infty(-1)^n\frac{\sin(n\pi y)}{n} = -\frac{\pi y}{2}$

$$\text{so } S = \frac{B}{\pi}\int_0^1 ye^{-By^2}(-\pi y)dy$$

$$= \tfrac{1}{2}\int_0^1(-2yBe^{-By^2})ydy$$

$$2S = ye^{-By^2}\Big]_0^1 - \int_0^1 e^{-By^2}dy.$$

Substituting in (2) leads to

$$\sum_0^\infty e^{-(2n+1)^2 B} = \tfrac{1}{2}\sqrt{\frac{\pi}{B}}\left[\tfrac{1}{2} + \sum_1^\infty (-1)^n e^{-(n\pi)^2/(4B)}\right] \qquad (3)$$

In the region where both sides converge reasonably quickly the equation (3) was checked by the substitution of B = 1 and 0.1.

The sum wanted is related to the integral of the left hand side.

$$\int_0^B \sum_0^\infty e^{-(2n+1)^2 B} = -\sum_0^\infty \frac{e^{-(2n+1)^2 B}}{(2n+1)^2} + \frac{\pi^2}{8} = \int_0^B \tfrac{1}{2}\sqrt{\frac{\pi}{B}}\left[\tfrac{1}{2} + \sum_1^\infty (-1)^n e^{-(n\pi)^2/(4B)}\right] dB.$$

$$\text{So } \frac{\pi^2}{8} - \sum_0^\infty \frac{e^{-(2n+1)^2 B}}{(2n+1)^2} = \tfrac{1}{2}\sqrt{B\pi} + \sum_1^\infty \int_0^B (-1)^n \frac{1}{\sqrt{B}}\, e^{-(n\pi)^2/(4B)}\, dB \ . \qquad (4)$$

Consider $\displaystyle\int_0^B \frac{1}{\sqrt{B}}\, e^{-(n\pi)^2/(4B)}\, dB.$

If $\dfrac{df(x)}{dx}$ is monotonically increasing in the interval (a,b) then

$$f(b)(b-a) > \int_a^b f(x)dx > f(a)(b-a).$$

$$f(B) = \frac{1}{\sqrt{B}}\, e^{-A/B}$$

so $\dfrac{df}{dB} = B^{-3/2} e^{-A/B}(A/B - \tfrac{1}{2}) > 0$ for $B < 2A$.

So for $B < 5$ $f'(B) > 0$ all n.

$$\text{So } \int_0^B \frac{1}{\sqrt{B}}\, e^{-n^2\pi^2/(4B)}\, dB < B\left(\frac{1}{\sqrt{B}}\, e^{-n^2\pi^2/(4B)}\right) = \sqrt{B}\, e^{-n^2\pi^2/(4B)}$$

For $B < 0.4$, $\sqrt{B} e^{-n^2\pi^2/(4B)} < 2 \times 10^{-3}\sqrt{B}$ for n = 1 and rapidly decreases with n. Thus the sum of the integrals on the right hand side of (4) is negligible compared to B.

$$\text{So for } B < 0.4 \quad \sum_0^\infty \frac{e^{-(2n+1)^2 B}}{(2n+1)^2} = \frac{\pi^2}{8} - \tfrac{1}{2}\sqrt{B\pi}.$$

Diffusion in a Sphere

The sphere is of radius a, diffusion coefficient k, and has initially zero concentration at all $r < a$. Its outer surface is held at a concentration C_o for a time θ, after which this concentration is zero. Time t is measured from this change in concentration.

From Crank (1957) p. 86, we have the concentration profile at time θ as

$$C/C_o = 1 + \frac{2a}{\pi r} \sum_{1}^{\infty} \frac{(-1)^m}{m} \sin\left(\frac{m\pi r}{a}\right) e^{-km^2\pi^2\theta/a^2}$$

By substituting $u = Cr$ in the diffusion equation, it is possible to use the solution given on p. 45 of Crank for the case of planar diffusion with constant concentrations on both boundaries. Using the above expression for C as the initial distribution, with zero concentration at time t at the boundary, we get

$$C = \frac{2}{ar} \sum_{n=1}^{\infty} \sin(n\pi r/a) e^{-kn^2\pi^2 t/a^2} \cdot$$

$$\cdot \int_0^a xC_o\left(1 + \frac{2a}{\pi x} \sum_{m=1}^{\infty} \frac{(-1)^m}{m} \sin(m\pi x/a) e^{-km^2\pi^2\theta/a^2}\right) \sin(n\pi x/a)dx$$

$$\int_0^a x\sin(n\pi x/a)dx = \frac{-a}{n\pi} \int_0^a x d(\cos(n\pi x/a)) = -(-1)^n \frac{a^2}{n\pi}$$

$$\int_0^a \sin(m\pi x/a)\sin(n\pi x/a)dx = 0 \text{ for } m^2 \neq n^2$$

$$\int_0^a \sin^2(m\pi x/a)dx = \int_0^a dx - \int_0^a \cos^2(m\pi x/a)dx = \tfrac{1}{2}a$$

$$\text{so } C = \frac{2aC_o}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} e^{-kn^2\pi^2 t/a^2} \sin(n\pi r/a)\left[e^{-km^2\pi^2\theta/a^2} - 1\right].$$

$$M = \int_0^a 4\pi Cr^2 dr = 4\pi \sum_1 X_n \int_0^a r \sin(n\pi r/a)dr$$

where X_n includes the r-independent terms of the expression for C,

$$\text{so } M = 8aC_o \sum_1^{\infty} \frac{-(-1)^{2n}a^2}{n^2\pi}\left[e^{-km^2\pi^2\theta/a^2} - 1\right] e^{-kn^2\pi^2 t/a^2}$$

$$= \frac{8a^3C_o}{\pi}\sum_1^{\infty} \frac{1}{n^2}\,(1-e^{-km^2\pi^2\theta/a^2})\; e^{-kn^2\pi^2 t/a^2}$$

$$= C'\sum_1^{\infty} \frac{1}{n^2}\,(1-e^{-Dn^2\theta})\; e^{-Dn^2 t}$$

where $C' = 8a^3C_o/\pi$ and $D = k\,\pi^2/a^2$.

If M is taken to be the total amount in all the N spheres on the surface, and the concentration in the sphere at equilibrium with a solution of concentration V is pV, then C' in the above expression is replaced by

$$C = 8Na^3pV/\pi .$$

From the formal similarity between this expression and that for the planar case, and the fact that

$$\frac{1}{n^2} = \pi^2/6,$$

the expression for x in terms of G(B) follows directly.

APPENDIX IV

A SEARCH FOR RADIO-COLLOIDS

REASON FOR THE SEARCH

An experiment was described in Chapter 6, in which the amount of phosphate removed from a solution upon adding aluminium ions appeared to be much greater than the amount of aluminium added, and not greatly dependent on the amount of aluminium added above a certain limit. This suggested that the assumption that the added carrier and the carrier-free material were chemically identical should be tested as far as possible.

It is well known (Wilson, (1966)) that dilute radioactive solutions often contain suspended radioactive material, called in general "radio-colloids", and often due to adsorption of the radioactive material on to small dust particles. If such materials were present in the solutions being used, and if they took a long time to come to isotopic equilibrium with the solution, then the interpretation of results could be seriously in error. If the particles were not as strongly adsorbed by the surface as the PO_4^{3-} ions, then the effective specific activity would be lower than the measured one, but if they were more strongly adsorbed, the effective specific activity would be higher.

POSSIBLE SOURCES OF COLLOIDAL MATERIAL

^{32}P Production Process

Some details of the production process for $^{32}PO_4$ used by the Australian Atomic Energy Commission at Lucas Heights, Sydney, were obtained from one of their representatives, who said that much the same procedure was used at Amersham. New silica apparatus is used each time, after being cleaned physically and with solvents. Redistilled sulphur is irradiated, and then the excess sulphur is distilled off, leaving a polyphosphate. At this stage carrier phosphate is added until the proportion of active material is about 10%, in order to reduce losses, and the mixture is refluxed with HCl to hydrolyse the polyphosphate. After diluting to pH 2, and passing through a cation-exchange column in hydrogen form, the product is tested by electrophoresis to check that the activity is present as phosphate.

The only major impurity in the fresh product is SiO_2, which can be removed by autoclaving, but with time, breakdown products due to radiolysis of the glass bottle may accumulate. The silica particles and breakdown products may be capable of adsorbing significant quantities of phosphate (Mellish et al (1964)).

Removal of the Radioactive Solution from its Bottle

A possible source of particles is introduced when removing solution from the rubber stoppered bottle with a hypodermic syringe. The conventional needles are nickel or chromium plated steel, with a brass hub, so that there is a possibility of iron particles being dislodged by the acid phosphate solution. The needles were always rinsed before use with distilled water in a chromic-acid-cleaned beaker, but this seemed a weak point in the technique. Some needles made from a platinum alloy, with a poly-fluorinated-hydrocarbon hub, were ordered from The Hamilton Company, Whittier, California, but these did not arrive in time to be used. A technique which was used once was to remove the rubber stopper from the bottle, and transfer the contents to a press-cap glass bottle with a glass dropper, but it was felt that the radiation hazard & danger of spillage made the use of a platinum needle and a syringe preferable.

TESTS FOR PRESENCE OF COLLOIDAL MATERIAL

Filtration

The concern with the possibility of radio-colloid effects was initiated by some experiments which suggested that the radioactive material was more strongly sorbed than the carrier, so an experiment was carried out where a mixture of active and inactive phosphate was filtered through an asbestos filter, and the concentration of the active and inactive phosphate measured independently before and after the filtration.

To 20 ml of 10^{-4}M. inactive phosphate in a 25 ml stoppered flask was added a few drops of $^{32}PO_4$, and then 2.0 ml of 1.6×10^{-5}M $AlCl_3$. After shaking to mix the solutions thoroughly, 1.00 ml. samples were taken at known times after mixing the active and inactive phosphate, these samples being placed in a small Hirsch funnel containing a few grams of Gooch asbestos on top of a circle of filter paper. The solution was sucked through into a clean test tube placed in a Buchner flask, and the filter rinsed with a little distilled water, which was also collected. The filtrate was transferred to a 25 ml volumetric flask, 4 ml of the reagent described by Murphy and Riley (1962) was added, and the volume made up to 25 ml with distilled water.

