THE ELECTROMIGRATION OF INORGANIC IONS IN PAPER

by

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1. Preface.

The separation of ions by migration in filter paper under the influence of an electric field is basically a simple technique, but one that is extremely versatile. It is particularly adapted to small amounts of material, and in the field of radiochemistry it appears well suited for dealing with "carrier-free"materials. Although this procedure has received most attention from biochemists, and is often an adjunct to free electrophoresis so frequently used when dealing with proteins, in recent years it has been applied to the separation of inorganic ions. As yet, however, there has been little practical use made of work in the latter field. The method is almost entirely empirical. Very little is understood about the processes occurring. Indeed, many of the factors which influence the movement of an ion in moist paper have received only cursory attention from workers in the field. The theoretical considerations which have been proposed to cover the phenomena are largely untested experimentally, particularly as they apply to small ions such as inorganic ones. The work described herein was undertaken in part to investigate the variables involved, and, where possible, to compare observed results with theoretical predictions, and also to make some separations that might be of interest from a radiochemical point of view.

Although this technique is superficially similar to paper chromatography, the two procedures differ fundamentally. Chromatography depends on the distribution of the materials to be separated between a moving and a stationary phase, while separations by electromigration depend only on different velocities of the particles under the external force. In principle, the stationary solid phase serves only to prevent mixing by convection, while the liquid phase is also stationary and provides a medium in which the ions may move -- perhaps as a complex with it. Liquid flow and sorption by the solid may occur, and may be used to aid in a separation, but they do not form an essential part of the method.

2. Terminology.

In spite of the widespread use of this technique, no universally accepted term for it exists. Many names have been suggested and are in use in the literature, but all may be criticized on one ground or another. The term electrophoresis, coupled with an indication of the porous solid phase (as paper electrophoresis) is probably the most popular. However, since electrophoresis is normally associated with colloidal particles, Martin (1) has proposed the use of the word ionophoresis for ions. Zone electrophoresis (or zone ionophoresis) has been suggested for electromigration in an anticonvectant medium (2), thus distinguishing this technique from the free or moving boundary technique. Durrum (3) has criticized this, arguing that it emphasizes a non-essential point.

Electrochromatography has been suggested (4,5), but this tends to imply too great a contribution from chromatographic effects to be suitable as a general term. It is best reserved for those techniques in which the separation is achieved by a flow of solvent (other than accidental electroosmotic or capillary flow) in conjunction with an electric field. Such procedures have also been called electrochromatophoresis (6).

Ionography has been suggested by McDonald (7) to describe all migration in a stabilized medium brought about by an electric field. This fails to describe the force causing the movement, however.

Electromigration has also received considerable usage, and although McDonald criticizes it as being too general (8), it seems to give the clearest description of the process, and will be used throughout this thesis. The major disadvantage of this term is that it does not lead to a name for the piece of material containing the separated substances, while the others give electropherogram, electrochromatogram, or ionogram rather naturally. One perhaps could coin a term such as "electromigram" or "electrogram" if one were necessary.

One other term worthy of note is electrorheophoresis, introduced by Macheboeuf (9) to describe the process when evaporation is a factor deliberately introduced. It thus describes a special technique.

The porous material in which the migration is carried out is usually referred to as the supporting medium. Filter paper is used most commonly, but any material which is porous and a non-conductor of electricity may be employed. The supporting medium is moistened with a conducting solution which is best called the background electrolyte, although terms such as carrier electrolyte or buffer solution are also used. The volume of background electrolyte per unit weight of supporting medium has been termed the absorbance or the wetness.

The zone mobility (often just mobility) of a substance under the conditions of electromigration is defined as the velocity, under unit potential gradient, of the spot, or zone, of the substance moving. It is normally taken as the velocity of the geometric centre of the zone without regard for distribution in it.

3. Historical Development.

The technique of separating charged substances in solution by causing them to migrate in an electric field goes back many years and is related to much work that is not directly a part of separatory procedures. It is further complicated by following a number of paths-migration in gels, in tubes packed with porous or granular materials, in paper strips, and in free solution. Early reports which utilized some of the now basic techniques of the paper strip method appear to have been almost entirely overlooked by later workers; the method as it exists today was actually developed nearly simultaneously, and more or less independently , by many investigators. The historical treatment to be given will deal primarily with early applications to inorganic separations. In many instances the basic developments took place in the biochemical field, but these will be indicated only when they are inextricably linked with subsequent inorganic work. A much more complete history is given by McDonald (8).

Electromigration of ions in stabilized media -- i.e., in systems where convection is prevented -- goes back to the work of Lodge (10), who in 1886 attempted to measure ionic velocities in a tube of gelatin stabilized electrolyte. This basic technique was first employed for the separation of inorganic ions by Kendall and co-workers during the 1920's (11-16). They carried out the migrations in tubes filled with agar gel. The separations studied included Ra from Ba, Hf from Zr, certain rare earths, and even isotopes. To keep the zones sharp, an ion which moved faster than those to be separated was used in the electrolyte ahead of the migrants, while a slower one was used behind.

The method, although slow and cumbersome, gave promising results, but little interest was aroused in it.

In 1939, Strain (17) and Coolidge (18) set up the basis of the column technique and used it for biochemical separations, while in 1944 Lecoq (19) applied this method to inorganic separations. Also about this time, Brewer, Madorsky, et al (20, 21) reported the use of a related technique, electromigration in a packed tube in opposition to a flow of solvent (counter-current electromigration) to separate isotopes.

The use of a strip of filter paper in electromigration had been introduced in 1937 by Konig (22,23) and Berraz (4,24) had made inorganic separations on paper in 1943, but this work appears to have been largely overlooked. In the period 1948-1950, many workers, all more or less independently, reported the use of filter paper electromigration for biochemical separations. Both discontinuous strip techniques and continuous procedures appeared, and since that time the method has been firmly established. Its application to inorganic chemistry lagged somewhat. Garrison et al (25) separated some radioactive ions by electromigration in a stack of filter paper discs in 1949. In 1950, Kraus and Smith (26) used this technique to investigate complex formation of Hg^{++} in chloride solutions, and McDonald (7) tried to use it to determine the transference numbers of Ni, Cu, and SO_4 ions. In 1951, Lederer (27,28) and Strain (29) described a number of inorganic separations. The latter used both discontinuous and continuous techniques. It was only after 1953, however, that an appreciable number of inorganic separatory procedures appeared. These will be discussed in a later section.

4. Common Techniques.

(a) Discontinuous Strip Techniques.

Two basic arrangements have been developed for discontinuous electromigratory separations on paper strips. These are the open and closed strip techniques. In the former, the paper strip is suspended freely in a chamber which is saturated with vapour from excess background electrolyte. This is sometimes termed the moist chamber technique. Since dissipation of the heat generated in the strip by the current is brought about only by conduction through the air-space and evaporation of liquid from the paper, this type of procedure is generally limited to low voltages and currents. In the closed strip technique, cooling is achieved, and evaporation is prevented, by one of two methods: the strip may be clamped between two plates of glass, plastic, or insulated metal (the "sandwich" technique), or it may be immersed in an organic solvent which is immiscible with the background electrolyte solution.

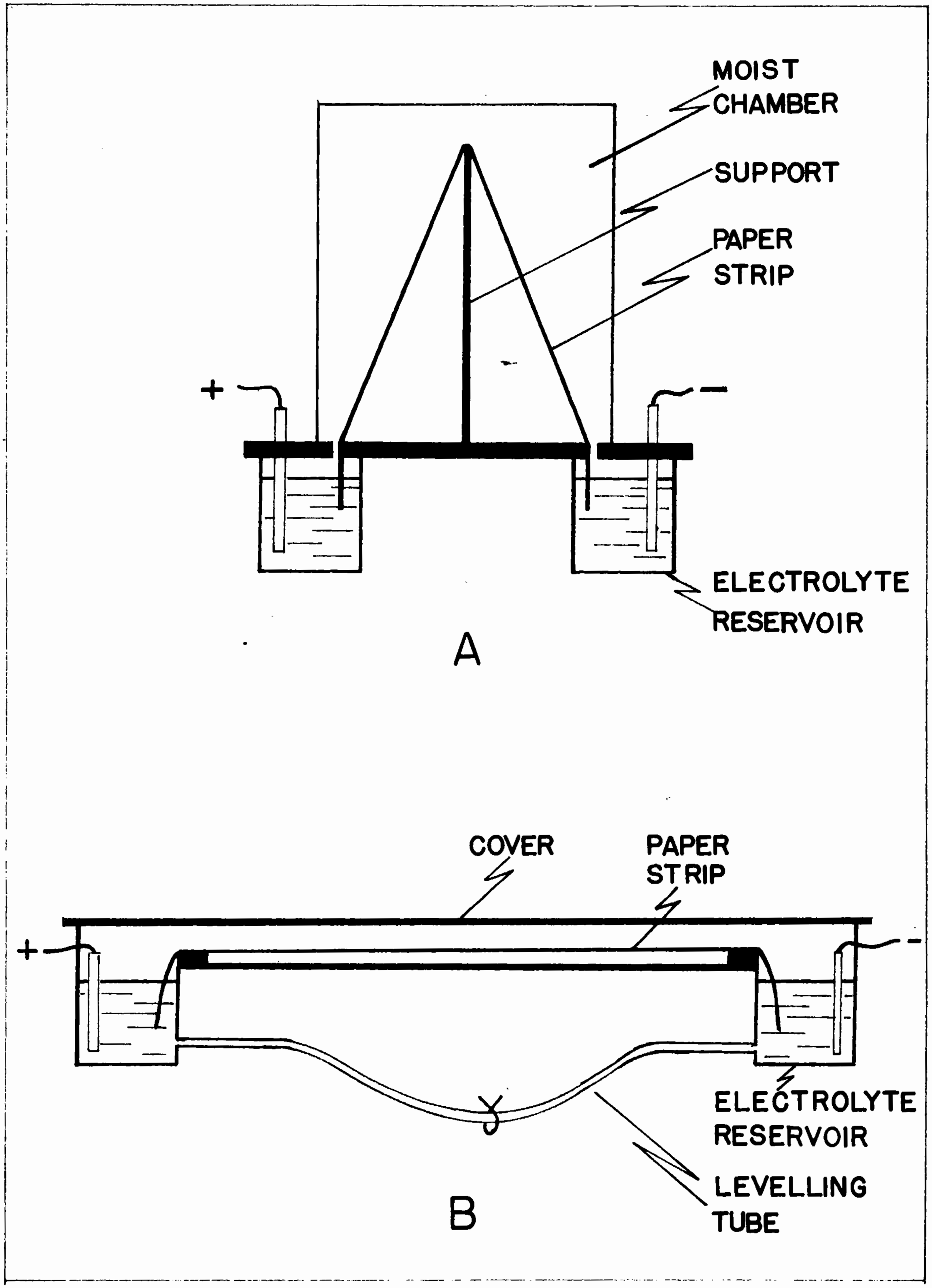
Several methods of suspending the strip have been described for the moist chamber technique. The simplest has been popularized by Durrum (30) and is illustrated in Fig. 1A.

Figure 1.

Types of apparatus for open strip electromigration procedures.

A. A hanging strip arrangement.

B. A horizontal strip arrangement.


MOIST CHAMBER
SUPPORT
PAPER STRIP
+
−
ELECTROLYTE RESERVOIR
A
COVER
PAPER STRIP
+
−
ELECTROLYTE RESERVOIR
LEVELLING TUBE
B

The strip is hung over the horizontal part of an inverted L-shaped glass rod, and the ends are allowed to dip into two vessels of background electrolyte solution which also contain the electrodes. These vessels are covered by a plastic plate containing slots for the ends of the strip, and a third vessel is inverted over the paper to form the moist chamber. Another popular arrangement (8,31), shown in primitive form in fig. 1B, has the strip pulled taut horizontally on a plastic frame.

With any open strip technique there is invariably evaporation from the strip, particularly when appreciable current is drawn. This results in a flow of electrolyte solution from the reservoirs at the ends of the strip toward the centre, and an increase in concentration of non-volatile electrolytes in the paper as water evaporates and more electrolyte is carried in (32). Some attempts have been made to increase the voltage that can be used with this type of apparatus. A simple procedure is to operate the instrument in a cold room or refrigerated cabinet. McDonald (33) has filled the air space with hydrogen or helium, since these are better heat conductors than air. The use of glycerol (34) to lower the vapor pressure of the electrolyte solution, or of acetone (35) to lower the partial vapour pressure of the water, has also been proposed. The former results in an increased viscosity of the background electrolyte with consequent slowing of the ions which counteracts some of the advantage of the higher voltage, and may also lead to handling difficulties.

The most convenient apparatus for the closed strip technique is the sort in which the strip is placed between two flat plates; a simple form of this system is shown in fig. 2A. This is similar to the design suggested by Kunkel and Tiselius (36). More elaborate systems involve cooling of the plates by attached cooling coils, the use of pressure regulating devices, and other refinements. Such designs have been operated at as high as 10,000 volts. Some of these, as well as the liquid sealed arrangement to be discussed next, have been reviewed by Michl (35).

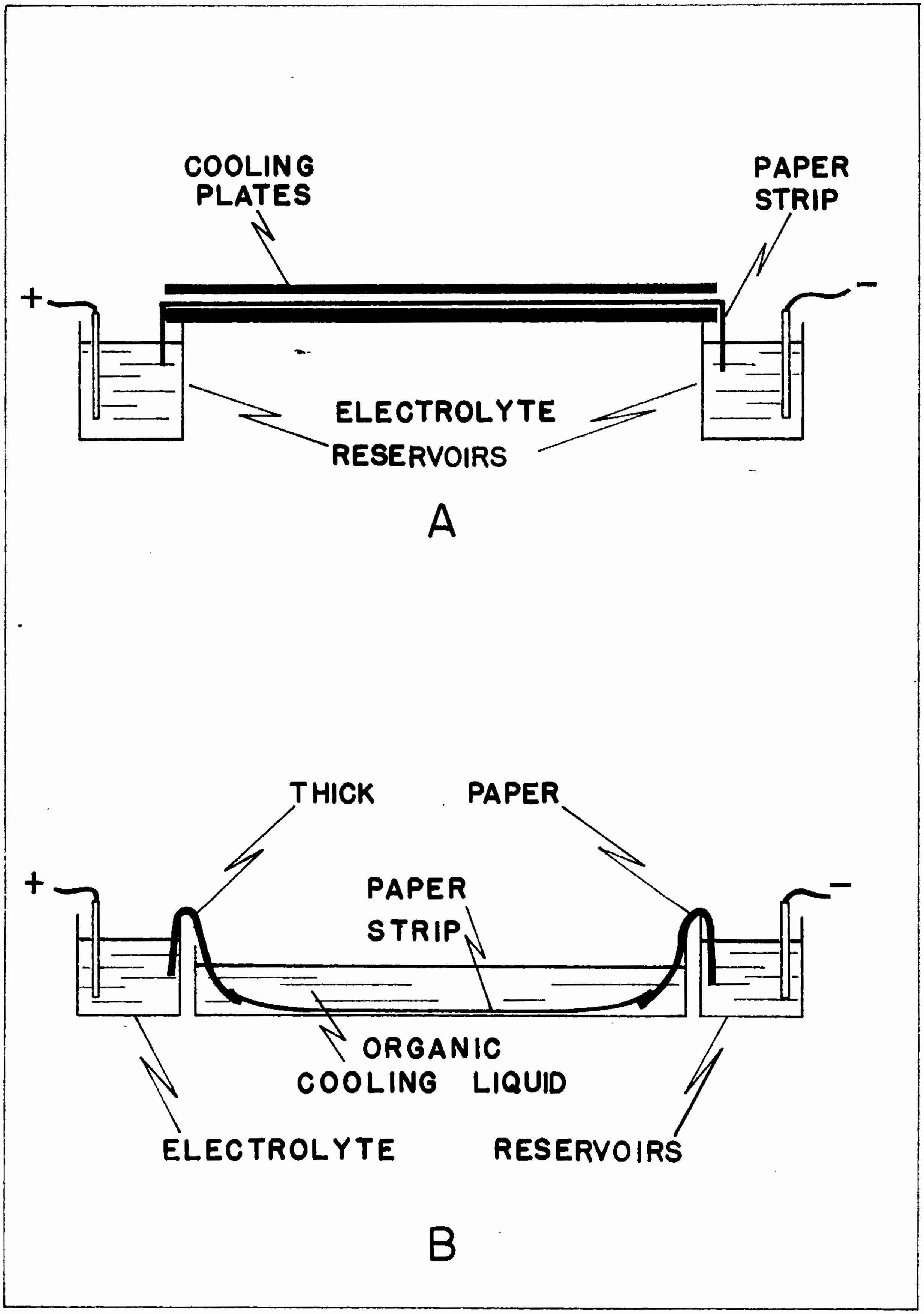
The non-conducting liquid sealed device, shown schematically in fig. 2B, is in effect a moist chamber with the air-space filled by a liquid. Such a device was pioneered by Cremer and Tiselius (37) who placed the paper between glass plates before immersing it in the liquid. It has been used in a number of similar forms without the glass plates. Cooling liquids have included chlorobenzene, toluene, heptane, and hexane, which are inflammable, and carbon tetrachloride. While the latter does not introduce the hazard of fire, it is toxic. Although this type of apparatus is capable of dissipating a large amount of heat, it is inconvenient, and introduces the danger of partition between the paper and the organic liquid.

Figure 2.

Types of apparatus for closed strip electromigration procedures.

A. Paper between cooling plates.

B. Paper immersed in organic liquid.


COOLING PLATES
PAPER STRIP
+
−
ELECTROLYTE RESERVOIRS
A
THICK
PAPER
PAPER STRIP
+
−
ORGANIC COOLING LIQUID
ELECTROLYTE
RESERVOIRS
B

It has become customary to divide electromigration procedures arbitrarily into low and high voltage techniques. The latter generally refers to operation with a voltage gradient greater than about 20 volts per centimetre. There is of course no fundamental distinction, but the high voltage technique requires more careful attention to cooling. As a rule, all high voltage work must be done by a closed strip technique, although not all closed strip operation is a high voltage method.

The open strip techniques are suitable only for low voltage work, and because of evaporation and the resulting change in concentration of electrolyte in the paper, and frequently also because of non-uniform absorbance along the strip, they are not satisfactory for the determination of zone mobilities. This is especially true if the centre of the strip is higher or lower than its ends. If experimental conditions are rigidly fixed, reproducible results may be obtained, but they have little real meaning. For separations, open strip techniques are quite suitable if low voltages are adequate.

For mobility measurements, the "sandwich" type of closed strip apparatus is most suitable. Since evaporation is practically wholly eliminated, there is no appreciable change in concentration of the electrolyte solution in the paper. The absorbance is in general more uniform since excess liquid which may be present near the ends of the strip is squeezed out by the plates. Much higher voltages can be used, and since the speed of an ion is dependent on the voltage gradient, separations can be carried out much more rapidly. There exists the possibility that a film of liquid may form between the paper and the cooling surface, and the migrant may travel partly through this film and partly through the paper, yielding a blurred zone. This is readily avoided if the paper is not too wet and if the cooling surface is hydrophobic.

If the paper strip is placed on a cooled surface, but the upper surface left free in a moist chamber, a combination of the open and closed strip techniques can be achieved (the semi-closed strip technique). Quite good cooling may be achieved this way, but evaporation is not entirely prevented.

A number of factors in the design of apparatus should be considered. All of the arrangements described above, and illustrated in Figs. 1 and 2, have the ends of the paper strip dipping into vessels of background electrolyte in which the electrodes are also placed. This is done to prevent products formed by electrolysis reactions at these electrodes from migrating directly onto the strip. These vessels are usually of large capacity so that these products are highly diluted, or the electrodes proper are separated by salt bridges or other arrangements. In order to prevent siphoning of liquid through the paper, the solution in the two vessels must be at the same level. This is assured by a levelling tube between them. This is normally closed while voltage is applied, but some workers (38) use a small bore tube which is left open during the run to eliminate changes in electrolyte level caused by electroosmosis.

Since filter paper is normally negatively charged, possibly because of dissociation of carboxyl groups, an applied potential tends to cause electrolyte solution to flow from the positive toward the negative electrode (39). The observed mobility of a substance, then, is the sum (or difference) of its own true electrical mobility and that of the electrolyte. Therefore, the contribution from liquid flow must be determined for mobility measurements. Many workers have used uncharged substances such as dextran, glucose, or hydrogen peroxide as flow indicators. Since these materials have no electrical mobility, their motion is assumed to follow that of the liquid. The value of such corrections is doubtful, however, because adsorption effects may not be the same for the migrant and the reference substance. That is, for either or both substances, the velocity of movement under the action of the flow of liquid may not be the same as the velocity of the liquid itself. Thus one must know to what extent, if any, chromatographic adsorption slows both substances. Such information is not readily obtained; ordinary determinations of the R_f

values * by a standard chromatographic technique may not be reliable since the experimental conditions are not the same. Moreover, R_F values are notoriously subject to variation with minor changes in technique. Corrections are often made in this manner, however.

In addition to the uniform electroosmotic flow, liquid may flow from the ends of the paper toward the centre by capillary action. This may take place if evaporation occurs, as was discussed previously, but it may also happen if the paper were not fully saturated with liquid initially. In the closed strip technique this flow may depend on the pressure of the plates. It is impossible to correct for, since it may vary with position on the strip and with time. Strauch and Andrec have dealt in detail with flow of electrolyte in both open (32) and closed (40) strip techniques.

Strain et al investigated electroosmotic flow with electrode vessels (41) and with the electrodes attached directly to the paper (42). They found in the latter case that there was no measurable movement of electrolyte. Although this may not be true under all conditions (40), in cases where Strain's observations can be confirmed, it is clearly advantageous to do away with the electrolyte

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* The R_F value of paper chromatography is defined as

$$R_F = \frac{\text{Movement of spot of substance}}{\text{Movement of advancing front of liquid}}.$$

It is related to the partition coefficient of the moving substance between the mobile and the fixed phase. As determined experimentally, it varies not only with the developing solvent and the paper, but also according to the manner of development (ascending, descending, etc.), length of paper used, and distance of the starting point from the solvent.

reservoirs, provided the effects of the electrolytic products can be eliminated. This will be discussed further in the experimental section.

Several specialized techniques have been used, and these will be mentioned briefly. By elevating one end of the strip, Dvorak and Grubner (43,44,45) obtained a continuous flow of electrolyte along the strip. By adjusting this flow so that it just cancels the electrical velocity of the slower component, it is possible to separate two substances having very small differences in mobility on a comparatively short strip of paper. This is a form of counter-current electromigration.

Another method of considerable interest is the "focussing" technique used by Kauman (46) and Hoch and Barr (47) for biological materials, and by Schumacher (48-54) in the inorganic field. As used for inorganic cations, the strip contains an agent capable of forming negatively charged complexes with the cations to be separated, and a gradient of concentration or pH such that at the anode end of the strip the ions would be non-complexed and positive, while at the cathode end they would be complexed and would have a negative charge. At some point along the gradient, the ions will have an effective zero charge provided the complexed and non-complexed forms are in rapid dynamic equilibrium. All the ions of a given kind will be concentrated in a very narrow region, the position of which depends on the stability of the complex.

The above mentioned methods are all linear. A radial method of electromigration has been developed in which the migrants are placed at the centre of a disc of paper and move toward the outer edge (55).

(b) Two Dimensional Techniques and Continuous Electrochromatography.

Two dimensional separations may be carried out on a square sheet of paper. The migrants are applied at a spot and migrate normally. The sheet then may be dried, remoistened with a second electrolyte, and the electromigration repeated with the electrodes now along the other two edges (56). Separation in one dimension may be brought about by paper chromatography (57), which may be done simultaneously with the electromigration, or the two processes may be carried out in successive steps.

This combination of electromigration and paper chromatography may be used to give a method for continuous separations which permits large amounts of material to be separated, and which may be used for preparative work. The usual arrangement consists of a "hanging curtain" of filter paper in a moist chamber. Electrodes are attached to the sides of the curtain, and a flow of electrolyte is set up perpendicular to the electric field. The materials to be separated are applied continuously at a point at the top, and fractions are collected from "drip-points" along the bottom. Such an apparatus is shown schematically in Fig. 3. Use of some devices of this type for inorganic separations is described by Strain (58, 59).

In order to speed up the solvent flow, McDonald (60, 61) has resorted to the use of centrifugal force, and rotates the sheet of paper at high speed in a horizontal position.

(c) Column and Gel Techniques:

In biochemical work, packed columns and slabs of various gels are in fairly common use. In the inorganic field there has been very little reported along these lines in recent years. Of interest is the work of Lederer and Cook (62) and Cetini (63) using agar and starch gels, respectively, and some studies of electromigration in ion exchange columns by Manecke (64) and Spiegler and Coryell (65,66). Techniques in use are described by Kunkel and Trautman (67); they are not of sufficient importance in inorganic chemistry to warrant further discussion here.

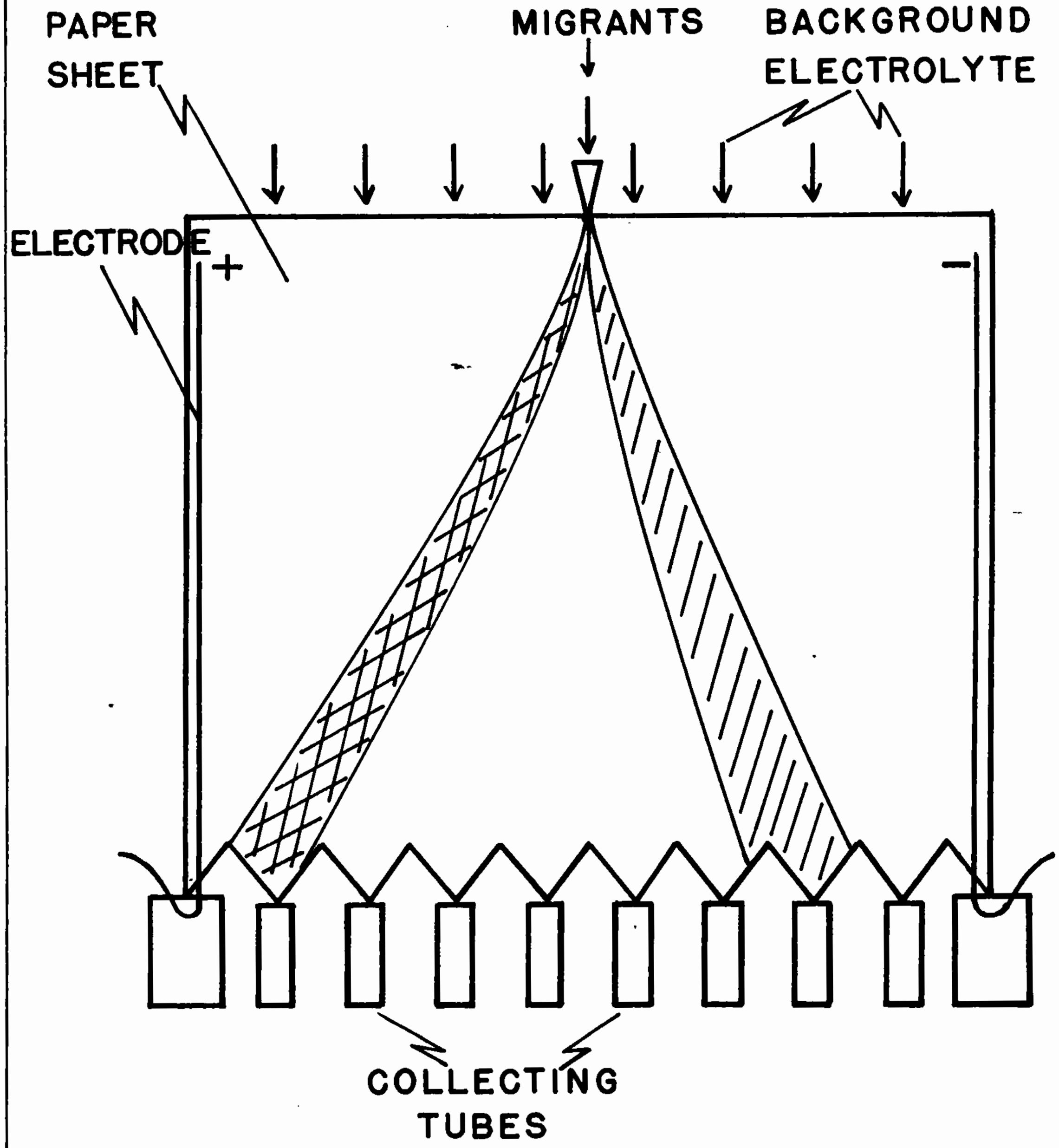
5. Factors Affecting the Electromigration of an Ion in Paper.

(a) General Considerations.

The velocity of electromigration of an ion in a porous medium such as paper is known to be affected by many factors. Theoretical treatments have been proposed for some of these, but this section will deal only with their qualitative aspects. Many of the factors have not been fully investigated experimentally, particularly as to how

<u>Figure 3.</u>

Schematic diagram of apparatus
for continuous electrochromatographic
separations.


PAPER SHEET
MIGRANTS
BACKGROUND ELECTROLYTE
ELECTRODE
+
−
COLLECTING TUBES

they affect small ions such as those under consideration here. This has been true partly because in order to elucidate them it is necessary to be able to obtain reproducible measurements of zone mobility under such conditions that all of the variables are known and controlable. Many of the techniques and types of apparatus used for separations are not suitable for this. In particular, evaporation of liquid from the strip must not occur, and flow of background electrolyte solution must be absent or corrected for; these points were discussed previously.

(b) Temperature.

An increase in temperature causes an increase in mobility, and a few temperature coefficients have been given for inorganic ions by Maki (68), Yasunaga and Shimomura (69), and Achiwa (70). These reports indicate that the increase is about the same as that in free solution, or about 2% per degree C. Therefore, reasonable temperature control is necessary for mobility determinations. The Joule heat generated in the strip must be dissipated efficiently, or the temperature in the paper may rise several degrees.

For an inorganic separation, the actual temperature is not of much importance as long as overheating leading to charring of the paper is avoided. In the closed strip technique, if the strip has a uniform resistance and the cooling surface offers an even, close contact, it is possible to operate at temperatures of 60 or 70 degrees C., with an aqueous background electrolyte solution. There are certain advantages to working at high temperatures. In the first place, the increased speed of the ions means that a given distance can be traversed in a shorter time, and secondly, the distance required to achieve a complete separation may be less, since, if the mobilities increase by say 2% per degree, then to a first approximation the difference in mobility will also increase by 2% per degree (71). Counteracting this, of course, is increased diffusion, which will tend to increase the size of the zones, and hence the distance required before they are completely separated. Complex formation and adsorption may also be influenced by temperature.

(c) Absorbance.

A very important factor which has been ignored by many workers who have given lists of mobilities in paper is the absorbance. The zone mobility of the migrant, which is always less than its mobility in free solution, increases as the amount of liquid per unit weight of paper increases, and would approach the free solution value if a sufficiently large amount of liquid could be present. The effect of this variable is quite considerable, and since it is almost never reported, practically none of the values of mobility quoted in the literature have any quantitative meaning. Certain workers have considered the effect of absorbance, and this topic will be dealt with more fully in the theoretical section.

(d). Concentration of the Migrant

The effect of the concentration of the migrant on its zone mobility has not been adequately studied experimentally, except perhaps in certain complex-forming systems. Marbach(38) found no difference when he used two concentrations of a protein, but this experiment is not conclusive.

Miller, Pickering, and Ward (72) claim that the mobility of inorganic ions is independent of their concentration unless they are adsorbed by the paper, and provided that their concentration is less than that of the background electrolyte. Sato, Norris, and Strain (73) confirm this, and also note that the mobility is decreased with increasing concentration if this is greater than that of the background solution. Strain(56) has also made some observations on this. In many cases, however, this work was done in systems where complex formation was likely to take place. Complicated behaviour may be observed if the ion is strongly adsorbed by the paper (73). In such cases increased concentration may result in an increase in average mobility since a smaller proportion is adsorbed. Such behaviour is usually accompanied by marked trailing and the formation of comet-shaped spots.

The size of the zone is certainly influenced by the amount of migrant present. It is well known that if the concentration of the initial zone is appreciably greater than that of the background electrolyte, the final zone may "smear" to a large size, and under such conditions separations become quite unsatisfactory. Maki has shown that in certain concentration ranges at least, the length of the migrated band of ion is directly proportional to the amount applied, and this was used for quantitative estimations of Ba and Al (68, 74-76).

(e) Composition of the Migrant Solution.

The composition of the applied solution, as distinct from its concentration, may influence the migration of a given ion. It is usually true that the ions in a mixture migrate independently, but this will not be so if interactions such as the formation of stable complexes are possible. The applied ions may remain complexed and migrate in an entirely unexpected manner. Workers (72,77) have studied the migration of complex ions in various media, and have found that some metal chelates, for instance, are undissociated even in 2% nitric acid.

Zinc offers a good example of the effects of this type of interference. A solution of the nitrate migrates in a non-complexing background electrolyte as a positive ion, but if it is applied with only a small excess of HCl, it remains motionless, or moves slightly as a negative ion. This can be due only to the formation of a fairly stable chloride complex.

Another case of interference between cations and anions has been described by Casinovi and Lederer (78). They found that when a solution of CsCl was applied alone to a strip of paper, the Cs moved normally, but when added with $K_4Fe(CN)_6$ it remained at the starting position. They attributed this to the formation of insoluble double ferrocyanides with zinc and other impurities in the paper.

Still another type of effect is given by Lederer (79). In separating Bi (III) from Cu (II) with HCl as the background electrolyte, he found that if the initial solution contained a high concentration of other acids such as HNO_3, the complex $BiCl_4^-$ was prevented from forming until Bi (III) had first migrated out of the starting region as a positive ion; it then formed the negative chloride ion and migrated back. This type of behaviour leads to the so-called "umkehreffekt" -- a substance is found to move in one direction for a short time at the beginning of electromigration, but with longer time it reverses its direction. This phenomenon also was noticed with proteins in the presence of excess electrolytes.

It is evident from this that the ions to be investigated are best applied in a solution of background electrolyte and with other ions absent, although it is usually sufficient to apply them as nitrates if a large excess of the acid is avoided.

(f) Nature of the Supporting Medium.

The supporting medium is not in practice the inert substance that it is in principle, and its effects on the migrating ions may amount to considerably more than just mechanical obstruction. The interactions between an inorganic ion and cellulose are complex. Cellulose paper contains ionizable groups which are capable of entering into ion exchange reactions; among these are carboxyl groups resulting in part from oxidation processes occurring during manufacture. Each type of paper has its own particular exchange capacity, and this may vary over quite wide values for various papers. A few values are given by Schröder (80). The presence of inorganic impurities in the paper may have a marked effect on adsorption (73), and several reports have been made comparing zone mobilities on washed and unwashed papers (70,81). The mobility is lower in unwashed paper. Presumably the impurity ions on the carboxyl groups or other exchange sites are more readily replaced by other metal ions than are the hydrogen ions which occupy these positions in the absence of impurities. It is also possible that the acid washing process has an effect on the fibre structure which alters the physical obstruction, but no evidence has been proposed for this.

Some work which has been done in determining the effects of adsorption in paper chromatography has been reviewed by Schröder (80) and Grüne (82); although this is not strictly applicable to electromigration, similar effects should be found. It is quite probable that adsorption, including ion-exchange adsorption, plays a part in controlling the electrical mobility in paper. Maki has made some studies of this (83) which will receive further consideration in the theoretical section.

A given ion may take part in specific interactions. For example, Bi(III) usually migrates very slowly, and its speed increases as its concentration in the initial zone increases (73). This, together with the fact that it usually trails, is indicative of strong adsorption. Work by Jakovác and Lederer (84) on electromigration in cellulose and glass papers and in the presence of glycerol indicates that Bi(III), and also Cu(II) and Sb(III), form complexes with polyhydroxy compounds, and may therefore form strong linkages with certain groups in cellulose. The adsorption in such cases is due to formation of a complex compound, and need not be completely reversible.

In any event, different zone mobilities are observed when only the type of paper is changed. Part of the difference may be due to different physical parameters such as the fibre structure of the paper or the absorbance, but it is certain that adsorption processes frequently have an effect.

(g) Nature of the Background Electrolyte Solution:

Most important of the factors influencing zone mobility is the nature and concentration of the background electrolyte solution used. From what is known from conductance it would be expected that an increase in ionic strength would result in a decrease in mobility, and that the viscosity of the medium would also be important. The most significant effect of the background electrolyte lies in its ability to form complexes with the migrant. By suitable choice of complexing agent as background electrolyte, various ions may be made to have an effective positive, negative, or neutral charge, and the electromigratory behaviour thus controlled to a considerable extent. Complexing agents have been used in many separations.

The effect of pH on inorganic ions is important only in so far as it affects complex formation, and in relation to amphoteric ions. Experimental studies which bear out the above statement have been carried out by Maki

(68), Achiwa (70), and Yasunaga and Shimomura (85). Consden, Gordon, and Martin (86) have dealt with the calculation of the optimum pH for separation of weak electrolytes such as amino acids, but this has little application in the inorganic field and will not be dealt with here.

In addition to any influence which the concentration of the background electrolyte may have on the zone mobility, it has an important effect on the size and shape of the final spot. The increase in size of the zone when the migrant concentration exceeds that of the background electrolyte has already been mentioned (p. 23). Achiwa (70) has given examples of the variation in size and shape of migrated zones in various concentrations of background electrolyte; they become elongated and trail in the most dilute cases, while at higher concentrations they are small and circular. Adsorption as indicated by R_f values increases with decreasing concentration of electrolyte, and results in an overall slowing of the motion.

6. Factors to be Considered in a Useful Separation Procedure.

The following factors should be considered in a separation - particularly one of radiochemical interest. First of all, to be of real use the separation should be rapid. For this, a fairly high voltage technique is preferable. In order to use a high voltage without drawing an unduly high current, background electrolytes of low conductivity are necessary. Weakly dissociated acids and bases are very suitable, but complexing and other considerations must be taken into account. Too low a concentration must be avoided because excessive elongation of the zones may occur. Often, voltage must be sacrificed in favour of the complexing power of a more highly conducting solution.

Conditions under which marked trailing occurs are not satisfactory. Trailing may occur when small amounts of material are strongly adsorbed while the bulk continues to migrate. The reverse, a streak of low concentration extending in advance of the main zone of migrant, can also be met with if the concentration of the background electrolyte is too low. Such an effect can be produced as well by material which migrates continuously from a slightly soluble precipitate. Trailing means that a long distance of migration is required in order to achieve complete separation, if indeed one can be obtained at all under these circumstances, and also leads to contamination of one zone with a low concentration of another migrant. This contamination may escape detection, particularly if chemical tests are used. In addition, trailing may make recovery difficult if this is required.

For some uses it may be necessary to remove the material from the strip after separation; this can be done by an elution technique. An excess of foreign substances in the eluted solution is often undesirable, so that it is sometimes advantageous to use a background electrolyte which can be removed easily, as by evaporation. The paper itself may contain impurities which can be eluted with the desired ions, and these also may exert a disturbing influence on the migration itself. An acid-washed paper is useful in this respect; non-cellulose papers such as glass or cellulose acetate have advantages from this point of view, and the former in particular is more resistant to attack from certain chemicals, but they may be more difficult to handle.

As a rule, this technique is not successful with high concentrations of material, and if one component of the applied mixture is present in large amounts, it may "smear" over a large area. The maximum amount of substance which can be handled depends on the width of the strip and the kind and thickness of the paper. In the field of radiochemistry, this technique has most promise in the separation of nearly "carrier-free" materials from one another, for the high concentration effects are eliminated.

Finally, the shape of the paper should be considered. Although this factor is of no consequence if chemical detection of the separated zones is used, it is important with radioactive substances. Square sheets of paper as are used in the two-dimensional discontinuous techniques, and other irregular shapes, cannot be scanned readily by automatic devices, and cutting the paper into segments for individual measurement also becomes a problem. The method of autoradiography remains suitable, but this is much less convenient than a "counting" technique. A narrow strip as is used in most ordinary procedures is most convenient.

7. Theoretical.

(a) Relationship Between Free Solution Mobility and Zone Mobility:

The main object of most theoretical treatments in this field has been to relate the observed zone mobility of a substance to its mobility in free solution. This problem was first treated fundamentally by Kunkel and Tiselius (36), and later by Edward (87), who modified their treatment. The model which they used, although admittedly naive, seems to be the best available as yet. Moreover, it is one that has been used in other fields, such as geology, in dealing with porous materials.

According to this picture, a charged particle moving in paper must follow a crooked path or channel in going around the fibres. The actual distance which it travels is then greater than the apparent distance as would be measured from the displacement of the zone. This is illustrated in Fig. 4A. By the same reasoning, if the fibres are non-conducting the voltage gradient seen by the particle is less than the apparent voltage drop, since the former occurs through the longer crooked channel which contains the conducting solution.

The conductance K of a column of liquid having a volume V, a cross-sectional area A, and of specific conductivity k, and which is between electrodes a distance L apart, is

$$K = \frac{kA}{L} = \frac{kV}{L^2} \quad . \qquad --- 1$$

If now a volume of non-conducting solid is added, the conductance becomes K'. Assuming that the volume of liquid V now finds itself in winding channels of length L' which are formed by the solid, as illustrated in Fig. 4A, then

$$K' = \frac{kV}{L'^2} \quad , \qquad --- 2$$

similarly. From 1 and 2,

$$\frac{K'}{K} = \frac{(L)^2}{(L')^2} \qquad --- 3$$

and from Fig. 4A, $\frac{d}{d'} = \frac{L}{L'}$. d represents the apparent distance travelled by the zone, and d' the real distance through the channel.

The free solution mobility of the migrant is

$$U_F = \frac{d'L'}{tE} \qquad --- 4$$

where E is the voltage applied at the electrodes and t is the time of migration. The apparent mobility in paper, that is, the zone mobility is defined as

$$U_Z = \frac{dL}{tE} \qquad --- 5$$

Hence, $$\frac{U_Z}{U_F} = \frac{dL}{d'L'} \qquad --- 6$$

or $$U_Z = PU_F \qquad ---6a$$

Kunkel and Tiselius called P the tortuosity factor, tacitly assuming that the entire difference between U_F and U_Z was due to this more tortuous path. P is related to the conventional tortuosity factor used in the study of flow in porous media (88). Edward, on the other hand, prefers to give P a more functional meaning, according to the relation $P = \frac{K'}{K}$. Realizing that P defined in such a manner may include effects of adsorption, for instance, he prefers the term obstructive factor.

