CATIONIC EQUILIBRIA IN SELECTED SOILS AND SOIL MATERIALS

by

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ABSTRACT

The relationship between exchangeable potassium and AR_e^K was studied for four agronomically-important soils of the O.F.S. Region and two commercial clays. Some attention was also given to the Q/I and Gapon relationships for these soils and clays. The effects of some factors, e.g. sodium level and clay:solution ratio, on these parameters were also investigated.

Linear relationships between K_{ex} and AR_e^K were found for all soils and clays used. In most cases the graphs relating K_{ex} to AR_e^K had intercepts different from zero. At extremely high levels of K saturation in bentonite the slopes of the graphs changed and different linear relationships were obtained, the slopes of the upper portions being lower than those of the lower portions.

At high K_{ex} levels a fairly good numerical similarity between $-\Delta K^o$ and K_{ex} was found in most cases. At K_{ex} levels near EK^o, i.e. that level of K_{ex} where AR_e^K becomes zero, $-\Delta K^o$ decreased relative to K_{ex}. At these low K_{ex} levels $-\Delta K^o$ was therefore not a good indication of K_{ex}.

PBC^K proved to be a very constant property of a soil or clay, being unaffected by most experimental conditions and by level of K saturation. The PBC^K values of these soils were very low. PBC^K of bentonite was strongly influenced by clay:solution ratio when ΔK values were expressed as me per 100g clay.

Increased sodium levels changed the relationships between K_{ex} and AR_e^K, but did not cause poorer relationships between these two parameters. The magnitude of the effect of sodium was a function of the amount of sodium brought into the system and the latter was largely a function of the CEC of a soil.

CHAPTER 1

INTRODUCTION

1.1 GENERAL

In soil fertility studies it is of the greatest importance to obtain a realistic way to describe a soil's power to supply any specific plant nutrient to plants over short and over longer periods of time. Thus far only limited success has been achieved for most nutrient elements in this respect.

The main problem seems to be that any given plant nutrient in the soil is incorporated in a wide range of different chemical compounds and that a dynamic equilibrium exists between these chemical compounds. Contributions of different chemical forms of the element to its so-called "plant-available" fraction vary greatly. Furthermore, when a given amount of the element which occurs in a form is removed by means of either chemical extraction or extraction by plant roots, this loss is compensated by replenishment from other forms. The degree and speed of replenishment vary for different soils and for different soil conditions. Both the speed and the degree of replenishment of the plant-available fraction influence the power of the soil to supply the specific element to plants growing in that soil. These differences in replenishing power further complicate the problem of determining the "plant-available" fraction of any given element in soils.

Other factors, such as poor soil physical conditions, may also influence the uptake of nutrient elements by plants. Shortages or excesses of other essential elements will also affect the quantity and concentration of a given element in the plant. In studies on the "plant-available" fraction of an element it is assumed that care is taken that all these other factors are at an optimum and will not have a significant effect on the obtained results. Also, if any of these abnormalities occur under field conditions it must be corrected for before any other steps are taken. As far as the supplying power of a soil for any specific element is

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concerned, there seems to be four important aspects which must be taken into consideration. These are:

1. The power of the soil to supply in the plant's needs at any specific moment.

2. The power of the soil to keep on doing this throughout the growing season.

3. The power of the soil to recover its original supplying power before the start of the next cropping season.

4. The power of the soil to keep on doing this for a large number of years.

Plant roots feed mainly from the soil solution. The immediate power of a soil to supply a given nutrient to a plant at any given moment will therefore be closely related to the concentration, or rather the activity, of the ions of that nutrient in the soil solution at that moment. The speed, or intensity, of nutrient supply to and uptake by plant roots will thus be governed by the activity of the ions in the soil solution.

In most soils the actual concentration (or activity) of any plant nutrient in the soil solution at any given moment is very low and will be depleted totally within an extremely short period if it is not replenished at a fast rate from some other source. Under soil conditions this fast replenishment occurs from those forms of the nutrient which are in immediate equilibrium with the soil solution. Those forms which are in immediate equilibrium with the soil solution constitute the so-called "labile pool" of the element in the soil.

Because of the quick and dynamic equilibrium which exists between the labile pool and the soil solution, the concentration of a given nutrient ion in the soil solution at any given moment will be governed by the amount in the labile pool. It can thus be stated that the intensity of nutrient supply at any given moment will be governed by the quantity in the labile pool because of its influence on the composition of the soil solution.

For phosphorus the labile pool in the soil can be determined radio-isotopically by means of the L-value technique (Russell & Marais, 1955). The S-value of the soil can be determined by shaking a given amount of soil with a solution containing a specified phosphorus concentration (Marais, 1955). The quantity of phosphorus which the soil sorbs from the solution is the so-called S-value. Laker (1964) determined L- and S-values and phosphorus uptake by plants from limed and unlimed plots on an acid soil from Outeniqua Experimental Farm near George. It was found that lime caused a large increase in phosphorus uptake, but did not increase the L-value of the soil. The citric acid soluble phosphorus content of the soil was also not increased. The S-values of the limed plots were, however, considerably lower than those of the unlimed plots. This means that the solution in equilibrium with the limed soil had a higher P concentration than that of the unlimed soil.

For a very sandy soil from the North-western Orange Free State Laker (1964) also found a very low S-value despite an extremely low L-value and citric acid soluble phosphorus content. Marais (1955) and Russell, Tukey & Wittwer (1955) found no constant relationship between plant uptake of phosphorus and L-values. In all cases of abnormally low phosphorus uptake accompanied by high L-values, the soil had very high S-values. Marais and Laker (unpublished discussions) concluded that the labile pool alone is not sufficient to describe the short term phosphorus supplying power of a soil, but that two factors, a capacity factor and an intensity factor, are needed. The L-value seems to give the capacity factor and the S-value seems to indicate the intensity factor, a low S-value indicating high intensity.

It thus seems that, although the capacity factor or labile pool governs the composition of the soil solution, and hence the intensity factor, the relationship between these two components is influenced by so many factors that any one of these two alone will not be sufficient to fully describe the soil's power to supply the specific nutrient at any given moment.

For the nutrient cations, e.g. potassium, the labile pool is usually considered to be identical to the exchangeable fraction (e.g. Beckett, 1964b). Burger (1955) stated that: "It has been established that the exchangeable potassium content of a soil governs the immediate supply for plants at any given moment." He found no definite relationship between exchangeable potassium and water soluble potassium for a number of soils. This is not unexpected as the relationship between exchangeable potassium and potassium in the soil solution is affected by various factors. The most important of these are the properties of the soil's colloidal fraction and the composition of the complementary ions (Wiklander, 1955).

Burger (1955) defined water soluble potassium as that amount which occurs in soluble form under normal field conditions and which is relatively unbound by cation exchange forces. The normal procedure for determining water soluble ions in a soil is to extract the soil with water at some arbitrary soil: solution ratio. This cannot be taken as an indication of the activity of the ions under field conditions. Both Burger (1955) and Wiklander (1955) indicated that the relative relationship between the adsorbed and dissolved ions is changed by mere dilution. This led Wiklander (1955) to state that it is not feasible to shake a soil with water for the determination of the free salts originally present.

Schofield (1947) examined "a ratio law applicable to the equilibrium between the exchangeable cations of a soil and the cations dissolved in the soil solution." He defined his now well-known Ratio Law as follows: "When cations in a soil solution are in equilibrium with a large number of exchangeable ions, a change in the concentration of the solution will not disturb the equilibrium if the concentrations of all the monovalent ions are changed in one ratio , those of all the divalent ions in the square of that ratio and those of all the trivalent ions in the cube of that ratio."

Schofield (1947) percolated soils with solutions containing cations in different proportions. By means of trial and error a certain solution could be found that suffered little change upon percolation. This indicated an equilibrium between the soil solution and the soil's exchange complex, and it was assumed that the ratio between the cations in this percolating solution was identical to their ratio in the soil solution. This would, of course, give no indication of the actual concentration of each cation in the original soil solution. He also pointed out that the Ratio Law is valid "only for a soil containing no positive charges, or at least an overwhelming preponderance of negative changes."

Beckett (1964a) stated that the validity of Schofield's Ratio Law had not been confirmed experimentally for more than a few soils prior to 1964. In later studies made on approximately 40 different soils by himself and others, he proved (1964a) that Schofield's Ratio Law was valid for the ion pair K-(Ca+Mg). He also found that, for the purpose of the Ratio Law, Ca and Mg behaved identically and that they could be taken as a single ionic species.

Beckett (1964a) made an important contribution by devising an experimental procedure to obtain the equilibrium activity ratio for the ion pair K-(Ca+Mg) without relying upon trial and error methods. This procedure consists of shaking a number of samples of a soil with a series of solutions containing equal (Ca+Mg) concentrations but different K concentrations. When the ratio $K/\sqrt{Ca+Mg}$ in the shaking solution is too high the soil will withdraw K from the solution. Conversely the soil will release K to the solution. The amount of K withdrawn or released will be proportional to the difference between the activity ratio of a shaking solution and that of the soil solution. After plotting the amounts of K lost or gained against the ratio $K/\sqrt{Ca+Mg}$ in each equilibrium solution the equilibrium activity ratio $K/\sqrt{Ca+Mg}$ of the soil solution can be obtained by interpolation. The equilibrium activity ratio of the soil solution is the activity ratio where the soil neither looses nor gains potassium.

It must be emphasized again that the Ratio Law gives no indication of the actual activity of the potassium ions in the soil solution under field conditions, but only of the relative activity of potassium to the square root of the activity of calcium+magnesium. From a practical point of view this is not too great a disadvantage since a knowledge of the ratio between the different cations is perhaps more important in plant nutritional studies than a knowledge of the actual concentration of each cation. Since Ca+Mg constitutes by far the greatest proportion of the cations in most soils, the ratio of K to Ca+Mg is a determinative factor in the availability and uptake of potassium.

1.2 THE Q/I CONCEPT

After describing his method for determining the activity ratio $^{a}K/\sqrt{^{a}(Ca+Mg)}$ of the soil solution in equilibrium with the exchangeable cations, Beckett (1964a,b) concluded that the equilibrium activity ratio (or AR_e^K) satisfactorily describes the potential of the labile K in a soil or the availability of K to plants. He stipulated, however, that it only applies to soils in which calcium and magnesium are the dominant cations. He qualified this statement by remarking that: "AR_e^K is a measure of the 'intensity' of labile K in the soil. Different soils exhibiting the same value of AR_e^K may not possess the same capacity for maintaining AR_e^K while K is removed by plant roots. So to describe the K status of a soil we must specify not only the current potential of K in the labile pool but also the form of the quantity-intensity relation (Q/I relation) or the way in which the potential depends upon the quantity of labile K present."

According to Beckett (1946b) nearly all the labile K is in the form of exchangeable cations in field soils. The Q/I relation can therefore be described as the relation between the quantity of labile K, i.e. the quantity of exchangeable K (the quantity factor), and AR_e^K (the intensity factor). He quite rightly had the following intentions: "The aim of the work described here was to explore the form of the Q/I relations for a number of soils, by observing the changes in AR_e^K after small additions or removals of K, during periods too short for the mobilization of non-labile K, and in soil suspensions shaken well enough for there to be no diffusion gradients." A logical approach to this aim would consist of a series of experiments in which subsamples of each soil at different levels of exchangeable K were employed. The relationship between exchangeable K values and their corresponding AR_e^K values, determined by interpolation on the appropriate graphs, could then be found. Beckett (1964b) failed to pursue his original intentions. Instead he did not distinguish between AR^K and AR_e^K and between ΔK (the amount of K gained or lost by a soil shaken with solutions not in equilibrium with the soil solution) and exchangeable K. He actually determined only one AR_e^K value for each soil. Figure 1 of Beckett (1964b) illustrates this. He states:"Fig. 1 indicates how AR^K in the soil solution depends on the exchangeable K content of the LGS soil."

This statement leads one to expect a graph of the form illustrated in Fig. 1. Beckett, however, represents a graph of the form illustrated in Fig. 2 (redrawn from Beckett, 1964b). This is merely a graph of ΔK against AR^K, the graph which was devised to determine the true equilibrium activity ratio (AR_e^K) of the soil solution. The amounts of K lost or gained by the soil (ΔK), when shaken with a solution of which the original activity ratio is not in equilibrium with the soil solution, is described as the "exchangeable K content" of the soil. The properties of the latter are ascribed to the former (Beckett, 1964b).

He further stated: "......... so Fig. 1 is a very close approximation to the relation between the amount of labile K in the field soil (the quantity factor) and AR^K (the intensity factor)." This implies that the gains or losses of K (ΔK) are the quantity factor. It is not stated which one of the 57 ΔK values plotted in the figure represents the actual quantity of labile K in the field sample of the LGS soil.

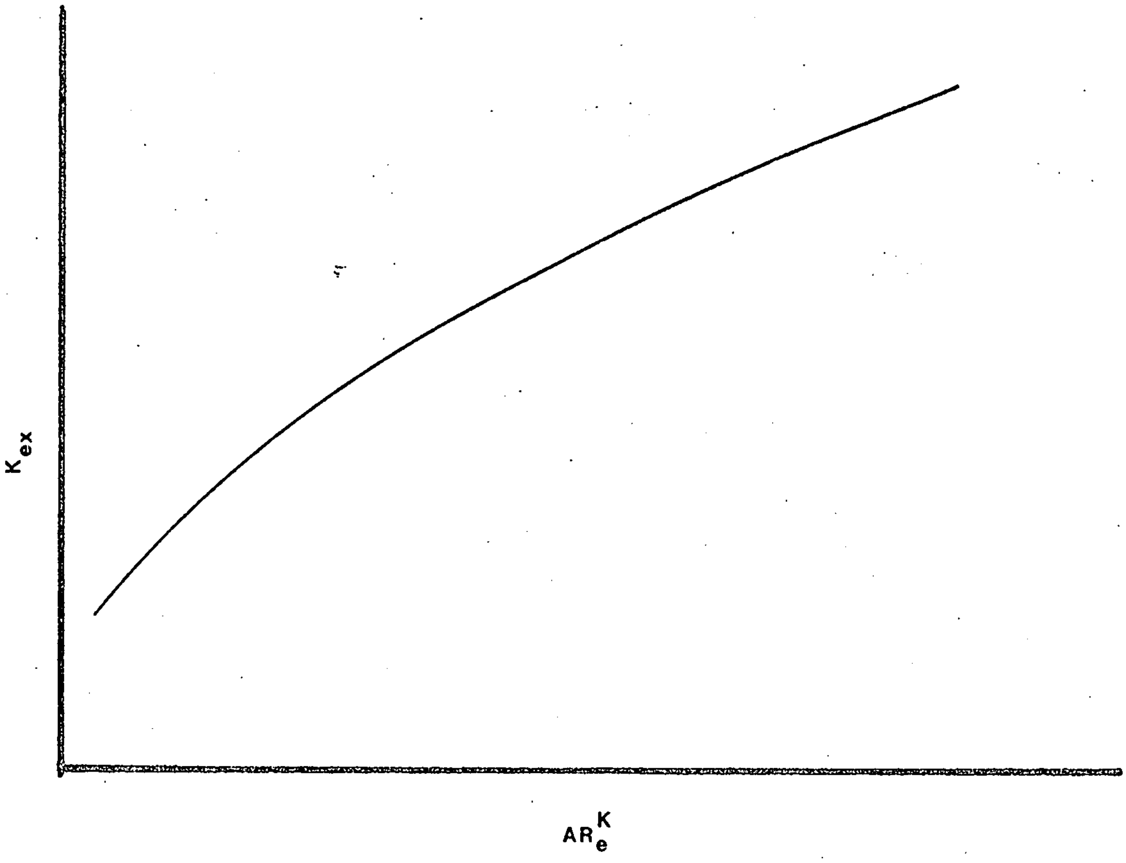

FIG. 1 Expected Q/I curve.

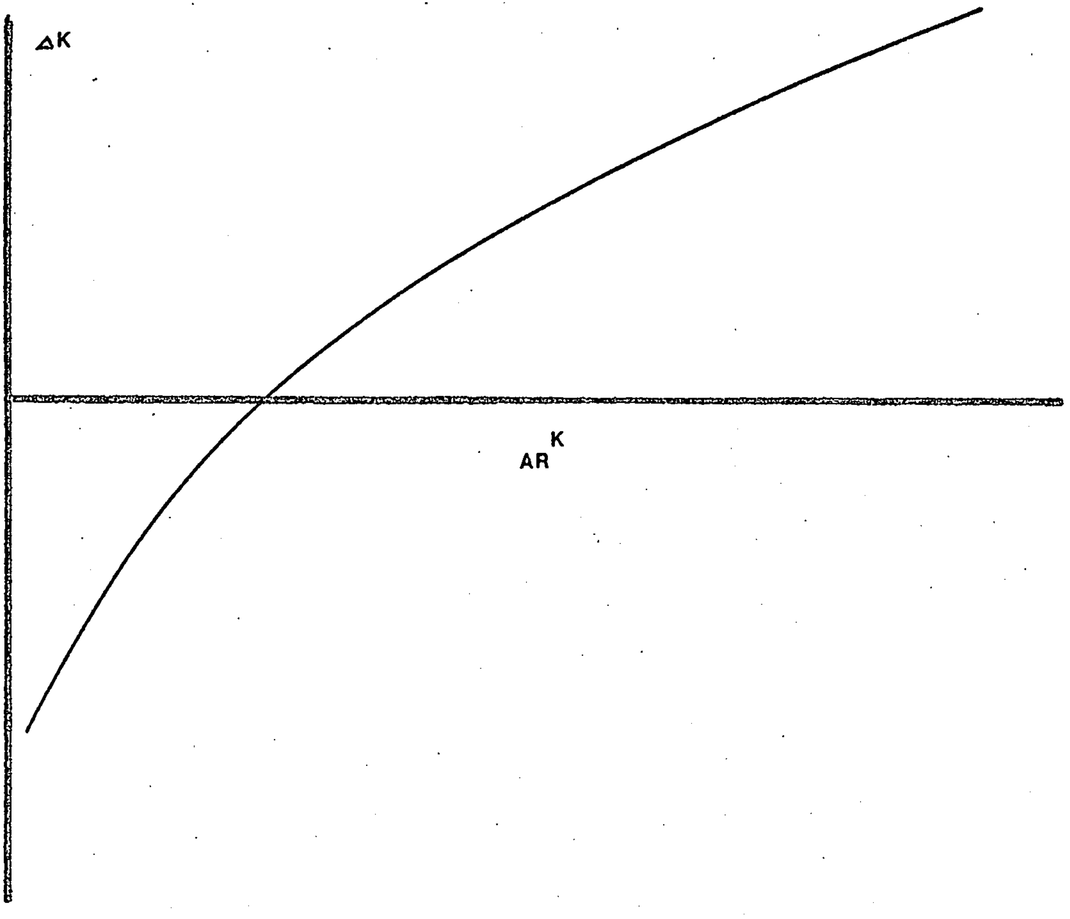

FIG. 2 Given Q/I curve.

Furthermore Beckett (1964b) stated that AR^K is the intensity factor. Fact is that AR^K can be changed simply by changing the potassium activity ratio of the equilibrating solution. If it is accepted that the equilibrium activity ratio of the soil is the intensity factor, AR_e^K (and no other AR^K value) is the only value which can be called the intensity factor. Beckett's aim to determine "....... the changes in AR_e^K after small additions or removals of K ...." was therefore not realised in his initial experiments. The reasons for this departure from his original aim are not clear.

If it is accepted that $-\Delta K^O$ (the value of ΔK where AR^K becomes zero) represents the quantity of labile K in the soil, then Beckett (1964b) determined the intensity of potassium supply (AR_e^K) for one specific quantity of labile K ($-\Delta K^O$) for each soil. He did use a Natal soil which received three K levels in one experiment, but did not comment very much about it.

It has already been pointed out that Schofield's Ratio Law (Schofield, 1947) does not enable one to determine the actual potassium concentration of the soil solution, but only the equilibrium ratio between potassium and the major cations, calcium and magnesium. As AR_e^K describes this equilibrium ratio the statement about Schofield's Ratio Law is also fully applicable to AR_e^K.

Beckett (1964b) also introduced another factor, viz. the "potential buffering capacity" or PBC^K. PBC^K is given by the slope of the graph which describes the relationship between ΔK and AR^K. According to Beckett (1964b) PBC^K "measures the amount of labile K that can be removed before AR^K falls by more than a given amount." It is really meant to indicate the ability of a soil to maintain a high potassium potential, that is a high intensity for supplying potassium (a high AR_e^K), when potassium is removed from the labile pool of the soil.

It must be kept in mind that the Q/I parameters (AR_e^K, $-\Delta K^O$ and PBC^K) are all properties of the labile pool which

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indicate the relationship between capacity and intensity in the labile pool. This is not meant to indicate the relationship between labile and non-labile K in a soil. The Q/I parameters are therefore expected only to indicate the potassium supplying power of a soil at a given moment or at most over relatively short periods (Beckett, 1964b). These parameters are not indicative of the long-term potassium supplying power of a soil.

Beckett's (1964a) conditions for the determination of Q/I relationships must be emphasized, the most important being:

1. The concentration of the soil solution must not be high enough for anions to penetrate the inner part of the double layer.

2. The exchange surface must not bear a significant proportion of positive charges.

3. All soils must have a comparable (Ca+Mg) status.

4. Ca and Mg must be the dominating exchangeable cations.

1.3 PURPOSE OF THE PRESENT STUDY

From results previously obtained in studies on phosphorus uptake (Laker, 1964) the author was convinced that the ability of a soil to supply a plant nutrient must be described by two factors, viz. a capacity factor and an intensity factor. It was also reasoned that the actual quantity of a nutrient in the labile pool would supply the capacity factor or quantity factor.

The Q/I concept of Beckett (1964b) provides a means to measure the quantity and the intensity factors. This quantity/intensity approach is undoubtedly of such potential usefulness that it deserves to be developed into the form that Beckett (1964b) originally intended. The first object of this study was therefore to obtain some information about the relationship between the quantity of exchangeable potassium and AR_e^K for a number of soils and clays. It was imperative to make certain other comparisons of factors like PBC^K and ΔK also.

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During the past few seasons large numbers of analyses done in the Department of Soil Science at the University of the Orange Free State (unpublished data) and at the Research Institute of the Orange Free State Region (unpublished data) showed exceptionally low potassium values in the leaves of sultana grapes suffering from "growth stunting disease" (groeistilstandsiekte) and cotton suffering from "red death" (rooidood). These low values could not always satisfactorily be accounted for by low exchangeable potassium values or by poor soil physical conditions, although both of these had significant effects. Three of the soils used in the present study are from the western irrigation areas. The potassium Q/I relationships of these soils may provide a means to an understanding of their potassium supplying power. The above mentioned "diseases" are of considerable economic importance.

Since sodium often occurs in significant amounts in these irrigated soils, the effect of this element on their Q/I relationships was also investigated.

It must be noted that the different experiments were conducted at different constant temperatures. This was an inevitable consequence of the fact that the Department of Soil Science does not have a constant temperature room at its disposal and that constant temperature facilities of other departments had to be used.

CHAPTER 2

THE RELATIONSHIP BETWEEN EXCHANGEABLE POTASSIUM AND AR_e^K FOR A TOPSOIL OF THE MANGANO SERIES

2.1 PURPOSE

In the previous chapter it was shown that the Q/I concept of Beckett (1964b) might prove very useful for describing the short term potassium supplying power of soils. The purpose of the present experiment was therefore to pursue Beckett's (1964b) proposal, viz. to vary the exchangeable potassium content of a specific soil and to determine Q/I relationships at these different potassium levels in order to note the effect on AR_e^K.

Beckett (1964b) also postulated that PBC^K will decrease as the potassium content of a given soil is increased. This statement could therefore also be verified for the soil which was used.

Only one soil was selected in order to ascertain whether the experimental procedures would give satisfactory results. The results were also to indicate what general patterns could be expected from subsequent experiments.

2.2 MATERIALS AND METHODS

2.2.1 The soil

The top soil of a profile of the Mangano series from Vaalharts was used. This is a fersiallitic loamy fine sand soil, occurring extensively on the Vaalharts Irrigation Scheme. Some properties of the soil are listed in Table 1.

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TABLE 1 - Some properties of the Mangano soil sample

CEC me %	pH (2:5 water)	Particle size distribution			
		Coarse sand %	Fine sand %	Silt %	Clay %
4.90	7.1	14.1	75.9	1.0	10.7

TABLE 2 - Ratios of potassium saturated: calcium saturated soil in the soil mixtures

Mixture no.	Potassium soil	Calcium soil
A	25	75
B	20	80
C	15	85
D	10	90
E	Original field soil	
F	0	100

TABLE 3 - Equilibrating solutions for determining AR_e^K

No.	Weight of soil (g) in 100 ml solution	KCl concentration in soln. (me/litre)
1	10	1.0
2	10	0.8
3	10	0.6
4	10	0.4
5	10	0.2
6	10	0
7	5	0
8	1	0

All solutions in 0.002 M $CaCl_2$

2.2.2 Preparation of the soil

To ensure that calcium would be the dominant exchangeable cation samples of the <2 mm soil were saturated with calcium and potassium respectively. Saturation was effected as follows: Into each of a number of 380 ml polythene sentrifuge tubes 100 g samples of soil were weighed, followed by addition of 200 ml of the appropriate saturation solution. Normal solutions of either $CaCl_2$ or KCl were used. The suspensions were shaken for 30 minutes in a mechanical shaking machine and left for another hour before centrifugation at 2000 r.p.m. The clear supernatant solutions were discarded. This procedure was repeated twice, but the suspensions were left over night before the final centrifugation. Excess soluble salts were removed by successive washings and centrifugation with 200 ml portions of 60% ethanol until chloride free by the silver nitrate test. These soil samples were brought over on to flat filter papers by rinsing with 60% ethanol and air dried. The air dry soil was then ground to pass a 2 mm sieve.

Samples of the calcium and potassium saturated soils were then mixed in the ratios shown in Table 2. The mixing was done as follows: The required quantities of each of the treated samples were weighed into glass sample bottles and their lids screwed on. The bottles were not filled more than half to facilitate good mixing and shaken for one hour in a mechanical shaking machine.

2.2.3 Determination of the Q/I parameters

From each of the soil mixtures (Table 2) six 10 g, one 5 g and one 1 g quantities were weighed into 250 ml Erlenmeyer flasks. To each set of samples the series of equilibrating solutions outlined in Table 3 were added.

In view of Beckett's (1964b) findings that the Q/I relationship is temperature dependent, the equilibration procedure was carried out in a contant temperature room at 27°C. The Erlenmeyer flasks were stoppered with rubber stoppers and left for one hour in order to attain

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the temperature of 27°C. The suspensions were then shaken mechanically for exactly one hour, immediately filtered into reagent bottles with ground-in stoppers and immediately stoppered after completion of filtration. Only then the filtrates were removed from the constant temperature room for further analysis. This means that the temperature of the suspensions were kept constant during the entire period in which the soil was in contact with the equilibrating solution.

Potassium, calcium and magnesium were determined in the filtrates and the ion activities were calculated according to a simplified Debye-Hückel equation (Maron & Prutton, 1958). The ΔK and AR^K values were calculated and a graph of ΔK versus AR^K was drawn for each of the six mixtures (A to F). The AR_e^K value of each mixture was obtained by interpolation or extrapolation, according to the method of Beckett (1964a,b). The $-\Delta K^o$ values were obtained by extrapolation of the linear parts of the graphs.

The exchangeable K content of each of the six mixtures (A to F) was determined by leaching with neutral IN ammonium acetate at a constant temperature of 27°C. Prior to leaching the bulk solution of IN ammonium acetate was left over night in the constant temperature room to attain the required temperature. Thus exchangeable potassium was also determined at the temperature at which the Q/I parameters were determined.

Potassium was determined on a Zeiss PF5 flame photometer and calcium and magnesium on a Techtron AA4 atomic absorption spectrophotometer.

2.3 RESULTS AND DISCUSSION

The series of Q/I curves obtained for the different mixtures containing varying exchangeable K levels are presented in Figure 3. From this figure the increases in AR_e^K values at increasing K_{ex} levels can be seen. The AR_e^K values obtained in this way were then used for further correlation studies.

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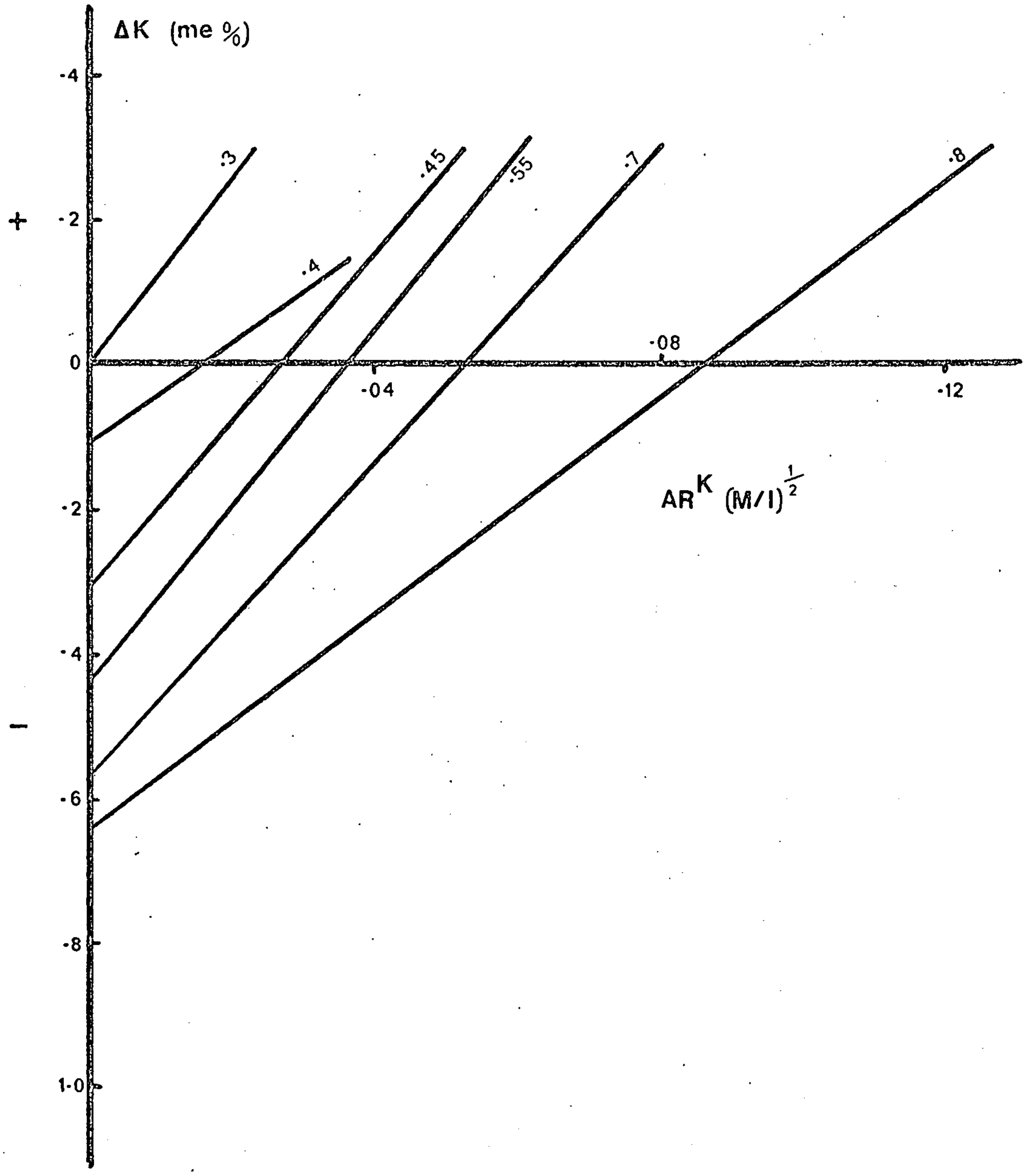

FIG. 3 Q/I relationships for the Mangano soil at different K_{ex} levels.

The values for exchangeable K and AR_e^K are given in Table 4. The relationship between exchangeable K and AR_e^K is shown in Figure 4. Figure 4 shows a linear relationship between exchangeable K and AR_e^K. AR_e^K becomes zero at an exchangeable K value of 0.32 me/100 g soil. With mixture F (Ca-saturated) an actual value of 0.00 was obtained. It can therefore not be argued that the line was extrapolated incorrectly and that the y-axis may be approached asymptotically at low AR_e^K values.

Beckett & Nafady (1967) found a linear relationship between AR_e^K and $K_{ex}:Ca_{ex}+Mg_{ex}$. They also found that the latter had a small positive value where AR_e^K became zero and stated that part of the potassium which was exchangeable with ammonium acetate did not contribute to the exchange equilibrium in the soil. Moss (1967) also found a linear relationship between AR_e^K and $K_{ex}:Ca_{ex}+Mg_{ex}$ for most, but not all, the soils he studied. His lines, however, all passed through the origin. Acquaye & MacLean (1966) also found that AR_e^K is related to water-soluble plus exchangeable K and to percentage K saturation of the samples.

Mixture F, which had an AR_e^K value of 0.00, consisted only of Ca-saturated soil (cf. Table 2). This sample could be expected not to contain any potassium exchangeable by this procedure. It contained, however, 0.3 me K^+/100 g soil exchangeable with ammonium acetate. This fraction may represent the K^+ adsorbed to specific sites. Skeen & Sumner (1970) came to a similar conclusion for K-Al exchange equilibria in different soil series.

Potassium adsorbed to specific sites therefore does not contribute to Beckett's quantity factor ($-\Delta K^o$) or his intensity factor (AR_e^K) for both are 0.00 at this exchangeable K level. This K fraction would thus make no contribution to the short-term potassium supplying power of this soil. Both the quantity and the intensity of the plant-available potassium, according to Beckett's concept, thus seem to depend only upon the potassium adsorbed to the non-specific exchange positions.

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TABLE 4 - Exchangeable K and AR_e^K values of mixtures of the Mangano soil

Mixture No.	Exchangeable K me %	AR_e^K (moles/litre)$^{\frac{1}{2}}$
A	0.80	0.08575
B	0.70	0.05200
C	0.55	0.03575
D	0.45	0.02650
E	0.40	0.01525
F	0.30	0.00000

TABLE 5 - Relationship between exchangeable K and $-\Delta K^O$ for the Mangano soil

Mixture No.	$-\Delta K^O$ me %	Exchangeable K me %	$\frac{-\Delta K^O}{\text{Exchangeable K}} \times 100\%$
A	0.645	0.80	81
B	0.570	0.70	81
C	0.445	0.55	81
D	0.310	0.45	69
E	0.160	0.40	40
F	0.000	0.30	0

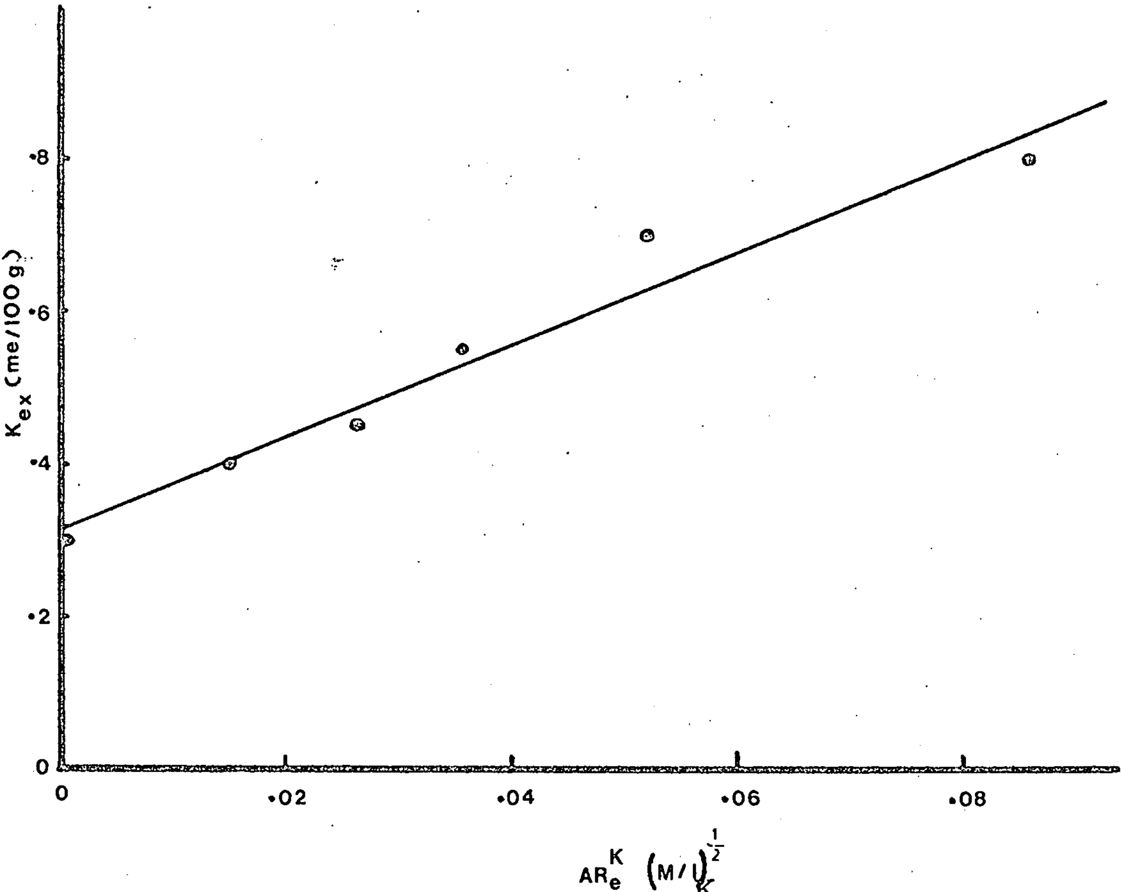

FIG. 4 Relationship between K_{ex} and AR_e^K for the Mangano soil.

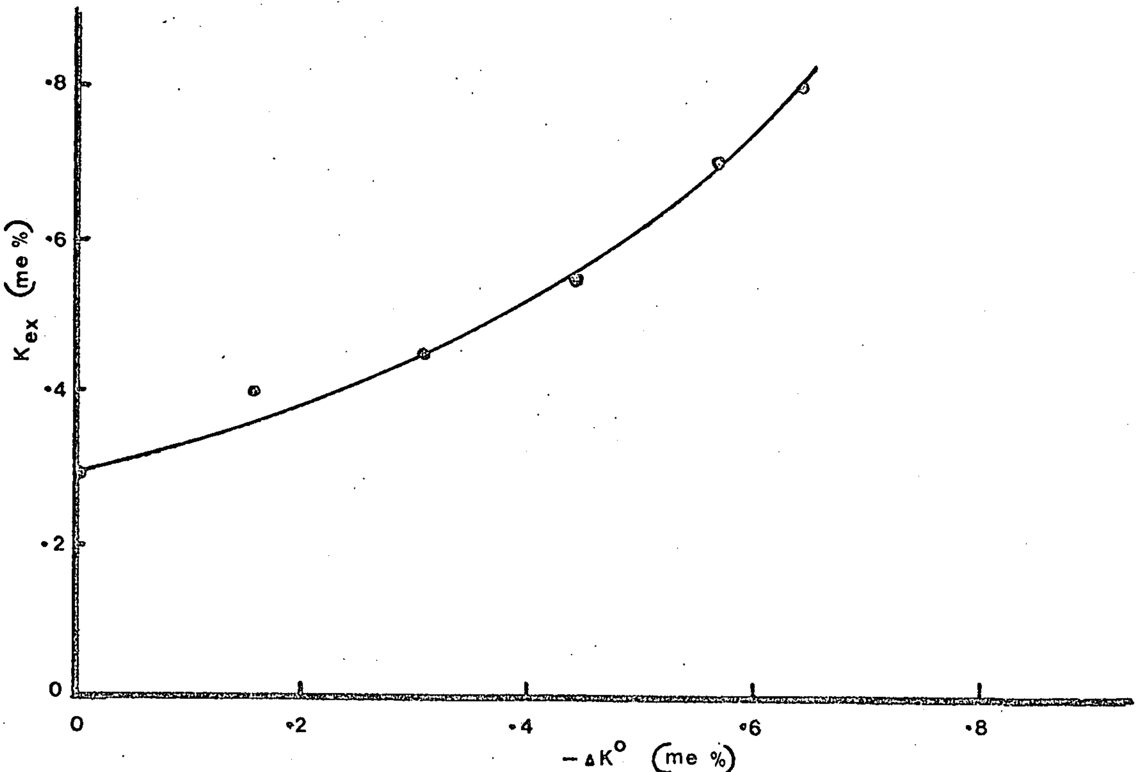

FIG. 5 Relationship between K_{ex} and $-\Delta K^O$ for the Mangano soil.

The fact that as much as 0.32 me/100 g soil of the ammonium acetate exchangeable K may not contribute to the quantity or intensity factors may be of great practical significance. Exchangeable K values of less than 0.32 me/100 g are common in this soil type, which is used extensively for irrigation farming purposes. In the past values as low as 0.20 me/100 g were regarded as sufficient, according to data obtained from literature as reviewed by Ulrich & Ohki (1966).

In spite of a linear relationship between exchangeable K and the intensity factor (AR_e^K) the relationship between exchangeable K and the quantity factor ($-\Delta K^o$) was curvilinear (Figure 5).

From Table 5 it is evident that $-\Delta K^o$ represented a constant fraction (81%) of the exchangeable potassium at the three highest K_{ex} levels. At lower K_{ex} levels, however, $-\Delta K^o$ represents a progressively smaller fraction of the corresponding K_{ex} values.

When the exchangeable K value for the specific sites, viz. 0.32 me/100 g, is subtracted from the total exchangeable K the remaining fraction may be taken as the non-specifically adsorbed K. Table 6 shows that $-\Delta K^o$ values are invariably larger than those of non-specifically adsorbed K. It may therefore be concluded that specifically adsorbed K contributes to some extent to $-\Delta K^o$. The calculated contributions of specifically adsorbed potassium at different potassium levels are also given in Table 6. From these it is evident that the contributions are relatively large and of a fairly constant value (average 0.17 me/100 g) at high levels of K_{ex} (mixtures A,B,C and D), but decrease rapidly thereafter, reaching a zero level at the lowest level of K.

Beckett's (1964b) claim that $-\Delta K^o$ provides a good indication of the exchangeable K (the capacity factor) was therefore affirmed for high levels of exchangeable K (above 0.55 me/100 g). K_{ex} values of this magnitude are, however, never found in field samples of this sandy soil. At the lower, more commonly experienced K_{ex} values $-\Delta K^o$ is not

related/..............

related to K_{ex} and therefore also not to the capacity factor. The relationship between $-\Delta K^{O}$ and non-specifically adsorbed potassium was relatively constant over a wider range of K_{ex} values. This relationship was, however, not as good as that between $-\Delta K^{O}$ and total K_{ex} for the few highest K_{ex} values.

The PBC^{K} values are given in Table 6. Although differences in PBC^{K} are relatively large, there is no general trend for PBC^{K} to decrease or increase with increases in exchangeable K. PBC^{K} can therefore be described as independent of the exchangeable K content of this soil. This is in agreement with results obtained by Beckett (1964b), although contradictory to what he expected. He expected PBC^{K} to decrease with increasing potassium saturation. In later experiments Beckett, Craig, Nafady & Watson (1966) and Beckett & Nafady (1967) also found PBC^{K} to be independent of potassium saturation. On the other hand Acquaye, MacLean & Rice (1967) and Le Roux & Sumner (1968) found increases in PBC^{K} at low potassium levels in soils.

The obtained independence of PBC^{K} of potassium level leads to the conclusion that PBC^{K} as such does not provide a measure of the potassium status of a soil at any given moment. According to Beckett (1964b) PBC^{K} "measures the amount of labile K that can be removed before AR^{K} falls by more than a given amount." Because of the substitution of AR^{K} for AR_{e}^{K} it was subsequently interpreted that PBC^{K} indicates how well a soil is buffered against decreases in AR_{e}^{K} when potassium is removed from the labile pool. Conversely this will, however, also mean that only small increases in AR_{e}^{K} will result from relatively large increases in the labile pool of a soil with a high PBC^{K}. It may therefore be reasoned that K fertilization will have relatively little effect on AR_{e}^{K} in such soils.

It is important to note that Beckett (1964b) stated that the potassium status of a soil can be characterized by any <u>two</u> of AR^{K}, PBC^{K} or $-\Delta K^{O}$.

From/..................

TABLE 6 - PBC^K at different K_{ex} levels and comparison of $-\Delta K^o$, "non-specifically" and "specifically" adsorbed potassium for the Mangano soil

Mixture No.	Exchangeable K me%	PBC^K me%/$(M/l)^{\frac{1}{2}}$
A	0.80	7.5
B	0.70	11.0
C	0.55	13.0
D	0.45	12.0
E	0.40	10.0
F	0.30	13.0

Mixture No.	$-\Delta K^o$ me %	"Non-specific" K_{ex} me %	Contribution of "specific" K_{ex} to $-\Delta K^o$ me %
A	0.645	0.500	0.145
B	0.570	0.400	0.170
C	0.445	0.250	0.195
D	0.310	0.150	0.160
E	0.160	0.100	0.060
F	0.000	0.000	0.000

From the present experiment it appears that the relationship between exchangeable K and AR_e^K should be a reliable measure of the potassium status of a soil. Furthermore it may be possible to characterize a given soil with regard to this relationship only once, and thereafter the determination of only one of these two parameters should enable the other to be found on a standard graph for that soil. It should also be possible to construct a standard graph for each soil type. For routine purposes only one of either K_{ex} or AR_e^K of any sample of that soil type need be determined to obtain both the quantity and intensity of its immediately available potassium.

Zandstra & MacKenzie (1968) found a good correlation between "available potassium" (extracted with 0.1N NH_4Ac and 0.5N H_2SO_4) and yields of oats, barley and maize. The only Q/I parameter which gave equally good results was the "K potential", given by $-\Delta K^o x\ PBC^K$. PBC^K is obtained by the equation $PBC^K = -\Delta K^o/AR_e^K$. The K potential is therefore given by $(-\Delta K^o)^2/AR_e^K$. Zandstra & MacKenzie (1968) found a good correlation between $-\Delta K^o$ and exchangeable K. The relationship between K_{ex} and AR_e^K should therefore also yield good correlations with crop yields.

Because K_{ex} can be determined faster and easier than AR_e^K, determination of K_{ex} will be preferred in routine laboratories. This will be sufficient to describe the potassium status of soils once calibration curves (standard curves) had been constructed for different soil types.

Based on the foregoing the following procedure is proposed for routine determinations of the potassium status of soils:

1. Choose good representative samples for each soil type which occurs in the region. Series which are subdivided into texture phases may be chosen for this purpose.

2. Saturate samples of each soil to different degrees with potassium. Determine K_{ex} and AR_e^K for each sample at a given constant temperature.

3/.....................

3. Construct a standard graph for each soil type by plotting K_{ex} against AR_e^K.

4. Subsequently only K_{ex} need be determined, on a routine basis, on all samples of characterized soil types received.

As more results are obtained on the relationship between K_{ex}, AR_e^K and potassium uptake by plants it will be possible to make ever more reliable predictions about K status in practice.

This proposed procedure is exquisitely dependent upon reliable soil maps. Unfortunately the latter are not yet available for large areas of the Republic of South Africa at present.

CHAPTER 3

THE RELATIONSHIP BETWEEN EXCHANGEABLE POTASSIUM AND AR_e^K FOR FOUR SOILS

3.1 PURPOSE

In view of the illuminating results for the Mangano top soil it was decided to include three other arable soils from the Orange Free State Region. In addition to the Mangano soil which was again included for comparison purposes, two alluvial soils from the Riet River Irrigation Scheme and a soil of the Estcourt series from the Eastern Orange Free State were selected for this investigation.

Arable soils constitute only a relatively small percentage of the total area of the Orange Free State Region. The four soil types of which representative samples were used in this investigation are of considerable economic importance in this Region. The Mangano series constitutes most of the irrigated area of the Vaalharts Irrigation Scheme. It is also extensively cropped to maize, wheat and sorghums in the Western Orange Free State, mainly under dry-land conditions. The two alluvial soils represent some of the most important irrigated soils under the Riet River Irrigation Scheme. The Estcourt soil from the Eastern Orange Free State is mainly used for dry-land cropping of wheat and maize. Indications of potassium deficiencies in crops grown on these soils were found lately.

3.2 MATERIALS AND METHODS

3.2.1 The Soils

Some properties of the soils used are summarized in Table 7. From this table it is evident that the sand fractions of the two Riet River soils and the Mangano soil are dominated by fine sand, but that the sand fraction of the Estcourt soil is dominated by coarse sand. The soils cover a range of clay contents and CEC values. The CEC of the clay fractions of the Riet River soils and the Estcourt

soil/...............