The optical density of the blue colour developed by the samples was measured on an SP 500 spectrophotometer, at a wavelength of 890 mμ, and compared with that of two samples which had been prepared as above except for the filtration. No phosphate was found to be washed out of the asbestos in a blank experiment, and the usual corrections for reagent blank and cell mis-match were made. The solutions were only weakly radioactive, and by using stoppered 4 cm cells, and a pro-pipette to fill and empty the cells, it was found to be possible to avoid contaminating the spectrometer.

After measuring the optical density of the samples 10 ml aliquots of the same, coloured, solutions were counted in a M6H liquid Geiger counter.

The specific activity of eight such samples taken over a period of 8 hours after mixing the solutions were equal to within 1%, except for one sample, and the mean of these was within 2% of the mean of the two unfiltered samples. There was generally a 5 to 10% decrease in the total activity of the filtered samples, compared with the unfiltered ones. This experiment showed that the adsorption in this case produced no change in the specific activity of the solution despite a significant adsorption on the asbestos, so that the suspected differences between active and inactive phosphate species were not prominent in this case.

A possible explanation for the negative result is that the original anomalous adsorption was found when using a phosphate solution which had been evaporated to dryness the day before, in order to increase the pH. The above measurements were carried out with the same phosphate solution, but 11 days after the evaporation, during which time the "sticky" phosphate may have adsorbed on to the glass, or decomposed to ionic phosphate.

Chromatography

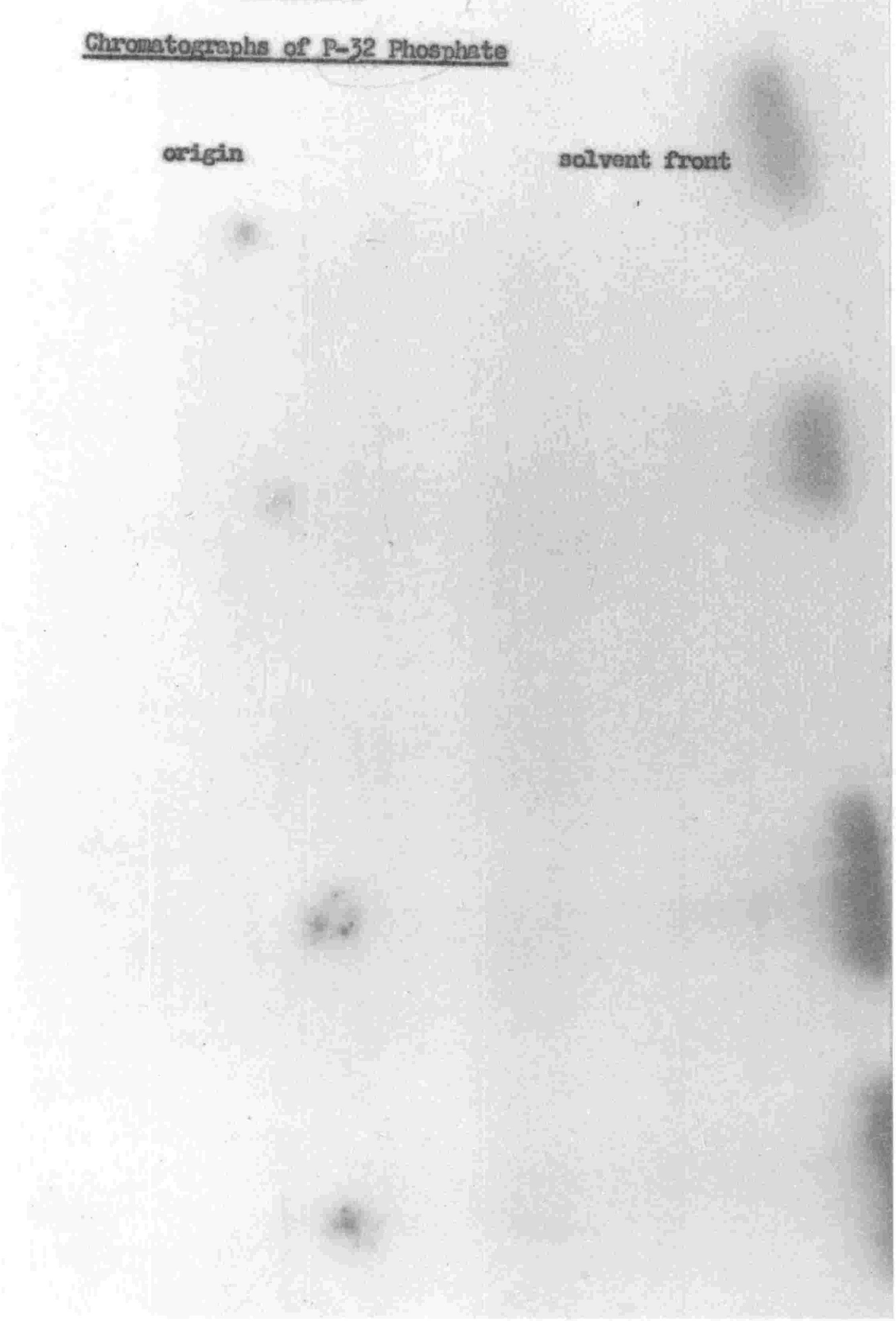
At attempt to distinguish various types of phosphate was made, using rising front chromatography. The paper was soaked in 10^{-4} KH_2PO_4 and dried, and 10^{-4}M. KH_2PO_4 was used as the solvent. Several spots of the "carrier-free" pH 5.5 $^{32}PO_4$ solution were put on the paper, and after letting the solvent nearly reach the top of the paper it was dried and autoradiographed. The autoradiograph (fig. IV.1) was then used to locate the active parts, which were cut out and counted.

It was found that about 4% of the activity in the drop was firmly stuck to the origin, while the rest ran with the solvent front. Because of the large amount of carrier present and the absence of "tailing" this could not be an exchange effect, and seems to indicate that some large or strongly adsorbing particles were present. Similar results were obtained when the phosphate was put on a wet, descending front chromatogram.

This technique should be developed in future so that by the choice of appropriate solvents, (and perhaps thin-layer chromatography), the components may be separated at positions between the origin and solvent front. The composition of the solutions might then be assumed with more confidence.

Fig. IV.1

Chromatographs of P-32 Phosphate



APPENDIX V

DETECTION BY COUNTERS OF THE RADIATION FROM RADIOACTIVE ATOMS

INTRODUCTION

This appendix describes the detection of the radiation emitted by some of the isotopes used in this thesis, with emphasis on calculating the efficiency of detection with the end-window Geiger counters used in much of the work. There is first a brief summary of nuclear phenomena, and a more detailed description of the electronic changes which follow an electron-nuclear interaction. The principles outlined are then applied to the description of the radiation from the four electron-capture isotopes used.

DESCRIPTION OF SOME DECAY PROCESSES

Beta Decay

In this process electrons with a continuous energy distribution are emitted from the nucleus. Only a few of them have the maximum energy. The most probable energy can be either zero, or somewhere between zero and the maximum energy, depending on the transition nature. Owing to a coincidental relationship between the energy spectrum and the energy loss mechanisms the attenuation of β decay electrons is approximately exponential.

Electron Capture

An orbital electron is captured, from one of the inner shells, usually the K or L. Some of the energy charge involved is carried off as a neutrino, which is undetectable. The product atom is left in an excited electronic state, owing to the absence of an orbital electron, and in the process of losing this energy X-rays and Auger electrons are emitted.

γ Radiation

The nuclear state resulting immediately from the beta emission or electron capture can be either the ground state or an excited state. If an excited state is formed the excess energy is usually lost by the immediate emission of electromagnetic radiation, usually having an energy somewhat greater than X-rays. In some cases a significant time delay is observed - the excited state is then called a metastable state. Often transitions occur to several excited states in series, each transition leading to separate γ rays. If there are no metastable states formed these will be "coincident" γ rays. These coincident γ rays will generally be emitted in different directions, so unless the detection efficiency is very high they can be regarded as independent emissions.

Internal Conversion Electrons

In some transitions there is a high probability that instead of a γ ray being emitted the energy is carried off by the emission of an orbital electron, with an energy equal to the γ ray energy minus the electron binding energy. This leaves the atom in an excited electronic state similar to that when electron capture occurs. However, the relative probabilities of internal conversion from the various electronic shells and sub-shells are different for the corresponding probabilities for electron capture, and this must be borne in mind when estimating the electronic effects resulting when both electron capture and internal conversion are occurring simultaneously.

The electrons emitted in internal conversion processes are monoenergetic, and although they have a fairly definite maximum range, which equals that of the maximum range of a continuous beta spectrum of maximum energy equal to the monoenergetic electrons, the absorption of the monoenergetic electrons is strongly dependent on the experimental arrangement (Evans, 1955), and it is not possible to talk of an absorption coefficient or half-thickness.

ELECTRONIC EFFECTS FOLLOWING DECAY

Energy Loss Mechanisms

Electron capture and internal conversion result in vacancies in the orbital electron shells, and in particular the K and L shells. If a K shell vacancy occurs it is filled by a transition of an electron from an outer (usually the L) shell, the energy change being carried off either as electromagnetic radiation (an X-ray), or by the emission of an electron from the atom. This electron, called an Auger electron, leaves behind a further vacancy in an L or higher shell, and this in turn fills up by either X-ray or Auger electron emission.

Thus electron capture and internal conversion are followed by a cascade of X-rays and Auger electrons, and it is sometimes necessary to be aware of the proportions of the different processes. In particular, when attempting to estimate the relative efficiency of using an end-window Geiger counter and using a scintillation counter to count γ-emitting electron capture isotopes, it is necessary to know what fraction of the total decays give rise to emission of K or L X-rays.

Calculation of the Number of Electron Shell Vacancies

The information needed to calculate the X-rays produced is not always available, if or available is scattered through several publications, and in forms which can only be converted to the required numbers after some considerable calculation. Probably the most useful single compilation at the time of writing is "The Radiochemical Manual" published by the Radiochemical Centre, Amersham, (Wilson, 1966). This book gives, as well as the more common useful data, the γ-ray and internal conversion intensities as fractions of the total number of transformations of the isotope, for most of the useful radio-isotopes.