The treatment of Kunkel and Tiselius has been criticized strongly by McDonald (8) and Marbach (38) on the grounds that the path followed by an ion when migrating under an electric field in free solution is tortuous in that it is random with a superimposed drift in the direction of the field. The path in paper is thus only somewhat more irregular, so that the difference is just one of degree, not of kind. The counter-argument to this is that in paper the superimposed drift is not in a straight line, but follows the crooked channel; this is implicit in assuming that the electric field follows this channel, as one does by considering the fibres to be electrically insulating.

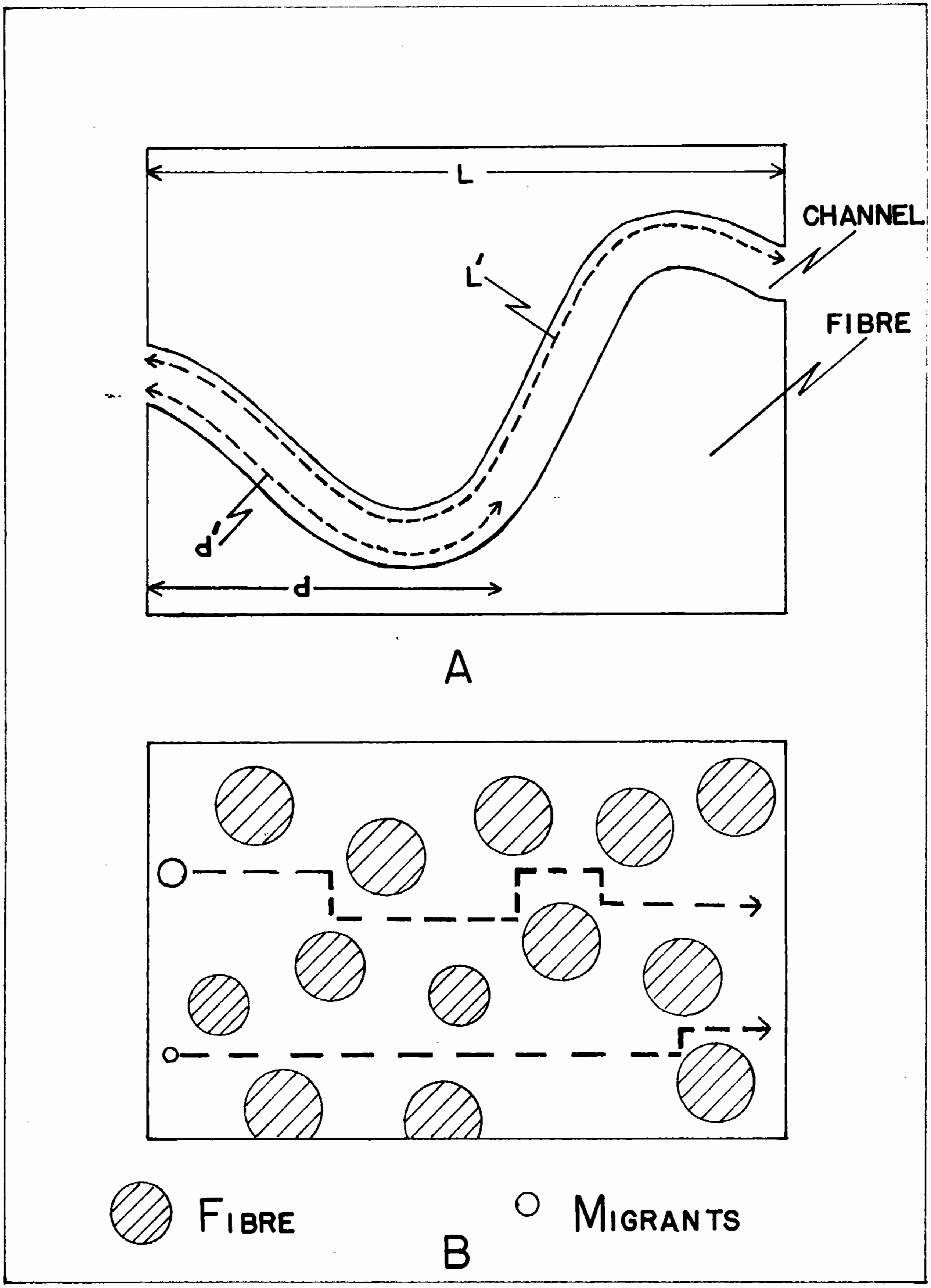
For proteins, Kunkel and Tiselius were able to obtain free solution mobilities, which were in reasonably

Figure 4

Migration of an ion through moist paper.

A. Model of Kunkel and Tiselius.

B. Model of McDonald.


L
CHANNEL
L'
FIBRE
d'
d
A
Fibre
Migrants
B

good agreement with independent measurements, from zone mobilities in paper. They concluded that if P is determined for a given paper, the value holds for all migrants in that paper. This can be true only if the obstruction is purely mechanical and no specific adsorption effects come into play. It also requires that all migrants follow the same path through the paper. This means that a small ion must not take "short-cuts" through channels that are too narrow for larger ions. Most of the experimental work pertaining to this theory has utilized proteins and thus has considered only very large and complicated molecules. For these it appears that while this treatment usually gives fairly good results, P does depend markedly on the migrant ion in some cases. No test of this theory using inorganic ions has been carried out heretofore.

McDonald prefers to consider electromigration in paper according to his "barrier theory" (8). His model is illustrated in Fig. 4B. The fibres act as barriers to the moving ions, which are slowed momentarily by striking them. The effect of these "barriers" will depend on the size of the ions. This model is in effect only the model of Kunkel and Tiselius, allowing for cross-linking of the channels and variation of their size.

In his theoretical treatment, McDonald does not make use of any physical model, but assumes that the slowing of an ion in paper can be expressed as a lowering of the activity of the ion by the paper without regard for the mechanism involved. Using conductance measurements of a bovine serum albumin solution in a cell containing varying amounts of paper, Marbach (38) found that conductivity, and hence the activity, decreased linearly with increasing ratio of paper to solution. Corrections were made for the displacement of solution by the inert volume of the paper. McDonald's treatment also requires that electroosmosis take place at a maximum and constant rate throughout the experiment; for this, the electrolyte reservoirs must be connected by an open siphon during the run.

The development of the equation used by Marbach and McDonald in relating zone mobility to mobility in free solution is as follows: the observed displacement d_o of the migrant is given by $d_o = d_e + d_{eo}$ --- 7, where d_e is the displacement due to electromigration alone, and d_{eo} that due to electroosmosis. But

$$d_e = \frac{d_F}{C} \qquad \text{- - - 8}$$

where d_F is the displacement in free solution, and C is the activity coefficient of the migrant, and

$$d_{eo} = \frac{D}{C} \qquad \text{- - - 9}$$

where D is the displacement of the background electrolyte caused by electroosmosis. It is assumed that the migrant will be slowed by the paper to the same extent when moving with a flow of solvent as when moving under an electric field. Combining 7, 8, and 9,

$$d_F = Cd_o - D \qquad --- 10$$

But D depends on the ratio of paper to electrolyte solution; McDonald assumes that

$$D = \frac{W_1}{W_2} P' \qquad --- 11$$

where W_1 is defined as the weight of solution forming a primary layer over the fibre, while W_2 is the weight of the excess liquid which fills the spaces between them. The term P' is a constant which is related to the osmotic coefficient. If R is taken as the "concentration" of the paper,

$$\frac{1}{R} = W_1 + W_2, \text{ or } W_2 = \frac{1}{R} - W_1 \qquad ---12$$

Combining now 10, 11, and 12,

$$d_F = Cd_o - \frac{W_1 P'}{\frac{1}{R} - W_1} \qquad --- 13$$

Dividing by time and (apparent) potential gradient, we find that

$$U_F = CU_z - \frac{W_1 h}{\frac{1}{R} - W_1} \qquad --- 14$$

where h may be regarded as the maximum electroosmotic mobility of the water molecules in the primary layer. The activity coefficient, C, can be determined from the variation of conductance with paper concentration. Since this is a linear relationship, C can be replaced by

$$C = \frac{1}{mR + 1} \qquad --- 15$$

where m is the slope of the line obtained when the activity coefficient is plotted against R. From two experimental determinations of zone mobilities at different absorbances (i.e., different values of R), the two remaining unknowns, W_1 and h, can be obtained.

We may reduce equation 14 to

$$U_F = \frac{U_z}{mR+1} - \frac{W_1 h}{\frac{1}{R} - W_1} \qquad ---16$$

This equation contains three parameters which must be determined from experiment if zone mobility is to be related to free solution mobility. The first of these, m, is assumed by McDonald to be constant for a given migrant. However, this quantity might very well depend on the nature of the background electrolyte. The experimental evaluation of C by Marbach may be criticized on the grounds that the physical arrangement did not really represent the situation which prevails during an electromigration experiment. From his description of the technique, it appears that his measurements were made in a cell containing free liquid as well as the saturated paper. W_1 and h, the remaining two parameters, vary with the nature of the background electrolyte solution, but are independent of the migrant. All three terms depend on the type of paper.

Crawford and Edward (89) have extended the

Kunkel-Tiselius model to cover the variation of the obstructive factor with absorbance, and, in certain cases, their results make it possible to calculate this quantity. Their treatment is based on the semi-empirical equation of Biefer and Mason (90) giving the conductance of pads of randomly oriented, non-swelling, non-conducting fibres, which in turn was obtained from the theoretical equation

$$K' = \frac{kf(\theta)A\epsilon}{L} \qquad ---17$$

As before, K' is the conductance of the moistened pad, k is the specific conductivity of the solution, A is the cross-sectional area of the pad plus solution, and L its length. ϵ is the void fraction of the pad;

$$\epsilon = \frac{V_L}{V_L + V_S} \qquad ---18$$

where V_L is the volume of the liquid, and V_S the volume of the solid fibres; $f(\theta)$ is an orientation factor which was originally equated to the void fraction on experimental grounds. Subsequent work (90) has shown that better agreement with experiment is obtained if $f(\theta) = \alpha\epsilon$, where α is a constant which is close to unity. Measurements with cellulose acetate, Dacron, nylon, and glass fibres gave a mean value for α of 0.955. Then

$$K' = \frac{kA\alpha\epsilon^2}{L} \ . \qquad ---19$$

Since $A = \frac{(V_L + V_S)}{L}$, substituting for

A and ϵ gives

$$\alpha\epsilon = \frac{K'L^2}{kV_L} \quad . \qquad --- 20$$

But $$P = \frac{K'}{K} = \frac{K'L^2}{kV_L}$$ from 2 and 3.

Thus, $$\alpha\epsilon = P \qquad --- 21$$

Now, the absorbance a is

$$a = \frac{V_L}{\text{Wt. of solid}} \quad .$$

Applying this to 18, we get

$$P = \alpha\left(\frac{a}{a + V_S}\right), \qquad --- 22$$

where V_S is the specific volume of the fibres.

Cellulose fibres are known to swell in aqueous solution. If X is the fractional increase in fibre volume which is effective in hindering ion migration, then

$$\epsilon = \frac{V_L - XV_S}{V_L + V_S} \quad . \qquad --- 23$$

Then, from equations 19, 2, and 3,

$$P = \alpha\left(\frac{a-2V_S X}{a+V_S}\right) \quad . \qquad --- 24$$

Crawford and Edward, using measurements of conductance of the moistened strip, found that values of X between 0.1 and 0.2 fitted most of their experimental obstructive factors for inorganic salt solutions; α was taken as unity.

From equation 22 it is possible to calculate the obstructive factor for non-swelling fibres such as glass, if the theory is correct. The only uncertain factor in the equation is α . This can be assumed to be unity with only a small error, or it can be taken as 0.96 from the work of Biefer and Mason. The expression $f(\theta) = \alpha\epsilon$, on which equations 22 and 24 depend, is admittedly empirical, but it does seem to be well founded experimentally.

The above model makes no allowance for specific interactions between the ions and the fibre. It is true that the values of P obtained from conductance measurements may include effects of adsorption and may therefore show a dependence on the ions used, but measurements made in this connection so far (89) have been with solutions of higher concentration than is usual for the ions in the moving zone, so that the paper is "overloaded". It is possible that adsorption effects at very low concentrations are more marked. Furthermore, the background electrolyte itself may well affect the way in which an ion interacts with the paper. This could not be shown from conductance measurements.

Although the treatment of Marbach and McDonald takes into account interactions between migrant and paper, it does not consider the influence of different background electrolytes on these interactions. Moreover, at least two experiments are required in each background electrolyte in order to determine the values of the remaining constants. For non-swelling fibres, the treatment of Crawford and Edward and Kunkel and Tiselius, although also empirical, is a much better starting point. For fibres which swell in solution, it is necessary to know the value of X, which in general may vary with the background electrolyte. Even here, however, Crawford and Edward's treatment contains only one unknown, and is much more readily applicable than is McDonald's.

There is no doubt that specific effects such as adsorption are important for many inorganic ions. Some authors have attempted to account for this by utilizing the R_F factors obtained from paper chromatography to give a measure of the slowing of an ion by adsorption. For example, Pucar and Jakovac (91) correct their mobilities according to the equation

$$U = m\left(\frac{U'}{R_F} - \frac{U'_e}{R_{Fe}}\right) , \qquad --- 25$$

where U' is the apparent mobility of the migrant in paper, U_e' the electroosmotic mobility of the indicator substance, R_F the chromatographic adsorption factor for the migrant, and R_{Fe} that for the indicator; m is a "porosity" factor, a constant for the paper. This equation can be rewritten in the notation used previously to yield

$$U_F = \frac{1}{P}\left(\frac{U_z}{R_F}\right) \quad \text{or } U_z = PR_FU_F \qquad --- 26$$

where U_z is corrected for electroosmosis. Pucar and Jakovac use the value of 0.84 for P, but they do not indicate how they obtained this.

Yasunaga and Shimomura (92) earlier used the same basic equation. They proposed the expression

$$\frac{d}{L_oR_F} = \text{Constant} , \qquad --- 27$$

where d is the distance travelled by the zone on the paper, and L_o is the calculated migration distance under the same conditions. The value of the constant should give the obstructive factor, although in their paper they do not relate equation 27 to the treatment of Kunkel and Tiselius. Equation 27 is in all respects equivalent to equation 26.

For several negative ions, the results of Yasunaga and Shimomura give about the same value, 0.84 to 0.87, for the constant, but for positive ions considerable variation was found. In some cases the values are greater than unity, reaching the exceedingly large value of 1.60 for Cu^{++}. However, in this paper no mention is made of any correction for electroosmotic flow of the background electrolyte. If this took place, the values of d obtained might be too high for positive ions and too low for negative ones. Even so, the possible values of the constant would be unusually high for the obstructive factor in cellulose paper, although again no absorbance data are given. The value of P given by the negative ions is about that used by Pucar and Jakovac (91).

Yasunaga and Shimomura explain some of the variation in the value of the constant on the basis that the assumed concentrations of the moving ions were not correct, and hence L_o is in error. Since they used the value of 0.1N, and the background electrolyte used was 0.1M $NaNO_3$, this is probably not too significant.

While the numbers themselves which were obtained are not too meaningful, nevertheless they do suggest that a uniform value for the obstructive factors of negative ions can be obtained if adsorption is considered. The relative R_F values are also interesting since very few such values are known for the type of electrolyte solution ordinarily used in electromigration. That for Cu^{++} is unusually low, as is its migration distance, and this would certainly indicate strong adsorption.

Maki has given experimental evidence to show that exchange adsorption can occur in filter paper (83,93), and has proposed that the zone mobility may be explained by an equation similar to those derived theoretically for adsorption chromatography. The equation proposed (83) is

$$U_z = \frac{U_F}{1 + \frac{a_S C_S}{a_L C_L}} = bU_F \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 28$$

where a_S is the volume of the stationary phase per gram of filter paper, C_S is the concentration of the solute in the stationary phase, a_L is the volume of the liquid per gram of paper, and C_L is the concentration of the solute in the solution phase. The factor b, which is equal to $\dfrac{1}{1 + \dfrac{a_S C_S}{a_L C_L}}$, was evaluated by measuring the amount of adsorption by a batch process as used for weak ion exchange resins; (b is equal to the ratio of the amount of the ion in question remaining in the liquid phase per gram of paper to that present before adsorption.) The amount of adsorption increased as the pH increased. This is the sort of behaviour which would be expected if the process were due to weakly acidic carboxyl groups. The agreement between b and $\frac{U_z}{U_F}$ determined from zone mobility measurements is good at the high and low ends of the pH range investigated, but a large difference is evident over much of the range. Only two ions were studied; Ni^{++} and Mg^{++}.

This treatment does not include a term for the slowing of the ions by purely mechanical obstruction, and therefore cannot be complete. Moreover, the given curves showing the ratio $\frac{U_z}{U_F}$ include some experimental points which are greater than unity, implying that the ion moved faster in paper than in free solution. This must be due to some factor which has been overlooked in the experimental technique. Apparently equilibrium was reached very slowly in the adsorption process. This makes it quite possible that the effect measured in this way is greater than that acting in a normal electromigration experiment where the ions do not have time to diffuse into the internal structure of the fibres.

Maki's whole treatment is just equivalent to stating that the zone mobility is equal to the free solution mobility multiplied by that fraction of the ions which is free to move at any instant. This is undoubtedly correct, provided a term for purely mechanical obstruction by the fibres is introduced. In other words, the zone mobility would be given by

$$U_Z = rPU_F \qquad ---29$$

where r is the fraction of the ions free to move at any instant. The problem now remains to find some reasonable method of evaluating r which will apply to the conditions which exist in paper electromigration. Values of R_F, obtained from paper chromatography, as used in equation 26 are not adequate. Maki has not presented sufficient data to permit any definite conclusions to be drawn, but it is unlikely that his method will be satisfactory either, although a modification of it may be. Then P must be evaluated in such a way that only mechanical effects are included. Equation 22 is suitable for non-swelling fibres. With cellulose fibres, P could be found in any system where r was known accurately, and the same P might then apply to all other ions in the same electrolyte. In other electrolytes, P might change if the swelling of the fibres were affected. Further variation of P with migrant ion would be possible if the fibres showed different degrees of permeability to the various ions. It is possible that cellulose fibres do, but unless the effects of adsorption can be isolated, the other phenomena are hidden.

Berbalk and Schier (94) have shown that the mobility of a weakly dissociated ion such as an organic acid ion depends on the degree of dissociation. This is reasonable, since the fraction of migrant which is not dissociated at a given instant is not able to move. They derive the differential equation

$$\left[\frac{\partial C(x,t)}{\partial t}\right]_x = -\alpha w V \left[\frac{\partial C(x,t)}{\partial x}\right]_t . \qquad 30$$

α is the degree of dissociation (i.e., the fraction of migrant present in ionic form at any time), w is the mobility of the ion under unit potential gradient, and V is the applied voltage gradient. The expression C(x,t) represents the distribution of migrant along the strip as a function of position x and time t. In the simplest case, the distribution will be represented by a symmetrical, gaussian-shaped curve, but the actual function need not be considered here. Weber has gone into this in some detail (95).

If this is the case, then after a time of migration t, the distribution function will be centered at a point

$$X = \alpha wVt.$$

In other words, the mobility will be

$$U = \alpha w. \qquad ---31$$

If w is taken to mean the speed of the ion in paper, then U is U_z. If, on the other hand, it is taken as the free solution mobility as Berbalk and Schier evidently mean it to be, then the zone mobility will be

$$U_z = \alpha wP = \alpha PU_F. \qquad ---32$$

This expression should give the zone mobility of the anion of a weak acid when moving in an acidic solution, for instance. U_F represents the actual velocity of the ion in free solution. In a salt solution or a basic electrolyte, $\alpha = 1$ and equation 31 reduces to equation 6a.

Although there are few instances where this equation is applicable to inorganic ions, the author feels that it can be extended to cover complex formation where several ions are present. Suppose the migrant zone contains two species, M_1 and M_2, in a state of rapid dynamic equilibrium. Let w_1 and w_2 be the actual velocities of these species (their free solution mobilities under conditions such that they are perfectly stable in a solution of the same viscosity and ionic strength), and let α_1 be the fraction of the total migrant present as M_1 at any instant. The fraction present as M_2 is $(1-\alpha_1)$. The migrant will spend part of the time moving as M_1, and the rest moving as M_2. Its net zone mobility will be

$$U_z = P(\alpha_1 w_1 + (1-\alpha_1)w_2)$$
$$= P[\alpha_1(w_1-w_2) + w_2]. \qquad --- 33$$

This equation may be extended to any number of species in equilibrium, since for n species,

$$U_z = P(\sum_{i=1}^{n} \alpha_i w_i). \qquad --- 34$$

It applies if w_2, say, is zero (an uncharged species) as well as when it has positive or negative values with respect to w_1. α_1 depends on the stability of the complex ion, and may be calculated at least in principle.

The equation is also good in the case of adsorption if the adsorbed species is considered as one of the members of the equilibrium with $w = 0$, and if the fraction which is adsorbed can be ascertained.

(b) Shape and Size of Migrant Zone.

Weber (95) has given a mathematical treatment of the shape of the zone to be expected in one and two-dimensional electromigration techinques. If no adsorption occurs, a symmetrical, gaussian distribution of concentration is established. Although the differential equation describing the concentration as a function of position which is derived when adsorption is considered does not lend itself to an explicit solution, qualitative discussion of it shows that the distribution is no longer symmetrical, but that the highest concentration occurs at the leading edge of the zone. A "comet-shaped" spot results. This is exactly the sort of behaviour which is found in many cases where adsorption is believed to be important. The mathematical details of this treatment are given in Appendix B.

Edward (96) has considered the connection between the concentration of migrant and the shape and mobility of the zone. The following argument is largely his. When a solution of migrant is applied to paper as a spot, two extreme situations may be visualized. In the first, the applied solution completely displaces the background electrolyte solution and is present on the paper in essentially the concentration at which it was applied initially. In the second extreme, the migrant solution mixes with a larger volume and concentration of background electrolyte so that the region of the zone is at practically the same concentration as the background electrolyte. Normally, some intermediate condition will exist, but when working with the very low concentrations of radioactive tracers used in much of the work described in this thesis, the second condition is very nearly approached. In many separations, however, the first extreme will be closer to the truth.

In the first case, the relative concentrations of the zone and background will affect the measured zone mobility, as will be seen from a consideration of the potential gradient along the strip. If the migrant is present in a zone of higher conductance than the background electrolyte, the real potential drop through the migrant zone will be less than that over the rest of the strip. As a result, the migrant will move more slowly than expected. But since the boundaries of the zone are not absolutely sharp, those migrant ions in the edges where the conductance is intermediate between that of the background and the bulk of the zone see a higher potential gradient, and thus move faster, than does the main body of these ions. Therefore, the leading edge of the zone becomes more and more extended; the trailing edge, on the other hand, is sharpened. This low concentration forward region continues to expand until the concentration in the zone has dropped sufficiently to make its conductance equal to that of the background electrolyte.

If, as in the second case, the migrant starts out in a zone that is effectively the same as the background electrolyte in the rest of the strip, no difference in potential gradient will exist and the zone will move with a constant size (neglecting diffusion) and with what may be called the "true" zone mobility.

The conductivity of a zone depends on both the concentration and the mobility of the ions in it. If we have a migrant $A^+ X^-$ and a background electrolyte $B^+ X^-$, and the concentrations and mobilities of A^+ and B^+ are C_A, u_A, and C_B, u_B, respectively, then, according to Edward, the zone containing A^+ will have the following behaviour in the first extreme. First, if $u_A = u_B$, then, when $C_A = C_B$, the concentration (i.e., size) of the migrant zone is unchanged. When $C_A > C_B$, the migrant zone elongates until $C_A = C_B$. If $C_A < C_B$, the zone contracts. Now, if $C_A = C_B$, then when $u_A > u_B$, the zone contracts, and when $u_A < u_B$, it expands. It may also be noted that a boundary is sharpened if the ion ahead of it has a higher mobility than the one behind it, while if the reverse is the case the boundary becomes blurred. Hence, while one boundary of a migrating zone is sharpened, the other becomes diffuse and a comet-shaped zone is formed with a "tail" that may either precede or follow it. This is in addition to the "comet-formation" brought about by adsorption.

EXPERIMENTAL

1. Apparatus and Techniques of Electromigration.

The closed strip technique was used for all experiments. Two pieces of apparatus were employed. One was operated at comparatively low voltages and was used primarily for mobility determinations, while the other provided a longer migration path and a higher voltage gradient for separations. In the first arrangement, the plates were of brass, 60 x 25 x 0.4 cm., in size. They were insulated electrically by polyethylene or polyvinyl-chloride film of a total thickness of about 0.01 inches. Water from a constant temperature bath was circulated through copper tubing which was soldered to the backs of these plates. The second apparatus was made of aluminum plates of dimensions 105 x 20 x 0.6 cm. Copper tubing was bolted to their backs for the circulation of cooling water. A schematic view of the arrangement is shown in Fig. 5A.

In order to withstand an electrical potential of 10,000 volts, a fairly thick insulation is necessary. Most plastic materials have a very low heat conductivity, so that overheating and consequent charring of the paper strip were often encountered at high voltages when such insulators were used. Of the possible insulating materials considered, mica combines the highest electrical break-down potential with the best heat conductivity, and therefore it was used. Commercial mica sheets 4 x 4 inches in size were split to the desired thickness and cemented along the centre of the plates to form a laminated sheet 4 inches wide extending from end to end. The thickness of this sheet was about 0.016 inches at the high-voltage end, but somewhat thinner over the main part. A thin film of polyethylene or polyvinylchloride was used to protect the mica. This insulation proved to be quite suitable, and had the advantage that if charring did occur, the mica remained undamaged. Over 0.6 watts/cm.^{2} could be handled.

The plastic, which was not a high quality material, was normally given a coating of Desicote*. This seemed to improve its electrical breakdown properties. It had little visible effect on the wetting of the surface, which was quite hydrophobic in any case.

To improve the contact between the cooling surfaces and the paper strip, weights usually were placed on the upper plate. With the first apparatus this was not necessary when the power limitations for mobility determinations were not exceeded. No differences in mobility were observed whether the weights were used or not. They aided the cooling when high currents were drawn, and in such cases 4 or 5 lead bricks, each weighing about 17 pounds, were used. The high voltage apparatus required weights for all runs

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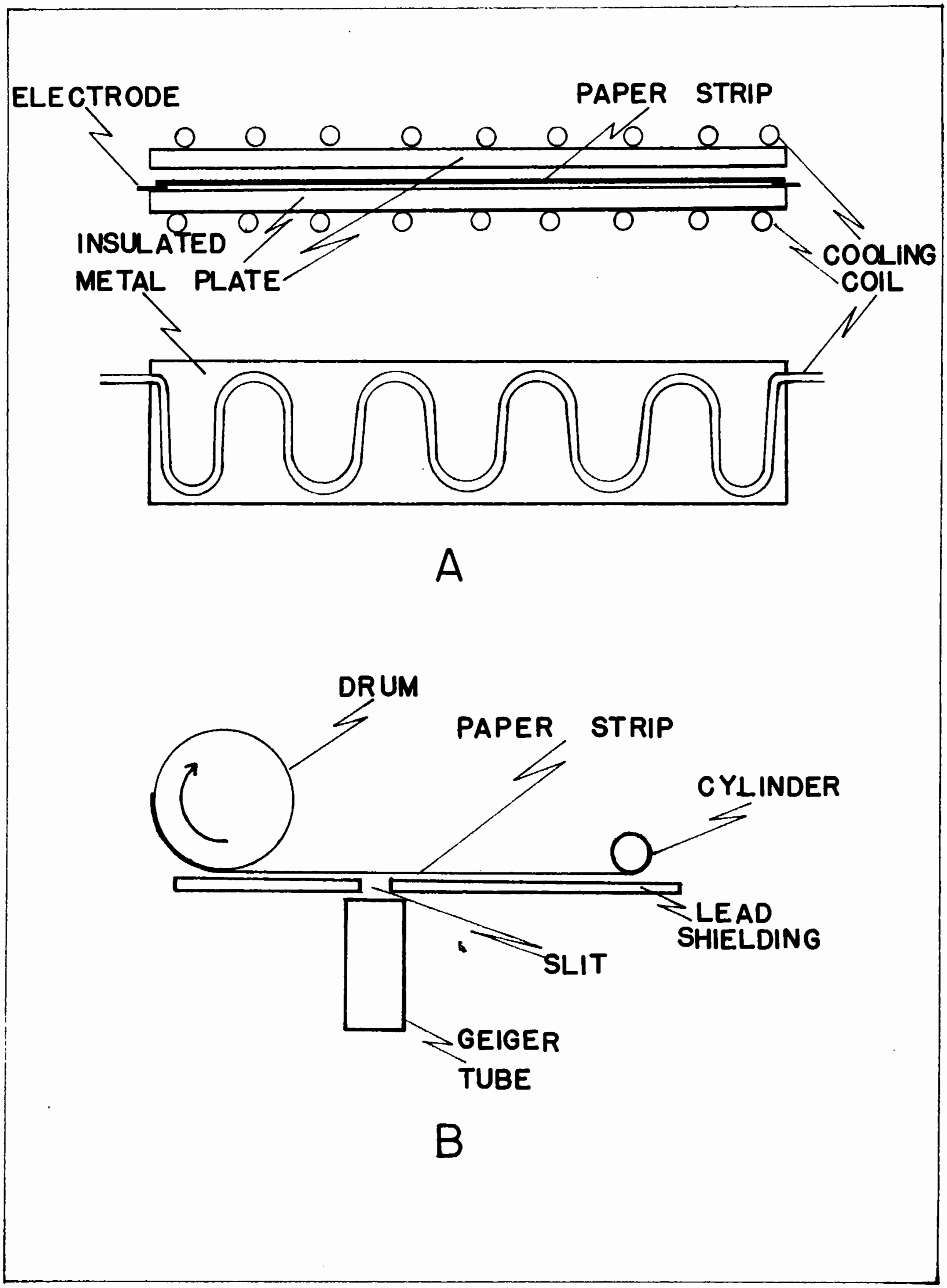
* Desicote-an organo-silicon preparation manufactured by Beckman Instruments, Inc., and used to render surfaces water repellent.

Figure 5.

A. The apparatus for electromigration, showing an edge view, and a view of the back of a cooling plate.

B. The scanner for the detection of radioactive zones on paper strips.


ELECTRODE
PAPER STRIP
INSULATED METAL PLATE
COOLING COIL
A
DRUM
PAPER STRIP
CYLINDER
LEAD SHIELDING
SLIT
GEIGER TUBE
B

since the upper plate was very light. Nine lead bricks, evenly spaced, were employed.

With the first apparatus, measurements with a thermocouple in contact with the paper showed that at an applied potential of 30 V/cm., a current of 1 milliampere could be carried for each centimeter width of the paper with an increase of less than 0.5° C., in the actual temperature of the strip. This was approximately the rise calculated by assuming equilibrium between the amount of heat generated in the paper and that conducted accross the polyethylene insulation (Appendix A). Mobility measurements were carried out below this upper limit.

Wood and Strain have shown (42) that electroosmotic flow of the background electrolyte is largely eliminated if the electrodes are placed in direct contact with the paper. This arrangement was employed here. When necessary, interference from electrolytic products was eliminated by moistening the zones at the ends of the paper with a suitable buffer solution which trapped the ions formed by electrolysis. For example, when acetic acid was used as background electrolyte, an ammonium acetate buffer zone at the cathode end of the strip prevented pH changes from occurring in the rest of the strip. This kept the voltage gradient in that part of the strip which was used for migration constant with constant voltage on the electrodes.

This procedure was chosen in preference to using electrolyte reservoirs and correcting for electroosmotic flow by means of an uncharged substance for the reasons discussed previously. When uncharged substances such as H_2O_2 were used as electroosmosis indicators in the technique as employed here, no measureable motion was detected except when cellulose acetate strips were used. With these, an obvious drying of the anode end of the strip occurred during a run, and motion of H_2O_2 was evident. Therefore, with this material, the usual correction was used. The distance of displacement of the H_2O_2 was never greater than 10% of the distance moved by the ions. Acetic acid was the background electrolyte in these experiments.

It may be argued that some movement of liquid takes place in all cases, but in any event in all other instances reported here it was so slight as to be undetectable, and its effect on the motion of the ions is entirely negligible. Any such motion would result in an absorbance gradient in the strip. Again, however, it is too small to have any effect except possibly with cellulose acetate.

In both pieces of apparatus, the electrodes were of platinum foil. They could be placed at the ends, or at any desired distance from the ends, of the plates, and electrical connection made to them by means of aluminum or copper ribbon. Thus any desired migration path up to the length of the plates could be used.

Voltages were measured by means of a vacuum tube voltmeter connected to platinum probes that were at some distance from the ends of the strip so that voltage drops across the electrodes and the buffer zones were not considered. Separate measurements showed that the voltage gradient in that part of the strip between the probes was uniform, and remained constant for the duration of an experiment.

In order to obtain known, reproducible absorbances of the paper, the desired volume of electrolyte was spread as uniformly as possible over the strip from a pipette. The buffer zones were moistened to the same absorbance. For mobility determinations, the electrolyte was allowed to spread for half an hour or more before the ion to be investigated was applied. The starting point was previously marked in pencil on the dry strip. This method of moistening the paper was quite satisfactory except at very low absorbances.

Most of the mobility values reported here represent the mean of three or more experiments, usually carried out with different voltage gradients and migration times. Lengths of paper available for migration varied in different experiments from 20 to 50 cm., and actual distances of migration ranged from 15 to 50 cm. In the case of some very slow ions, somewhat shorter migration distances were used. Reproducible mobility values were obtained which were independent of time, distance of migration, and potential gradient. The estimated errors amount to less than ± 5% of the quoted values in the most favourable cases, but are somewhat greater than this for slow ions and in very dilute background electrolyte solutions.

A source of direct current potential is required. A number of experiments were done using a Shandon model 2523 d.c. power pack with a maximum output of 1,000 volts, but most work was carried out with a Beta Electric model 1010-50 R & D power supply. This instrument gave an output which was continuously variable up to 10,000 volts, and could deliver a maximum current of 50 milliamperes. Its regulation was adequate, and the ripple, which leads to increased heating, was small.

2. Detection of Migrated Zones.

For the detection of radioactive ions, standard apparatus for the measurement of radioactivity was used. Usually, the part of the strip containing the zone was cut into sections 1 cm., (occasionally 0.5 cm.) broad, and each measured with a suitable radiation detector. In most cases, an end-window Geiger counter was employed, but for nuclides which emitted only gamma radiation, a "well-type" scintillation counter was used. Alpha radiation was measured with a 2π – proportional counter operated at the alpha plateau voltage. When separations were made of substances emitting gamma-rays of characteristic energies, identification of the zones was confirmed by means of the energy spectrum as determined by a hundred channel pulse height analyser using a 3 x 3 inch NaI crystal as detector. Other identities were confirmed by relative rates of decay.

For less tedious location of the zones, a "scanner" was constructed. This device is illustrated schematically in Fig. 5B. The strip was rolled onto a cylinder, and the free end attached to a drum which was rotated by means of a synchronous motor. The paper passed before a slit in lead shielding, and the radiation detected by a Geiger counter behind the slit. Pulses from the Geiger tube were passed into a counting rate meter which was used to drive a strip-chart recorder. From the known speeds of chart and strip, and from a reference point on each, the position of the active zone relative to the starting point follows.

In a preliminary design, the strip was wrapped around the drum, which rotated in front of the slit. This arrangement limited the length of the strip to the circumference of the drum, whereas the final design does not have such a limitation. Several strips can be taped together and run successively.

The speed of the paper past the scanning slit is determined by the speed of the motor and the circumference of the drum. By a proper choice of these this speed may be matched to the chart speed, or some multiple of it. The resolution of the scanner is better with a narrower slit, but at the same time the number of "counts" registered decreases, and with too narrow a slit comparatively low activities may be missed. In the design used, the slit width could be varied as required.

Although this type of scanner could be made quantitative by defining the slit-width and fixing the position of the Geiger tube and paper with respect to the slit, no such refinements were necessary for merely indicating the relative positions of the zones. The very simple construction used proved quite effective for locating substances which emitted energetic beta particles. Many scanners are described in the literature, most of them considerably more refined. The one described here is not a copy of any of them, but ideas from various sources influenced its design. The arrangement given by Muller and Wise (97) is of particular note, however.

Inactive migrants usually were detected by brushing the strip with a solution of a reagent giving a suitable colour test, or by exposure to H_2S . Reagents used are indicated in Table I.

3. Migrant Solutions.

There are certain advantages to using radioactive

Table I

Inactive ions and reagents used
for their detection.

Ion	Reagents
Ag (I)	Dithizone in CCl_4, or H_2S
Al (III)	Alizarin – NH_3
Bi (III)	Dithizone in CCl_4
Cd (II)	Dithizone in CCl_4, or H_2S
Co (II)	Rubeanic acid – NH_3, or H_2S
Cu (II)	Dithizone in CCl_4, or H_2S
Fe (III)	NH_4SCN, or H_2S
Ga (III)	Alizarin — NH_3
Hg (II)	Dithizone in CCl_4
In (III)	Alizarin – NH_3 or Dithizone in CCl_4
Ni (II)	Rubeanic acid – NH_3, or Dimethyl-glyoxime-NH_3, or H_2S
Pb (II)	Dithizone in CCl_4
Ti (IV)	Chromotropic acid.
Th (IV)	Alizarin — NH_3
V (III)	Cupferron
UO_2 (II)	Alizarin – NH_3
Zn (II)	Dithizone in CCl_4

materials in this work. The zones of migrant are very easily detected by their radiations so that chemical tests are unnecessary-a great advantage when working with the alkali metals, for example. Furthermore, exceedingly small amounts of material can be used, so that the ionic strength of the moving zone need not be appreciably different from that of the background electrolyte solution. Radioactive tracers permit the use of such dilute solutions that any effects of concentration on mobility are entirely negligible.

Inactive ions were used in some cases, particularly in separations where the effects of appreciable concentration were of no concern. When simple chemical tests are available, detection is more rapid than by radiochemical methods.

Na^{22}, Cs^{137}, Tl^{204}, (as Tl^{+}), Co^{60}, Zn^{65} and Cl^{36}, (as chloride) were the radioactive isotopes used in determinations of zone mobilities. Various others were used in separations. The Na^{22} was effectively "carrier-free" while the concentrations of the rest, although not known exactly, were in all cases much less than 0.001 molar. A minimum of foreign ions were present, but the solutions of the Tl, Co, and Zn were slightly acid with HNO_3.

Inactive Cu^{++}, Cd^{++}, and Fe^{+++} were used as 0.001 M. solutions of the nitrate, and some experiments with $Zn^{++}$and Co^{++}were done with similar inactive solutions. The volume of solution applied, both of active and inactive materials, was usually 10 microlitres, but over 50 microlitres could be used with no difficulty. It was felt that the smaller volume would result in a zone which was effectively of the same ionic concentration as the rest of the strip.

In general, similar solutions were used for separations whenever possible, but often higher concentrations (0.01 M) were used for better detection on the thicker paper employed. Where it may be important, details of the composition of the solutions used in a particular case will be noted.

4. Background Electrolyte Solutions.

Background electrolyte solutions were made up from reagent grade chemicals when possible, but only technical grades of the "complexones"* were available. Where a series of concentrations of a given electrolyte was used, the strength of the most concentrated was determined and the remainder made up from this stock solution by dilution.

5. Supporting Media.

The cellulose papers used in the experiments were Whatman Chromatography papers. No. 52 was used for most mobility determinations, and this and No. 3 MM for

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* The term "complexone" is often used when referring to a group of generally similar chelating agents of which ethylenediaminetetraacetic acid (EDTA) is the best known.

most separations. A few other grades were used in particular cases. Reeve Angel 934AH glass fibre paper, and "Oxoid" cellulose acetate electrophoresis strips* were also used for some measurements.

Paper contains more or less adsorbed water. No attempt was made to eliminate this; ordinary paper in equilibrium with the moisture in the air was used for all experiments. Absorbances are based on the weight of this "air-dried" paper. The consideration of the free portion of this adsorbed water would shift the absolute absorbance values slightly, but would have no real effect on any results given. Variation of this adsorbed water from day to day is insignificant for this work. That No. 52 paper at least is reproducible is indicated by the fact that several rolls, purchased at different times, all yielded the same zone mobility values for several ions. Mobilities measured 18 months apart were in agreement.

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* Manufactured by Courtaulds Ltd., for Oxo Ltd., and distributed by British Drug Houses.

RESULTS

The results of this research are collected in the tables and figures which follow. Most measurements of zone mobility and zone size were carried out with radioactive tracers, but those with copper, and some of those with other multivalent ions, were done with inactive substances as described in the experimental section. In those cases where both active and inactive migrants were used, no difference in mobility was observed. It is probable that the condition of the migrant zones in these cases approaches the second extreme discussed by Edward (96), and that the zone mobilities measured are the "true" zone mobilities.

The separations accomplished are illustrated in Figs. 19 to 34. Separations of non-radioactive substances are shown as tracings from the original strip. The heavy vertical line represents the starting position. All are of actual size except those in Figs. 19 and 21, which were reduced to one-half or three-quarters natural size by means of a pantograph. The diagrams show only the regions of the strip which contained the separated zones; the total length was appreciably greater than this (usually about 50 cm.). The separations of radioactive ions are presented in the form of histograms in Figs. 25 to 34.

Here, the counting rate given by each centimeter broad segment of the strip is plotted against its position in the strip; the starting point is the zero position, while distances toward the cathode are considered positive, and those toward the anode, negative. The relative heights of the different peaks have no meaning, since the detection efficiencies for the various nuclides are not the same. The actual counting rates are not relevant either, and have not been given.