TABLE 7 - Some properties of the four soils used

Soil	CEC me %	CEC/g clay me	Particle size distribution			
			Coarse sand %	Fine sand %	Silt %	Clay %
Riet River No. 2	16.24	0.68	2.0	63.0	12.3	24.0
Riet River No. 4	12.93	0.65	0.6	71.9	7.9	20.0
Mangano	4.90	0.46	14.1	75.9	1.0	10.7
Estcourt	9.10	0.66	68.4	8.7	9.3	13.7

TABLE 8 - New series of equilibrating solutions for determining AR_e^K

No.	KCl concentration in solution (me/litre)
1	2.4
2	2.0
3	1.6
4	1.2
5	0.8
6	0.4

All solutions in 0.002 M $CaCl_2$.

soil are practically similar, but that of the Mangano soil is significantly lower. X-ray diffraction studies failed to give conclusive indications of types of clay minerals present in these soils. The clay fractions of the two Riet River alluvial soils showed identical X-ray diffractograms and it may be concluded that they contain similar clay mineral suites. Clay mineral analysis by the method of Alexiades & Jackson (1966) indicated fair amounts of vermiculite in the soils of this region (unpublished data - Department of Soil Science, U.O.F.S.).

3.2.2 Preparation of the soils

Samples of each soil were saturated with calcium and potassium as described in section 2.2.2. For each soil a series of six mixtures was prepared. The ratios between potassium saturated and calcium saturated soil in the mixtures corresponded to those prepared for the previous experiment (cf. Table 2).

3.2.3 Determination of the Q/I parameters

It was considered that only the linear parts of the Q/I relationships are of importance, i.e. to find $-\Delta K^o$ by extrapolation, AR_e^K by interpolation or extrapolation and for calculation of PBC^K. The curved part does not affect these Q/I parameters. Furthermore Beckett & Nafady (1967) and Fariña (1970) indicated that there is much uncertainty about the extrapolation and interpretation of the curved part. Consequently it was decided to omit those solutions which gave the curved parts of the graphs in the previous experiment. The lowest potassium concentrations in the equilibrating solutions and the smaller amounts of soil (5g and 1g) were therefore omitted. Instead of these a number of solutions with higher potassium concentrations were added. This modification has the advantage that more points are obtained on the linear parts of the graphs without increasing the number of equilibrating solutions. More points on the linear parts of the graphs facilitate a more accurate calculation of the lines. All lines were calculated by means of the standard formula of y=a+bx. In order to simplify calculations the horizontal axis of each figure was taken as the y-axis. Skeen & Sumner (1970) adopted the same artifice.

The new series of equilibrating solutions is given in Table 8. In all cases 10g soil and 100ml equilibrating solution were used.

The rest of the procedure was identical to that described in section 2.2.3, except for a slightly higher temperature of 28°C. This change was not intentional, but unavoidable because of high ambient summer temperature.

3.3 RESULTS AND DISCUSSION

Linear relationships between K_{ex} and AR_e^K were found for all four soils, as illustrated in Figures 6 to 9. All four soils contained considerable quantities of K_{ex} when AR_e^K reached zero values. These K_{ex} values, designated EK^o, are given in Table 9. The general trend is that EK^o values are increased with increasing clay contents and CEC values of the soils. The EK^o value for the Riet River No.2 soil was almost double that of the Riet River No. 4 soil (0.73 and 0.37 me/100g respectively). It has already been pointed out that these soils contained identical clay mineral suites. The EK^o values for the Riet River alluvial soils are also higher than those of the Mangano and Estcourt soils with lower clay contents and CEC values.

The EK^o values for the Mangano and Estcourt soils were identical (0.12me/100g) despite greater differences in CEC values than those between the two Riet River soils. This may be due to differences in their clay fractions. From Table 7 it may be seen that the CEC values of the two alluvial soils and the Estcourt soil were identical at 0.66me/g compared with 0.46me/g for the Mangano soil. This may be taken as a fair indication of a difference in type of clay mineral. As was indicated in section 3.2.1 attempts by the author and others, e.g. Van der Merwe (1966) and unpublished data, were not successful in identifying the clay

minerals/................

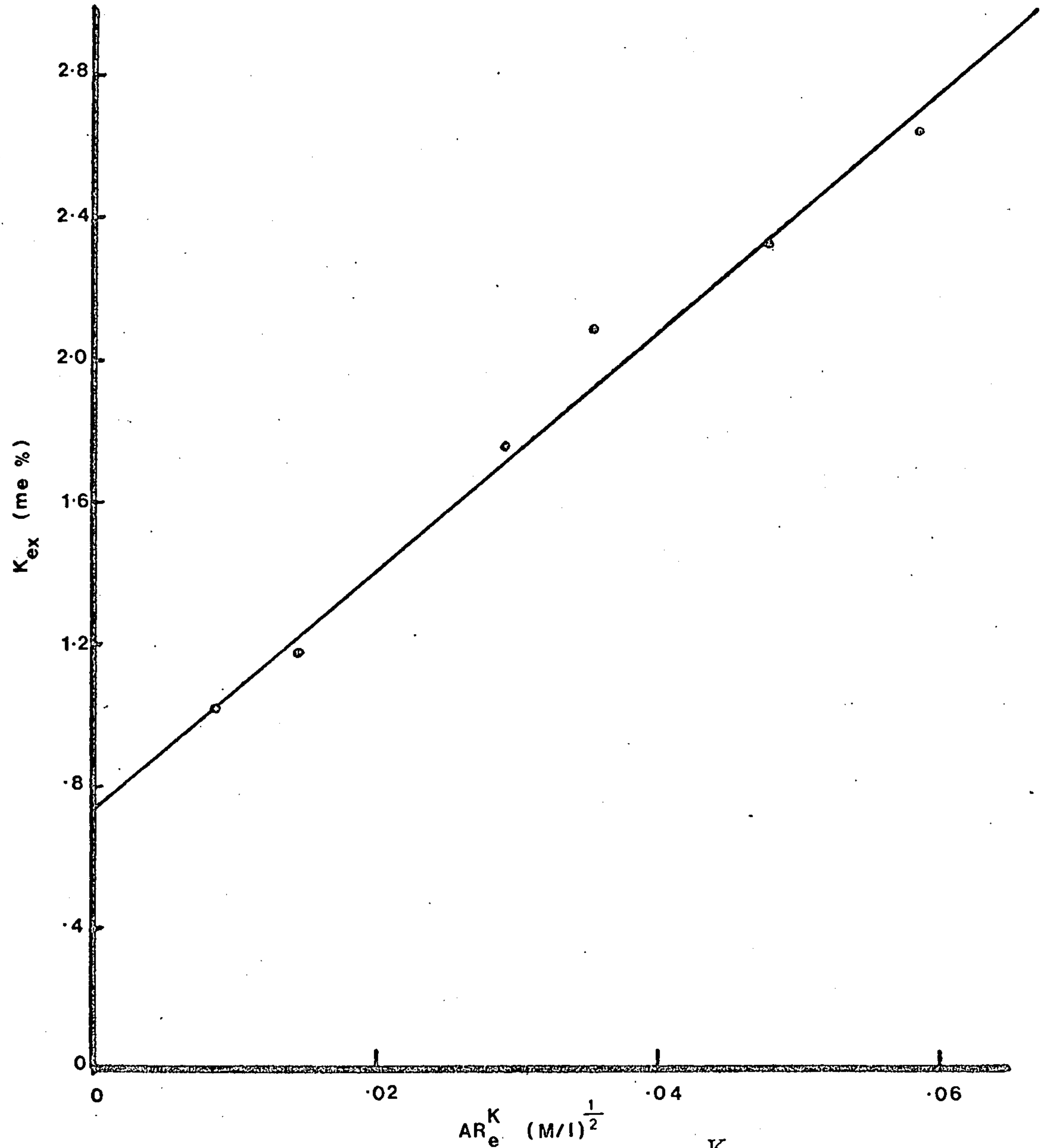

FIG. 6 Relationship between K_{ex} and AR_e^K for the Riet River No. 2 soil.

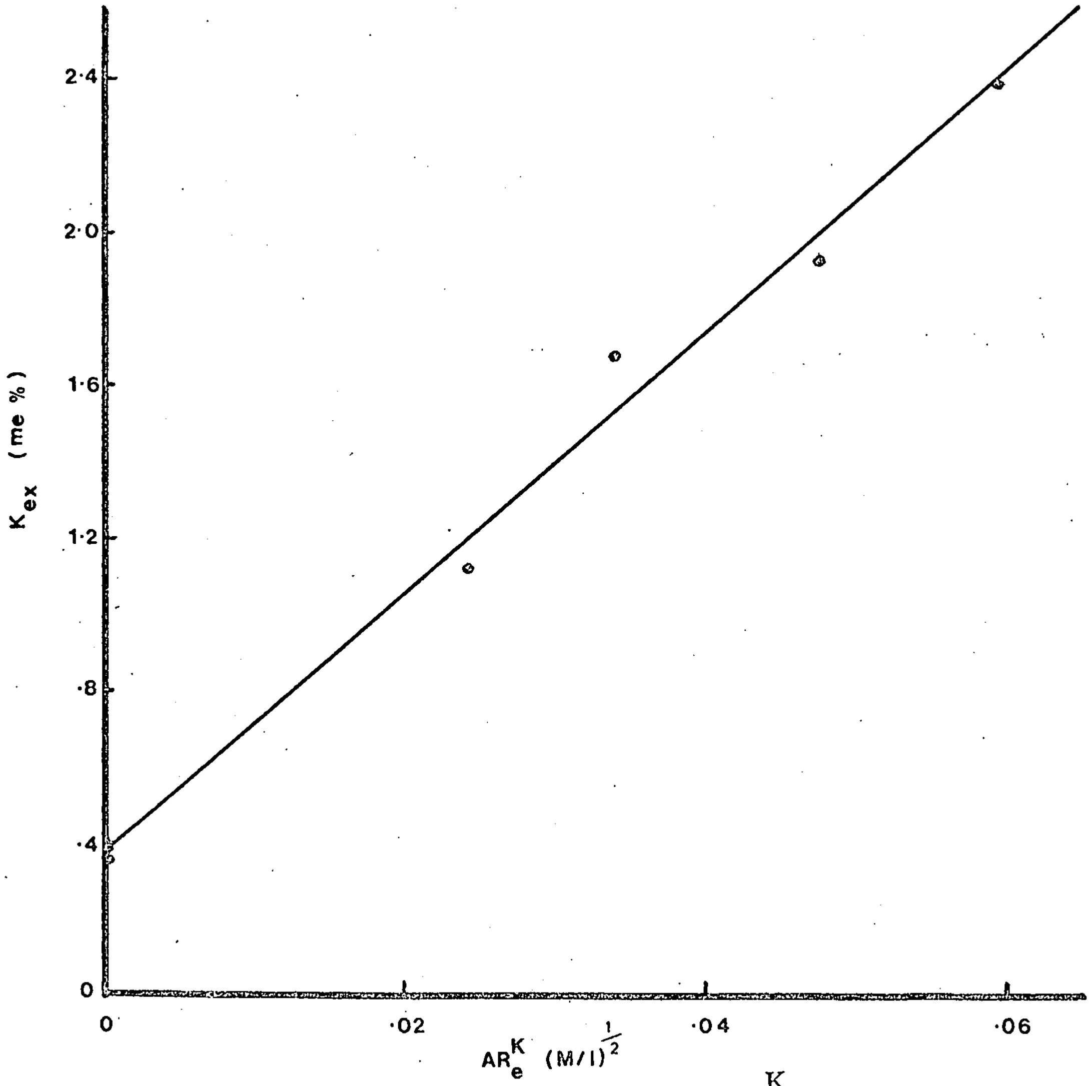

FIG. 7 Relationship between K_{ex} and AR_e^K for the Riet River No. 4 soil.

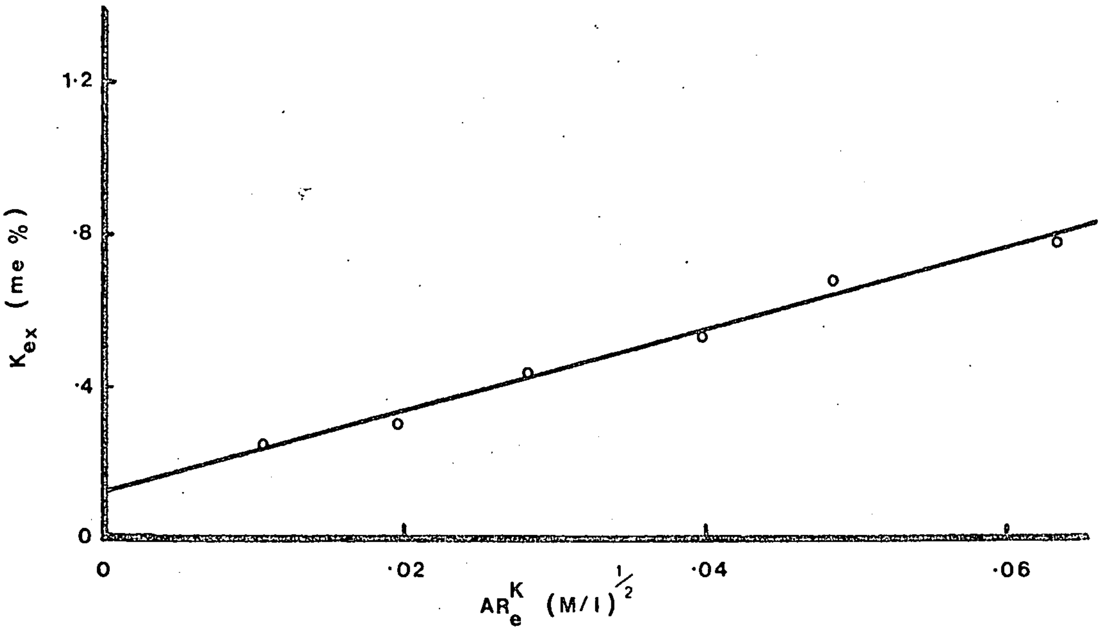

FIG. 8 Relationship between K_{ex} and AR_e^K for the Mangano soil (second experiment).

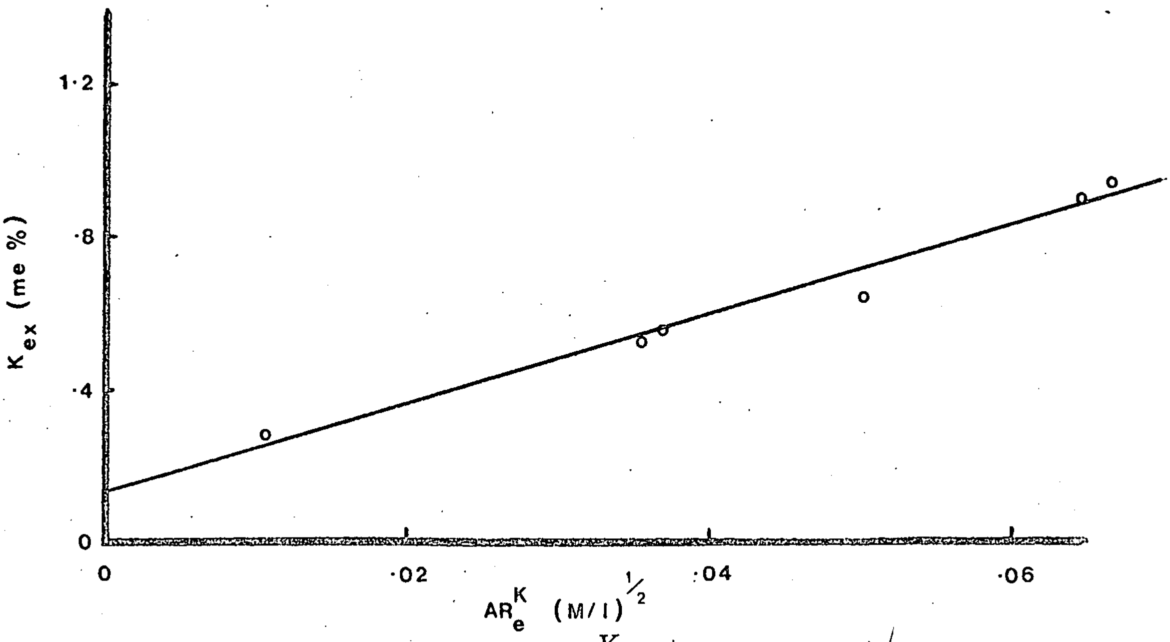

FIG. 9 Relationship between K_{ex} and AR_e^K for the Estcourt soil.

TABLE 9 - EK^{O} values for the four soils

Soil	EK^{O} me %
Riet River No.2	0.73
Riet River No.4	0.37
Mangano	0.12
Estcourt	0.12

TABLE 10 - PBC_{T}^{K} values for the four soils

Soil	PBC_{T}^{K} me %/$(M/l)^{\frac{1}{2}}$
Riet River No.2	33.69
Riet River No.4	34.23
Mangano	10.64
Estcourt	11.86

minerals present in these soils and therefore no better proof can be given concerning the possible effect of clay mineral type.

It must be noted that the EK^o value of the Mangano soil was only 0.12me/100g in this experiment compared to 0.32me/100g in the previous experiment. This change cannot be attributed to the change in temperature at which the experiment was conducted, as will be shown later.

The slopes of the final graphs of K_{ex} versus AR_e^K, which may be designated PBC_T^K, are given in Table 10. The values for the Riet River No.2 and Riet River No.4 soils were practically identical despite the fact that their clay contents and CEC values differed markedly and their EK^o values differed even more. It may therefore be concluded that PBC_T^K is dependent upon the type of clay mineral and independent of the amount of clay in these soils and that EK^o is dependent upon the amount of a specific type of clay mineral which is present in a soil.

The PBC_T^K and EK^o values for the Mangano and Escourt soils differed only slightly in spite of marked differences in other important properties.

The PBC^K values for all the mixtures of all 4 soils and the average value for each soil are given in Table 11, showing that the PBC^K values of the two Riet River soils were very similar. The PBC^K values for the Mangano and Estcourt soils were likewise very similar. The CEC's of the soils have therefore no effect on their PBC^K values. PBC^K was also independent of the level of potassium saturation in all four soils.

Both these facts are contradictory to what Beckett (1964b) expected, viz.: "........PBC^K should vary with $(K+Ca+Mg)_{ex}$ as a measure of the extent of colloid surface available for the exchange equilibrium and for a given value of $(Ca+Mg+K)_{ex}$ PBC^K will decrease with increasing K saturation as indicated already."

The/....................

TABLE 11 - PBC^K values at different potassium levels for the four soils

Soil and Mixture No.		PBC^K (me%/(M/l)$^{\frac{1}{2}}$)
Riet River No. 2	A	40.95
	B	41.89
	C	40.63
	D	39.68
	E	35.75
	F	37.73
Mean		39.44
Riet River No. 4	A	44.71
	B	38.04
	C	37.85
	D	44.62
	E	32.30
	F	33.05
Mean		38.43
Mangano	A	12.20
	B	13.67
	C	13.71
	D	10.44
	E	12.56
	F	11.34
Mean		12.32
Estcourt	A	16.77
	B	12.99
	C	12.67
	D	15.25
	E	11.89
	F	14.79
Mean		14.06

The fact that PBC^K is independent of both clay content and CEC of the soil is contradictory to the findings of Acquaye & MacLean (1966) and Zandstra & MacKenzie (1968). They found that PBC^K increased with increasing clay content. That PBC^K is independent of level of potassium saturation agrees with the results of Beckett & Nafady (1967) and Zandstra & MacKenzie (1968), but disagrees with those of Acquaye, MacLean & Rice (1967) and Le Roux & Sumner (1968).

With regard to plant uptake of potassium, Acquaye & MacLean (1966) found that "........ the PBC^K was a useful criterion of subsequent uptake of initially non-labile K." A high PBC^K would therefore be an indication that a soil is able to supply sufficient potassium to plants over a long period. In this respect the results of the present experiment present an unfavourable picture. The PBC^K values of both the Mangano and Estcourt soils were extremely low and even those of the two alluvial Riet River soils were relatively low. The ability of the former two soils to supply enough potassium to plants over a long period should accordingly be very poor. This deduction is actually verified by results of Stanton (1964) for a number of Orange Free State soils, including Estcourt and Mangano soils. Exchangeable K contents of the cultivated soils were much lower than those of the comparable virgin soils. Table 12, a summary of his Table 3, illustrates this. From the results of Beckett (1964b) and others it is evident that PBC^K values of higher than 100me/100g/$(M/l)^{\frac{1}{2}}$ are obtained for some soils.

It is significant that, although the EK^{o} value of the Mangano soil in this experiment was considerably lower than that in the previous experiment, the mean PBC^K values were practically unchanged (11.1 versus 12.32me/100g/$(M/l)^{\frac{1}{2}}$). Together with the fact that the PBC^K values for a given soil were not shifted in any direction by variations in exchangeable K levels this may serve as an indication that PBC^K is a constant property of any given soil. Furthermore, since mean PBC^K was independent of clay content for the otherwise similar Riet River soils it appears that PBC^K is a relatively constant property of the soils within a certain soil

series/...................

TABLE 12 - Comparison of the exchangeable K content of virgin and cultivated samples of different soils of the Orange Free State (from: Stanton, 1964)

Soil type	Number of samples	Exchangeable K (me %)
Highveld Pseudo-podzolic:		
Cultivated	24	0.27
Virgin	24	0.44
Fersiallitic:		
Cultivated	15	0.35
Virgin	15	0.43
Semi-arid brown:		
Cultivated	5	0.40
Virgin	5	0.70

TABLE 13 - The relationship between mean PBC^K and PBC^K_T for four soils

Soil	$\frac{\text{Mean } PBC^K}{PBC^K_T}$
Riet River No. 2	1.17
Riet River No. 4	1.12
Mangano	1.16
Estcourt	1.19
Mean	1.155

series. Le Roux (1966) found unexpectedly large differences between the PBC^K values of different samples within some soil series. Some of his soils did, however, not conform to the conditions which allow reliable determinations of AR_e^K and hence PBC^K, viz. absence of excess positive charges, a fair degree of base saturation and dominance of $Ca^{++}+Mg^{++}$, as put forward by Beckett (1964a,b). Schofield (1947) pointed out that the Ratio Law is not valid in the case of such soils.

Another interesting phenomenon is that although the properties and the PBC^K values of the four soils differed much, the ratios between mean PBC^K and PBC_T^K were practically identical for all four soils (Table 13). This must be related to the linear relationship between $-\Delta K^O$ and K_{ex} (Figures 10 to 13) and between $-\Delta K^O$ and AR_e^K (Figures 14 to 17) for all four soils. Furthermore the slopes of the lines relating $-\Delta K^O$ to K_{ex} were practically identical for all four soils.

At high K_{ex} levels a good correlation between K_{ex} and $-\Delta K^O$ was again recorded (Table 14), the numerical size of the corresponding values being remarkably similar. At low K_{ex} levels, comparable tot field levels, the relationship was again unfavourable, the contribution of $-\Delta K^O$ to total K_{ex} decreasing as K_{ex} decreases. In the usual determination of Q/I parameters some authors, e.g. Beckett (1964b), simply took $-\Delta K^O$ as a measure of K_{ex}, which they regarded as the true capacity factor. For the present soils $-\Delta K^O$ evidently corresponds to K_{ex} only at relatively high K_{ex} levels, but not at normal field K_{ex} levels, especially in arable soils depleted in K_{ex}.

For all four soils there was some correlation between $-\Delta K^O$ and non-specifically adsorbed K at all K_{ex} levels (Table 15). At high K_{ex} levels the correlation between $-\Delta K^O$ and non-specifically adsorbed K was not as good as that between $-\Delta K^O$ and total K_{ex}. Whereas there was a good numerical similarity between $-\Delta K^O$ and K_{ex} at high K_{ex} levels, there was not such a good similarity between $-\Delta K^O$ and non-specifically adsorbed K. It should be noted that

Zandstra/..............

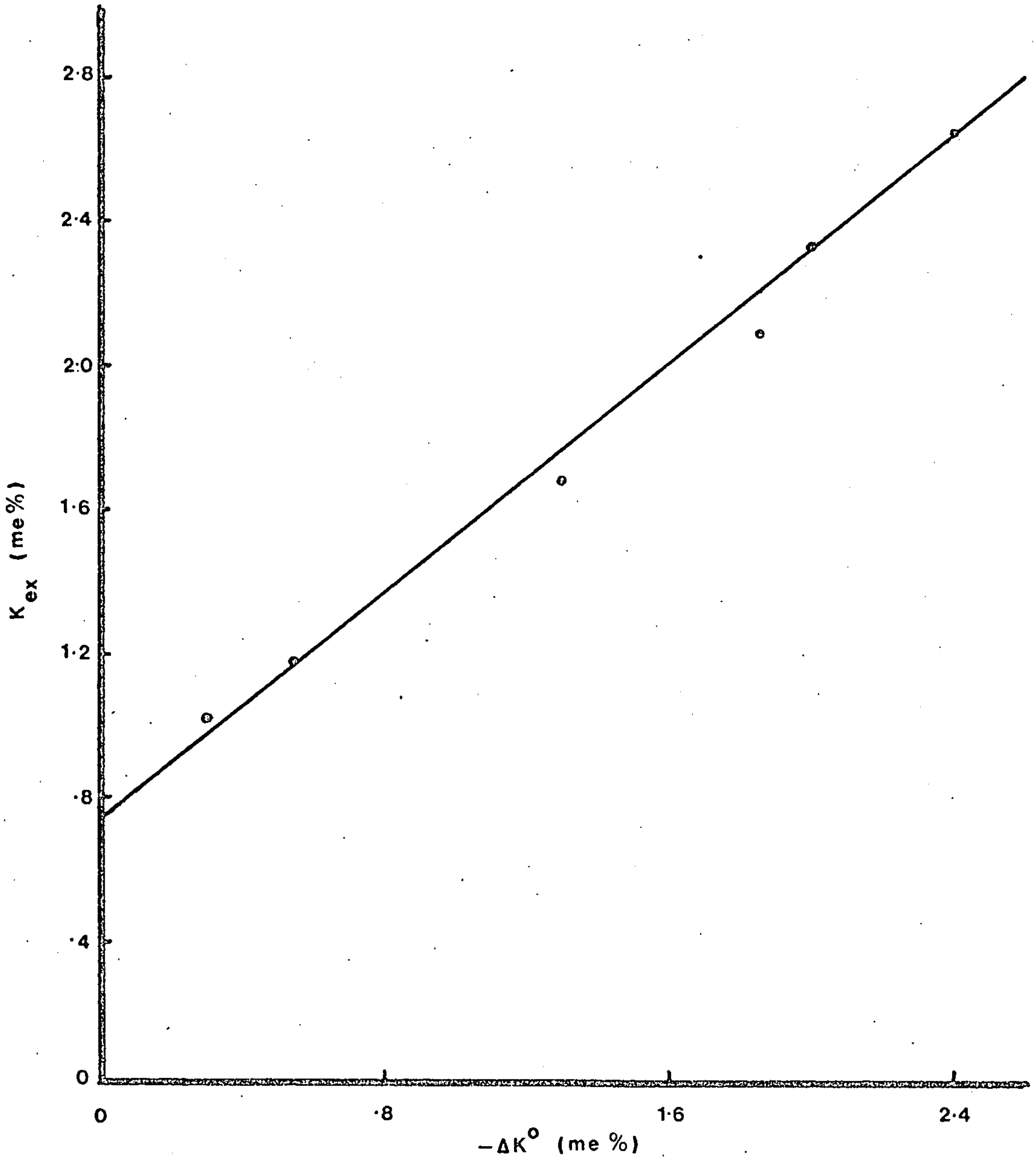

FIG. 10 Relationship between K_{ex} and $-\Delta K^o$ for the Riet River No. 2 soil.

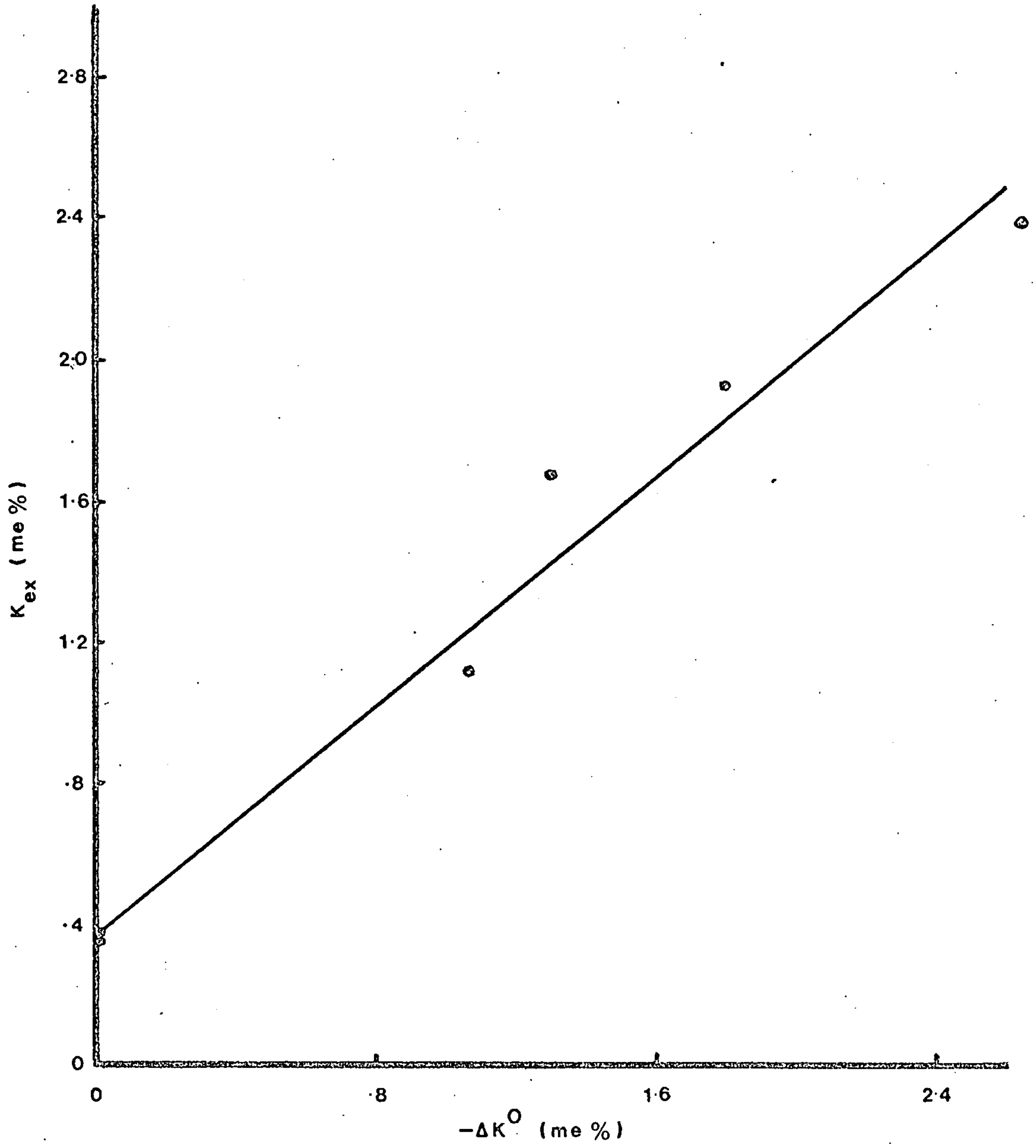

FIG. 11 Relationship between K_{ex} and $-\Delta K^O$ for the Riet River No. 4 soil.

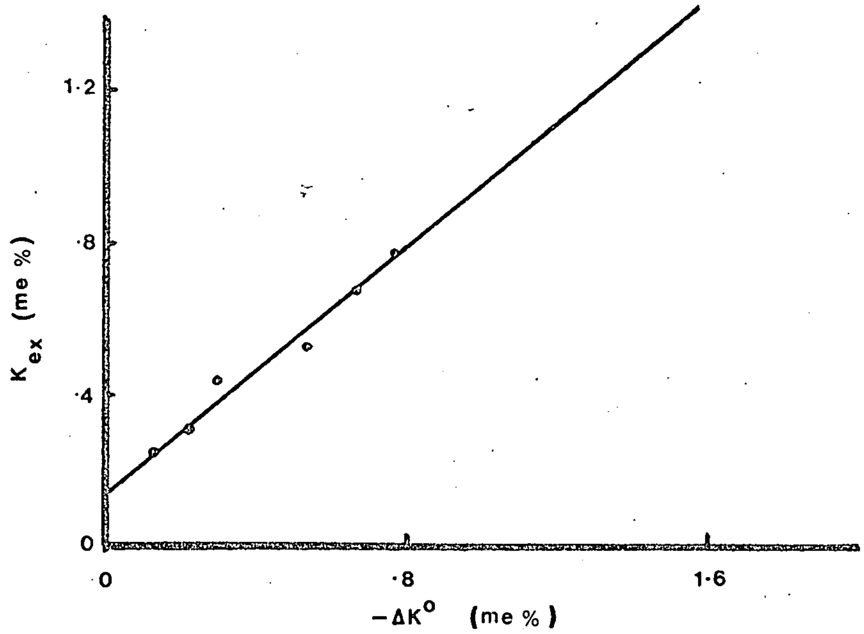

FIG. 12 Relationship between K_{ex} and $-\Delta K^{o}$ for the Mangano soil (second experiment).

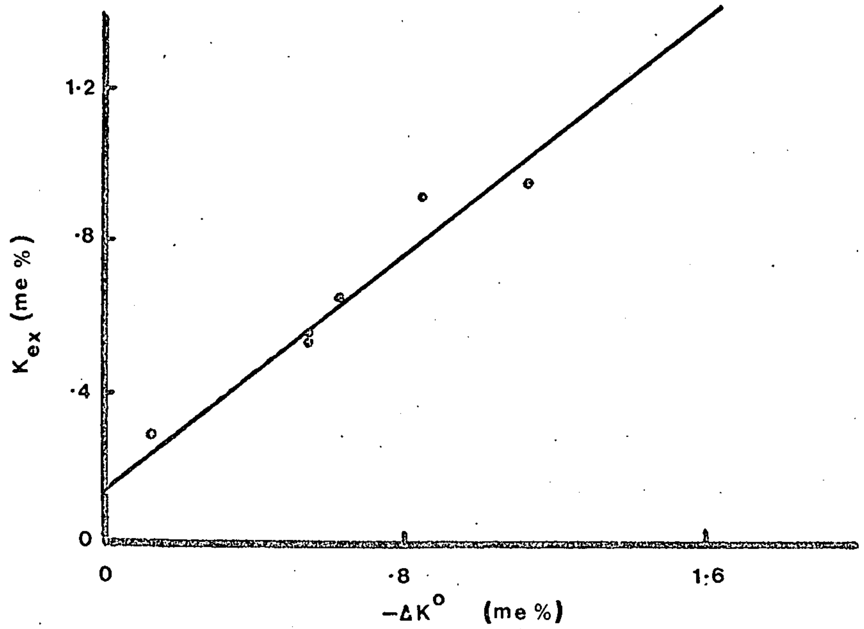

FIG. 13 Relationship between K_{ex} and $-\Delta K^{o}$ for the Estcourt soil.

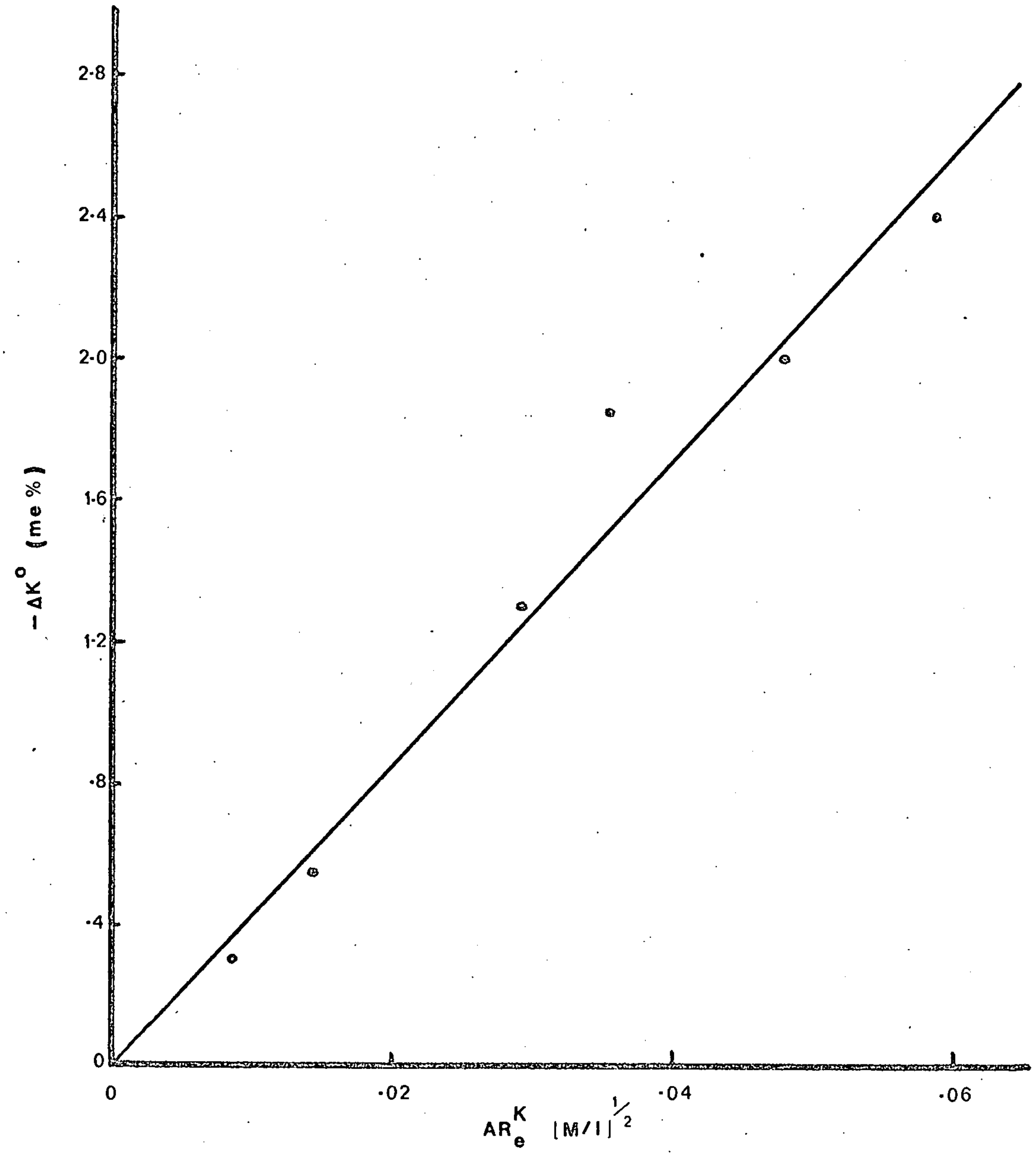

FIG. 14 Relationship between - ΔK^o and AR_e^K for the Riet River No. 2 soil.

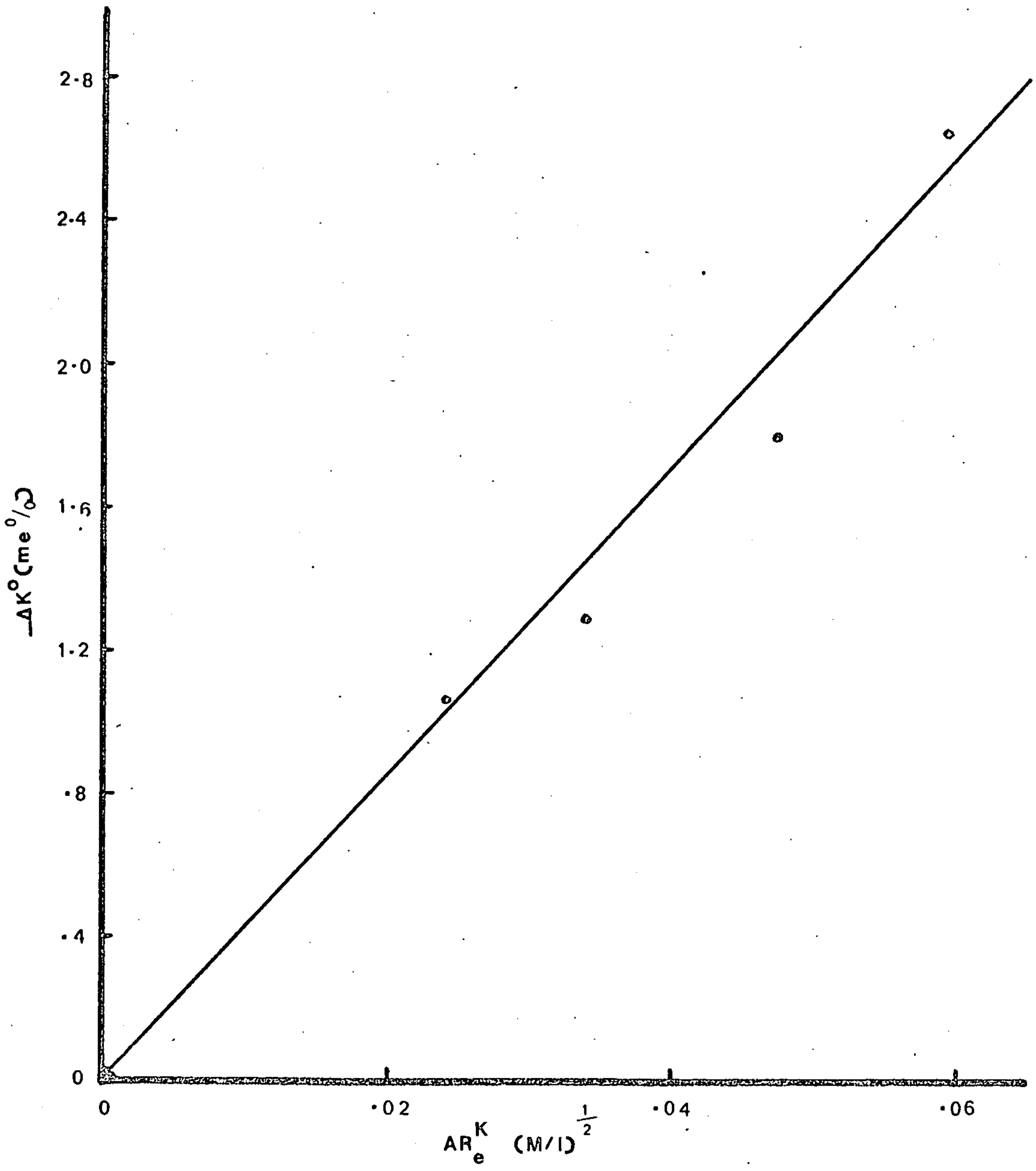

FIG. 15 Relationship between - ΔK^{O} and AR_e^K for the Riet River No. 4 soil.

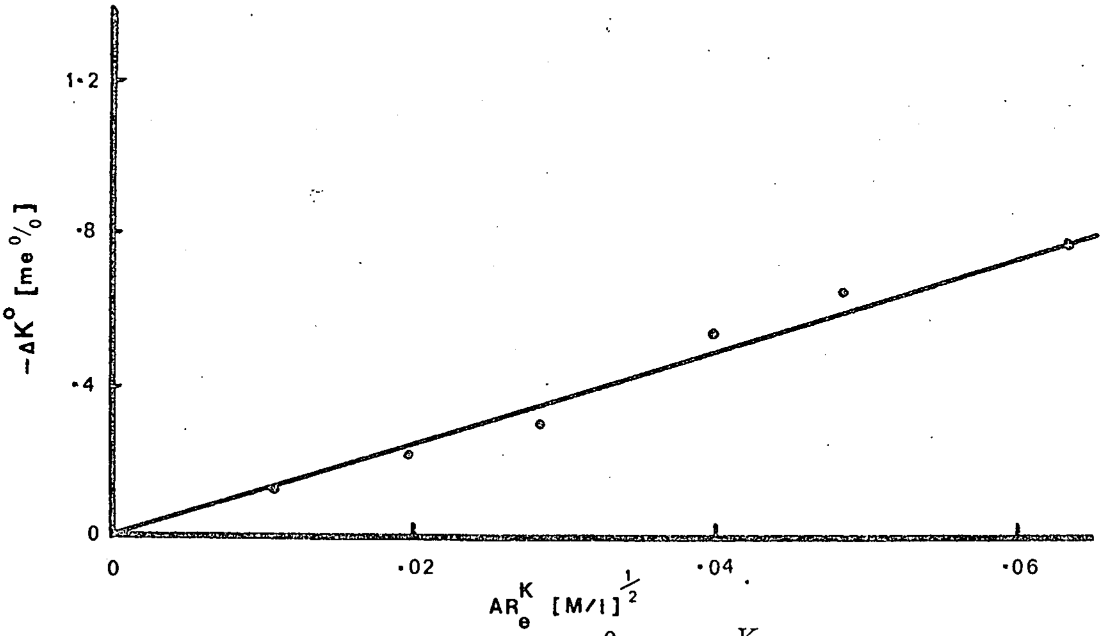

FIG. 16 Relationship between $-\Delta K^0$ and AR_e^K for the Mangano soil (second experiment).

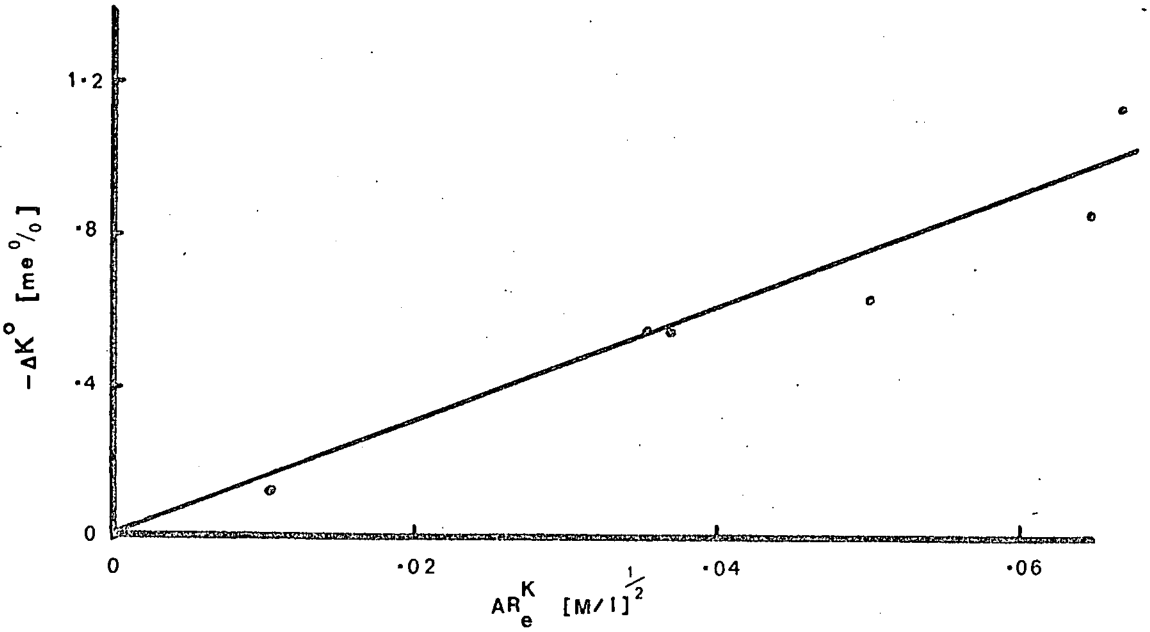

FIG. 17 Relationship between $-\Delta K^O$ and AR_e^K for the Estcourt soil.

TABLE 14 - Relationship between exchangeable potassium and $-\Delta K^o$ for four soils

Soil	K_{ex} me%	$-\Delta K^o$ me%	$\frac{-\Delta K^o}{K_{ex}}$x100%
Riet River No. 2	2.640	2.40	91
	2.325	2.00	86
	2.088	1.85	89
EK^o=0.73	1.683	1.30	77
	1.181	0.55	47
	1.018	0.30	30
Riet River No.4	2.390	2.65	111
	1.931	1.80	93
	1.675	1.30	78
EK^o=0.37	1.119	1.07	96
	0.388	0.00	0
	0.369	0.00	0
Mangano	0.775	0.77	99
	0.675	0.65	96
	0.531	0.54	102
EK^o=0.12	0.438	0.30	69
	0.313	0.22	70
	0.250	0.13	52
Estcourt	0.950	1.13	118
	0.906	0.85	94
	0.653	0.63	96
EK^o=0.12	0.556	0.55	99
	0.531	0.55	104
	0.294	0.13	43

TABLE 15 - Relationship between "non-specifically adsorbed" K and $-\Delta K^{o}$ at different total K_{ex} levels for four soils

Soil	"Non-specific"K me %	$-\Delta K^{o}$ me %	$\frac{-\Delta K^{o} x100}{\text{Non-spec.K}}$ %	Difference between $-\Delta K^{o}$ and non-specific K me %
Riet River No.2	1.910	2.40	126	0.490
	1.595	2.00	125	0.405
	1.358	1.85	136	0.492
	0.953	1.30	137	0.347
	0.451	0.55	122	0.099
	0.288	0.30	104	0.012
Riet River No. 4	2.005	2.65	132	0.645
	1.561	1.80	115	0.239
	1.305	1.30	100	-0.005
	0.749	1.07	143	0.321
	0.018	0.00	0	-0.018
	0.000	0.00	0	0.000
Mangano	0.655	0.77	118	0.115
	0.555	0.65	117	0.095
	0.411	0.54	131	0.129
	0.318	0.30	94	-0.018
	0.193	0.22	114	0.027
	0.130	0.13	100	0.000
Estcourt	0.830	1.13	136	0.300
	0.786	0.85	108	0.064
	0.533	0.63	118	0.097
	0.436	0.55	126	0.114
	0.411	0.55	134	0.139
	0.174	0.13	75	-0.044

Zandstra & MacKenzie (1968) found that $-\Delta K^{o}$ was much larger than so-called "available potassium" in their experiments.