Other pieces of information needed if electronic transitions are to be calculated are the ratio of capture in the K shell to that in the other shells, and the corresponding ratio for internal conversion. This information is more difficult to come by, but a source of information which is extensive, even if somewhat old, is the compilation of nuclear data by Strominger, Hollander and Seaborg (1958).

In most cases the ratio of L capture to K capture can be found approximately from the theoretical curve published by Rose and Jackson, (1949). From this curve a number can be found, which when multiplied by the square of the ratio of the energies of the neutrinos emitted in L and K capture, gives the ratio of L to K capture. If the neutrino energy is much greater than the electron binding energy of a few KeV, then this energy ratio very nearly equals 1, so the curve can be used directly. For atomic numbers from 20 to 50 the ratio of L to K capture when the neutrino energy is high ranges from 0.08 to 0.12. However, it is necessary to check that the energy effect is unimportant, for in some cases, such as ^{75}Kr, ^{193}Pt, ^{202}P6 or ^{205}P6 very little, if any, capture occurs from the K shell. If the internal bremsstrahlung end-point energy is given, this may be taken as equal to the neutrino-energy, and this should be compared with the K-shell binding energy. As long as it is greater than a few hundred KeV, the variation from the given curve should be unimportant.

The internal conversion process is comparatively complicated, and the probabilities are generally used to find out the properties of nuclear energy states. This means that if sufficient data is available to calculate the required information, this information is usually available as a direct experimental measurement. The probability of internal conversion is greater for inner shell electrons than outer ones.

Fluorescence Yields

The capture and conversion data may be used to find the number of initial K and L shell vacancies produced. It is then necessary to consider the relative probabilities of X-ray and Auger electron emission. This probabilitiy is described by the "fluorescence yield", ω. The ratio of the number of K X-rays emitted to the total number of K vacancies is called ω_K, and similarly for the other shells.

Slack and Way (1959) give graphs of the variation in ω_K and ω_L with atomic number, and there is a very great difference in the values for low and high atomic number. Below Z = 18, $\omega_K < 0.1$, while above Z = 50, $\omega_K > .85$. The graph of ω_L does not extend below Z = 40, at which value $\omega_L = 0.06$, and rises linearly so that at Z = 70 $\omega_L = 0.25$. It is clear that very few L X-rays will be produced in the lighter elements.

From the K-fluorescence yield and the probability of Auger electron emission from various shells, Slack and Way have calculated the number of L vacancies formed as the result of initial K-vacancies, and presented the results as a graph, which ranges from 1.5 at Z = 24 to 1.0 at Z = 44 and 0.8 at Z = 73.

Once the number of initial vacancies produced in the various shells is known, one can calculate the total electronic effects.

RADIATION FROM ^{57}Co

Primary Radiation

The radiations from ^{57}Co, which decays by 100% E.C., are given in the Radiochemical Manual as -

Transition Energy	% γ-rays	% I.C. electrons
14 KeV	8.2	81.6
122 KeV	88.8	1.0
136 KeV	8.8	1.2

The percentages are the number of γ-rays or electrons expressed as a fraction of the number of nuclei which undergo decay. The total is greater than 100% because of emission of radiations in cascade.

Owing to its simple decay scheme this information is easily found also from the data given by Strominger et al, which gives the relative γ-ray intensities and the ratio of internal conversion electrons to γ-rays. In most cases this is difficult.

Calculation of X-Rays

Moussa and Juilliard (1956) have measured the ratio of L to K capture, and obtained the value 0.2 ± 0.16. Using this number we find that 80% of the captures produce K vacancies and 20% produce L vacancies. The 122 and 136 KeV internal conversion electrons will contribute negligibly to the L shell vacancies (K/L is about 7). The 14 KeV internal conversion K/L ratio is 8.9 (Strominger et al.) so that internal conversion overall produces 9% of L vacancies and 78% K vacancies.

The total of K-shell vacancies is 160%, which leads (at the rate of 1.4 L vacancies per K vacancy, found in Slack and Way (1959)) to 220% L vacancies, giving a total number of L vacancies of about 250%.

The K fluorescence yield is 0.33 (Slack and Way), so that 52% of the decays give K X-rays. Assuming an L fluorescence yield of 0.03, (a great extrapolation is used for this) 7% of decays would give L X-rays.

Significant Radiations

The internal conversion electrons from the 14 KeV level have a range in aluminium of only about 0.2 mg/cm^2, so would be quite undetectable in the present counters. Thus the radiations and proportions which could affect the Geiger counter are -

X-Rays	K (8 KeV)	52%
	L (0.7 KeV)	7%
I.C. Electrons		
	about 120 KeV	2%
γ rays	14 KeV	8%
	122 KeV	89%
	136 KeV	9%

Experimental Determination of the Most Significant Radiation

Preliminary experiments suggested that a very soft component was responsible for most of the count rate observed with the EW3H end-window Geiger counter. The problem of whether the L X-rays or electrons were responsible was resolved by plotting the variation in count rate with absorber thickness for two absorber materials of different atomic number. The photo-electric cross-section for photon interaction, on which the X-ray attenuation largely depends, is very strongly dependent on the atomic number of the absorber, (approximately as Z^4), so the transmission curves were obtained using, in one case, aluminium, and in the other, polythene film (which for the purposes of this experiment is almost entirely carbon). The attenuation of electrons is independent of atomic number.

The results of the experiment are shown in fig. V.1, and it is clear that the radiation is a combination of photons and electrons. The electrons and photons are initially attenuated at the same rate in aluminium, so the effect of the electrons is only noticeable as a slight flattening off of the curve near zero thickness. However, in polythene, the electrons are attenuated at the same rate as in aluminium, but the photons are attenuated about twenty times slower. This leads to the sharp discontinuity once the electrons have been absorbed.

It turns out that about 60% of the initial count rate is due to electrons, and 40% to photons. In principle it is possible to separate by graphical analysis, the contributions due to photons with various energies, but the graphs obtained did not separate convincingly into separate terms, possibly because the geometry of the detection system was not such as to ensure measurement of only that radiation which had not interacted with the absorber.

The conclusion that the internal conversion electrons are important is clear. It may be established that their energy is about 120 KeV by noting that the deviation from the linear part corresponding to photon absorption in polythene occurs at about 15 mg/cm^2, which, after allowing another 2 mg/cm^2 for the end window and 2 mg/cm^2 for the air, agrees very well with the expected maximum range of the electrons (18 mg/cm^2).

The approximate slope of the photon attenuation graphs shows that the photons are about 10 KeV in energy, and so they are the K X-rays and 14 KeV γ-rays.

X-Ray Efficiency of the Geiger Counter

The ratio of counts from the electrons and photons is about $1\frac{1}{2}$ to 1. However the relative proportions of high energy electrons to 10-20 KeV photons is about 1 to 30. Thus the efficiency of counting these photons is only about 2% that of counting the electrons. Since the electrons are likely to be counted with something approaching 100% efficiency, the low energy photons must be counted with only about 2% efficiency.

The above measurements suggest that the EW3H Geiger counter is a somewhat inefficient way of detecting ^{57}Co. When the work on ^{57}Co was started, a comparison was made between the EW3H and a scintillation counter, and a result was obtained which suggested that they were of comparable efficiencies. At the time, it was believed that X-rays were being detected by the EW3H, so this result was not surprising. Subsequent comparisons have shown that the EW3H has about 5% of the efficiency of the Philips scintillation counter used. The original measurement must have been in error, possibly because of overloading of the electronics. This will not affect any of the conclusions of the experiments performed, because these were all based on ratios of counts with the same counter.

RADIATION FROM ^{67}Ga

The nuclear information in the following table of radiations from ^{67}Ga was obtained from the Radiochemical Manual, and the information on X-rays calculated as in the ^{57}Co case.

Transistion Energy (KeV)	% γ-ray	% I.C.
92	42	29
182	24	
206	2.5	
300	22	
390	7	
K X-ray	55	
L X-ray	5	

From the information on the relative efficiencies of detecting internal conversion electrons and X-rays, it is clear that most of the counts obtained with an EW3H Geiger counter will be due to the electrons.

A comparison was made between the count rate obtained with the EW3H, and that obtained with two scintillation counters (a Nuclear Enterprises one with a 1" crystal, and a Philips one with a 2" well crystal), under comparable geometrical conditions. The rates of the scintillation counters were very similar, and that of the EW3H was about 64% of this.

Because of its lower background, and comparable efficiency, the EW3H was the preferred counter.

RADIATION FROM ^{131}Cs

^{131}Cs decays by pure electron capture, with no γ-rays, so that the only radiations which can be detected are the xenon K and L X-rays, at 30 KeV and 4 KeV. Strominger et al (1958) quote a value of L to K capture of 0.1, so that the initial vacancies are roughly 10% in the L shell and 90% in the K shell. From Slack and Way (1959) it is found that for Z = 55 there are about 0.9 L shell vacancies per K shell vacancy, so that overall about the same number of L shell and K shell vacancies are formed.

The K fluorescence yield is about 0.9, so that about 80% of captures give rise to 30 KeV X-rays. The L fluorescence yield is about 0.16, so that about 14% of captures give rise to 4 KeV X-rays.

The efficiency of a counter for detecting radiation depends on the probability of interaction of the radiation with the counter. For X-rays of the present energy, this probability is inversely proportional to the cube of the energy, because interaction is almost solely by the photoelectric effect. Thus the efficiencies of a counter for the 30 KeV and 4 KeV X-rays may be very different.