Various temperatures were used for the separations, but a large number were carried out at 25° C., since they were run alternately with experiments on zone mobilities, and the same constant temperature bath was used for both pieces of apparatus. The latter measurements were done chiefly at 25° C., because this is a standard temperature for physico-chemical measurements. The actual temperature of the strip during a high voltage separation may be three or four degrees higher than that nominally given because of the heat produced by the electric current.

Whatman No. 3 MM paper was used for all separations except where another type is specifically indicated. The absorbance employed with this paper was about 1.1 ml./g., but no great care was taken to attain this value precisely, nor to have the absorbance uniform.

While it was always possible to reproduce the sequence of migration for a given set of ions under specified conditions, the actual mobilities are not reproducible. This is particularly true in the "complexone" electrolytes, where a great deal of variation in both absolute and relative mobilities was encountered from run to run. This may be due partly to the fact that the concentration of the initial migrant zone was often too high to give the "true" zone mobility, and was not always the same, and partly because of the small differences in absorbance and temperature which undoubtedly existed from run to run.

Table II

Zone mobilities of several positive ions in various concentrations of acetic acid.

Ion	Concentration of Acetic Acid moles/litre	U_z cm.^{2} v^{-1} sec^{-1} x 10^5	P_{app}
Cs^+	0.01	27.8	0.35
	0.02	28.8	0.36
	0.04	31.2	0.40
	0.06	34.5	0.44
	0.59	30.9	0.43
	1.18	28.8	0.43
	2.36	25.1	0.43
	5.89	16.2	0.38
Na^+	0.06	24.8	0.49
	0.59	22.1	0.47
	1.18	20.7	0.48
	2.36	18.1	0.48
	5.89	13.4	0.49
Tl^+	0.06	27.0	0.36
	0.59	25.4	0.36
	2.36	21.1	0.37
	5.89	13.4	0.32
Zn^{++}	0.06	15.7	0.30
	0.59	15.8	0.33
	1.18	16.1	0.35
	2.36	12.6	0.32
	3.40	10.7	0.31
	5.89	7.7	0.27
Cd^{++}	0.06	14.9	0.30
	0.59	15.3	0.33
	1.18	15.1	0.36
	2.36	11.6	0.32
	3.40	9.4	0.29
	5.89	6.9	0.26
Cu^{++}	0.06	10.2	0.18
	0.59	10.4	0.20
	1.18	11.0	0.22
	2.36	9.0	0.21
	3.40	7.2	0.19
	5.89	5.1	0.17

Note: Absorbance 0.96 ml/g., Whatman No. 52 paper, 25.0 ± 0.5° C.

Table III

Zone mobilities of some positive ions in various concentrations of ammonium hydroxide.

Ion	Concentration of NH_4OH, moles/litre	U_z $cm.^2\ v^{-1}sec^{-1} \times 10^5$	P_{app}
Cs^+	0.06	28.9	0.37
	0.61	26.1	0.34
	1.22	25.4	0.33
	2.4	23.8	0.33
	6.1	21.5	0.33
Na^+	0.06	21.3	0.42
	0.61	19.9	0.41
	2.4	19.6	0.43
	6.1	17.9	0.43
Tl^+	0.06	15.6	0.21
	0.61	12.4	0.17
	1.22	11.8	0.16
	2.4	10.7	0.15
	6.1	9.5	0.15
$Ag(NH_3)_2^+$	0.06	18.9	
	0.61	18.0	
	1.22	17.8	
	6.1	16.5	

Note: Absorbance 0.94 ml./g., Whatman No. 52 paper, 25.0 ± 0.5°C.

Table IV

Zone mobilities of Cs^+ in various concentrations of citric acid.

Concentration of citric acid, moles/litre	U_z $cm.^2\ v^{-1}sec^{-1} \times 10^5$	P_{app}
0.07	33.1	0.45
0.32	27.3	0.42
1.30	16.4	0.44

Note: Absorbance 0.96 ml./g., Whatman No. 52 paper, 25.0 ± 0.5°C.

Table V

Zone mobilities of Cl^- in various concentrations of acetic acid and ammonium hydroxide.

Background electrolyte; concentration in moles/ litre	U_z $cm.^2v^{-1}sec^{-1} \times 10^5$	P_{app}
0.02 M Acetic Acid	15.2	0.20
0.06 " " "	30.3	0.39
0.59 " " "	26.3	0.37
1.18 " " "	24.1	0.36
2.36 " " "	20.1	0.35
5.89 " " "	16.0	0.38
0.6M NH_4OH	24.8	0.33
2.4M "	24.0	0.34
6.1M "	22.2	0.34

Note: Absorbance 0.96 ml./g., Whatman No. 52 paper, 25.0±0.5°C.

Figure 6.

Zone mobility vs. concentration for Cs^+ in acetic acid. Absorbance 0.96 ml./g., Whatman No. 52 paper, 25.0 ± 0.5°C.

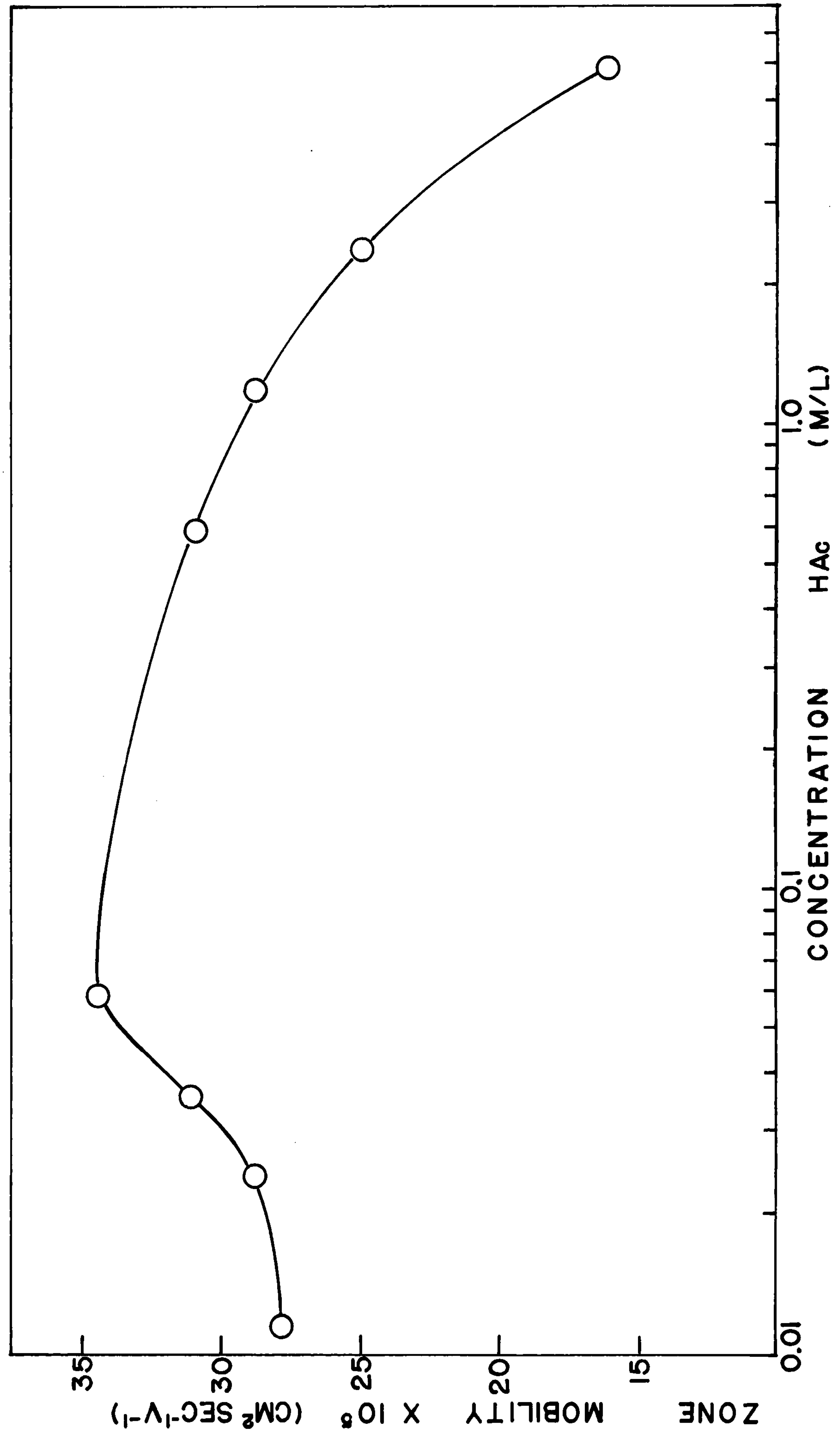
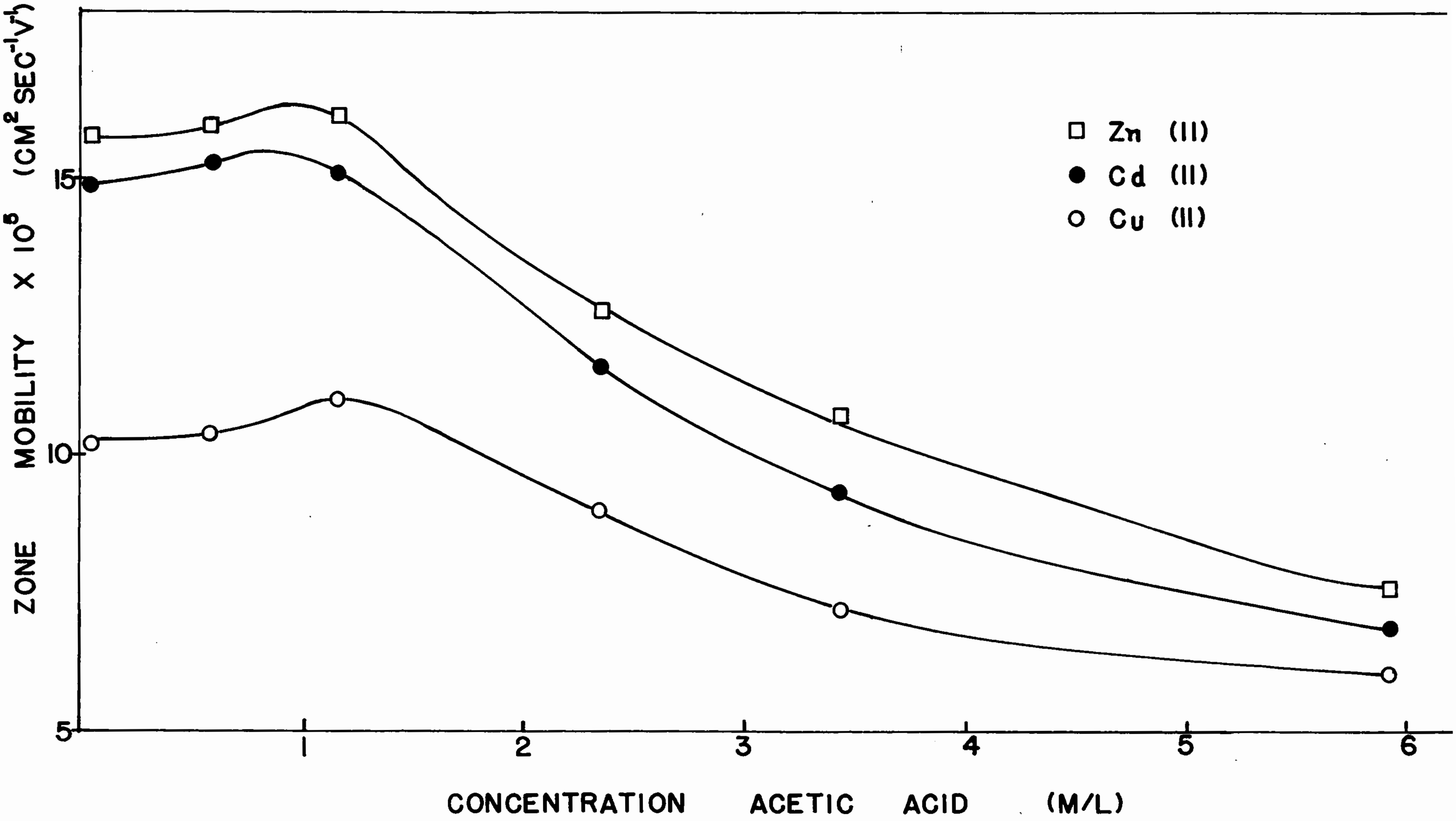

ZONE MOBILITY X 10⁵ (CM² SEC⁻¹V⁻¹)
35
30
25
20
15
0.01
0.1
1.0
CONCENTRATION HAc (M/L)

Figure 7.

Zone mobility vs. concentration for Cu^{++}, Cd^{++}, and Zn^{++} in acetic acid. Absorbance 0.96 ml./g., Whatman No. 52 paper, 25.0 ± 0.5°C.


□ Zn (II)
● Cd (II)
○ Cu (II)
ZONE MOBILITY X 10^{5} (CM^{2} SEC^{-1}V^{-1})
15
10
5
1
2
3
4
5
6
CONCENTRATION ACETIC ACID (M/L)

<u>Figure 8.</u>

Apparent obstructive factor vs. exchange capacity of the paper for Cu^{++}. Background electrolyte 2.36M acetic acid, absorbance 0.96 ml./g., 25.0 ± 0.5°C.

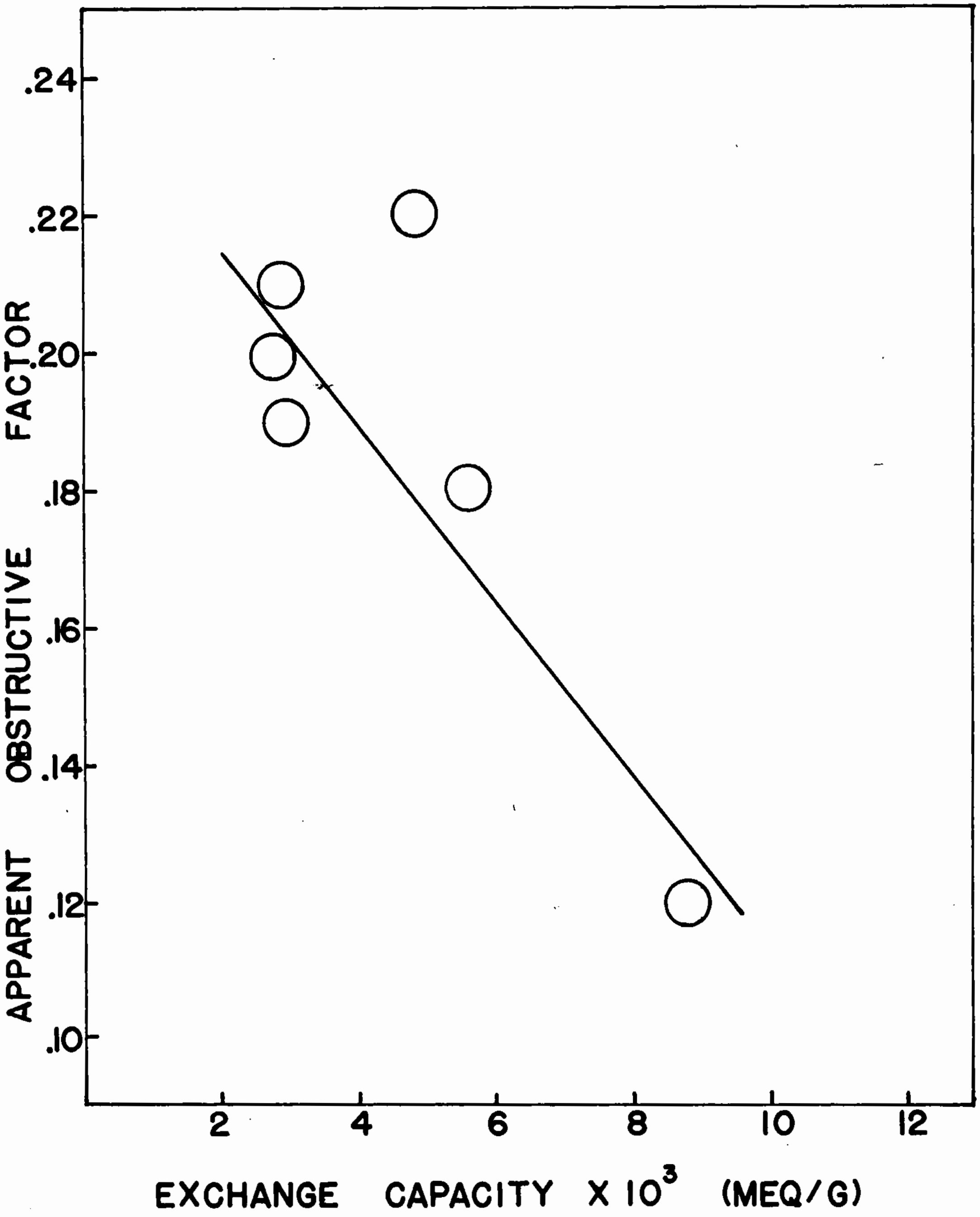

APPARENT OBSTRUCTIVE FACTOR
.24
.22
.20
.18
.16
.14
.12
.10
2
4
6
8
10
12
EXCHANGE CAPACITY X 10^3 (MEQ/G)

Table VI

Variation of zone mobility with paper type for several ions

Whatman Chromatography paper number	Exchange Capacity meq./g.	U_z cm.^{2}v^{-1}sec^{-1} x 10^5				P app			
		Cu^{++}	Zn^{++}	Cd^{++}	Na^+	Cu^{++}	Zn^{++}	Cd^{++}	Na^+
7	0.0027	8.4	12.2	11.1	16.5	0.20	0.31	0.30	0.43
52	0.0028	9.0	12.6	11.6	18.1	0.21	0.32	0.32	0.48
42	0.0029	8.2	13.5	11.8	-	0.19	0.34	0.32	-
4	0.0049	9.2	13.5	12.0	-	0.22	0.34	0.33	-
1	0.0056	7.5	10.1	8.5	-	0.18	0.26	0.23	-
20	0.0089	4.9	12.5	11.1	16.9	0.12	0.32	0.30	0.44

Note: Background electrolyte 2.36M acetic acid, absorbance 0.96 ml./g., 25.0 ± 0.5°C.

Table VII

Zone mobilities in Whatman No. 41H paper at several absorbances.

Absorbance ml./g.	U_z(cm.^{2}v^{-1}sec^{-1}) x 10^5 Cu^{++}	 Zn^{++}	 Cd^{++}
0.67	3.1	4.5	4.4
0.79	4.3	5.7	6.1
0.95	5.4	7.2	7.0

Note: Background electrolyte 2.36M acetic acid, 5 ± 1°C.

Table VIII

Zone mobilities in Whatman No. 52 paper at several absorbances.

Absorbance			U_z(cm^{2}v^{-1}sec^{-1}) x 10^5			
ml./g.	Cu^{++}	Zn^{++}	Cd^{++}	Co^{++}	Ni^{++}	Fe^{+++}
0.77	3.7	5.6	5.3	5.7	5.3	1.4
0.96	5.4	7.8	7.1	7.2	6.9	2.1
1.12	6.8	9.6	8.8	9.0	8.2	2.6
1.28	8.2	11.1	9.7	-	-	-

Note: Background electrolyte 2.36M acetic acid, 5 ± 1°C.

Figure 9.

Zone mobility vs. absorbance for several ions in 2.36M acetic acid background electrolyte and Whatman Nos. 52 and 41H papers. 5 ± 1°C.

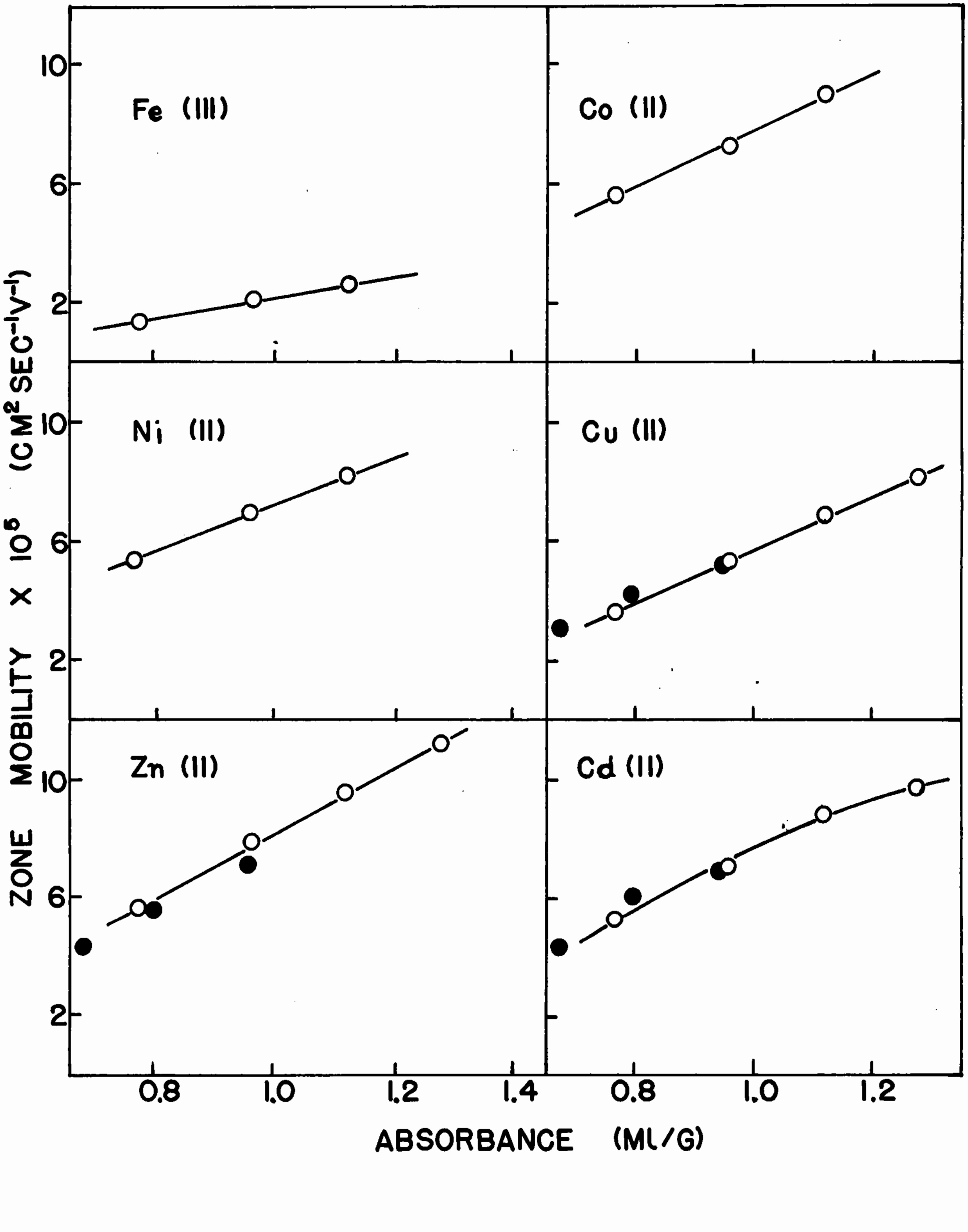

Fe (III)
Co (II)
Ni (II)
Cu (II)
Zn (II)
Cd (II)
ZONE MOBILITY X 10^5 (CM^2 SEC^{-1}V^{-1})
10
6
2
0.8
1.0
1.2
1.4
ABSORBANCE (ML/G)
○ WHATMAN No. 52
● WHATMAN No. 41 H

Table IX.

Zone mobilities of Cs^+ at various absorbances in several background electrolytes.

Background Electrolyte	Absorbance ml./g.	U_z cm.^{2}v^{-1}sec^{-1} x 10^5	P_{app}
0.02M Acetic Acid	0.47	11.2	0.14
	0.71	19.3	0.24
	0.72	20.9	0.26
	0.79	22.8	0.29
	0.86	25.1	0.32
	0.96	28.8	0.36
	1.06	31.6	0.40
	1.14	34.0	0.43
0.06M Acetic Acid	0.72	24.8	0.32
	0.84	29.7	0.38
	0.96	34.5	0.44
	1.08	38.1	0.49
	1.20	39.1	0.50
2.36M Acetic Acid	0.72	17.8	0.30
	0.84	22.2	0.38
	0.96	25.1	0.43
	1.08	29.3	0.50
	1.20	31.1	0.53
5.89M Acetic Acid	0.72	11.8	0.27
	0.78	12.5	0.29
	0.84	13.8	0.32
	0.90	15.3	0.36
	0.96	16.2	0.38
	1.08	18.3	0.43
	1.20	18.8	0.44
1.22M NH_4OH	0.72	22.6	0.30
	0.94	25.4	0.33
	1.20	28.7	0.38
0.32M Citric Acid	0.72	18.7	0.29
	0.84	23.9	0.37
	0.96	27.3	0.42
	1.08	30.3	0.47
	1.20	33.0	0.51

Note: Whatman No. 52 paper, 25.0 ± 0.5°C.

<u>Figure 10</u>.

Zone mobility vs. absorbance for Cs + in several background electrolytes. Whatman No. 52 paper, 25.0 ± 0.5°C.

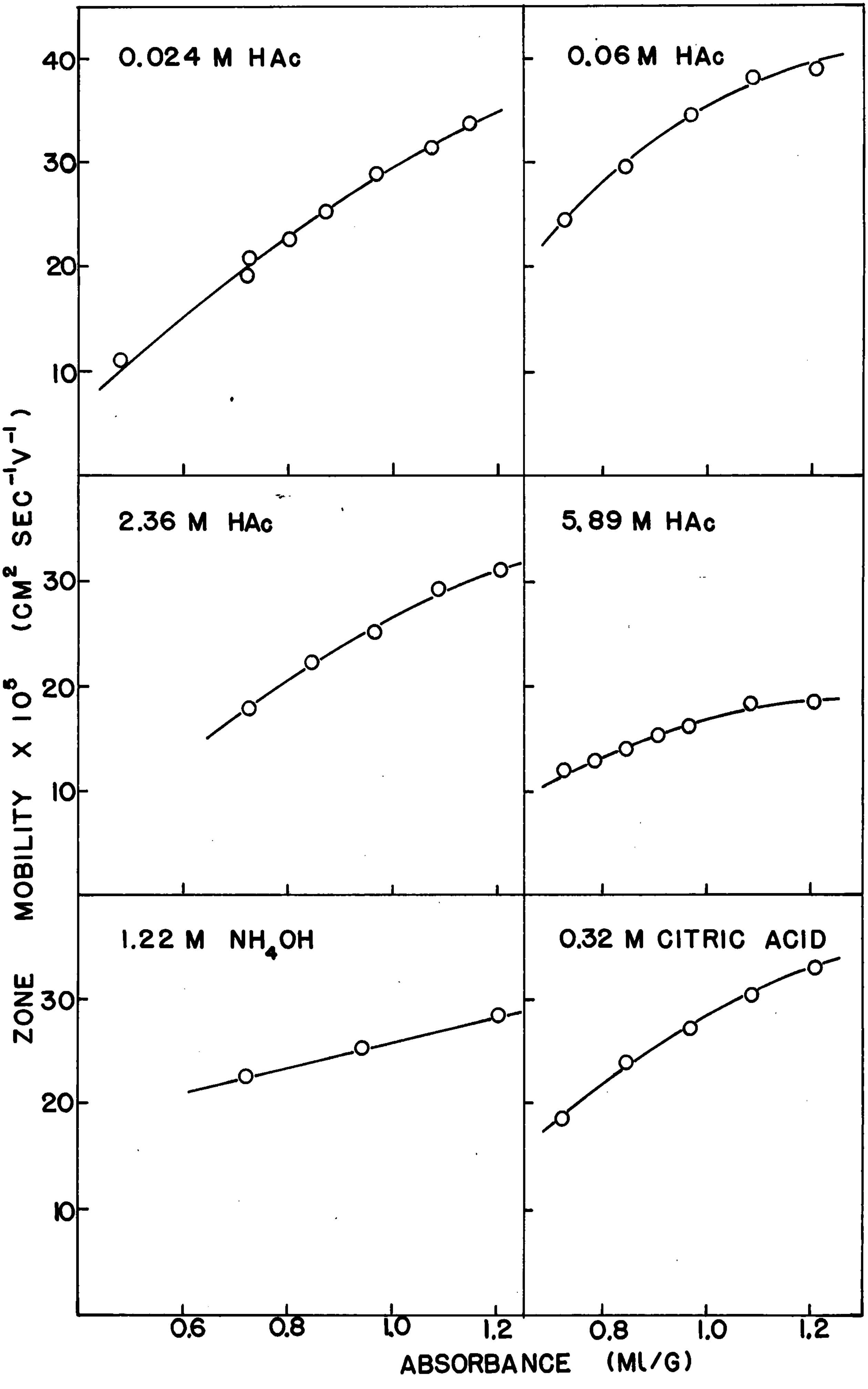

0.024 M HAc
0.06 M HAc
2.36 M HAc
5.89 M HAc
1.22 M NH₄OH
0.32 M CITRIC ACID
ZONE MOBILITY X 10⁵ (CM² SEC⁻¹V⁻¹)
ABSORBANCE (ML/G)
10
20
30
40
0.6
0.8
1.0
1.2

Figure 11.

Comparison of calculated and experimental (or apparent) obstructive factors as a function of absorbance for Cs^+ in several background electrolytes. The curves are calculated from equation 24, using the values of X indicated. The circles represent experimental points. Whatman No. 52 paper, 25.0 ± 0.5°C.

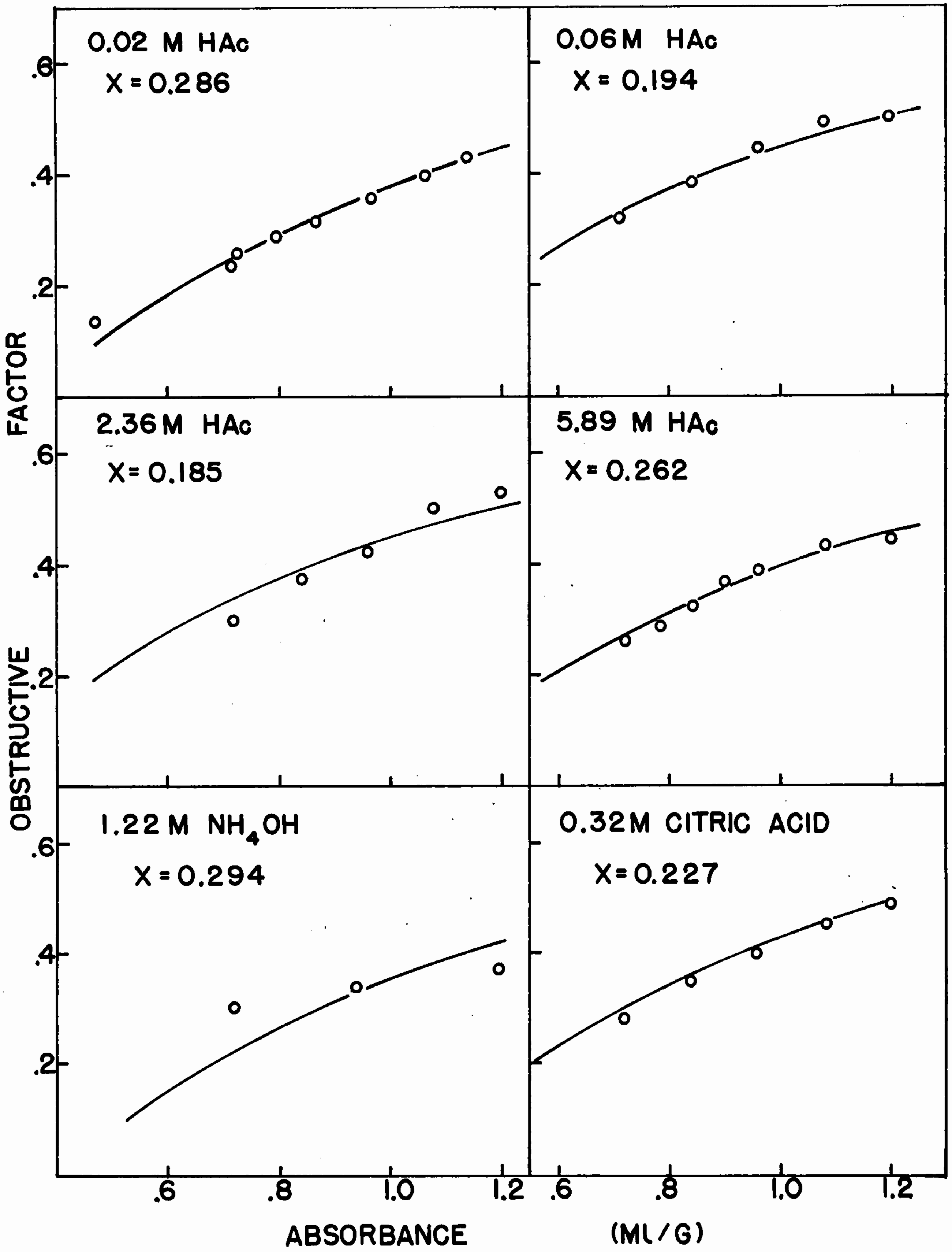

0.02 M HAc
X = 0.286
0.06M HAc
X = 0.194
2.36 M HAc
X = 0.185
5.89 M HAc
X = 0.262
1.22 M NH$_4$OH
X = 0.294
0.32M CITRIC ACID
X = 0.227
OBSTRUCTIVE FACTOR
.6
.4
.2
.6
.8
1.0
1.2
ABSORBANCE (Ml/G)

Table X.

Variation of the apparent obstructive factor in the presence of the swelling agent thiourea.

		1.18M Acetic Acid		1.18M Acetic Acid-1M thiourea	
Ion	Paper (Whatman)	U_z $cm^2v^{-1}sec^{-1}$ x 10^5	P_{app}	U_z $cm.^2v^{-1}sec^{-1}$ x 10^5	P_{app}
Na^+	52	20.7	0.48	21.4	0.51
	31 double thickness	17.3	0.40	18.8	0.45
	3MM	19.8	0.46	21.4	0.51
Cs^+	52	28.8	0.43	29.1	0.45
	31 double thickness	24.6	0.35	27.2	0.42
	3MM	27.5	0.41	30.7	0.47

Note: Absorbance 0.96 ml./g., 25.0 ± 0.5°C.

Table XI.

Zone mobilities of some ions in Reeve Angel 943AH glass fibre paper with acetic acid as background electrolyte.

Ion	Concentration of Acetic Acid moles/litre	U_z cm.^{2}v^{-1}sec^{-1} x 10^5	P_{app}
Na^+	0.01	23.6	0.47
	0.04	31.5	0.62
	0.06	33.0	0.66
	0.59	34.1	0.73
	1.18	33.7	0.78
	2.36	29.9	0.80
	5.89	23.1	0.85
Cl^-	0.59	49.5	0.66
	1.18	47.0	0.71
	2.36	41.3	0.71
	5.89	23.9	0.69
Zn^{++}	0.01	Ca. 34	Ca. 0.6
	0.12	34.0	0.66
	0.59	31.2	0.64
	2.36	25.9	0.66
	5.89	19.0	0.66
Cu^{++}	0.01	Ca. 22	Ca. 0.4
	0.12	23.0	0.42
	0.59	21.4	0.40
	2.36	17.1	0.43
	5.89	11.8	0.38

Note: Absorbance 3.36 ml./g., for Na^+ and Cl^-, 3.96 ml./g., for Zn^{++} and Cu^{++}.

Figure 12.

Comparison of experimental zone mobilities of Na^+ in acetic acid with those calculated from the free solution mobility with the aid of equation 22. Reeve Angel 934AH glass fibre filter paper, absorbance 3.36 ml./g., 25.0 ± 0.5°C.

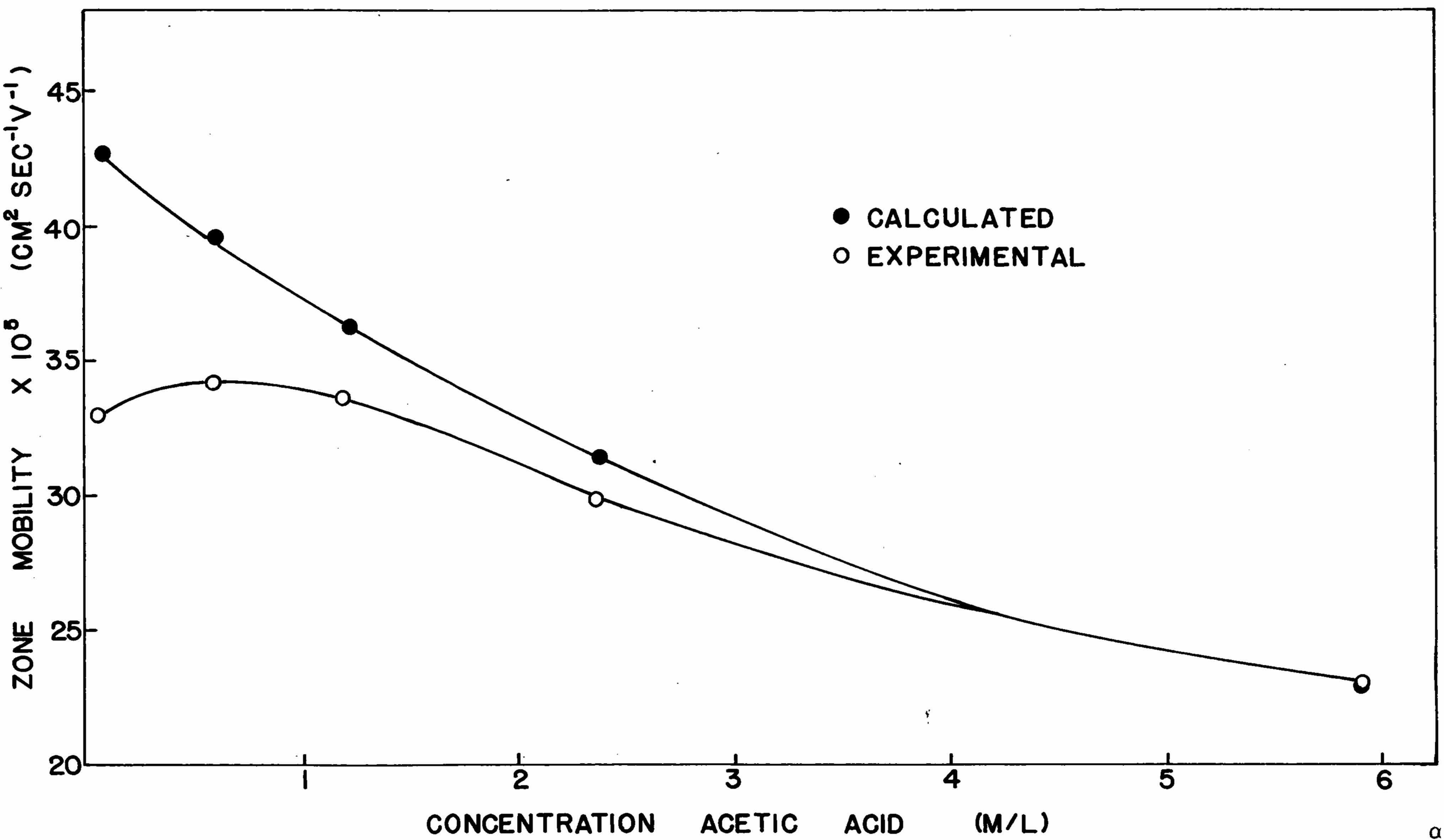

ZONE MOBILITY X 10⁵ (CM² SEC⁻¹V⁻¹)
45
40
35
30
25
20
CALCULATED
EXPERIMENTAL
1
2
3
4
5
6
CONCENTRATION ACETIC ACID (M/L)

Figure 13.

Comparison of experimental zone mobilities of Cl^- in acetic acid with those calculated from the free solution mobility with the aid of equation 22. Reeve Angel 934AH glass fibre filter paper, absorbance 3.36 ml./g., 25.0 ± 0.5°C.

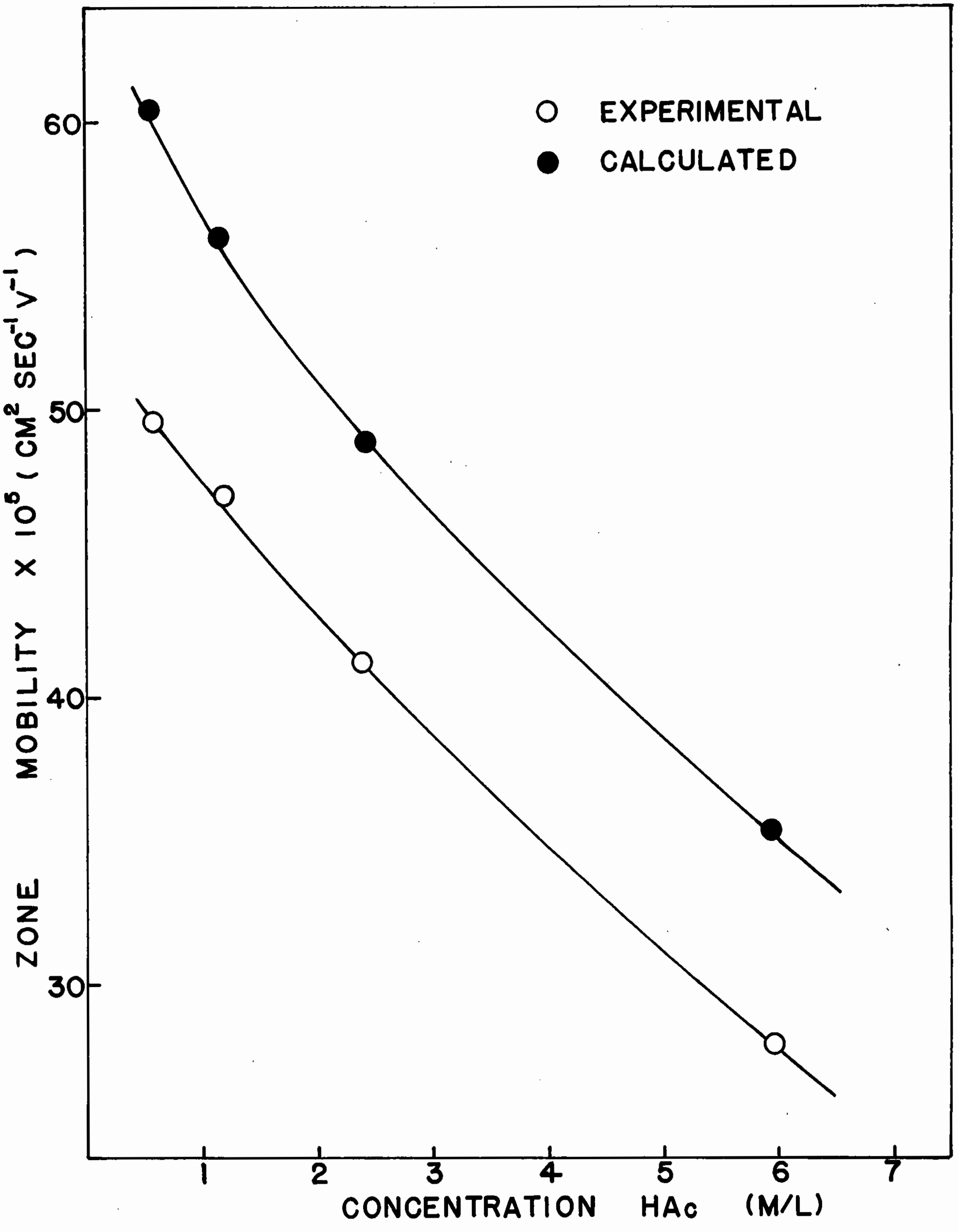

○ EXPERIMENTAL
● CALCULATED
60
50
40
30
ZONE MOBILITY X 10^5 (CM^2 SEC^{-1} V^{-1})
1
2
3
4
5
6
7
CONCENTRATION HAc (M/L)

Table XII

Zone mobilities of Na^+ in cellulose acetate with acetic acid background electrolyte.