More attention need be given to the fact that a constant ratio (1.12 to 1.19) was found between mean PBC^{K} and PBC^{K}_{T} for all four soils (refer to Table 13). The most important aspect is not that a relationship was found between PBC^{K} and PBC^{K}_{T}, but that the ratio describing this relationship was constant for different soil types. This fact introduces the possibility that PBC^{K}_{T} can be calculated from a single Q/I determination.

If the factor of 1.155, the mean found for these four soils, can be accepted as a constant factor for these soils it will enable one to construct a graph of K_{ex} against AR^{K}_{e} for any unknown member of these soil types simply by using a field sample of the soil and without subjecting it to a series of time-consuming pretreatments, as was proposed in the previous chapter.

It will, however, not be sufficient to do only a Q/I determination. The Q/I determination will give one value of AR^{K}_{e} and will allow calculation of PBC^{K}_{T}, but it will not give EK^{o}. Not only is EK^{o} a very important value, but without it one cannot draw the correct graph of K_{ex} against AR^{K}_{e}. To eliminate this problem it is necessary that the exchangeable K of the sample on which the Q/I study was done, must be determined. By plotting this value of K_{ex} against the obtained value of AR^{K}_{e} an actual point on the graph is obtained. The obtained PBC^{K} value and the factor of 1.155 can now be used to calculate and construct a standard graph for that soil without the need of any further determinations.

The coefficients of variation of the PBC^{K} determinations on the four soils are given in Table 16. They are not very good (mean 10.33%) in view of the fact that specially prepared samples were used throughout. The variations are, however, normal for soil studies. The construction of a standard graph by means of the method described above may thus not have the desired degree of accuracy. The more tedious method described in the previous chapter should therefore be preferred on this score.

TABLE 16 - The coefficients of variation of PBC^K for four soils

Soil	Coefficient of Variation of PBC^K (%)
Riet River No. 2	5.80
Riet River No. 4	14.00
Mangano	8.38
Estcourt	13.15
Mean	10.33

By using this standard graph for a particular soil type it should suffice to determine only K_{ex} of any sample of that particular soil type to describe its potassium status. From the above a point on the standard graph could be found relating the K_{ex} value to the corresponding AR_e^K value for that sample. This means that both the capacity and the intensity factors of a sample are easily obtained. This reasoning is based on the provision that the ratio between PBC^K and PBC_T^K is a definite constant factor.

It must be noted at this point that the normal field samples of all four soils which were used fitted the curves of K_{ex} against AR_e^K perfectly together with the specially prepared samples. This can be taken as an indication that the properties of these field samples were such that they conformed to the Ratio Law and that the Q/I concept is applicable to them without any reservations.

CHAPTER 4

THE EFFECT OF VARYING SODIUM CONCENTRATIONS ON THE RELATIONSHIP BETWEEN EXCHANGEABLE POTASSIUM AND AR_e^K FOR TWO SOILS

4.1 PURPOSE

Beckett (1964a,b) stated that when the Q/I technique is applied to a soil significant amounts of cations other than Ca^{++},Mg^{++} and K^+ should not be present. For soils with appreciable Al^{+3} Tinker (1964a) found that the value for Al^{+3} must be included in the equation for the calculation of the Q/I parameters. Le Roux (1966), however, found that other cations did not influence calculation of Q/I parameters for certain soil series from Natal.

In cultivated soils of the Orange Free State Region sodium is the only other cation, apart from calcium, magnesium and potassium, which frequently occur in significant amounts, especially in certain irrigated soils. Sodium may therefore prove to be a problem in the determination of Q/I relationships for some of these soils. For this reason the influence of Na^+ on the Q/I relationships of two irrigated soils was investigated. The effect of Na^+ on both the calculation of the Q/I parameters and the relationship between K_{ex} and AR_e^K was examined.

4.2 MATERIALS AND METHODS

4.2.1 The soils

Top soil samples of the Mangano series and the alluvial Riet River No. 2 soil, described in section 3.2.1, were selected for this study.

4.2.2/...............

4.2.2 Preparation of the samples

Samples of the soils were saturated with Ca^{++} and K^+ as described in section 2.2.2. Other samples were saturated with Na^+ by treatment with NaCl. To obtain samples of variable Ca^{++}:K^+:Na^+ ratios quantities of the soil saturated with either Ca^{++}, K^+ or Na^+ were mixed as outlined in Table 17.

4.2.3 Determination of the Q/I parameters

Six 10g samples of each mixture were weighed into 250ml Erlenmeyer flasks and 100ml of equilibrating solutions no. 1 to 6 respectively were added. The equilibrating solutions corresponded to those given in Table 8. The suspensions were then left in a constant temperature room for one hour, shaken for one hour and filtered as outlined in section 2.2.3. Exchangeable potassium was displaced by leaching with 1N NH_4Ac at the same temperature.

This experiment was conducted at 20°C.

4.3 RESULTS AND DISCUSSION

The results for this experiment were firstly calculated in the usual way, i.e. without including Na^+ in the Q/I equation.

For both soils and at all three levels of sodium saturation linear relationships between K_{ex} and AR_e^K were again recorded (Figures 18 to 23). The AR_e^K, K_{ex} and PBC^K values are given in Table 18 and those of EK^o, PBC_T^K and the ratios between mean PBC^K and PBC_T^K in Table 19.

The overall averages of PBC^K for both soils did not differ significantly from those found for the same soils in the previous experiment - 13.60 against 12.32me/100g/$(M/l)^{\frac{1}{2}}$ for the Mangano soil and 40.10 against 39.44me/100g/$(M/l)^{\frac{1}{2}}$ for the Riet River No. 2 soil. Thus PBC^K again proved to be a very constant property of a soil and is not even significantly influenced by large variations in the temperature at which the Q/I parameters are determined. In the present experiment both soils showed a general tendency for average PBC^K to decrease with increasing degree of sodium saturation.

TABLE 17 - Mixing ratios of potassium, calcium and sodium saturated soil for the sodium experiment

Mixture No.	Potassium saturated soil	Calcium saturated soil	Sodium saturated soil
A	5	95	0
B	5	75	20
C	5	55	40
D	10	90	0
E	10	70	20
F	10	50	40
G	15	85	0
H	15	65	20
I	15	45	40
J	20	80	0
K	20	60	20
L	20	40	40

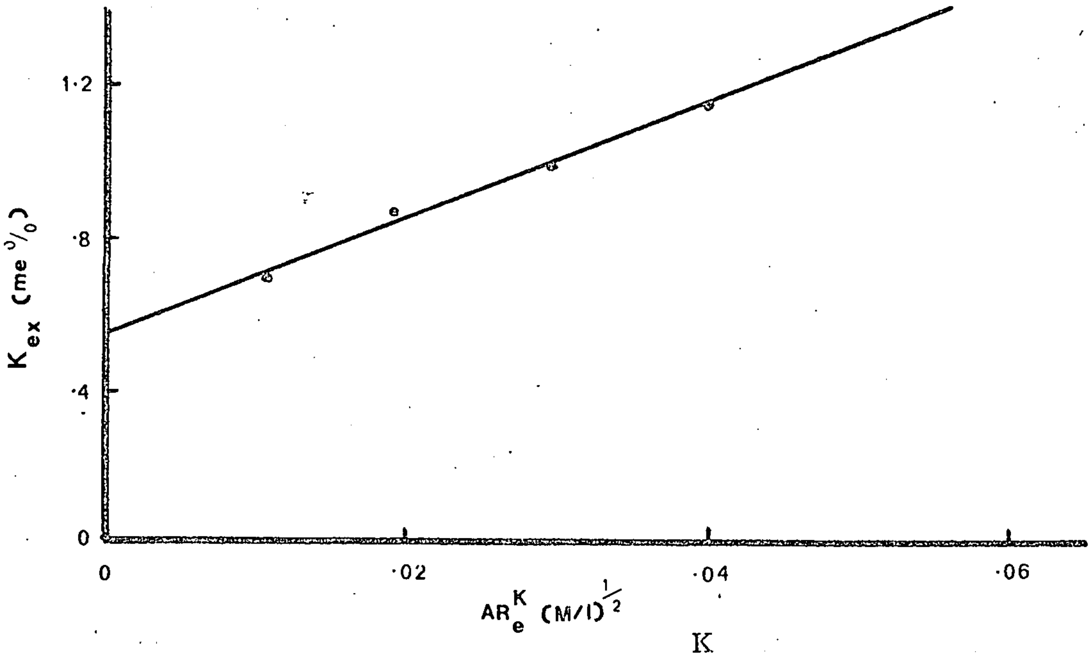

FIG. 18 Relationship between K_{ex} and AR_e^K for the Riet River No. 2 soil - no Na-soil in mixture.

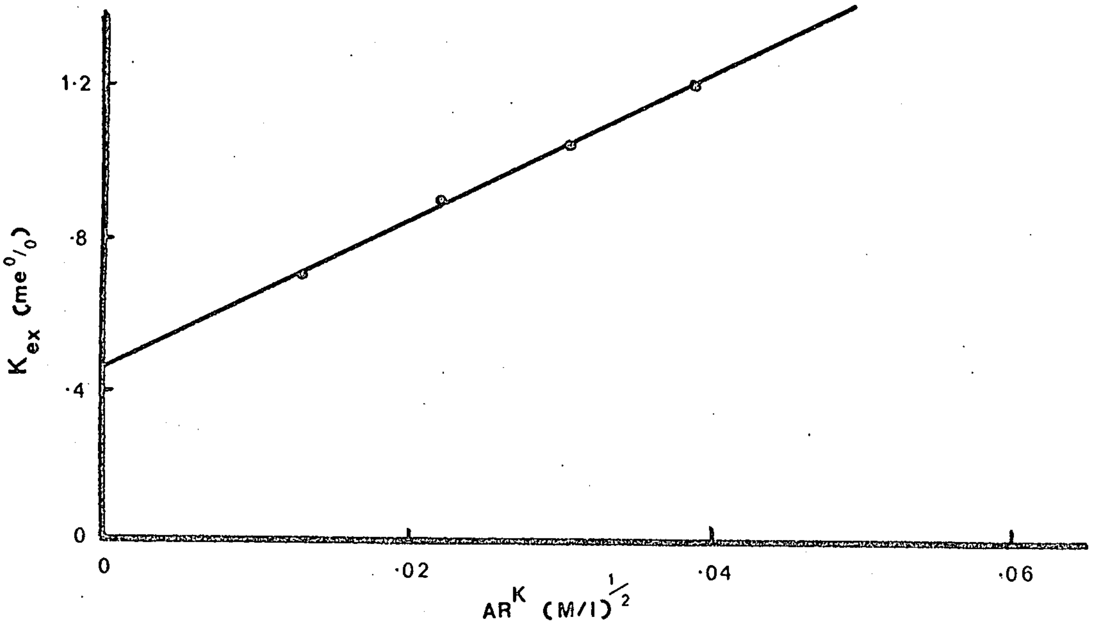

FIG. 19 Relationship between K_{ex} and AR_e^K for the Riet River No. 2 soil - 20% Na-soil in mixture.

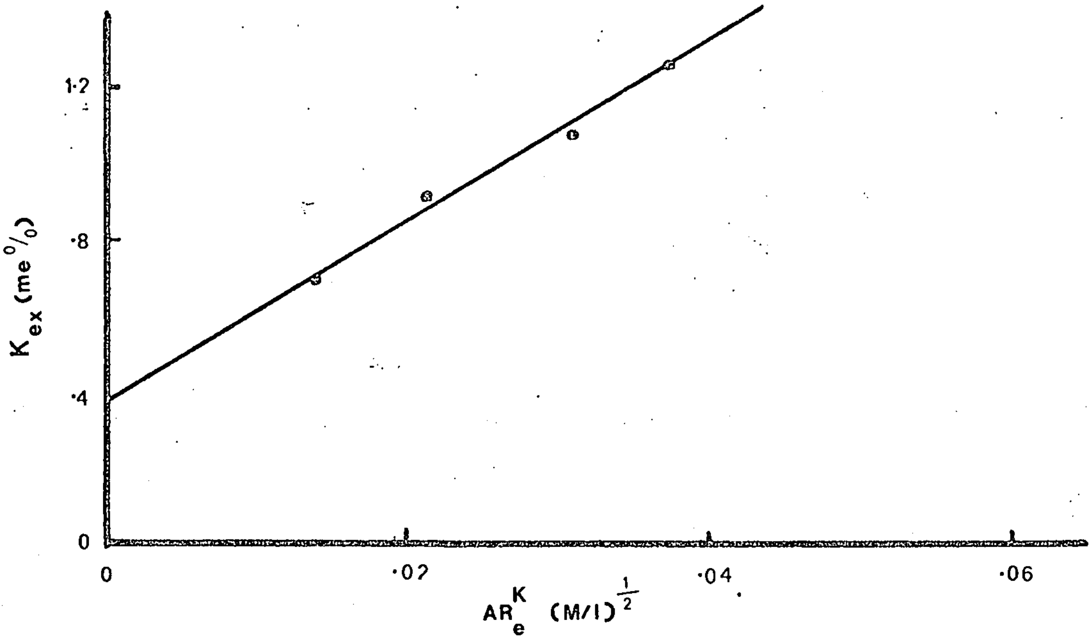

FIG. 20 Relationship between K_{ex} and AR_e^K for the Riet River No. 2 soil - 40% Na-soil in mixture.

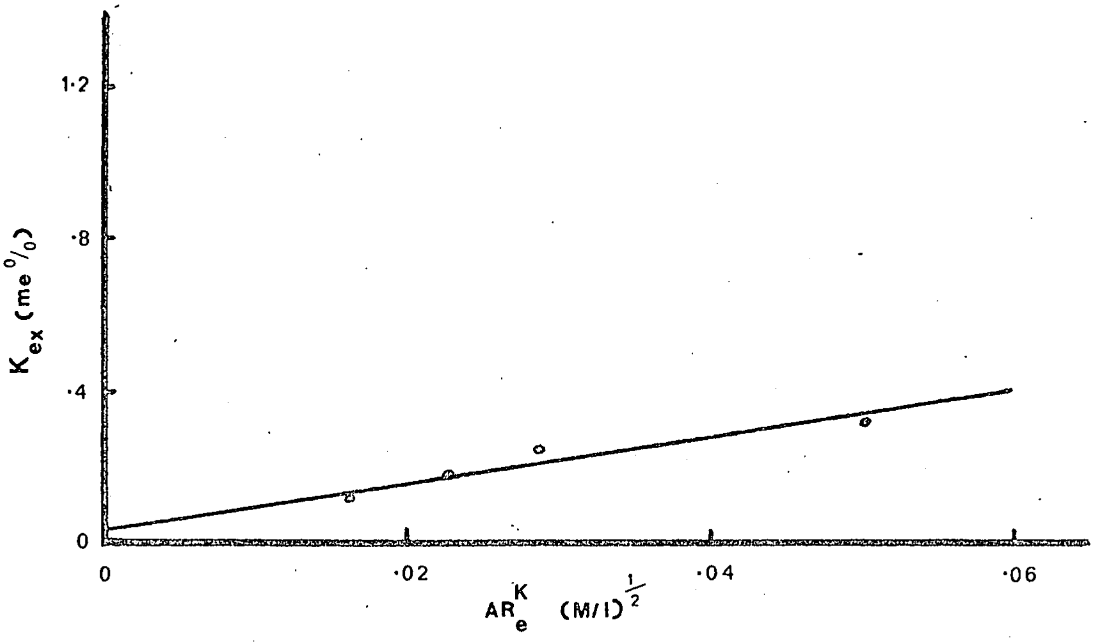

FIG. 21 Relationship between K_{ex} and AR_e^K for the Mangano soil - no Na-soil in mixture.

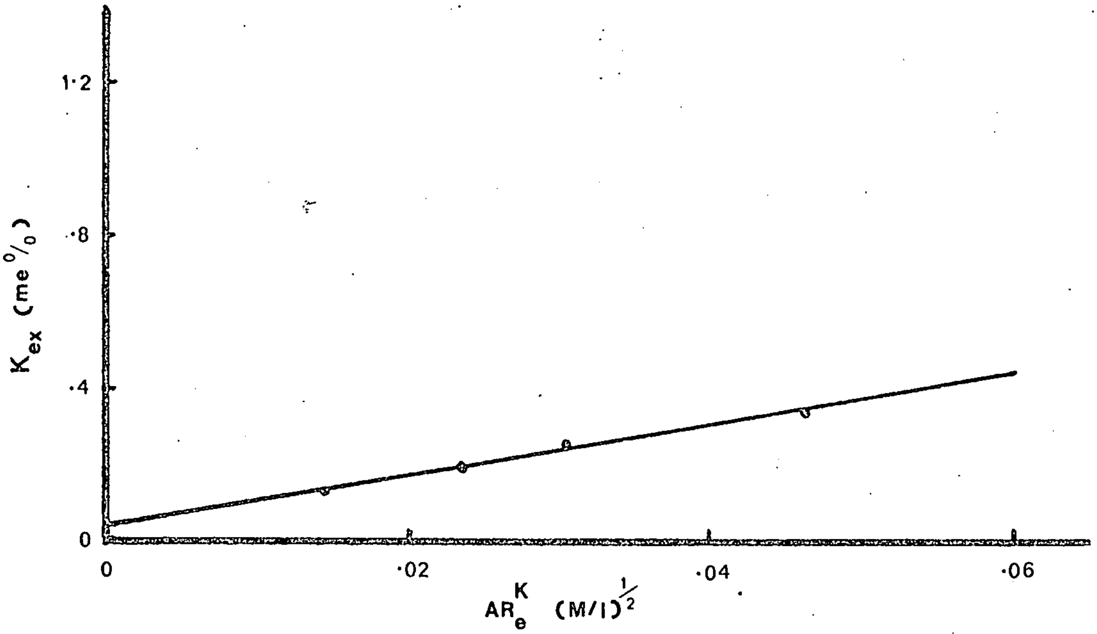

FIG. 22 Relationship between K_{ex} and AR_e^K for the Mangano soil - 20% Na-soil in mixture.

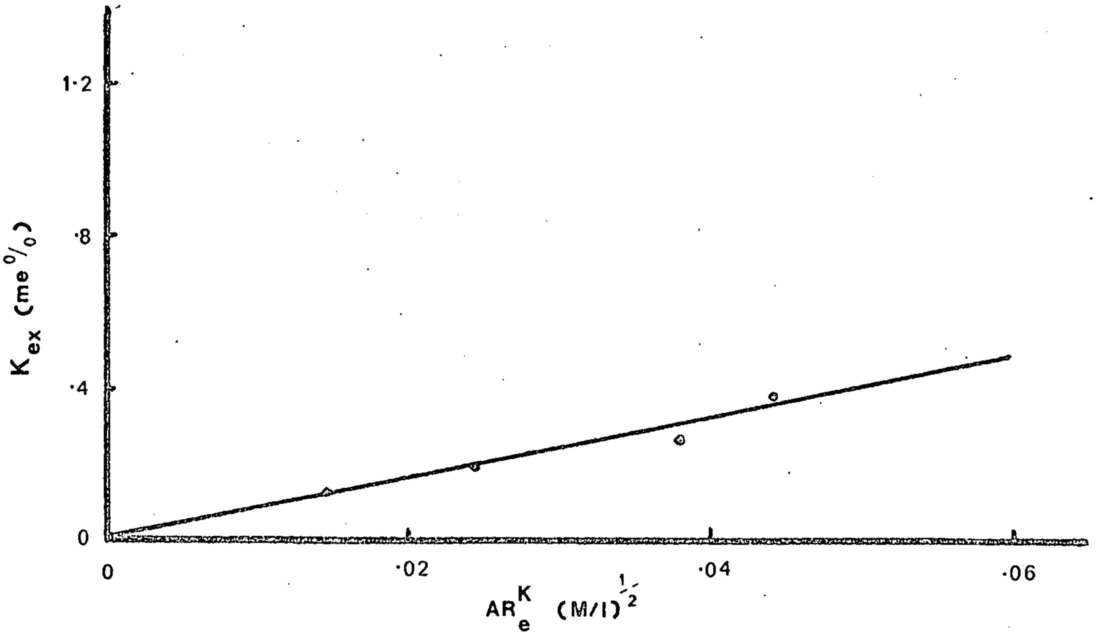

FIG. 23 Relationship between K_{ex} and AR_e^K for the Mangano soil - 40% Na-soil in mixture.

TABLE 18 - AR_e^K and PBC^K values at different K_{ex} and sodium levels for two soils

Soil	Percentage sodium soil	K_{ex} me %	AR_e^K $(M/l)^{\frac{1}{2}}$	PBC^K me %/$(M/l)^{\frac{1}{2}}$
Riet River No.2	0	0.700	0.01086	44.09
	0	0.875	0.01908	44.35
	0	0.990	0.02968	40.36
	0	1.150	0.03996	35.72
	0		Mean	41.13
	20	0.700	0.01324	48.22
	20	0.900	0.02223	33.24
	20	1.035	0.03067	41.96
	20	1.200	0.03898	39.46
	20		Mean	40.72
	40	0.700	0.01414	47.21
	40	0.925	0.02156	37.11
	40	1.080	0.03092	38.04
	40	1.265	0.03726	31.41
	40		Mean	40.10
Mangano	0	0.123	0.01632	15.10
	0	0.183	0.02263	16.69
	0	0.255	0.02891	17.00
	0	0.323	0.05028	9.68
	0		Mean	14.62
	20	0.135	0.01457	13.14
	20	0.198	0.02357	15.76
	20	0.263	0.03037	16.47
	20	0.340	0.04627	10.65
	20		Mean	14.01
	40	0.135	0.01485	16.18
	40	0.198	0.02452	10.07
	40	0.273	0.03804	10.48
	40	0.388	0.04437	12.00
	40		Mean	12.18

These decreases are, however, so small and the mutual variations within each set of samples so large that they are not significant.

In contrast to the constancy of the average PBC^K it was found that the average values of PBC^K_T of both soils were now much lower than in the previous experiment (Table 19). For the Mangano and Riet River No. 2 soils these values were 7.09 and 19.29me/100g/$(M/l)^{\frac{1}{2}}$ compared to 10.64 and 33.60me/100g/$(M/l)^{\frac{1}{2}}$ respectively. Because the mean PBC^K values remained constant and PBC^K_T values decreased considerably the ratios of mean PBC^K to PBC^K_T were much higher in this instance. The average value for all sodium levels of the Mangano soil was 1.97, compared to 1.16, and that for the Riet River No. 2 soil was 2.14, compared to 1.17. At the two lower levels of sodium saturation the PBC^K_T values of the Mangano soil were fairly similar, but at the highest level of sodium saturation PBC^K_T was higher (Table 19). The Riet River No.2 soil showed a systematic large increase in PBC^K_T with increasing level of sodium saturation. Because the mean PBC^K values were relatively unaffected by level of sodium saturation and PBC^K_T values were increased, the ratio describing the relationship between mean PBC^K and PBC^K_T decreased with increasing sodium saturation for both soils.

The EK^O values of both soils were lower in the present experiment than in the previous one. The values obtained with the series without sodium can best be compared with the values obtained in the previous experiment. The EK^O value of the Mangano soil decreased from 0.12me/100g to 0.04me/100g and that of the Riet River No. 2 soil from o.73me/100g to 0.555me/100g. In the three experiments with the Mangano soil EK^O decreased from 0.32me per 100g in the first experiment to o.12/100g in the second and to 0.04me/100g in the third. There were time lags of several months between the execution of consecutive experiments and the decreases may perhaps be ascribed to prolonged storage in tightly closed tins. Fresh samples from the tins were, however, saturated with the required cations immediately prior to the execution of each experiment so that each experiment was

actually/...............

TABLE 19 - EK^{o}, PBC_{T}^{K} and the ratio between mean PBC^{K} and PBC_{T}^{K} at different sodium levels

Soil and sodium level	EK^{o} me %	PBC_{T}^{K} me %/(M/l)$^{\frac{1}{2}}$	$\frac{\text{Mean } PBC^{K}}{PBC_{T}^{K}}$
Riet River No. 2:			
0 % Na	0.555	15.04	2.73
20 % Na	0.460	19.17	2.12
40 % Na	0.380	23.67	1.62
Mean		19.29	2.14
Mangano:			
0 % Na	0.040	6.20	2.34
20 % Na	0.045	6.62	2.12
40 % Na	0.000	8.45	1.44
Mean		7.09	1.97

actually done on a set of freshly prepared samples. The applied potassium was therefore not in contact with the soil for long periods, and long-term fixation or release of potassium could not be the cause of these differences.

The EK^{o} values of the Mangano soil were practically equal at the two lower levels of sodium saturation, but lower at the highest level. The Riet River No. 2 soil showed a gradual, fairly large, decrease in EK^{o} with increasing sodium saturation. The amount of exchangeable K which does not contribute to the intensity factor (AR_{e}^{K}) thus decreases with increasing sodium saturation. This fraction of the exchangeable potassium has also been described as the potassium which is adsorbed to specific sites. This means that sodium saturation affected the specific adsorption of potassium by these soils. The highly hydrated sodium ion probably opened up some of the interlayer surfaces and made these sites available for normal non-specific cation exchange reactions. As has been indicated in section 3.2.1 clay mineralogical studies by the method of Alexiades & Jackson (1966) indicated fair amounts of vermiculite in the soils of this Region. The results of Scott & Smith (1966) on the susceptibility of interlayer potassium in micas to exchange with sodium may provide an explanation for the observed effect of sodium on EK^{o}. They found very rapid changes in K content and increases in basal spacing of vermiculite upon treatment with sodium. They observed that interlayer K in micas is easily exchanged by sodium and further states: "NH_4 can be used to replace the K held on external surfaces of contracted mica particles, but interlayer K in an expanded component of the sample may be trapped and not replaced by the NH_4 ions. On the other hand, if Na is used, variable amounts of interlayer K in the contracted mica may be removed along with that in the expanded mineral."

This may also fit in with the observation that, in contrast to the lower EK^{o} values at higher levels of sodium saturation, at any given amount of potassium-saturated soil in a mixture there was a general tendency for total exchangeable potassium to increase with increasing amounts of sodium-saturated soil in the mixture (Table 18). The effect became

increasingly/..........

increasingly larger at higher K levels for each soil.

For the alluvial Riet River No.2 soil $-\Delta K^{o}$ and K_{ex} were again numerically of a similar order of magnitude (Table 20). For the Mangano soil $-\Delta K^{o}$ was now numerically much larger than K_{ex}. Where no sodium-saturated soil was included in the mixture the Riet River No. 2 soil gave a curvilinear relationship between $-\Delta K^{o}$ and AR_{e}^{K} (Figure 24). At 20 and 40 per cent sodium-saturated soil added the relationships were linear (Figures 25 and 26). At the two lower levels of sodium added the Mangano soil gave good linear relationships at the lower potassium levels (Figures 27 and 28). In each case the highest level of K_{ex} gave an odd point out. Where 40 per cent sodium-saturated soil was added a linear distribution of all points were found for this soil (Figure 29).

Thus far only results which were calculated in the normal way were given.

AR^{K} values were also calculated by introducing the activity of sodium ions into the equilibrated solutions into the Q/I equation. This means that the normal Q/I equation

$$AR^{K} = \frac{a_{K}}{\sqrt{a_{(Ca+Mg)}}} \quad \ldots\ldots\ldots\ldots\ldots(1)$$

was changed to

$$AR^{K} = \frac{a_{K}}{a_{Na+}\sqrt{a_{(Ca+Mg)}}} \quad \ldots\ldots\ldots\ldots(2)$$

The AR^{K} values calculated by equation (2) are lower than those calculated by equation(1) because only the denominator is increased by the term a_{Na}. The differences between the comparable AR^{K} values calculated by means of the two equations increased with increasing sodium saturation. ΔK values are independent of the change in calculation, but different AR_{e}^{K} values were obtained by plotting the new AR^{K} values against ΔK. Figure 30 gives an example of the effect of method of calculation on Q/I curves for the same set of results. The results in Table 21 show how the AR_{e}^{K} values changed by introducing a_{Na} in the equation.

The/....................

TABLE 20 - Relationship between K_{ex} and $-\Delta K^o$ at different sodium levels

Soil	Percentage sodium soil	K_{ex} me %	$-\Delta K^o$ me %	$\frac{-\Delta K^o}{K_{ex}}$x100%
Riet River No. 2	0	1.150	1.427	124
	0	0.990	1.198	121
	0	0.875	0.846	97
	0	0.700	0.474	67
	20	1.200	1.538	128
	20	1.035	1.287	124
	20	0.900	0.739	82
	20	0.700	0.638	91
	40	1.265	1.170	92
	40	1.080	1.176	109
	40	0.925	0.800	86
	40	0.700	0.668	95
Mangano	0	0.323	0.487	151
	0	0.255	0.491	193
	0	0.183	0.378	207
	0	0.123	0.246	200
	20	0.340	0.493	145
	20	0.263	0.500	190
	20	0.198	0.370	187
	20	0.135	0.191	141
	40	0.388	0.465	120
	40	0.273	0.399	146
	40	0.198	0.245	124
	40	0.135	0.240	178

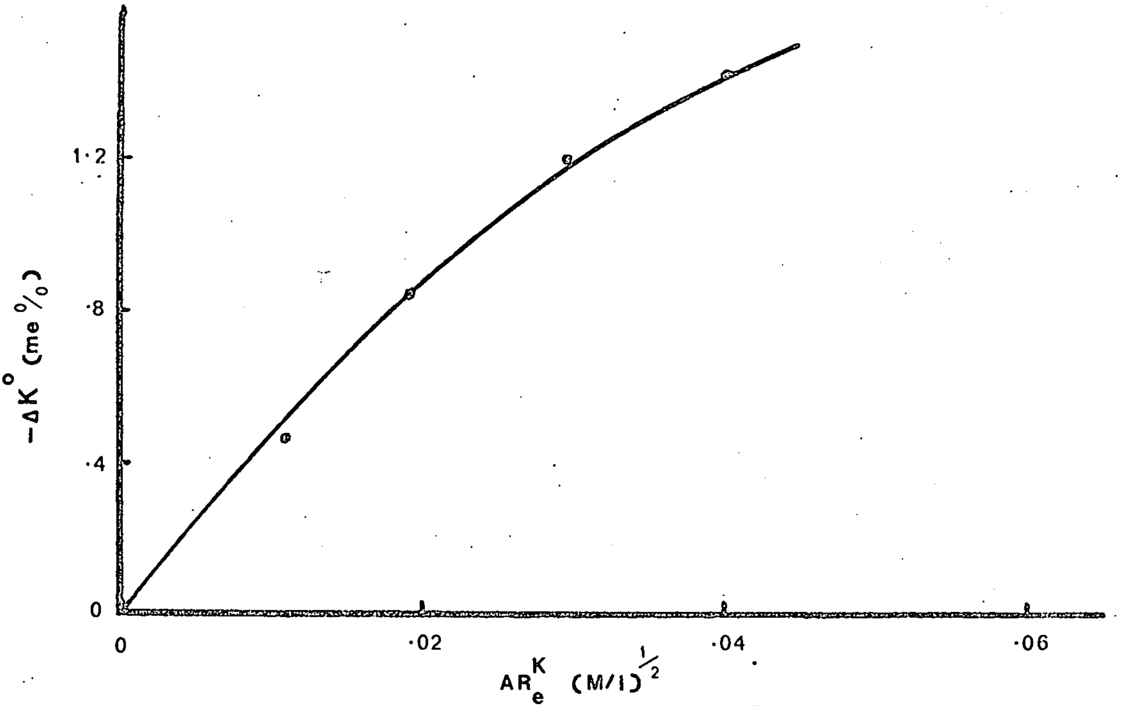

FIG. 24 Relationship between $-\Delta K^o$ and AR_e^K for the Riet River No. 2 soil - no Na-soil in mixture.

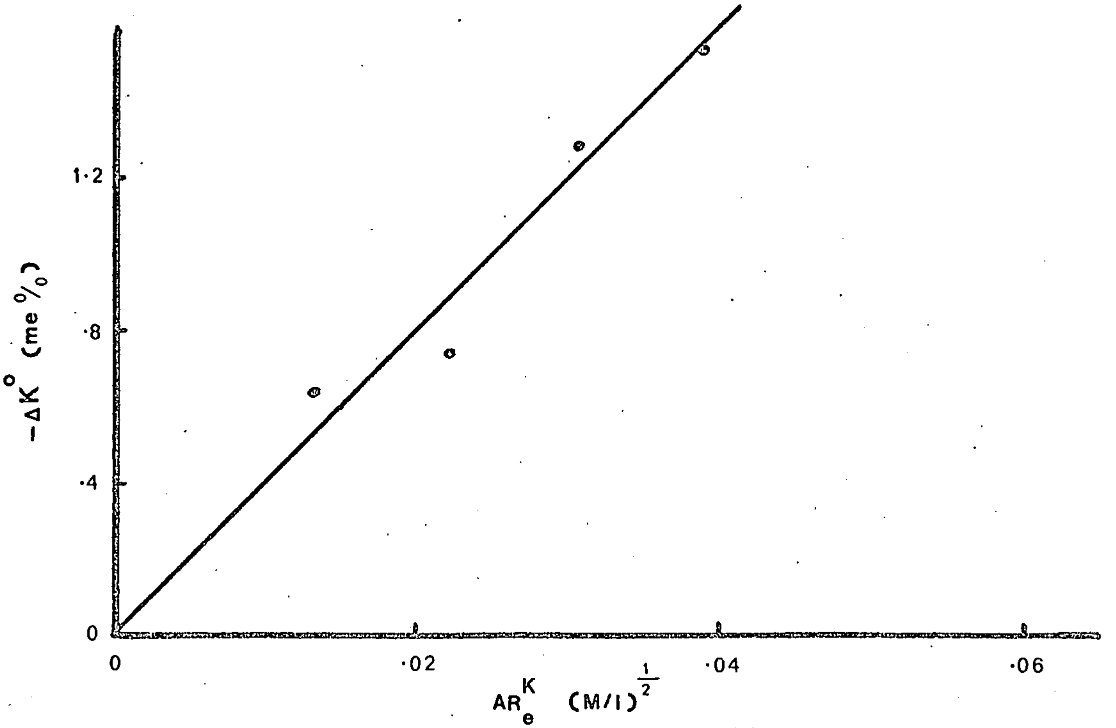

FIG. 25 Relationship between $-\Delta K^o$ and AR_e^K for the Riet River No. 2 - 20% Na-soil.

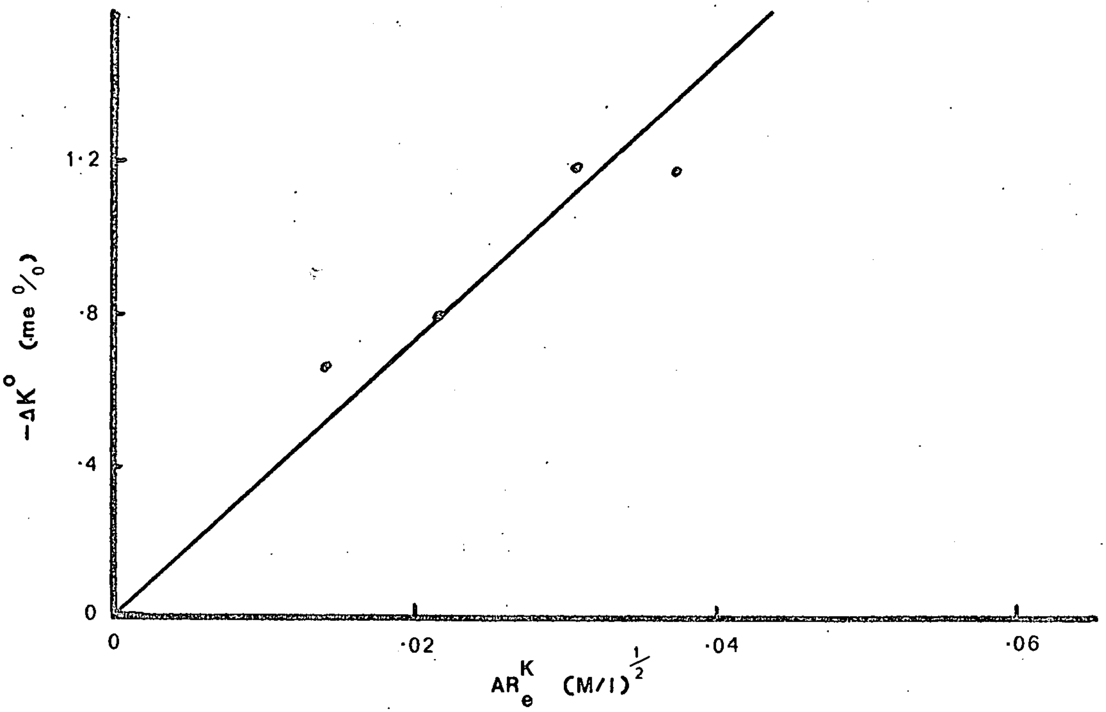

FIG. 26 Relationship between $-\Delta K^{O}$ and AR_e^K for the Riet River No. 2 soil - 40% Na-soil in mixture.

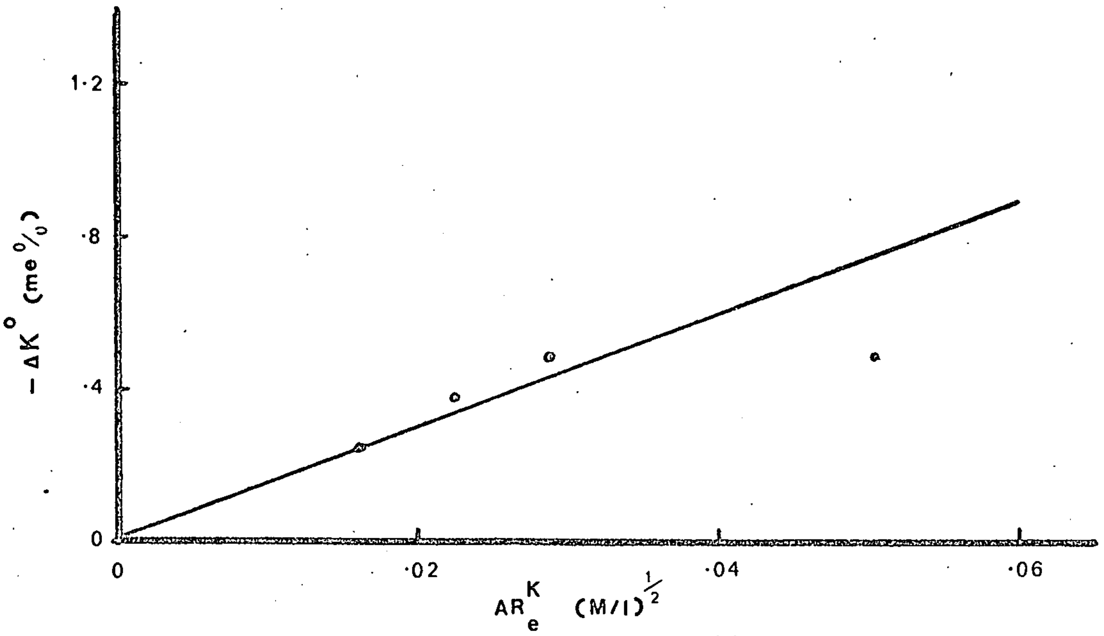

FIG. 27 Relationship between $-\Delta K^{O}$ and AR_e^K for the Mangano soil - no Na-soil in mixture.

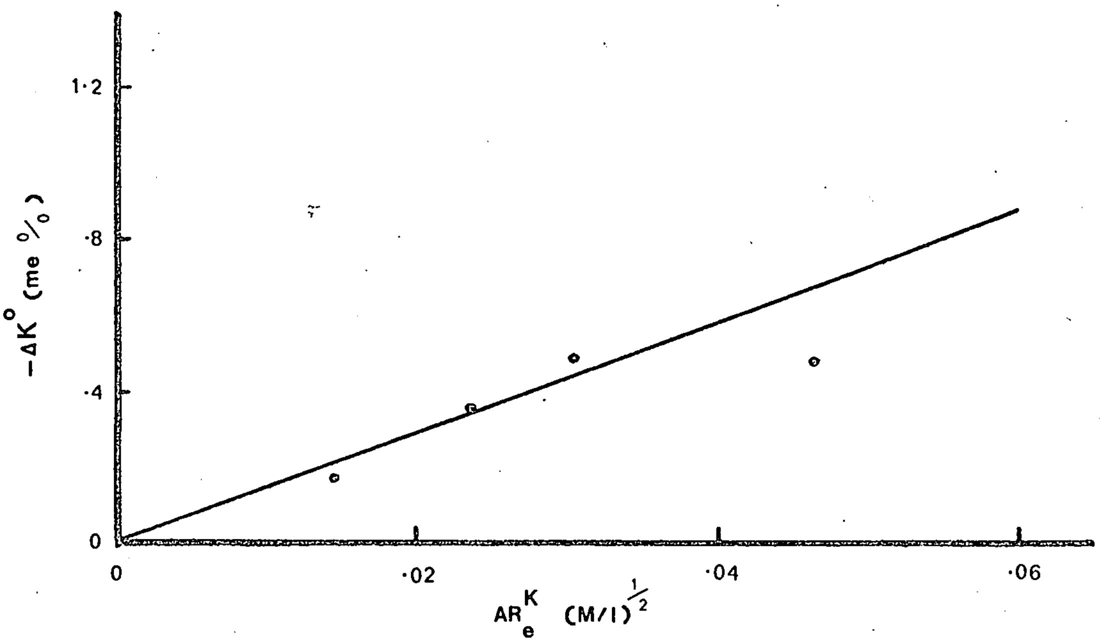

FIG. 28 Relationship between $-\Delta K^o$ and AR_e^K for the Mangano soil - 20% Na-soil in mixture.

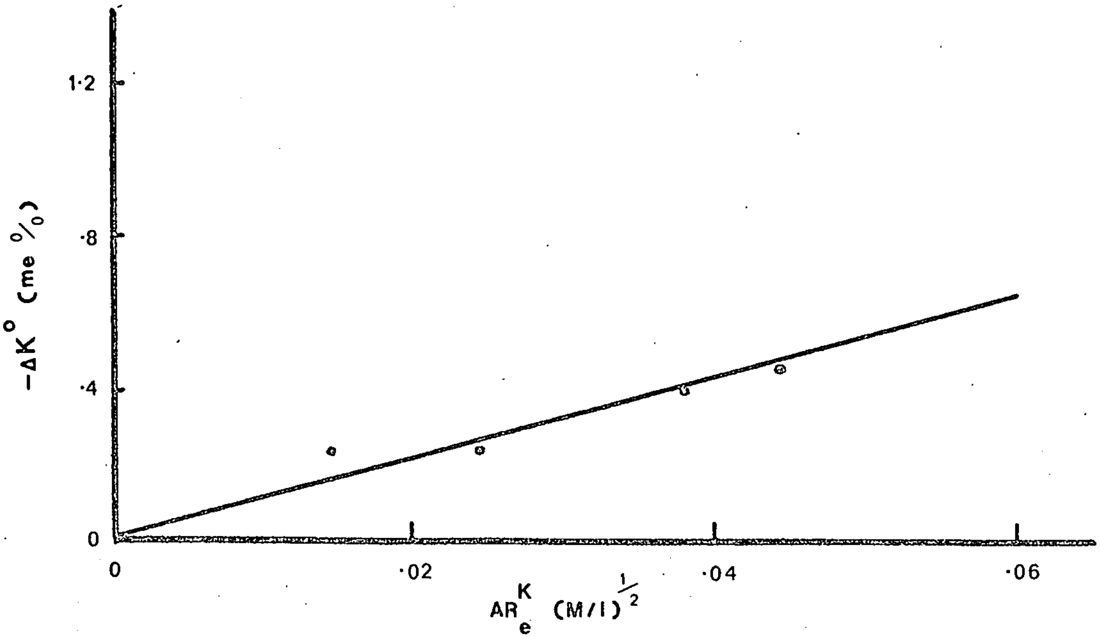

FIG. 29 Relationship between $-\Delta K^o$ and AR_e^K for the Mangano soil - 40% Na-soil in mixture.

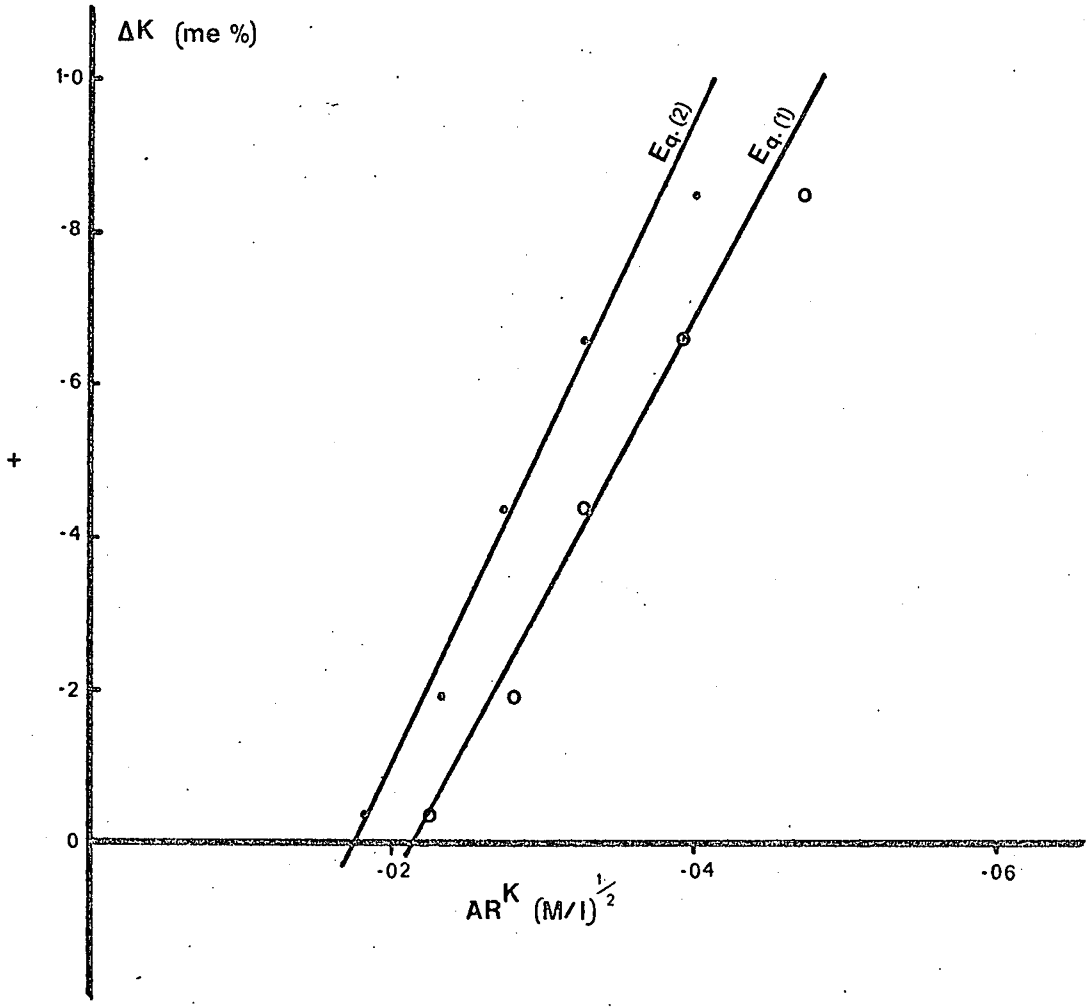

FIG. 30 Effect of incorporation of sodium into the equation for calculating AR^K on the Q/I relations of mixture F of the Riet River No. 2 soil:

Equation (1) - Sodium not incorporated.
Equation (2) - Sodium incorporated.