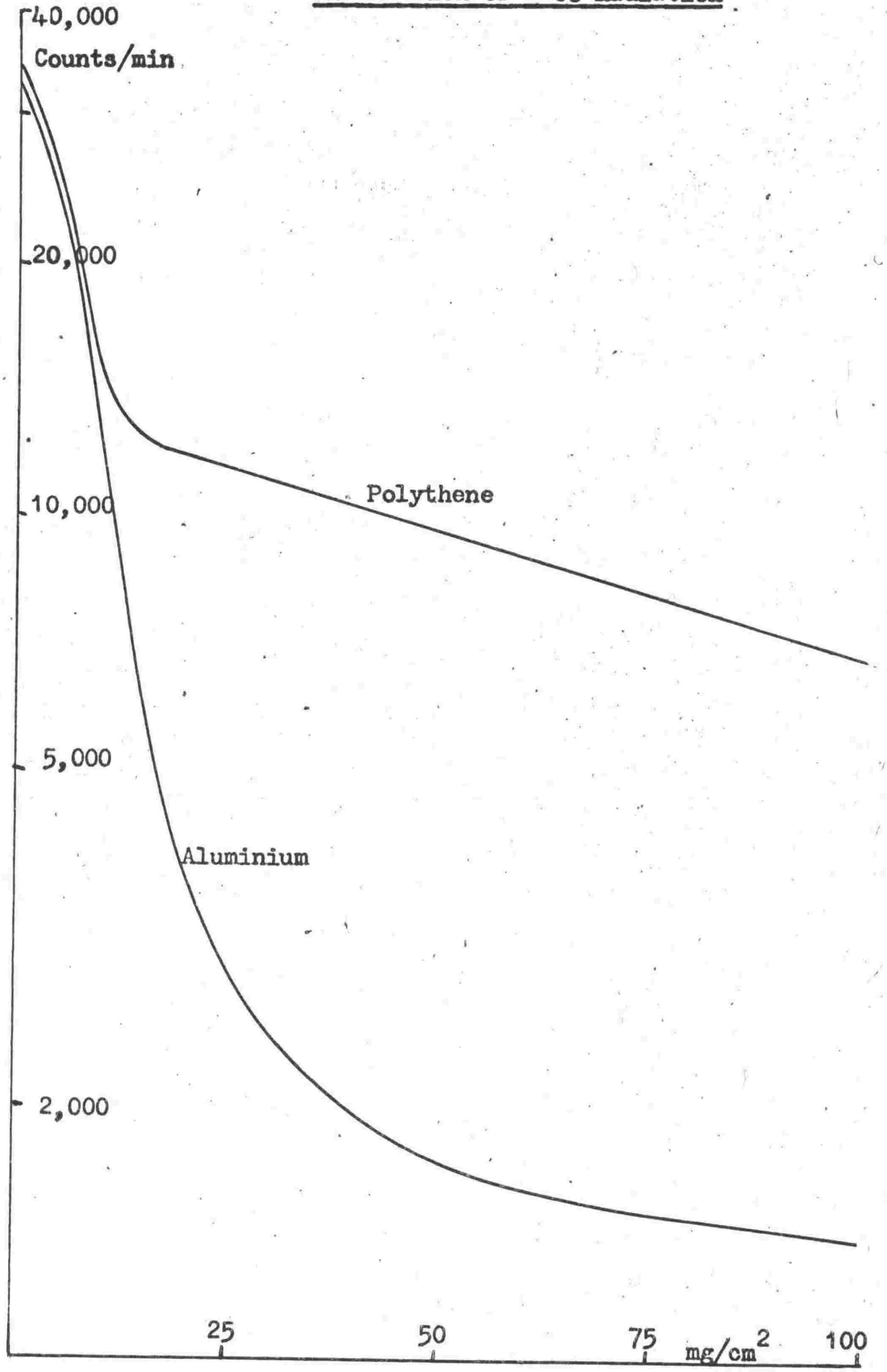
The efficiency is $(1 - e^{-\sigma x})$, where the cross-section for interaction with the material in the counter is σ, and x is the amount of material in the sensitive volume of the counter. For the EW3H counters, $(1 - e^{-\sigma x})$ is small at about 10 KeV, so that σx is small, and so $(1 - e^{-\sigma x}) = \sigma x$. The relative efficiency for 4 KeV and 30 KeV X-rays is therefore approximately equal to the ratio of their cross sections, which is in turn equal to $30^3/4^3 = 400$. Even allowing for the fact that the approximation to the exponential may not be very good for the 4 KeV X-ray, it is clear that most of the radiation detected with the EW3H will be L X-rays.

RADIATION FROM ^{55}Fe

^{55}Fe decays by pure electron capture, with no γ-ray. The only radiation of significance to Geiger counters is the manganese K X-ray at 5.9 KeV. (The L X-rays would be few in number because of the small fluorescence yield, and they would also have too low an energy to have a useful range in air.). It would be expected from the ^{57}Co measurements that the efficiency of counting the X-rays produced would be very low with the EW3H, so that a great saving in the amount of isotope needed could be made by using a counter designed especially for X-rays. Such a counter would have a low-Z window, and a high-Z gas at high pressure.

Fig. V.1

Attenuation of ^{57}Co Radiation



APPENDIX VI

DETECTION OF ELECTRON-CAPTURE ISOTOPES BY AUTORADIOGRAPHY

DETECTION BY X-RAY FILM

The Film Used

The film used in most of the autoradiography was Kodak Royal Blue Medical X-ray film, which has two layers of sensitive emulsion 12μ thick, on a plastic base 200μ thick. The emulsion is protected by a 2μ thick layer of gelatin. No information was available on the emulsion composition, but a reasonable figure would probably be about 2 grams/ml of AgBr, with gelatin and other ingredients bringing the density up to about 2.5 grams/ml. As far as the X-rays are concerned, only the high atomic number constituents are important, so we can assume the emulsion is 2.4 mg/cm^2 of atomic number about 40. The base and protective overcoat can be regarded as mainly carbon ($Z = 6$) with density 1 gm/cm^3.

Detection of 10 KeV X-Rays

This energy is somewhat greater than that from ^{57}Co or ^{67}Ga K vacancies, or ^{131}Cs L vacancies, but it gives an indication of the type of behaviour expected. Since the cross-section varies as $(h\gamma)^{-3}$ the exact behavious must be individually calculated.

In the AgBr 10 KeV X-rays would have a ½-thickness of about 10 mg/cm^2, and in the base and gelatin about 200 mg/cm^2. This means that about 20% of the incident photons would be stopped in the first emulsion layer, about 75% of them would reach the second layer, and about 15% would be absorbed in the second layer. Thus approximately equal intensities should be found on both faces. The attenuation of 5 KeV X-rays would be 8 times greater, so that these would be almost all stopped in the first emulsion layer.

Detection of 1 KeV X-Rays

These could be L X-rays from ^{57}Co or ^{67}Ga. The protective coating is about .2 mg/cm^2. Since the ½-thickness of 1 KeV X-rays is about .8 mg/cm^2 in aluminium, and is approximately proportional to Z^4 when no absorption edges interfere, the attenuation in this layer should be very small. The emulsion being 2.4 mg/cm^2, of high Z material, then all the X-rays will be absorbed in the first emulsion layer.

Detection of Auger Electrons

The maximum range of 10 KeV electrons is about .2 mg/cm^2, independent of the atomic number, so that none of the Auger electrons from ^{57}Co or ^{67}Ga will penetrate the protective coating.

Detection of Internal Conversion Electrons from ^{57}Co

The electrons from the 14 KeV level of ^{57}Fe (from ^{57}Co) will be mostly of similar energy to the Auger electrons, and thus not detected.

The other electrons have energy about 100 KeV, which have a range of about 15 mg/cm^2. Thus little attenuation is produced by the protective gelatin coating, while the first emulsion layer is about a fifth of the maximum range of the particles, and the base is greater than the maximum range. Thus exposure from 100 KeV internal conversion electrons would be only in the first emulsion layer.

Conclusions Regarding ^{57}Co and ^{67}Ga Detection

It would be expected that most of the K X-rays would be stopped in the first side of the film, as would all the L X-rays and high energy internal conversion electrons. One side of the film would therefore be exposed much more than the other. This was found to happen.

HIGH RESOLUTION AUTORADIOGRAPHY

For this work Ilford G5 emulsion was used, as a stripping film with 5 microns of emulsion on a 10 micron base. With this technique the emulsion is in direct contact with the sample, so that all radiations, including Auger electrons, enter the emulsion.

Barkas (1963) is a source of much information about nuclear emulsions, but mainly from the point of view of the observation of the tracks of nuclear particles. From this reference it was learned that the density of AgBr in nuclear emulsions is generally greater than in other emulsions, being about 3 gm./ml. The size of undeveloped grains in G5 emulsion is about 0.3μ, but with the plating-out of silver which occurs with developers such as D19, the developed grains are about twice this size.

Low energy electrons, such as those from tritium, ($E_{\beta \max}$ = 18 KeV, mean energy 5.5 KeV) give no tracks because their range is so low. A 10 KeV electron has a range of 0.9μ, and a 100 KeV one 50μ in nuclear emulsion. The low energy electrons give isolated grains, indistinguishable in nature from the background fog.

It is clear that around a point source of ^{67}Ga or ^{57}Co should be a region of about one micron radius in which all the silver halide grains are exposed by K-LL Auger electrons. The L X-rays will also be mostly stopped in this region, but the K X-rays would travel much further, with a half-thickness of about 30μ. With an emulsion layer a few microns thick the exposure would be entirely due to L X-rays and Auger electrons, so that resolution to within a few microns should be possible.

AMENDMENTS TO PROGRAM DESCRIPTIONS

R. Hoare, September, 1967.

Program UCHH04: This program has been modified so that, when choosing the range of the log (count rate) scale, the upper range is set by the greatest count rate in the range hours [i] to hours [j], and the lower range is set by the smallest rate in that range, unless that rate is 1.0001.

Program UCHH12A:

Plots percentage count rate versus log (hours).

Program UCHH12B:

Plots percentage count rate versus sqrt (hours). No account is taken of word generator keys, but either form of data tape will be accepted.

After drawing the first graph, the data tape is examined to see if the character "R" is in the reader. If so, the values of "countmax" and

maximum values of its coordinates countmax and sqrt (hoursmax). Countmax will be a percentage countrate. The data tape will end with

time↑ divisorR countmax hoursmaxⒽ e.g. 267↑ 12340R 5 2 Ⓗ

Program UCHH12C:

Plots percentage count versus 1/sqrt(hours).

Comments for H12B apply.

APPENDIX VII

USE OF THE ELLIOTT 503 COMPUTER FOR DATA PROCESSING, WITH PROGRAMMES UCHH04, UCHH11 AND UCHH12

The programmes have been written for the Elliott 503 computer owned by the Applied Mathematics Division of the Department of Scientific and Industrial Research, and use the Algol programming language. The programme and data are both read in from paper tape, and the data is output on a lineprinter and a graphical plotter.