Concentration of Acetic Acid, moles/litre	U_z cm.^{2}v^{-1}sec^{-1} x 10^5	P_{app}
0.59	ca. 38*	ca. 0.8
1.18	32.0	0.74
2.36	27.5	0.73
5.89	17.3	0.64

Note: Absorbance 1.80 ml./g., 25.0 ± 0.5°C. P calculated from equation 22 is 0.69.

* Very great motion of electrolyte.

Table XIII

Variation of size of zone with initial concentration of migrant solution.

Background electrolyte solution	Zone length (cm.) with initial Na^+ concentration of: 0M*	0.005M	0.025M
0.005M sodium acetate	4.0	4.0	5.8
0.01M sodium acetate	2.5	2.5	4.5
0.005M potassium acetate	3.5	4.5	8.5
0.01M potassium acetate	2.5	4.0	7.0

* "Carrier-free" solution.

Note: Migrant is Na^+ in solution as sodium acetate.

Absorbance 0.96 ml./g., Whatman No. 52 paper, 25.0 ± 0.5°C.

Table XIV

Effect of initial migrant concentration on zone mobility and zone size in 2.36M acetic acid.

Concentration of migrant solution, moles/litre.	U_z $cm.^2v^{-1}sec^{-1} \times 10^5$	Relative zone length ≠
0*	18.1	1
0.02	17.7	1.14
0.05	17.3	1.36
0.10	16.5	1.43
0.50	14.9	2.7
1.00	-	3.2

* "Carrier-free" solution.

≠ Relative to the size of the zone given by the "carrier-free solution".

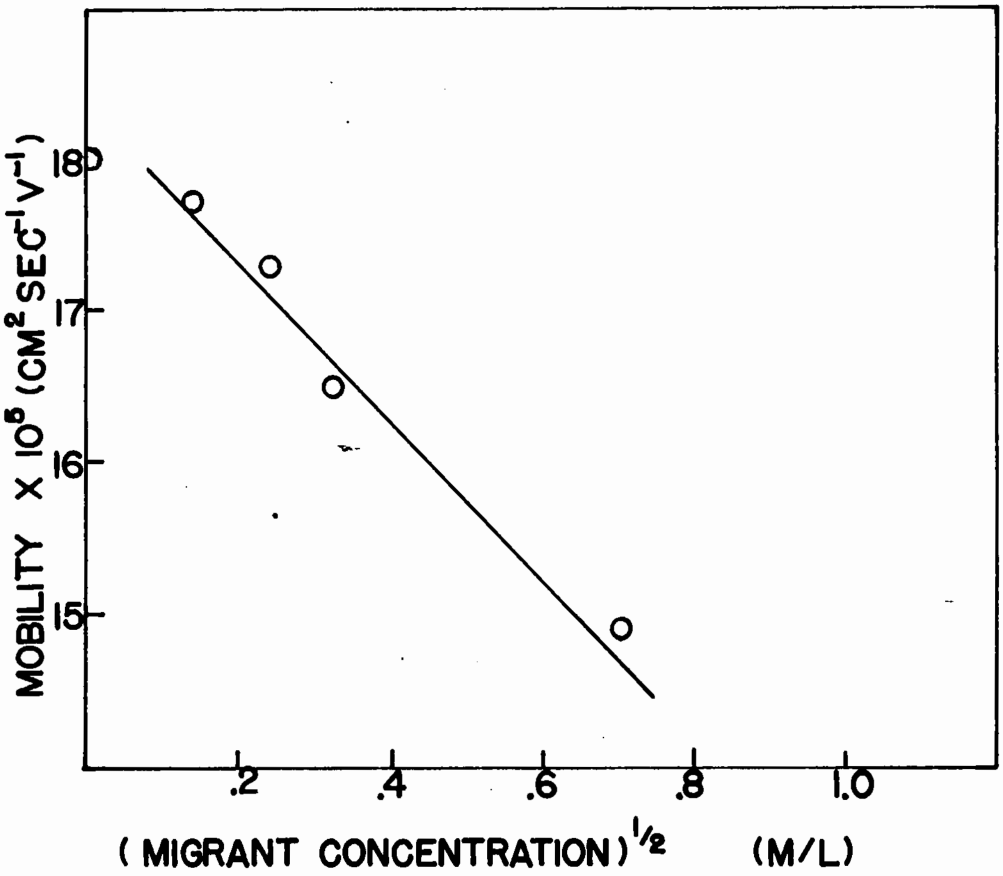
Note: Migrant is Na^+. Absorbance 0.96 ml./g., Whatman No. 52 paper, 25.0 ±0.5°C.

Figure 14.

Zone mobility vs. the square root of the migrant concentration for Na^+ in 2.36M acetic acid. Absorbance 0.96 ml./g., Whatman No. 52 paper, 25.0 ± 0.5°C.

Figure 15.

Relative zone length vs. the square root of the migrant concentration for Na^+ in 2.36M acetic acid. Absorbance 0.96 ml./g., Whatman No. 52 paper, 25.0 ± 0.5°C.


MOBILITY X 10⁵ (CM² SEC⁻¹ V⁻¹)
18
17
16
15
.2
.4
.6
.8
1.0
(MIGRANT CONCENTRATION)^1/2 (M/L)

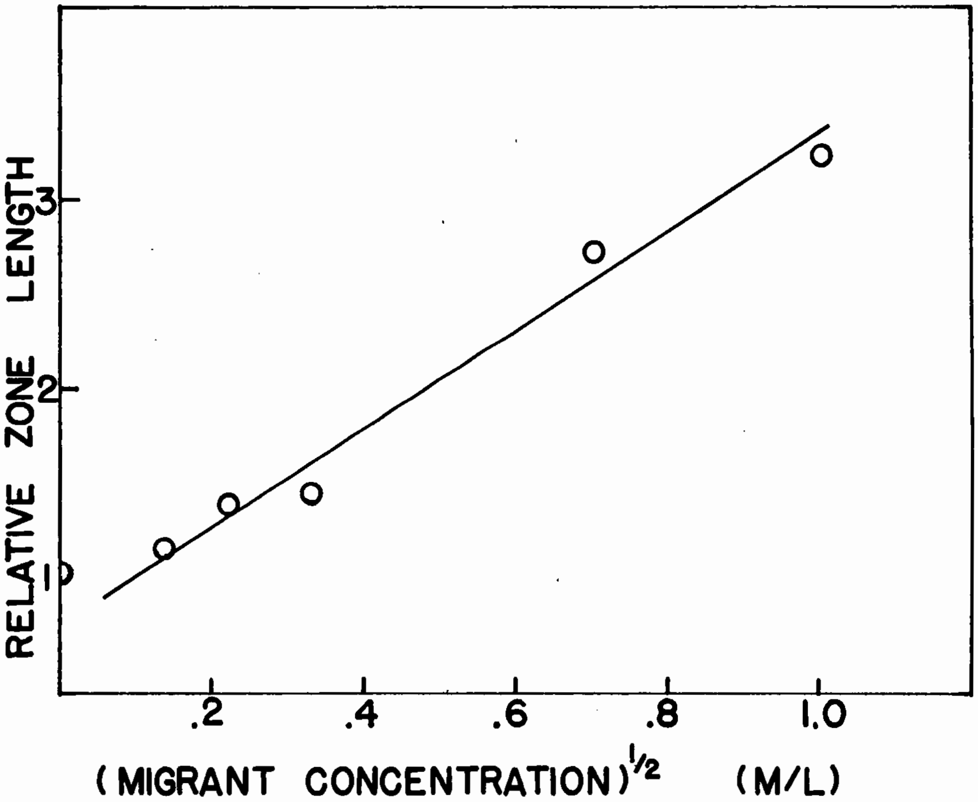

RELATIVE ZONE LENGTH
3
2
1
.2
.4
.6
.8
1.0
(MIGRANT CONCENTRATION)^1/2 (M/L)

Table XV

Effect of foreign ions present in the initial migrant solution on the zone mobility and zone size of Na^+ .

Initial Concentration of HCl in migrant solution, moles/litre.	U_z of Na^+ $cm.^2 v^{-1} sec^{-1} \times 10^5$	Relative zone length*
0	20.7	1
0.001	20.7	1.1
0.012	19.9	1.3
0.12	16.7≠	2.0

* Relative to zone length given by "carrier-free" Na^+ with no HCl present.

≠ Zone elongated with trailing.

Note: Background electrolyte 1.18M acetic acid, Absorbance 0.96 ml./g., Whatman No. 52 paper, 25.0 ± 0.5°C.

Table XVI

Effect of Temperature on Zone Mobility.

Ion	Background electrolyte	Temperature °C.	U_z cm.^{2}v^{-1}sec^{-1} x 10^5	P_{app}
Cs^+	1.18M Acetic Acid	25	28.8	0.43
		30	30.5	0.42
		35	33.7	0.42
		39	38.0	0.42
	1.22M NH_4OH	25	26.1	0.35
		30	28.2	0.35
		35	30.5	0.35
		39	34.3	0.36
Tl^+	1.18M Acetic Acid	25	24.0	
		28	25.4	
		30	25.8	
		35	28.3	
		39	31.3	
Cu^{++}	1.18M Acetic Acid	25	11.0	
		30	11.5	
		35	12.6	
		39	14.1	
	0.01M Oxalic Acid	25	-9.8	
		30	-10.6	
		35	-11.6	
		39	-12.0	
Co^{++}	0.01M Oxalic Acid	25	4.8	
		30	5.3	
		39	6.6	

Note: Absorbance 0.96 ml./g., Whatman No. 52 paper.

All temperatures ± 0.5°C. A negative zone mobility indicates motion toward the anode.

Figure 16.

Zone mobility vs. temperature for several ions in various background electrolytes. Absorbance 0.96 ml./g., Whatman No. 52 paper.

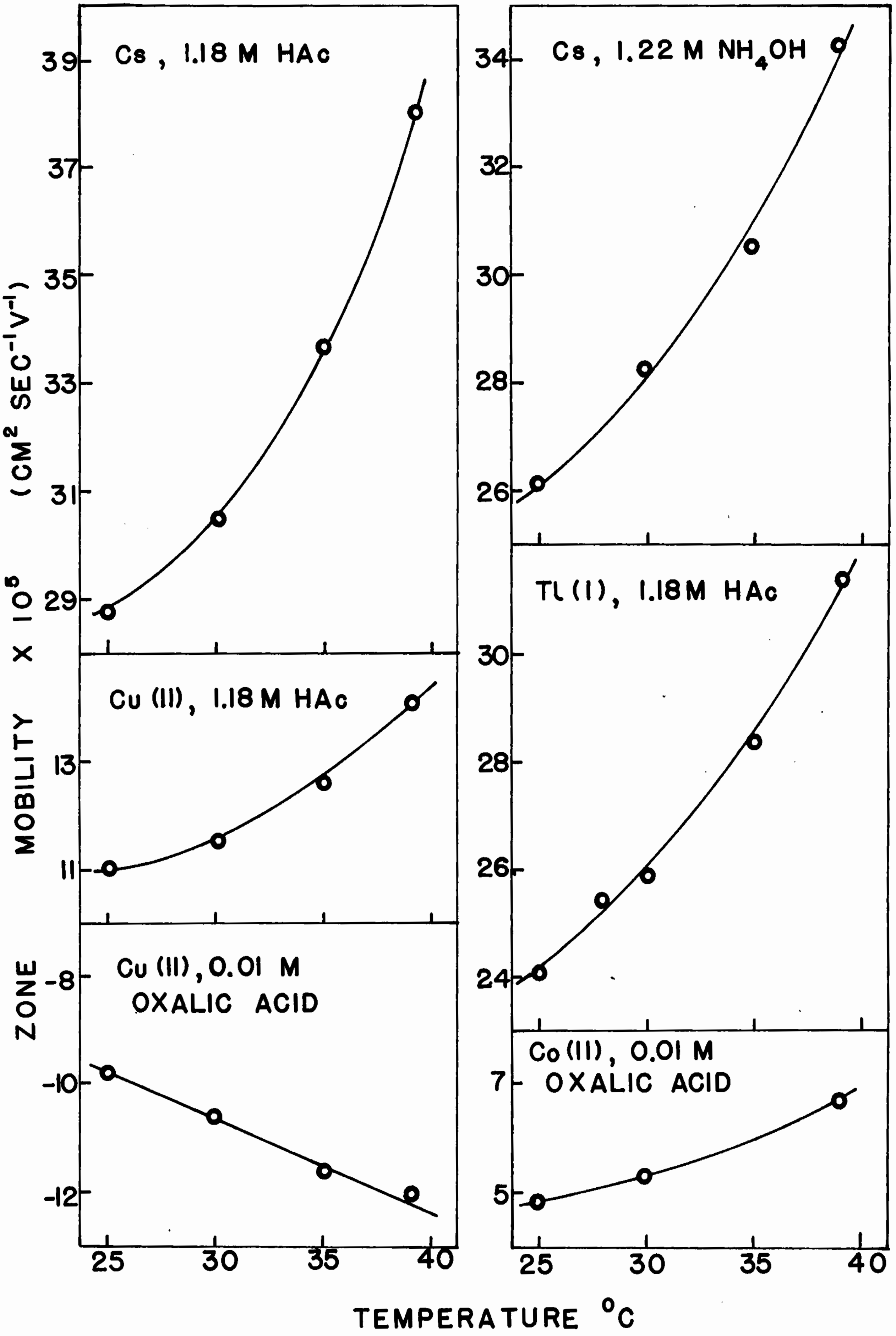

Cs , 1.18 M HAc
Cs , 1.22 M NH$_4$OH
Tl (I), 1.18M HAc
Cu (II), 1.18 M HAc
Cu (II), 0.01 M OXALIC ACID
Co (II), 0.01 M OXALIC ACID
ZONE MOBILITY X 10^5 (CM^2 SEC^{-1}V^{-1})
TEMPERATURE °C
39
37
35
33
31
29
34
32
30
28
26
30
28
26
24
13
11
-8
-10
-12
7
5
25
30
35
40

Figure 17.

Behaviour of Ag(I) in various EDTA solutions at 25°C.

A. Ag(I) in 0.01M EDTA- 0.06M NH_4OH. 33v/cm., 53 min.

B. Ag(I) in 0.01M EDTA- 1.2M NH_4OH. 40v/cm., 150 min.

C. Ag(I) in 0.01M EDTA- 6.1M NH_4OH. 33v/cm., 35 min.

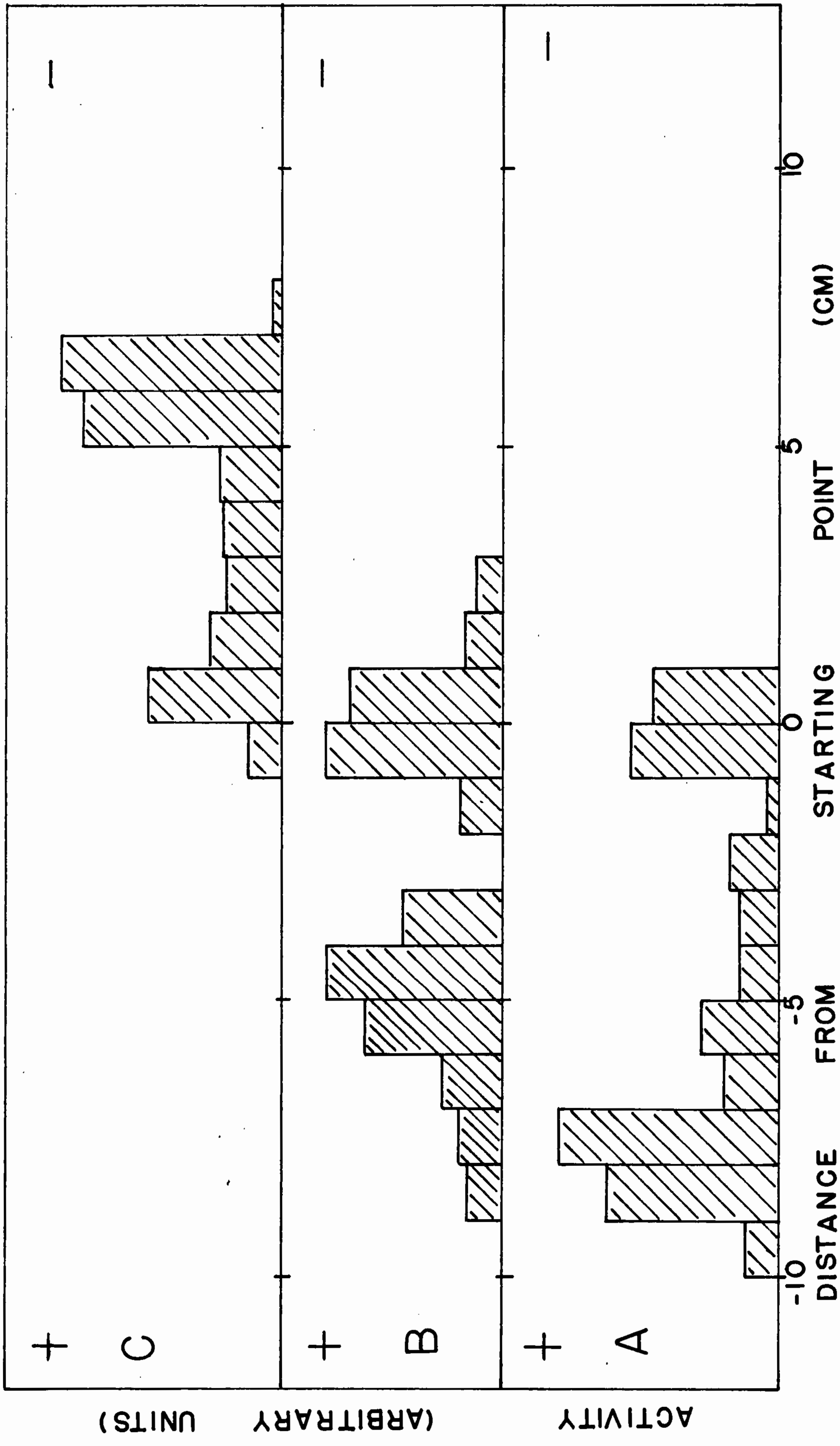

A
B
C
+
−
-10
-5
0
5
10
DISTANCE FROM STARTING POINT (CM)
ACTIVITY (ARBITRARY UNITS)

Figure 18.

Behaviour of Ag(I) in various EDTA solutions at 25°C.

A. Ag(I) in 0.03M EDTA- 0.1M NH_4OH.
33v/cm., 150 min.

B. Ag(I) in 0.03M EDTA- 1.2M NH_4OH.
20v/cm., 140 min.

C. Ag(I) in 0.03M EDTA- 6.1M NH_4OH.
20v/cm., 60 min.

D. Ag(I) in 0.03M EDTA- 6.1M NH_4OH.
20v/cm., 135 min.

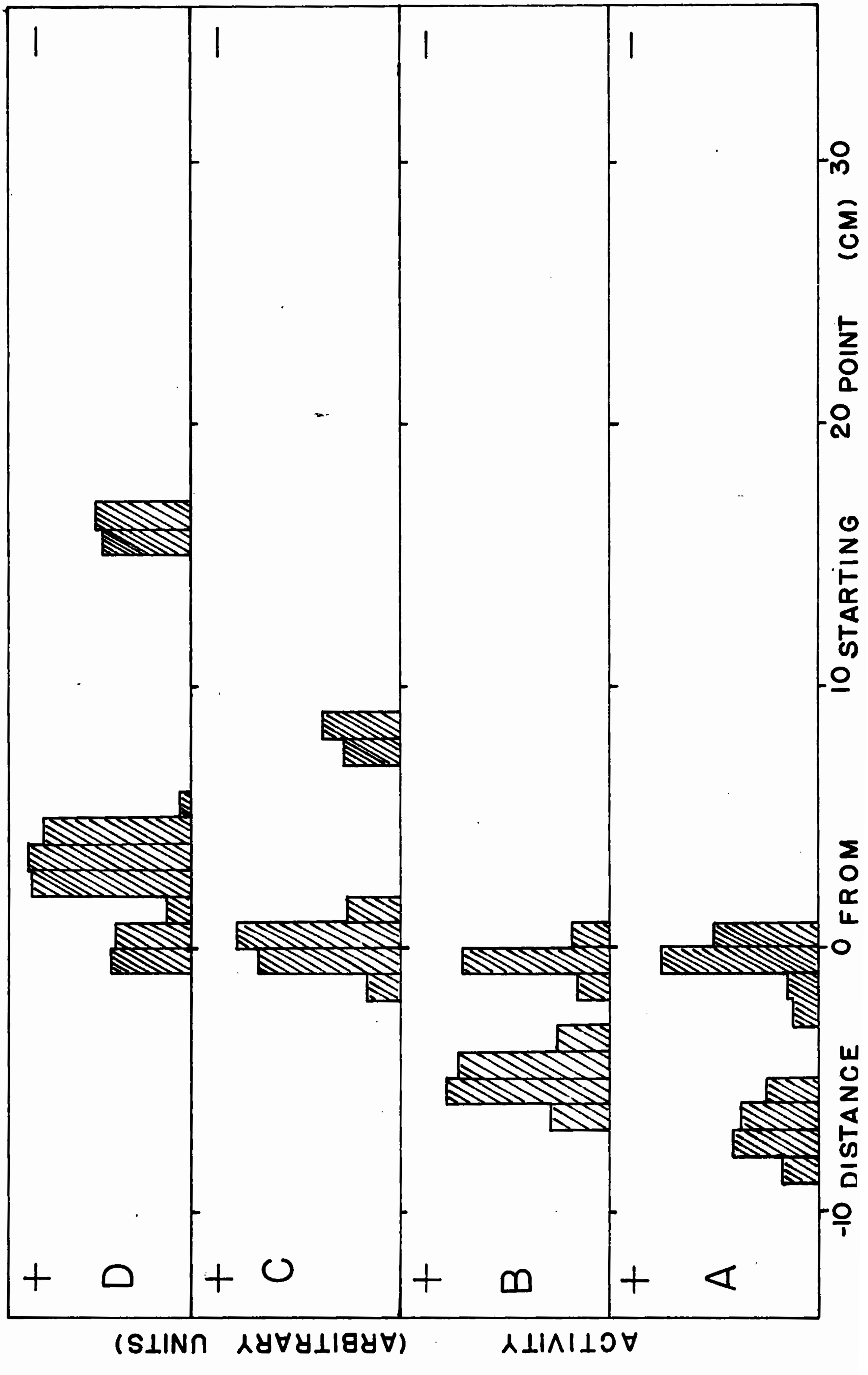

A
B
C
D
+
−
-10
0
10
20
30
DISTANCE FROM STARTING POINT (CM)
ACTIVITY (ARBITRARY UNITS)

Figure 19.

A. Separation of Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) in 0.01M oxalic acid. 60v/cm., 55 min., 39°C. Scale ½.

B. Separation of Fe(III), Co(II), Ni(II), and Cu(II) in 0.01M oxalic acid. 150v/cm., 15 min., 35°C. Scale ½.

C. Separation of Co(II), Ni(II), and Cu(II) in 0.01M oxalic acid. 160v/cm., 10 min., 35°C. Scale 3/4.

D. Separation of Co(II), Ni(II), and Fe(III) in 0.015M citric acid. 160v/cm., 10 min., 39°C. Scale 3/4.

E. Separation of Zn(II), Cu(II), and Ga(III) in 0.1M tartaric acid. 80v/cm., 28 min., 25°C. Scale 3/4.

F. Separation of Ag(I), Cd(II), and In(III) in 0.01M oxalic acid. 120v/cm., 9 min., 39°C. Scale 3/4.

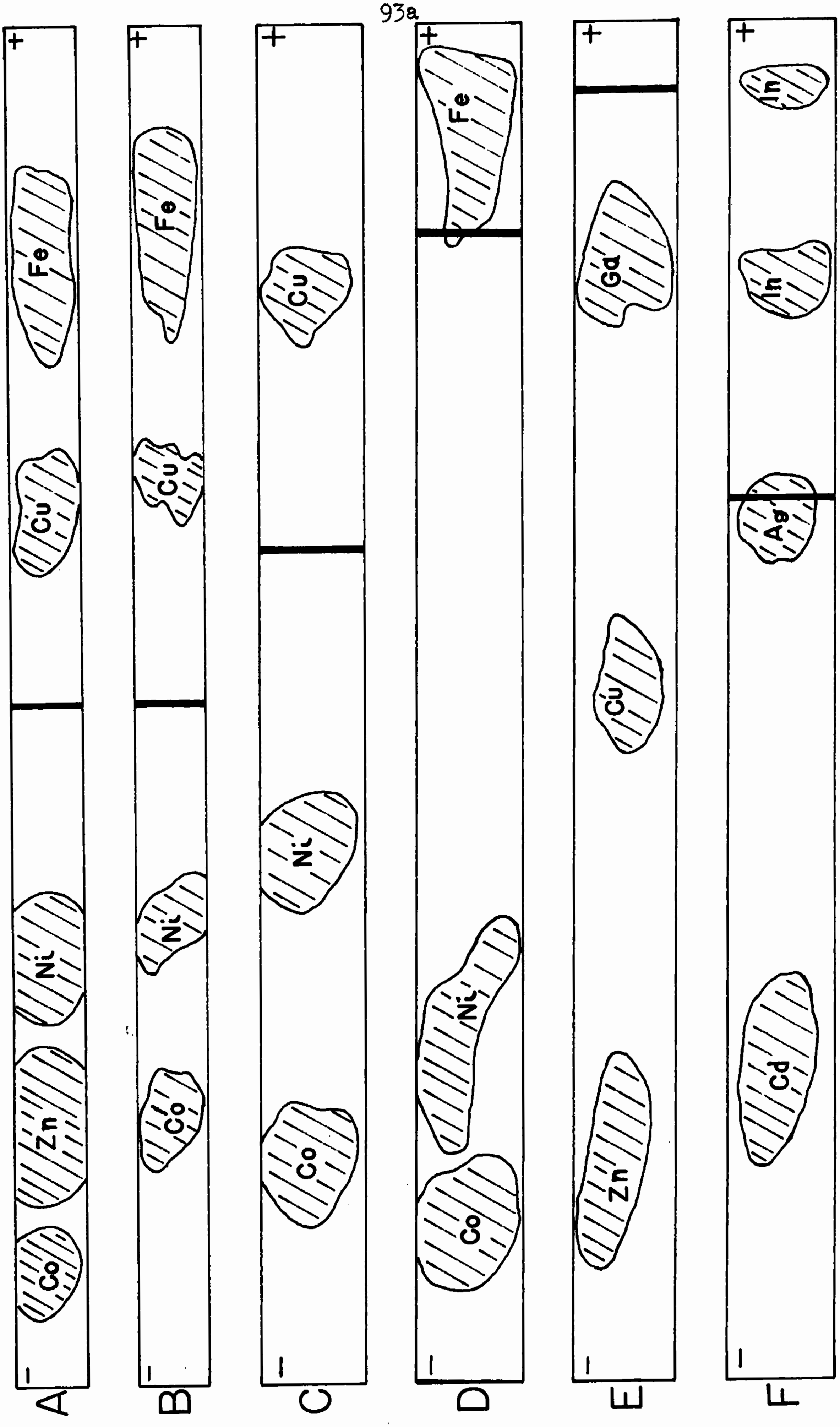

A
+
Fe
Cu
Ni
Zn
Co
-
B
+
Fe
Cu
Ni
Co
-
C
+
Cu
Ni
Co
-
D
+
Fe
Ni
Co
-
E
+
Ga
Cu
Zn
-
F
+
In
In
Ag
Cd
-

Figure 20.

A. Separation of Co(II), Ni(II), and Fe(III) in 0.01M oxalic acid. 160v/cm., 7 min., 39°C.

B. Separation of Ni(II), Cu(II), and Zn(II) in 0.01M oxalic acid. 160 v/cm., 9min., 39°C.

C. Separation of Cu(II), Zn(II), and Ga(III) in 0.01M oxalic acid. 130v/cm., 10.5 min., 30°C.

D. Separation of Cu(II), Zn(II), and Ga(III) in 0.015M citric acid. 120v/cm., 12 min., 30°C.

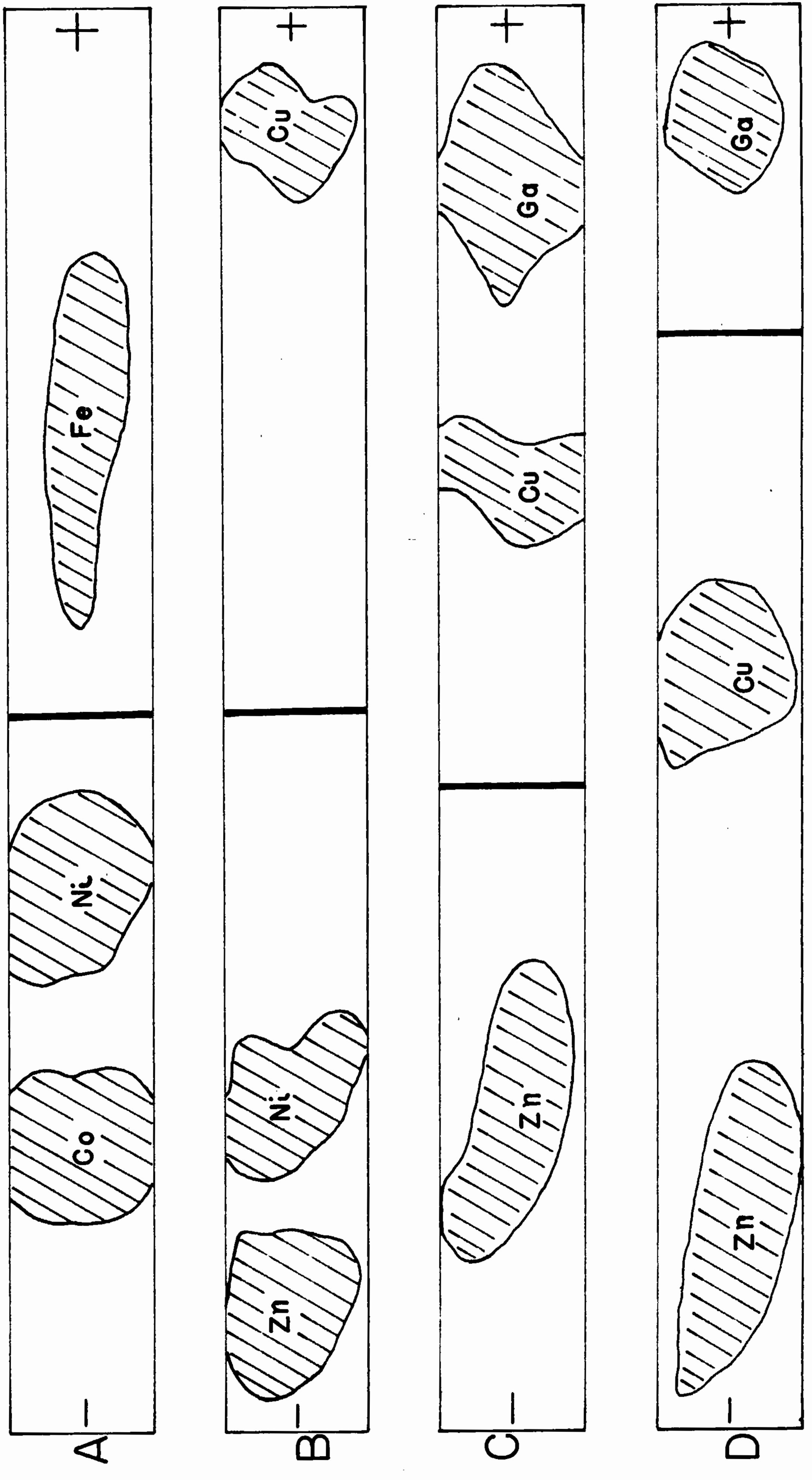

A
−
+
Co
Ni
Fe
B
−
+
Zn
Ni
Cu
C
−
+
Zn
Cu
Ga
D
−
+
Zn
Cu
Ga

Figure 21.

A. Separation of Ag(I), Cd(II), and In(III), utilizing a zone of HCl to prevent streaking of silver. 0.1M lactic acid, 80v/cm., 31 min., 35°C. Scale ½.

B. Separation of Ag(I), Cd(II), and In(III) with KCN added to the migrant solution before application. 0.1M tartaric acid, 80v/cm., 24 min., 35°C. Scale 3/4.

C. Separation of Zn(II), Cd(II), and Hg(II) in 0.1M tartaric acid. 80v/cm., 29 min., 25°C. Scale ½.

D. Separation of Zn(II), Cd(II), and Hg(II) in 0.1M lactic acid. 80v/cm., 29 min., 25°C. Scale ½.

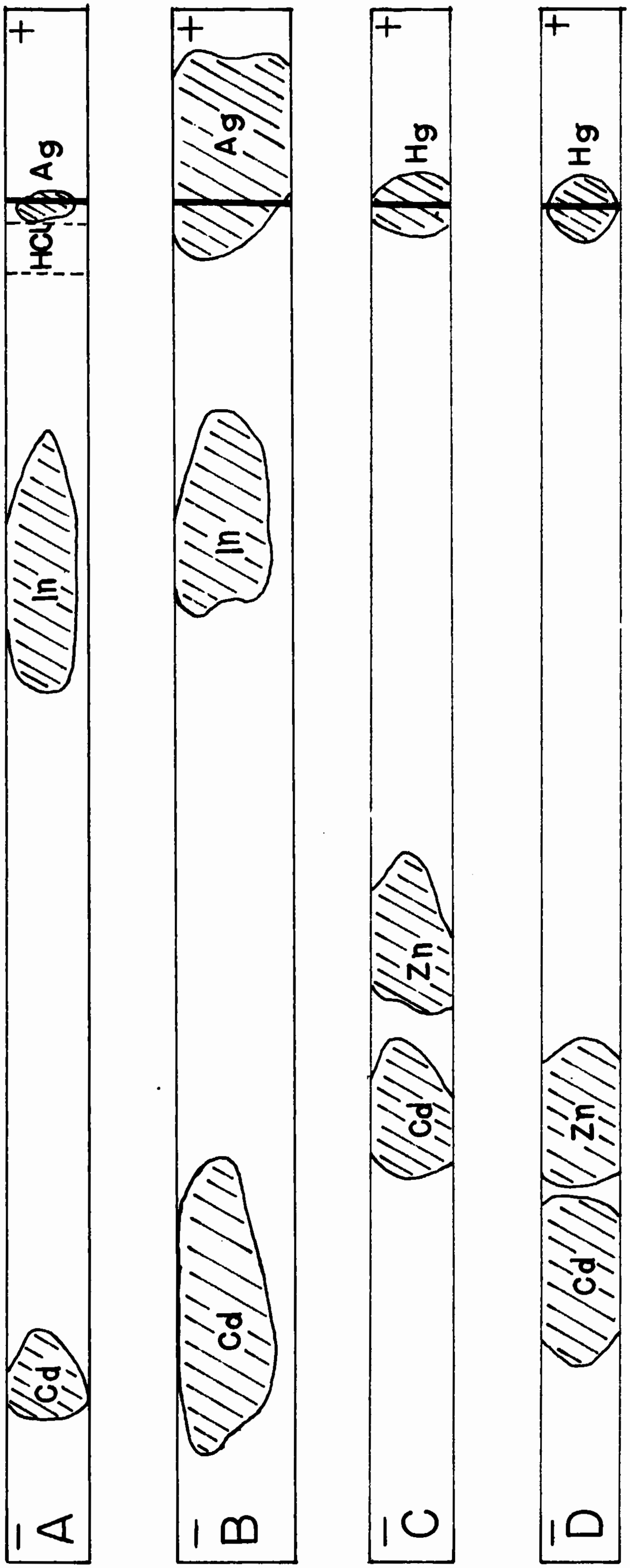

A
B
C
D
−
+
Cd
In
HCl
Ag
Hg
Zn

Figure 22.

Behaviour of Ag(I) in several electrolytes.

Whatman No. 52 paper, 25°C., in all cases. The silver was in solution in dilute HNO_3.

A. In 5.89M acetic Acid. 35v/cm., 42 min. Amount of silver applied: less than 2×10^{-6}g., in a volume of 0.01 ml.

B. In 5.89M acetic acid. 25v/cm., 60 min. Amount of silver applied: 3×10^{-5} g., in a volume of 0.02ml.

C. In 0.3M citric acid. 35v/cm., 35 min. Amount of silver applied: less than 2×10^{-6} g., in a volume of 0.01 ml.

D. In 6.1M NH_4OH. 35v/cm., 33 min. Amount of silver applied: less than 2×10^{-6} g., in a volume of 0.01 ml.

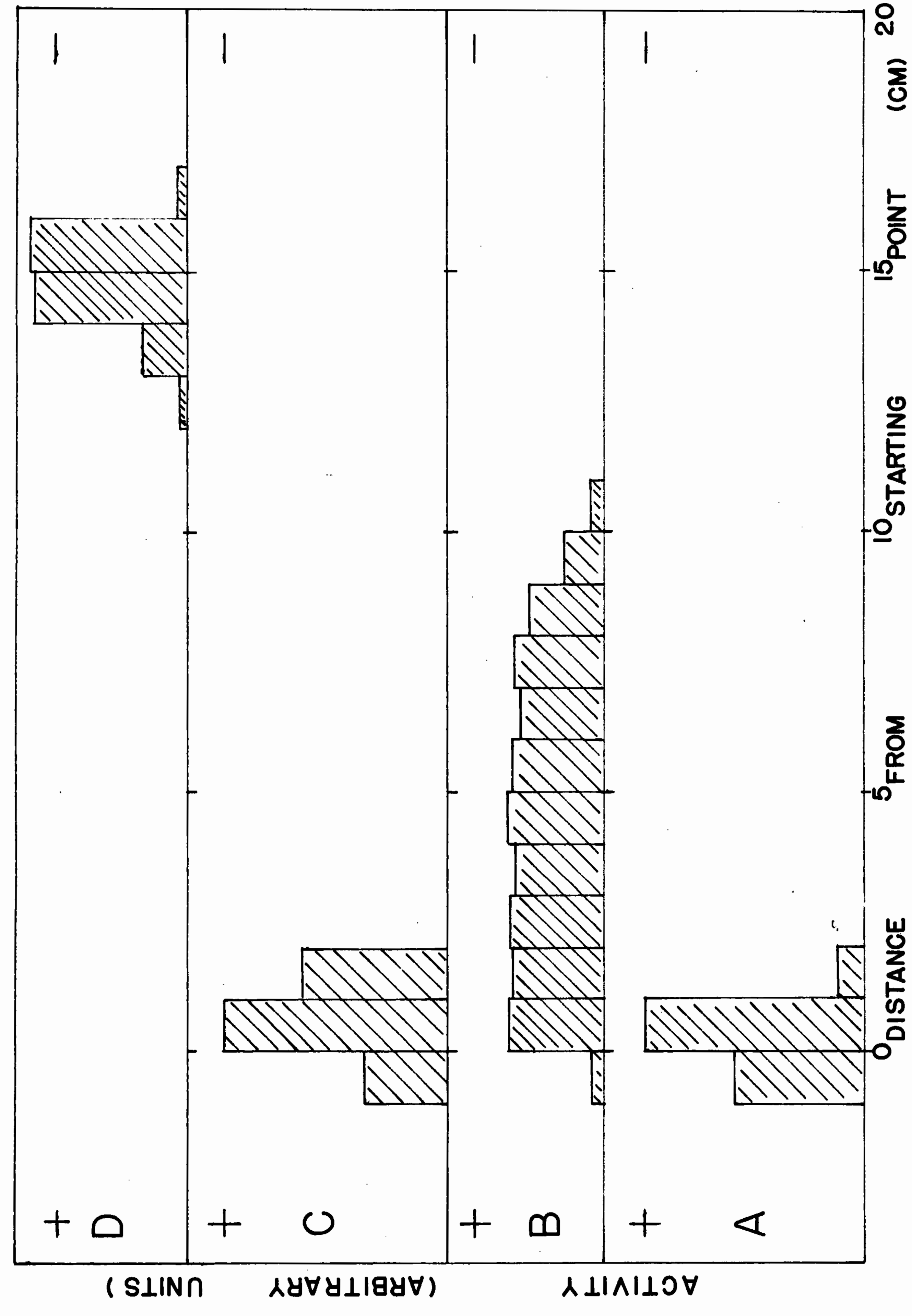

A
B
C
D
+
−
0 DISTANCE
5 FROM
10 STARTING
15 POINT
20 (CM)
ACTIVITY (ARBITRARY UNITS)

Figure 23.