TABLE 21 - Effect of calculation method on AR_e^K

Soil and mixture no.		AR_e^K Equation (1)	$(M/l)^{\frac{1}{2}}$ Equation (2)	Difference	% Difference
Riet River no.2	A	.01086	.01081	.00005	0.5
	D	.01908	.01899	.00009	0.5
No sodium	G	.02968	.02953	.00015	0.5
	J	.03996	.03978	.00018	0.5
	B	.01324	.01223	.00101	7.6
20% sodium	E	.02223	.02064	.00159	7.2
	H	.03067	.02843	.00224	7.3
	K	.03898	.03615	.00283	7.3
	C	.01414	.01213	.00201	14.2
40% sodium	F	.02156	.01764	.00392	18.2
	I	.03092	.02583	.00509	16.6
	L	.03726	.03129	.00597	16.0
Mangano:	A	.01632	.01622	.00010	0.6
	B	.02263	.02249	.00014	0.6
No sodium	G	.02891	.02876	.00015	0.5
	J	.05028	.04999	.00029	0.6
	B	.01457	.01427	.00030	2.1
20% sodium	E	.02357	.02299	.00058	2.5
	H	.03037	.02972	.00065	2.1
	K	.04627	.04526	.00101	2.2
	C	.01485	.01423	.00062	4.2
40% sodium	F	.02452	.02352	.00100	4.1
	I	.03804	.03649	.00155	4.1
	L	.04437	.04266	.00171	3.9

The constancy of the relative decreases in AR_e^K at each level of sodium saturation for both soils (given as percentages) is noteworthy. In spite of this remarkable constancy at a given sodium level for a given soil, the magnitude of the effect was quite different for the two soils. For the Mangano soil the difference was approximately 0.1% for each one per cent of sodium-saturated soil included in the mixture and o.4% for the Riet River No.2 soil.

This effect may possibly be related to the difference in CEC values of the two soils, viz. 4.90me/100g for the Mangano soil and 26.24me/100g for the Riet River No.2 soil. Table 22 illustrates the average percentage differences in AR_e^K values, the CEC values and the ratios of these values between the two soils. It is evident from these ratios (notably at the 20% sodium level) that the effect of introducing sodium into the equation is most probably related to the CEC of the soil.

The CEC's of the respective soils determine the total amount of sodium brought into the systems. The calculated milli-equivalents Na^+ in each soil mixture are given in Table 23. The Riet River No. 2 soil with 3.25 and 6.50me% Na^+ contributed more sodium to the equilibrium solution through exchange with adsorbed sodium ions by calcium and potassium ions of the equilibrating solutions than the Mangano soil with 0.94 and 1.88me% Na^+ respectively at the 20% and 40% sodium levels. The comparable a_{Na} levels are given in Table 24. It is thus evident that these varying a_{Na} values are the cause of the apparently anomalous behaviour of the two soils. When the ratios between the % difference in AR_e^K and me% sodium for both soils and at both sodium levels (Table 23) are examined it is noteworthy that a constant value is obtained. Percentage sodium saturation and CEC therefore singly and collectively affect the AR_e^K of a soil.

The PBC^K values of the graphs for the values calculated by means of equation (2) were higher than those of the graphs calculated by means of equation (1), as can be seen by comparing Tables 18 and 25. This is a direct consequence of the fact that the AR^K values were decreased by using equation (2) but Δ K values were not affected. The absolute

TABLE 22 - Relationship between the % differences in AR_e^K due to method of calculation and CEC of the soils

Factor	Soil		$\frac{\text{Riet River No. 2}}{\text{Mangano}}$
	Riet River No.2	Mangano	
% Difference in AR_e^K at 20% Na	7.35	2.225	3.30
% Difference in AR_e^K at 40% Na	16.25	4.075	3.99
CEC	16.24	4.90	3.31

TABLE 23 - Ratios between calculated quantities of sodium added and % differences in AR_e^K due to calculation method

Sodium calculation	Na^+ added me%	% Difference in AR_e^K	$\frac{\text{\% Difference}}{\text{me \% } Na^+ \text{ added}}$
Riet River No.2:			
$16.24 \times \frac{20}{100}$	3.25	7.35	2.3
$16.24 \times \frac{40}{100}$	6.50	16.25	2.5
Mangano:			
$4.90 \times \frac{20}{100}$	0.94	2.225	2.4
$4.90 \times \frac{40}{100}$	1.88	4.075	2.2
		Mean	2.35

TABLE 24 - Activities of sodium ions in equilibrium solutions

Sodium activities (Moles x 10^{-3} / litre)			
20% Na soil added		40% Na soil added	
Riet River No.2	Mangano	Riet River No.2	Mangano
2.0768	0.7346	-	1.3343
2.0453	0.6779	3.8258	1.2667
2.0817	0.6764	3.8153	1.2650
2.1751	0.6794	3.7384	1.3589
2.0702	0.7616	3.8073	1.3910
1.9169	0.6809	3.5658	1.2720
2.1924	0.5420	3.4096	1.2912
2.1756	0.7684	3.8688	1.2680
2.2600	0.7670	3.9450	1.3554
2.1773	0.7690	3.8199	1.3147
2.2001	0.8952	3.8420	1.3919
1.9967	0.6818	3.5673	1.1829
2.0734	0.7358	-	1.3469
2.1766	0.7681	3.8662	1.2957
2.1696	0.7667	3.9860	1.2536
2.1737	0.7249	3.8233	1.2830
2.0313	0.8974	3.7960	1.3533
2.0507	0.6824	3.5599	1.1508
2.0768	0.7506	3.2880	1.3628
2.1766	0.8143	3.7347	1.2283
2.1701	0.7627	3.8484	1.3096
2.0850	0.7258	3.8624	1.2312
2.1624	0.7859	3.8429	1.2228
2.0009	0.6251	3.7175	1.1405
Mean: 2.1131	Mean: 0.7364	Mean: 3.7514	Mean: 1.2863

TABLE 25 - PBC^K values for two soils as calculated with equation (2)

Soil	Percentage sodium soil	K_{ex} me %	PBC^K me %/(M/l)$^{\frac{1}{2}}$
Riet River No. 2	0	0.700	44.86
	0	0.875	44.29
	0	0.990	40.47
	0	1.150	35.75
	0	Mean	41.59
	20	0.700	51.09
	20	0.900	35.35
	20	1.035	43.88
	20	1.200	41.07
	20	Mean	42.84
	40	0.700	57.31
	40	0.925	42.43
	40	1.080	44.80
	40	1.265	37.67
	40	Mean	45.56
Mangano	0	0.123	15.14
	0	0.183	16.70
	0	0.255	17.07
	0	0.323	9.74
	0	Mean	14.66
	20	0.135	13.32
	20	0.198	16.17
	20	0.263	16.80
	20	0.340	10.87
	20	Mean	14.29
	40	0.135	16.61
	40	0.198	10.47
	40	0.273	10.89
	40	0.388	12.37
	40	Mean	12.59

TABLE 26 - EK^{o}, PBC_T^K and ratio between mean PBC^K and PBC_T^K at different sodium levels, calculated by equation (2)

Soil and sodium level	EK^{o} me %	PBC_T^K me %/$(M/l)^{\frac{1}{2}}$	$\frac{\text{Mean } PBC^K}{PBC_T^K}$
Riet River No. 2:			
0% Na	0.555	15.17	2.74
20% Na	0.460	20.64	2.08
40% Na	0.380	28.45	1.60
Mean		21.42	2.14
Mangano:			
0% Na	0.040	6.23	2.35
20% Na	0.045	6.78	2.11
40% Na	0.000	8.77	1.44
Mean		7.26	1.97

and relative increases were again much higher for the Riet River No.2 soil than for the Mangano soil. For both soils the differences also increased with increasing sodium saturation.

Introduction of sodium into the equation did not have a significant effect on the EK^o values (Tables 19 and 26). PBC_T^K values were increased by the new calculation as a consequence of the decrease in AR_e^K values (Tables 19 and 26). For both soils and at all sodium levels the relative increases in PBC_T^K were similar to the relative increases in mean PBC^K (Tables 18 and 25). The ratios between mean PBC^K and PBC_T^K were therefore independent of whether sodium was introduced into the equation or not (Tables 19 and 26).

In conclusion it can be stated that sodium had a significant effect on some Q/I parameters. The magnitude of these effects are directly correlated with the total amounts of sodium introduced into the system and not with the relative amounts. In this respect the CEC of the soil plays an important part. Some effects of sodium could not be eliminated by merely introducing a_{Na} into the equation for calculating AR^K. Some parameters, e.g. ΔK, are independent of the equation used for calculating AR^K. Others, e.g. EK^o, are not significantly affected by the method of calculation.

It is evident that high sodium saturation affects the Q/I relationships directly in a number of ways, especially in a soil with a high CEC. These relationships may therefore not be considered valid in saline soils. On the other hand it may be reasoned that saline members of a given soil type cannot be compared with its non-saline members on this basis, but that comparisons within a group of saline soils could be valid. When selecting samples of a given soil type for comparative Q/I studies, e.g. for correlations within a specific series, it will therefore be necessary to distinguish between saline and non-saline members of that series, especially on finer textured soils. This will fit in well with the new South African soil classification system of Van der Eyk, Macvicar & De Villiers (1969) as amended (unpublished) in which soils within any specific series are now separated into different soil phases on the basis of salinity.

CHAPTER 5

Q/I RELATIONSHIPS OF TWO CLAY MINERALS

5.1 PURPOSE

The foregoing experiments brought forward a number of illuminating conclusions concerning the relationships between Q/I parameters and exchangeable K levels of soil samples. Since cation exchange reactions are largely a function of the nature of the exchanger, and hence the type of clay mineral, this experiment was designed to investigate the effect of amount of clay mineral present and clay mineral type on these relationships. A perusal of the available literature reveals that only little attention had been given to this aspect of Q/I relationships in experimental work.

In this experiment most attention was focussed on the effect of both quantity and type of clay mineral on the Q/I parameters.

5.2 MATERIALS AND METHODS

5.2.1 The clays

Bentonite (Riedel-De Haën bentonit) and kaolinite (B.D.H. collo-kaolin) were selected as representatives of 2:1 and 1:1 silicate clay minerals respectively. CEC values of the clay samples were determined by the usual method of leaching with IN NH_4Ac. Values of 64.80 and 4.33 me/100g clay were recorded for the bentonite and kaolin respectively. The CEC of the bentonite was therefore comparable in size to those of the clay fractions of three of the soils used in the previous experiments (cf. Table 7).

5.2.2 Preparation of the samples

Separate samples of each clay were saturated with Ca^{++} and K^{+} respectively, by the same procedure as described for the soil samples (cf. section 2.2.2). Dried and ground calcium and potassium saturated samples of each clay were mixed in the series of ratios indicated in Table 27. The CEC of each mixture was determined and it was proved that the

mixing/.................

TABLE 27 - Mixing ratios for the clays

Mixture No.	Potassium clay %	Calcium clay %
A	25	75
B	20	80
C	15	85
D	10	90
E	5	95

TABLE 28 - Cation exchange capacities of bentonite and kaolin at different K_{ex} levels

Clay	Mixture No.	K_{ex} me %	CEC me %
Bentonite	A	16.50	63.8
	B	12.25	65.4
	C	9.45	64.4
	D	7.00	65.4
	E	3.00	64.9
	Mean		64.8
Kaolin	A	0.46	4.17
	B	0.40	4.43
	C	0.29	4.22
	D	0.28	4.43
	E	0.07	4.38
	Mean		4.33

mixing ratios did not influence the CEC of any one of the clays (Table 28).

The shaking solutions used, were identical to those used in the previous two experiments, as given in Table 8 (cf. sections 3.2.2 and 4.2.2).

5.2.3 Determination of the Q/I parameters

Of each bentonite mixture six samples of 0.3g each (series a), six samples of 0.6g each (series b) and six samples of 0.9g each (series c) were weighed into 250ml Erlenmeyer flasks. The six samples of each series were treated with 100ml quantities of shaking solutions 1 to 6 respectively.

Of each kaolin mixture six samples of 7.5g each (series d), six of 15.0g each (series e) and six of 22.5g each (series f) were weighed into 250ml Erlenmeyer flasks. The six samples of each series were treated with 100ml quantities of shaking solutions 1 to 6 respectively.

The experiment was conducted at 28°C and the determination of the Q/I parameters were done as described in section 2.2.

5.2.4 Calculation of K_{ex} and ΔK

For both bentonite and kaolin K_{ex} and ΔK were firstly calculated as me/100g clay. This the usual way for calculating K_{ex} and ΔK.

In experiments with soil, values for K_{ex}, ΔK and EK^{o} are usually expressed in me/100g soil. When a ratio of 10g soil to 100ml shaking solution is used, as in the previous experiments, this is equivalent to 100g soil per 1000ml shaking solution. The clay fraction of any low-humus soil is the main source of its exchange sites and therefore regulates its cation exchange properties, including the Q/I parameters. It was therefore decided to express these parameters for bentonite also as me/1000ml equilibrating solution. This should give an indication of what can be expected when 10g soil samples containing 3%, 6% or 9% bentonite respectively were used. This would represent a series of sandy

soils/.................

soils containing different quantities of an identical montmorillonitic clay. As the quantities of kaolin used were already large, values for kaolin were not given as me/1000ml shaking solution.

5.3 RESULTS AND DISCUSSION

5.3.1 Values for bentonite as per 100g clay

The values for the Q/I parameters obtained in this way, should give an indication of the effect of different clay:solution ratios on the Q/I parameters at low clay: solution ratios.

For all three quantities of bentonite per 100ml shaking solution there was a linear relationship between K_{ex} and AR_e^K at the four lower levels of potassium saturation (Figures 31 to 33). The points for the highest level of potassium saturation in each case deviated from the line. The pattern of deviation was similar in all three cases, i.e. that the value of AR_e^K was smaller than required to fit the line.

The total curves did not fit a quadratic equation as well as the four lower points fitted a linear equation. It appears that other factors might have affected the K exchange relationships at the high level of potassium saturation. This level is, however, seldom reached in practice and should therefore not be considered a serious problem in normal soil studies.

PBC^K values for each of the three quantities of bentonite remained relatively constant at the different levels of K saturation and no definite trend was apparent (Table 29). PBC^K must therefore be considered as being independent of level of K saturation. This is in accordance with the results obtained with soils. On the other hand Le Roux & Sumner (1968) found that "there is an increase in PBC^K with decreasing K saturation" for illite and kaolinite. The values for bentonite are extremely high and increase with decreasing amount of clay. This increase is most pronounced at the smallest quantity of clay.

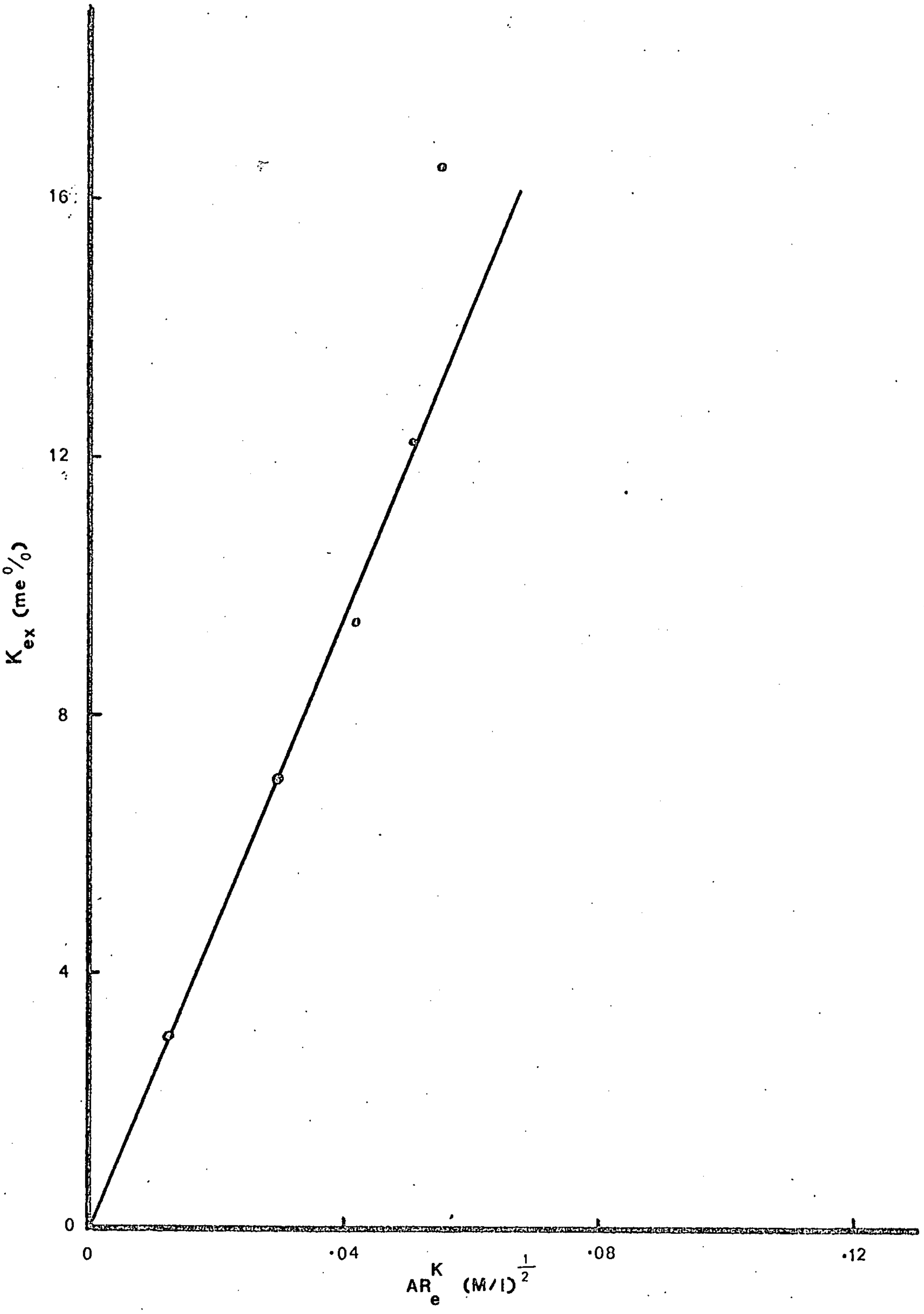

FIG. 31 Relationship between K_{ex} and AR_e^K for series a of bentonite when K_{ex} is expressed as me per 100 grams of clay.

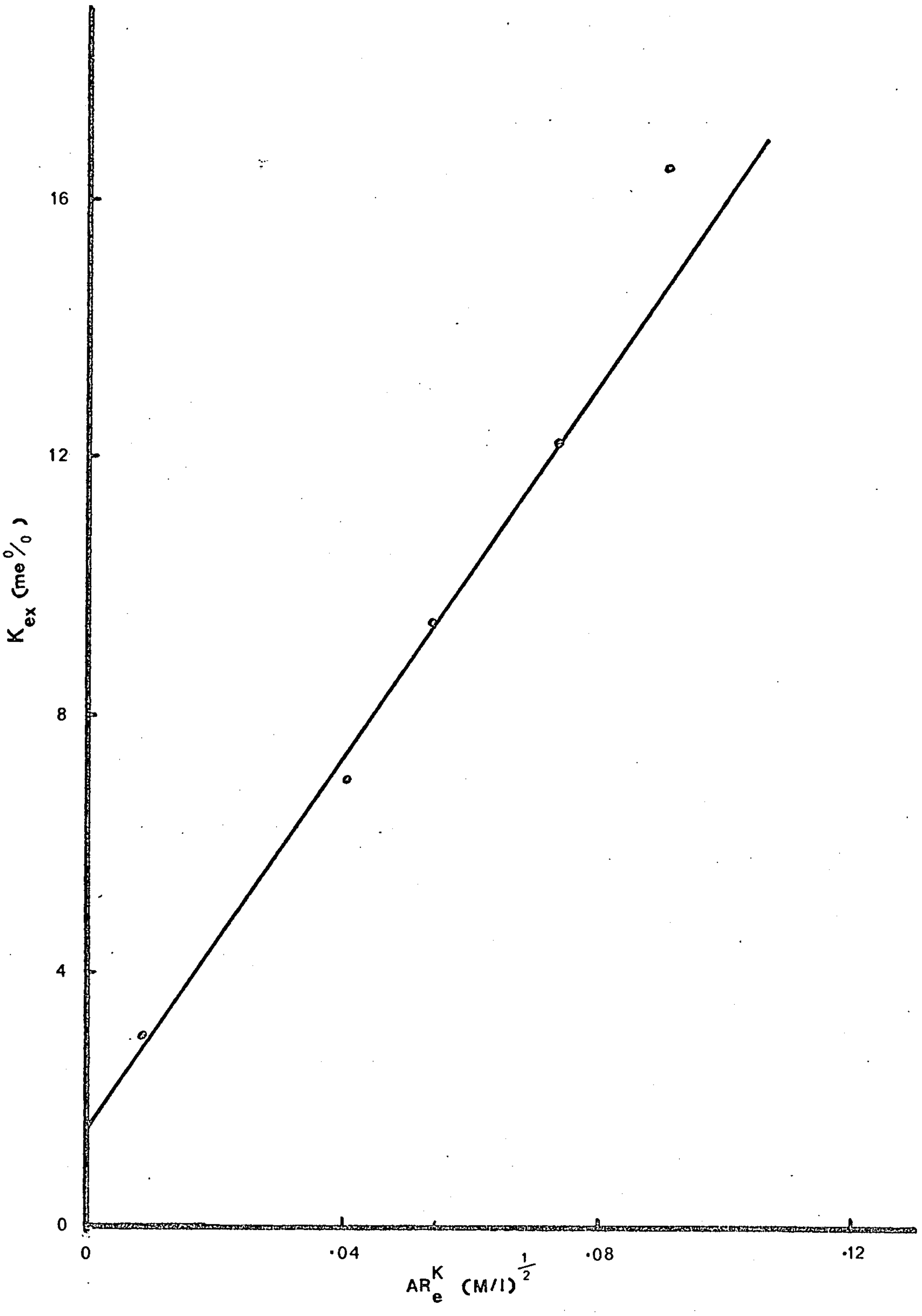

FIG. 32 Relationship between K_{ex} and AR_e^K for series b of bentonite when K_{ex} is expressed as me per 100 grams of clay.

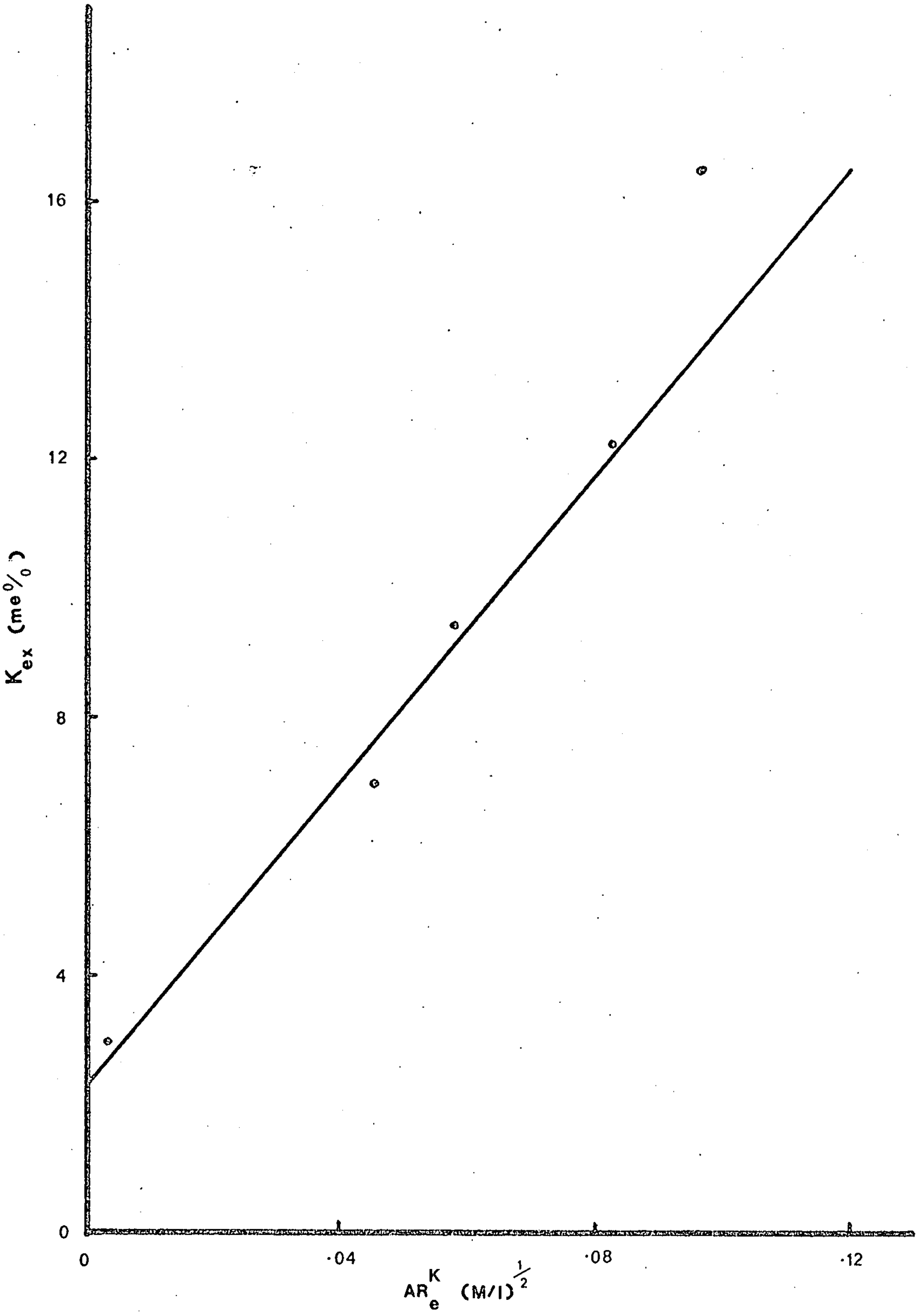

FIG. 33 Relationship between K_{ex} and AR_e^K for series c of bentonite when K_{ex} is expressed as me per 100 grams of clay.

TABLE 29 - PBC^K values for bentonite calculated as per 100 grams of clay

Quantity of clay per 100 ml	K_{ex} me %	PBC^K me $\%/(M/l)^{\frac{1}{2}}$
0.3g	16.50	635.7
	12.25	515.3
	9.45	449.0
	7.00	445.0
	3.00	487.0
	Mean	506.4
0.6g	16.50	232.2
	12.25	241.0
	9.45	292.7
	7.00	297.8
	3.00	241.2
	Mean	261.0
0.9g	16.50	200.1
	12.25	200.2
	9.45	297.2
	7.00	287.6
	3.00	169.4
	Mean	230.9

PBC_T^K also shows a sharp increase with decreasing quantity of clay (Table 30 and Figure 34). This increase is also most pronounced at the smallest quantity of clay. The ratio between mean PBC^K and PBC_T^K was relatively constant for the three quantities of clay (2.14, 1.85 and 1.96). These ratios are fairly similar to those found for the two soils in the sodium experiment (cf. Table 19, section 4.3).

EK^o values were obtained by extrapolating the lines describing the linear relationships between K_{ex} and AR_e^K at the four lower levels of potassium saturation. These values are given in Table 31. For the smallest quantity of bentonite EK^o was 0.00. For the two larger quantities EK^o increased with increasing quantity of clay. EK^o was thus related to the clay content of the equalibrating suspension for a given type of clay. This supports the results obtained for the two Riet River soils.

When expressed as milli-equivalents per 100 grams of clay, K_{ex} is of course independent of the quantity of clay used for equilibration at any specific level of K saturation of the clay. The K_{ex} values are therefore identical for the three quantities of clay (Table 32). The $-\Delta K^o$ values decreased with increasing quantity of clay at any level of potassium saturation (Table 32). $-\Delta K^o$ values were much higher than K_{ex}, except at very low potassium levels as found in samples bE and cE. From the latter it is again evident that $-\Delta K^o$ becomes only a small fraction of K_{ex} at any K_{ex} value near EK^o. This tendency was also found for the soils in the previous experiments as well as for kaolin, as will be shown later (section 5.3.3).

AR_e^K values were also affected by the quantity of clay in the suspension (Table 32). At any specific level of potassium saturation AR_e^K is increased with increased quantity of clay. These increases in AR_e^K can be ascribed to the fact that more potassium is brought into the system when larger quantities of clay are used. At equilibrium more potassium is consequently found in the solution phase to be in equilibrium with the larger quantity of potassium in the adsorbed phase. The activities of calcium and magnesium

TABLE 30 - Mean PBC^K, PBC_T^K and the ratio between mean PBC^K and PBC_T^K for bentonite as per 100 grams of clay

Quantity of clay per 100 ml	Mean PBC^K me %/$(M/l)^{\frac{1}{2}}$	PBC_T^K me %/$(M/l)^{\frac{1}{2}}$	$\frac{\text{Mean } PBC^K}{PBC_T^K}$
0.3g	506.4	236.0	2.15
0.6g	261.0	143.2	1.82
0.9g	230.9	118.1	1.96

TABLE 31 - EK^O values for bentonite as per 100 grams of clay

Quantity of clay per 100 ml	EK^O me %
0.3g	0.00
0.6g	1.60
0.9g	2.33

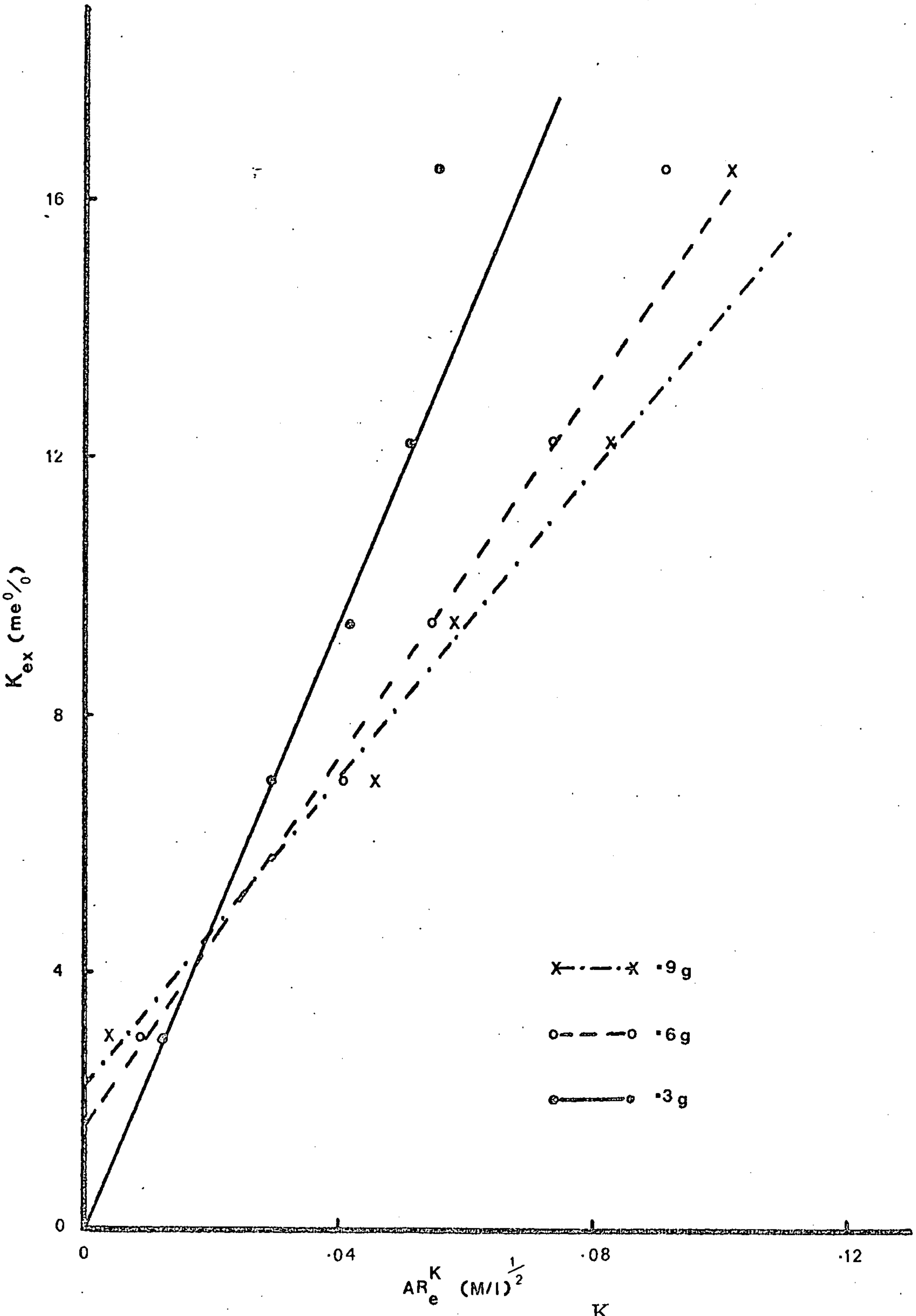

FIG. 34 Relationship between K_{ex} and AR_e^K for different quantities of bentonite per 100 ml shaking solution when K_{ex} is expressed as me per 100 grams of clay.

TABLE 32 - AR_e^K, K_{ex}, $-\Delta K^o$ and the ratios between $-\Delta K^o$ and K_{ex} for bentonite, as per 100 grams of clay

Quantity of clay per 100 ml	AR_e^K $(M/l)^{\frac{1}{2}}$	K_{ex} me %	$-\Delta K^o$ me %	$\frac{-\Delta K^o}{K_{ex}}$ x100%
0.3g	0.0552	16.50	36.00	218
	0.0508	12.25	26.00	213
	0.0418	9.45	18.66	197
	0.0297	7.00	13.33	191
	0.0125	3.00	6.00	200
0.6g	0.0911	16.50	20.50	124
	0.0736	12.25	18.84	154
	0.0540	9.45	17.34	183
	0.0407	7.00	12.00	171
	0.0086	3.00	2.00	67
0.9g	0.1014	16.50	20.00	121
	0.0827	12.25	16.44	134
	0.0578	9.45	16.89	179
	0.0454	7.00	13.11	187
	0.0037	3.00	0.56	19

in the equilibrium solutions remain relatively constant and thus the higher potassium activities lead to higher AR_e^K values. It is evident that AR_e^K is largely a function of the quantity of adsorbed potassium in the system and this quantity is determined by the level of K saturation, clay content and CEC of the clay. The same conclusion was reached for a_{Na} in the previous experiment (section 4.3). It is, however, important to note the effect of EK^o on the relationship between AR_e^K and quantity of exchangeable K brought into the system. AR_e^K is zero at EK^o and, as EK^o is larger for larger quantities of clay, this means that AR_e^K becomes zero at higher K_{ex} levels for larger quantities of clay. This is the cause of the results for the lowest level of K saturation, where AR_e^K decreases with increasing clay content. For the larger quantities of clay the corresponding K_{ex} values are much nearer to EK^o than for the smaller quantities.

The decreases in AR_e^K and increases in $-\Delta K^o$ and PBC^K with decreasing quantities of clay, and especially the fact that these decreases and increases become far more pronounced for the smallest quantity of clay, are noteworthy in relation to the patterns found in the usual Q/I studies described in literature. In those studies a curved lower part is induced in the Q/I relationship by introducing a set of shaking suspensions containing progressively smaller quantities of clay or soil per constant volume of equilibrating solution. These smaller quantities of soil or clay are only shaken with equilibrating solutions containing no potassium initially. The ΔK values obtained by shaking smaller quantities of soil or clay are always smaller (or larger negative) than those obtained by shaking larger quantities of soil or clay with the same equilibrating solution. The decreases in ΔK values become progressively larger as the quantities of clay or soil used for shaking are decreased progressively. This trend is similar to the pattern indicated by the results of the present experiment. Each of the points obtained by using a smaller quantity of soil or clay for shaking would therefore represent only one point of a separate linear graph which would have been obtained had each of the smaller quantities been shaken with the whole

series/....................

series of shaking solutions. This may be an indication that the curved part of the Q/I relationship is largely an artificially induced factor and not a characteristic of the Q/I relationship.

The curved part of the Q/I relationship is not used for obtaining any of the Q/I parameters $-\Delta K^O$, AR_e^K and PBC^K. Beckett (1964b) and others stated that by extrapolation of the curved part of the Q/I graph a measure of the non-exchangeable K content of a soil is obtained. Both Beckett & Nafady (1967) and Fariña (1970), however, indicated that extrapolation of this line, tending to be asymptotic, involves too much uncertainty to be of real value. It would seem that the curved part is only of little value and confuses the Q/I concept rather than serving any specific purpose. It may be better to omit it and concentrate more on the upper linear part of the graph which is the actual relationship which gives all the Q/I parameters.

The fact that clay:solution ratio affected all three Q/I parameters, viz. $-\Delta K^O$, AR_e^K and PBC^K should be taken into consideration. It seems to indicate that the choice of any specific clay:solution ratio or soil:solution ratio for general routine use would be relatively arbitrary and empirical like all the other methods for determining "available" plant nutrients. It has already been indicated that large differences in Q/I parameter values between different clay: solution ratios occur mainly at very low clay:solution ratios.

5.3.2 Values for bentonite as per 1000ml shaking solution

Whereas the previous calculations primarily gave an indication of the effect of clay:solution ratio (or soil: solution ratio) on Q/I parameters, the calculation used here will give an indication of the effect of varying clay content on the Q/I parameters of soils containing the same clay mineral species.

Firstly the effect of the method of calculation should be considered briefly. It should be noted that AR^K remains the same, because AR^K is a characteristic of the equilibrating solution after attaining equilibrium with the

solid/................

solid phase. Furthermore it is a ratio and not an absolute value.

ΔK is influenced directly and strongly because it is expressed in milli-equivalents per any chosen weight of clay or soil. In each series, that is for each weight of clay used for shaking, all ΔK values will vary with the same ratio between the two different calculations. This ratio is given by the ratio between the quantities of clay in terms of which ΔK is expressed. The case where 0.3g clay was used per 100ml shaking solution can be taken as an example. When ΔK values are calculated as me/1000ml shaking solution it means that ΔK values are given as me/3g clay. In the previous section it was given as me/100g clay. The ratio will thus be $\frac{3}{100}$ or 0.03. Likewise $-\Delta K^{O}$ and PBC^{K} values change in the same ratio as ΔK. The conversion ratios for 0.6 and 0.9g/100ml are 0.06 and 0.09 respectively.

Because AR^{K} values remain unchanged and the relative changes in ΔK values are equal, AR_{e}^{K} values remain unchanged irrespective of the method of calculation of ΔK. This is illustrated in Figure 35 where the Q/I graphs for the same set of values, but calculated by the two methods, are given.

K_{ex} values are expressed in the same units as ΔK and therefore the relative changes in the K_{ex} values from me/100g to me/3, 6 or 9g will be the same as those in ΔK. This means that the ratios describing the relationships between K_{ex} and $-\Delta K^{O}$ will not be affected by the method of calculation.

Furthermore, as K_{ex} values change with a constant ratio and AR_{e}^{K} values remain unchanged it means that PBC_{T}^{K} will also change with the same ratio as K_{ex} for each set of samples. From what has been said previously it is evident that for a certain set of values mean PBC^{K} and PBC_{T}^{K} will change in the same ratio and consequently the ratio describing the relationship between them will remain unaltered.

EK^{O} will change with the same ratio as K_{ex}, PBC_{T}^{K}, ΔK, $-\Delta K^{O}$ and PBC^{K}. These are all the parameters which are changed by the method of calculation. The parameters which remain unchanged are AR^{K}, AR_{e}^{K}, the ratio between K_{ex} and $-\Delta K^{O}$ and the ratio between mean PBC^{K} and PBC_{T}^{K}.

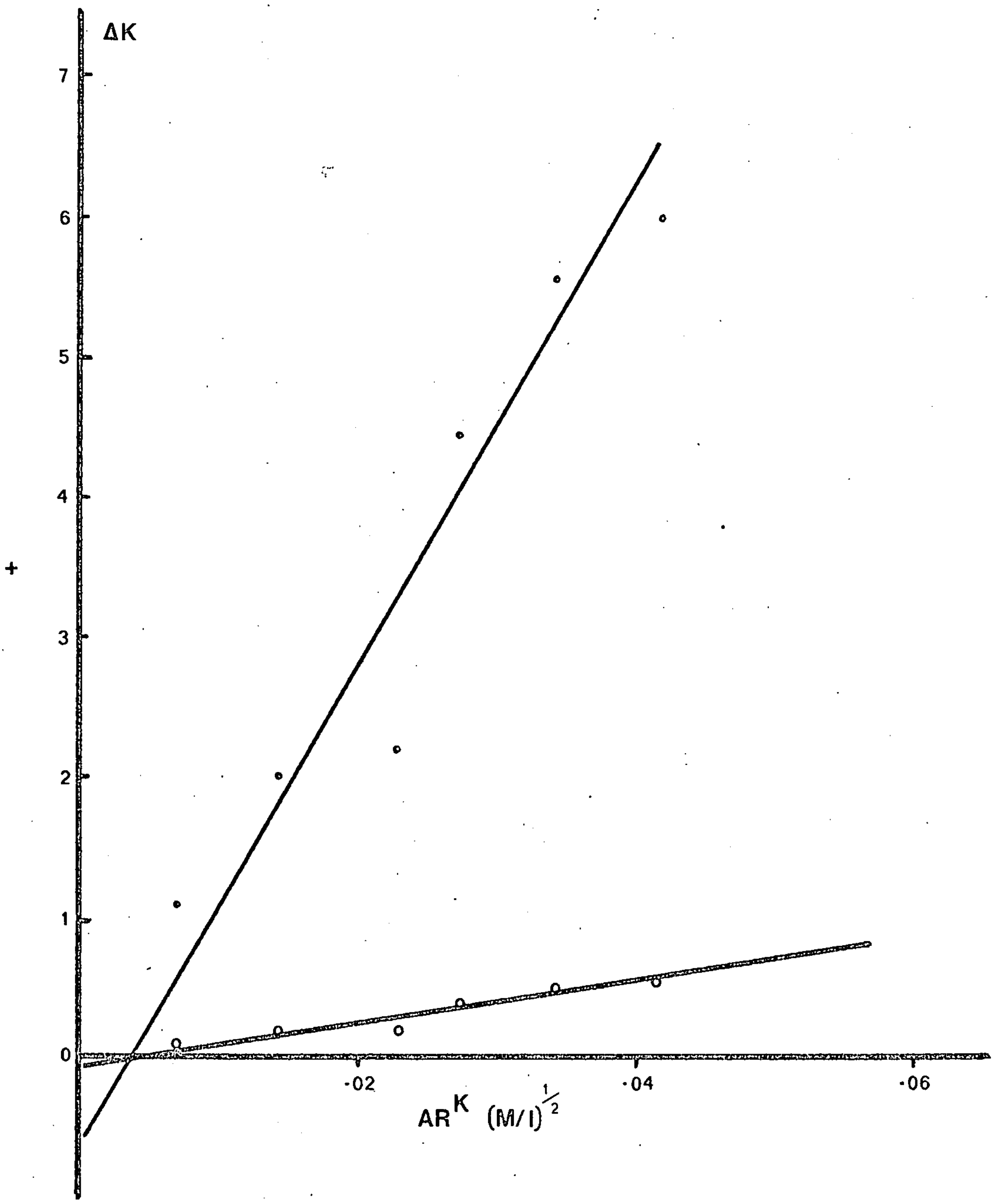

FIG. 35 Effect of way of expression of ΔK on the Q/I relations of mixture E, series c, of bentonite:

●——● ΔK as me %.

○——○ ΔK as me/1000 ml.

The actual results obtained for bentonite when calculated as me/1000ml are discussed below:

For all three quantities of bentonite the relationship between K_{ex} and AR_e^K remained linear for the four lower levels of potassium saturation, but the points at the highest level again deviated from the lines (Figure 36).

The EK^O values obtained by extrapolating the linear parts of the graphs for the relationship between K_{ex} and AR_e^K are given in Table 33. For 0.3g bentonite EK^O was again 0.00. For 0.6 and 0.9g bentonite EK^O increased in correspondence to the increases in quantity of clay. EK^O was thus directly correlated with quantity of clay of a given type in this instance.

PBC^K values were relatively constant and independent of level of K saturation (Table 34). Mean PBC^K and PBC_T^K values and the ratios between them are given in Table 35. For 0.3 and 0.6g clay the mean PBC^K values were relatively constant at 15.19 and 15.86 respectively, but for 0.9g it was slightly higher at 20.78. There was a gradual small increase in PBC_T^K with increasing quantities of clay (7.68, 8.59 and 10.63 10.63). These values are of the same order as those found for the sandy soils (cf. section 3.3).

The most notable difference found between the two methods of calculation is that the graphs giving the relationship between K_{ex} and AR_e^K cross each other when K_{ex} is expressed as me/100g clay, but are more or less parallel to each other when expressed as me/1000ml. In the latter case there is, furthermore, no sharp increase in mean PBC^K and PBC_T^K with decreasing quantity of clay.

5.3.3 Values for kaolin as per 100 grams of clay

The quantities of kaolin per 100ml of shaking solution were chosen to give CEC values more or less comparable to those of the bentonite quantities used (Table 36).

The most important result obtained with kaolin is that there was a linear relationship between K_{ex} and AR_e^K for all levels of potassium saturation and for all three quantities of clay (Figures 37 to 39). There was no deviation from linearity at the highest level of K saturation

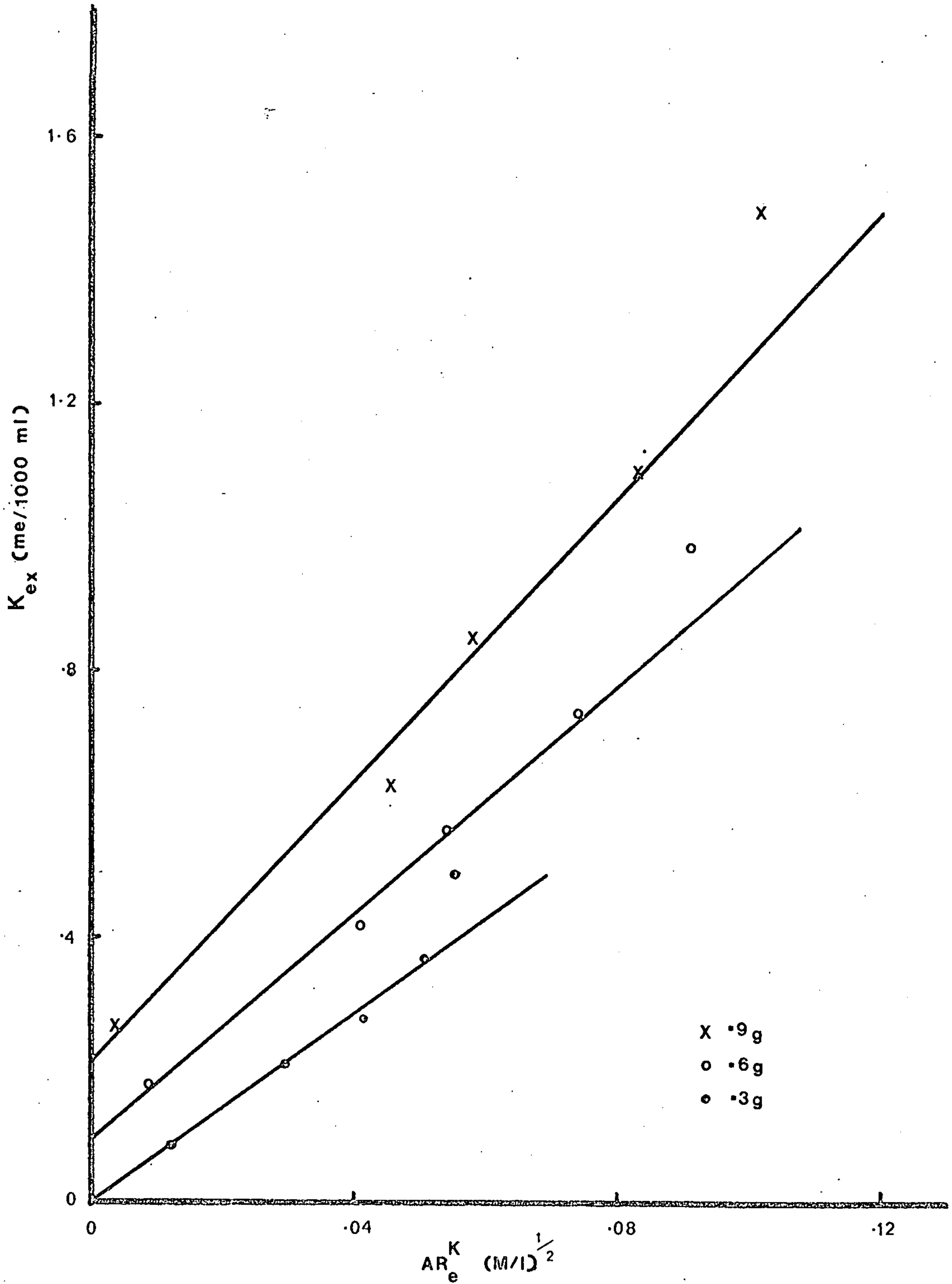

FIG. 36 Relationships between K_{ex} and AR_e^K for different quantities of bentonite per 100 ml shaking solution with K_{ex} expressed as me per 1000 ml shaking solution.