The first sections of all the programmes are very similar, being designed to read in the experimental data, and calculate the count rate and time for each point, after allowing for the ratemeter range, chart speed, small errors when ranges are changed, attenuating filters introduced to extend the range of radioactivity measurable, dead time of counters, background and decay. After printing this information on the lineprinter, it is further processed and output on the graphical plotter, in a way which depends on the particular programme.

One aim of the programmes is to reduce to the minimum the amount of mental work done by the person taking readings from the charts. The data is fed in as numbers corresponding to the percentage of full scale chart reading, and the number of time divisions from an arbitrary, adjustable zero point. In order that these can be converted to count rates and times, various other numbers are fed in as required.

The unit of time used is the hour.

The unit of count rate used is the number of counts/minute.

DATA INPUT

The names of parameters specified in the data tape are -

runNo	The experiment identification number - up to three figures but no letters allowed in this code.
j	The number of data points - choose a number greater than the number counted, in case a small error has been made.
lambda	The decay rate (i.e., $0.693/t_{\frac{1}{2}}$) of the isotope, in hrs^{-1} - (for ^{32}P, $\lambda = 2.02 \times 10^{-3}$)
timefactor	The number of hours per time division. If you are taking points every $\frac{1}{3}$", at a chart speed of 1"/hr, then timefactor = 0.333, and "time" (see below) = 1, 2, 3 etc. Exactly equivalent is to put timefactor = 1 and time = 0.333, 0.667, 1.0, etc. Less writing is entailed by the first method, if more than a few points are involved.
ratefactor	The number of counts/<u>min</u> (nominal) for full scale reading. If, as when using the printer, the actual number of counts in a specified interval are being measured, then ratefactor $= \frac{100}{\text{time for interval}}$

scalefactor	Allows for differences in the reading of the ratemeter observed sometimes when the range is changed, by assuming that the new scale is proportional to the old one. It is the ratio of the apparent count rate on the old range to that on the new range. If on the old range, of full scale reading S_1, the reading was X_1, and on the new one, full scale = S_2, the reading is X_2, then scalefactor is $\frac{100S_1X_1}{100S_2X_2} = \frac{10X_1}{3X_2}$ or $\frac{3X_1}{X_2}$, depending on which scale change is made.
filterfactor	Is the ratio of the number of counts/minute before the change to that after the change. It is necessary to allow for deadtime and background in the calculation of this factor.
deadtime	must be expressed in minutes. (0.6 m S. = 10^{-5} min.)
background	is in counts/minute.
timestep	This is used when there is a constant time = timestep between data points.
timeshift	is the elapsed time in hours from the start of the run to any point where a change is made in the value of timefactor. This is also used to enable counting of time divisions to start at any convenient place, in order to avoid fractions of divisions, and to avoid writing "time" to 3 figures when it gets up in to the hundreds - merely increasing timeshift by the appropriate number enables small (0-100) values of "time" to be used.

time	is the number of time divisions measured from the last change in timeshift. "time" has dimensions of <u>distance</u> along chart. For very long runs it may be convenient to measure time in days (e.g. 1000 hrs = 30.42 days), in which case timefactor = 24.
record	is the % of full scale chart reading, usually. If it is the actual number of counts, then put ratefactor = 100/ (the time for which the count was taken).

CALCULATION OF COUNT RATES

The time (hours[i]) and count rate (count[i]) for each point, characterised by the index, i, are calculated as follows -

```
hours[i]:=  timeshift + time* timefactor
count[i]:=  record*ratefactor*scalefactor/100
count[i]:=  (count[i]/(1-deadtime*count[i]) - background)*
            filterfactor*exp(lambda*hours[i])
```

(the symbol := means "set the value of the variable on the left equal to the present value of the expression on the right").

Different values of i correspond to the different pairs of time and record.

PREPARATION OF DATA TAPE

The numbers must be written on the data tape in the right order, for the computer cannot identify the numbers in any other way.

The first number is runNo
second number is j
third number is lambda

In normal operation we have

fourth number is deadtime
fifth number is background

These parameters remain fixed for the whole run.

Next follows a set of parameters as follows -

timefactor, ratefactor, scalefactor, filterfactor and timeshift, in that order.

This set is repeated each time it is desired to change the value of one of these parameters during a run.

Then come the values of time and record, in that order (e.g., 0.333, 97, 0.667, 84, 1, 75, etc.)

After reading the first two groups of numbers the computer reads the tape in groups of two numbers until it finds that the character immediately after the last "record" number is one of five "buffer" characters - any other characters except numbers are ignored. On finding one of these buffers, it performs the following operations -

buffer	operation
*	reads new set of parameters, e.g. when change ratefactor - all the numbers in the set must be written in, even if the values are the same as before.
↑	end of data - must follow the last value of "record".

buffer	operation
A	On reading this, the computer sets "timestep" equal to the next number on the tape, and then reads each number as a value of "record". Each time it reads a number it advances "time" by the value of "timestep".
X	indicates a missing value of record - it causes "time" to be increased without calculating "count" when running in the time-stepping mode.
B	causes the computer to read "time" and "record" alternately again.

A, B or X cannot occur after the first value of "timeshift" but may occur after subsequent values, (i.e., there must be a "time", "record" pair at the start of a run.

The data to be fed into the computer is written out by the user on to 503 Algol Programme forms, copies of which are available from the University Flexowriter operator. The completed forms are punched up by the Flexowriter operator, to give a typewritten copy and a punched tape. After checking the copy for errors, the tape, along with the programme tape and a 503 work sheet, which contains instructions to the computer operator, are handed in to the computer.

Layout of numbers on the programme sheet is unimportant to the computer, which reads the tape sequentially. Checking of the typed copy is much easier with a neat and systematic layout.

Buffer characters must immediately follow a value of record or timeshift (or another X in the case of X). After reading a number, if the next character is not a buffer, the computer ignores all non-numerical characters, and moves the tape along to the next numerical character. This means that identifying labels can be used on the data tape.

PROCESSING AND OUTPUT

The programmes in this set vary in the form in which the processed data is output. All of them give an initial output on the line-printer of the value of "count" and "hours" calculated for each point, together with the index "i" which indicates the position in the data sequence. The range of the data is $0 < \text{hours}[i] < 10{,}000$ and $1 < \text{count}[i] < 100{,}000$. If $\text{count}[i] \leq 0$ then it is set equal to 1.0001. This must be watched if filters are used to alter count rates during a run. If, as may occur when using a scintillation counter, count[i] is greater than 10^5 counts/minute it is possible to work in counts/second, provided appropriate units are used for "deadtime", "ratefactor" and "background".

The output is followed by graphical output, the form of which depends on which programme is being used.

Other general notes about the programme concern the selection of different paths in the data processing section. This is done by choosing certain settings of the "word generator keys", which are an array of switches on the computer control console, labelled WG1, WG2 etc. up to WG39. The desired position of the first few of these keys must be stated in the work sheet submitted with the programme and data to the computer operator. If WG1 is down, then "deadtime" and "background" are read in as data along with, and between, "filter-factor" and "timeshift", instead of at the start, after "lambda".

This can be useful if one or other of these is known to have changed during a run.

A simplified flow chart is shown in fig. VII.1 and VII.2, and should be of some help in understanding the use of the buffers, and other aspects of the processing calculations.

THE WORK SHEET

One of these must be submitted when putting the tapes in for a run, for it tells the computer operator how to set the machine up. Filling out of the form should be obvious. The version HO4 is available in RLB code (which the machine reads directly without translation) while the others are in Algol. The equipment used is reader (1), lineprinter, and plotter. When the Algol versions are used it is necessary to ask for the procedure "plot" to be inserted.

The positions of word generation keys one to four should all be specified as the required values (up or down).

PROGRAMME UCHH12

This version produces a graph of the logarithm of the time, versus the count rate expressed as a percentage of some number which is input as an additional piece of data. When this programme is being used the data tape must contain this number after the arrow buffer which designates the end of the ordinary data. This number can easily be added to a tape produced without it, providing the "halt" character usually on the end of the tape is erased. It will not affect the running of this data tape on other programmes. For an adsorption experiment this number (called "divisor") would be the decay-corrected equilibrium count rate, while for a desorption experiment it would be the extrapolated initial count rate. The graph output has the percentage count rate from 0 to 100% on a 5" long ordinate scale, and the logarithm of the time in hours on a 9" long abscissa, from −3 to +4. All points are plotted except those falling outside the range of the axes, or whose "count" values are less than 1% different from the previous value of count to be plotted.

After output of the graph the values of percentages and log (hours[i]) are output on the lineprinter, in the same format as the initial data, and the programme waits for another set of data.

PROGRAMME UCHH04

Programme UCHH04 is designed to plot the log of "count" against "hours", and then to read in two numbers from the control typewriter of the computer, which specify what section of the graph is to be regarded as a straight line, for purposes of calculating an exponential term. It calculates this straight line, using a least squares fit to the specified points, outputs the value of halflife and intercept on the control typewriter, and subtracts the values of this line from the remaining points. It also draws the calculated line on the graph. It then prints the new set of values of "count" on the lineprinter, draws the graph and proceeds exactly as before.

The graph scales are calculated automatically so that the data will just fit the page. There is provision here for a choice of presentation. If WG4 is up then a continuous line is drawn between the data points - this is inelegant, but fast. If WG4 is down, then a small cross is drawn at each point.

After drawing the graph the message "Type line ends" appears on the control typewriter. If the user is in the computer room, he can look at the graph and see that certain points are on a good straight line. One axis of the graph (the y - axis) has a few divisions, corresponding to the log of 10, 10^2 etc, and is the "count" axis. The other is marked every $\frac{1}{2}$ inch or so, and labelled with numbers 1, 2, 3, 4 or 0, 2, 4, 6 or 0, 4, 8, 12 etc, together with a number in scaled form written above the axis. This number $1_{10}2$ (=100) etc. is the number by which the numbers below the axis must be multiplied in order to find the time in hours. To specify the section of graph to which a straight line is to be fitted, the time co-ordinates of the ends of the section are found, in terms of the numbers on the axis, i.e., you do not multiply by the factor above the line. Interpolation between the labelled time markings is allowed. These co-ordinates do not have to refer to actual points - the programme selects points within the limits you choose.