A. Separation of Hg(II), Tl(I), and Pb(II) in 0.01M oxalic acid. 200v/cm., 7 min., 41°C.

B. Separation of Tl(I), Pb(II), and Bi(III) in 0.01M oxalic acid. 200v/cm., 6 min., 41°C.

C. Separation of Hg(II) and Bi(III) in glass fibre paper with 0.1M tartaric acid. 24v/cm., 43 min., 25°C.

D. Separation of Hg(II), Pb(II), and Bi(III) using a zone of 0.1M HBr in a strip moistened with 0.01M oxalic acid. Nominal voltage gradient 80v/cm., 30 min., 39°C. Tl(I) was separated in the same experiment, but is not shown; it has moved far toward the negative electrode.

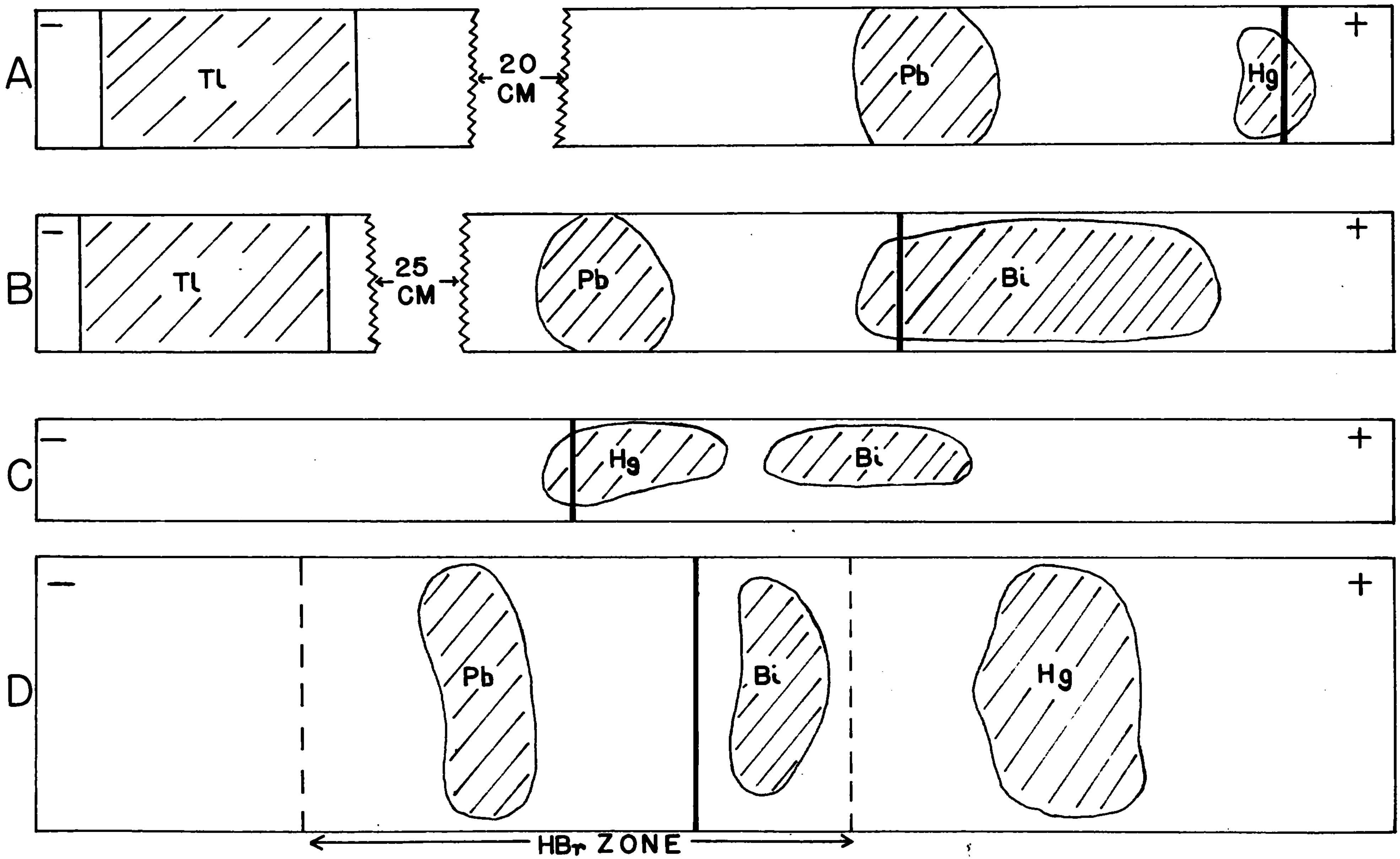

A
B
C
D
−
+
Tl
Pb
Hg
Bi
20 CM
25 CM
HBr ZONE

Figure 24.

A. Separation of Zn(II), Cd(II), and Hg(II) in 0.01M oxalic acid. 200v/cm., 5 min., 41°C.

B. Separation of Al(III), In(III), and Ga(III) in 0.1M tartaric acid. 80v/cm., 42 min., 25°C.

C. Separation of Al(III), In(III), and Ga(III) in 0.1M lactic acid. 100v/cm., 28 min., 35°C.

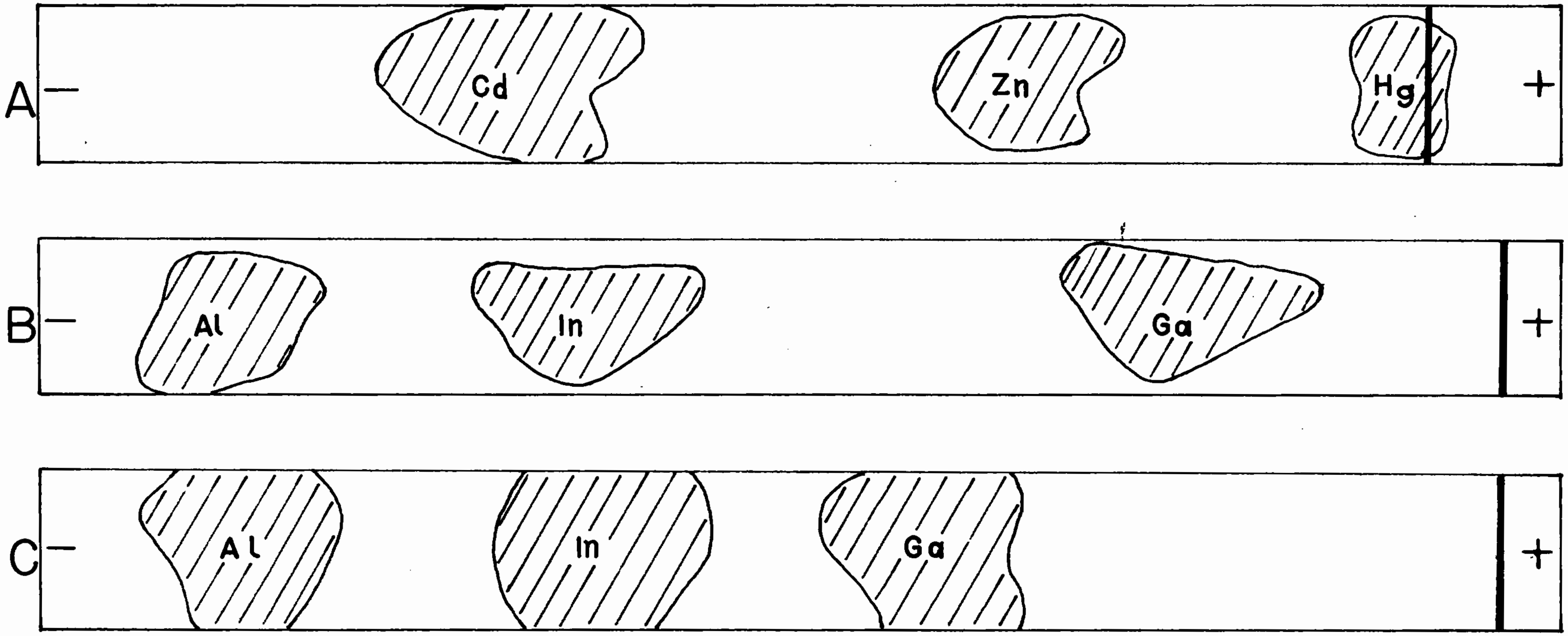

A
−
Cd
Zn
Hg
+
B
−
Al
In
Ga
+
C
−
Al
In
Ga
+

Figure 25.

A. Separation of Na^+ and Cs^+ in 2.36M acetic acid. 35v/cm., 50 min., 25°C.

B. Separation of Na^+ and Rb^+ in 1.18M acetic acid. 80v/cm., 28 min., 25°C.

C. Separation of Na^+, K^+, and Cs^+ in 0.15% ammonium acetate. 60v/cm., 63 min., 25°C.

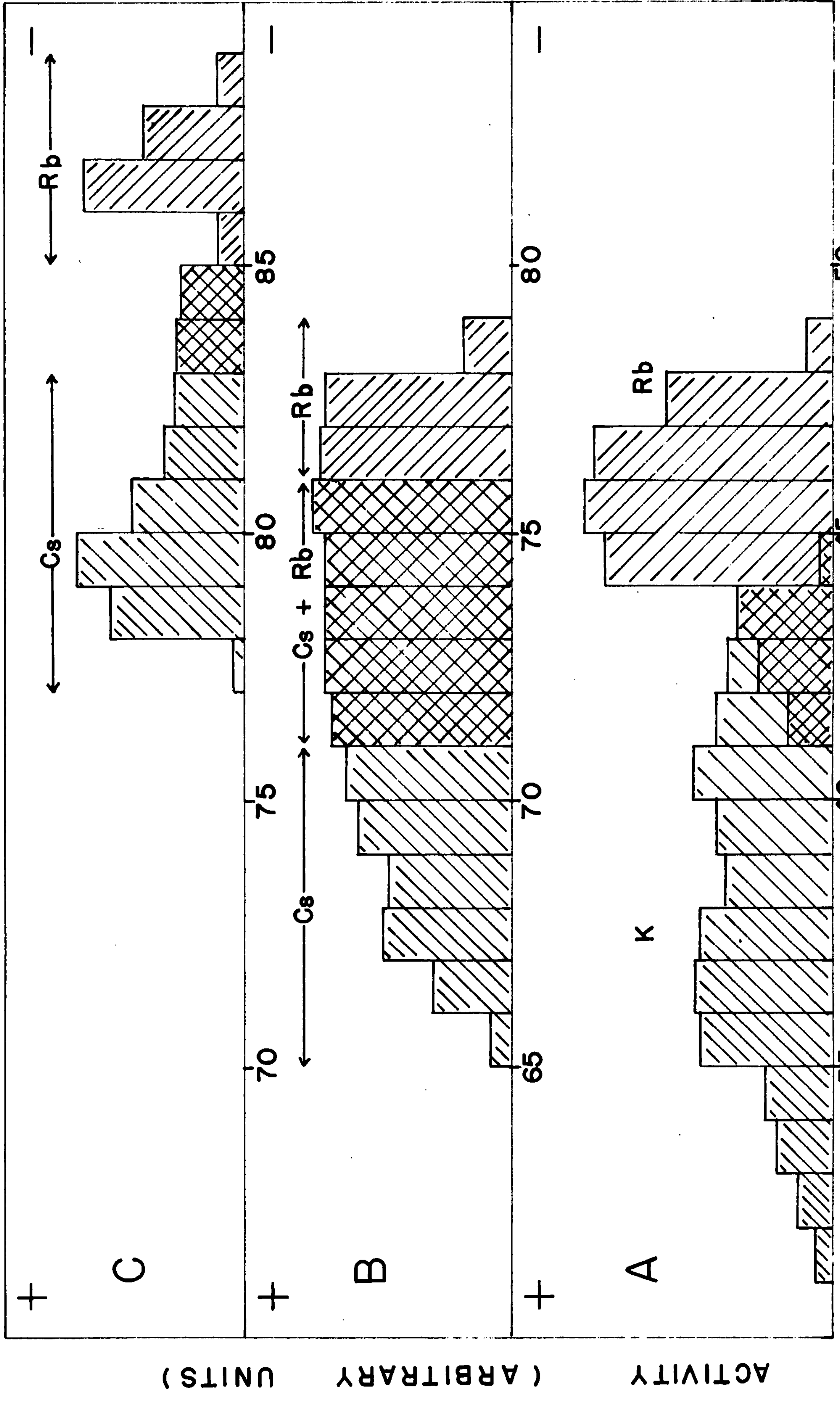

ACTIVITY (ARBITRARY UNITS)
DISTANCE FROM STARTING POINT (CM)
A
B
C
+
−
K
Rb
Cs
Cs + Rb
35
40
45
50
65
70
75
80
85

Figure 26.

A. Partial separation of K^+ and Rb^+ in 0.015M ammonium acetate. 60v/cm., 43 min., 25°C.

B. Partial separation of Rb^+ and Cs^+ in 5.89M acetic acid. 50v/cm., 130 min., 25°C.

C. Partial separation of Rb^+ and Cs^+ in 1.18M acetic acid in 1M thiourea. 70 v/cm., 70 min., 25°C.

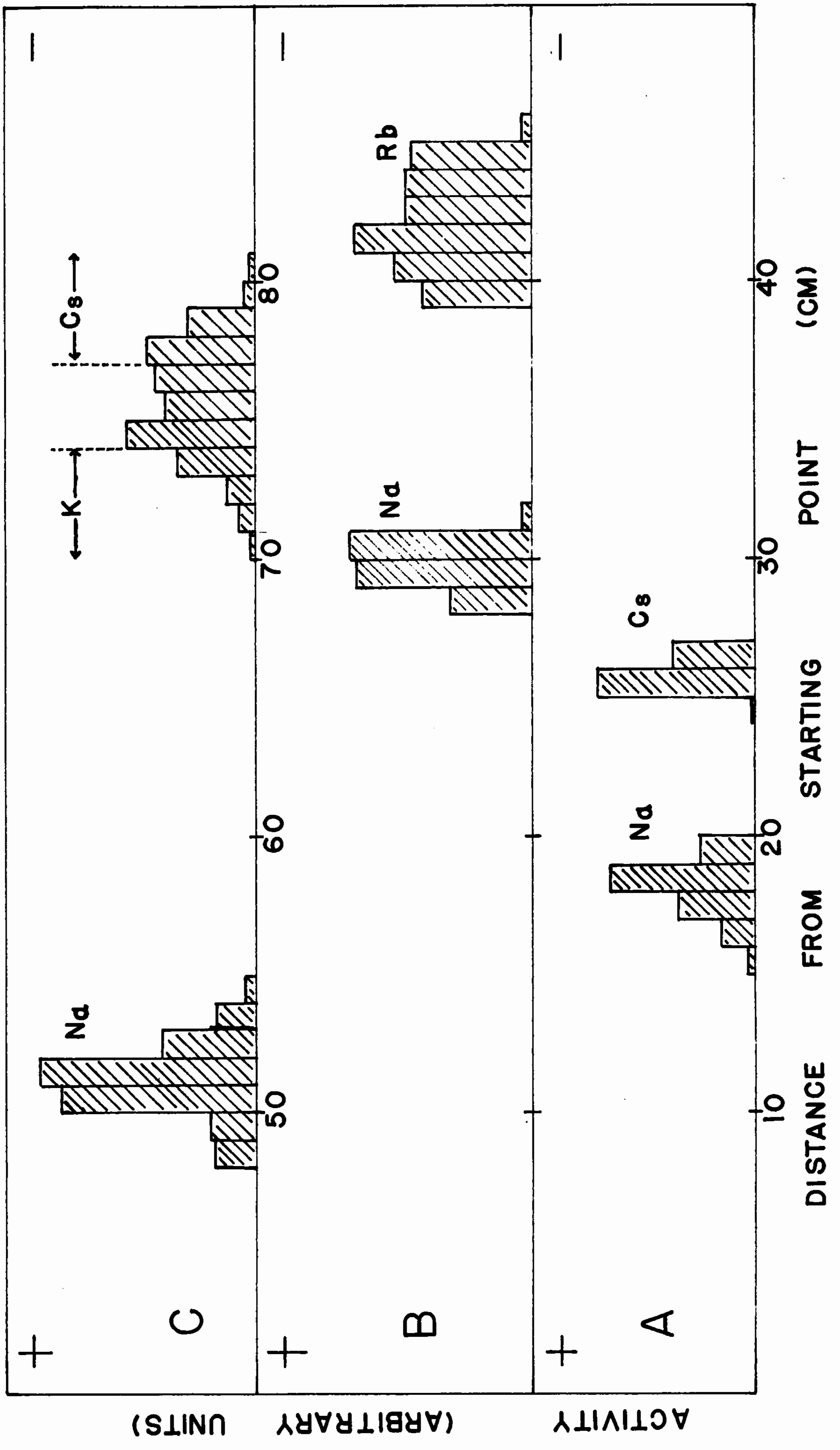

A
B
C
+
−
Na
Cs
Rb
K
10
20
30
40
50
60
70
80
DISTANCE FROM STARTING POINT (CM)
ACTIVITY (ARBITRARY UNITS)

Figure 27.

Separation of some univalent cations.

A. Separation of Na^+, Cs^+, and Tl^+ in 0.01M EDTA-6.1M NH_4OH. 20v/cm., 27 min., 25°C., Whatman No. 52 paper.

B. Separation of Na^+, Cs^+, Tl^+, and Ag^+ in 0.01M EDTA-1.2M NH_4OH. 50v/cm., 24 min., 25°C. Whatman No. 52 paper.

C. Separation of Na^+, Cs^+, Tl^+, and Ag^+ in 0.01M EDTA-6.1M NH_4OH. 50v/cm., 38 min., 25°C. Whatman No. 52 paper.

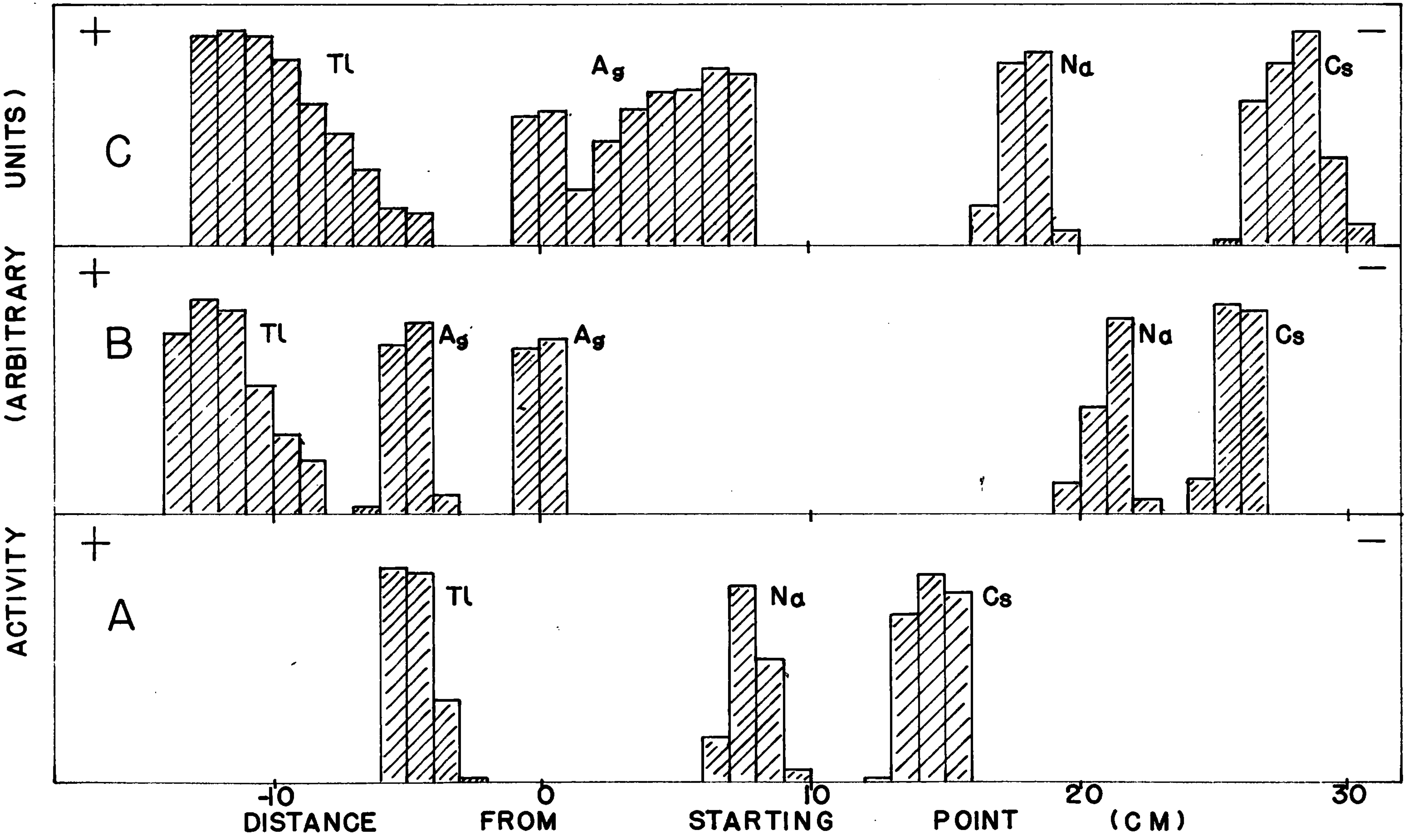

+
−
C
B
A
Tl
Ag
Na
Cs
Tl
Ag
Ag
Na
Cs
Tl
Na
Cs
ACTIVITY (ARBITRARY UNITS)
-10
0
10
20
30
DISTANCE FROM STARTING POINT (CM)

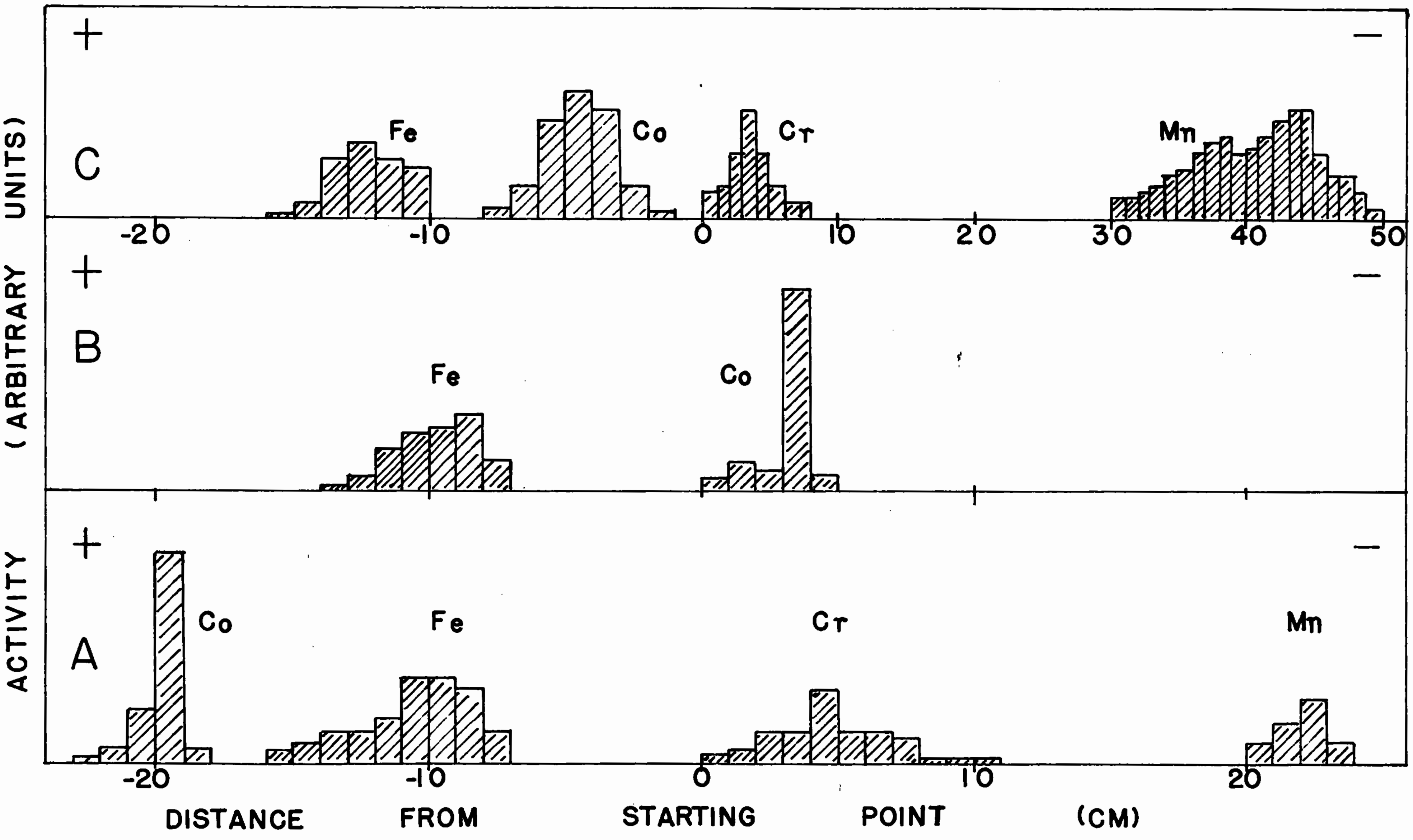
Figure 28.

Separation in "complexone" background electrolyte solutions.

A. Cr(III), Mn(II), Fe(III), and Co(II) in 0.01M HEDTA-0.06M NH_4OH. 80v/cm., 114 min., 25°C.

B. Fe(III) and Co(II) in saturated NTA in water. 70v/cm., 140 min., 25°C.

C. Cr(III), Mn(II), Fe(III), and Co(II) in 0.01M NTA-0.06M NH_4OH. 75v/cm., 116 min., 25°C.


ACTIVITY (ARBITRARY UNITS)
C
B
A
+
−
Fe
Co
Cr
Mn
-20
-10
0
10
20
30
40
50
DISTANCE FROM STARTING POINT (CM)

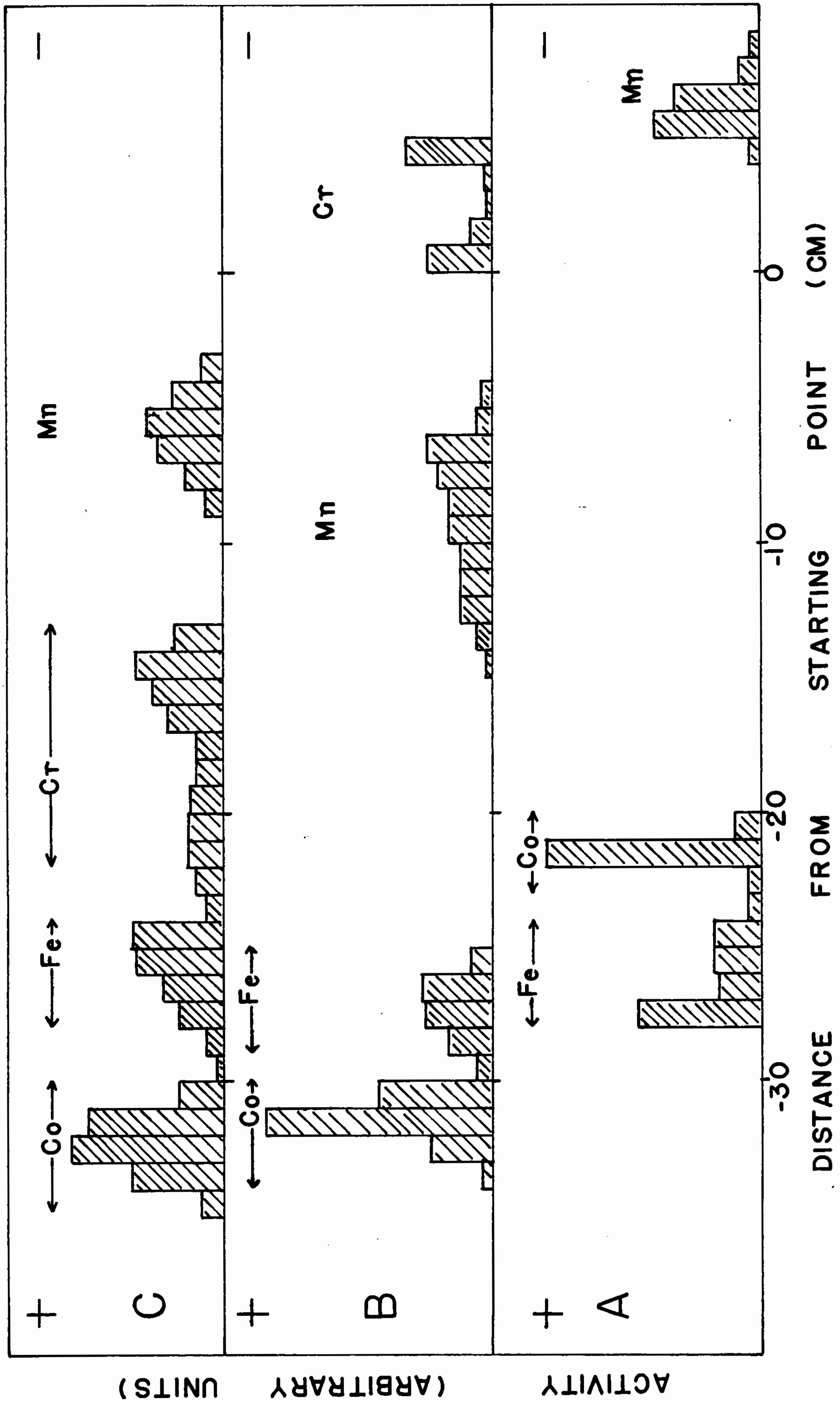
<u>Figure 29</u>.

Separations in "complexone" background electrolyte solutions.

<u>A.</u> Mn(II), Fe(III), and Co(II) in saturated EDTA in water. 70v/cm., 144 min., 25°C.

<u>B.</u> Cr(III), Mn(II), Fe(III), and Co(II) in 0.01M EDTA-0.06M NH_4OH. 70v/cm., 129 min., 25°C.

<u>C.</u> Cr(III), Mn(II), Fe(III), and Co(II) in 0.03M EDTA-0.1M NH_4OH. 50v/cm., 123 min., 25°C.


+
−
C
←Co→
←Fe→
←Cr→
Mn
B
←Co→
←Fe→
Mn
Cr
A
←Fe→
←Co→
Mn
-30
-20
-10
0
DISTANCE FROM STARTING POINT (CM)
ACTIVITY (ARBITRARY UNITS)

<u>Figure 30</u>.

Separation of molybdenum and technetium as the molybdate and pertechnate ions.

<u>A.</u> in 0.15% ammonium acetate. 60v/cm., 55 min., 30°C.

<u>B.</u> in 1.18M acetic acid. 100v/cm., 25 min., 30°C.

<u>C.</u> in 1.2M NH_4OH. 80v/cm., 45 min., 30°C.

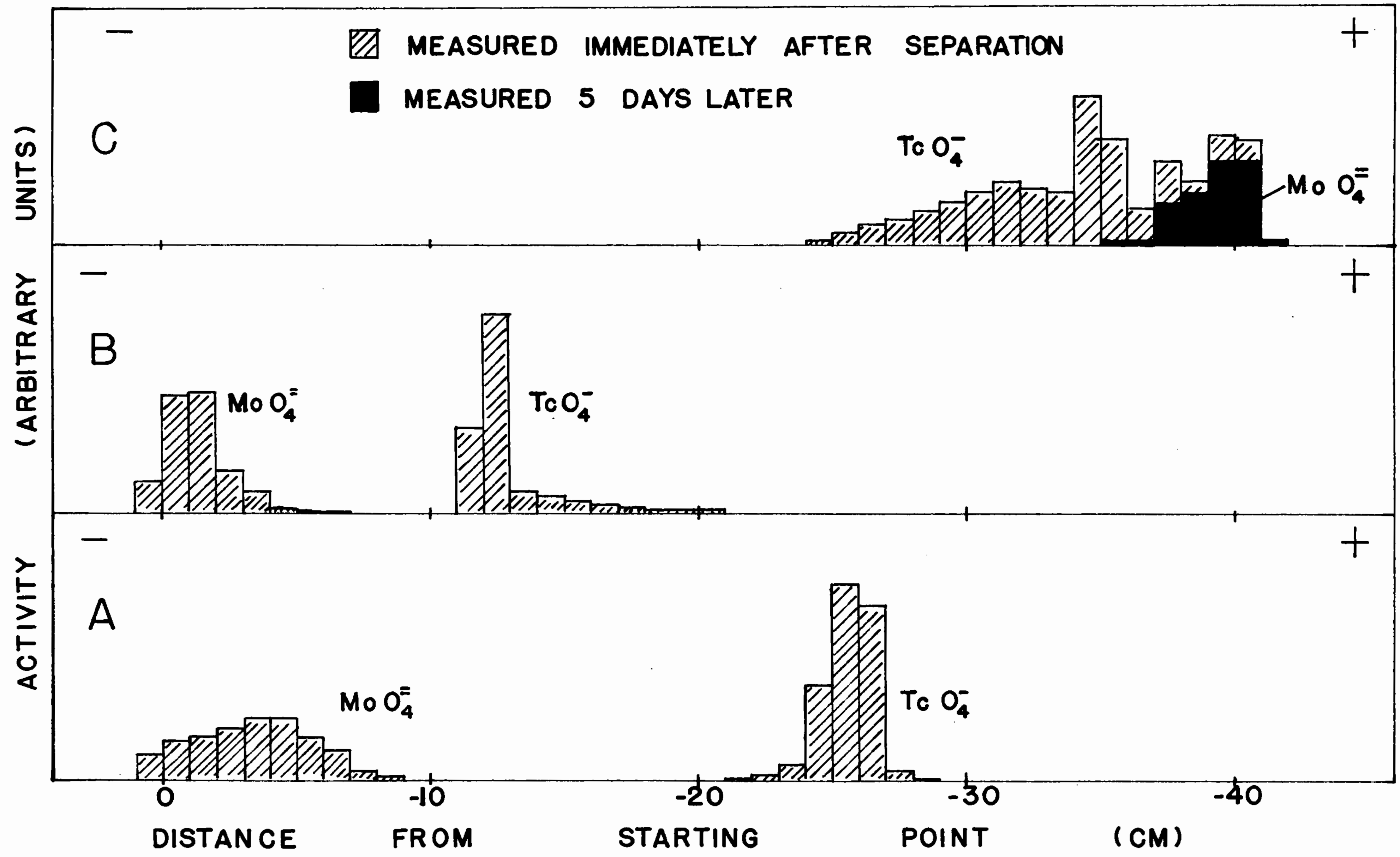

MEASURED IMMEDIATELY AFTER SEPARATION
MEASURED 5 DAYS LATER
C
B
A
−
+
TcO_4^-
$MoO_4^=$
(ARBITRARY UNITS)
ACTIVITY
0
-10
-20
-30
-40
DISTANCE FROM STARTING POINT (CM)
1048

Figure 31.

Separation of Ra D, E, and F (Pb^{210}, Bi^{210}, and Po^{210}).

A. in saturated EDTA in water. 90v/cm., 30 min., 41°C.

B. in 0.01M NTA-0.06M NH_4OH. 90v/cm., 22 min., 41°C.

C. in 0.01M DCTA-0.06M NH_4OH. 80v/cm., 42 min., 33°C.

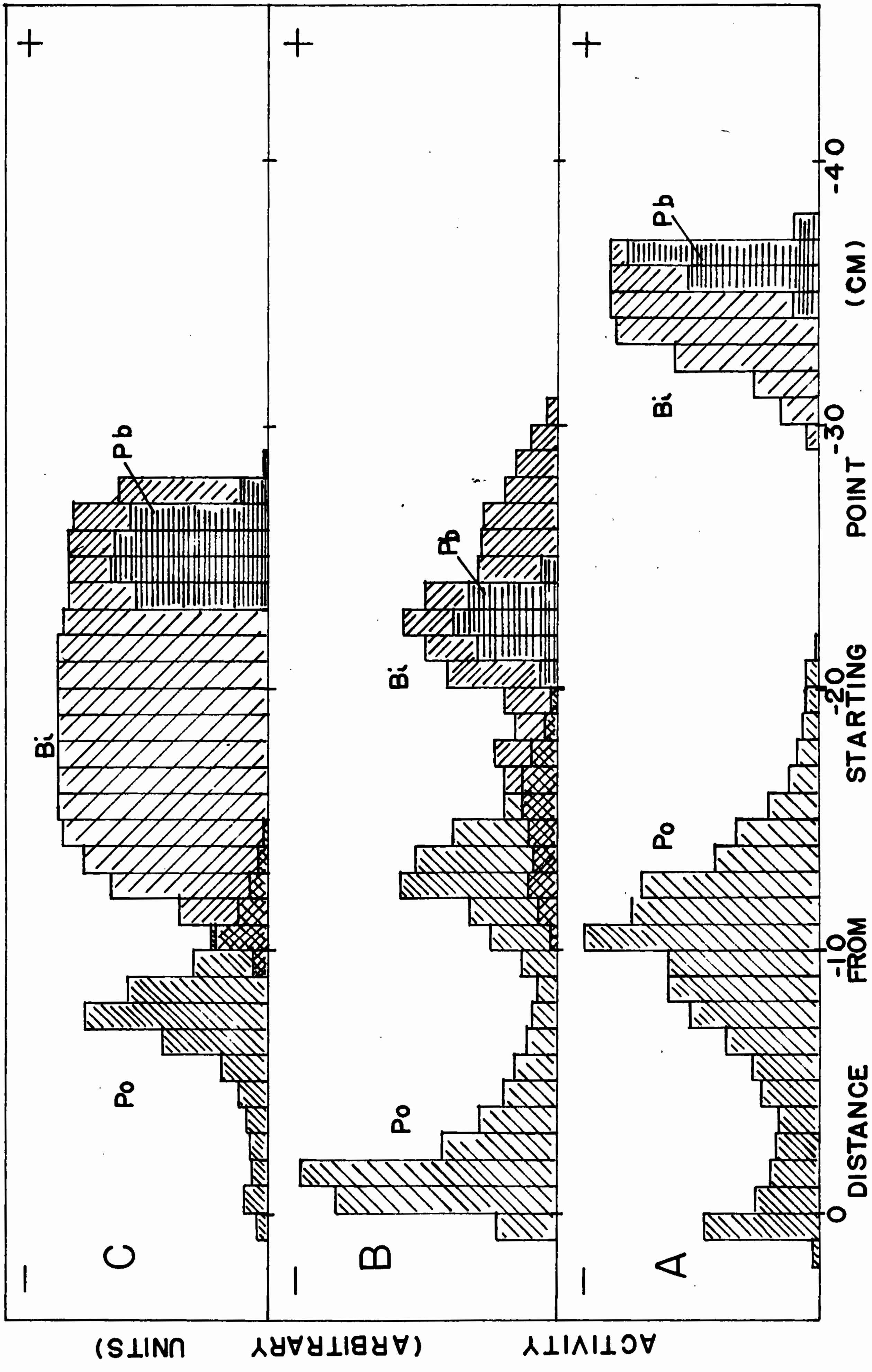

C
B
A
Po
Bi
Pb
+
−
0
-10
-20
-30
-40
DISTANCE FROM STARTING POINT (CM)
ACTIVITY (ARBITRARY UNITS)

Figure 32.

A. Separation of Rb, Sr, and Y in 1.18M acetic acid. 120v/cm., 8 min., 35°C.

B. Separation of Rb, Sr, and Y in 0.015M citric acid. 180v/cm., 5 min., 35°C.

C. Separation of Cs, Ba, and La in 1% citric acid. 160v/cm., 8min., 33°C.

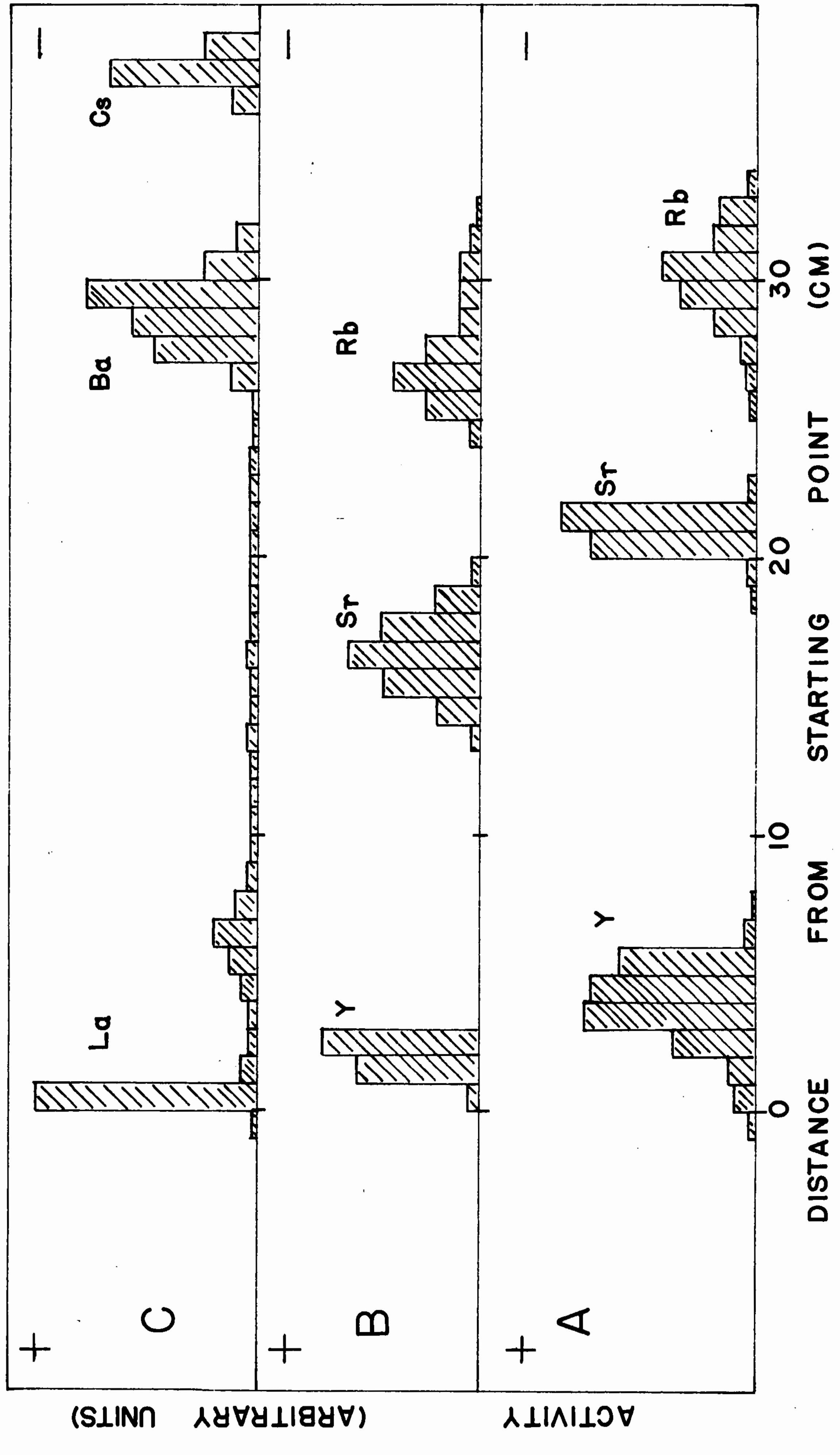

A
B
C
+
−
La
Ba
Cs
Y
Sr
Rb
0
10
20
30
DISTANCE FROM STARTING POINT (CM)
ACTIVITY (ARBITRARY UNITS)

Figure 33.