TABLE 33 - EK^o values for bentonite calculated as per 1 000ml of shaking solution

Series no.	EK^o me/litre
a	0.000
b	0.096
c	0.210

TABLE 34 - PBC^K values for bentonite as per 1000ml equilibrating solution

Series No.	Mixture No.	$PBC^K (me\%/(M/l)^{\frac{1}{2}})$
a (0.3g/100ml)	A	19.07
	B	15.46
	C	13.47
	D	13.35
	E	14.61
	Mean	15.19
b (0.6g/100ml)	A	13.93
	B	14.46
	C	17.56
	D	17.87
	E	14.47
	Mean	15.66
c (0.9g/100ml)	A	18.01
	B	18.02
	C	26.75
	D	25.88
	E	15.25
	Mean	20.78

TABLE 35 - Mean PBC^K, PBC^K_T and the ratio between mean PBC^K and PBC^K_T for bentonite as per 1000ml shaking solution

Series No.	Mean PBC^K $me\%/(M/l)^{\frac{1}{2}}$	PBC^K_T $me\%/(M/l)^{\frac{1}{2}}$	$\frac{\text{Mean } PBC^K}{PBC^K_T}$
a	15.19	7.08	2.15
b	15.66	8.59	1.82
c	20.78	10.63	1.96

TABLE 36 - Cation exchange capacities of weights of clay used per 100ml shaking solution

Clay	Series no.	CEC of clay per 100 ml
Bentonite	a	0.194
	b	0.389
	c	0.583
Kaolin	d	0.325
	e	0.650
	f	0.974

TABLE 37 - EK^{o} and PBC_{T}^{K} values for kaolin calculated as per 100 grams of clay

Series no.	PBC_{T}^{K} me%/$(M/l)^{\frac{1}{2}}$	EK^{o} me%
d	12.21	0.109
e	13.20	0.053
f	11.19	0.088

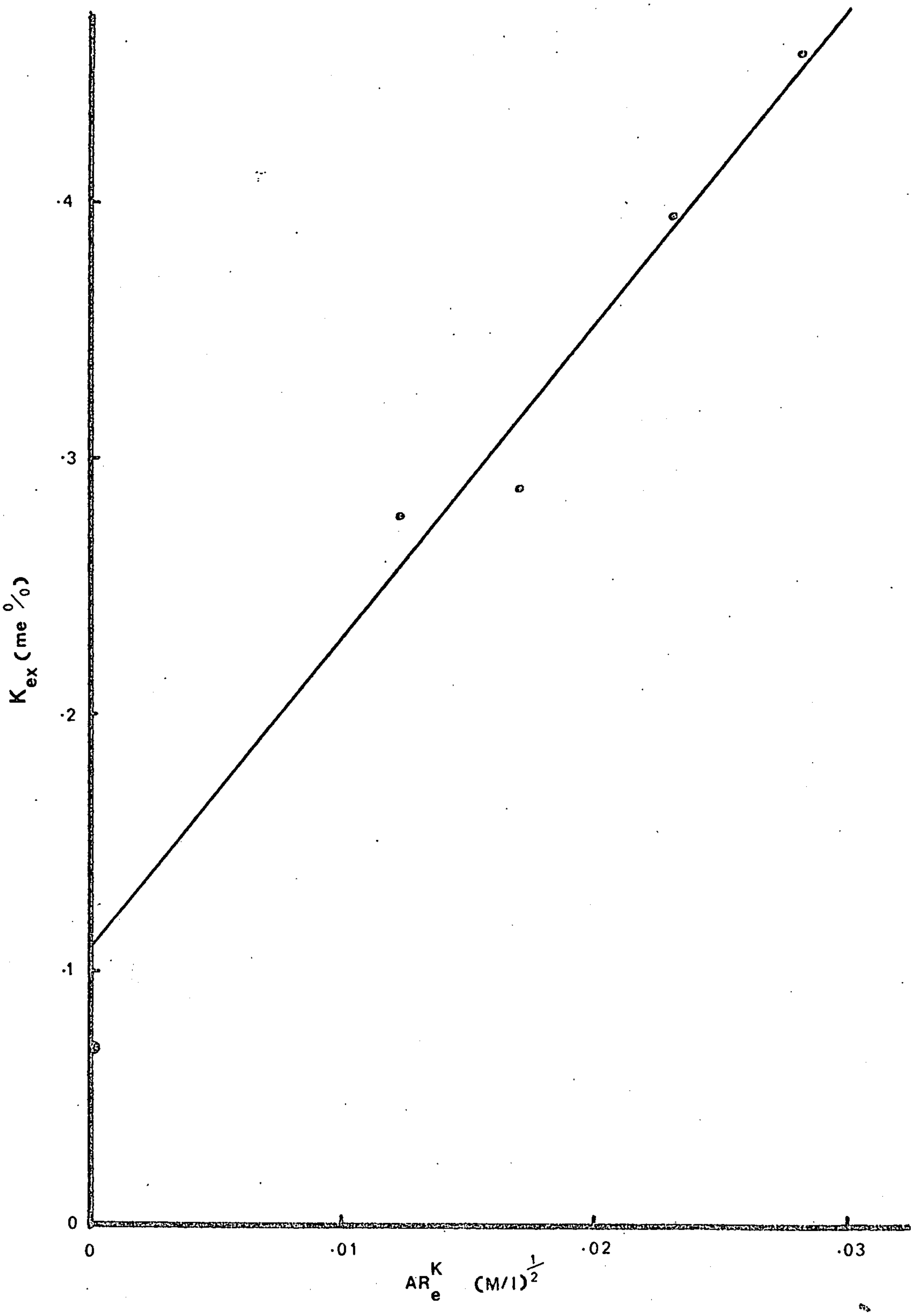

FIG. 37 Relationship between K_{ex} and AR_e^K for series d of kaolin.

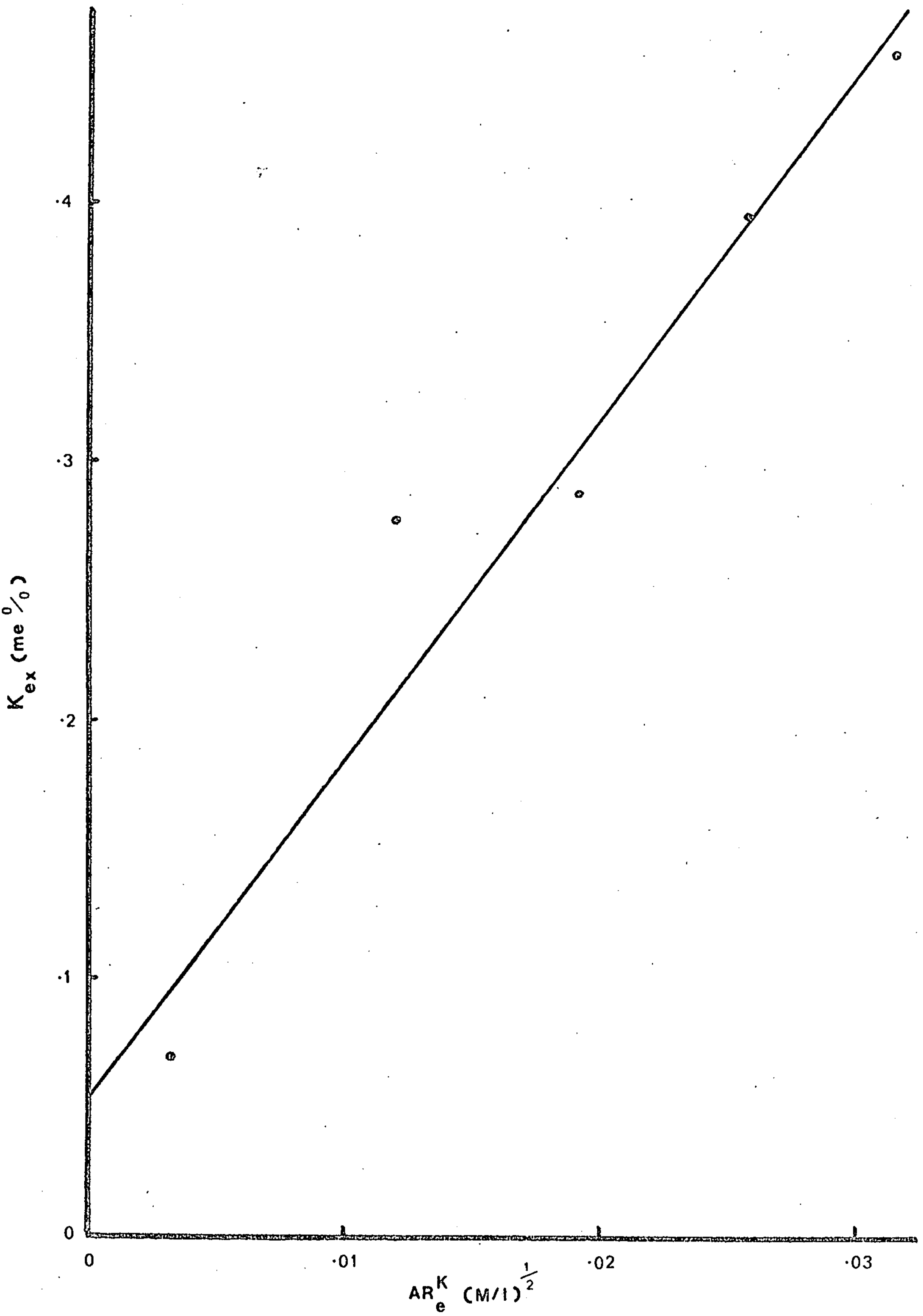

FIG. 38 Relationship between K_{ex} and AR_e^K for series e of kaolin.

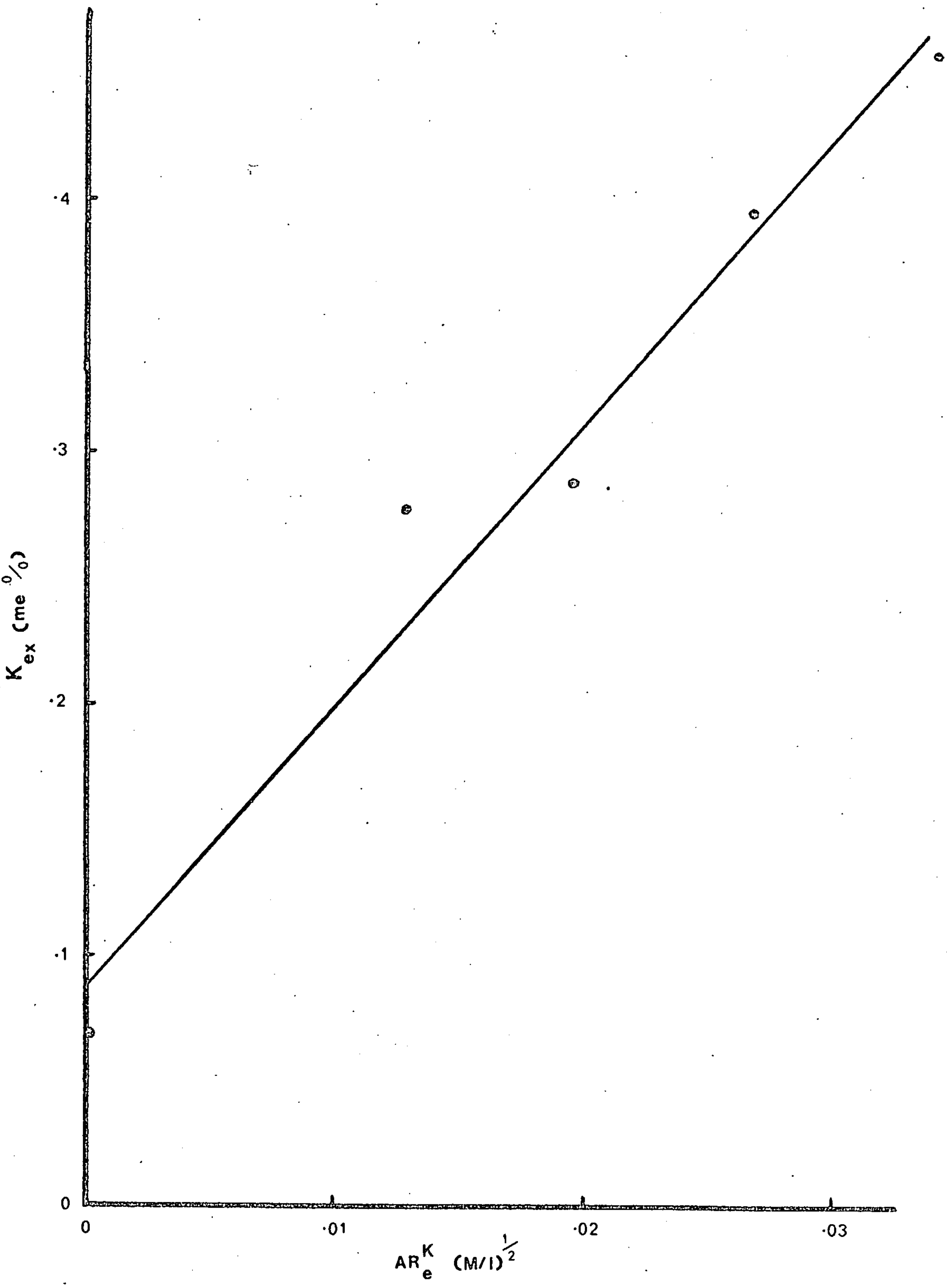

FIG. 39 Relationship between K_{ex} and AR_e^K for series f of kaolin,

as in the case of bentonite.

The PBC_T^K values for the three kaolin quantities did not differ significantly (Table 37). EK^o varied much (Table 37), but showed no general trend. It was lowest for 15.0g kaolin and highest for 7.5g kaolin with 22.5g in an intermediate position.

PBC^K values were constant and independent of level of potassium saturation for all three quantities of clay (Table 38). As can be seen the PBC^K values for kaolin were much lower than the corresponding PBC^K values for bentonite (i.e. per 100g clay). The ratio between the mean PBC^K for bentonite (333.3) and kaolin (16.42) was 20.30 and the ratio between the CEC of bentonite (64.80me/100g) and kaolin (4.33me/100g) was 14.97. The magnitude of the ratios was therefore roughly of the same order. When the values for the extremely low bentonite quantity (0.3g) is omitted the ratio between the means for bentonite (245.8) and kaolin (16.42) is 14.97 too. It must be kept in mind that the smallest quantity of bentonite in all respects differed much from the others.

The ratios describing the relationships between mean PBC^K and PBC_T^K for kaolin were lower than for bentonite (Tables 30 and 39).

For all three quantities of clay $-\Delta K^o$ values were numerically similar to the corresponding K_{ex} values at higher levels of potassium saturation (Table 40). At lower levels $-\Delta K^o$ values were much smaller than K_{ex} and actually dropped to zero at levels of K_{ex} approaching EK^o.

It can thus be stated that the results obtained with kaolin support the results obtained in the other experiments. This is especially true for the linear relationship between K_{ex} and AR_e^K, the relationship between K_{ex} and $-\Delta K^o$ and the independence of PBC^K from level of potassium saturation (K_{ex}).

TABLE 38 - PBC^K values for kaolin as per 100 grams of clay

Series no.	Mixture no.	PBC^K (me%/(M/l)$^{\frac{1}{2}}$)
d	A	16.93
	B	21.07
	C	20.97
	D	13.64
	E	12.69
e	A	21.62
	B	16.64
	C	18.21
	D	19.03
	E	17.83
f	A	12.70
	B	14.65
	C	13.08
	D	13.83
	E	13.35

TABLE 39 - Mean PBC^K and the ratio between mean PBC^K and PBC^K_T for kaolin

Series no.	Mean PBC^K me%/(M/l)$^{\frac{1}{2}}$	$\frac{\text{Mean } PBC^K}{PBC^K_T}$
d	17.06	1.40
e	18.67	1.41
f	13.52	1.21

TABLE 40 - K_{ex}, $-\Delta K^o$ and the ratio between $-\Delta K^o$ and K_{ex} for kaolin as per 100 grams of clay

Quantity of clay per 100ml	K_{ex} me%	$-\Delta K^o$ me%	$\frac{-\Delta K^o}{K_{ex}} \times 100\%$
7.5g	0.457	0.47	102
	0.395	0.48	122
	0.288	0.35	123
	0.278	0.16	58
	0.070	0.00	0
15.0g	0.457	0.68	149
	0.395	0.43	109
	0.288	0.33	116
	0.278	0.25	91
	0.070	0.05	76
22.5g	0.457	0.43	94
	0.395	0.39	99
	0.288	0.25	88
	0.278	0.17	61
	0.070	0.00	0

CHAPTER 6

THE INFLUENCE OF HIGH LEVELS OF POTASSIUM SATURATION ON THE RELATIONSHIP BETWEEN EXCHANGEABLE POTASSIUM AND AR_e^K FOR BENTONITE

6.1 PURPOSE

In a previous experiment with bentonite (section 5.3.1) it was found that the point describing the relationship between K_{ex} and AR_e^K at the highest level of potassium saturation (25% K) invariably deviated from linearity. The present experiment was designed to include a series of high potassium levels, up to 40% K saturation, in order to investigate the relationship between K_{ex} and AR_e^K at these very high levels of potassium saturation.

As the pattern was very similar for the three quantities of bentonite used in the previous experiment only one of these (0.9g per 100ml) was chosen. In addition a larger quantity (2.7g per 100ml) was also included to represent soils with a higher clay content.

6.2 MATERIALS AND METHODS

6.2.1 The clay

The same bentonite described in section 5.2.1 was used. The only difference was that fresh samples were saturated with calcium and potassium respectively.

6.2.2 Preparation of the samples

Samples of the clay were saturated with calcium and potassium as described in section 5.2.2. Calcium saturated and potassium saturated samples of the clay were mixed in the ratios shown in Table 41.

The/.....................

TABLE 41 - Mixing ratios for bentonite, including high potassium levels

Mixture no.	% K-clay	% Ca-clay
A	5	95
B	10	90
C	15	85
D	20	80
E	25	75
F	30	70
G	35	65
H	40	60

The equilibrating solutions were identical to those in Table 8.

6.2.3 Determination of the Q/I parameters

Of each mixture given in Table 41 six samples of 0.9g each (series a) and six samples of 2.7g each (series b) were weighted into 250ml Erlenmeyer flasks. Each series of six samples were treated with 100ml quantities of equilibrating solutions 1 to 6 respectively.

The experiment was conducted at 27°C.

6.2.4 Calculation of K_{ex} and ΔK

K_{ex} and ΔK were again calculated both as milliequivalents per 100g clay and as me per 1000ml shaking solution (to imitate 10g of soil used). The motivations for this are the same as for the previous experiment (section 5.2.4).

6.3 RESULTS AND DISCUSSION

6.3.1 Values as per 100g clay

For both quantities of bentonite there was again a linear relationship between K_{ex} and AR_e^K at the four lower levels of K saturation (Figures 40 and 41). At the four higher levels of potassium saturation there were also linear relationships between K_{ex} and AR_e^K, but the gradients of these lines were markedly smaller than those of the lines for the lower levels of potassium saturation.

For 0.9g of clay the point for mixture E deviated from the line for the lower levels of potassium saturation in the same way as in the previous experiment. This means that AR_e^K for mixture E was again relatively too low. From this pattern it could logically be expected that, if the high levels of potassium saturation should show a systematic deviation from the pattern for the lower levels, it should be in the form of a line with a steeper slope. This was not the case, however, as is evident from Figure 40. Because of the position of point E there is thus a region where the two lines seem to overlap. This region is indicated by the dotted lines. In this region either the

line/................

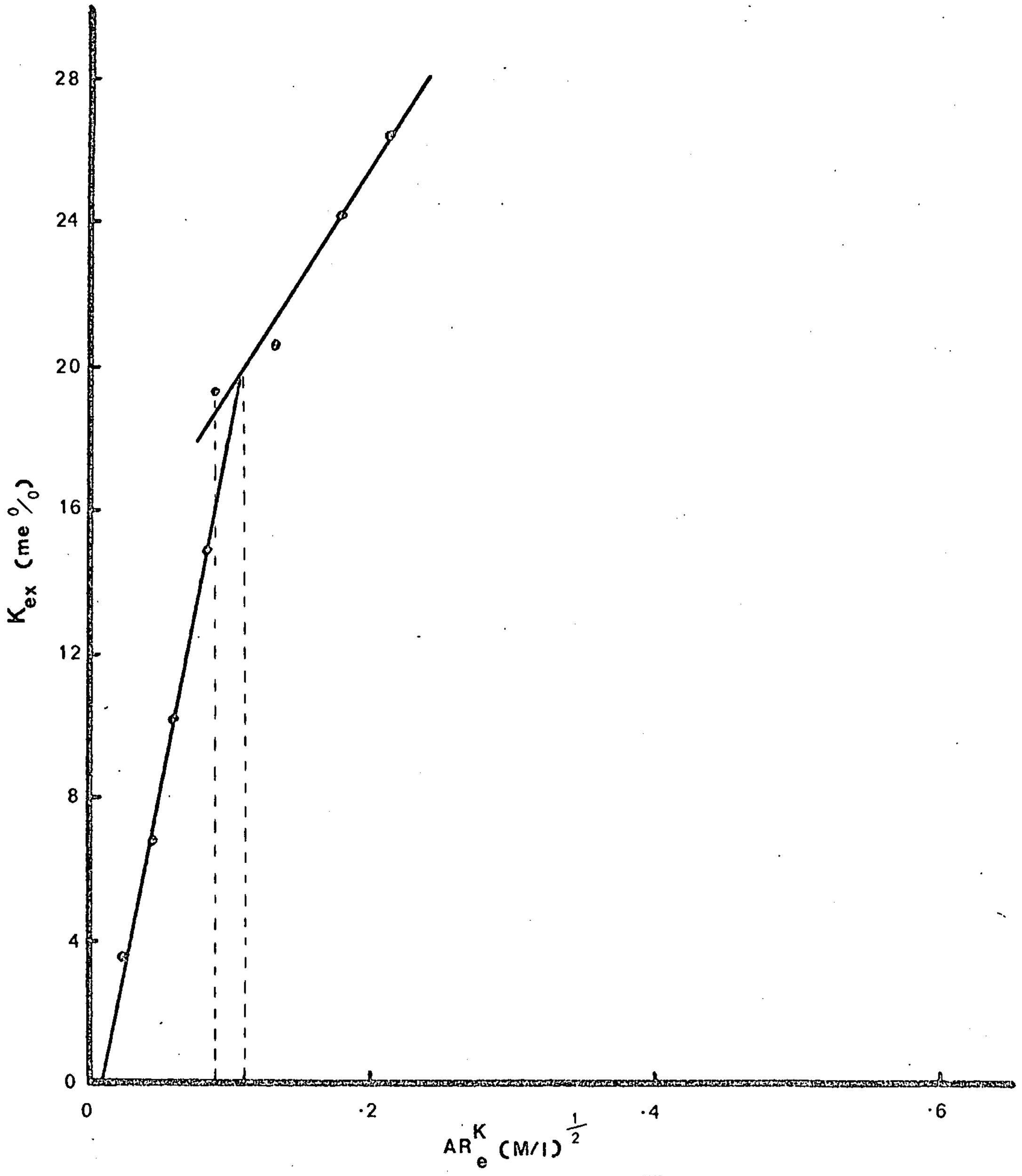

FIG. 40 Relationship between K_{ex} and AR_e^K for series a of the high K experiment with bentonite when K_{ex} is expressed as me per 100 g clay.

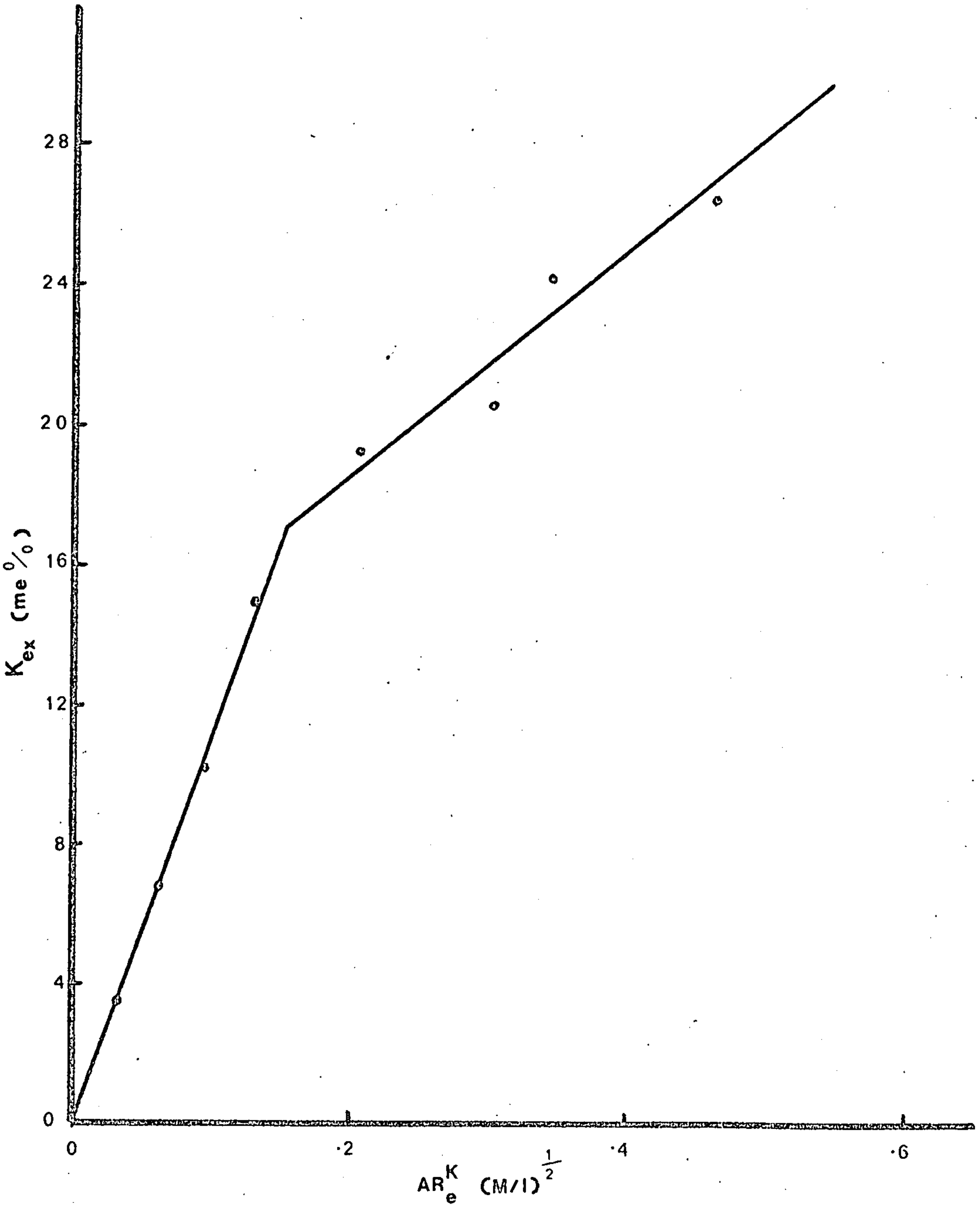

FIG. 41 Relationship between K_{ex} and AR_e^K for series b of the high K experiment with bentonite when K_{ex} is expressed as me per 100 g clay.

line for the higher K_{ex} levels or the one for the lower levels can be used and both may be considered to be valid.

Where 2.7g of clay was used, there was no abnormal deviation of point E and there was a clear difference between the line relating the four lower points and the line relating the four higher points (Figure 41).

For each quantity of clay PBC_T^K at the four higher levels of K_{ex} was consequently much lower than PBC_T^K at the four lower levels (Table 42). When referring to lower and higher levels of K_{ex} it must be remembered that the level of K saturation, where the change in slope occurs, actually is a very high level of K saturation compared to normal field values. The four lower levels are therefore not all really low levels of K saturation. It is more correct to state that PBC_T^K becomes lower at extremely high levels of K saturation of the exchange complex of the clay. In the present experiment PBC_T^K was much higher than in the previous experiment for corresponding K_{ex} levels and quantity of clay, but again showed a sharp decrease with increasing quantity of clay (Tables 30 and 42).

From Figures 40 and 41 it is furthermore evident that two different EK^o values could be found for each quantity of clay, one by extrapolating the line for the four higher K_{ex} levels and one by extrapolating the line for the four lower levels. In contrast to the previous experiment, the EK^o values found by extrapolating the lines for the four lower K_{ex} levels, were zero. This pattern of decrease in EK^o in successive experiments is similar to that found in the experiments with soils. It is obvious that the EK^o values for the lines relating the four higher K_{ex} levels are irrelevant because it can never be reached due to the changes in slopes of the lines once the K_{ex} values drop below a certain critical level.

Figures 40 and 41 also indicate that for both quantities of clay AR_e^K was relatively much higher at the higher levels of K_{ex} than at the lower levels of K_{ex}. This seems to indicate that potassium was much less strongly adsorbed relative to calcium and magnesium at the higher K_{ex} levels than at the lower ones. The Gapon relation-

ships/...............

TABLE 42 - Mean PBC^K, PBC_T^K and the ratio between mean PBC^K and PBC_T^K for bentonite, including high K_{ex} levels, as per 100 grams of clay

Series and mixtures No.	Mean PBC^K me%/(M/l)$^{\frac{1}{2}}$	PBC_T^K me%/(M/l)$^{\frac{1}{2}}$	$\frac{\text{Mean } PBC^K}{PBC_T^K}$
a, A - D	230.1	201.6	1.14
a, E - H	180.1	61.1	2.95
b, A - D	124.9	115.7	1.08
b, E - H	54.4	32.6	1.67

TABLE 43 - PBC^K values for bentonite, including high K_{ex} levels, per 100g clay

Series no.	Mixture No.	K_{ex} me %	PBC^K me%/(M/l)$^{\frac{1}{2}}$
a 0.9g/100ml	A	3.56	255.4
	B	6.91	187.8
	C	10.19	264.3
	D	15.00	212.9
	E	19.38	278.4
	F	20.63	168.9
	G	24.25	137.5
	H	26.50	135.7
b 2.7g/100ml	A	3.56	135.7
	B	6.91	135.9
	C	10.19	114.9
	D	15.00	113.9
	E	19.38	70.6
	F	20.63	51.3
	G	24.25	54.3
	H	26.50	41.3

ships for this experiment did not confirm this postulation. These effects are discussed in more detail in section 7.6.

For both quantities of clay the mean PBC^K values for the four lower levels of K_{ex} were much higher than those for the four higher levels of K_{ex} (Table 43). The differences were more pronounced for 2.7g clay than for 0.9g clay per 100ml equilibrating solution. The mean PBC^K value for the four lower levels of K_{ex} for 0.9g of clay (Table 43) was remarkably similar to that found for the corresponding K_{ex} levels with the same quantity of clay in the previous experiment (Table 29). The values were 230.1 and 230.9 $me/100g/(M/l)^{\frac{1}{2}}$ respectively. This again/ confirm the results obtained with the soils, viz. that the mean PBC^K for a given range of K_{ex} levels is a very constant property of a soil or clay, despite some variation among individual PBC^K values. For any level of K saturation PBC^K was also higher for the smaller quantity of clay (Table 43). This confirmed the trends found in the previous experiment.

For the lower levels of K saturation the ratios of mean PBC^K to PBC^K_T were just above 1 (Table 42). These values were of the same order as those found in the experiment with the four soils (section 3.3). At the higher levels of K saturation these ratios were much higher (Table 42).

At any level of K saturation $-\Delta K^o$ values were also higher for the smaller quantity of clay (Table 44). This is in accordance with the results of the previous experiment. The ratios between $-\Delta K^o$ and K_{ex} exhibit a peculiar pattern. For both quantities of clay the mean ratios for the four lower levels of K saturation were distinctly higher than those for the four higher levels (Table 44). Furthermore these ratios decreased with increasing quantity of clay. The values for the four higher levels of K_{ex} for 2.7g clay showed a marked constancy around 0.75.

6.3.2 Values as per 1000ml shaking solution

Different linear relationships between K_{ex} and AR^K_e were again obtained for the four lower and the four higher levels of K_{ex} for both quantities of clay (Figures 42 and 43).

At/......................

TABLE 44 - K_{ex}, $-\Delta K^{o}$ and the ratio between $-\Delta K^{o}$ and K_{ex} for bentonite, including high K_{ex} levels

Series No.	K_{ex} me %	$-\Delta K^{o}$ me %	$\frac{-\Delta K^{o}}{K_{ex}}$ x100%
a 0.9g/100ml	26.50	28.80	109
	24.25	24.58	101
	20.63	22.41	109
	19.38	25.36	131
	15.00	18.13	121
	10.19	16.41	161
	6.91	9.33	135
	3.56	6.87	193
b 2.7g/100ml	26.50	19.08	72
	24.25	18.71	77
	20.63	15.52	75
	19.38	14.69	76
	15.00	14.93	100
	10.19	11.22	110
	6.91	8.59	124
	3.56	4.67	131

TABLE 45 - Mean PBC^{K}, PBC_{T}^{K} and the ratio between mean PBC^{K} and PBC_{T}^{K} for bentonite, including high K_{ex} levels, per 1000ml

Series and mixtures No.	Mean PBC^{K} me%/(M/l)$^{\frac{1}{2}}$	PBC_{T}^{K} me%/(M/l)$^{\frac{1}{2}}$	$\frac{\text{Mean } PBC^{K}}{PBC_{T}^{K}}$
a, A-D	20.71	18.15	1.14
a, E-H	16.21	5.50	2.95
b, A-D	33.72	31.24	1.08
b, E-H	14.68	8.81	1.67

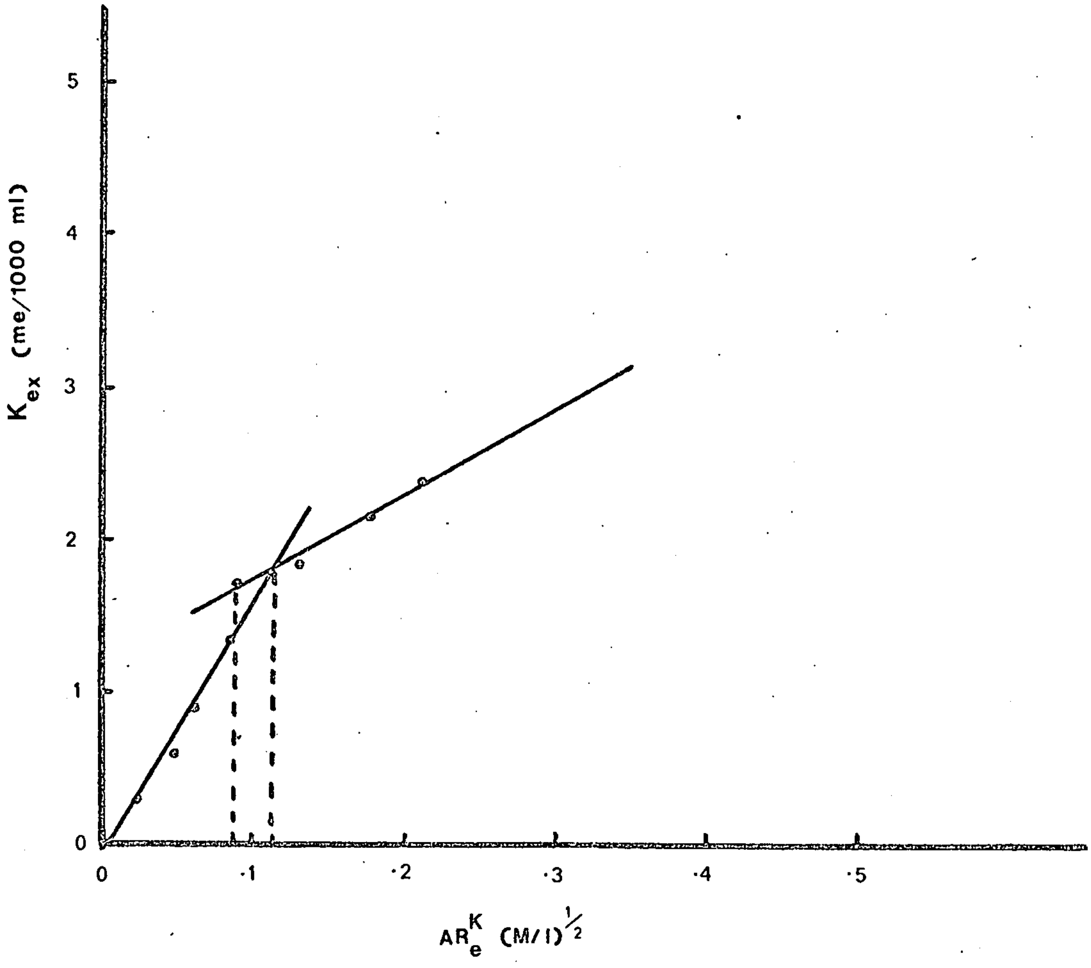

FIG. 42 Relationship between K_{ex} and AR_e^K for series a of the high K experiment with bentonite when K_{ex} is expressed as me per 1000 ml shaking solution.

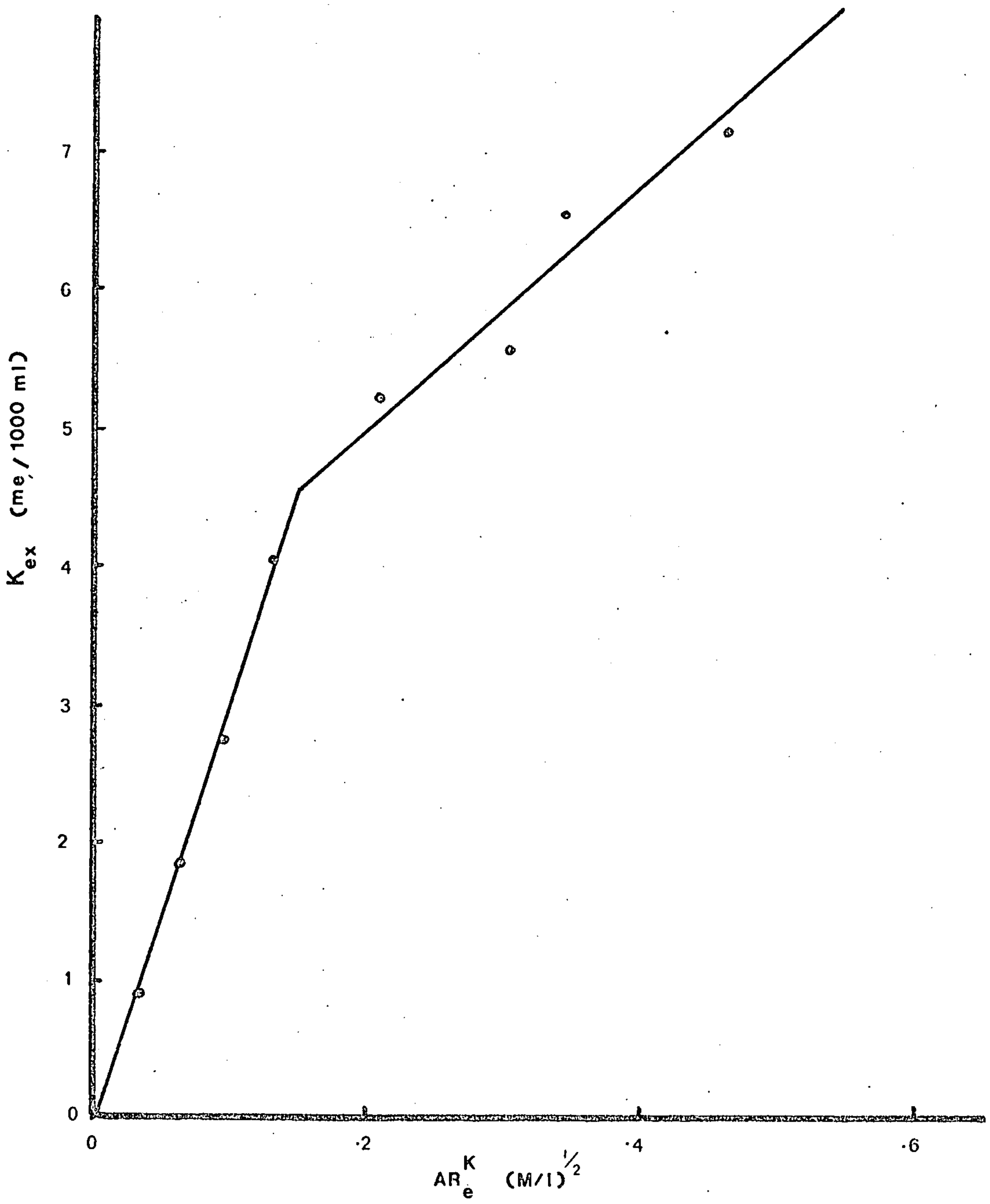

FIG. 43 Relationship between K_{ex} and AR_e^K for series b of the high K experiment with bentonite when K_{ex} is expressed as me per 1000 ml shaking solution.

At the four lower levels of K_{ex} mean PBC^K was also higher for the larger quantity of clay than for the smaller quantity (Table 45). At the higher K_{ex} levels PBC^K did not differ significantly between the two quantities of clay. PBC_T^K values were higher for the larger quantity of clay than for the smaller quantity both at the higher and at the lower levels of K_{ex} (Table 45). The mean PBC^K and PBC_T^K values for the lower levels of K_{ex} were again comparable to those for the soils with comparable clay contents and showed the same trends of change with increasing clay content as the soils (cf. sections 3.3 and 5.3.2). Soils with 9 and 27% clay would be represneted by the two quantities of clay used in this experiment, provided that other particle size fractions of soils do not significantly contribute to cation exchange relationships. The latter was confirmed by Sander & Grobler (1970).

CHAPTER 7

GAPON RELATIONSHIPS OF THE EXPERIMENTAL DATA

7.1 GENERAL

In all the experiments described in the previous chapters linear relationships were found between K_{ex} and AR_e^K. These relationships are Gapon-like in nature. The equations describing the lines can be written as:

$$K_{ex} = b.AR_e^K + a \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

$$\text{or} \quad K_{ex} = b. \frac{a_K}{(a_{Ca} + a_{Mg})^{\frac{1}{2}}} + a \quad \ldots\ldots\ldots \quad (4)$$

The Gapon exchange equation is:

$$\frac{K_{ex}}{Ca_{ex} + Mg_{ex}} = K_G. \frac{a_K}{(a_{Ca} + a_{Mg})^{\frac{1}{2}}} \ldots (5)$$

where K_G is the Gapon constant for potassium.

Equation (4) differs from the Gapon equation (5) in two respects. The factor $(Ca_{ex} + Mg_{ex})$ is omitted and an intercept is introduced. When $(Ca_{ex}+Mg_{ex})$ is dominant, as required by Beckett (1964a), this factor is relatively constant. The necessity for the introduction of an intercept into the Gapon equation was also found by Marques (1964) and Skeen & Sumner (1970).

As almost all necessary data were available, it was quite easy to calculate the Gapon relationships for the different experiments. Only the values of $(Ca_{ex}+Mg_{ex})$ were required additionally. For his so-called "saturated system" Marques (1964) did not, however, determine $(Ca_{ex}+Mg_{ex})$, but merely calculated it by subtracting K_{ex} from CEC. $(Ca_{ex}+Mg_{ex})$ was therefore calculated in the same way for the present study, except for the experiment with different sodium levels.

In these studies of Gapon relationships AR_e^K had to be used, as AR_e^K is the only true indication of the activity ratio in equilibrium with a certain exchange ratio (ER), given by $\frac{K_{ex}}{(Ca_{ex} + Mg_{ex})}$. The Gapon relationship obtained

by/....................

by using AR_e^K to indicate $\frac{a_K}{(a_{Ca} + a_{Mg})^{\frac{1}{2}}}$ may therefore be described as the true Gapon relationship for any soil or clay. This would, furthermore, mean that the Gapon equation and Schofield's (1947) Ratio Law are combined.

Usually K_G is determined by equilibrating soil samples with any chosen solution containing potassium and calcium and determining the activities of potassium and calcium plus magnesium in the equilibrium solution. The exchangeable cations are then replaced with another, mostly ammonium, and determined. The activity ratios obtained in this way are similar to the AR^K values obtained in Q/I studies. The exchange ratio for any AR^K value can be obtained by using the original K_{ex} value of the soil sample and the ΔK value for the specific equilibrating solution. By adding ΔK to the original K_{ex} the K_{ex} value in equilibrium with the corresponding AR^K value is obtained in an indirect way. The corresponding exchange ratio can consequently be calculated from these indirect values and will therefore be called the "indirect exchange ratio". This calculation is illustrated in Table 46, where the data for an initial K_{ex} of 0.80me K/100g soil for the Mangano soil in the first experiment are given.

7.2 GAPON RELATIONS FOR THE MANGANO SOIL IN THE FIRST EXPERIMENT (cf. Chapter 2)

The first important feature is that a good linear relationship between AR_e^K and $\frac{K_{ex}}{(Ca_{ex} + Mg_{ex})}$, the exchange ratio or ER, was found (Figure 44). This means that a good linear Gapon-like relationship was found between AR_e^K and the original exchange ratios of the samples. The intercept of the line was at an ER value of 0.06599 and the slope of the line was 1.6232. Moss (1967) also found a linear relationship for a number of soils, but he did not find an intercept different from zero. It has been pointed out, however, that an intercept is in accordance with the results of Marques (1964) and Skeen & Sumner (1970).

From/.....................

TABLE 46 - Calculation of indirect exchange ratios for a sample of the Mangano soil with an initial K_{ex} level of 0.80 me%

CEC (me%)	Initial K_{ex} (me%)	ΔK (me%)	Equilibrium K_{ex} (me%)	Equilibrium Ca_{ex} (me%)	Indirect ER
a	b	c	d=b+c	e=a-d	d/e
4.90	0.80	-0.300	0.500	4.400	0.1136
4.90	0.80	-0.400	0.400	4.500	0.0889
4.90	0.80	-0.500	0.300	4.600	0.0652
4.90	0.80	-0.470	0.330	4.570	0.0722
4.90	0.80	-0.495	0.305	4.595	0.0664
4.90	0.80	-0.530	0.270	4.630	0.0583
4.90	0.80	-0.588	0.212	4.688	0.0452

TABLE 47 - K_G values at different exchange ratios for the Mangano soil as calculated with AR_e^K

Exchange Ratio	K_G $(M/l)^{-\frac{1}{2}}$
0.1971	2.3
0.1667	3.3
0.1264	3.5
0.1011	3.8
0.0889	5.8
0.0652	∞

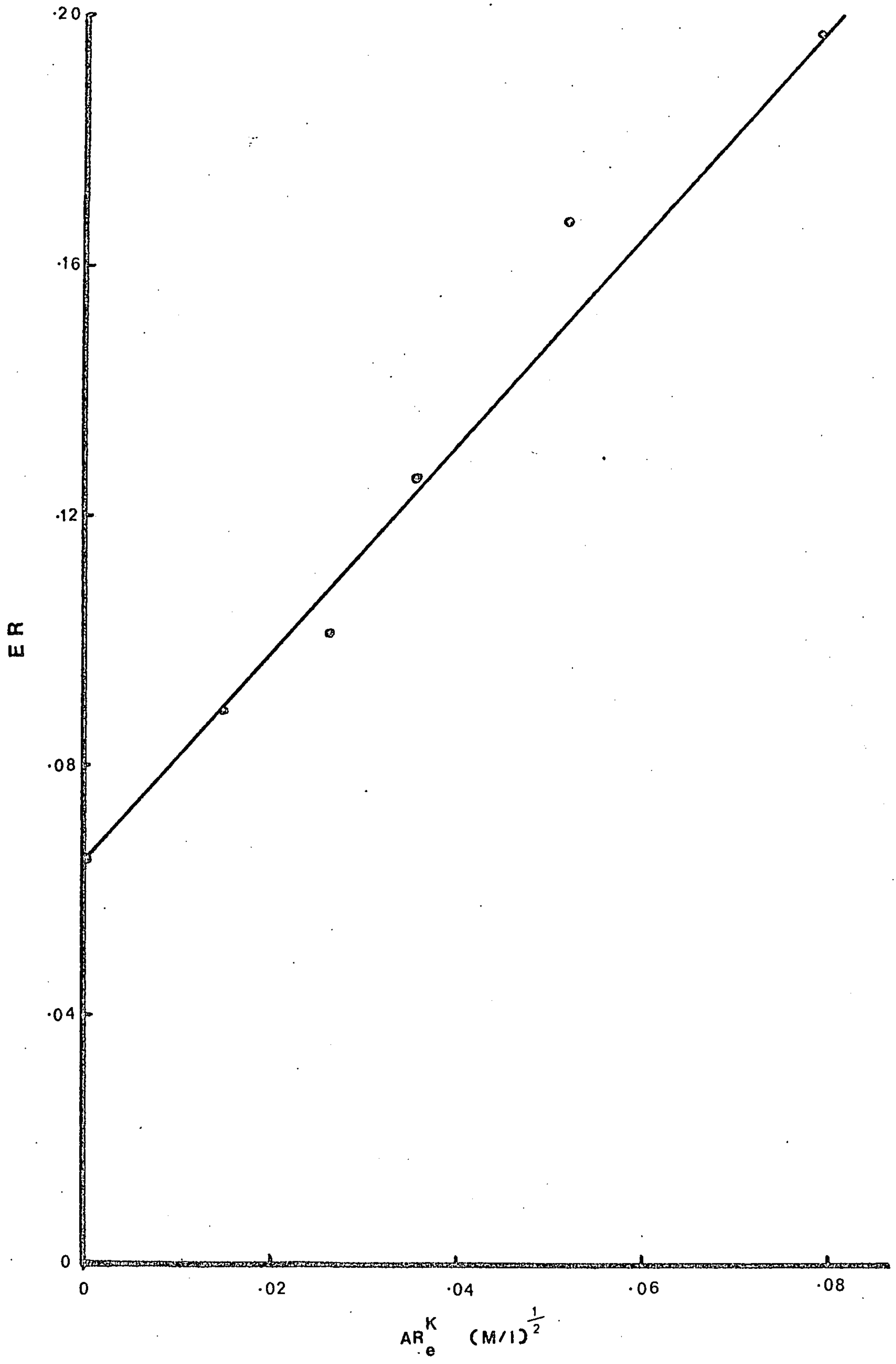

FIG. 44 Relationship between the exchange ratio (ER) and AR_e^K for the Mangano soil.