These time co-ordinates are typed by the operator on the control typewriter, the smaller one first, and a space or other non-numerical character between them and after the last. The programme then continues, does the fit to the points, subtracts the calculated curve, and replots the points which did not lie in the section chosen. "Halflife" and "intercept" are output on the control typewriter, followed by "type line ends". The process can then be repeated.

If the first of the numbers input is zero and the other is not, then after calculating the line in the normal way, the complete set of halflives and intercepts, and the percentage of each intercept relative to the sum of the intercepts, are output on the lineprinter. The programme then returns to the start, ready to accept another set of data. If both numbers are zero then the intercepts etc. are immediately output and the programme returns to the start again - this is used to reject a run.

There are some points to make concerning the details of the programme. The graph plotter is a comparatively slow way of putting out data. To help speed up the process without affecting the accuracy, not all of the data is actually put on the graph. If a point would have to be drawn on the graph with a separation of less than 1% of the full scale distance from the last point plotted, it is left off the graph, although still included in any calculations. Any point which would not fit on the paper is also omitted, and a message "point i out of range" where i is the appropriate index, is output on the lineprinter. In the process of working out the best fit line all points less than $\frac{1}{4}$ or greater than 4 times their neighbouring points are rejected - this guards against ridiculously large or small values upsetting the mean.

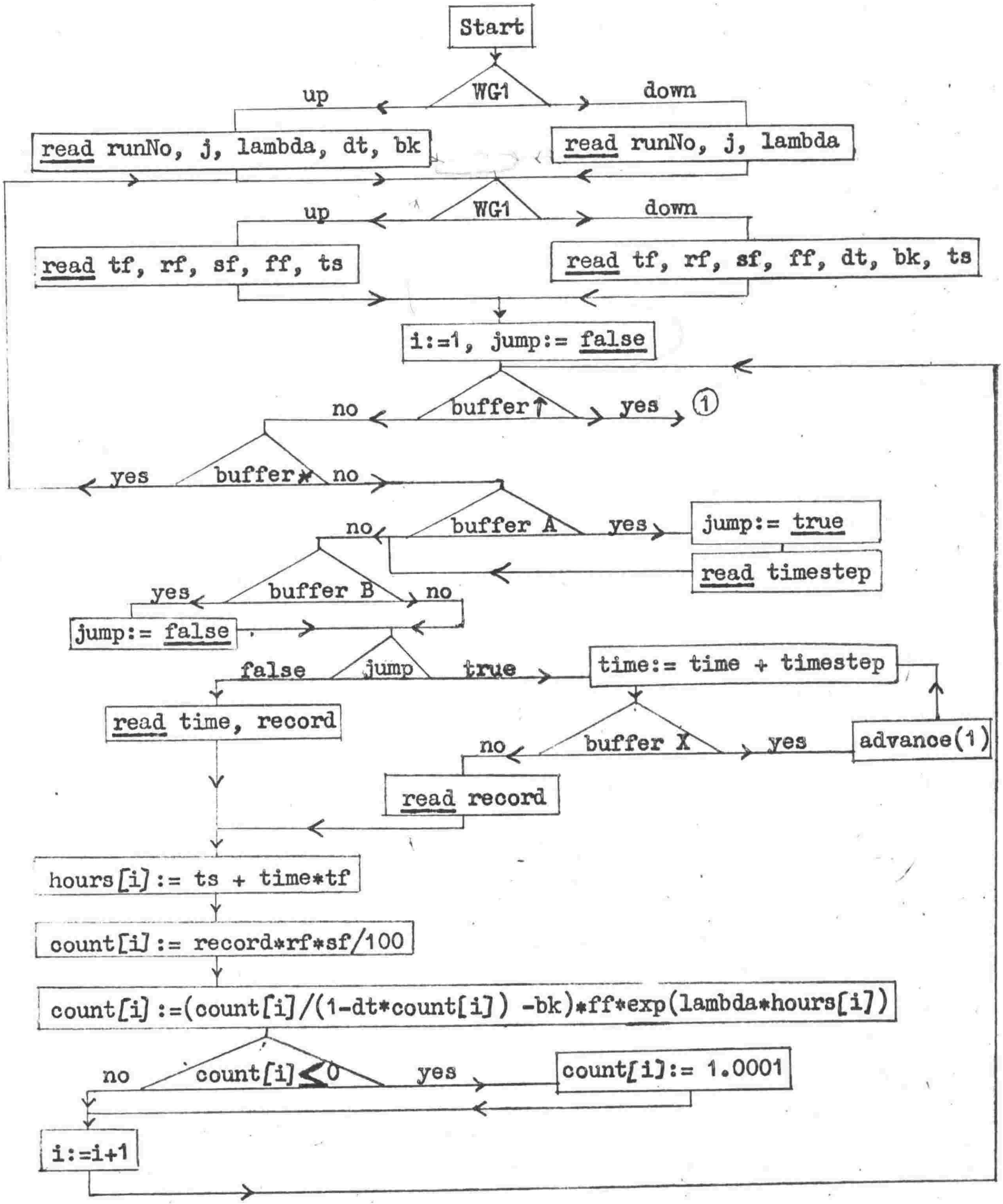
If WG2 is down, a message "backfix =" is typed out, and the programme waits for a value of "background" to be typed in. This was intended to be used if it was suspected, after observing the graph, that a better line would result from a different value of "background". In this case, after changing WG2, and typing "repeat", the data tape would be read in again. After reading the first few numbers the message "backfix =" would appear, the operator would type the desired new value, and the processing would continue.

If WG3 is down, a message "lambda=" appears. A new value for "lambda" can be entered as with "backfix". This facility was intended to show whether long halflives are in fact infinite if a slightly different decay constant is assumed.

PROGRAMME UCHH11

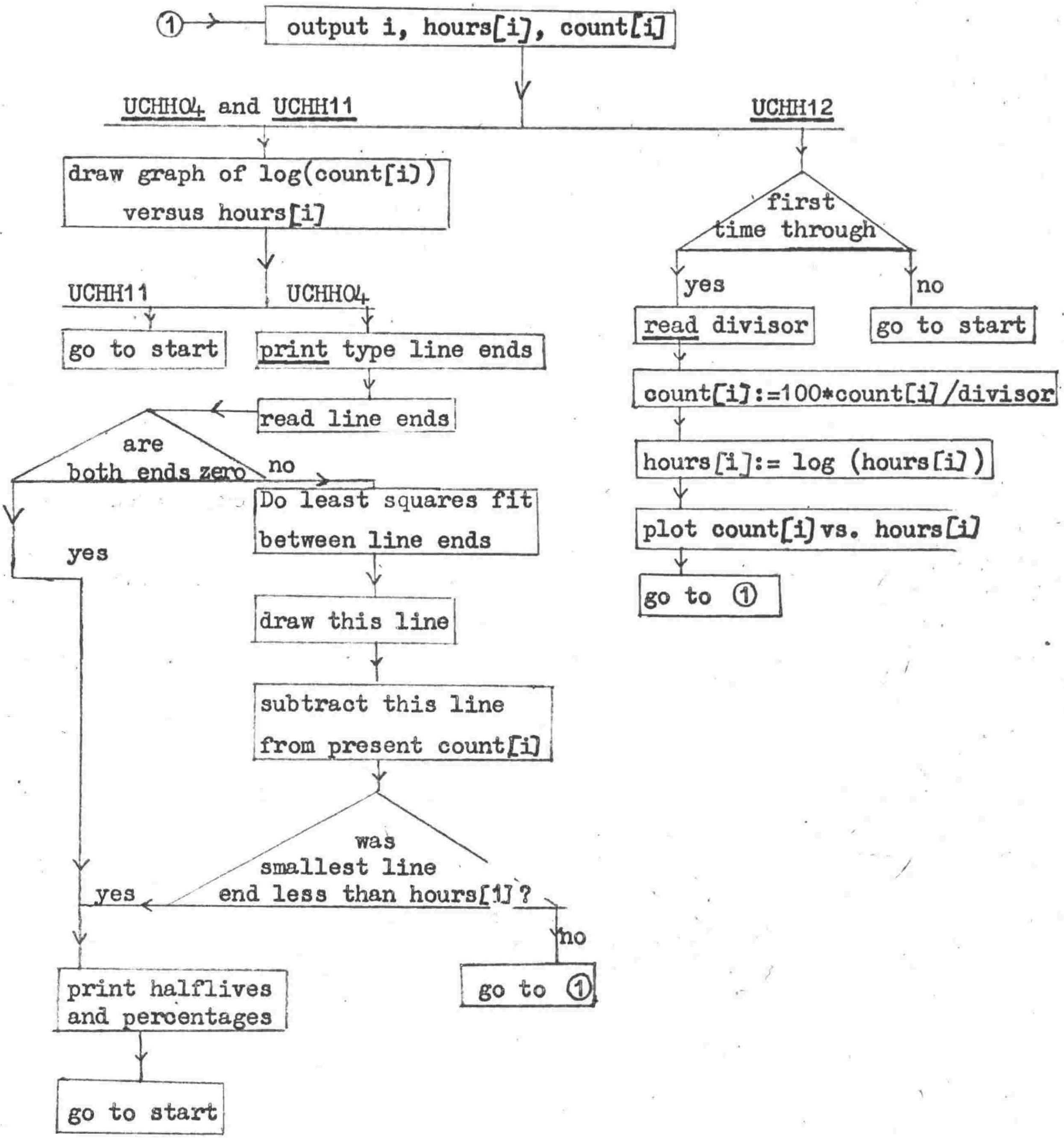
This programme is based on UCHH04, and provides the same output, except that on drawing the first graph of log(count(i)) versus hours(i), it returns to the start, ready for another set of data.