Separation of Sr and Y in EDTA background electrolyte solutions:

A. saturated EDTA in water. 120v/cm., 8.5 min., 30°C.

B. 0.01M EDTA-1.2M NH_4OH. 75v/cm., 35 min., 30°C.

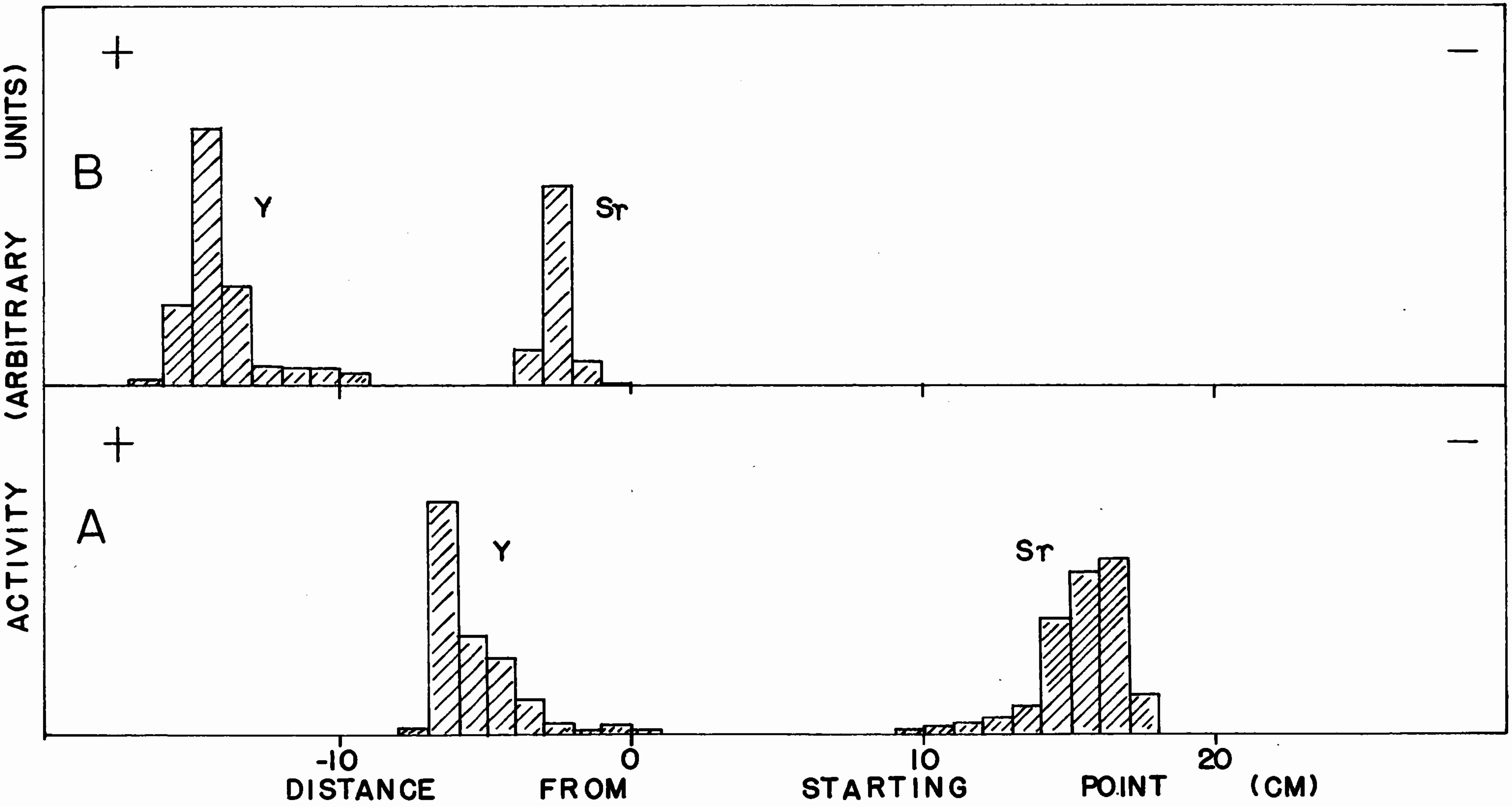

B
A
+
−
Y
Sr
Y
Sr
ACTIVITY (ARBITRARY UNITS)
-10
0
10
20
DISTANCE FROM STARTING POINT (CM)

Figure 34.

Separations of Ba and La in EDTA background electrolyte solutions.

A. Saturated EDTA in water. 180v/cm., 9 min., 33°C.

B. 0.01M EDTA-1.2M NH_4OH. 80v/cm., 37 min., 33°C.

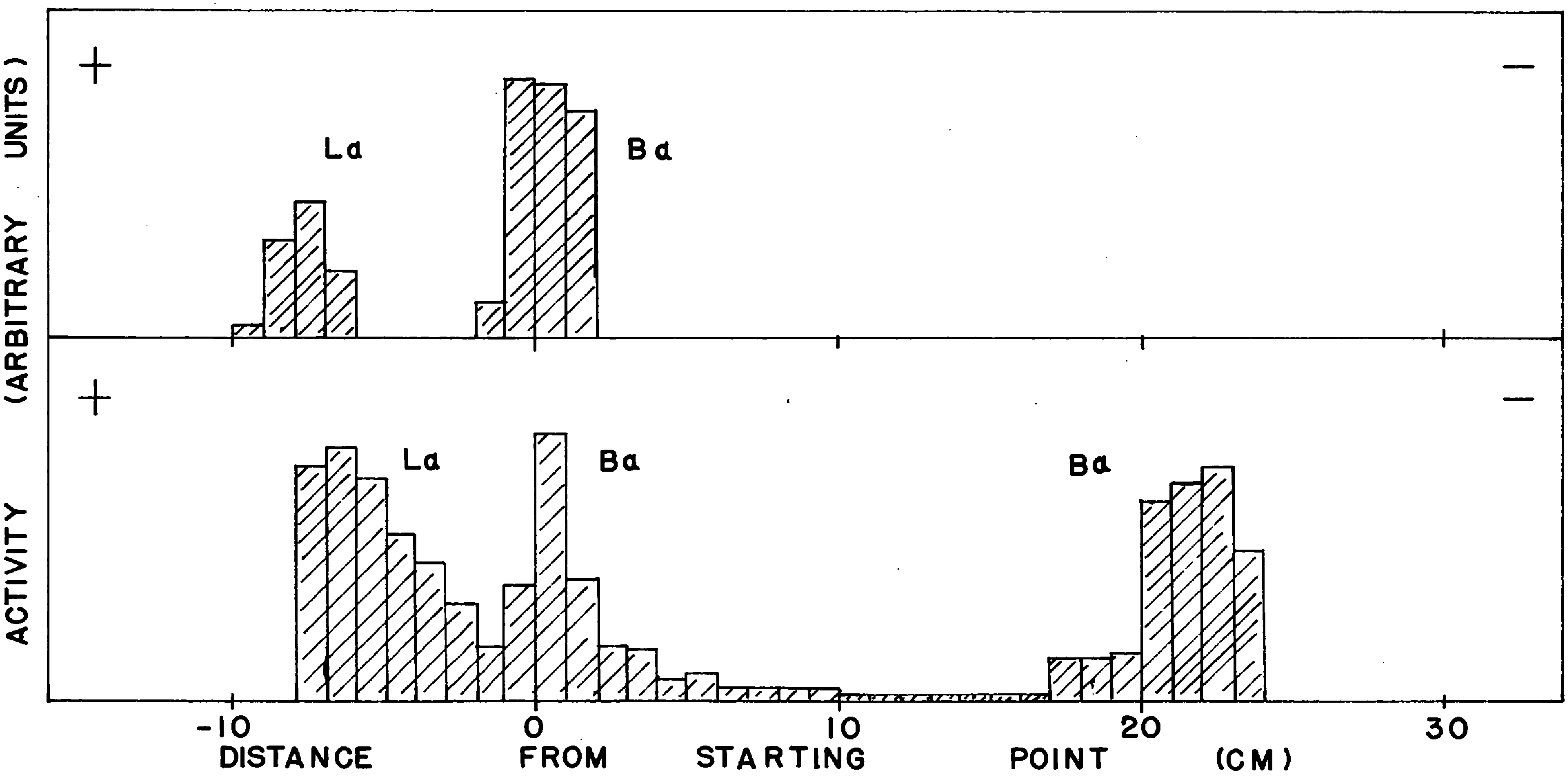

ACTIVITY (ARBITRARY UNITS)
+
−
La
Ba
+
−
La
Ba
Ba
-10
0
10
20
30
DISTANCE FROM STARTING POINT (CM)

Table XVII

Migration Sequences of a Number of Ions in Several Electrolyte Solutions.

Ions in brackets have similar mobilities; the faster was not determined.

The starting point is indicated by the symbol : .
Ions to the left of this move as cations, those to the right as anions.

Acetic acid of concentration 1-2M.
Tl(I), Co(II), Ni (II), Zn(II), Ga(III), Cd(II),
Pb(II), Cu(II), In(III), Fe(III), :

0.01M oxalic acid.
Tl(I), Cd(II), Co(II), Zn(II), Ni(II), Pb(II), : In(III),
Cu(II), Al(III), (Ga(III) + Fe(III)), In(III).

0.015M citric acid.
Tl(I), Cd(II), Co(II), (Ni(II) + Zn(II)), (Pb(II) + Cu(II)), :
Fe(III), (Al(III) + In(III)), Ga(III).

0.1M tartaric acid.
Tl(I), Cd(II), (Co(II) + Zn(II)), Ni(II), Pb(II), Cu(II),
Al(III), In(III), Ga(III),: Fe(III).

0.1M lactic acid.
Tl(I), Cd(II), (Co(II) + Zn(II)), Ni(II), Pb(II),
Cu(II), Al(III), (Fe(III) + Ga(III)),:

In addition Ag(I), Hg(II), and Bi(III) are adsorbed by the paper and are found near the starting position in these electrolytes.

Table XVIII

Migration Sequences of Cr(III), Mn(II), Fe(III), and Co(II) in some Complexone Electrolyte Solutions.

Brackets indicate the enclosed ions have very similar mobilities.

The starting point is represented by the symbol :. Ions to the left of this move as cations, those to the right as anions.

Complexone Solution	Migration Sequence	Remarks
Sat'd. EDTA in H_2O	Mn : (Cr + Co), Fe	Co, Cr have same mobility.
Sat'd. NTA in H_2O	Mn, Cr, Co,: Fe	Mn, Cr not complexed. Co near start.
0.01M HEDTA in H_2O	Mn, Cr, : Fe, Co	Mn, Cr not complexed. Fe zone diffuse about start.
0.01M EDTA in 0.06M NH_4OH	Cr, : Mn, (Fe + Co)	
0.01M NTA in 0.06M NH_4OH	Mn, Cr, : Co, Fe	
0.01M HEDTA in 0.06M NH_4OH	Mn, Cr, : Fe, Co	Cr zone diffuse.
0.01M DCTA in 0.06M NH_4OH	: Mn, (Cr + Fe + Co)	Cr zone diffuse Fe, Co of same mobility.
0.01M EDTA in 1.2M NH_4OH	: Cr, (Mn + Fe), Co	
0.01M NTA in 1.2M NH_4OH	: Cr, (Co + Mn + Fe)	

Table XVIII
(continued)

Complexone Solution	Migration Sequence	Remarks
0.01M HEDTA in 1.2M NH_4OH	Cr: Co, Cr, (Mn + Fe)	Cr forms two zones. Mn zone diffuse.
0.01M DCTA in 1.2M NH_4OH	: (Cr + Fe), Co, Cr, Mn	Cr forms two zones; one remains at start and overlaps Fe.
0.03M EDTA in 0.1M NH_4OH	: Mn, Cr, Fe, Co	Cr zone diffuse; tends to overlap Mn.
0.03M NTA in 0.1M NH_4OH	Mn : (Cr + Co), Fe	Cr, Co zones diffuse. Cr tends to spread on both sides of start.
0.04M EDTA in 0.1M NH_4OH	: Mn, (Cr + Fe), Co	Cr tends to be diffuse.

DISCUSSION

The results of this investigation divide themselves naturally into two main parts. One of these deals with a study of the variables which affect zone mobility, and an application of theoretical treatments to the data obtained. The other, which is more qualitative, deals with separations.

1. Zone Mobility Measurements.

(a). The Apparent Obstructive Factor and Its Variation with Migrant and Electrolyte.

The zone mobilities of a number of ions were measured as a function of the concentration of several background electrolytes. The experimental zone mobility was compared, when possible, to the free solution mobility U_F. This makes it possible to evaluate an apparent obstructive factor, which may be defined as

$$P_{app} = \frac{\text{zone mobility}}{\text{free solution mobility}} = \frac{U_Z}{U_F} .$$

If the simple theory of electromigration in porous media given in the theoretical section were correct, P_{app} would have a value independent of the nature of the background electrolyte solution, and of the migrating ion. Some variation with ionic size might be expected if this were comparable to the dimensions of the channels available for migration. In actual fact, P_{app} will include all effects which act to slow an ion moving in paper, including adsorption as well as mechanical obstruction. Variation of P_{app} for different ions and in different solutions will be a reflection of the action of specific effects. The size of any change in P_{app} will be an indication of the relative magnitude of such interactions.

The free solution mobility, U_F, of the ion in question in the solution used as background electrolyte, must be estimated. This has been done starting from the ionic conductance at infinite dilution and taking into account the effects of ionic strength and viscosity. One must consider the effects of foreign ions and uncharged molecules on the ion studied. This makes an accurate calculation of U_F very difficult. For example, the value of the dielectric constant, which enters into all conductance equations, is probably appreciably different in 6M acetic acid from what it is in pure water, but no satisfactory allowance can be made for such changes. Fortunately, all solutions used have quite a low ionic strength, so that the correction given by the limiting form of the Onsager equation (98), taking the constants to be those for water, probably serves as well as those which could be obtained from more complicated expressions. In any event, all theoretical treatments are largely untested under conditions such as exist in this case. In many of the solutions, the change in mobility due to ionic strength alone is small compared with the effects of viscosity. Therefore, in this work, the corrections for ionic strength have been made using the Onsager equation, and this result divided by the relative viscosity to get U_F. The answer, although perhaps crude, is not likely to involve an error greater than that in the zone mobilities which are experimentally determined.

Tables II, III, IV, and V give zone mobilities and apparent obstructive factors for several ions moving in various concentrations of some electrolytes. Data for acetic acid show that above a certain concentration, all ions show the same effect of decreasing zone mobility with increasing concentration, and for a given univalent ion, P_{app} remains fairly constant with concentration in this region. In most cases, P_{app} is lower in the most concentrated solution used, 5.89M, but whether this is real, or is due to erros in estimating U_F in this solution, is open to question.

In the case of the bivalent ions Zn^{++}, Cd^{++}, and Cu^{++}, P_{app} decreases slightly but regularly with increasing acetic acid concentration beyond 1M. Again, this may be due to errors in the estimation of U_F, since the correction would be less reliable for bivalent ions than for univalent ones. This change may be largely ignored if we consider only relative values in similar concentrations of acetic acid.

When the concentration of the background electrolyte solution falls below a certain value, there is a marked decrease in the zone mobility; this is illustrated in Figs. 6 and 7. The reduction in mobility sets in at a concentration which seems to be characteristic of the valence of the migrating ion, since the maximum mobility occurs at about 0.06M for univalent ions, but at 0.5 to 1M for bivalent ones. Extensive measurements in this region are available only for Cs^+. Here, the decrease is nearly linear with concentration. The cause of this decrease may be an increase in adsorption of the metal ions as the number of other ions and molecules available becomes small. Elongation of the zones, which is sometimes an indication of adsorption (95), occurs.

When P_{app} is compared for various ions at similar concentrations of acetic acid, a very considerable variation from ion to ion can be seen. Of the ions studied, Na^+ has the highest value of P_{app}, and is evidently least hindered. It is followed by Cs^+ and Tl^+. The bivalent ions are all more hindered than the univalent ones. Zn^{++} and Cd^{++} have nearly identical apparent obstructive factors, while Cu^{++} has the lowest and is most hindered. Since the latter is known to be adsorbed by paper (56, 84, 99), this is not surprising.

The results in NH_4OH are similar to those in acetic acid, but P_{app} is lower in each case. Only univalent ions were used. Zn^{++}, Cd^{++}, and Cu^{++}all form positively charged ammonia complexes, but their mobilities in paper are quite low. Data are included for the $[Ag(NH_3)_2]^+$ ion. Silver is strongly adsorbed by the paper when it is not complexed, and when present at very low concentrations it has a zone mobility which is close to zero. It migrates much more rapidly in NH_4OH where it forms the ammonia complex, and trailing even in 0.06M NH_4OH is not excessive. Since U_F for the species $[Ag(NH_3)_2]^+$ could not be estimated, P_{app} is not given.

The data in Table IV for Cs^+ in citric acid also fall into the general pattern shown by the other electrolytes.

A negative ion such as Cl^- might have different adsorptive properties with respect to cellulose, but for the most part there seems to be little difference in its behaviour as shown in Table V. P_{app} is about the same for this ion in both acetic acid and NH_4OH.

(B). Effects of Type of Paper.

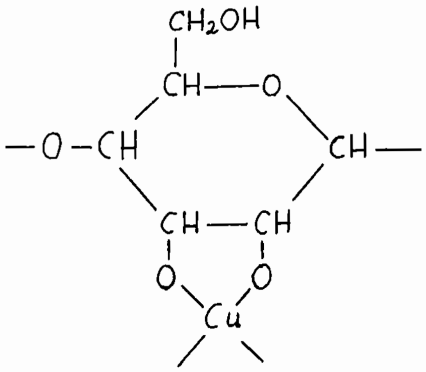
The variation of zone mobility and apparent obstructive factor for some ions in various types of filter paper is given in Table VI. The background electrolyte was 2.36M acetic acid. The so-called exchange capacity was determined by the method of Ultee (100). In this procedure, the maximum area attained by a known amount of Pb^{++} ions applied to the paper and chromatographed with distilled water is used to determine the "concentration" of ion exchange sites, mostly carboxyl groups, in the paper. It may be doubted that all of the adsorption of the Pb^{++} is due to an ion-exchange process rather than to some other form of interaction such as complex formation as postulated for some metal ions by Jakovac and Lederer (84). However, the results given by this method are claimed to agree with those obtained by other methods for the determination of the carboxyl content of paper.

For Cd^{++}, Zn^{++}, and Na^{+}, P_{app} seems to be completely independent of exchange capacity, since for the papers having the highest and lowest values (Whatman Nos. 20 and 7, respectively), the same value of P_{app} is obtained. Lower apparent obstructive factors, and hence more slowing of the ions, is given by Whatman No. 1 paper, which has an intermediate exchange capacity, but Whatman No. 4 paper, which has nearly the same capacity, shows a value of P_{app} which is as large as any other.

In the case of Cu^{++}, the behaviour is not the same. With this ion, there is a rough correlation between P_{app} and exchange capacity, as shown in Fig. 8. Whatman No. 4 paper is the only one showing particularly poor agreement, and it yields an unusually large value of P_{app}.

The zones obtained were all compact except in those papers which showed the highest obstructive factors. Thus, Cu^{++}(but not Zn^{++},Cd^{++}, or Na^{+}) exhibited a "comet-shaped" spot in Whatman No. 20 paper, while $Zn^{++}$and Cd^{++} were slightly elongated in Whatman No. 1.

It may be concluded from these results that Cu^{++}undergoes a different sort of reaction with the paper than do the other ions investigated. This is in agreement with the previous observations that it is strongly adsorbed by paper. It appears that the interaction occurs with ion-exchange sites on the paper, since P_{app} follows their concentration, but it may not be an ion-exchange reaction. Jakovac and Lederer (84) have proposed the formation of a complex between Cu (II) and cellulose, and copper-cellulose complexes have been proposed to account for the solubility of cellulose in certain copper solutions (101). However, these complexes have been presumed to form with the oxygen atoms from two adjacent hydroxyl groups to give the following structure for one cellulose unit:



The CH_2OH side-chain may be oxidized to a carboxyl or an aldehyde group.

This does not explain the parallelism with ion exchange capacity if we assume that Ultee is correct in asserting that the lead is adsorbed by exchange on carboxyl groups and not by a similar reaction to copper. However, interactions in which an oxygen attached to the carboxyl group forms one of the coordinate bonds with copper cannot be ruled out. It is possible to write down chelate rings involving this group, but steric effects were not considered. The lack of any relationship between the exchange capacity and P_{app} for Na^+, Zn^{++}, and Cd^{++} indicates that this factor is not generally of appreciable importance in the electromigration of ions in ordinary paper.

Tables VII and VIII, and Fig. 9, show the mobilities of Cu^{++}, Cd^{++}, and Zn^{++} in Whatman Nos. 41H and 52 papers at several absorbances at 5°C. There is no difference in the mobility of a given ion in these two papers under similar conditions.

(c) Effect of Absorbance.

Variation of zone mobility and obstructive factor with change of absorbance is an important factor which has not been adequately studied heretofore. The results given in Tables VII, VIII, and IX, and in Figs. 9 and 10, show how zone mobility varies with absorbance for several ions in several background electrolyte solutions, and some of these results are compared with the theoretical predictions of Crawford and Edward as given in equation 24. The data of Table VIII and Fig. 9 show the zone mobilities of Fe^{+++}, Co^{++}, Ni^{++}, Cu^{++}, Zn^{++}, and Cd^{++} in 2.36M acetic acid at 5°C. in Whatman No. 52 paper. The plots are in most cases linear, but the precision of the measurements is not sufficient to show the slight curvature which would be present if equation 24 were valid.

Results for Cs^{+} in a variety of background electrolyte solutions at 25°C. are shown in Table IX and Fig. 10. They show the same nearly linear form as do the previous examples. In Fig. 11, the apparent obstructive factor is compared with the obstructive factor calculated from equation 24 with X, the swelling factor, chosen to give the best over-all fit for the experimental data. The experimental points agree very well with the calculated curve in most instances.

The value of X required to give this agreement is interesting if X is regarded as a measure of the increased obstruction due to the reduction of the void fraction by the swollen fibres. In acetic acid, values of X of 0.19 are required at concentrations of 0.06M and

2.36M. Intermediate concentrations would be fitted by the same X, since P_{app} is constant for Cs^+ over this concentration range. In 0.02M and 5.89M acetic acid, where P_{app} is small, X must be taken as 0.29 and 0.26, respectively. There seems to be no reason to assume that there is any particular increase in the degree of swelling of the fibres in these concentration regions. X is evidently reflecting an increased hindrance to ion migration, but this hindrance need not be due to simply a change in the physical dimensions of the fibres which makes the path more tortuous, or removes liquid from the available path by trapping it in the fibres.

The values of X found by Crawford and Edward in their experiments (89) ranged from about 0.10 to 0.21, with a mean value of 0.156. However, the types of solutions and the means of evaluating the obstructive factors were not the same as those used here.

(d) Effect of Swelling Agents.

Variation of the obstructive factor when a swelling agent* such as thiourea is present has been investigated. Table X contains the results. A background electrolyte

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* Solutions of a number of substances produce a marked increase in the degree of swelling of cellulose fibres. Thiourea is one of these (102).

solution of 1M thiourea in 1.18M acetic acid was used, since the low ionic strength of thiourea alone leads to blurred zones. The apparent obstructive factors for Cs^+ and Na^+ in this electrolyte were compared to those obtained in 1.18M acetic acid. Determinations were made in 3 grades of Whatman chromatography paper: No. 52, acid washed and hardened, No. 31 double thickness, acid washed, and No. 3MM, neither acid washed nor hardened. In all cases, P_{app} is higher in thiourea, indicating that less hindrance is encountered. The difference is negligible in No. 52 paper, but it is significant in the other two types.

These results indicate that increased swelling does not lower the zone mobility. It is known, however, that much of the increased volume of swollen cellulose fibres is still available for ion transport (103, 104). It is possible that when thiourea is present, the increase in fibre size is accompanied by an increase in the fraction of the fibre through which the ion can travel. This may be equivalent to a loosening of the fibre structure on a very microscopic scale. Alternatively, the thiourea may reduce adsorption and thus lead to an increase in P_{app}. It is impossible to explain the variations of P_{app} with background electrolyte solution and with the migrant only on the basis of swelling of the fibres. The very important factor of adsorption must be considered, and it is undoubtedly this which is responsible for much of the change. The degree of swelling which is effective in hindering ion migration is probably not much different from one solution to another (except perhaps for certain special cases) and is very likely of the order of 0.1 to 0.2.

The value of X chosen to fit a set of experimental results will also reflect adsorption. In effect, a certain volume of space (that occupied by the adsorption forces) is unavailable for normal ion movement. (It is not proposed to give this "volume" a physical meaning, and in fact ion movement does occur in it if the adsorption is reversible. Nevertheless, variation in the volume term X can be used in equation 24 to account for changes in P_{app} due to adsorption.) The equilibrium constant between the ions in the sorbed and non-sorbed state, as well as the number of adsorption sites present per gram of paper, will determine the size of the effect.

(e) Zone Mobilities in Glass Fibre Paper.

Fibres such as glass do not swell in aqueous solution, so it should be possible to apply equation 22 to electromigration in such media. In Figs. 12 and 13 and Table XI the zone mobilities of Na^+, Cu^{++}, Zn^{++}, and Cl^- in Reeve Angel 934AH glass fibre paper are given with acetic acid as background electrolyte. Glass paper seems to adsorb some ions to a much greater extent than does cellulose paper. Both Cs^+ and Tl^+ showed very extensive trailing and seemed to be irreversibly adsorbed to an appreciable extent; therefore no useful measurements could be made with them. Na^+ behaved well in acetic acid of concentration greater than 1M, perhaps because of the excess sodium already in the glass. $Zn^{++}$and Cu^{++}both formed reasonably compact zones. No trailing of Zn^{++} was found when radioactive Zn^{65} was used as a tracer. Only inactive copper was used, and although it is possible that a low concentration trail was left that could not be detected chemically, the zones seemed sharp.

The calculated value of P, assuming v_s to be 0.43 and α to be 0.96, is 0.84 at the absorbance used for Na^+ and Cl^-. It is 0.86 for the experiments with Zn^{++} and Cu^{++}. In the high concentration region (above 1M) the calculated value of U_z for Na^+agrees quite well with the experimental values (Fig. 12). The experimental mobilities for Cl^- are lower than those calculated, indicating that adsorption is important here (Fig. 13). The behaviour of Na^+ is reasonable if it is assumed that the adsorption sites on the glass are already saturated with sodium.

$Cu^{++}$and Zn^{++} also exhibited an apparent obstructive factor much smaller than the calculated obstructive factor. Cu^{++} is much more hindered than Zn^{++}, as it was in cellulose paper.

With glass paper the ascending chromatographic technique also gave an indication of adsorption, since these ions, particularly Cu^{++}, extended back from the solvent front to form an appreciable "tail". The spot of Cu^{++} in these experiments was about twice as long as that of Zn^{++}. Values of R_F (measuring from the centre of the spot to get the distance moved by the ions) are probably meaningless, but they gave a product of PR_f of 0.70 for Cu^{++}, and 0.80 for Zn^{++} in 5.89M acetic acid. These are still greater than P_{app}. Although they have no quantitative value, these results do confirm that there is adsorption of some kind, and that Cu^{++} is more strongly adsorbed than Zn^{++}. The fact that the value of PR_F is still greater than P_{app} simply indicates that the chromatographic R_F factor is not an adequate means of determining the effects of adsorption in electromigration, and this was expected. It is also quite possible that a different chromatographic technique would yield different R_F values.

Similar experiments with Tl^+, Cd^{++}, Zn^{++}, and Cu^{++} in Whatman No. 52 paper with 5.89M acetic acid as solvent showed that Cu^{++} trailed more than any of the others, but it did not trail to the same extent as in glass paper. The value of $\frac{P_{app}}{R_F}$ did not approach constancy for these four ions in this case either.

(f). Zone Mobilities in Cellulose Acetate Paper.

Zone mobilities of Na^+ measured in strips of cellulose acetate paper are given in Table XII. These results may be subject to considerable error because of the appreciable electroosmotic flow of background electrolyte toward the cathode. Although corrections were made for this, their reliability may be questioned. Furthermore, the absorbance of the strip must tend to increase toward the cathode, and the magnitude of the effect of this on the final mobility is unknown.

It may be seen that the values of P_{app} are usually slightly greater than the calculated value of 0.69. This would be expected if the electroosmotic correction were not large enough. Since the Na^+ ions are migrating into a region of higher absorbance than that nominally used, their speed may be further increased. In 5.89M acetic acid, where P_{app} is smaller than 0.69, electroosmosis was a minimum. It increased with decreasing concentration, as does P_{app}. The only conclusions which may be drawn from these data is that P_{app} and the calculated value of P are not greatly different. No indication of adsorption was observed, and the zones of Na^+ were quite sharp.

A further difficulty encountered in working with cellulose acetate as supporting medium was in moistening the strip with background electrolyte. When a pipet was employed as in the technique used here, the amount of liquid which was required in order to avoid dry spots resulted in a medium which was almost "flooded". The limited amount of work done with this material indicates that further experiments with it would be well worth while, but a modified technique for moistening the strip to the desired absorbance would have to be developed, and motion of the background electrolyte solution would have to be considered more carefully.

Swelling of the cellulose acetate was neglected in calculating the value of P given previously. Swelling does occur with cellulose acetate in aqueous media, and consideration of this would make P still smaller. The magnitude of this effect cannot be estimated. From the data obtained, it would appear that swelling does not have a great influence in slowing the moving ions.

(g). Effect of Migrant Concentration on Zone Size and Mobility.

Table XIII lists the results of some measurements of spot size when the migration of Na^+ at various concentrations was carried out in sodium acetate and potassium acetate background electrolytes. A fixed volume of 0.02 ml., of solution containing Na^+ (as acetate) was applied. The spot size is smaller in more concentrated background electrolytes, and in sodium acetate the spot remained the same size until the migrant concentration exceeded that of the background solution. Beyond this, the zone became quite large. In potassium acetate, the spot expanded as the Na^+ concentration was increased, and was quite large when an initial concentration of 0.025M Na^+ migrated in 0.005M potassium acetate.

The actual zone mobilities did not change much in the various background electrolyte solutions. In the 0.005M solutions, U_z was about 19.0 cm.^{2} sec^{-1}v^{-1}, while in 0.01M solution it was about 18.0 cm.^{2}sec^{-1}v^{-1}. No significant variation in mobility was noted with change in concentration of the migrant solution.

The zone mobility and size of Na^+ in 2.36M acetic acid was determined for various initial concentrations of migrant solution. The volume applied was always 0.01 ml.; these data are given in Table XIV and are plotted in Figs. 14 and 15. It was found that in this case the zone mobility decreased with increasing Na^+ concentration, and that the variation was linear with the square root of the initial concentration of the migrant. When the concentration of the migrant solution was greater than 0.5M, the size of the spot became too large for reliable mobilities to be obtained. The mobility of 0.5M Na^+ had decreased by 17%

with respect to that of the carrier-free solution. In Fig. 15, one sees that the length of the zone increased linearly with the square root of the initial migrant concentration. In both graphs, the best straight line intersects the values for the mobility and relative length of zone at a value of concentration that is close to the ionic strength of the acetic acid. This tends to indicate that there is little effect on mobility or zone size unless the concentration of the migrant exceeds that of the ionized part of the background electrolyte. The situation in the more concentrated migrant solutions here probably approaches the first condition described by Edward.

Variation of the ionic strength of the initial zone shows (Table XV) that the presence of foreign ions in the initial zone can affect the subsequent migration of the ion in question. Here, "carrier-free" Na^+ was applied with increasing amounts of HCl. A total of 0.02 ml., was always used. The mobility of the Na^+ is only slightly affected when it is applied in 0.012M HCl, but when it is applied in 0.12M HCl, the zone mobility is substantially decreased and the zone becomes quite broad. This is due to trailing; the main peak was not affected very much. This can be due only to the high ionic strength of the initial zone, since the moving zone would be freed rapidly from the excess H^+ and Cl^- ions. The background electrolyte in these experiments was 1.18M acetic acid.

(h). Effect of Temperature.

The effects of temperature on zone mobility have been investigated for several ions in several background electrolytes over the temperature range 25°C. to 39°C. The data are summarized in Table XVI and are shown graphically in Fig. 16. In general, the variation in mobility is that which would be expected from the variation of the free solution mobility. P_{app}, where it can be evaluated, is constant with temperature, indicating that there is no change in the interactions between the ions and the paper with temperature in this range. The only example where the form of the mobility-temperature curve is unusual is for the case of the Cu^{++} in oxalic acid, where the copper forms a negatively charged oxalate complex. Increased temperature results in a smaller increase in mobility than would be expected. This could be due to a reduction in the stability of the complex species. The average change in mobility for the other ions is slightly more than 2% per degree in going from 25°C to 39°C.

2. Separations

(a). General.

The separations described in this thesis were meant primarily to be illustrative. No really detailed study of any particular group of ions was made, although separations, in some cases very rapid ones, were achieved for almost all of those investigated. A few of these were of systems of considerable interest from a radiochemical point of view. For the most part, organic acid background electrolyte solutions were used. These were chosen because they have the power of forming complexes with many metal ions, and at the same time their electrical conductance is low, permitting the use of high voltages without an unduly high current being drawn. Since these acids are only weakly dissociated, changes of pH due to electrode reactions are more readily eliminated than would be the case with a salt solution of similar conductance, for instance. In order to determine the optimum conditions for the separation of a given group of ions, variation of pH and concentration, which affect complex formation, would have to be investigated. This was not done. Nevertheless, the separations achieved show that the method may be very powerful even with a minimum of care in selecting the conditions.

The separations undertaken include many of elements of successive atomic numbers, since such combinations are often encountered in radiochemical work. In some cases, such adjacent elements have such different chemical properties that separation is not difficult, but this is by no means always the case. Moreover, it must be realized that two ions with very different chemical properties may migrate similarly in many electrolytes. As a general rule, univalent positive ions move more rapidly than bivalent ones of similar atomic numbers when complexing agents are not present. However, specific adsorption by the supporting medium may counteract this. Thus, Rb^+ is faster than Sr^{++}, Cs^+ is faster than Ba^{++}, and Tl^+ is faster than Pb^{++}, but Ag^+ is slower than Cd^{++} under similar conditions because it is very strongly adsorbed by the paper.

From separations made at various temperatures, it was concluded that a temperature in the neighbourhood of 35°C was most suitable from the points of view of speed, resolution, and operation of the apparatus.

The paper used for most of the separations was Whatman No. 3MM. This is a fairly thick paper, and has been used widely in electromigration work. It has the disadvantage that it is not acid-washed, and hence contains a rather large amount of inorganic impurities. For many purposes it might be advantageous to work with an analytical grade of paper. Whatman No. 52, which was used for most work on mobility determinations, is excellent except for the fact that it is thin and holds only a small amount of liquid. Such papers are more subject to localized drying and charring than are thicker papers. Also, at the same absorbance and with a fixed method of application, the amount of migrant which they can contain per unit area is less, so that a given amount of migrant solution will result in a larger zone on the thin paper than on a thicker type.

Background electrolytes capable of forming complexes with the migrant ions are most useful in the separation of metal cations. Weak complexing is often better than strong, since many anionic complex species have comparatively low mobilities and require a long time for separation. This is particularly true of some of the "complexone" species. For similar elements, it is best to work in a region of pH or concentration where the complexes are unstable, and some, at least, of the ions continue to move as cations, but sufficiently complexed to have their mobilities affected. Under these condtions, it is the relative stabilities of the complexes which are most important. Both the non-complexed cation and a complex ion will be in equilibrium with one another; more than one complex species may also be present. Normally, there will be a rapid exchange among the various ions involved. Then, the mobility of a given migrant will depend on the mobility of each form, and the fraction of time which the ion spends in that form. This will be related to the stability of the complex species. Equation 34 of the theoretical section deals with this problem. In some cases, two or more species may be formed which do not exchange with one another rapidly. These may then separate to give more than one zone of the same migrant. A number of instances of this type of behaviour have been reported in the literature. The following are only a few examples. Maki (105) found that Fe(III) formed two cationic zones in certain concentrations of KSCN background electrolyte; presumably these were due to the ions $[Fe(SCN)]^{++}$ and $[Fe(SCN)_2]^{+}$. Platinum forms two zones of opposite charge in HCl, and palladium does the same in NH_4Cl and in sodium citrate solutions (106). Sn(II) forms 6 to 8 zones in sodium citrate electrolyte, depending on the concentration (107), and Ru(III) forms multiple zones under many circumstances, including as many as 8, four of each sign, in 0.1M lactic acid (99). It is probable that many of the very broad zones which are sometimes observed are due to an intermediate state between the slow exchange giving multiple zones, and the rapid dynamic equilibrium which yields a single sharp zone. A few examples of the formation of more than one zone were encountered in this work. Most notable was the formation of two anionic spots by In(III) in 0.01M oxalic acid solution.

Of further interest along these lines is the behaviour of Ag(I) in solutions of EDTA and ammonium hydroxide. In this case, there is competition between the ethylenediaminetetraacetate ions and the ammonia molecules, both of which form complexes with silver. The silver-ammonia complexes have a single positive charge, while the effective charge on the silver-EDTA complex undoubtedly depends on the pH of the solution, which determines the ionization of the carboxyl groups. It is probably -2 or -3 in the solutions used here.

The usual coordination number of Ag(I) is only two, and the coordinate bonds are 180° apart. This means that most chelate rings will be strained, and therefore the formation of such complexes is not favoured over interactions with simple ligands (108). For this reason, the stability of the EDTA complex is of the same order as that of the ammonia complex.

In Fig. 17, some results of the electromigration of Ag(I) in 0.01M EDTA solutions are shown. In 0.01M EDTA in 0.06M NH_4OH, most of the silver moves as an anion, but it trails back to the start very appreciably, and a second major peak remains motionless here. When a more concentrated ammonia solution is used, (1.2M NH_4OH), similar behaviour is observed, but the anionic and motionless peaks have separated. In still stronger ammonium hydroxide, (6.1M), the anionic species is no longer evident. Most of the silver moves as a cation, trailing back to the usual peak at the starting position. Fig. 18 shows similar results in 0.03M EDTA in ammonium hydroxide solutions. The individual anionic peaks are completely separated from the motionless peaks, and all zones tend to be sharper. When the ammonium hydroxide concentration is increased to 6.1M, a cationic zone is formed as in the more dilute EDTA solution, but it separates completely from that remaining at the starting point

(Fig. 18C). It represents a much smaller proportion of the total silver present than did the corresponding zone in the 0.01M EDTA solution. In Fig. 18D, the migration has been allowed to proceed for a longer time, and the silver remaining at the starting point is seen to have split into two parts, one having a very low cationic mobility.

The state of the motionless silver is as yet unknown. In solutions of ammonium hydroxide alone, silver does not remain fixed by adsorption at the starting point, although it does in many other solutions. Neither does there seem to be any reason why a precipitate should form here. On the other hand, it is difficult to imagine a complex with zero charge in this system. An effective zero charge could arise from equilibrium between anionic and cationic species, but such an equilibrium would have to be very insensitive to the ammonium hydroxide concentration to yield the results shown here.

A review of all inorganic separations carried out by electromigration in paper will be given in the appendix. For this reason, little will be said in the following sections about previous work on the ions considered.

(b). Separations in some Organic Acids.

(i). Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ga(III).

Little difficulty was encountered in separating these ions in groups of three of consecutive atomic number, and some separations involving four and five of them were carried out. Of the background electrolytes used, 0.01M oxalic acid proved to be most suitable. This solution is capable of forming many complexes of appreciable stability even in solutions which are sufficiently dilute to have a low conductance.

The ions of this group were first caused to migrate in <u>acetic acid solution</u>, where little complex formation is to be expected. Co(II) and Ni(II) show nearly the same mobilities, and Zn(II) and Ga(III) are only slightly slower, so that separation of these four ions is not convenient in this electrolyte. Fe(III) is very slow, and Cu(II), although also slow, is sufficiently faster to permit a reasonably easy separation from it. Co(II), Ni(II), and Zn(II) are all fast enough to be separated from copper and iron, while gallium is easily separated from iron, but is more difficult to separate from copper here.

It has been reported (56,99) that Cu(II) is strongly adsorbed by paper, and this seems to be the case here for both Cu(II) and Fe(III). The latter, in particular, tended to form elongated spots.

In <u>0.01M oxalic acid</u> background electrolyte, Fe(III) forms a negatively charged complex and moves toward the anode as a comet-shaped zone. Cu(II) also forms a negatively charged complex, but one which moves more slowly than that of Fe(III) so that separation is quite easy.