From the equation $ER=K_G.AR_e^K+a$, it is evident that K_G, the Gapon constant, is given by the slope of the line, which is 1.6232 in this case. The normal values of K_G at the different levels of K_{ex}, when K_G is calculated by means of the original Gapon equation, i.e. without the introduction of an intercept and simply by dividing AR_e^K into the corresponding exchange ratios, are given in Table 47. The Gapon ratios calculated in this way were not constant and differed vastly from the value for the slope of the relating ER and AR_e^K. At the higher K_{ex} levels K_G was relatively constant, but at low K_{ex} levels K_G increased sharply and an infinite value was found at a K_{ex} value of 0.30me per 100g soil, which is EK^o or the K_{ex} value at which AR_e^K becomes zero. The results are illustrated in Figure 45. The curve is similar to those of Marques (1964) and Skeen & Sumner (1970).

According to Marques (1964) it is assumed that the Gapon constants, calculated by dividing the activity ratio into the exchange ratio, are to some extent a measure of the retaining power of a clay for potassium in relation to calcium. Marques (1964) took the increase in K_G at decreasing K_{ex} levels as a justification for the hypothesis that the intercept, significantly different from zero, is due to potassium "fixation" or at least a very marked increase in the retaining power of clay for potassium with decreasing amounts of K in the system. He further indicated that the specificity of K adsorption can be explained by the existence of two different types of exchange sites with widely varying exchange constants.

The linearity of the graph relating ER to AR_e^K (Figure 44) at all K_{ex} levels higher than EK^o indicates that the retaining power of this soil for potassium relative to calcium for all the exchange sites above EK^o is constant. These will represent the planar sites.

At EK^o the value of AR_e^K becomes zero, which means that the Gapon constant for all K_{ex} levels lower than or equal to EK^o is infinite. Zero AR_e^K values are often reported in literature. From the above it is evident that significant increases in AR_e^K upon increased potassium saturation of the

exchange/.................

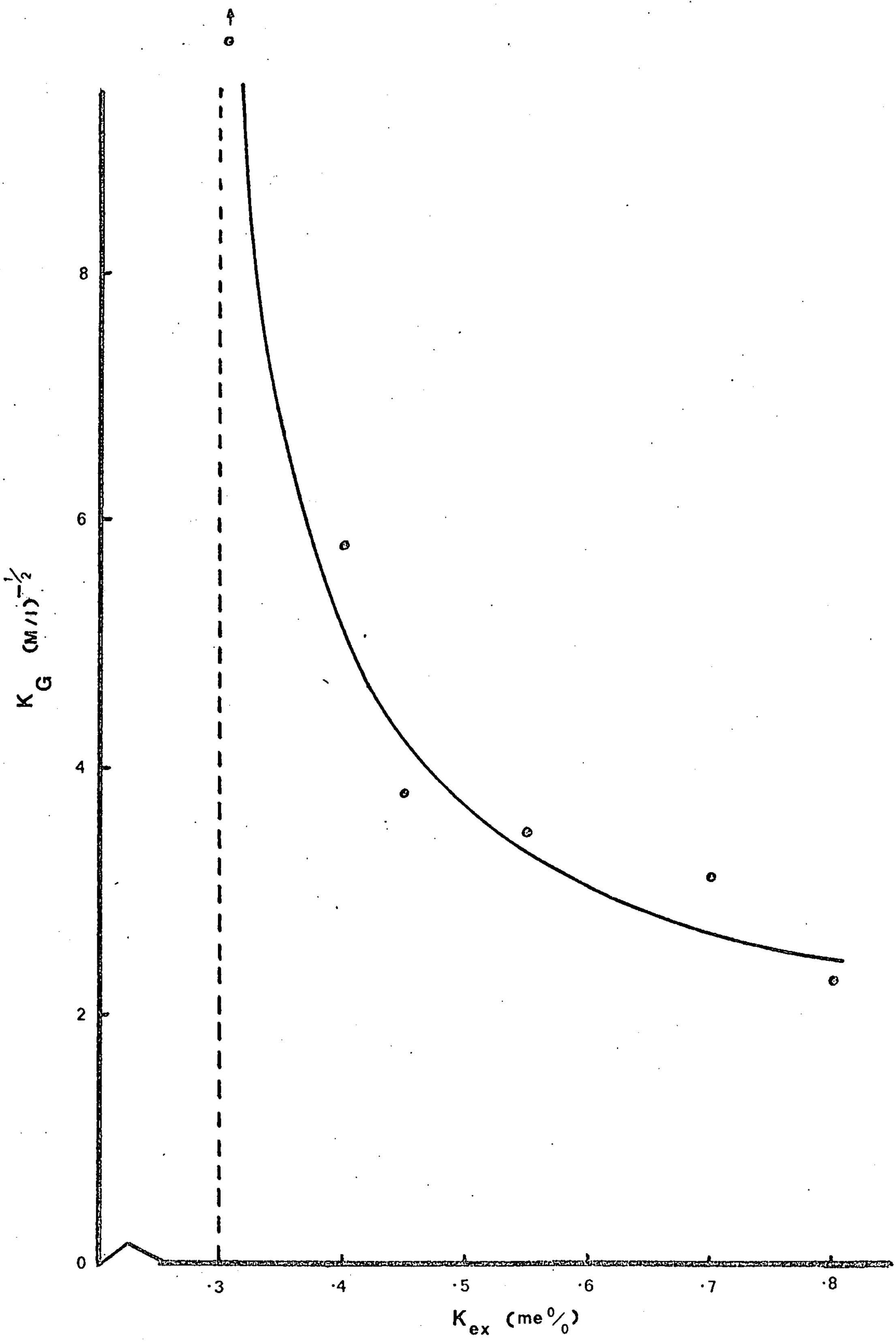

FIG. 45 Relationship between K_G and K_{ex} for the Mangano soil (The line was not fitted).

exchange complex of the soil can only be expected when the level of potassium saturation is higher than EK^o.

Gapon relationships by using AR^K and the indirect exchange ratio were calculated for each level of initial K saturation, i.e. for each mixture of the soil. These results are illustrated in Table 48 and Figures 46 to 51. From these it is evident that at the three higher levels of initial K saturation fairly good linear relationships between indirect ER and AR^K_e were obtained. The graphs for the three sets of values did not differ significantly as both the slopes and the intercepts of the lines were similar. The slopes of these lines were slightly higher and the intercepts much lower than those of the total line relating ER to AR^K_e. For the three lower levels of K saturation curvilinear relationships between indirect ER and AR^K were obtained. The constants for the linear upper parts of these graphs were calculated and are given in Table 48. The most striking effect is the increase in the intercept at the lower initial K_{ex} levels to give values of the same order as that of the line relating ER to AR^K_e. The curved parts of the latter graphs were given by the equilibrating solution containing no potassium initially and shaken with different quantities of soil.

The initial K_{ex} levels for which curvilinear relationships were found, and where the increases in the intercept of the linear part occurred, were those at which the relationship between $-\Delta K^o$ and K_{ex} broke down.

K_G values, obtained by the original Gapon equation, i.e. by simply dividing AR^K into the corresponding indirect ER values, increased with decreasing K concentration in the original equilibrating solutions and especially with decrease in initial K_{ex} level (Table 49).

7.3 GAPON RELATIONS FOR THE FOUR SOILS (cf. Chapter 3)

For all four soils extremely good linear relationships were found between ER and AR^K_e, as can be seen in Figure 52. The graphs for the Mangano and the two alluvial Riet River soils were close together, but that for the Estcourt soil

differed/...........

TABLE 48 - Equations for lines relating indirect ER and AR^K at different initial K_{ex} levels for the Mangano soil

Initial K_{ex} me%	Regression equation
0.80	$ER=1.8788AR^K+0.02813$
0.70	$ER=2.1022AR^K+0.03100$
0.55	$ER=2.1940AR^K+0.02914$
0.45	$ER=2.0308AR^K+0.03904$ *
0.40	$ER=1.7599AR^K+0.06132$ *
0.30	$ER=2.9440AR^K+0.06862$ *
Final line	$ER=1.6232AR_e^K+0.06599$

(*For linear part of the graph)

TABLE 49 - K_G values by dividing AR^K into indirect ER at different initial K_{ex} levels for the Mangano soil

K_G $(M/l)^{-\frac{1}{2}}$					
0.80*	0.70*	0.55*	0.45*	0.40*	0.30*
3.1	3.4	3.3	-	4.2	6.7
2.8	2.8	2.9	3.7	5.1	7.6
2.1	2.9	3.8	4.1	5.6	9.2
2.9	3.8	4.0	4.6	7.3	12.4
3.4	4.0	4.0	5.2	9.1	15.8
3.9	4.6	5.0	6.5	12.7	27.4
5.8	7.0	8.9	6.5	14.1	26.6

(*Initial K_{ex} level, as me%)

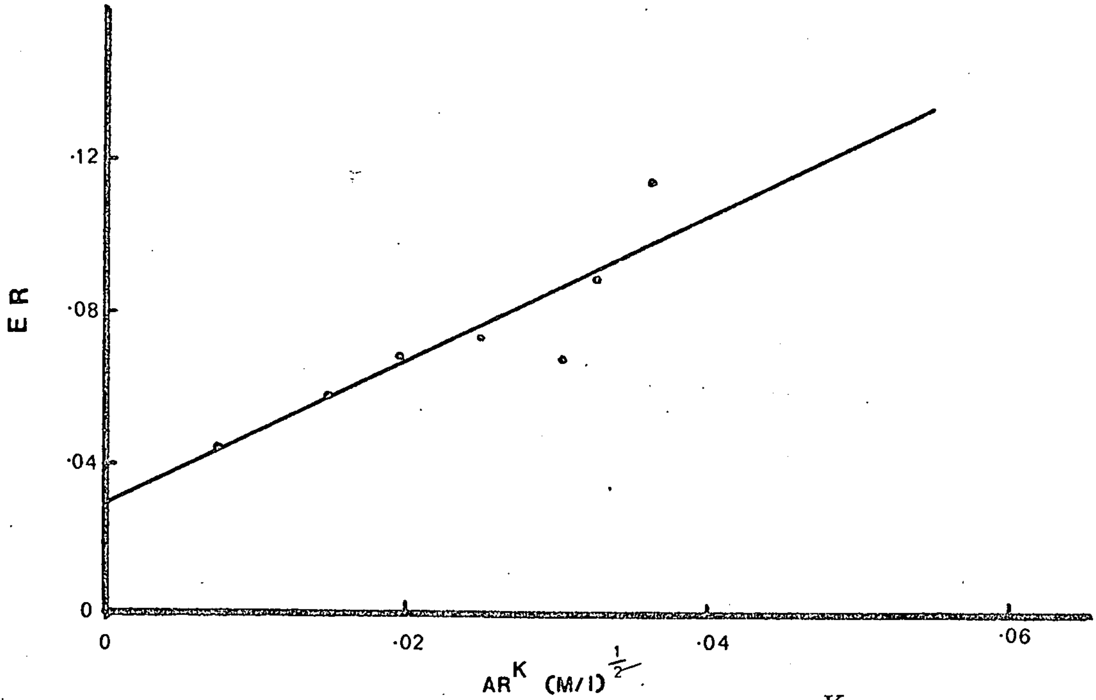

FIG. 46 Relationship between indirect ER and AR^K at an initial K_{ex} level of .80 me % for the Mangano soil.

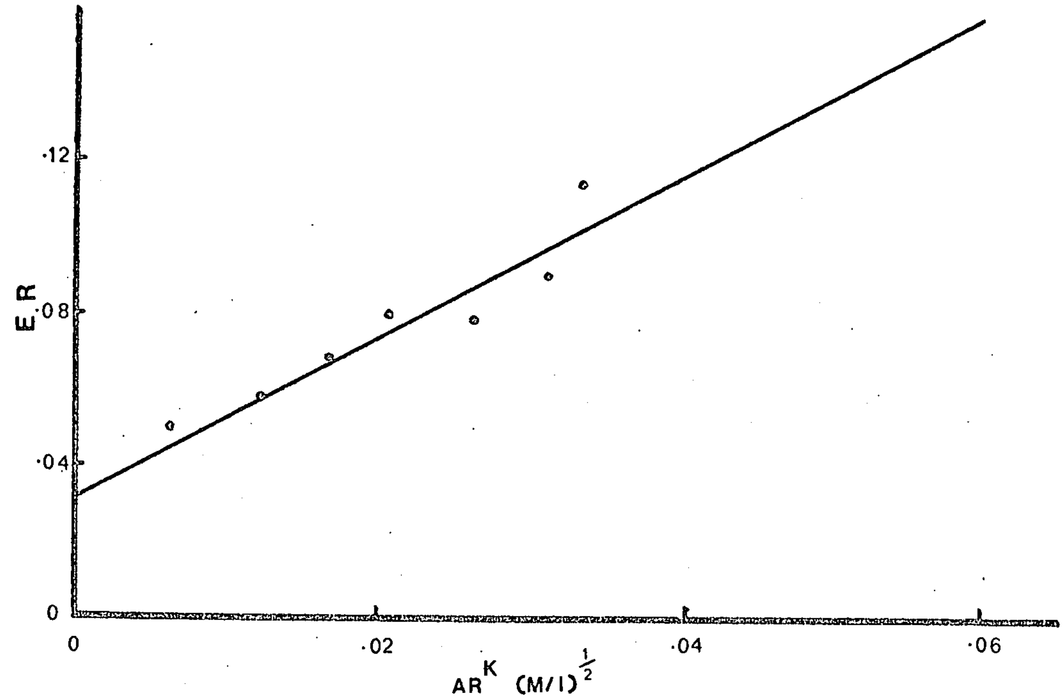

FIG. 47 Relationship between indirect ER and AR^K at an initial K_{ex} level of .70 me % for the Mangano soil.

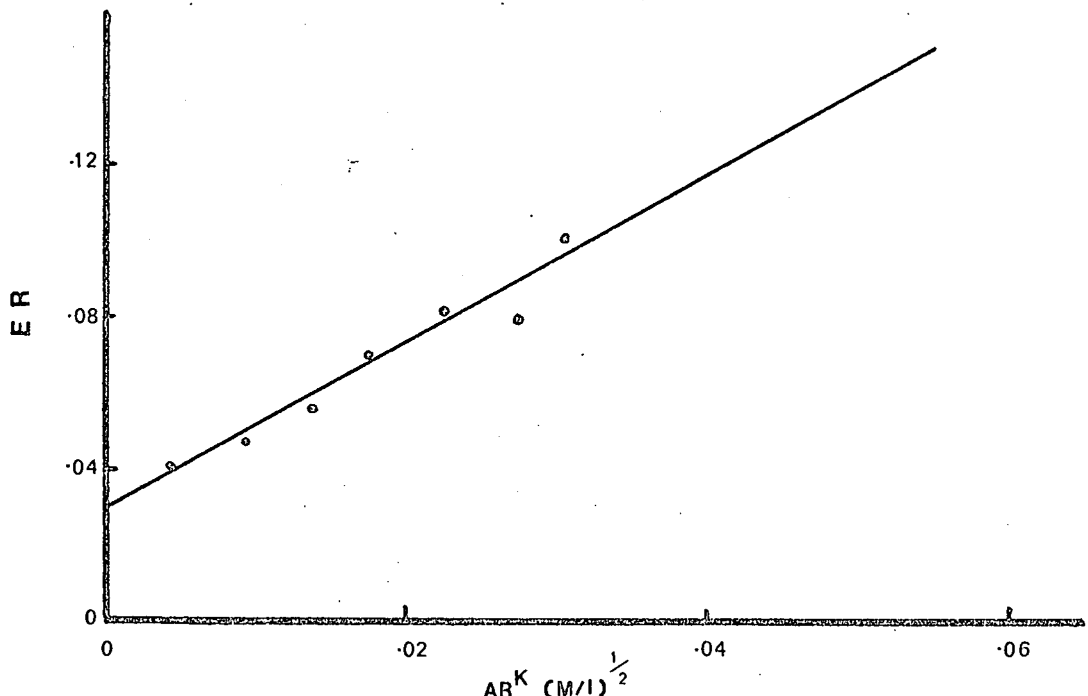

FIG. 48 Relationship between indirect ER and AR^K at an initial K_{ex} level of .55 me % for the Mangano soil.

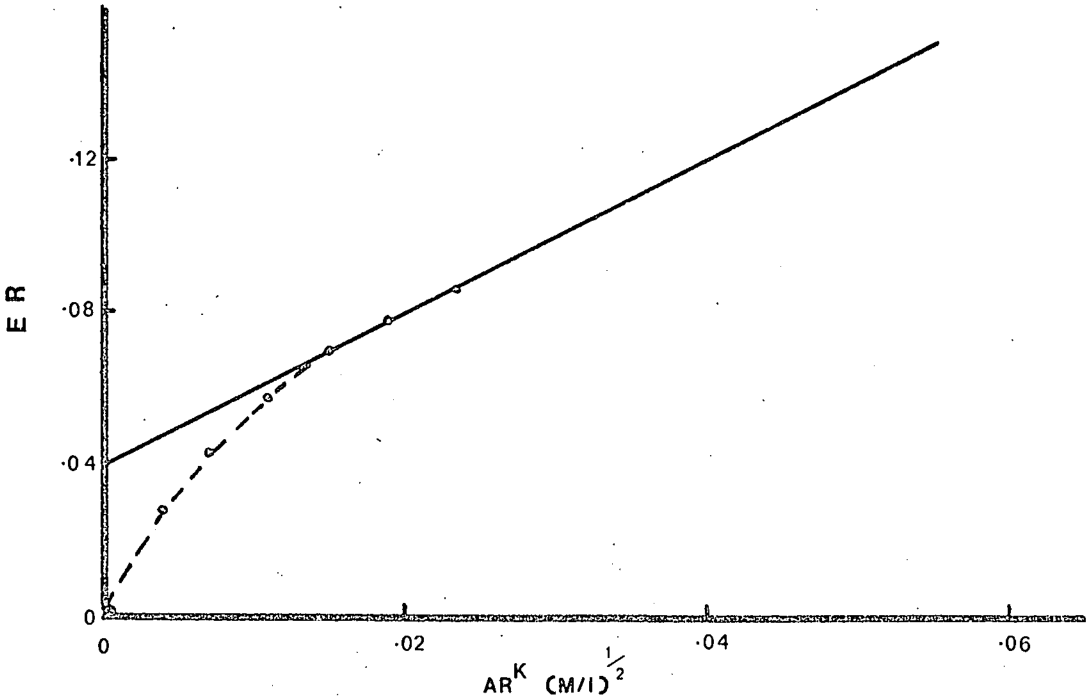

FIG. 49 Relationship between indirect ER and AR^K at an initial K_{ex} level of .45 me % for the Mangano soil.

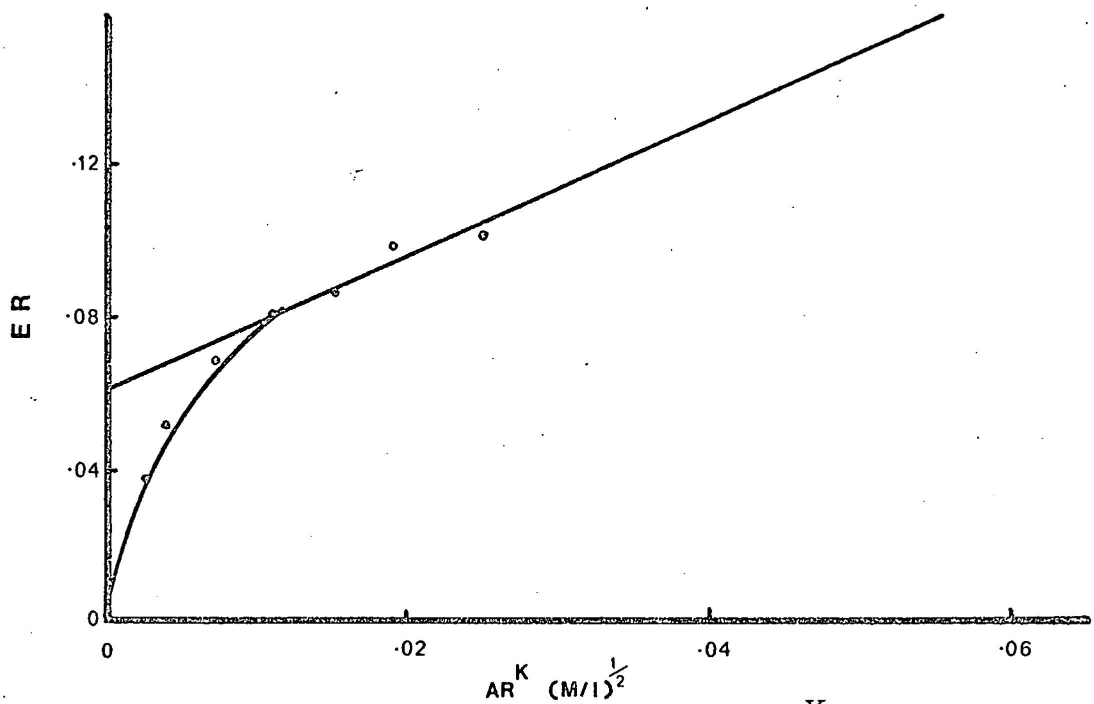

FIG. 50 Relationship between indirect ER and AR^K at an initial K_{ex} level of .40 me % for the Mangano soil.

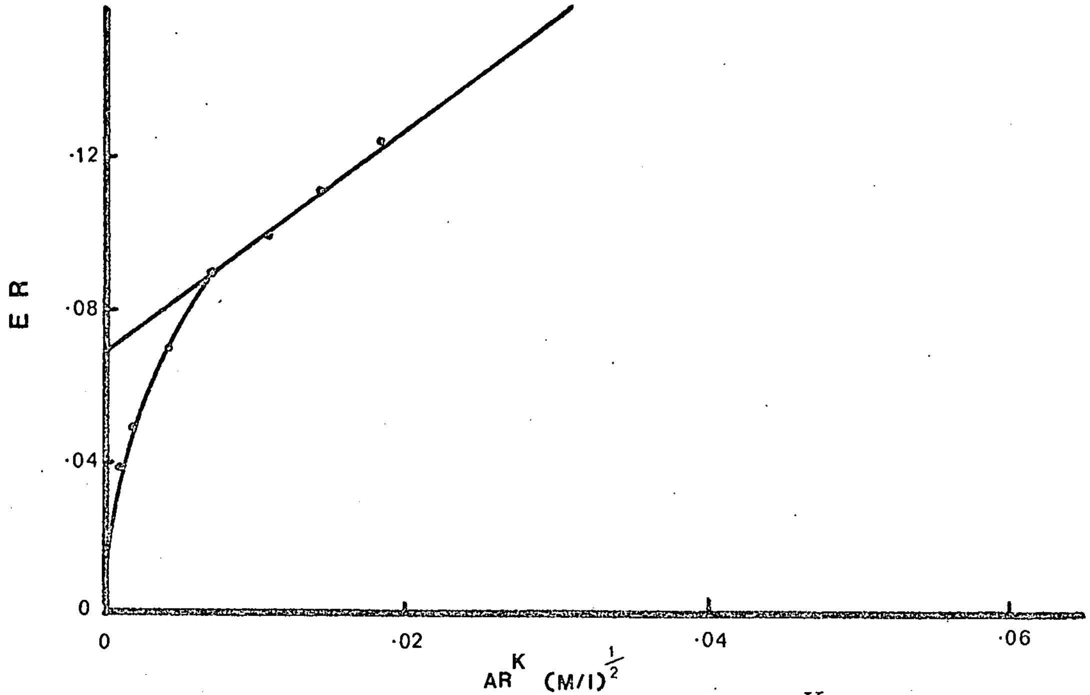

FIG. 51 Relationship between indirect ER and AR^K at an initial K_{ex} level of .30 me % for the Mangano soil.

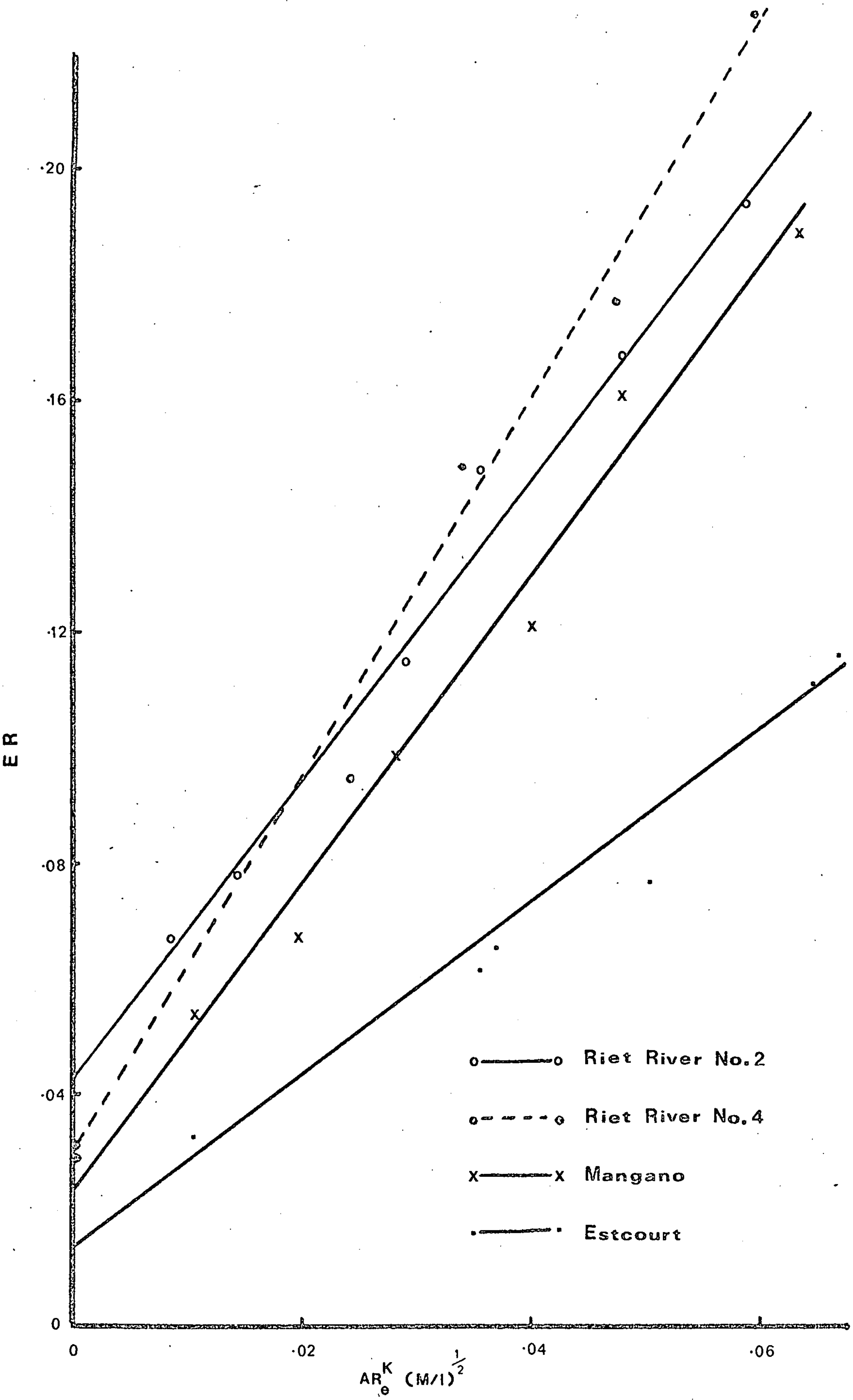

FIG. 52 Relationship between ER and AR_e^K for four soils.

differed markedly from the former. It is significant that it was not the three soils, of which the CEC of the clays were almost identical, which gave fairly similar graphs. The CEC of the clay of the Mangano soil was much lower than those of the others.

The relative differences between the intercepts of the lines were different from those of K_{ex} versus AR_e^K. The intercepts of K_{ex} versus AR_e^K for the Mangano and Estcourt soils were the same, but in this case that of the Mangano soil was almost twice as high as that of the Estcourt. For K_{ex} versus AR_e^K the intercept of the Riet River No. 4 soil was almost three times as high as that of the Mangano, but for ER versus AR_e^K their intercepts were of the same order. The relative differences between the intercepts of Riet River No.2 and Riet River No. 4 were also smaller in the case of ER versus AR_e^K than in the case of K_{ex} versus AR_e^K.

The relative differences between the slopes of the lines were also changed. For K_{ex} versus AR_e^K the slopes for the Mangano and Estcourt soils were similar, but for ER versus AR_e^K that of the Estcourt soil is much lower than that of the Mangano. For ER versus AR_e^K the slope of the line for the Mangano soil is similar to that for Riet River No.2 and that of Riet River No. 2 differed somewhat from that of Riet River No. 4. For K_{ex} versus AR_e^K the slope of the line for the Mangano soil differed vastly from that of the Riet River No. 2 soil and those of the two Riet River soils were similar.

The above changes in the relative differences between the intercepts and the slopes of the lines were caused by the fact that the CEC of the soils were vastly different. The higher the CEC of a soil, the smaller is the change in ER for equal changes in K_{ex} and the smaller is the intercept ER^o relative to EK^o. As a result of this the relationship between ER and AR_e^K will give no indication of the changes in AR_e^K which can be expected upon equal changes in K_{ex} in different soils. ER and AR_e^K are both ratios and therefore no absolute total value figures in the relationship between them. On the other hand K_{ex} and EK^o are both

absolute/.................

absolute values. From a practical point of view a knowledge of the relationship between K_{ex} and AR_e^K therefore seems more important than a knowledge of the relationship between ER and AR_e^K.

It is evident that the relative retaining power of all four soils for potassium relative to calcium is constant for all K which is adsorbed in excess of EK^o. Actual zero AR_e^K values were obtained for the Riet River No. 4 soil, which is an indication that this relationship is constant absolutely from EK^o. At and below EK^o the Gapon constants are infinite.

The normal K_G values for all four soils, obtained by simply dividing ER with AR_e^K, are given in Table 50. For each soil K_G was a relatively constant value at higher levels of K_{ex}. At K_{ex} levels nearer to EK^o increases in K_G occurred. At EK^o the value of K_G became infinite. K_G approached a vertical line, drawn through EK^o, asymptotically. This was best illustrated by the data obtained for the Riet River No. 4 soil (Figure 53). It should be noted that the constant K_G values, at the higher levels of K_{ex}, for the two Riet River soils and the Mangano soil were practically similar (Table 50 and Figure 53). These were the three soils for which the lines relating ER to AR_e^K were fairly similar. The constant K_G value for the Estcourt soil was much lower.

Gapon relations for all four soils were also calculated by using AR^K and indirect ER values. These results are illustrated in Table 51 and Figures 54 to 77. When comparing these results with those of the previous experiment it must be kept in mind that higher K concentrations were used in the equilibrating solutions in the present experiment.

The general tendency was, similar to the previous experiment, that the slopes of the lines for each soil were of the same order and generally slightly higher than those for the lines relating ER to AR_e^K. Furthermore there was, with some exceptions, a general increase in the intercept with decreasing initial level of K_{ex}. In all cases the

TABLE 50 - K_G values at different exchange ratios for four soils as calculated with AR_e^K

Soil	ER	K_G $(M/l)^{-\frac{1}{2}}$
Riet River No.2	0.1941	3.3
	0.1675	3.5
	0.1477	4.2
	0.1154	4.0
	0.0784	5.4
	0.0670	7.8
Riet River No.4	0.2268	3.8
	0.1755	3.7
	0.1493	4.4
	0.0948	3.9
	0.0311	∞
	0.0295	147.5
Mangano	0.1893	3.0
	0.1611	3.3
	0.1213	3.0
	0.0987	3.5
	0.0675	3.4
	0.0538	5.0
Estcourt	0.1166	1.7
	0.1111	1.7
	0.0769	1.5
	0.0656	1.8
	0.0618	1.7
	0.0329	3.1

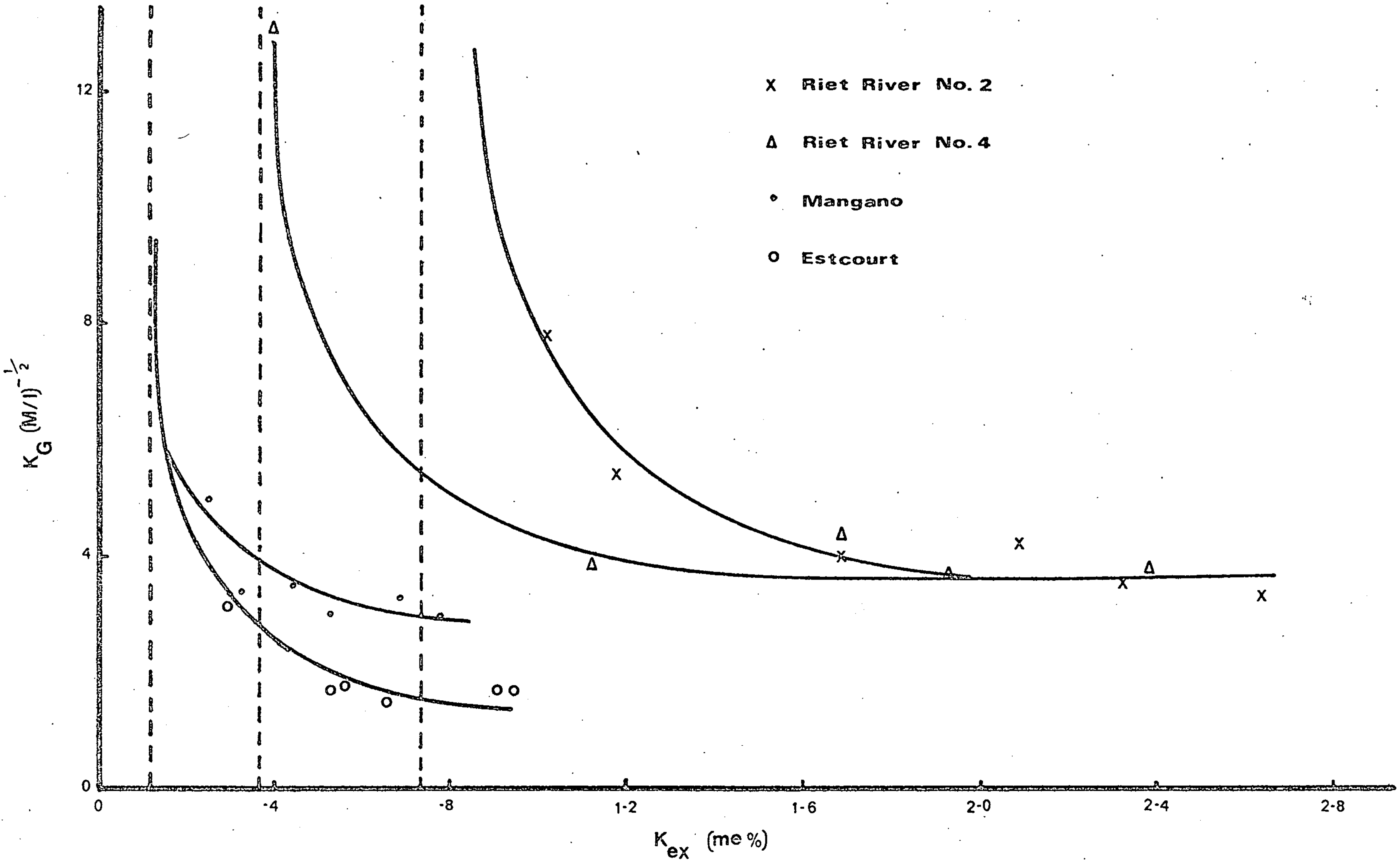

FIG. 53 Relationship between K_G and K_{ex} for four soils (Lines not fitted).

TABLE 51 - Equations for lines relating indirect ER and AR^K at different initial K_{ex} levels for four soils

Soil	Initial K_{ex} me%	Regression equation
Riet River No.2	2.640	$ER=3.2101AR^K+0.00239$
	2.325	$ER=3.3175AR^K+0.00762$
	2.088	$ER=3.1546AR^K+0.03590$
	1.683	$ER=2.9508AR^K+0.03037$
	1.181	$ER=2.6217AR^K+0.04217$
	1.018	$ER=2.5862AR^K+0.04504$
	Final line	$ER=2.5959AR_e^K+0.04416$
Riet River No.4	2.390	$ER=3.9218AR^K-0.01705$
	1.931	$ER=3.7852AR^K-0.00496$
	1.675	$ER=3.7439AR^K+0.02280$
	1.119	$ER=3.8292AR^K+0.00434$
	0.388	$ER=2.7735AR^K+0.03141$
	0.369	$ER=2.7453AR^K+0.03065$
	Final line	$ER=3.2627AR_e^K+0.02794$
Mangano	0.775	$ER=2.9842AR^K-0.00656$
	0.675	$ER=3.5042AR^K-0.01018$
	0.531	$ER=3.2968AR^K-0.00907$
	0.438	$ER=2.6407AR^K+0.02431$
	0.313	$ER=2.6842AR^K+0.01713$
	0.250	$ER=2.6856AR^K+0.03201$
	Final line	$ER=2.7060AR_e^K+0.02030$
Estcourt	0.950	$ER=2.0560AR^K-0.02345$
	0.906	$ER=1.5944AR^K+0.00534$
	0.653	$ER=1.4221AR^K+0.00404$
	0.556	$ER=1.7765AR^K+0.00002$
	0.531	$ER=1.7414AR^K+0.00017$
	0.294	$ER=1.3403AR^K+0.02087$
	Final line	$ER=1.4779AR_e^K+0.01219$

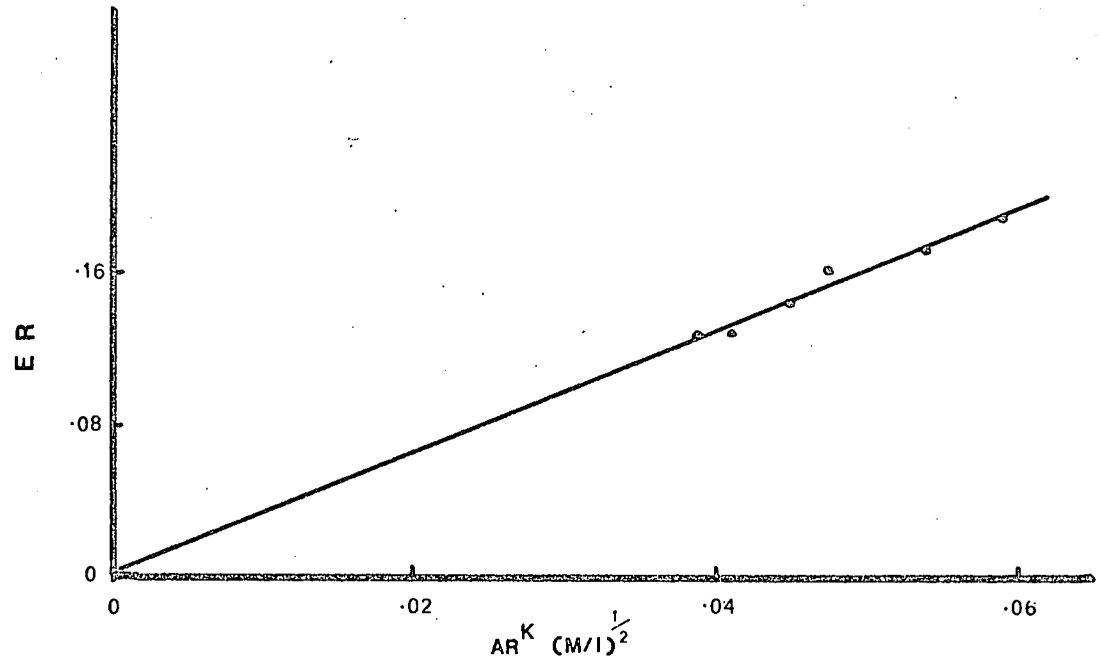

FIG. 54 Relationship between indirect ER and AR^K at an initial K_{ex} level of 2.64 me % for the Riet River No. 2 soil.

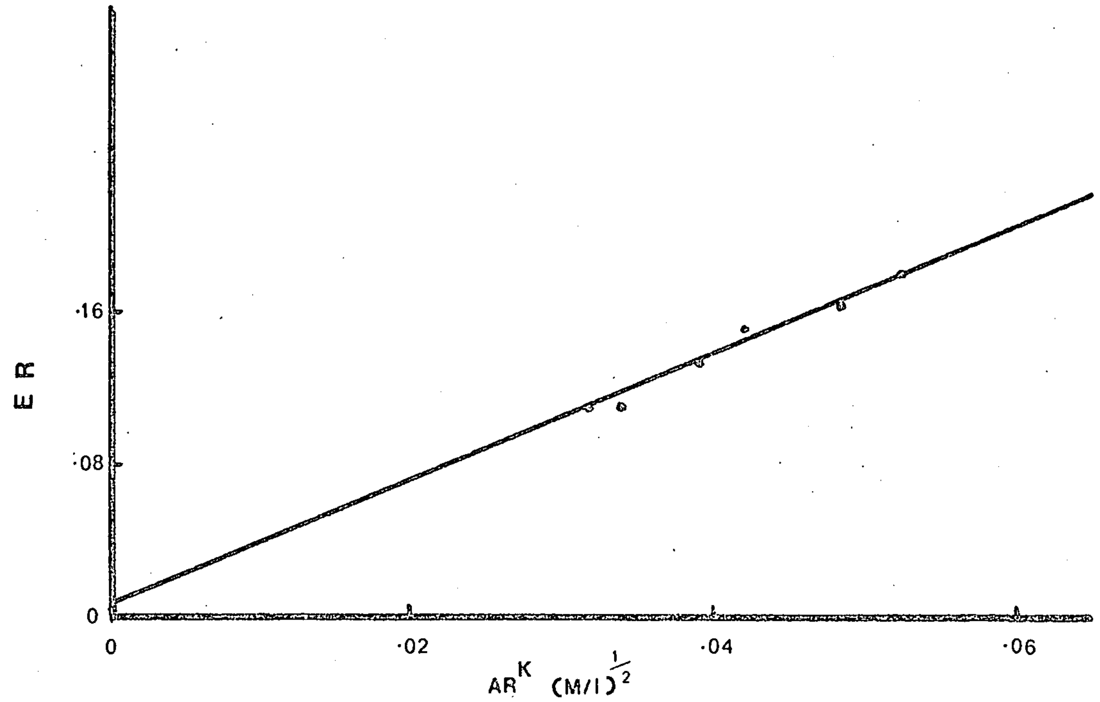

FIG. 55 Relationship between indirect ER and AR^K at an initial K_{ex} level of 2.325 me % for the Riet River No. 2 soil.

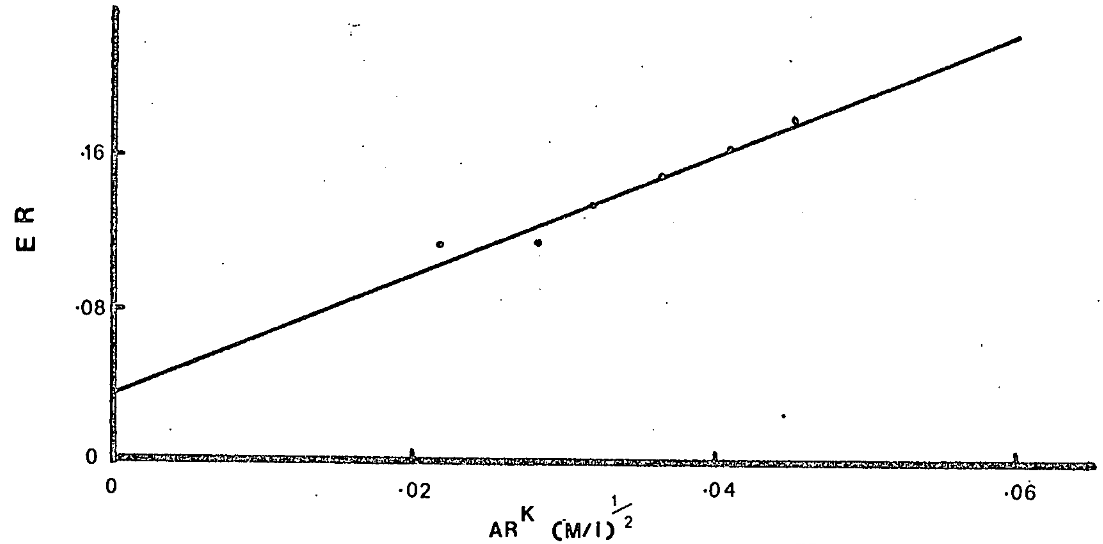

FIG. 56 Relationship between indirect ER and AR^K at an initial K_{ex} level of 2.088 me % for the Riet River No. 2 soil.

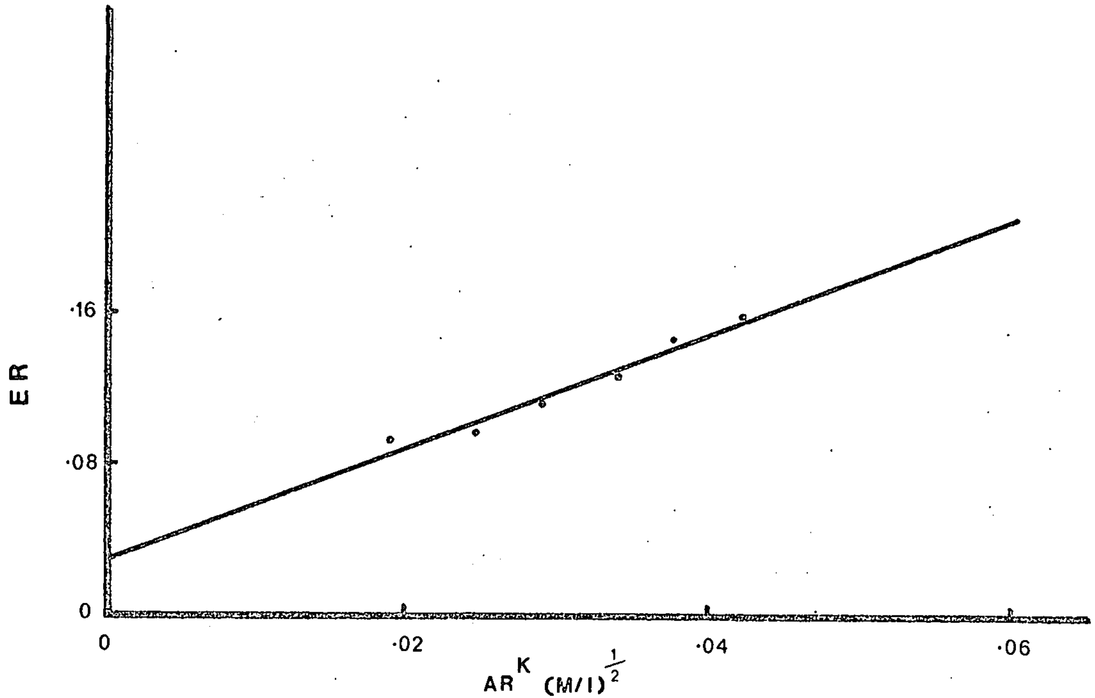

FIG. 57 Relationship between indirect ER and AR^K at an initial K_{ex} level of 1.683 me % for the Riet River No. 2 soil.