Fig. VII.1 **DATA PROCESSING**



DATA OUTPUT

Fig. VII.2



```
UCHH12;
begin real time,timefactor,record,ratefactor,scalefactor,filterfactor,
          deadtime,background,timeshift,lambda,timestep,shift;
     integer i,j,runNo,b;
     Boolean jump;
     switch ss:=start ;
     Boolean procedure sense(j);
          value j;
          integer j;
          begin integer i;
               i:=1;
               elliott(7,0,0,0,6,7,j);
               elliott(5,0,8191,0,2,3,i);
               sense:=i=1
          end;
     shift:=0 ;
start:if sense(1)then read runNo,j,lambda else read runNo,j,lambda,deadtime,background;
     sameline ;
     print punch(3),££L?Run?,runNo,££L??;
     begin array hours[0:j],count[1:j];
          switch S1:=L1,L2,L3,L4,L5;
          i:=1; b:=0 ; hours[0]:=1₁₀6 ;jump:=false;
        L1:if sense(1) then read timefactor,ratefactor,scalefactor,filterfactor,
                                 deadtime,background,timeshift
                    else read timefactor,ratefactor,scalefactor,filterfactor,
                                timeshift;
        L2:goto if buffer (1,£↑?)then L5 else L4;
        L4:goto if buffer(1,£*?)then L1 else L3;
        L3:if buffer(1,£A?) then begin jump:=true;read timestepend;
           if buffer(1,£B?) then jump:=false;
           if jump then begin switch S5:=L25;
                         L25:time:=time+timestep;
                                if buffer(1,£X?) then  begin advance(1); goto L25 end;
                                read record
                                end
                 else read time,record;
```

```
    hours[i]:=timeshift + time*timefactor;
    count[i]:=record*ratefactor*scalefactor/100;
    count[i]:=(count[i]/(1-deadtime*count[i])-background)*filterfactor*exp(lambda*hours[i]);
    if count[i]≤0 then count[i]:=1.0001 ;i:=i+1; goto L2;
L5:j:=i-1; i:=1; lineprinter; digits(3);
    begin integer m,n,s,t;
          switch S2:=L6,L7,L8;
       L8:s:=checki(jdiv4);t:=sdiv50;n:=0;lineprinter;
       L7:ifn<t then m:=50 else m:=checki(s-n*50);
          topofform ; print££L? Run?,runNo,£,page?,n+1,££L?programH12? ;
          if b=1 then print £log10(hours)and percent count£L?? ;
          print ££L2?index   time      rate       index   ?,
                            £time     rate       index   ?,
                            £time     rate       index   ?,
                            £time     rate £L2??;
       L6: sameline;printdigits(4),i,prefix(££S2??),freepoint(4),hours[i],
          freepoint(5),count[i],digits(7),i+m,freepoint(4),hours[i+m],
          freepoint(5),count[i+m], digits(7),(i+2*m),freepoint(4),
          hours[i+2*m],freepoint(5),count[i+2*m],digits(7),i+3*m,
          freepoint(4),hours[i+3*m],freepoint(5),count[i+3*m],££L??;
          if i<m+200*n then begin i:=i+1;goto L6end else n:=n+1;
          if m=50 then begin i:=i+151;goto L7 end;
          if i+3*m+1≤j then begin print ££L2? index   time     rate?,££1??;
                                 for i:=i+3*m+1 step 1 until j do
                                       print sameline,digits(4),i, prefix(££S2??),freepoint(4),
                                             hours[i],freepoint(5),count[i],££1??;
                            end
    end;
    topofform ;
```

```
        if b=1 then goto start ;
        begin real divisor ;
            integer a ;
            procedure drawcross(e,f) ;
                real e,f ;
                begin movepen(e-2/130,f) ; drawline(e+2/130,f) ;
                    movepen(e,f+2/5) ;   drawline(e,f-2/5) ;
                end ;
            read divisor ; a:=1 ;
            if shift<1 then setorigin(50,130,5,1) ;
            movepen(0,shift) ; drawline(0,shift+100) ; drawline(0.05,shift+100) ;
            for i:=1 step 1 until j do if count[i]/divisor>1or count[i]/divisor<0
                                       or hours[i]<1₁₀-3 or hours[i]>1₁₀4
                then print ££l?point?,i,£ out of range£l??
                else begin count[i]:=100*count[i]/divisor ;
                        hours[i]:=0.4343*ln(hours[i]) ;
                        if hours[i]<hours[i-1] or count[i]<count[a]-1 or count[i]>count[a]+1
                        then begin drawcross(hours[i]+3,count[i]+shift) ; a:=i end ;
                    end ;
            movepen(7,shift) ;
            for a:=6 step -1 until 0 do
                begin drawline(a,shift) ; drawline(a,shift+2) ; movepen(a-0.1,shift-2) ;
                    print plotter(10,1),a-3 ; movepen(a,shift)
                end ;
            movepen(0.4,shift+10) ; print plotter(20,1),runNo,£/H12? ;
            shift:=shift+120 ; b:=1 ; goto L5 ;
        end ;
    end ;
end ;
end ;
```

```
UCHH04;
begin real time,timefactor,record,ratefactor,scalefactor,filterfactor,
           deadtime,background,timeshift,lambda,backfix,timestep;
     integer i,j,runNo,b;
     Boolean jump;
     Boolean procedure sense(j);
          value j;
          integer j;
          begin integer i;
               i:=1;
               elliott(7,0,0,0,6,7,j);
               elliott(5,0,8191,0,2,3,i);
               sense:=i=1
          end;
     if sense(1)then read runNo,j,lambda
               else read runNo,j,lambda,deadtime,background;
     sameline ;

     print punch(3),££L?Run?,runNo,££L??;
     if sense(2)then begin print punch(3), £backfix = ?;   read reader(3),backfix end;
     if sense(3)then begin print punch(3), £lambda = ?; read reader(3),lambda end;
     begin array hours[1:j],count[1:j],halflife[1:10],intercept[1:10];
          switch S1:=L1,L2,L3,L4,L5,L11;
          i:=1;b:=0;
          jump:=false;
       L1:if sense(1) then read timefactor,ratefactor,scalefactor,filterfactor,
                                deadtime,background,timeshift
                    else read timefactor,ratefactor,scalefactor,filterfactor,
                               timeshift;
          if sense(2)then background:=backfix;
       L2:goto if buffer (1,£↑?)then L5 else L4;
       L4:goto if buffer(1,£*?)then L1 else L3;
```

```
  L3:if buffer(1,£A?) then begin jump:=true;
                                 read timestep
                           end;
     if buffer(1,£B?) then jump:=false;
     if jump then begin switch S5:=L25;
                    L25:time:=time+timestep;
                        if buffer(1,£X?) then  begin advance(1); goto L25 end;
                        read record
                  end
            else read time,record;
     hours[i]:=timeshift + time*timefactor;
     count[i]:=record*ratefactor*scalefactor/100;
     count[i]:=(count[i]/(1-deadtime*count[i])-background)*filterfactor*exp(lambda*hours[i]);
     if count[i]≤0 then count[i]:=1.0001 ;
     i:=i+1;
     goto L2;
  L5:j:=i-1; i:=1;
     lineprinter;
     digits(3);
     topofform;
L11: begin integer m,n,s,t;
           switch S2:=L6,L7,L8;
           b:=b+1 ;
           L8:s:=checki(jdiv4);
           t:=sdiv50;
           n:=0;
           lineprinter;
        L7:ifn<t then m:=50
                 else m:=checki(s-n*50);
           topofform ; print££L? Run?,runNo,£/?,digits(1),b,£,page?,n+1,££L?? ;
           print ££L2?index   time     rate      index   ?,
                            £time    rate      index   ?,
                            £time    rate      index   ?,
                            £time    rate £L2??;
```

```
   L6: sameline;printdigits(4),i,prefix(££S2??),freepoint(4),hours[i],
      freepoint(5),count[i],digits(7),i+m,freepoint(4),hours[i+m],
      freepoint(5),count[i+m], digits(7),(i+2*m),freepoint(4),
      hours[i+2*m],freepoint(5),count[i+2*m],digits(7),i+3*m,
      freepoint(4),hours[i+3*m],freepoint(5),count[i+3*m],££L??;
      if i<m+200*n then begin i:=i+1;
                              goto L6
                        end
                  else n:=n+1;
      if m=50 then begin i:=i+151;
                         goto L7
                   end;
      if i+3*m+1≤j then begin print ££L2? index   time     rate?,££1??;
                              for i:=i+3*m+1 step 1 until j do
                                    print sameline,digits(4),i, prefix(££S2??),freepoint(4),
                                          hours[i],freepoint(5),count[i],££1??;
                        end
end;
topofform ;

comment The next section graphs count against hours, and calculates
        the exponential terms, under control from the keyboard;
begin real p;
      integer n;
      switch S3:=L9;
      for n:=6 step -1 until -2 do
      begin if hours[j]/10↑n>4 then begin p:=4*(10↑(n-1));
                                           goto L9
                                     end;
            if hours[j]/10↑n>2 then begin p:=2*(10↑(n-1));
                                           goto L9
                                     end;
            if hours[j]/10↑n>1 then begin p:=1*(10↑(n-1));
                                           goto L9
                                     end
      end;
```

```
L9:begin real scaa,scao;
        integer px,py,f,z,a;
        switch S4:=L10 ;
        procedure drawcross4(e,f,scaa,scao);
              real e,f,scaa,scao;
              begin movepen(e-2/scaa,f);
                    drawline(e+2/scaa,f);
                    penraise;
                    movepen(e,f+2/scao);
                    drawline(e,f-2/scao)
              end;
              if b≠1 then movepen(0,(f-z)*1.2) ;
        px:=checki(entier(hours[j]/p)+1);
        scaa:=1000/(p*px) ;
        f:=entier(0.4343*ln(count[1]))+1;
        z:=entier(0.4343*ln(count[j]));
        py:=checki(f-z );
        if py<0 then begin print punch(3),£f-z<0?;gotoL10 end ;
        scao:=checkr(500/py);
        setorigin(50,scaa,scao,1);
        axes(p,1,px,0,py,0);
        movepen(p,py-0.2) ;printplotter(20,1),£Run?,runNo,£/?,digits(1),b;
        for a := f step -1 until z do begin movepen(p/10,a-z) ;
                                            print plotter(10,1),digits(1),a
                                      end ;
        begin for a:=1 step 1 until px do
              begin movepen(p*a-p/5,-10/scao);
                    print plotter(10,1),digits(2),entier(p*a/(10↑(n-1))+0.1)
              end;
              movepen(p*(px-4),25/scao);
              print plotter(20,1),£m?,digits(1),(n-1) ;
        end;
```

```
py:=1;
fori:=1 step 1 until j do
     if 0.4343*ln(count[i])>f or 0.4343*ln(count[i])<z
          or ( hours [i]<0 and i≠1)or hours [i]>hours[j]
      then print ££1??,£point ?,i,£ out of range ?,££1??
     else if hours[i]>hours[py]+hours[j]/100 or i=1
     thenbegin py:=i;
                 if sense(4) then drawcross4(hours[i],0.4343*ln(count[i])-z,scaa,scao)
                 else begin if i=1 then movepen(hours[i],0.4343*ln(count[i])-z)
                                   else drawline(hours[i],0.4343*ln(count[i])-z)
                 -
                        end
          end ;
movepen(hours[j],-0.25*(f-z)) ;
begin integer k,l, stops,points;
     real  sumxy,sumx,sumy,sumx2,numerator,denominator,
           subtract,hoursk,hoursl;
     for i:=1step1until jdo count[i]:=.4343*ln(count[i]);
     print punch(3),££L? Type  line ends ?;
     read reader(3),hoursk,hoursl;
     if (hoursk<₁₀-5and hoursl <₁₀-5 )then goto L10;
     if hours[1]>hoursk *10↑(n-1)then k:=1 else
     for i:=1,i+1 while hours[i]< hoursk *10↑(n-1)do
          k:=i;
     for i:=k,i+1 while hours[i] < hoursl *10↑(n-1) do
          l:=i;
     points:=l-k+1;
     sumxy:=sumx:=sumy:=sumx2:=0;
     fori:=kstep 1 until l do
     begin if i≠1 then begin Boolean A,B,C,D,E;
                            A:=count[i-1]<count[i+1];
                            B:=count[i]<count[i-1]-0.6;      D:=count[i]<count[i+1]-0.6;
                            C:=count[i]>0.6+count[i+1];      E:=count[i]>0.6+count[i-1];
                            if(A and B) or (not A and D) then count[i]:=count[i-1] else
                            if(A and C) or (not A and E) then count[i]:=count[i+1]
                 end;
```

```
          if hours[i]≥hours[k] then begin     sumxy:=sumxy + count[i]*hours[i];
                                              sumx:=sumx+hours[i];
                                              sumy:=sumy+count[i];
                                              sumx2:=sumx2+hours[i]*hours[i]
                                           end
          else points:=points -1
     end;
     numerator:=checkr(points*sumxy-sumx*sumy);
     denominator:=checkr(points*sumx2-sumx*sumx);
     halflife[b]:=-0.3010*denominator/numerator;
     numerator:=checkr(sumx2*sumy-sumx*sumxy);
     intercept[b]:=exp(2.3026*numerator/denominator);
     print ££L??,punch(3),££L?halflife = ?,sameline,freepoint(5),
          halflife[b],£intercept = ?,freepoint(5),
          intercept[b];
     movepen(hours1*10↑(n-1),ln(intercept[b])/2.3026-.301*hours1*10↑(n-1)/halflife[b]-z);
     drawline(0,0.4343*ln(intercept[b])-z) ;
     for i:=1 step 1 until k do
     begin subtract:=exp(ln(intercept[b])-(0.693/halflife[b])*hours[i]);
          count[i]:=checkr(exp(2.3026*count[i])-subtract);
          if count[i]<1 then count[i]:=1.0001
     end;
     j:=k-1;
     if hoursk≤-5 or k=1 then goto L10;
     i:=1
  end;
  goto L11;
 L10:movepen(0,(f-z)*1.2) ;
end ;
end ;
```

```
            freepoint(5);
            topofform; tab[3]:=20; tab[6]:=38;
            print££15?Results of run number ?,runNo,££14??;
            intercept[10]:=0;
            for i:=1step 1untilbdointercept[10]:=intercept[10]+intercept[i];
            print ££t2? halflife£t2?intercept£t3?percentage£12??;
            if b≠1 then
            for i:=1 step 1 until b do
                   if halflife[i]>1
                   then print££t2??,halflife[i],££t?hours£t??,intercept[i],££t?counts/min£t??,
                              freepoint(3),(intercept[i]/intercept[10])*100,££L??
                   else if(halflife[i]<1and halflife[i]>0.01667)then
                        beginhalflife[i]:=halflife[i]*60;
                              print££t2??,halflife[i],££t?minutes£t??,intercept[i],££t?counts/min£t??,
                                    freepoint(3),intercept[i]/intercept[10]*100,££L??
                        end
                  else begin halflife[i]:=halflife[i]*3600;
                              print££t2??,halflife[i],££t?seconds£t??,intercept[i],
                                    ££t?counts/min£t??,freepoint(3),(intercept[i]/intercept[10])*100,££L??
                        end;
            topofform;
      end
      end ; restart
end
end
end;
```