Ga(III) also forms an anionic zone, but its mobility is very similar to that of the iron complex. It is thus readily separated from Cu(II), but not from Fe(III) here. Co(II), Ni(II), and Zn(II) all move as positive ions. Cobalt moves about twice as fast as nickel, and zinc is only slightly slower than the former. All of the ions in this group with the exception of Fe(III) and Ga(III) can be separated from one another in this electrolyte. Fig. 19A shows such a separation, carried out in 55 minutes at 39°C with a potential gradient of 60v/cm. Much more rapid separations can be achieved if Zn(II) is not to be separated from Co(II) or Ni(II), and if higher voltage gradients are used. Fig. 19B shows the complete separation of Fe(III), Co(II), Ni(II), and Cu(II) in 15 minutes at 150v/cm., and Figs. 19C, and 20A and B give separations of Fe(III), Co(II), and Ni(II); and Ni(II), Cu(II), and Zn(II); and Co(II), Ni(II), and Cu(II), respectively, in less than 10 minutes at 160v/cm. A separation of Zn(II), Cu(II), and Ga(III) in this electrolyte in about 10 minutes at 130v/cm., is shown in Fig. 20C.

In <u>0.015M citric acid</u> as background electrolyte, there seemed to be a greater tendency for some of these ions to form very elongated zones. Fe(III) again forms a negatively charged complex, but this extended as a streak from the starting point. Ga(III) also formed an anionic zone, and although it moves as a compact zone, it is too slow to be separated easily from iron. All other ions are cationic in this electrolyte. Co(II) is slightly faster than Ni(II), but these two ions, and Zn(II), have mobilities that are quite similar. Cu(II) forms a slowly moving positive ion and is readily separated from the rest. In more concentrated citric acid solutions, the absolute mobilities are lower, but the relative values do not change greatly. Some of the more diffuse zones are sharper, however.

Only zinc, copper, and gallium are separated more satisfactorily in citric acid than in oxalic acid, this is illustrated in Fig. 20D. Twelve minutes at 120v/cm., were required. The separation of Fe(III), Ni(II), and Co(II), is shown in Fig. 19D; this took 10 minutes at 160v/cm.

Gross (109) found that in 0.05M citric acid at pH 5.5, Co(II), Ni(II), and Fe(III), and Cu(II) all formed anionic complexes of fairly high mobilities (listed in order of increasing mobility). Considerable change in behaviour can be brought about by variation of pH, since this affects complex formation quite strongly.

In <u>0.1M tartaric acid</u>, Fe(III) again forms a negative complex, but one which trails appreciably. All others migrate as positive ions. Ga(III) forms a very slowly moving zone, while Cu(II) is faster and Zn(II) much faster. The separation of these three ions is very easy in this electrolyte; that shown in Fig. 19E required 28 minutes at only 80v/cm. Zn(II) and Co(II) have similar mobilities here, while Ni(II) is intermediate between these and the slower Cu(II).

Ga(III) and Fe(III) are readily separated in this electrolyte, since they move in opposite directions. The only drawback is that the zone of Fe(III) is large and diffuse.

In 0.1M lactic acid, all of the ions of this group migrate as cations. Fe(III) moves very slowly and with trailing, and Ga(III) is also very slow. Co(II) and Zn(II), the fastest ions here, have very similar mobilities, while Ni(II) is only slightly slower. While separations are possible, other electrolytes are better.

Strain and co-workers have used 0.1M lactic acid for many separations, including some ions of this group (99). The sequence of mobilities which they give is (in order of decreasing mobility) Co, Ni + Zn, Cu, whereas that found here is Co + Zn, Ni, Cu.

(ii). Ag(I), Cd(II), In(III). Although these ions have different valencies, their separation is complicated by the fact that Ag(I) is strongly adsorbed by the paper. If only a small amount of it is present, it usually remains at the starting position, but as its concentration in the initial zone goes up, it tends to form a long cationic streak. The mobility of the leading edge of this zone increases with the initial concentration, and may be fairly high. Only if a strong complex can be formed does silver migrate satisfactorily; it does in ammonium hydroxide, for instance, where the ion $[Ag(NH_3)_2]^+$ forms.

Although no attempt was made to separate these three ions in this electrolyte, it was established that Cd(II) is considerably slower than Ag(I) here. The behaviour of In(III) was not investigated, but it is probable that it would form a precipitate.

In <u>acetic acid</u>, Cd(II) is faster than In(III), and if Ag(I) is present in trace quantities so that it remains at the starting point, a separation is possible.

In <u>0.01M oxalic acid</u>, a good separation can be obtained; this is shown in Fig. 19F, which represents a migration at 160v/cm., for 8 minutes. Ag(I) forms a compact zone at the starting position when present in small amounts, while Cd(II) moves rapidly as a positive ion. In(III) forms two quite distinct zones. Both move as negatively charged species, one having twice the speed of the other.

Moeller (110) has established that a dioxalatoindate ion $[In(C_2O_4)_2(H_2O)_2]^-$, is formed in alkali oxalate solutions. The trioxalatoindate complex, $[In(C_2O_4)_3]^{-3}$, has not been found definitely, but similar species are known for the chemically similar Al(III) and Ga(III). It appears likely that these two complex ions are responsible for the two zones which occur. One other indium oxalate complex ion, $[InC_2O_4]^+$, has been reported to be stable in aqueous oxalic acid solutions (111), but this has a positive charge and cannot be one of those found here.

In <u>0.015M citric acid</u>, In(III) forms only one anionic zone, but it tends to trail. Ag(I) also smears more than in oxalic acid. Cd(II) travels fairly rapidly as a cationic species, and a separation may be carried out here also, provided the amount of silver is small. However, the zones of Ag(I) and In(III) are not sharp, and may overlap at the starting point unless a long migration time is used. More concentrated citric acid should result in sharper zones.

The behaviour of these ions in both <u>0.1M tartaric acid</u> and <u>0.1M lactic acid</u> is similar. Cd(II) forms a fairly rapidly moving positive ion, In(III) a slower positive ion, and Ag(I) remains at the starting line, but as usual tends to "streak" toward the cathode, and may overlap the In(III) zone.

The tendency of Ag(I) to form a long streak from the starting position toward the cathode can interfere with many separations, since, if the amount of Ag(I) present is appreciable, the velocity of the leading edge of this zone may be greater than that of Cd(II). Two methods of preventing this streaking of silver have been tried, and both were successful in improving the separations of these three ions.

In the first method, a narrow zone (4 or 5 cm., broad) a short distance on the cathode side of the starting line was moistened with dilute HCl. The Ag^+ and Cl^- ions migrate toward each other, and AgCl is precipitated in the narrow region between the starting point and original edge of the HCl band. There need be no worry here that a streak of silver will migrate away from the AgCl, as has been found to occur with other precipitates (56), because the low concentration of Ag^+ so produced will be completely adsorbed by the paper, and will not move. The Cd(II) moves through the HCl zone and is not appreciably affected. The In(III) zone does the same, although it may become somewhat smeared and elongated. The HCl zone must be sufficiently dilute that chloride complexes of Cd(II) and In(III) are not formed to any great extent. Separations of this sort have been carried out in both tartaric and lactic acids. A separation in the latter is shown in Fig. 21A, which represents migration for 31 minutes at 80v/cm. Presumably this technique would work at least as well in other background electrolytes, but none were tried.

The second method, which was also successful, consisted of adding a little KCN to the original solution of migrants before application to the paper. The $[Ag(CN)_2]^-$ complex is sufficiently stable that the silver tends to move toward the anode. (Under the conditions employed, it didn't move appreciably). The Cd(II) and In(III) were unaffected. Such a separation is shown in Fig. 21B in <u>tartaric acid</u>; <u>lactic acid</u> is equally suitable. The experiment illustrated required 24 minutes at 80v/cm.

Strain (56) has reported a fairly high mobility for Ag(I) as a positive ion in lactic acid, and made no report of adsorption at the starting point. Sato, Norris, and Strain (99) did not report adsorption in lactic, tartaric, or acetic acids. Experiments with Ag^{110} as tracer showed that while that part of the silver which moved did so rapidly, there was always a trail back to the original position. Although the separations shown were made with inactive silver, radioactive silver was used in some experiments to establish its behaviour even in concentrations which were too small to be detected chemically. Some results of electromigration of silver are shown in Fig. 22, for several electrolytes, including NH_4OH where it migrates well. The failure of other workers to detect the adsorption may be due to use of a different type of paper which did not give adsorption, or to the use of chemical tests which failed to detect the low concentration tail and showed only the leading edge, which might well have a higher concentration.

(iii). Hg(II), Tl(I), Bi(III), Pb(II). The separation of these ions is rendered difficult by the fact that both Hg(II) and Bi(III) are strongly adsorbed by the paper, and move very slowly under most conditions. In fact, they both behave similarly to Ag(I) which was discussed previously, although the tendency to streak is less pronounced. The adsorption capacity of the paper may be greater for these ions than for Ag(I). Tl(I) is readily separated from the rest since it moves as a very fast cation unless complexed with strong ligands.

In 0.01M oxalic acid, Pb(II) travels as a positive ion of fair speed, but it is much slower than Tl(I). Hg(II) remains virtually motionless, while Bi(III) tends to move as a negative ion, but does not leave the starting point entirely. Separations of Tl(I), Pb(II), and Hg(II), or of Tl(I), Pb(II), and Bi(III), have been carried out in 6 to 7 minutes at 200v/cm., (Figs. 23A and B), but Hg(II) and Bi(III) cannot be separated from one another here.

In 0.015M citric and 0.1M lactic acids, and in almost any concentration of acetic acid, much the same behaviour is observed. All ions but Bi(III) and Hg(II) can be separated. Sato, Norris, and Strain (73) observed similar behaviour in 0.1M lactic acid. They also reported adsorption of the lead which was not noticed here.

In 0.1M tartaric acid, Bi(III) showed the strongest tendency to migrate as an anionic complex, but it still refused to leave the starting position entirely. Hg(II) showed almost no tendency to move. That this is due to interaction with the cellulose is indicated by the behaviour of these two ions in glass fibre paper as shown in Fig. 23C. This shows a separation of Hg(II) and Bi(III) in 0.1M tartaric acid in glass paper. Both Bi(III) and Hg(II) form anionic species, but the Hg(II) complex moves more slowly than that of Bi(III), and a separation is possible. Chemical tests failed to detect any trailing of the Bi(III) zone. Although Pb(II) might be separated from Bi(III) and Hg(II) in glass paper, the fourth ion, Tl(I), shows irreversible adsorption on the glass and certainly would overlap the former zone.

In order to obtain a separation of all four ions, halide complexes were used. Pucar (112) has made a study of some ions which form halide complexes, and from his work it was decided that the complexes formed in 0.1M HBr would be most suitable. In order to avoid the high conductance of a strip completely moistened with 0.1M HBr, a region only a few centimeters broad about the starting line was moistened with this electrolyte; the rest of the strip contained 0.01M oxalic acid, but almost any electrolyte could be used because only Tl(I) travels in it to any extent. Best results were obtained if the HBr zone extended about 10 cm., in the cathode direction, and 5 cm., in the anode direction, from the starting line. Under these conditions, Bi(III) moved slowly as a negative ion, Hg(II) acted as an appreciably faster negative ion, and Pb(II) and Tl(I) remained as cations. The Pb(II) zone did become enlarged and blurred if it migrated out of the HBr region and into the oxalic acid, but if the migration were stopped before this, all zones were fairly compact. The Tl(I) was not affected on moving into the oxalic acid region. The movement of the ions in the HBr zone was slow, perhaps because the true voltage gradient across this more highly conducting region was low. The separation illustrated in Fig. 23D required 30 minutes at 80v/cm. The Tl(I) zone is not shown as it has moved very far toward the negative electrode.

(iv). Group IIb: Zn(II), Cd(II), Hg(II).

Separation of ions of the same valence and in the same group of the periodic table is sometimes difficult, but the ions of the elements in this region may be separated readily by virtue of their different complexing behaviour with many ligands. The results are particularly interesting in that they show how complexing varies with the members of such a group.

Group IIb is very easily separated in 0.01M oxalic acid; at 200v/cm., and 41°C., the complete separation takes only 5 minutes (Fig. 24A). All of these ions migrate as cations in this background electrolyte, but Hg(II) moves hardly at all because of adsorption. Cd(II) travels almost exactly twice as fast as does Zn(II), indicating that the interactions between Zn(II) and oxalate ions are greater than with Cd(II). This migration sequence is in contrast to that in non-complexing electrolytes such as acetic acid, and in free solution, where Zn(II) has a slightly higher mobility.

The reversal of the migration sequence of Zn(II) and Cd(II) also occurs in citric, tartaric, and lactic acids, but the difference in the mobilities of zinc and cadmium is less, indicating that the complex formation is weaker. Separations of the ions of this group in 0.1M tartaric and lactic acids are illustrated in Figs. 21C and D. A migration time of 29 minutes at 80v/cm., was used in each case.

(v). Group IIIa; Al(III), Ga(III), In(III).

Ions of group IIIa, Al(III), Ga(III), and In(III), have also been separated from one another. The fourth member of this group, thallium, can be separated easily from the others since the mobility of Tl(I) (the stable valence state) is appreciably greater than that of the others in the electrolyte solutions considered.

As was mentioned previously, In(III) forms two anionic zones in 0.01M oxalic acid. Both Al(III) and Ga(III), also form anionic species in this electrolyte, but they yield only one zone. It is possible that under other conditions of concentration or pH they might also yield two zones. The mobilities of the gallium and aluminum complexes are similar, and they fall between the two indium zones. Thus, separations in this background electrolyte are not obtained readily.

In 0.015M citric acid, all three ions again form negatively charged species, but the zones tend to be elongated. Ga(III) moves more rapidly than In(III) or Al(III), which move at about the same rate.

A good separation can be obtained in 0.1M tartaric acid; this is illustrated in Fig. 24B. The experiment shown took 42 minutes at 80v/cm. As can be seen, all ions are cationic here. Al(III) forms the fastest moving zone, followed by In(III). Ga(III) is slowest.

An equally good separation was obtained in 0.1M lactic acid. That shown in Fig. 24C required 28 minutes at 100v/cm. The order of migration is the same as that shown in tartaric acid, but the Ga(III) zone moves more rapidly relative to the others. These results indicate that of this group, gallim has the greatest tendency to form complexes.

C. Alkali Metals and other Univalent Cations.

An attempt was made to separate the ions Na^+, K^+, Rb^+, and Cs^+, utilizing radioactive tracers to simplify detection. Previous workers have established that potassium, rubidium, and cesium have very similar zone mobilities, while sodium is slower, and lithium, the first member of this family, slower still (109,113,114,115). This behaviour of the K^+, Rb^+, and Cs^+would be expected from the fact that their free solution mobilities are also quite similar, and there seems to be very little chance of influencing their mobilities by complex formation. Most attempts to separate K^+, Rb^+, and $Cs^+$by electromigration in paper have been unsuccessful. Only Gross (109) has reported their separation. The migration sequence which he found was, in order of decreasing mobility, Rb, Cs , K. This is the same order as exhibited by the free solution mobilities at 25°C. The ratios of these mobilities in free solution is 0.943:1:0.993 at this temperature.

In the work done in this research, no difficulty was encountered in separating Na^+ from the other three ions. Figs. 25A and B show the separation of Na^+ from Cs^+ and Rb^+, respectively. The background electrolyte used had little effect on the separation. K^+, Rb^+, and Cs^+ always formed zones which overlapped, and wile partial separations were obtained, a complete separation was not. The size of the zone after migration of a distance of 80 to 90 cm., was 10 to 15 cm., for a single ion in both Whatman No. 3MM and No. 52 papers. As a rule, much of this size was due to a comparatively low concentration trailing region. Ammonium acetate yielded sharper zones than did acetic acid or ammonium hydroxide, but it did not give much improvement in the separation. A mixture of 1M thiourea in 1.18M acetic acid also gave better results than acetic acid alone. The reason for the large size of the zone is not clear. Other ions which were allowed to migrate over the same distance usually were sharper. The cause was certainly not a high concentration of migrant.

Fig. 25C shows the separation of Na^+ from K^+ and Cs^+; the latter two show a large area of overlap, but the gamma-ray spectra showed that part of each is free from the other. Fig. 26A shows a partial separation of Rb^+ and K^+.

The plot was obtained by measuring the strip twice; once immediately after separation, and again 6 days later when all of the radioactive potassium (K^{42}, with a half-life of 12.8 hours) had decayed away. These measurements give the total amount of Rb plus K, and the amount of Rb, respectively. A large portion of each zone is free of the other element. This was obtained after a short migration of less than 50 cm. Undoubtedly better results could be obtained with a longer migration path. However, the K^+ region in particular is already very broad. In other runs of about the same distance, similar behaviour was observed.

Partial separations of Cs^+ and Rb^+ are shown in Figs. 26B and C. In the first, done in <u>acetic acid</u>, a large area of overlap occurs. This is much smaller in the second case, where almost all of each zone is free of the other ion. The electrolyte used here is a mixture of <u>thiourea</u> and <u>acetic acid</u>. The zones are much sharper in this electrolyte. Other runs in this solution did not exceed 80 cm., distance, and showed a greater overlap, but still yielded large uncontaminated areas of each zone. Gamma ray spectra were used to determine the purity in these cases.

Some separations of alkali metals from other univalent cations Ag(I) and Tl(I) were also undertaken. No problem is encountered with Ag(I) in trace amounts since it is strongly adsorbed at the starting point. Tl(I) has a high mobility when moving in an uncomplexed form as in acetic acid, and here it is only slightly slower than Cs^+. A distance of nearly 80 cm., is required for their separation under these circumstances. By forming suitable complexes as with ethylenediaminetetraacetic acid (EDTA) which does not react with the alkali metals, the separation of alkali -Tl(I)-Ag(I) is accomplished readily.

Some separations of cesium, sodium, silver, and thallium in EDTA are illustrated in Figs. 27A, B, and C. The behaviour of Ag(I) in such solutions has been discussed.

(d). Separations of some Ions in Complexone Solutions.

The electromigration of a number of ions was investigated in some "complexone" solutions with a view to investigating the applicability of these compounds in separations. The complexones used were:

ethylenediaminetetraacetic acid (EDTA),
nitrilotriacetic acid (NTA),
1,2-diaminocyclohexanetetraacetic acid (DCTA), and hydroxyethyl-ethylenediaminetriacetic acid (HEDTA),

in various concentrations of ammonium hydroxide. EDTA, NTA, and HEDTA were also used in aqueous solution without addition of ammonia. The latter was used as a 0.01M solution here, but saturated solutions of the other two were employed. These are about 0.0007M for EDTA, and 0.008M for

NTA*. The ions considered in most detail were Cr(III), Mn(II), Fe(III), and Co(II), but Ni(II), Cu(II), and Zn(II) were also investigated. Since many of the complexes formed are so stable that they interfere with chemical spot tests, radioactive ions were used in most cases.

A number of disadvantages in the use of these electrolyte solutions became apparent. The first of these is that there is often a tendency for the zones to "smear" or trail. This usually can be reduced with higher concentrations of complexone, but this results in a higher current being drawn, and reduces the maximum voltage gradient which can be used. The mobilities of the anionic complexes formed are usually low, necessitating a long migration time to begin with. Thus, these solutions are not good for very rapid separations.

The work reported here merely gives an indication of the possibilities held by such systems. The best separation of a given group of ions can only be found by a careful study of the effects of pH and concentration of the complexing medium on the electromigration of each one.

As can be seen from the accompanying table of migration sequences for Mn(II), Cr(III), Fe(III), and Co(II), (Table XVII), the complexing power indicated by the formation of anionic species increases as the pH increases-i.e., in

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*Solubility data were taken from technical bulletins distributed by Geigy Industrial Chemicals, 89 Barclay Street, New York.

solutions containing more ammonium hydroxide. Of the four complexones used, EDTA and DCTA usually form more stable complexes than do NTA and HEDTA. They also have an additional carboxyl group which can result in a higher negative charge on the complex.

Cr(III) and Mn(II) do not form anionic complexes in aqueous NTA or HEDTA solutions, but in EDTA, Cr(III) yields a negatively charged zone. Fe(III) and Co(II) form the strongest complexes in nearly all cases. Oddly enough, while Cr(III) forms an anionic zone in aqueous EDTA solution, and Mn(II) does not, in 0.01M EDTA-0.06M NH_4OH solution, the Mn(II) zone is anionic while that of Cr(III) has become cationic. The Mn(II) complexes retain a greater anionic mobility in more strongly basic solutions, but Cr(III) becomes anionic again. There very often is a tendency for Cr(III) to form a large zone and in 0.01M HEDTA-1.2M NH_4OH, and also in 0.01M DCTA-1.2M NH_4OH, it forms two zones. In the first case these have opposite charges. Of the other ions, Ni(II) and Cu(II) form complexes which are quite stable and comparable to those of Co(II) in mobility, while the Zn(II) complexes seem to be weaker and slower, but still move as anions.

Representations of some separations are shown in Figs. 28 and 29. The times required were long. In many cases there is overlap of the zones, although in the examples shown this was slight, and most of each zone is uncontaminated. Purity was checked by the gamma-ray spectra.

In a saturated solution of <u>NTA in water</u>, Fe (III) and Co(II) are very well separated (Fig 28B). Cr(III) and Mn(II) both move comparatively rapidly as positive ions, and under the conditions used they have moved off the strip. By stopping the experiment sooner, these two ions could be obtained in separate form. In Fig 29A, Fe(III), Co(II), and Mn(II) are shown separated in saturated EDTA in water. Cr(III) has almost exactly the same mobility as Co(II) under these conditions, and the separation of Cr(III), Mn(II), and Fe(III) can be carried out similarly. The best separation of all four ions was achieved in 0.01M EDTA in 0.06M NH_4OH (Fig. 28A). The zones are large, but they are well separated. A good separation also occurs in 0.01M NTA in 0.06M NH_4OH (Fig. 28C). Separations of Cu(II), Ni(II), Co(II), and Zn(II) in these solutions were not satisfactory, since, under the conditions employed, the first three of these ions all have similar mobilities.

Use of "complexones" in the separation of Ag(I), Tl(I), and the alkali metals has been given, and their use in the separation of lead, bismuth, and polonium, as well as strontium and yttrium, and barium and lanthanum, will be mentioned in later sections.

It is not necessary to use a background electrolyte containing the "complexone" in order to work with these complex species. Macek and Pribil (77) found that many of them were quite stable in non-complexing electrolytes. When a number of ions were migrated as "complexone" complexes in 1.18M acetic acid, it was found that Cu(II) moved as an anion when complexed with all but NTA, but showed thr greatest negative movement as the DCTA complex. Fe(III) and Co(II) remained stable anionic complexes for all four "complexones", but Ni(II) moved very slightly and Zn(II) was cationic, indicating that the complex had broken up. All movements were small, however, and no separations were attempted. This technique might prove to be very useful, however, in comparing the stabilities of such complexes in various media.

(e). Molybdenum and Technetium.

Radioactive Mo^{99} decays with a half-life of 67 hours to Tc^{99m}. The latter in turn decays to the long-lived Tc^{99} by means of an isomeric transition having a half-life of 6 hours. It is useful to have a simple means of separating the daughter Tc^{99m} from the parent Mo^{99} . The molybdenum used in these investigations was isolated as the molybdate ion, $MoO_4^{=}$, from the products of the fission of thorium. The technetium is produced as the pertechnate ion, TcO_4^{-}, and is carrier-free.

The molybdate ion is readily precipitated as molybdic acid if the basic solution in which it exists is acidified. The presence of a precipitate on the paper offers the danger that small amounts of material may migrate away from it continuously to give a streak if it has a slight solubility.

In this case, there is also the possibility that the Tc present may be adsorbed in the molybdic acid crystals, and will be unable to migrate. As will be seen, in cases where molybdic acid seems to have precipitated, no difficulties from these two factors are evident.

Experiments were carried out in ammonium acetate, acetic acid, and ammonium hydroxide background electrolytes. Figs. 30A and B show the separations obtained in the former two. In 0.15% ammonium acetate solution, at 60v/cm., the illustrated separation required 55 minutes (Fig. 30A). The distance between the molybdenum and technetium zones amounts to 12 cm., and no detectable activity remained in it. Measurements of the amount of activity in the technetium zone at several times showed that it decayed to background with the approximate half-life expected for this isotope, and from this and an examination of the gamma-ray spectrum it can be concluded that this region contained no radioactive contaminants. The molybdenum region is broad, but symmetrical. It has moved slightly as a negative ion. In Fig. 30B, a similar separation is given in 1.18M acetic acid. This required 25 minutes at 100v/cm. Again, the separation is good and no contamination of the technetium zone was found. The molybdenum zone has moved slightly, but it is probably precipitated here. There is a slight tendency for it to streak, but not to any harmful extent. An unusual feature which was always found in this electrolyte is the long tail containing a small amount of Tc which is seen to extend ahead of the main technetium zone. No explanation can be given for this unless a negative ion of Tc having a greater mobility is present. This does not seem likely.

In ammonium hydroxide, complete separation could not be accomplished even after migration of 40 cm. There is no question here of precipitation of molybdic acid. The molybdate ion has a slightly greater mobility than that of the TcO_4^- ion. The results of this experiment are shown in Fig. 30C. The radioactivity was measured immediately after separation, and again 5 days later when all of the original Tc^{99m} had decayed. This gives the limits of the $MoO_4^=$ zone, but it does not give the position of the leading edge of the TcO_4^- zone. However, most of the latter zone is free from molybdenum.

(f). Ra D, E, and F. (Pb, Bi, and Po).

Ra D (Pb^{210}), its daughter RaE(Bi^{210}) and the third member of the series, RaF(Po^{210}), are of considerable interest radiochemically. Pb^{210} decays with a 20 year half-life, emitting a low energy beta-particle and a gamma-ray. Bi^{210} in turn decays by beta emission with a five day half-life to Po^{210}, which is an alpha-emitter with a half-life of 138 days. These nuclides are readily identified by their characteristic radiations.

Separation of these isotopes proved to be difficult. Both Bi and Po tend to form diffuse broad zones when they migrate. Bismuth tends to be strongly adsorbed unless strongly complexed, and polonium almost always trails from the starting point as a negative ion. It is possible to separate lead from bismuth in the electrolytes discussed in section b(iii). Lead can be removed as a cation while bismuth and polonium remain near the starting point.

Bismuth and polonium could be separated in strong complexing agents. A few "complexone" solutions were tried, and saturated EDTA in water proved to be most suitable. This separation is shown in Fig. 31A. The polonium zone is broad and somewhat irregular, but no bismuth or lead remain in it. It is thus possible to isolate pure Po in this way. By cutting away that part of the paper containing the lead and bismuth, and extracting the portion containing the polonium with HCl, most of the Po can be recovered.

The bismuth and lead form reasonably sharp zones in this electrolyte, but they are not separated after a migration of 38 cm. Lead is slightly faster than bismuth, and a longer migration might give a separation, but this was not attempted.

In 0.01M NTA-0.06M NH_4OH, as shown in Fig. 31B, no complete separation could be achieved. Both the polonium and the bismuth form extended zones, while the lead migrates in the centre of the bismuth zone. Most of the polonium remains near the starting point, however, and this part is free of bismuth and lead.

In a saturated solution of NTA in water, the situation is similar. The bismuth forms a very broad zone having two peaks. Most of the polonium again remains near the starting position, and is free of the other two elements, but small amounts of it extend well into the Bi-Pb region after a migration of nearly 40 cm.

In 0.01M HEDTA in water, both bismuth and polonium extend from the starting point a long distance toward the anode. The lead, although it does not trail, is found well inside the bismuth zone. This electrolyte solution is not at all suitable.

In 0.01M EDTA-0.06M NH_4OH, polonium moves more rapidly as an anion, although it trails back to the starting position. After a run of 40 minutes at 80v/cm., the leading edge of the polonium zone overlapped the trailing edge of the bismuth zone, while the lead was found at the leading edge of the latter region.

Very similar results were obtained with 0.01M DCTA -0.06M NH_4OH, but the polonium was relatively slower than the bismuth, giving better results. This is shown in Fig. 31C. Again, separation of bismuth and lead would require a much longer migration.

Thus, it is possible to separate Ra D from the mixture Ra D, E, and F in weakly complexing (or non-complexing) media, and to separate Ra F from the other two in some "complexone" solutions. A zone of Ra E completely free from both Ra D and Ra F could not be obtained in the migration times allowed, but in some cases a large fraction of this zone was free from contamination.

Other works on the separation of Pb, Bi, and Po in lactic acid have been described by Sato and co-workers (73,99). There was always some overlap of the polonium and bismuth zones in their work, but the detection was by autoradiography and the extent of the overlap is not clear. Lead was well separated, however.

(g). Rb(I), Sr(II), and Y(III), and Cs(I), Ba(II), and La(III).

Strontium and yttrium, and barium and lanthanum, are very important pairs of elements radiochemically. Y^{90} and La^{140} are radioactive daughters produced by the decay of Sr^{90} and Ba^{140}, respectively. They are all produced in nuclear fission reactions.

The separations of Sr and Y, and of Rb, Sr, and Y, proved to be quite easy. Rubidium has a greater cationic mobility than does either strontium or yttrium, and can be separated from these two elements in almost any background electrolyte solution. In non-complexing media, Y(III) is much slower than Sr(II) and the simultaneous separation of all three of these ions may be carried out in acetic acid, for example, as shown in Fig. 32A. At 120v/cm., only 8 minutes were required for this. In 0.015M Citric acid, where there may be some complexing, the yttrium forms a sharper zone. The separation shown in Fig. 32B required only five minutes at 180v/cm. No contamination of the Y^{90} zone with Sr^{90} or any other radioactive substance could be detected.

It was also found possible to separate Sr(II) and Y(III) in EDTA solutions. Rb(II) could also be separated here even more easily since its mobility is not appreciably affected, but it is not shown. In saturated EDTA in water, Y(III) moves as an anion, while Sr(II) is still cationic (Fig. 33A). Both zones trail back toward the starting point, but not excessively. In 0.01M EDTA in 1.2M NH_4OH, both Sr(II) and Y(III) are anionic, but Y(III) is faster. Again, the latter trails slightly, but a complete separation is readily obtained (Fig. 33B). More complicated behaviour is encountered in 0.01M EDTA in 0.06M NH_4OH. Y(III) moves as an anion, and presents no problem. It can be obtained free of Sr(II). The behaviour of the Sr(II) varied in several experiments with this electrolyte. It forms two species here; one is cationic, while the other is motionless or slightly anionic. However, the relative amounts of strontium in these two forms varied greatly from one experiment to the next. In some cases, a very small amount showed movement as a cation, while in others, the amount which remained near the starting position was almost negligible. In 0.01M EDTA in 6.1M NH_4OH, both strontium and yttrium showed similar anionic mobilities, and were not separated.

The behaviour of Cs(I), Ba(II), and La(III) is similar to that of the previous three ions. Again, Cs(I) is readily separated from the other two by virtue of its higher mobility. A striking difference lies in the behaviour of barium when moving as a cation. Although the bulk of the barium moves as does strontium, there is invariably a trailing of a small amount back to the starting point. Although this phenomenon was looked for with strontium, no trace of it was found. It was suspected that the cause might be precipitation of barium by trace amounts of sulfate ions in the paper. With Whatman No. 3MM paper, such impurities would be expected. However, the same behaviour was given by Whatman No. 52 paper, which is acid washed and contains much less inorganic matter. It is still possible that enough sulfate remains even in this paper to give rise to the observed trailing. This behaviour is illustrated in <u>citric acid</u> in Fig. 32C. The separation of Cs is not affected, but the lanthanum at the starting line contains some barium.

Because of this trailing, it is possible to separate La(III) completely from Ba(II) only in electrolytes where the former is anionic. This is the case in EDTA solutions. <u>In EDTA-water solution</u>, a good deal of barium remains at the starting point (Fig.34A) and overlaps the trailing part of the La(III) zone. This sort of behaviour was not found with Sr(III) in the same solution; in Fig. 33A no detectable amount of strontium remains at the starting line. The case in 0.01M EDTA in 0.06M NH_4OH is similar to that with strontium, but the two barium zones seem to be more nearly equal. In 0.01M EDTA in 1.2M NH_4OH, the separation obtained is good, and the zones are sharp with no overlap or trailing (Fig. 34B).

(h). Others.

Thorium and uranium (as Th(IV) and UO_2(II)) were investigated briefly in several background electrolytes. It was found that in acetic acid, thorium moved a good deal faster than did the uranyl ion, so that a separation was possible. Both were cationic. In citric acid, on the other hand, both were anionic but slow and with similar mobilities.

Vanadium and titanium were investigated as the chloride complexes of V(III) and Ti(IV), but neither showed any appreciable motion in citric, oxalic, or acetic acids, or in some "complexone" solutions. No further work was done with these substances.

Copper and silver, elements of the same family, may be separated in non-complexing media if all the silver can be forced to remain at the starting point as by precipitation with HCl. Alternatively, the copper can be removed as an anionic oxalate complex while the silver remains at or near the starting point.

CONCLUSIONS

1. The Variables.

The following points may be summarized from the study of the variables which affect the zone mobility.

(a). The variation of the apparent obstructive factor with absorbance follows the form of the semi-empirical equation proposed by Crawford and Edward (89). Since the swelling factor is not known, the obstructive factor cannot be calculated for cellulose papers. In general, the apparent obstructive factor is different for each ion and background electrolyte, although it may be constant for a given ion in a fixed electrolyte over large regions of concentration. Part of the difference may be due to different physical obstruction by the fibres by virtue of varying degrees of permeability toward the ions, but more probably the chief cause lies in specific adsorption effects. A reasonable approximation of the zone mobility can be calculated at any absorbance by using some average value of X in equation 24. This will be greatly in error only for comparatively few ions such as those which are strongly adsorbed as is Cu(II). In complex-forming media, no means of estimating the zone mobility exists unless the various species in equilibrium, and the mobilities and relative stabilities of each, are known. In most cases, these data are not available.

(b). When thiourea, a substance which increases the swelling of cellulose fibres, is present, the obstructive factor is not decreased as would be expected from equation 24, but rather the hindrance encountered by the ion is, if anything, reduced. This may be the result of lessened adsorption in the presence of thiourea, or it may be due to an increase in the fraction of the swollen fibre which is available for ion transport.

(c). The extent of adsorption on cellulose papers as indicated by values of the apparent obstructive factor does not depend on the ion exchange capacity of the paper for most ions. Ion exchange groups may be important in the hindrance of some strongly adsorbed ions such as Cu(II), but this is not necessarily through an ion exchange mechanism.

(d). For non-swelling fibres such as glass, zone mobilities calculated from free solution mobilities and the obstructive factor given by equation 22 agree quite well when there is no adsorption. For most ions, however, there seems to be a very large amount of adsorption by the glass, and this is specific to a great extent.

(e). The calculated value of the obstructive factor for cellulose acetate is close to the experimental value of P_{app} in the case of Na^+, but experimental difficulties prevent the making of accurate measurements with this supporting medium.

(f). Under certain circumstances, the zone mobility may decrease, and the zone length increase, linearly with the square root of the concentration of the migrant solution when this exceeds the ionic strength of the background electrolyte. A high ionic strength in the initial migrant zone may result in distortion of the final zone.

(g). The effect of temperature on zone mobility is just that which would be expected from the behaviour of the conductance in free solution. Interactions between the ions and the paper do not seem to be affected appreciably over the range of temperature investigated. The behaviour in complex-forming systems as the temperature is changed may be influenced by variation of the stability of the complex species, and in this respect some temperature control may be of importance in separation procedures.

2. General Considerations Regarding Separations.

The following considerations may be given for the general application of this technique to separations. The points are chiefly those which would be of interest when separating radioactive materials, although many of them are applicable equally to inactive substances.

(a). Very rapid separations may be accomplished with high voltage gradients. Some separations required as little as five minutes. Elevated temperatures are advantageous.

The increase in size of the zone caused by enhanced diffusion at higher temperatures is negligible, at least if the separation does not require a very long time.

(b). Very small amounts of material can be separated; this includes "carrier-free" radioactive substances. The maximum amount of material which can be handled in a discontinuous strip technique is also small, however, and this constitutes a major limitation of the method.

(c). Information may be obtained about the identity of unknown ions. An unknown can be migrated side by side with a number of known species to give a direct comparison of mobilities. In many cases, it is not necessary to know the identity of all of the substances present in a mixture in order to separate them if runs are made in a few different background electrolyte solutions.

(d). It is often possible to obtain information about the nature and stabilities of complex ions in solution. In any system, the effective charge on the ion is determined readily. In this way, the technique may well prove to be of use in fundamental studies of inorganic chemistry as well as in problems of separation.

(e). The paper strip containing the separated substances is handled very easily. For many uses, such as half-life determinations and the investigation of gamma-ray spectra, the material may be measured directly on the paper without further treatment. Other quantitative measurements can be made if proper calibration is performed; in particular, the relative amounts of the radioactive migrants in the separated zones are determined readily.

(f). Removal of separated material from the paper, if this is necessary, may present a problem in some cases. In any event, it forms an additional, time-consuming step.

(g). Although movement along the strip is usually quantitative, in a few cases there may be irreversible adsorption of small amounts of material on the paper which leads to a continuous deposition of migrant along the path followed by the moving zone. If the amount which is adsorbed irreversibly is large enough in relation to the total amount of migrant present, no motion will take place. Although this does not seem to be a very common occurrence, it is necessary to investigate every system for this effect when quantitative separations are necessary. Harbottle (116) has found that by soaking the paper in a solution containing the species which is strongly adsorbed, and then washing out the excess, irreversible adsorption of the migrant is more or less eliminated. Apparently, the adsorption sites are saturated in this way. With this treatment, a substance which normally forms a large "smear" moves as a sharp zone. If the migrant is radioactive, the presence of inactive ions of the same element throughout the strip does not interfere with detection of the zone. In the cases where this has been used, the ions taken up originally are held irreversibly, since they do not exchange with the migrating radioactive ones. This approach may be very useful in the elimination of the trailing caused both by irreversible adsorption and by precipitation by small amounts of impurities in the paper.

SUMMARY AND CONTRIBUTION TO KNOWLEDGE

1. The existing theoretical treatments relating the electromigrational zone mobility of an ion in paper to its free solution mobility (i.e., the mobility which the ion would have when migrating in the background electrolyte solution in the absence of paper) have been considered and evaluated.

2. Apparatus was designed, and a technique developed, which allow zone mobilities of ions migrating in paper under an electric field to be measured under conditions such that the factors which influence this migration are known and controllable. In particular, temperature and absorbance could be chosen at a desired value, and flow of background electrolyte solution by electroosmosis or capillary action was eliminated.

3. A second piece of apparatus was constructed for separations. This provided a total migration path of any length up to 100 cm., and could withstand an applied potential of 10,000 volts.

4. The apparent obstructive factor, defined as the ratio of the zone mobility of an ion to its mobility in free solution, was introduced, and used to indicate the relative hindrance encountered by a number of ions in various systems.

This gives an indication of the relative amount of interaction between the ions and the paper in these cases. In general, the apparent obstructive factor has a characteristic value for each ion in each background electrolyte solution, and although it may be constant over a large range of concentration of the background solution, it decreases markedly, indicating greater interaction, in very dilute solution.

5. The effect of the type of paper on the zone mobility and apparent obstructive factors of several ions in acetic acid background electrolyte was investigated, and an attempt was made to correlate the results with the ion exchange capacities of the papers. Only Cu^{++}, an ion which shows an unusually large amount of interaction, gave any correlation at all. It was concluded that only in special cases does the exchange capacity of ordinary papers have any direct relationship to the zone mobility, and even here the mechanism of interaction may not be an exchange process.

6. The variation of zone mobility with absorbance, a very important factor which frequently has been overlooked, was studied extensively in several systems. For Cs^+ in Whatman No. 52 paper, the experimental values of the apparent obstructive factors were compared with the values calculated from equation 24 which was proposed by Crawford and Edward (89). The experimental points agree very well with the

calculated curves. However, equation 24 contains a factor for the swelling of the paper. This is not known, and was chosen in each case to give the best fit. The swelling factor obtained in this way also included effects of adsorption, so that no real estimate of its magnitude with respect to only mechanical obstruction could be obtained. These data do show that the form of equation 24 is consistent with experiment.

7. The influence of thiourea, a substance which enhances the swelling of cellulose in aqueous solutions, on the apparent obstructive factors for Cs^+ and Na^+ in three types of paper, showed that the increased swelling did not result in an increased hindrance. This may be due to a decrease in adsorption which offsets the purely mechanical effects, or to an increase in the fractional volume of the fibres now permeable to the migrant ions.

8. The behaviour of some ions was studied in Reeve Angle 934AH glass fibre papers, and it was found that for Na^+, the zone mobility could be calculated fairly well from equation 22 of Crawford and Edward if the background electrolyte were not too dilute. Equation 22 gives the mechanical obstruction, and contains no unknown terms. For other ions, there was always an appreciable amount of adsorption which hindered them much more than predicted by the equation. A term for the effect of adsorption must be introduced in order to calculate zone mobilities from free

solution mobilities, but no independent method of evaluating the adsorption term yet exists.

9. Experiments were carried out with Na^+ in cellulose acetate paper, and although accurate measurements could not be made because of experimental difficulties, the experimental and calculated obstructive factors had similar values.

10. The zone length given by Na^+ was investigated with various concentrations of migrant and background electrolyte. It was found that the zones were smaller in higher concentrations of background electrolyte, and in a given electrolyte, increased with increasing migrant concentration, particularly when this exceeded the concentration of the background solution. This point confirms earlier observations on different systems. The effect depends to some extent on the nature of the background electrolyte. Further, it was found that in acetic acid, the zone length increased, and the zone mobility decreased, linearly as the square root of the migrant concentration increased. It was also noted that an excess of foreign ions in the initial zone could result in slowing and elongation of the migrant zone even when the excess ions did not move with it.

11. Finally, measurements of zone mobilities in several systems over the temperature range 25°C. to 39°C., confirmed previous reports that the effect is about the same as

would be expected in free solution; the temperature coefficient is of the order of 2% per degree C. It was also established that the apparent obstructive factor for Cs^+ in acetic acid and ammonium hydroxide did not vary with temperature. In the case of complex species, where a change in temperature alters the stability, anomalous results may be evident.