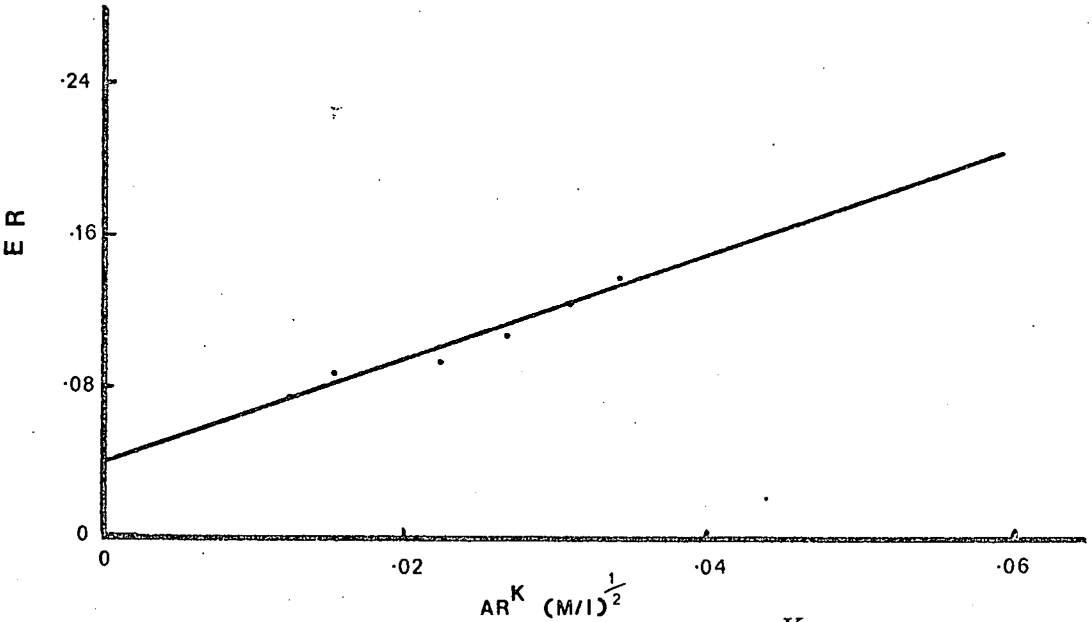

FIG. 58 Relationship between indirect ER and AR^K at an initial K_{ex} level of 1.181 me % for the Riet River No. 2 soil.

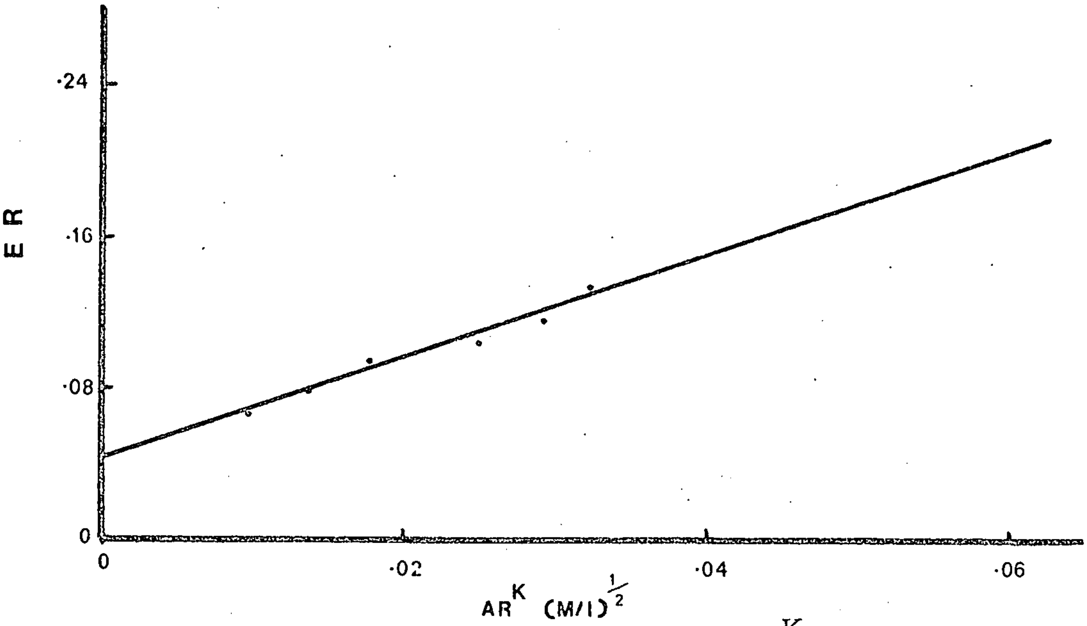

FIG. 59 Relationship between indirect ER and AR^K at an initial K_{ex} level of 1.018 me % for the Riet River No. 2 soil.

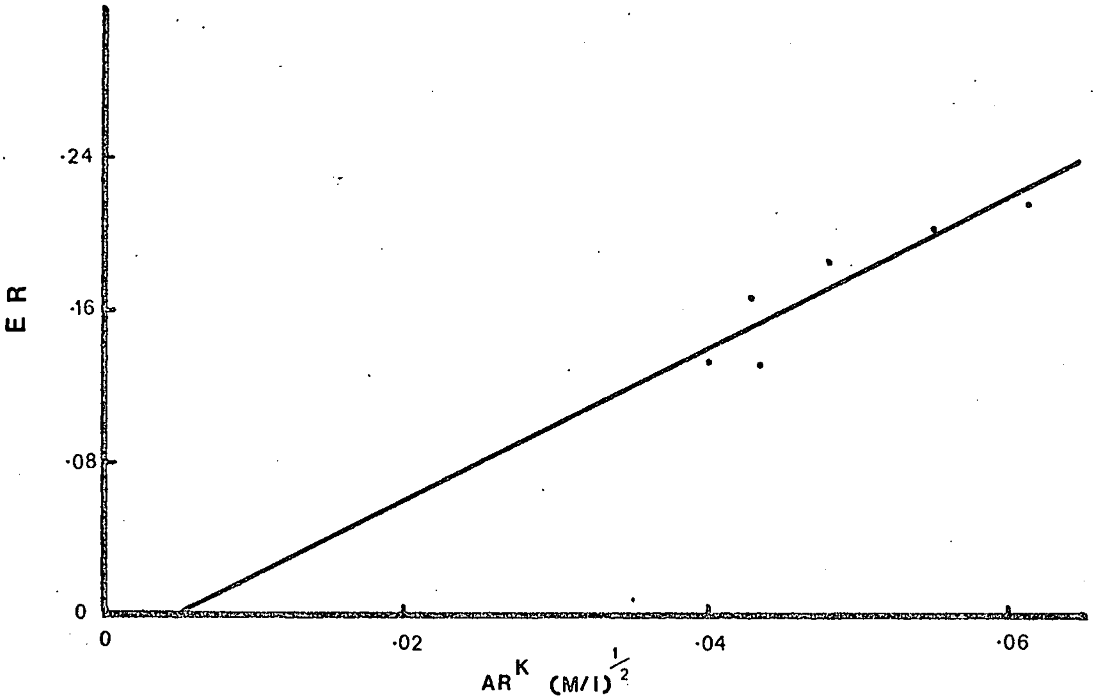

FIG. 60 Relationship between indirect ER and AR^K at an initial K_{ex} level of 2.39 me % for the Riet River No. 4 soil.

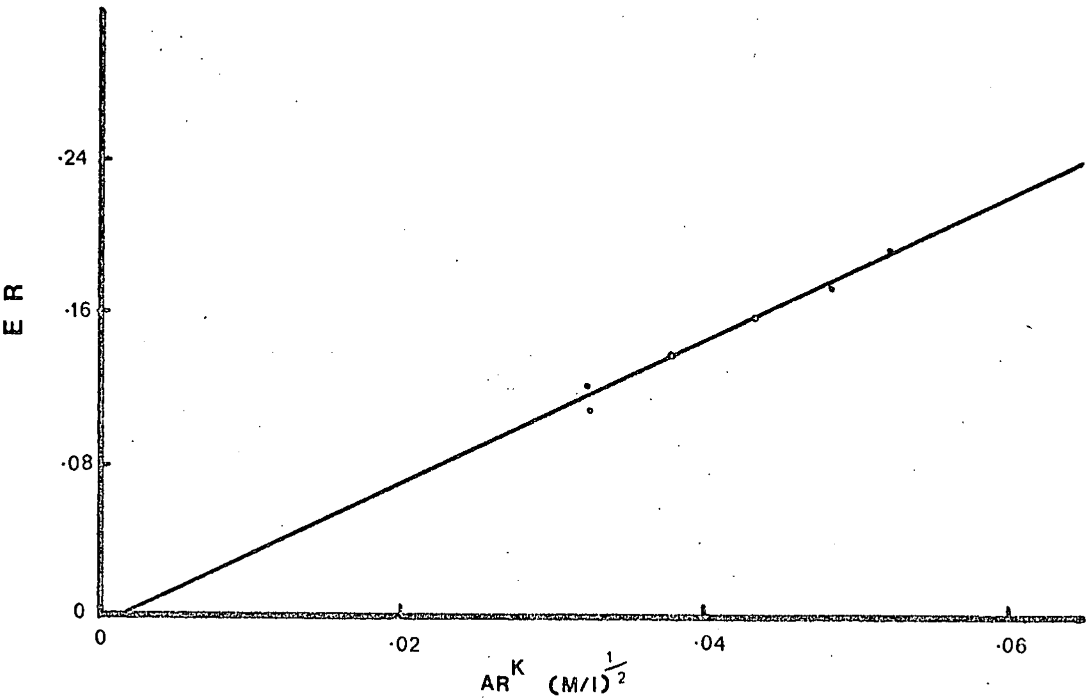

FIG. 61 Relationship between indirect ER and AR^K at an initial K_{ex} level of 1.931 me % for the Riet River No. 4 soil.

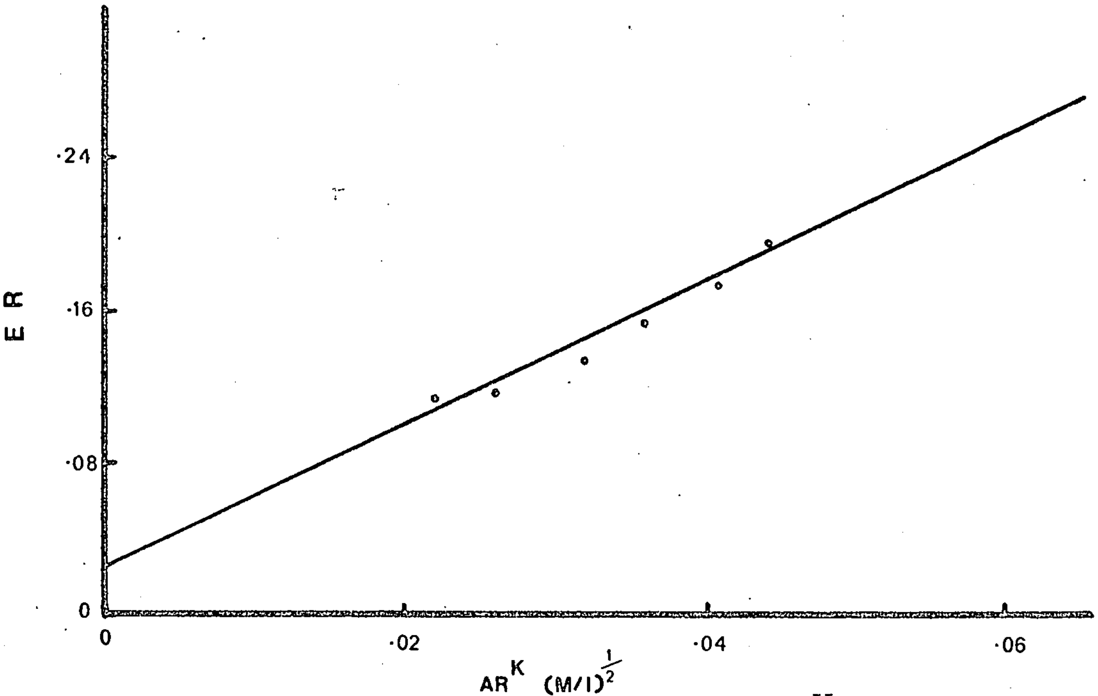

FIG. 62 Relationship between indirect ER and AR^K at an initial K_{ex} level of 1.675 me % for the Riet River No. 4 soil.

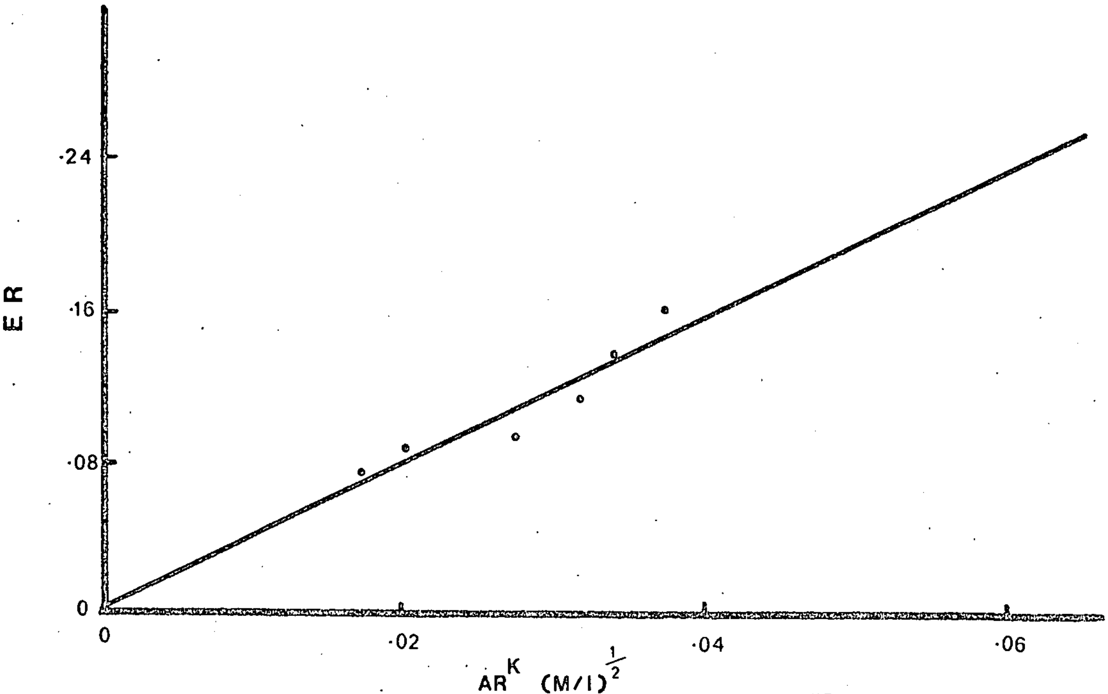

FIG. 63 Relationship between indirect ER and AR^K at an initial K_{ex} level of 1.119 me % for the Riet River No. 4 soil.

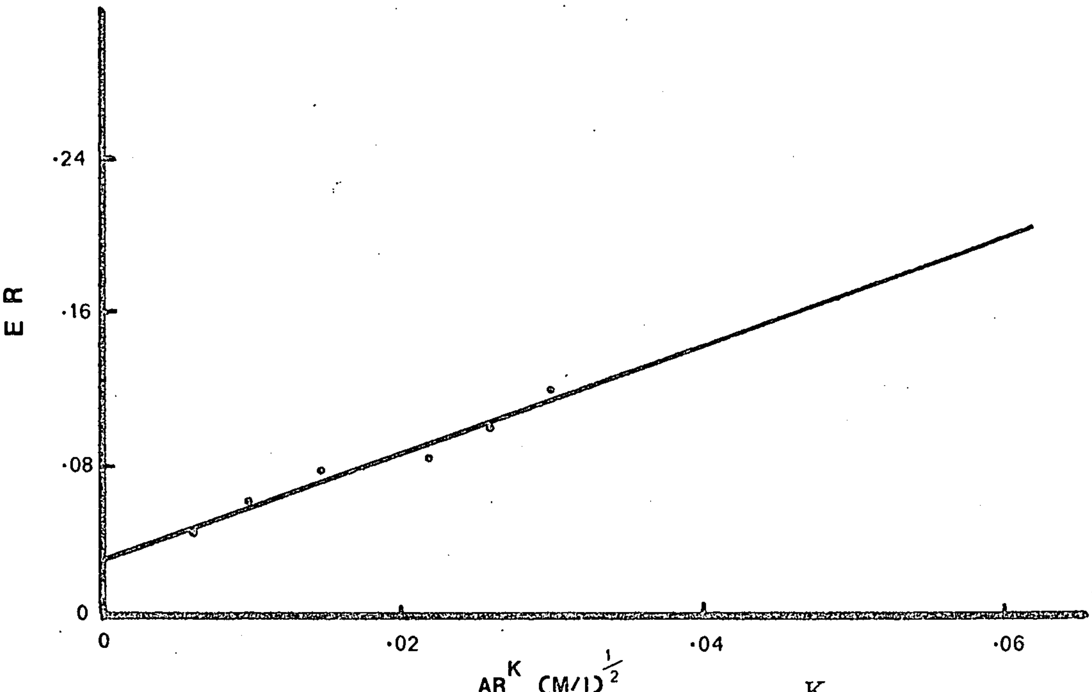

FIG. 64 Relationship between indirect ER and AR^K at an initial K_{ex} level of .388 me % for the Riet River No. 4 soil.

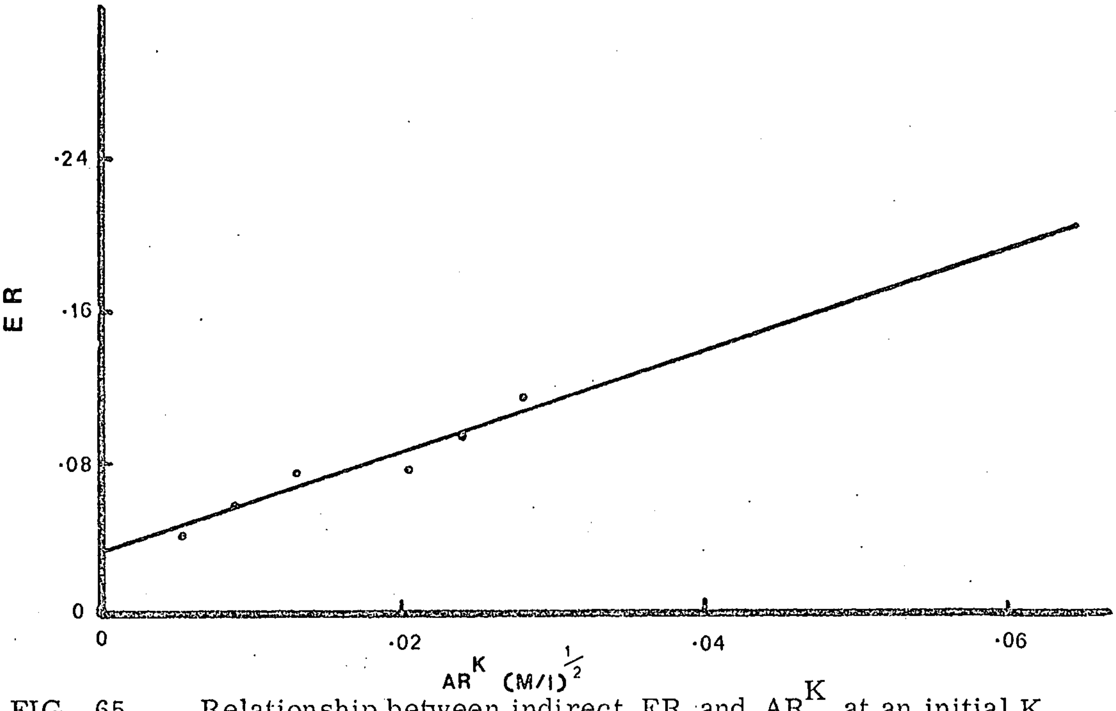

FIG. 65 Relationship between indirect ER and AR^K at an initial K_{ex} level of .369 me % for the Riet River No. 4 soil.

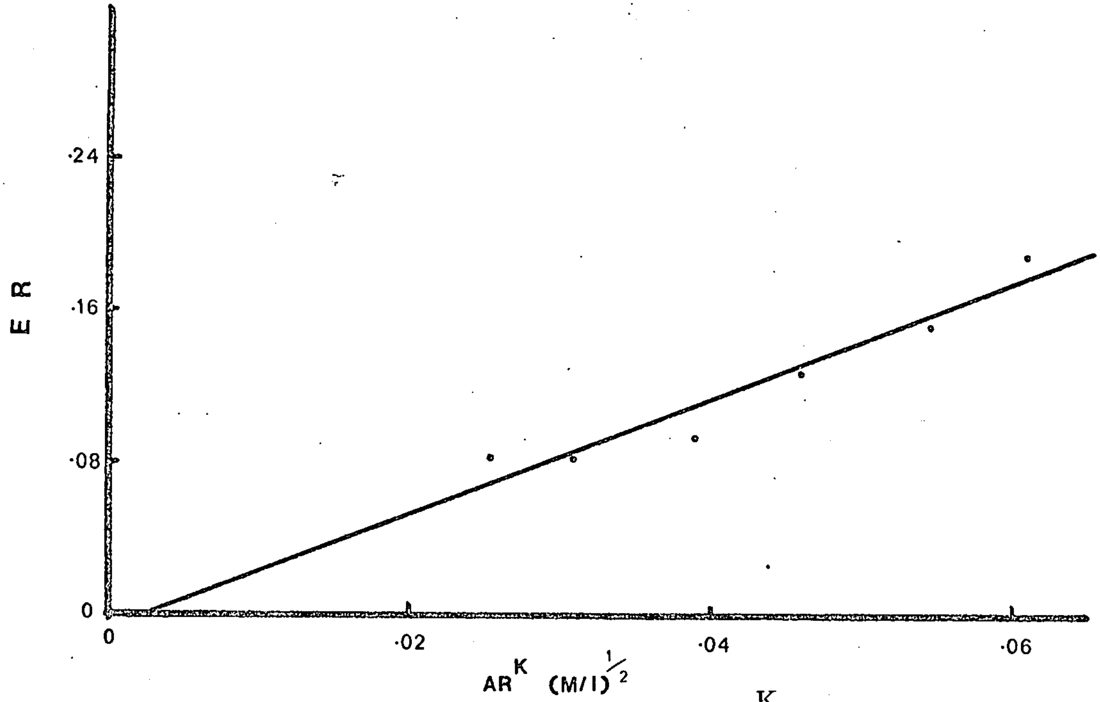

FIG. 66 Relationship between indirect ER and AR^K at an initial K_{ex} level of .775 me % for the Mangano soil.

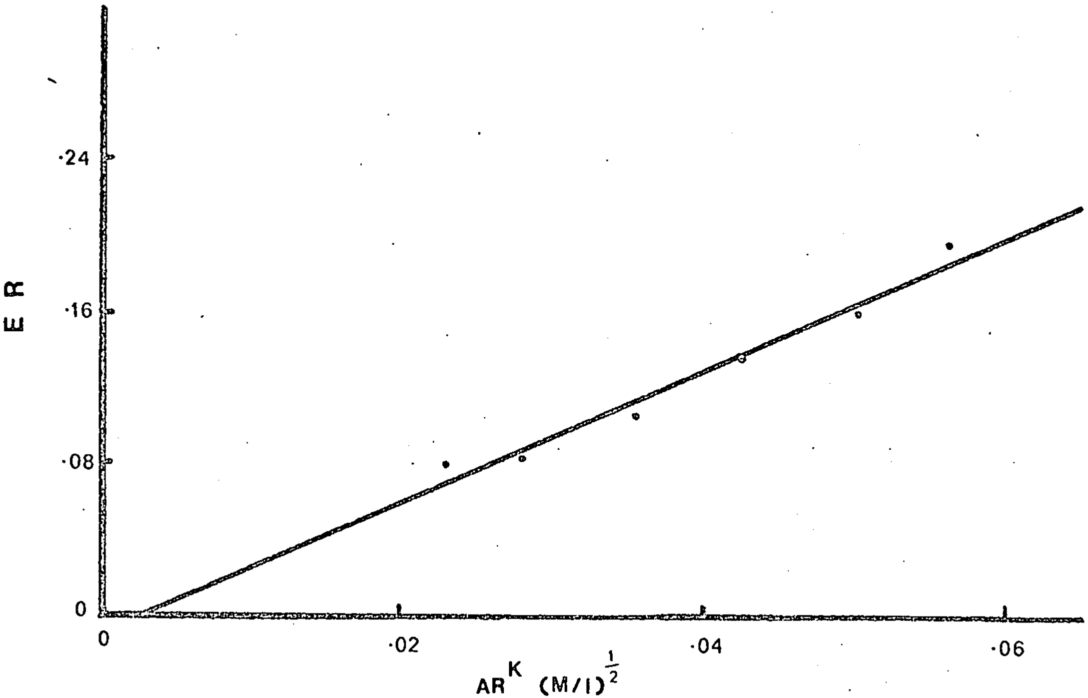

FIG. 67 Relationship between indirect ER and AR^K at an initial K_{ex} level of .675 me % for the Mangano soil.

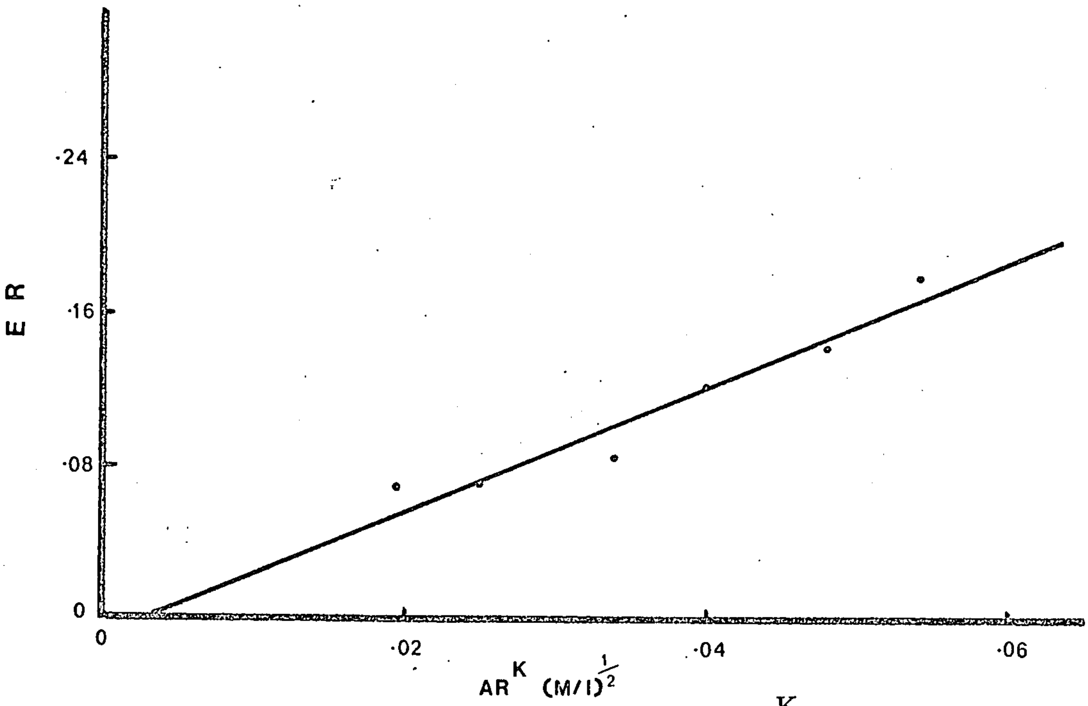

FIG. 68 Relationship between indirect ER and AR^K at an initial K_{ex} level of .531 me % for the Mangano soil.

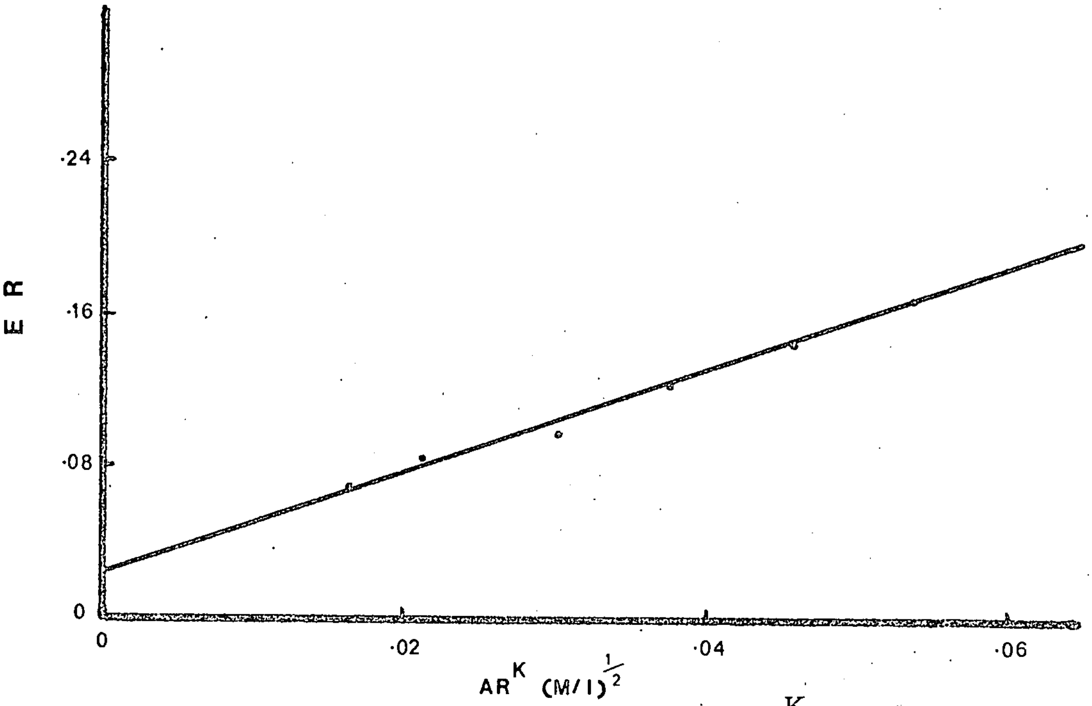

FIG. 69 Relationship between indirect ER and AR^K at an initial K_{ex} level of .438 me % for the Mangano soil.

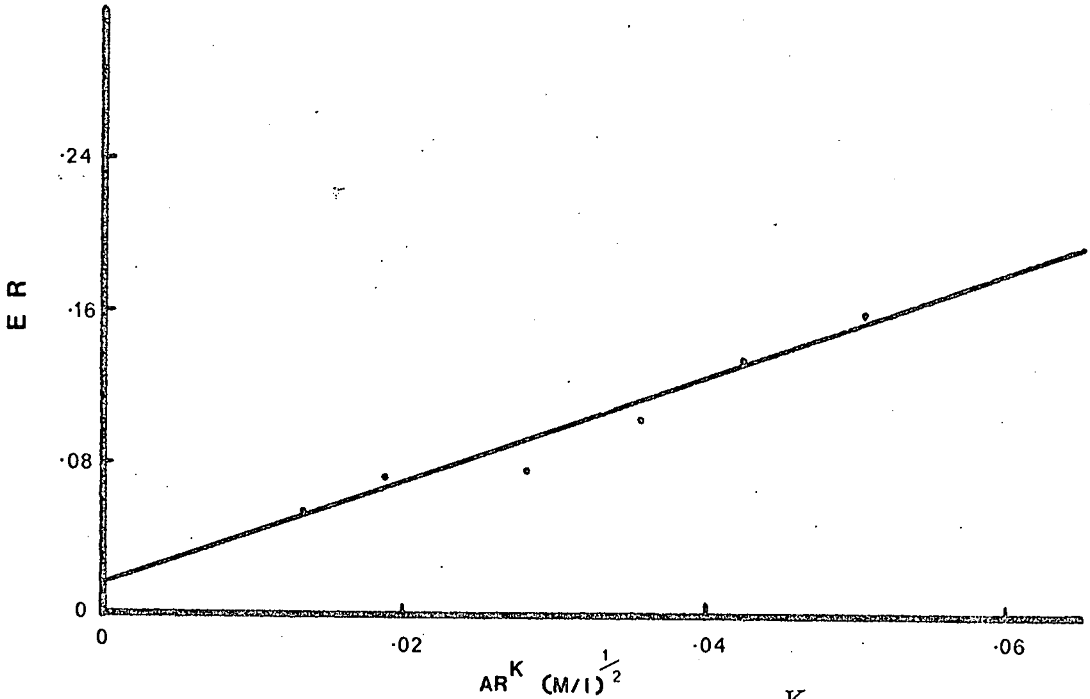

FIG. 70 Relationship between indirect ER and AR^K at an initial K_{ex} level of .313 me % for the Mangano soil.

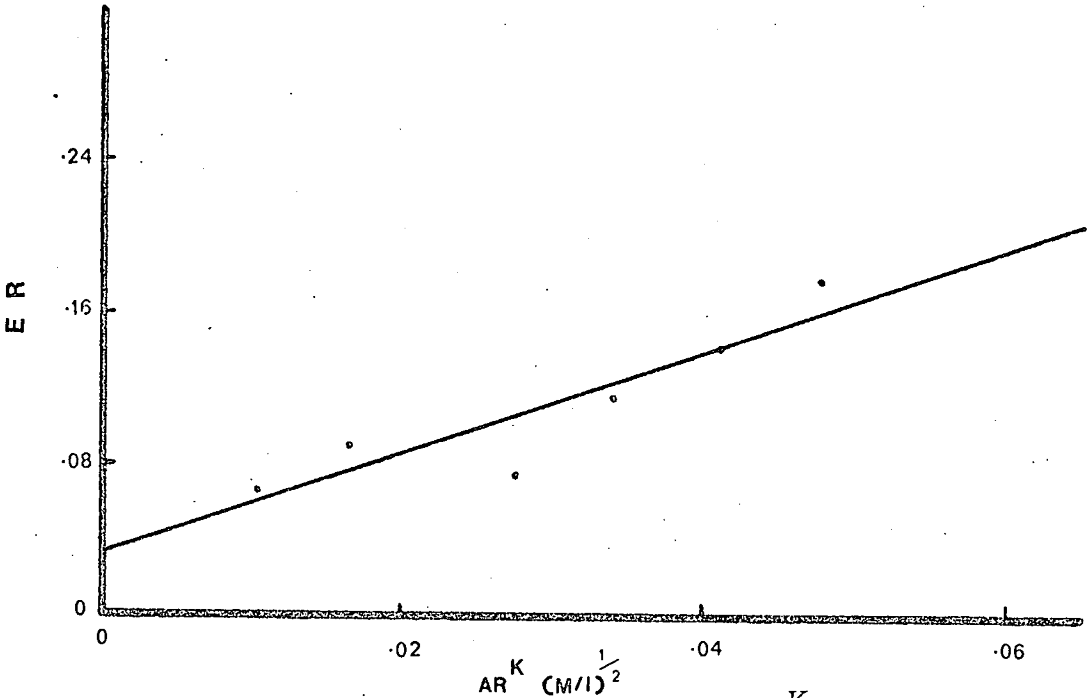

FIG. 71 Relationship between indirect ER and AR^K at an initial K_{ex} level of .250 me % for the Mangano soil.

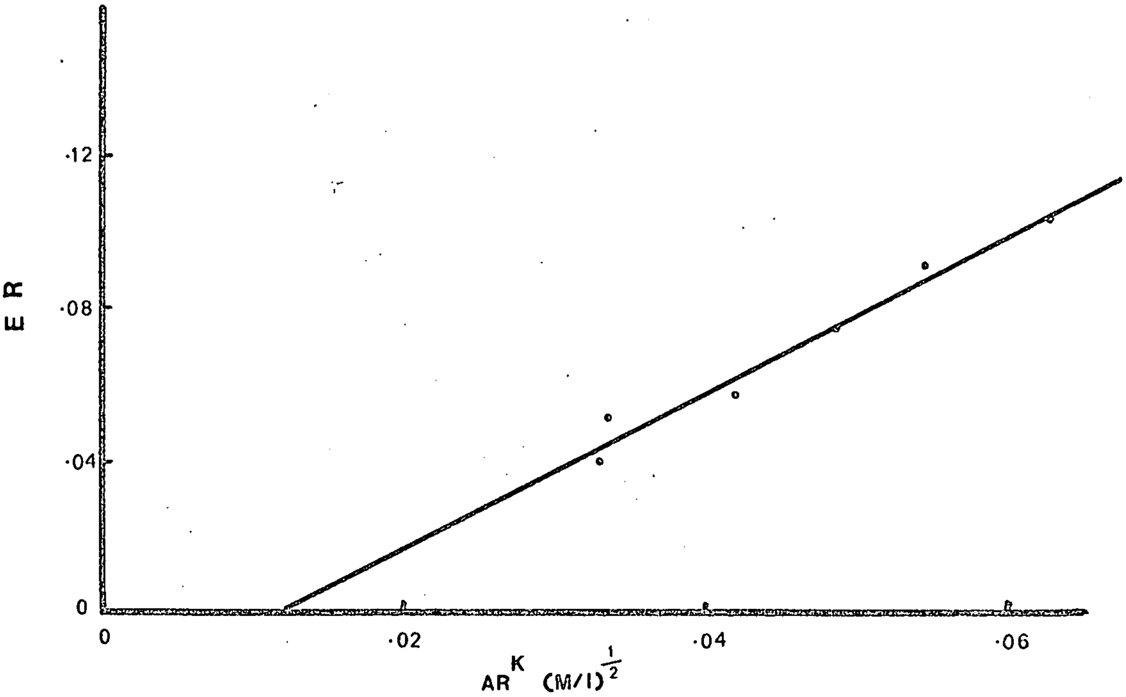

FIG. 72 Relationship between indirect ER and AR^K at an initial K_{ex} level of .95 me % for the Estcourt soil.

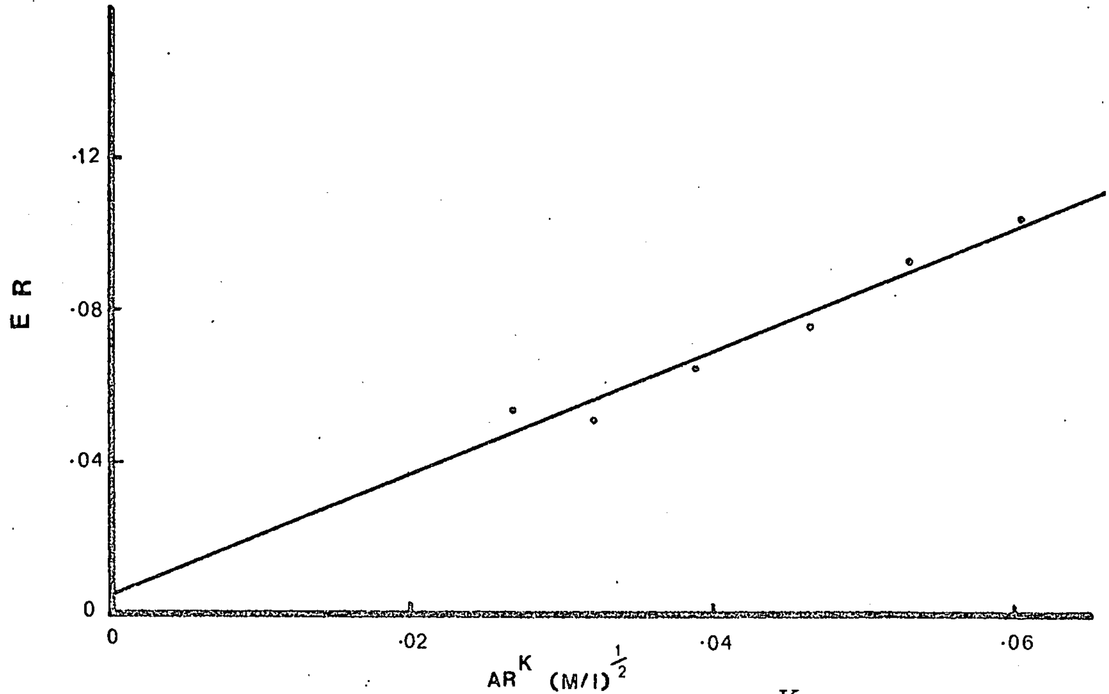

FIG. 73 Relationship between indirect ER and AR^K at an initial K_{ex} level of .906 me % for the Estcourt soil.

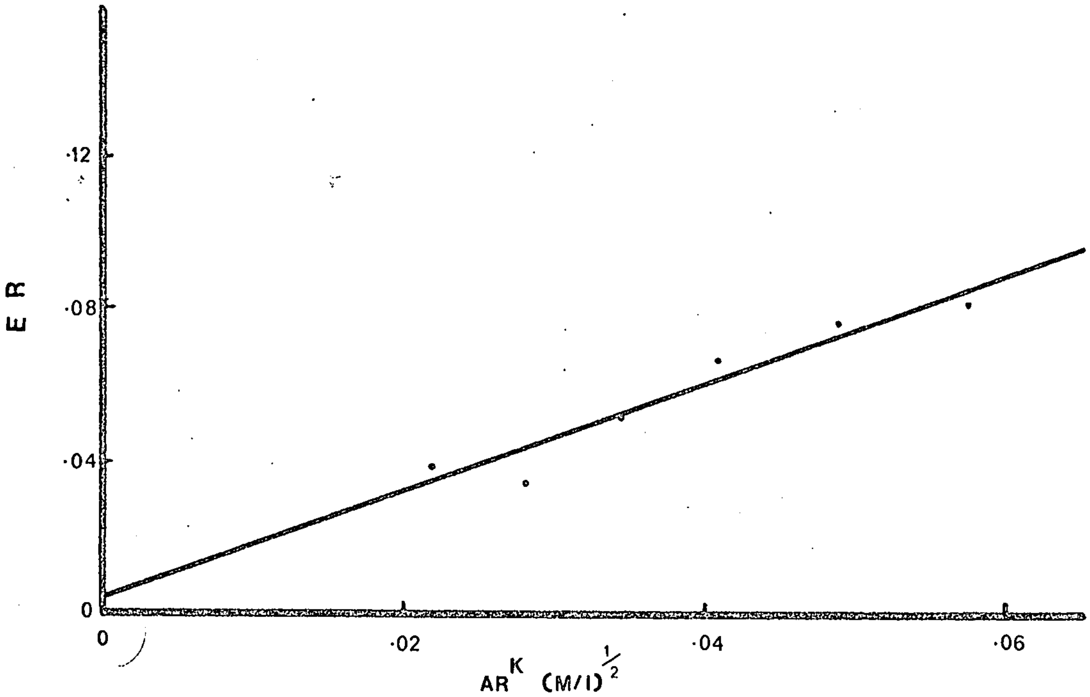

FIG. 74 Relationship between indirect ER and AR^K at an initial K_{ex} level of .653 me % for the Estcourt soil.

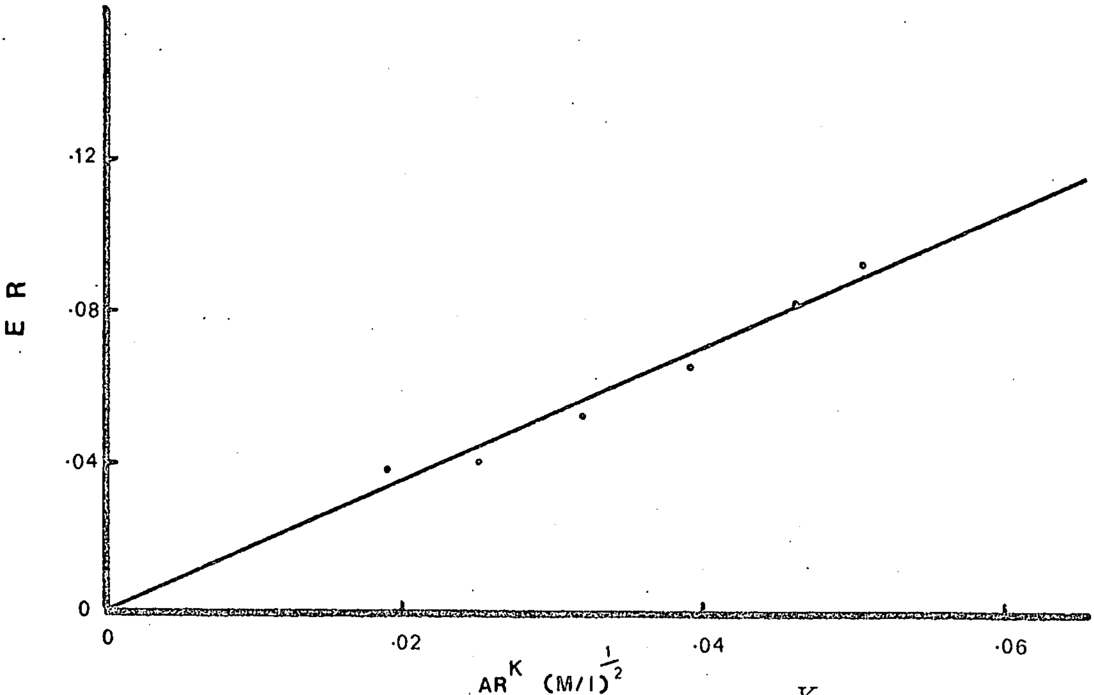

FIG. 75 Relationship between indirect ER and AR^K at an initial K_{ex} level of .556 me % for the Estcourt soil.

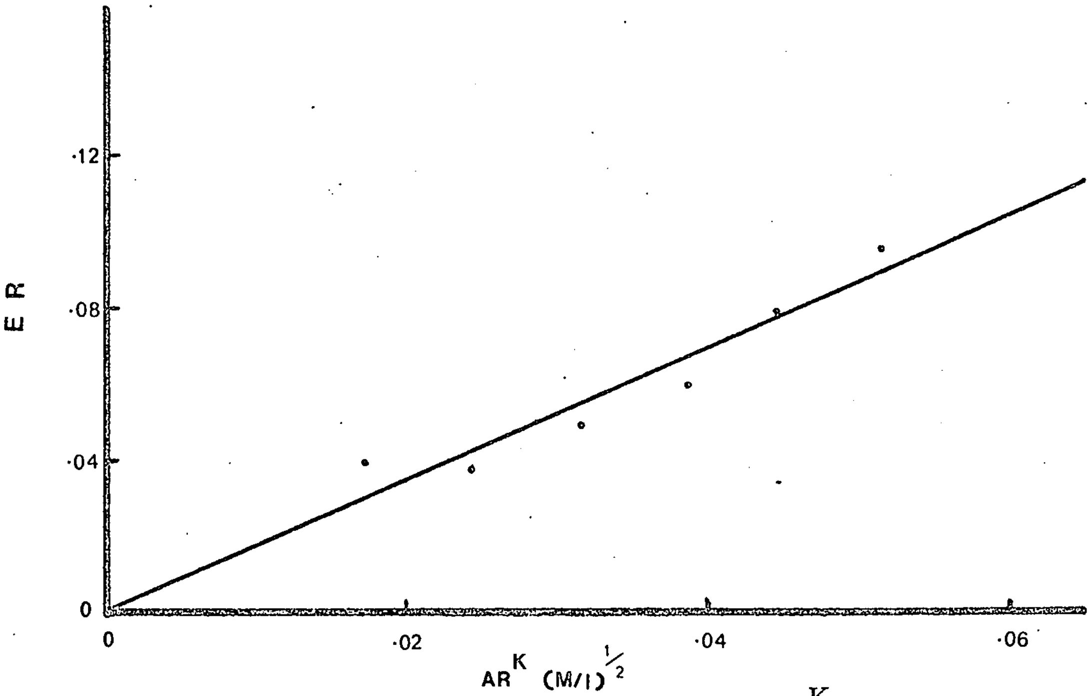

FIG. 76 Relationship between indirect ER and AR^{K} at an initial K_{ex} level of .531 me % for the Estcourt soil.