APPENDIX VIII

TABLE OF $\sqrt{t+1} - \sqrt{t}$ FOR $0.01 < t < 100$

for $t < 0.01$ use $1 - \sqrt{t}$ for $t > 100$ use $\frac{1}{2\sqrt{t}}$

	0	1	2	3	4	5	6	7	8	9
.01	.905	.901	.896	.893	.889	.885	.882	.878	.875	.872
.02	.869	.866	.863	.860	.857	.854	.852	.849	.847	.844
.03	.842	.839	.837	.835	.833	.830	.828	.826	.824	.822
.04	.820	.818	.816	.814	.812	.810	.808	.806	.805	.803
.05	.801	.799	.798	.796	.794	.793	.791	.789	.788	.786
.06	.785	.783	.782	.780	.779	.777	.776	.774	.773	.771
.07	.770	.768	.767	.766	.764	.763	.762	.760	.759	.758
.08	.756	.755	.754	.753	.751	.750	.749	.748	.746	.745
.09	.744	.743	.742	.741	.739	.738	.737	.736	.735	.734

	0	1	2	3	4	5	6	7	8	9
.1	.733	.722	.712	.703	.694	.685	.677	.669	.662	.655
.2	.648	.642	.636	.630	.624	.618	.613	.607	.602	.597
.3	.593	.588	.583	.579	.575	.570	.566	.562	.558	.555
.4	.551	.547	.544	.540	.537	.533	.530	.527	.524	.521
.5	.518	.515	.512	.509	.506	.503	.501	.498	.495	.493
.6	.490	.488	.485	.483	.481	.478	.476	.474	.472	.469
.7	.467	.465	.463	.461	.459	.457	.455	.453	.451	.449
.8	.447	.445	.444	.442	.440	.438	.437	.435	.433	.431
.9	.430	.428	.427	.425	.423	.422	.420	.419	.417	.416

APPENDIX VIII

	0	1	2	3	4	5	6	7	8	9
1.	.414	.400	.388	.376	.366	.356	.348	.339	.332	.325
2.	.318	.312	.306	.300	.295	.290	.285	.280	.276	.272
3.	.268	.264	.261	.257	.254	.251	.247	.244	.242	.239
4.	.236	.234	.231	.229	.226	.224	.222	.220	.218	.215
5.	.213	.212	.210	.208	.206	.204	.203	.201	.199	.198
6.	.196	.195	.193	.192	.191	.189	.188	.187	.185	.184
7.	.183	.182	.180	.179	.178	.177	.176	.175	.174	.173
8.	.172	.171	.170	.169	.168	.167	.166	.165	.164	.163
9.	.162	.161	.161	.160	.159	.158	.157	.157	.156	.155

	0	1	2	3	4	5	6	7	8	9
1	.1543	.1475	.1414	.1361	.1313	.1270	.1231	.1195	.1163	.1132
2	.1104	.1078	.1054	.1031	.1010	.0990	.0971	.0954	.0937	.0921
3	.0905	.0891	.0877	.0864	.0851	.0839	.0828	.0817	.0806	.0796
4	.0786	.0776	.0767	.0758	.0750	.0741	.0733	.0725	.0718	.0711
5	.0704	.0697	.0690	.0684	.0677	.0671	.0665	.0659	.0654	.0648
6	.0643	.0638	.0632	.0627	.0623	.0618	.0613	.0609	.0604	.0600
7	.0595	,0591	.0587	.0583	.0579	.0575	.0572	.0568	.0564	.0561
8	.0557	.0554	.0550	.0547	.0544	.0541	.0538	.0535	.0531	.0529
9	.0526	.0523	.0520	.0517	.0514	.0512	.0509	.0506	.0504	.0501

APPENDIX IX

TABLE OF VALUES OF Bt CORRESPONDING TO VALUES OF F =

$$F = 1 - \frac{8}{\pi^2} \sum_{1}^{\infty} \frac{1}{(2n+1)^2} e^{-(2n+1)^2 Bt}, \text{ from } F = 0.01 \text{ to } 0.99$$

100F	Bt	100F	Bt	100F	Bt	100F	Bt
1	.0002	26	.1310	51	.5033	76	1,217
2	.0008	27	.1413	52	.5240	77	1.260
3	.0017	28	.1519	53	.5450	78	1.304
4	.0031	29	.1630	54	.5665	79	1.351
5	.0048	30	.1744	55	.5885	80	1.399
6	.0070	31	.1862	56	.6110	81	1.451
7	.0095	32	.1984	57	.6340	82	1.505
8	.0124	33	.2110	58	.6575	83	1.562
9	.0157	34	.2240	59	.6816	84	1.623
10	.0194	35	.2374	60	.7063	85	1.687
11	.0234	36	.2512	61	.7316	86	1.756
12	.0279	37	.2653	62	.7576	87	1.830
13	.0328	38	.2798	63	.7842	88	1.910
14	.0380	39	.2948	64	.8116	89	1.997
15	.0436	40	.3101	65	.8398	90	2.093
16	.0496	41	.3258	66	.8688	91	2.198
17	.0560	42	.3418	67	.8986	92	2.316
18	.0628	43	.3583	68	.9294	93	2.449
19	.0700	44	.3752	69	.9612	94	2.603
20	.0775	45	.3924	70	.9940	95	2.786
21	.0855	46	.4062	71	1.028	96	3.009
22	.0938	47	.4249	72	1.063	97	3.297
23	.1025	48	.4439	73	1.099	98	3.702
24	.1116	49	.4633	74	1.137	99	4.395
25	.1211	50	.4831	75	1.176		

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