12. Results were given showing the complicated behaviour of Ag(I) in electrolytes composed of ethylenediaminetetraacetic acid and NH_4OH. Invariably, the silver formed at least two zones; one remained motionless while the others were anionic or cationic, depending on the amount of ammonia present. The extent of adsorption of Ag(I) by paper in non-complexing media was shown also. When present in very small amounts, it does not migrate at all, but when present in larger amounts, it may form a long "smear" extending from the starting point.

13. A number of metal cations were studied in acetic, oxalic, citric, tartaric, and lactic acids, and high voltage separations were obtained for them. The groups of elements considered in this respect were those of the first long period from iron to gallium, inclusive; silver, cadmium, and indium; mercury, thallium, lead, and bismuth; group IIb; and group IIIa (except boron).

14. The alkali metal ions were investigated, but a complete separation of potassium, rubidium, and cesium could not be obtained. Partial separations were made, however. Some separations of the alkali metals from other univalent cations were carried out also.

15. Some chelating agents of the ethylenediaminetetraacetate type were used as background electrolytes in the electromigration of some elements of the first transition series. The purpose was to investigate the effectiveness of these compounds in this technique. The anionic complexes formed were found to have low mobilities, so that separations were slow.

16. The pertechnate ion, produced by the radioactive disintegration of molybdenum in solution as the molybdate ion, was separated from its parent in acetic acid and in ammonium acetate electrolytes.

17. The separation of lead, bismuth, and polonium in the mixture of Ra D, E, and F was studied. Both bismuth and polonium were found to trail or form very large zones, but it was possible to obtain either lead or polonium completely free from any of the others. Bismuth could be separated from lead readily, but it could not be separated from both lead and polonium in one run. "Complexone" solutions were found useful here.

18. Separation of rubidium, strontium, and yttrium was carried out in five minutes. Separations were done in acetic

and citric acid solutions, and in some ammonium ethylenediaminetetraacetate electrolytes.

19. Similar work was done with cesium, barium, and lanthanum, but barium was found to deposit along its migration path. This may have been due to precipitation by trace amounts of impurities in the paper. Separation of these elements was nevertheless accomplished, and the barium zone was kept sharp by using a suitable complexing agent.

APPENDICES

APPENDIX A

The Temperature of the Paper Strip

The temperature of the paper strip in the "sandwich" type of closed strip apparatus can be calculated if it is assumed that there is an equilibrium between the amount of heat produced by the electric current, and the amount conducted away. It also is necessary to assume that heat is generated, and removed, uniformly over the entire strip. This will apply to the type of apparatus used here, where the cooling plates are maintained at a constant temperature and heat is transferred to them through the electrical insulation.

The amount of heat (in calories) Q_p, produced in the paper strip in time t is

$$Qp = \frac{EIt}{4.2}$$

where E is the voltage applied, and I is the current flowing through the strip. The quantity of heat conducted away Qc, in the same time is

$$Qc = \frac{K(Ts-Tp)\,At}{d}$$

where K is the specific heat conductivity of the insulator, A is the total area across which heat may flow, d is the thickness of the insulator, and Ts-Tp is the difference in temperature between the strip and the cooling plates.

At equilibrium,

$$T_s - T_p = \frac{EID}{4.2\,KA} \qquad {}^{o}C.$$

Values of K are:	polyethylene	8×10^{-4} cal/sec/cm°C.
	polyvinylchloride	4×10^{-4} "
	mica	18×10^{-4} "

APPENDIX B

Mathematical Treatment of the Shape of the Zone

Weber's treatment of the shape of the zones formed in electromigration in paper (95) was discussed qualitatively. The following is his mathematical treatment.

The concentration of the migrant is a function of position x and time t ; i.e. $C = C(x,t)$. Let the substance move under the electric field with a velocity v in the x direction. In a period of time Δt the increase in amount of substance ΔN in the increment of strip Δx will be

$$\Delta N = v\left[C(x) - C(x-\Delta x)\right]\Delta t + D\left[\left(\frac{\partial c}{\partial x}\right)_{x+\Delta x} - \left(\frac{\partial c}{\partial x}\right)_{x}\right]\Delta t$$

where D is the diffusion co-efficient. Dividing by $\Delta x \, \Delta t$ and going to the limit,

$$\frac{\partial c}{\partial t} = -v\frac{\partial c}{\partial x} + D\frac{\partial^2 c}{\partial x^2}$$

$$\text{if} \quad \frac{\Delta N}{\Delta x} = \Delta c$$

Appendix B

If at $t = 0$ we assume that all of the migrant is concentrated in a narrow band across the paper, we can solve and obtain an expression for C as a function of position and time.

$$C = \frac{K}{2\sqrt{\pi D t}} \exp\left[- \frac{(x \quad vt)^2}{4Dt}\right]$$

where K is a constant of integration. This represents a symmetrical, gaussian distribution.

If adsorption takes place, the situation is more complicated. Let C_1 be the concentration of the migrant which is free to move, and C_2 its concentration in the adsorbed phase. The total concentration is still C so that $C = C_1 + C_2$.

We assume that C_1 is a function of the total concentration, i.e.

$$C_1 = C_1(C)$$

Then

$$\frac{dC_1}{dC} = C_1'(C) \, ; \qquad \frac{d^2C_1}{dC^2} = C_1''(C) \, .$$

Therefore

$$\frac{dC_1(C)}{dx} = \frac{dC_1}{dC}\frac{dC}{dx} = C_1'(C)\frac{dC}{dx} \, .$$

The previous differential equation becomes

$$\frac{\partial C}{\partial t} = -v \frac{\partial C_1(C)}{\partial x}$$

since only the mobile phase takes part in electromigratory movement. Diffusion has been neglected.

We can set

$$C = f[x + j\,(t)] \, .$$

Appendix B

Then

$$\frac{\partial C}{\partial t} = f\left[x+j(t)\right] j'(t) = -v\, C_1'(C)\, f'\left[x - j(t)\right] .$$

Therefore,

$$j'(t) = -v C_1'(C),$$

or

$$j = -v C_1'(C) t,$$

neglecting the constant of integration.

Then,

$$C = f\left[x - v C_1'(C) t\right] .$$

$$\frac{\partial C}{\partial x} = f'\left[x - v C_1'(C) t\right] \left[1 - v t \frac{\partial C_1'(C)}{\partial x}\right]$$

$$= f'\left[x - v C_1'(C) t\right] \left[1 - v t\, C_1''(C) \frac{\partial C}{\partial x}\right],$$

If we assume that the adsorption is linear with concentration so that

$C_1''(C) = 0$ then $\frac{\partial C}{\partial x} = f'\left[x - v C_1'(C) t\right]$;

although this expression cannot be solved explicitly, its shape can be determined from qualitative considerations - as was indicated in the theoretical section of this thesis.

APPENDIX C

A Review of Inorganic Separations by Electromigration in Paper

No complete collection of inorganic separations made by electromigration in paper strips is available; one of the best partial compilations is given by Blasius (1). It was thought desirable to give as comprehensive a review as possible here. The arrangement given below is arbitrary. No system of grouping of ions can be completely satisfactory, since those considered in various investigations have been chosen so widely. Often, the prime factor governing selection of the ions studied seems to have been ease of detection.

The work which can be considered historical - i.e., most of that done before 1950, and some work in packed columns and gels, will not be considered here. The "focussing" technique of Schumacher, in which a complexing gradient is used, will not be discussed either although it has given some striking results. Work with this method has dealt with a few metal cations from most of the groups below, so references to it are given (2-6).

For convenience, the literature references covered in this review are collected and numbered separately from those which appear in the rest of the thesis. Papers appearing in both lists are treated independently in each.

A few lists of relative zone mobilities of some ions have been given. These may be useful in indicating whether a proposed separation is feasible. Such values for anions in 0.1N NaOH are given by Grassini and Lederer (7) and in $(NH_4)_2\ CO_3$ by Gross (8) and by Lederer (9).

Cetini has given zone mobility values for cations in lactic acid - $Na_2\ CO_3$, HCl - potassium biphthalate, and sodium citrate (10), while Maki has reported some in organic solvents (11). In addition, Cetini has studied a large number of cations in NaOH-potassium biphthalate and in NaOH - lactic acid of various pH values, and some anions in ammonium acetate, in a starch gel (12). A number of separations were reported here also.

The following may also be of interest, although they do not include actual separations. De Angelis et al have considered the variation of the mobilities of Co, Mn, Fe, Zn, Cu, Pb, Al, and Mg as a function of pH in 0.05 M citric acid, 0.01M SCN^- solution, and KNO_3 (13). Yasunaga and Shimomura have also studied the effect of pH on very many anions and cations in $NaNO_3$, KCNS, and tartaric acid electrolytes (14). Achiwa has studied a number of factors influencing the movement of many anions (15).

(a) The Alkali and Alkaline Earth Ions

Separation of the alkali metals by paper electromigration has been carried out by a few workers, but the difficulty in detecting these ions on paper has offered a considerable obstacle. Flame photometry has been used, but this is tedious. The alternative has been to use a background electrolyte such as ammonium carbonate which is easily volatilized, leaving an alkali metal compound which can be detected by an acid-base indicator.

Radioactive tracers, which offer the best means of detection, have so far seen little use.

The most difficult ions to separate of the alkali metals are K^+, Rb^+, and Cs^+. These have very similar mobilities. The Separation of Li^+ and Na^+ from the rest and from each other is not difficult.

The alkaline earth ions are in many ways similar to the alkalis; the mobilities of Ca, Sr, Ba, and Ra are very similar. Each alkaline earth ion migrates more slowly than the corresponding alkali metal ion. Moreover, the former can form anionic complexes, thus giving a much wider scope for separatory procedures.

Migrants	Background Electrolyte	Remarks	Ref.
Mg, Li, Na K	$(NH_4)_2 CO_3$	Separated all in 35 min. at 30 V/cm K, Rb, Cs could not be separated. Relative mobilities are Mg(0.34), Li (0.53), Na(0.72), K(Rb, Cs)(1.00)	16
Mg, Li, Na, K, Rb, Cs	0.1M $(NH_4)_2$- CO_3	Separations at 100v/cm. Complete in 37 min. Rb and Cs still very close together. Migration sequence (in order of increasing mobility) Mg, Li , Na, K, Cs, Rb	17

Migrants	Background Electrolyte	Remarks	Ref
Mg, Li, Na, K, Rb	NH_4 OH	All but K and Rb separated	18
Na, K	NH_4 Cl-HCl	Linear and radial techniques. A more fundamental study of the conditions for separations	19
Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Ra	H Cl, lactic, tartaric, and citric acids and their ammonium salts, EDTA at several pH values, and others	K, Rb, Cs, could not be separated. Ba, Ca separated in di- and tri-ammonium citrate, but Sr overlapped both. In NH_3-EDTA solutions of pH $>$ 6, alkaline earths anionic and easily separated from alkalis.	20
Mg, Ca, Sr, Ba	0.05M citric acid, pH 5.5.	All separated in 45 min. at 100 v/cm. Also some separations from group (c) and (d) ions.	17
Mg, Ca., Sr, Ba	0.007 M citric acid in 5 N NH_4OH,	Electromigration, and discontinuous electrochromatography	21
Mg, Na, K, and anions	ethanol-acetic acid-ammonium acetate	Discontinuous electrochromategraphy. Most of separation due to chromatographic effects. Electromigration separated only cations and anions.	22
Mg, Ca, Sr, Ba.	0.1N NH_4Cl, 0.1N NH_4NO_3, and others	Sr and Ba could not be separated. Ternary mixtures separated in given electrolytes. Binary mixtures separated in other electrolytes.	23

Mg, Ca, Sr, Ba.	$Na_4P_2O_7$-HCl of pH 3.2.	Sr, Ba have similar mobilities, but ternary mixtures not involving this pair were separated.	24
Ca-Ba; Ba-La; Sr-Y; Sr-Ba.	0.05 M lactic acid	Sr-Ba only partially separated	25
Sr, Ba	Methanol - acetone - HCl		11
Ca-Sr Ca-Ba	HPO_3; pH 1.5		26
Ca-Sr	(HPO_3); pH 1.75	Also separated Ba from Zn, Pb, Fe, and Co, Al, Fe	26
Sr-Ba		discontinuous electrochromatography	27
Ra from Pb, Bi, and Po	0.1 M lactic acid	Separation of Ra from its decay products	28
Sr-Y, Rb, Cs, Ca, and others	0.1M lactic acid	A few separations	28

Mach has used this technique in determining the radiochemical purity of Na, K, Rb, and Sr of this group. (29).

Arnikar (30) has studied the electromigration of alkali metals in asbestos paper at 350°C with fused $NaNO_3$, as background electrolyte. Mobilities $(10^4 \mathrm{cm}^2\ \mathrm{sec}^{-1}\ \mathrm{v}^{-1})$ are:

Li (3.75), Na (4.16), K (3.74), Rb (3.58),

Cs (3.38). Cs and K were not separated in 45 cm. due to extensive low concentration regions behind and ahead of the main zones.

b) Sc, Y, the Rare Earths, and the Actinide Elements

The rare earth elements and their homologues have such similar mobilities and chemical properties that separations by electromigration are quite difficult.

Eu-Pm-Ce	0.035 M tartaric acid - 0.015 M diammonium tartrate	Eu, Pm anionic; Ce cationic. Separation accomplished.	31
(Pr(Pm))(Ce)-(Y(Nd))-Sc	0.1M lactic acid	Separations accomplished. Ions in brackets had same mobilities.	31
Sc, Sm, Nd, Y, Pr, Ce, La, Ac	citric acid - NH_3 pH 7-8	Too short a migration distance for good separations to be achieved.	32
Sc, Sm, Nd, Y, Pr, La, Ac.	1% citric acid	As above	33
Ce, Y, U, Sr, Cs, Nb, Zr	0.1M lactic acid	Continuous electrochromatography. Some ordinary electromigration separations reported also	28

U02, Co, Fe (III)		Migrated as "complexone" complexes in various background electrolytes	40
$U0_2$ and ions of groups (c), (d) (e) and (g)	0.05 M citric acid, pH3.1, and other values	Separated in 30 min at. 140 v/cm	17
Th (IV) $U0_2$ (II) and others	Many	Deals with the members of the 3rd analytical group. See section (c) and (g)	41
U02, Th, Pu	0.1 M lactic acid	Separated as radioactive tracers. Pu formed long, diffuse zone, overlapping both others	28
$U0_2$ from Pt, Pd, Bi, and Fe	Many	UO_2 separated from the rest. Migration sequences given. Chiefly binary mixtures	42

Bachelet et al have given the direction of migration of UO_2 (II) in many electrolytes, but no separations or quantitative information is given (43).

Maki has separated the rare earths in monazite (44) by the method of outline in ref. (34).

(c), Cr, Mn, Fe, Co, Ni, Zn, Al.

Since these ions offer considerable scope for the use of complexing agents of various sorts, they have been investigated extensively.

Fe (III), Co (II), Ni (II)		These ions, those of the copper and arsenic groups, and Au, Pd, Pt, considered	45
Fe (III), Co (II), Ni (II),	Alcoholic KCNS - N/2 HCl	Separation readily accomplished	46
Co (II), Ni (II),	1NH Cl 7% KCNS in 66% ethanol	Ni anionic, Co remains cationic. Separation as above	47
Fe (III), Co (II), Ni (II), Zn (II), Al (III), Ba (II)	HPO_3, pH, 1.5. $(HPO_3)_3$, pH 1.6 and 1.75	Separations from each other and from some copper and arsenic group ions. Quaternary mixtures considered	26
Fe (III), Zn (II), Co (II), Ni (II), Al (III), and the copper group	Many	Chiefly a separation of Fe (III) from the others. Only pairs of ions were separated	48
Zn (II), Mn(II), Co (II), Ni (II), and the copper group	Many	Zn and Mn separated from each other and the rest. Migration sequences given	49
Zn, Co, Ni, and the copper and arsenic groups	Many	Chiefly deals with the separation of members of the arsenic group from the others	50

Appendix C

Co, Ni, Ag and the copper group	Many	Chiefly deals with the separation of Ag and Hg from many other ions, including Co and Ni	51
Fe (II), Fe(III), Co, Ni, Zn, Al	0.05 M citric acid at various pH values	High voltage separations from each other and other ions of groups (b), (d), (e), and (g)	17
Co, Ni, and the copper group	Many	Separations from quaternary mixtures with copper group ions	52
Fe (III), Co(II), Al (III), and others	Many	Separations of these ions from some of groups (b) and (g) (The 3rd analytical group.) Only a few separations of quaternary mixtures obtained	41
Ni, Zn, Co, Mn	KCN at pH 6.0 Many others tried.	Co, Zn always formed overlpping zones in KCN. Complete separation of any 3 possible	53
Ni(II), Co (II), Mn (II), Zn (II), Al (III), Cr (III), Sn (II), Sb (V)	0.1M ammonium tartrate in 4N NH_4 OH. Other proportions used also.	Co-Ni-Mn-Zn, and Sb(V)-Sn (II) - Cr (III), Al (III) were the groups separated	54
Fe, Al, and $CrO_4^=$ from As, Sb, Sn	$Na_4P_2O_7$ - H Cl; pH 2.4	Studied quaternary mixtures only	24

Mn, Co, Ni, Zn,	ethanol - acetone - H Cl	Separation of Ni, Co, and Mn from Zn	11
Fe(II) - Fe (III)- Co (II) - Cd (II) - Pb (II) - Cu (II).	2N acetic acid - 0.6 N Formic acid	Sequence (in order of decreasing speed) Fe (II), Co, Cd, Pb, Cu, Fe (III). Fe (II) and Co zones very close together	55
Fe, Ni, Co, Al		Discontinuous elctro-chromatography	27
Mn, Co, Ni, Zn, Fe, Al, CrO_4, Cu, Ag.	Many	One and two dimensional techniques. Not all separated in one experiment	56
Fe(III) - Co. Fe(III) - Mn; Fe(III)-Mg; Al-Tl-As(III)	0.05 M malonic acid- - 0.01 M Acetic acid	Continuous separations using a tapered paper sheet	57
Fe (II), Ni, Co, Cu.	1% NaK Tartrate	Continuous electrochromatography of the α, α'-dipyridyl complexes. They are all anionic, sequence of mobilities Fe > Ni > Co > Cu. 1-10 phenanthroline complexes also studied	58
Fe (II) - Fe (III)	1% NaK Tartrate	Continuous electrochromatography. Fe (II) as α, α'-dipyridyl complex, Fe (III) as acetylacetone complex	58
Fe(II)- Fe (III)	0.1N H_2SO_4	Separation in 90 min at 10 V./Cm Fe,(II) faster	59

Fe(II)-Ni(II) ; Fe(II)-Cr(III); Fe(II)-Fe(III);	1% citric acid and 0.5% NaK Tartrate	Continuous electrochromatography Fe(II) present as α,α'-dipyridyl complex, FePy2 (II). Also sep. Fe(II)-Fe (III)-FePy$_2$ (II).	60
Fe(III), Co, UO_2		"Complexone" complexes in several electrolytes	40
Ni-CrO_4 Ni-Cu.	I M acetic acids 0.I M Lactic acid	Used for quantitative analysis after elution	61
Fe(III)-Ni; Ni-Ag; Ni-Cu-Cd-Ag; Al-Co-Fe(III)	Several	Two dimensional discontinuous technique; chromatography used in one dimension	62
Ni-Cu; Ni-Cr O_4 Fe(III)-Al; Fe(III)-Ni-Cu-Ag	Several	Continuous electrochromatography	62
Fe(III) from group (b) and (g) elements	HF, and H Cl-HF	See groups (b) and (g)	38, 39
Fe(III), Cr. Al, Mn, and ;group (a), (d) and (e)	0.007 M citric acid in 5N NH_4 OH, and others	Electromigration and discontinuous electrochromatography	21

In addition. separation of some precious metals from some ofthese ions are given by Mukerjee (63, 64, 65). (See group (f))

d.) The Copper Group (Cu, Cd, Hg (II), Pb, Bi) and Ag, Hg(I), Tl, Po.

The copper group ions have been studied quite extensively, since they form complexes with many reagents, and are all readily detected on paper. The other ions frequently have been considered with the copper group in separations by electromigrations.

Cu-Bi-Hg(II)	0.5 N Na Cl	Separation done in agar gel	66
Cu-Bi-Hg (II)	0.5 N H Cl	Also separated Cu, Hg (II) and As (III) from Au, Pd, and Pt	45
Cu, Cd, Bi, Hg (II), As	1N H Cl	Also separated Cu from Au, Pd, and Pt	67
Cu, Cd, Pb, Bi, Hg (II) Tl (1) and elements of groups (b), (c), (e) and (g)	0.05 citric acid at various pH values	Ions separated from each other and from ions of other groups. A high voltage separation	17
Hg(II) - Pb(II)-Ag	3N NH_4 OH; 30% formic acid; 0.5M citric, lactic, acetic, and tartaric acids	Could not obtain complete separations under the conditions used. Reported two zones formed by Ag in many of these electrolytes	68

Cu, Cd, Hg (II), Pb, Bi.	0.1, 0.5, and 1.0N H Cl	Separation complete in 15 min. at 12 v/cm. Cu cationic at all concentrations, Bi, Hg (II) anionic	46
Cu, Cd, Pb, Bi, Co, Ni	Many	Separation of quaternary mixtures	52
Cu, Cd, Hg (II), Pb, Bi.	0.1N K Cl; several others	K Cl gave best separation, other electrolytes also gave separation	69
Hg (II), Pb, Ag, Tl (I)	1N Na Cl, KCl, KCN, and several others	Separations complete in 3 hrs. Other electrolytes failed to give complete separations	70
Cu, Cd, Hg (II), Pb, Bi	Na Cl - HCl-glycine, pH 1.8	Bi motionless, Hg (II) anionic, remainder cationic	71
Cu, Cd, Pb, Bi, Ni, Fe(III)	HPO_3, pH 1.5; $(HPO_3)_3$, pH 1.6	Separations of some ions from group ('c'), and well as the copper group ions	26
Ag, Hg (II), Cu, Cd, Pb, Bi, Co, Ni	Many	Chiefly a separation of Ag and Hg (II) from the others	51
Cu, Cd, Pb, Bi, Ag, Fe, Be, Al, Zn, Co.	Many	Separations of pairs only	48
Cu, Cd, HgII)	0.1N KCl H Cl of various concentrations	Chiefly a study of migrational behaviour. Separations not given.	72, 73
Cu, Cd, Hg (II), Pb, Bi	1, 2, and 4 N H Cl	Excellent separations, but the high conductivity means that much heat is produced	74

Cu, Cd, Hg (II), Pb, Bi	K Cl, K Br, and HB r at various concentrations	Best separation in 0.5 N K Br, or 0.5 N H Br. As above, high conductance causes much heating, but separations in less than 1 hr are possible. Much information given about the behaviour of halide complexes	75
Cu, Cd, Hg (II), Pb, Bi		One-and two-dimensional separations	56
Cu-Ag; Cd-Ag-Bi-Al; Tl (I) - Al; Tl (I)-Al-As (III)	0.01M EDTA in 1M NH_4 OH. 0.05 M ammonium malonate. 0.05 M citric acid; and others	Continuous separations	57
Cu, Cd, Pb, Co, Fe (III), Fe (II)	2 N acetic acid - 0.6N Formic acid	See section (c)	55
Bi, Pb, and Groups (b) and (g)	HF and HF-HCl mixtures	See section (b)	38
Cu-Ni	0.1M lactic acid	Used for quantitative analysis after elution	61
Cu-Cd	aqueous acetic acid-pyridine	Cd fasterthan Cu	76
Ag-Pb-Hg(II); Cu-Cd-Pb-Bi-Hg(II).		Discontinuous electro-chromatography	27

Ag - Ni; Cu-Ni; Hg(I)-Pb-Ag; Hg (II)-Ag; (Hg-Bi)-(Cu-Pb-Cd); Ni-Ag-Cd-(Cu-Co-Fe)	Many	Discontinuous electrochromatography. Ions in bracket formed overlapping zones	62
Cu-Ag-Ni-Fe	A basic tartrate-oxalate mixture. Others also used	Continuous electrochromatography. The electrolyte given separated all	62
Cu, Cd, Bi, Ag, Pb, Hg (II)	0.007 M citric acid in 5 N NH_4 OH, and others	Electromigration, and discontinuous electrochromatography. Ions of groups (a), (c) and (e) considered also	21
Cu from Pd and Pt	1N HCl	Cu is cationic, others anionic	77
Pb - Bi - Po-Ra	0.1M lactic acid	Separation of Ra decay products - including RaD, E and F Bi is adsorbed near the starting point, Po moves slowly as an anion. Po, Bi zones overlap somewhat	25, 28

Separation of some precious metals from some of these ions has been given by Mukerjee (63, 64, 65) (See group (f)). Separation of Zn and Mn from these ions is given in (49), and As, Sb, and Sn, from the copper group in (50). Separation of Cu from Fe (II), Ni, and Co was given in (58).

(e) The Arsenic Group (As, Sb, Sn)

This group of ions has been fairly well studied. For some separations involving separation of the oxyanions of these ions ($AsO_4^=$ for example) from other common anions, see section (l).

Sb, Sn, As, Cd	0.05 M Citric acid, pH 5.5	Also considered many other ions of groups (b) (c), (d), and (g)	17
Sb - Sn		Group (c) ions and Au, Pd, and Pt also considered	45
Sb- Sn	1 N H Cl	Also separated As from Cu and Hg (II), and Au, Pd, Pt.	67
As, Sb, Sn	Many	Separated in pairs. All three ions could not be separated in one run	69
S b (V), Sn (II), Al (III), Cr(III)	0.1M ammonium tartrate - 4 N NH_4OH	Complete separation in 4 hrs. at 4 v/cm	54
As (III), Sb (III) Sn (II)	0. 1 M triethanolamine- 0. 1M ammonium tartrate		24
As, Sb, Sn, Ag, Pb, Cu, Bi, Cd, Zn, Ca, Ni	Many	Separation of binary and ternary mixtures of these ions	30

As, Sb, Sn	0.02 M lactic acid - 0.02 tartaric acid- 0.04 M alanine, and others	Discontinuous and continuous electrochromatography	62
As, Sb, Sn		Discontinuous electrochromatography	27
As(V), Sb(III)	0.007 M citric acid - 5 N NH_4OH, and others	Also considered ions of groups (a), (c) and (d)	21
As, Sb, Pt, Pd, Ru, Au	Many	Chiefly a separation of As and Sb from the rest. It is claimed here that Sn cannot be separated from the Pt metals by electromigration because of chemical interaction.	42
As, Sb, Sn, Al, Fe (III), $CrO_4^{=}$	$Na_4P_2O_7$ - HCl, pH 2.4		24

Garrison et al separated radioactive arsenic in carrier-free form from a $Cu(OH)_2$ precipitate by electromigration in a stack of filter-paper discs (78). Maki has separated Sb (III) from Ni, Cu, and Fe (III), using solutions of complex phosphates as background electrolytes (26).

(f) The Platinum Metals (Ru, Rh, Pd, Os, Ir, Pt) and Au

This group has been quite thoroughly investigated by a few workers. Complicated behaviour may occur in some systems - for example, Sato reports that Ru (III) forms as many as 8 zones in 0.1 M lactic acid (28).

Pt (IV) Pd (II), Rh (III), Ir (IV)	EDTA solutions of various pH values	In 0.1M EDTA at pH9, complete separation of all 4 in 45 min. at 15 v/cm. Rh (III) precipitated at starting point; Pd, Pt move in that order toward anode.	79, 80
Pt (IV)-Pd(II); Pd(II)-Ir(IV); Rh (III) Ir (IV); Rh(III)-Pt(III); Rh(III)-Pd(II)-Ir (IV)	Various EDTA solutions	Continuous electrochromatography. Separations as shown	79, 80
Pd(II), Pt(IV), Ir (IV), Rh(III), Ru (III), Os (IV), Au (III)	Several	Separations of quaternary mixtures studied	81, 82
Pt, Pd, and ions of groups (c) and (d)	Many	H Cl and sodium citrate best electrolytes. Separations chiefly of binary mixtures	63
Ru (III), Pt, Pd, and ions of groups (c) and (d)	Many	Ru (III) separated from Pt and Pd in KCN, $NaNO_2$, and H Cl. Separation of Ru (III), from binary mixtures with other ions also given.	64

Pt, Pd, Ru, Au., and some ions of groups (c) and (d)	Many	Au separated from Pt in KSCN and Oxalic acid, from Pd in KSCN, and from Ru in KCl and KSCN. Separation of Au from some ions of groups (c) and(d) also given	65
Os (IV) and Copper group ions	Many	Separation of Os (IV) from the others	42
Pt, Pd, UO_2, Fe (III)		Separation of UO_2 from the rest in binary mixture	42
Pt, Pd, Ru, Au, As, Sb		As, Sb separated from the rest in binary mixture	42
Pd, Au	IN Na Cl	Separation in agar gel Present as Pd Cl_2 , and Na Au Cl_4	66

Cu has been separated from Au, Pd, and Pt in H Cl(45, 67). It may be noted here that Lederer claims that Rh-Pt and Rh - Pd cannot be separated reliably by paper electromigration (83).

(g) Ti, V, Zr, Nb, Mo, Tc, Ta, W, Re

These elements are not easy to work with, but some very good studies have been made of a few systems.

Ti (IV), Zr (IV), Th (IV), Fe, (III), Al (III), Cr (III), UO_2 (II), Be (II)	Several	Separations of binary, ternary, and a few quaternary mixtures were made. Mobilities of these ions are generally low.	41
Ti (IV), Zr (IV), Ta (V), Nb (V), Pa (V), Fe (III), Bi (III), Pb (IV), Th (IV), Po (III), U (VI)	HF, and HF- H Cl mixtures of various concentrations	Zr - Pa - Fe; Zr - Nb; Zr - Pa - U- Th; and a few other separations are given	38
Ti (IV), Zr (IV), Ta (V), Nb (V), Pa (U), Fe (III), U (VI)	5% HF - 5% H Cl and 1% HF - 1% H Cl	Zr - Pa - U, and Zr - Pa, Fe separated	39
Mo (IV), V (IV), Ti (III), and elements of groups (a), (b), (c), (d) and (e)	0.05 M citric acid, pH 2.9 Other pH values also used	Other elements also studied, and some separated from this group	17
Ti, V, Mo	0.5N H Cl	Separated as the per - ions	84
Nb - Ta	Citric acid - potassium citrate, p H 3.42	In first electrolyte, Nb faster	85
	Oxalic acid-ammonium oxalate	Two zones, are formed by Ta in the second electrolyte; one coincides with Nb zone. This is a detailed study.	85
W - Mo	Oxalic acid of various concentrations and pH	MoO_4 = faster than WO_4 =	86

Nb - Ta	Sodium borate - Na OH in various proportions	Tantalate much slower than niobate. Separation accomplished in .01 M NaOH - .01 M $Na_4B_2O_7$ at pH 10.15, or in 0.01 M Na OH	86
$MoO_4^=$ $WO_4^=$ $Cr\ O_4^=$, and Cr^{+3}	0.1M ammonium citrate, and 0.1M lactic acid	Cr^{+3} - $CrO_4^=$; $CrO_4^=$ - W $O_4^=$; Cr $O_4^=$ - Mo $O_4^=$ separated in ammonium citrate. Lactic acid gave best separation of $MoO_4^=$ and $WO_4^=$	87
Tc - Re and Tc - Re - Mo	Hydrazine sulfate - hydrazine hydrate, pH 9;	TcO_4^- and ReO_4^- have similar mobilities. These electrolytes reduce Tc (VII) to Tc (IV) without affecting Re (VII)	88
	1% Sn Cl_2 in 1 M H Cl;	In first electrolyte, Tc (IV) slow but cationic, ReO_4^- anionic. Mo $O_4^=$ also separated here (faster than ReO_4^-)	
	0.1M HBr; 1M HI	In second electrolyte, Tc cationic, Re streaks as anion	
		Tc is cationic, Re anionic in the last two	

Garrison et al separated carrier-free Nb from a Mn O_2 precipitate, and Nb and Zr from Y and rare earths, by electromigration in a stack of filter-paper discs moistened with 1 M ammonium oxalate (78).

h) Inorganic Ions of N, P, S, Se, Te

Section (i) will deal with phosphates, sulfates, and others when considered in relation to other common anions. It will also cover CN^- and SCN^-.

NH_4^+, $N_2H_6^+$, NH_3OH^+, NO_3^-, NO_2^-, $N_2O_3^-$, $N_2O_2^=$	0.001 N H_2SO_4 Na_2SO_4 - Na OH Na_2SO_4- Na OH- Fe $(OH)_3$ Na_2SO_4 - Ag_2SO_4	A mixture of all of these could be resolved in 3 runs	89
$S^=$, $S_2O_3^=$, $SO_3^=$, $SO_4^=$	8 N NH_4OH		90
$S_3O_6^=$, $S_4O_6^=$, $S_5O_6^=$	1% sodium potassium tartrate	Continuous electro-chromatography	60
$SeO_3^=$ - $TeO_3^=$	0.5N H Cl		91
$SeO_3^=$, $SeO_4^=$, $TeO_3^=$, $TeO_4^=$	O.IN H_2SO_4, and o.4 N Na_2SO_4	Mobilities: $SeO_4^= > SeO_3^= > TeO_3^= > TeO_4^=$ Complete separation in 3 hours at 7.5 v/ cm in latter electrolyte	92
$S_2O_3^=$, and di-, tri-, tetra-, penta-, and hexa-thionate ions	A phthalate electrolyte	Mobility decrease with increasing number of S atoms	93
Thiosulfate, Tri-, tetra-, and pentathionates, seleno-and tellurodithionates and tetrathionates	As above	Se lowers the mobility with respect to the corresponding S compound; Te lowers it still more	94

Sulfite, thiosulfate, and other photographic reducing agents	Citric acid - phosphate mixture of pH 7		95
SO_4^{-2} - PO_4^{-3}	0.5N HCl	Separation of "carrier-free" radioactive materials	91
$H_2PO_4^-$, HPO_4^{-2}, PO_4^{-3}	Phosphoric acid	A comparison of mobilities	96
Oxyacid anions of phosphorus	0.1M acetic acid, and 0.1M lactic acid	long (2 m.) migration paths. radioactive species employed. Used also for identification.	97
Various polyphosphate ions	borax - H_3BO_3- NaCl buffer of pH 8.5	trimeta-, tetrameta-, mono, di-, tri-, and tetra-phosphates, and others from commercial preparations	98
Various condensed phosphate ions	a number of buffer solutions at various pH values		99
Various condensed phosphate ions	NaOH - borate buffer, and others	A high voltage technique. mono-, di-, tri-, trimeta-, tetrameta-phospates, among others, were separated	100
Condensed phosphate ions	sodium borate - NaOH, pH 10	Continuous electrochromatography	101
Phosphate - Silicate	Sodium borate - NaOH, and others	Silicate slower than phosphate	86

(i) Some Common Anions

Some metal anions such as $CrO4^{=}$ also appear in references listed in their respective sections. Phosphates are treated here in relation to other common anions, but separation of various phosphate ions from one another is covered in section (h).

PO_4^{-3}, CNS^-, Cl^-, Br^-, and cations	ethanol - acetic acid - ammonium acetate	Discontinuous electro-charmatography. Most of the separation is due to chromatographic effects; electromigration separated only the anions and cations	22
Cl^-, Br^-, I^-	0.1 to 2.5 M lactic acid	Discontinuous electro-chromatography	102
BrO_3^- - Br^-; IO_3^- - I^-; AsO_3^- - $AsO_4^{\equiv}$	0.01 M Na OH	Separation of products of Szilard - Chalmers reactions	103
PO_4^{-3}, AsO_3^-, AsO_4^{-3}	1M formic acid	Other anions of groups 2 and 3 also studied	90
$Cr_2O_7^{-2}$, PO_4^{-3}, CNS^-, $Fe(CN)_6^{-3}$, $Fe(CN)_6^{-4}$	0.5 M lactic acid	$Cr_2O_7^{-2}$ decomposed during migration	104
$Fe(CN)_6^{-4}$ - $Fe(CN)_6^{-3}$.	0.5N H Cl	Separation in 50 min at 5 V/cm	91

$Fe(CN)_6^{-4-}$ $Fe(CN)_6^{-3}$	0.1N K Cl		46
PO_4^{-3}-SO_4^{-2}	0.5N H Cl	Separation of "carrier-free" radioactive material	91
Phosphate-silicate	Sodium borate - NaOH, and others	Silicate slow	86
ClO_3^- - BrO_3^- - IO_3^-; ClO^- - ClO_2^- - ClO_3^-		Separation of 1st 3 in 50 min., 2nd 3 in 30 min. at 40 v/cm Mobilities $IO_3^- < BrO_3 < ClO_3^-$ $ClO_2^- < ClO_3^- < ClO^-$.	105

Mach has used electromigration in paper to check the radiochemical purity of solutions containing radioactive P, S, Cl, and I (29).

(j) Separation of Metal Complex Ions

A number of workers have used electromigration in paper to separate various complex ions of some metals, and others have used it to investigate the behaviour of a metal ion in complex-forming systems. The latter will not be dealt with here.

Kawamura et al (106, 107, 108) have studied the qualitative and quantitative separation of chromium complexes this way. Separations of $[Cr(H_2O)_6]^{+3}$, $[Cr(H_2O)_4(C_2O_4)]^{+}$ $[Cr(H_2O)_3(C_2O_4)(OAc)]$, $[Cr(H_2O)_2(C_2O_4)_2]^{-}$

$[Cr(C_2O_4)_3]^{-3}$ and similar species with the ligands SO_4^{-2}, SCN^-, and NH_3 were made. A good separation was achieved in 0.33 N $HClO_4$ in 1 hr. at 13 v/cm. Distances moved were proportional to the charge on the ion.

Maki has separated some complexes of Cr (III) in an H Cl - K Cl electrolyte (109). At 4 v/cm., 2.5 hrs. were required to separate $[Cr(H_2O)_4\ Cl_2]^+$, $[Cr(H_2O)_5\ Cl]^{+2}$, and $[Cr(H_2O)_6]^{+3}$.

Under similar conditions, Cr 2 (SO4) 3 can be separated into the species $[Cr(H_2O)_6]^{+3}$ and $[Cr(SO_4)]^+$.

Shuttleworth has investigated sulfate complexes of Cr (III) by electromigration in 0.05 N HNO_3 (110), while Kertes and Lederer have studied these complexes using S^{35} as tracer. (III). The kinetics of complex formation was followed in this way.

Bighi and Trabanelli (112) separated the complex ions $[Co(NH_3)_6]^{+3}$, $[Co(NH_3)_5\ Cl]^{+2}$ $[Co(NH_3)_4(NO_2)_2]^+$ and $[Co(NH_3)_3(NO_2)_3]$ as well as similar Cr (III) species, by continuous electrochromatography in 0.25% NH_4Cl.

Maki (113,114) has separated the ions $[Co(NH_3)_6]^{+3}$, $[Co(NH_3)_5\ NO_2]^{+2}$ cis and trans $[Co(NH_3)_4\ (NO_2)_2]^{+}$, $[Co(NH_3)_3(NO_2)_3]$, $[Co(NH_3)_2\ (NO_2)_4]^{-}$, and $[Co(NO_2)_6]^{-3}$ by a discontinuous strip technique in a chloride solution.

Rauscher and Harbottle (115) separated the complex species $[Co(CN)_6]^{-3}$, $[Co(CN)_5\ H_2O]^{-2}$, $[Co(CN)_4\ (H_2O)_2]^{-1}$, and $[Co(CN)_4\ (NH_3)_2]^{-1}$ as well as Co^{+2} in an acetate buffer. These were products of the Szilard - Chalmers reaction in potassium cobalticyanide, and the method was used as an aid in identifying the species as well as estimating their relative amounts.

(k) Separations of Particular Radiochemical Interest

A number of separations have been made which are of particular interest in one or another branch of radiochemistry. The earliest of these is the separation of "carrier-free" activities from precipitates of other elements in a stack of filter-paper discs moistened with a suitable electrolyte, made by Garrison et al (78) . Elements separated include Nb from MnO_2, and Nb and Zr from Y and the rare earths in ammonium oxalate solution, and As from

$Cu\ (OH)_2$ in H Cl. Other separations of interest include that of Ra D, E, and F by Sato et al (25, 28), the separation of "carrier-free" $P^{32}O_4{}^{-3}$ and $S^{35}O_4{}^{-2}$ from one another by Lederer. (91), and the separation of Ca^{45} from $P^{32}O_4$ from each other and from other radioactive contaminants, by continuous electrochromatography by Sato et al (116). Schumacher has also used his focusing technique to separate "carrier-free" radioactive materials (3).

Separations of the products of Szilard-Chalmers reactions in potassium cobalticyanide have been made by Rauscher and Harbottle (115), and these separations, as well as those of the products of similar reactions in alkali bromates and iodates, and in arsenic pentoxide, have been described by Jach, Kawahara, and Harbottle (103). Sato et al have done analogous work with phosphates (117).

Mach has used electromigration in paper to estimate the radiochemical purity of P^{32}, S^{35}, Na^{22}, K^{42}, Rb^{86}, I^{131}, and Sr^{90}, and recommends it as a routine method for such purposes (29).

Finally, Zimakov et al (118) have used this method to determine quantitatively all of the ions of Ce, Y, Sr, Zr, Nb, Ru, and Cs in a solution of fission products. By carrying out electromigration in 0.1N H Cl, 0.1N NaOH, and 2% $K_4\ Fe\ (CN)_6$ electrolyte solutions, and using standardized techniques for measuring various sections of the strips, one can obtain quantitative estimates of each of these substances rapidly.

(1) Miscellaneous

The separation of isotopes by electromigration procedures has been studied by a number of workers. This has been treated in a recent review by Chemla (119), and will not be discussed further.

Maki has used the zone length to give a method of quantitatively estimating Ba and Al. With proper standardization, the estimation was accurate to within 10% over the range of 150 to 1500 micrograms of Ba, and 25 to 500 micrograms of Al (120). Others have eluted the separated substances from the strip for analysis by standard methods. Schumacher also has adapted his technique for quantitative analysis (5).

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