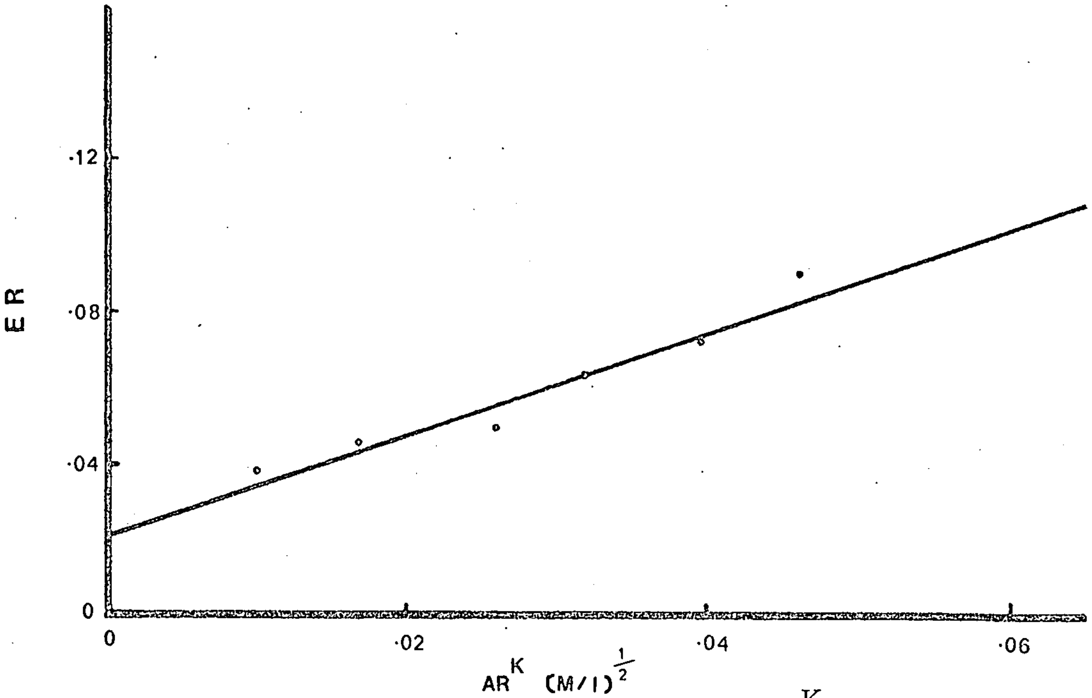

FIG. 77 Relationship between indirect ER and AR^{K} at an initial K_{ex} level of .294 me % for the Estcourt soil.

lines for the lowest one, or at most two, initial K_{ex} levels for each soil gave by far the best approximation to the line relating ER to AR_e^K for a given soil (Table 51). For the Riet River No. 2 soil the line for the lowest initial K_{ex} level was quite remarkably similar to the line relating ER to AR_e^K, the regression equations being : ER = $2.5959AR_e^K$ + 0.04416 (for the total line) and ER = $2.5862AR^K$ + 0.04504 (for an initial K_{ex} of 1.018me per 100g).

In almost all cases the experimental data fitted the Gapon-like linear equation ER = $b.AR^K$ + a very well and in some cases quite remarkably well, expecially if the small number of observations available for each line is taken into account. On the other hand it is noteworthy that no general equation can be obtained for any one of the soils by combining the results obtained with the various initial K_{ex} levels. For each soil such a general equation can be obtained for a small number of initial K_{ex} levels in a limited range. The factor prohibiting a general equation for a soil is the large changes in the values of the intercepts.

7.4 THE EFFECT OF SODIUM ON THE GAPON RELATIONS OF TWO SOILS (cf. Chapter 4).

Both the Mangano and the Riet River No. 2 soils gave linear relationships between ER and AR_e^K at all three levels of sodium saturation (Figures 78 and 79). In this experiment Ca_{ex} was determined and not calculated by subtracting K_{ex} from CEC. This was necessary because of the differences in sodium levels. Except for the highest sodium level of the Mangano soil, all the lines again had intercepts different from zero.

With the exception of the highest sodium level of the Mangano soil the intercepts of the lines relating ER to AR_e^K increased slightly with increasing sodium level and did not decrease as was the case with the intercepts of the lines relating K_{ex} to AR_e^K. The slopes of the lines relating ER to AR_e^K also increased with increasing sodium levels. These increases in the intercepts and the slopes of the lines were caused by the fact that Ca_{ex} was decreased with increasing quantity of sodium in the system. The denomi-

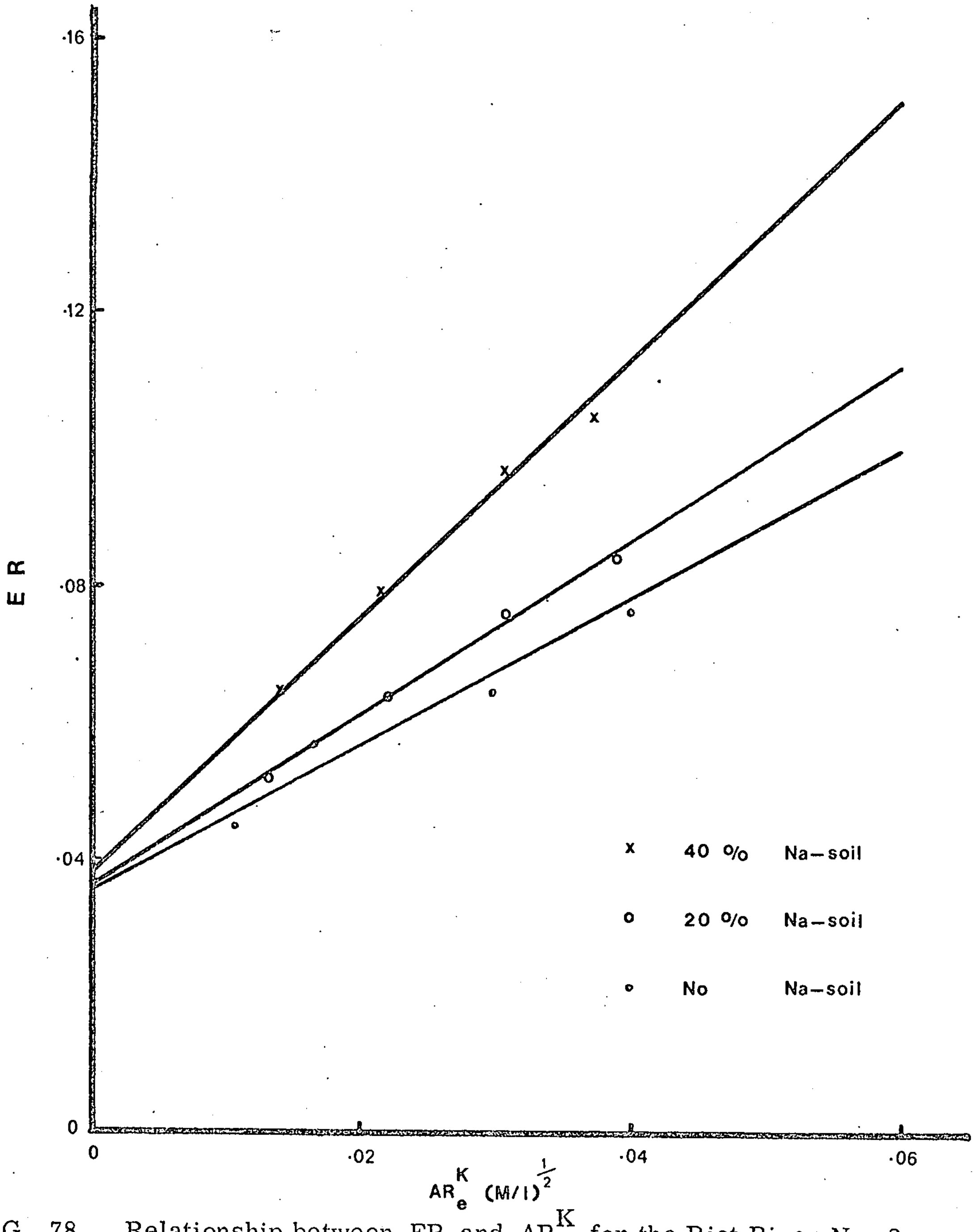

FIG. 78 Relationship between ER and AR_e^K for the Riet River No. 2 soil at different levels of sodium saturation.

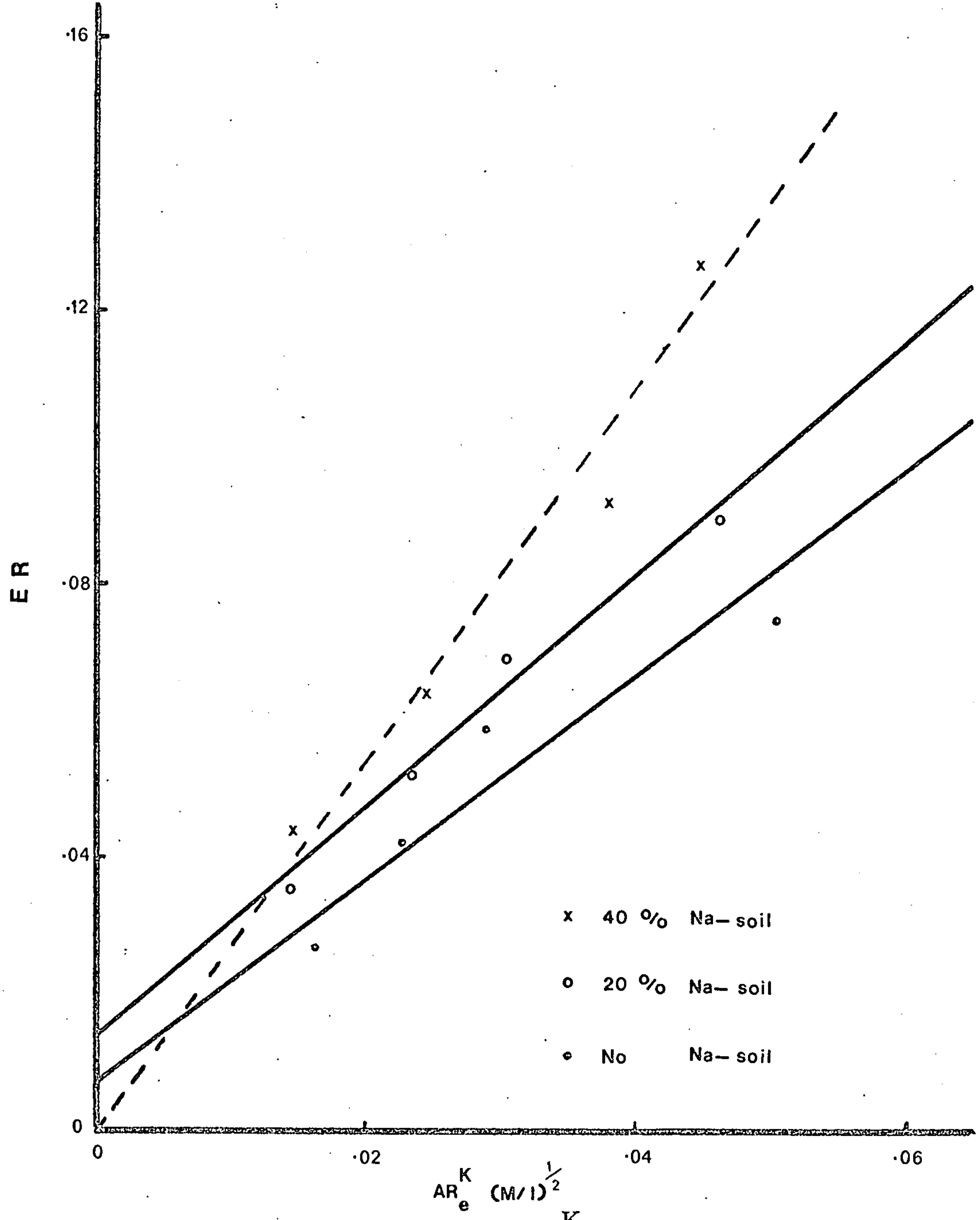

FIG. 79 Relationship between ER and AR_e^K for the Mangano soil at different levels of sodium saturation.

nators of the exchange ratios were therefore decreased by increasing sodium levels and the ratios were consequently increased.

The normal K_G values for both soils, obtained by dividing AR_e^K into ER, are given in Table 52. The values again were fairly similar for the two soils, being higher with increasing level of sodium saturation (Table 52 and Figures 80 and 81). The latter can be ascribed to the fact that less calcium soil was present with increasing quantities of sodium soil added and this caused a decrease in amount of exchangeable calcium in the soil. Because K_{ex} stayed relatively constant for each level of K saturation the exchange ratios were therefore increased.

Whereas K_G was increased at high sodium levels, the levels of exchangeable K where K_G became infinite were decreased (Figures 80 and 81). It was illustrated best by the Riet River No. 2 soil, but the Mangano soil showed a similar tendency. This supports the statement (in Chapter 4) that it seems as if high sodium levels "opened up" some of the more specific sites where potassium is normally adsorbed very tightly. Such potassium will then be more freely available to plants and this may partially explain the synergistic effect of high sodium concentrations on plant-uptake of potassium at low potassium levels on some soils as found by Heimann (1958, 1966) and others.

Relationships between AR^K and the indirect ER could only be calculated for the treatments where no sodium was added. These results are given in Table 53 and Figures 82 to 89. It is evident that the data fitted the Gapon-like equation well, especially in the case of the Riet River No.2 soil which gave r values ranging from 0.9860 to 0.9976. The intercepts again increased with decreasing level of K_{ex}, although the results for the Mangano soil was rather inconsistent. The slopes of the lines remained relatively constant and were practically similar for the two soils. The slopes, however, differed much from those for the total lines. The smaller number of observations obtained within some sets of samples were caused by fungus development, despite the taking of precautionery measures.

7.5/..................

TABLE 52 - K_G values for two soils at different sodium levels as calculated with AR_e^K

Soil	Sodium soil in mixture	ER	K_G $(M/l)^{-\frac{1}{2}}$
Riet River No.2		0.0762	1.9
		0.0649	2.2
	0%	0.0569	3.0
		0.0450	4.2
		0.0842	2.2
		0.0764	2.5
	20%	0.0643	2.9
		0.0517	3.9
		0.1050	2.8
	40%	0.0973	3.1
		0.0797	3.7
		0.0651	4.6
Mangano		0.0751	1.5
		0.0593	2.1
	0%	0.0426	1.9
		0.0270	1.7
		0.0895	1.9
		0.0692	2.3
	20%	0.0521	2.2
		0.0355	2.4
		0.1272	2.9
	40%	0.0925	2.4
		0.0649	2.6
		0.0443	3.0

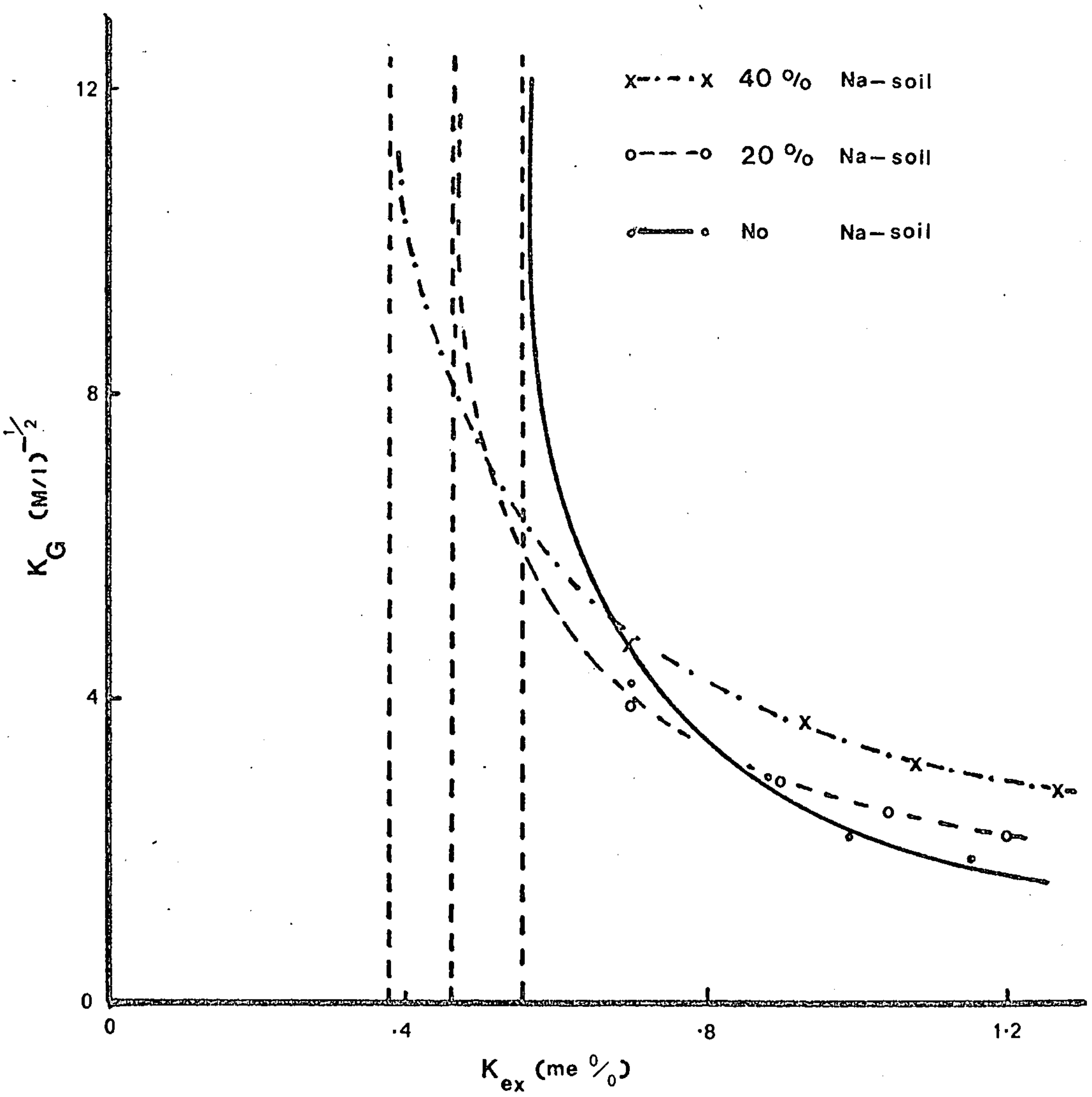

FIG. 80 Relationship between K_G and K_{ex} for the Riet River No. 2 soil at different sodium levels. (Lines not fitted)

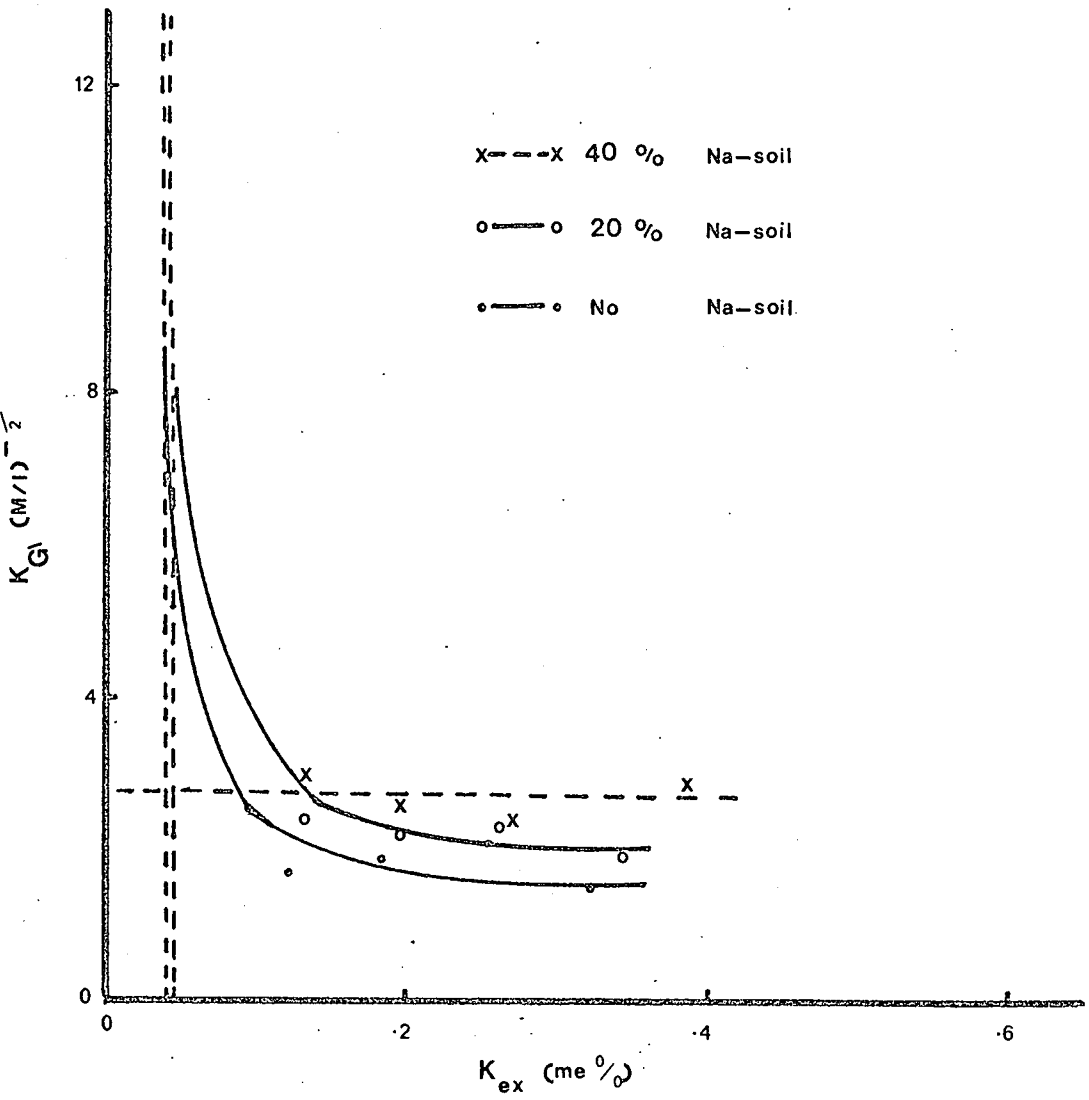

FIG. 81 Relationship between K_G and K_{ex} for the Mangano soil at different sodium levels. (Lines not fitted)

TABLE 53 - Equations for lines relating indirect ER and AR^K at different initial K_{ex} levels for the sodium experiment

Soil	Initial K_{ex} me%	Regression equation
Riet River No.2	1.150	$ER=2.4818AR^K-0.0224$
	0.990	$ER=2.7729AR^K-0.0167$
	0.875	$ER=3.0351AR^K+0.0000$
	0.700	$ER=3.1540AR^K+0.0112$
	Final line	$ER=1.0319AR_e^K+0.0350$
Mangano	0.323	$ER=2.0412AR^K-0.0336$
	0.255	$ER=3.7560AR^K-0.0525$
	0.183	$ER=3.0147AR^K-0.0271$
	0.123	$ER=3.2206AR^K-0.0274$
	Final line	$ER=1.3301AR_e^K+0.0117$

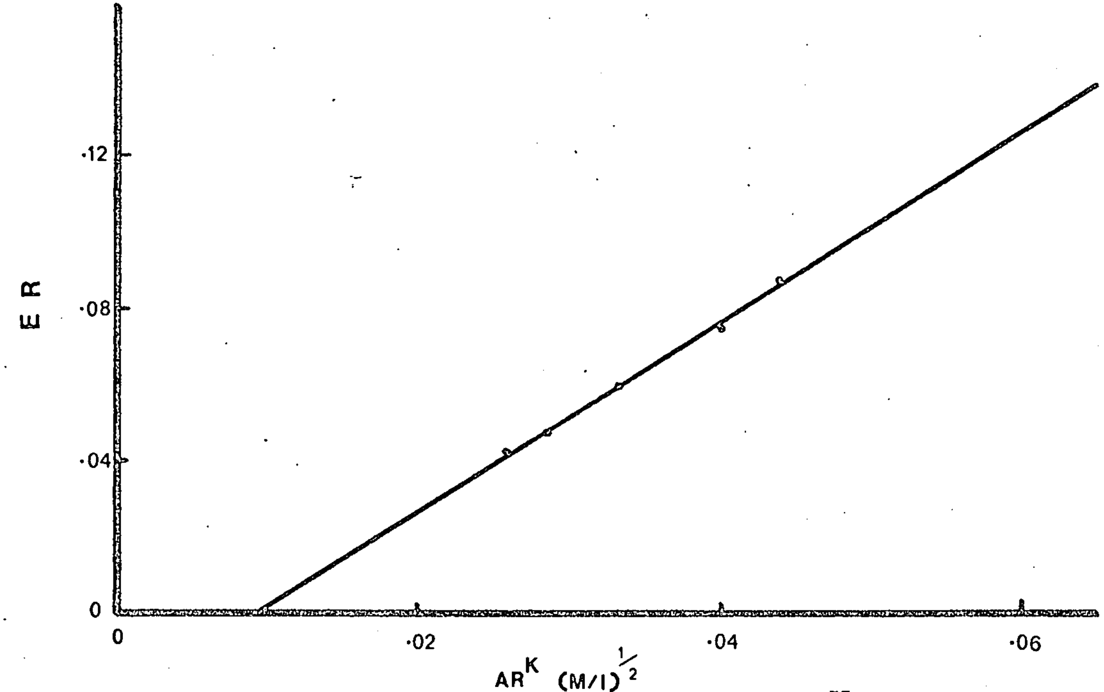

FIG. 82 Relationship between indirect ER and AR^K at an initial K_{ex} level of 1.150 me % for the Riet River No. 2 soil.

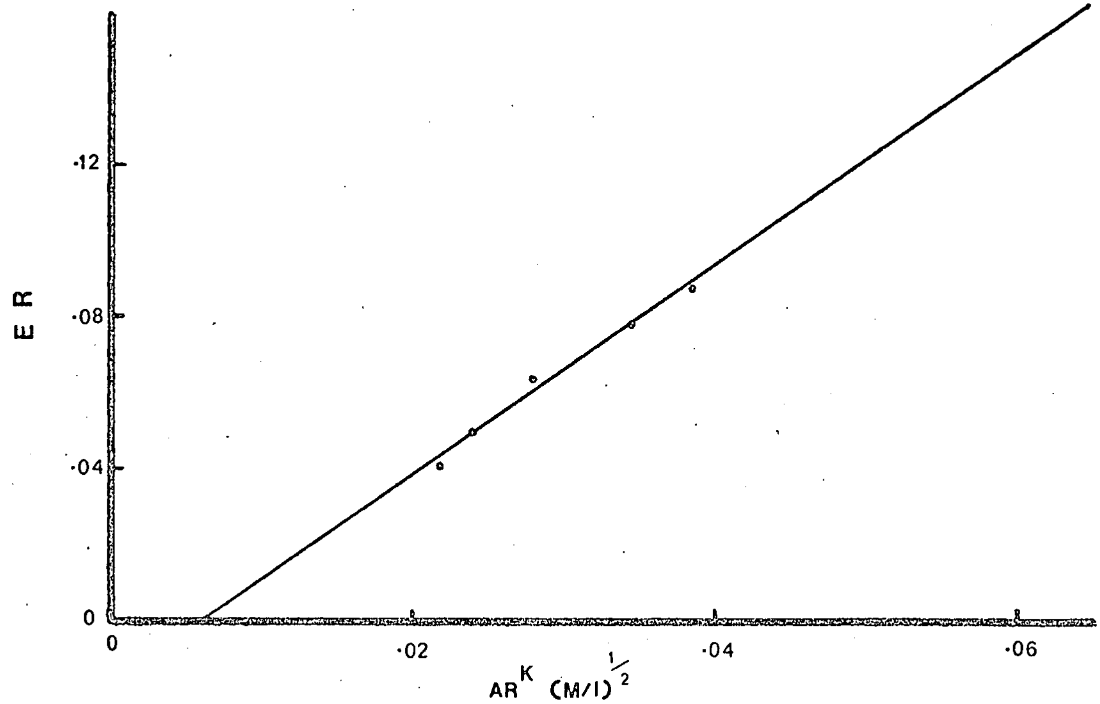

FIG. 83 Relationship between indirect ER and AR^K at an initial K_{ex} level of .990 me % for the Riet River No. 2 soil.

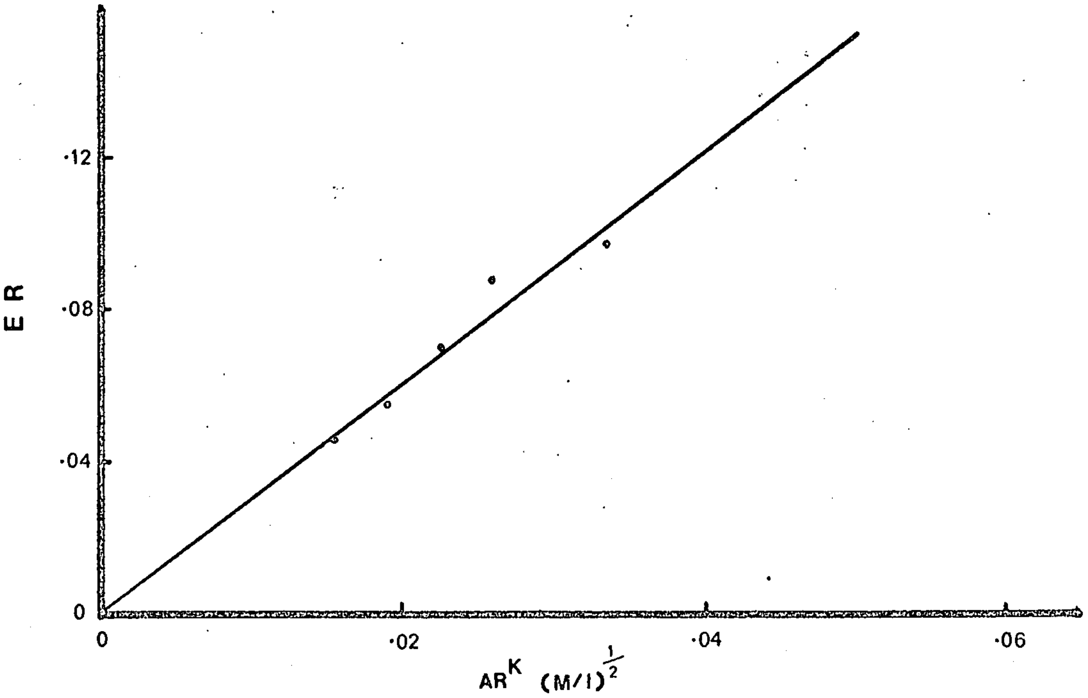

FIG. 84 Relationship between indirect ER and AR^K at an initial K_{ex} level of .875 me % for the Riet River No. 2 soil.

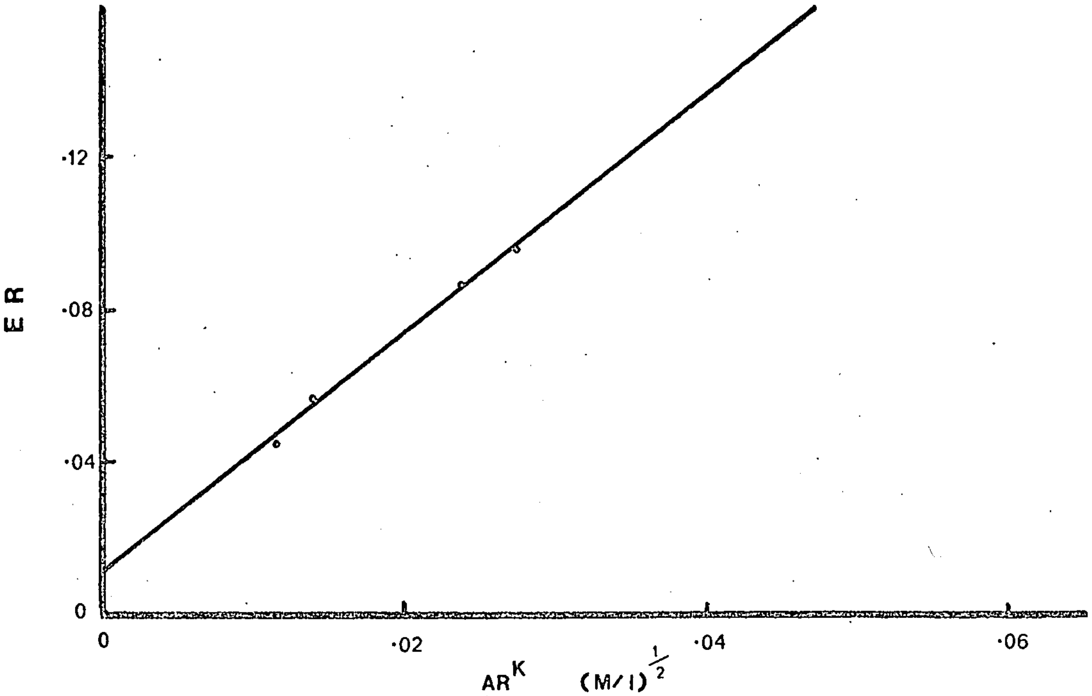

FIG. 85 Relationship between indirect ER and AR^K at an initial K_{ex} level of .700 me % for the Riet River No. 2 soil.

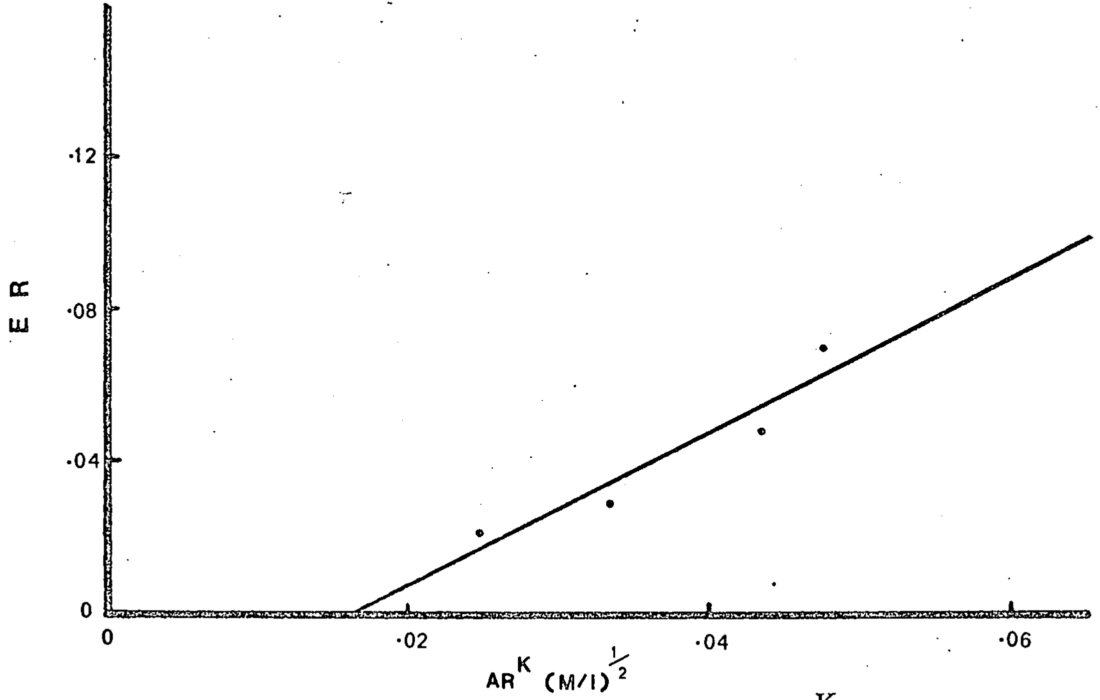

FIG. 86 Relationship between indirect ER and AR^K at an initial K_{ex} level of .323 me % for the Mangano soil.

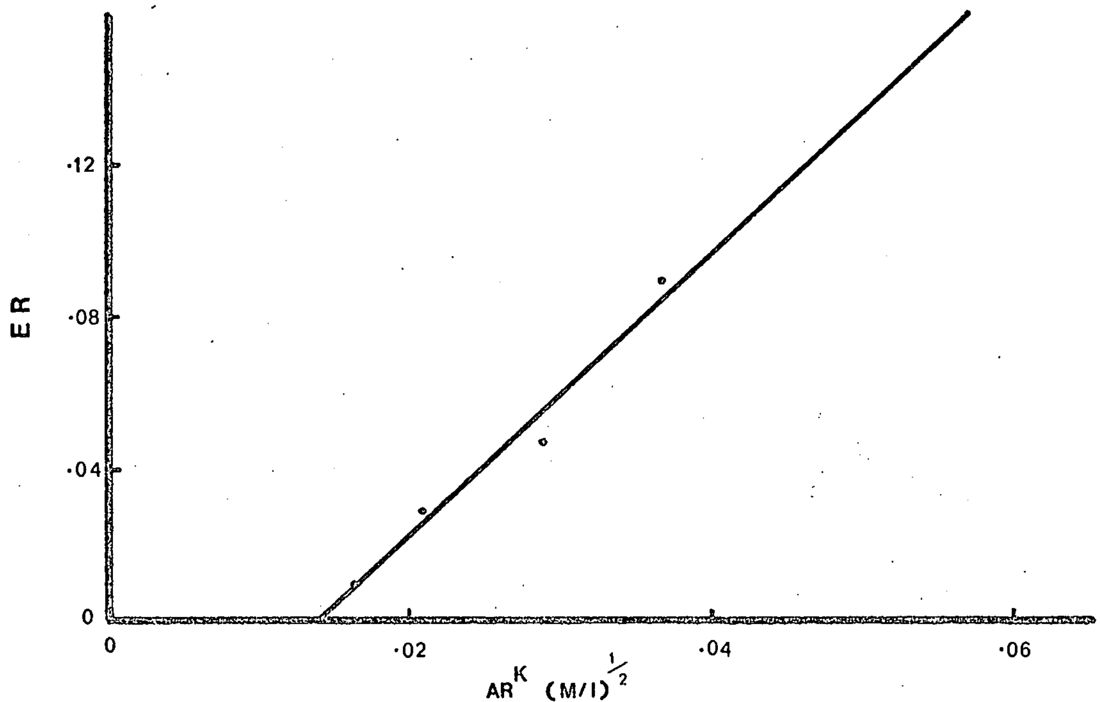

FIG. 87 Relationship between indirect ER and AR^K at an initial K_{ex} level of .255 me % for the Mangano soil.

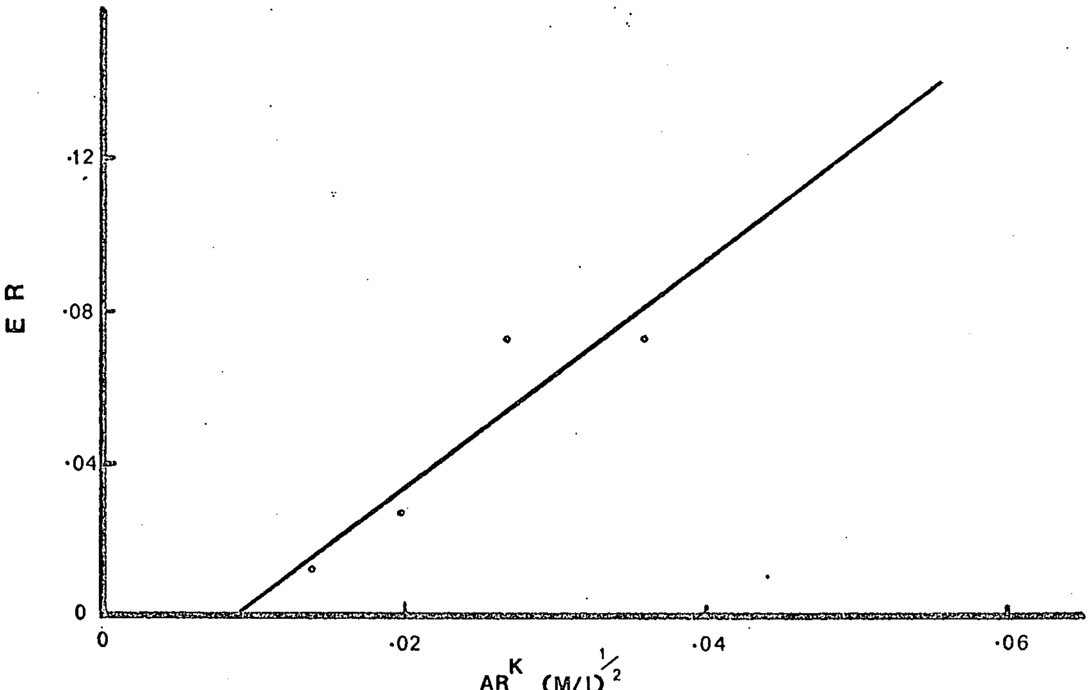

FIG. 88 Relationship between indirect ER and AR^K at an initial K_{ex} level of .183 me % for the Mangano soil.

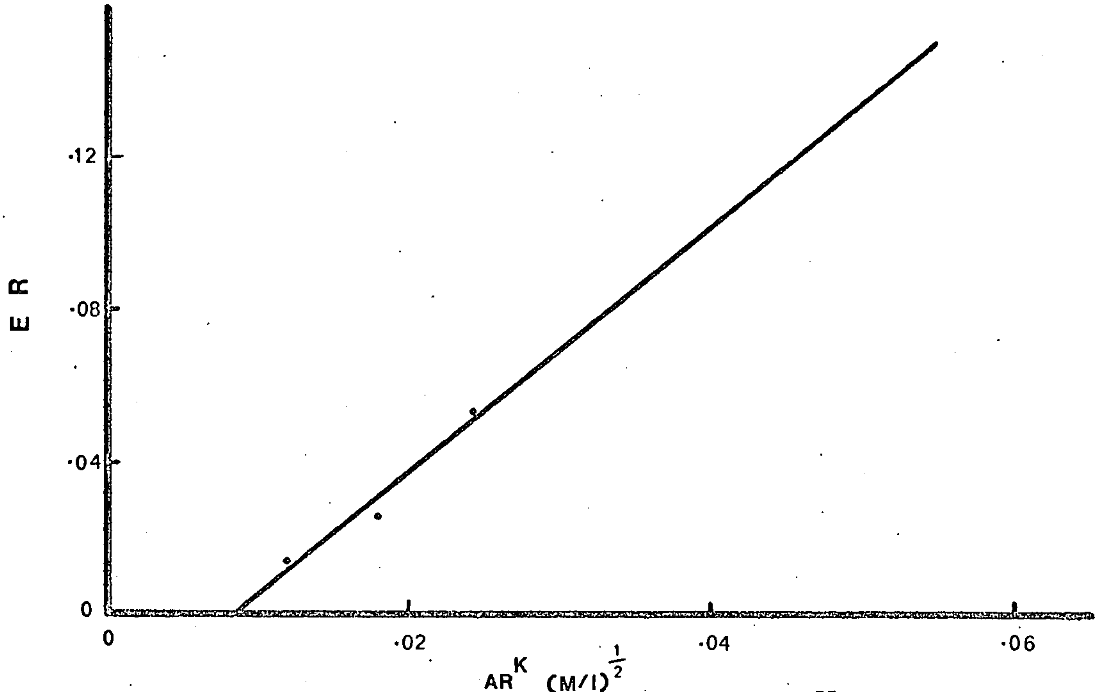

FIG. 89 Relationship between indirect ER and AR^K at an initial K_{ex} level of .123 me % for the Mangano soil.

7.5 GAPON RELATIONS FOR BENTONITE (cf. Chapter 5)

In Chapter 5 it was pointed out that the results for kaolin were rather inconsistent, probably because too large quantities of clay per 100ml equilibrating solution were used, and it was decided not to include those results in this section. Only the derived results for bentonite were therefore included in this section.

The exchange ratio (ER) is a ratio and not an absolute value and will be the same, independent of whether actual values are given as per 1000ml equilibrating solution or as per 100g clay. It was shown that AR_e^K is also not affected by the way of expression. The Gapon constants will therefore not be affected by the way of expression. K_{ex} values are given as me per 100g clay. Ca_{ex} was again calculated by subtracting K_{ex} from CEC of the bentonite.

For all three quantities of clay used the relationships between ER and AR_e^K were not linear but curved (Figure 90). The two larger quantities again gave intercepts different from zero. The intercepts increased with increasing quantity of clay used. The curved graphs for the relationships between ER and AR_e^K may point to an inconsistent or poor Gapon relationship. Marques (1964) and Moss (1967), however, also found curved relationships for some soils or soil clays.

The normal K_G values for all mixtures and quantities of clay, calculated by dividing AR_e^K into ER, are given in Table 54. It is evident that at higher K_{ex} values, where K_G is relatively constant, K_G increased with decreasing quantity of clay used per 100ml equilibrating solution. The relationships between K_{ex} and K_G are shown in Figure 91. EK^O, the K_{ex} value at which K_G becomes infinite (because AR_e^K becomes zero), increased with increasing quantity of clay. This means that with increasing clay content the lowest experimental value of K_{ex} (3.00me per 100g, mixture E) was nearer to the line which is approached asymptotically by the curve. This is illustrated by the K_G values for mixture E. For 0.3g of clay EK^O was zero and therefore K_G cannot increase at the lowest K_{ex} levels. Consequently K_G for mixture E remains low. For 0.6g clay the K_{ex} value of

mixture/..............

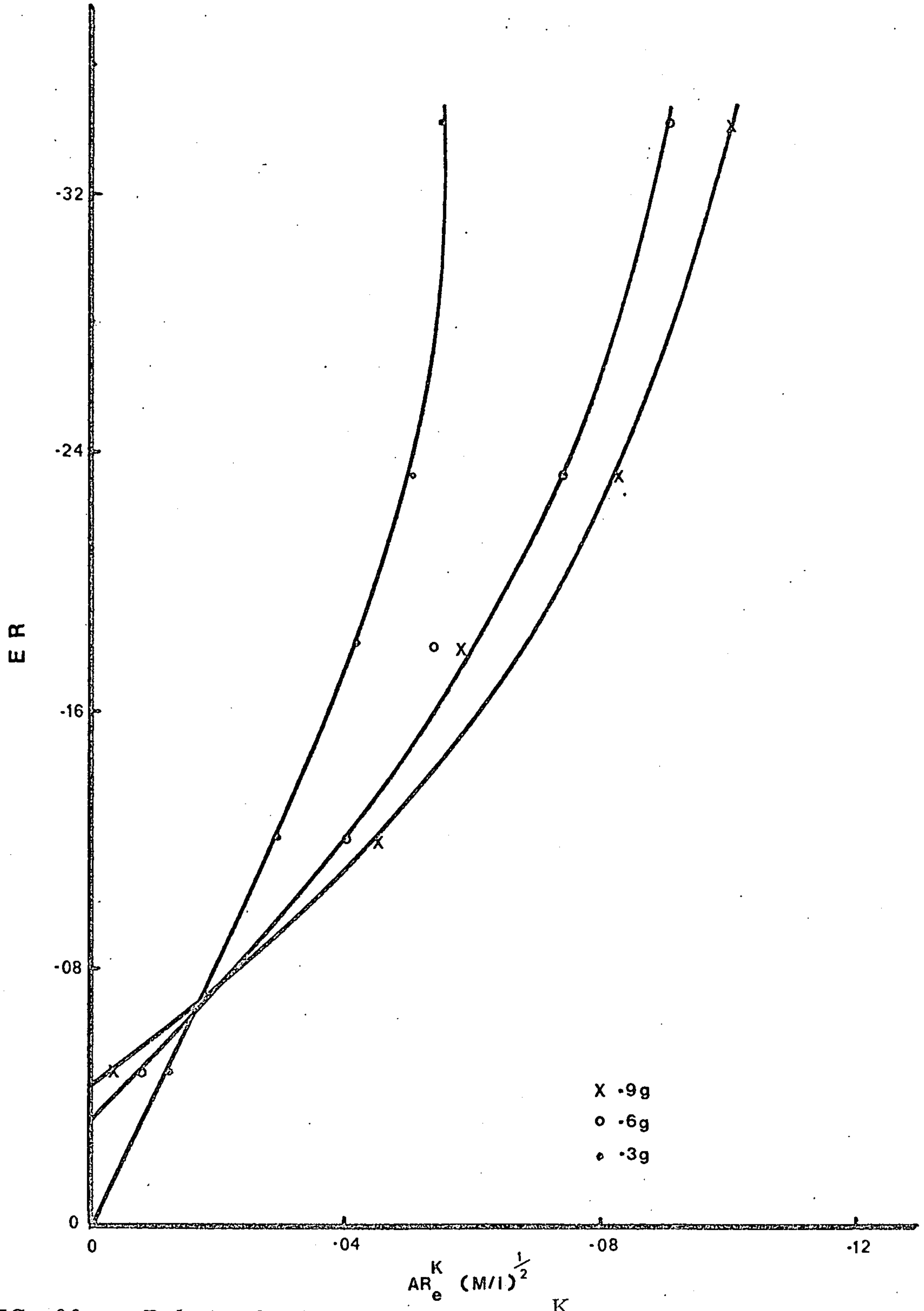

FIG. 90 Relationship between ER and AR_e^K for different quantities of bentonite per 100 ml shaking solution.

TABLE 54 - Exchange ratios and K_G values for bentonite

Quantity of clay per 100 ml	ER	K_G $(M/l)^{-\frac{1}{2}}$
	0.3416	6.2
	0.2331	4.6
0.3g	0.1771	4.1
	0.1211	4.1
	0.0485	3.9
	0.3416	3.7
	0.2331	3.2
0.6g	0.1771	3.2
	0.1211	3.0
	0.0485	5.6
	0.3416	3.4
	0.2331	2.8
0.9g	0.1771	3.0
	0.1211	2.7
	0.0485	13.1

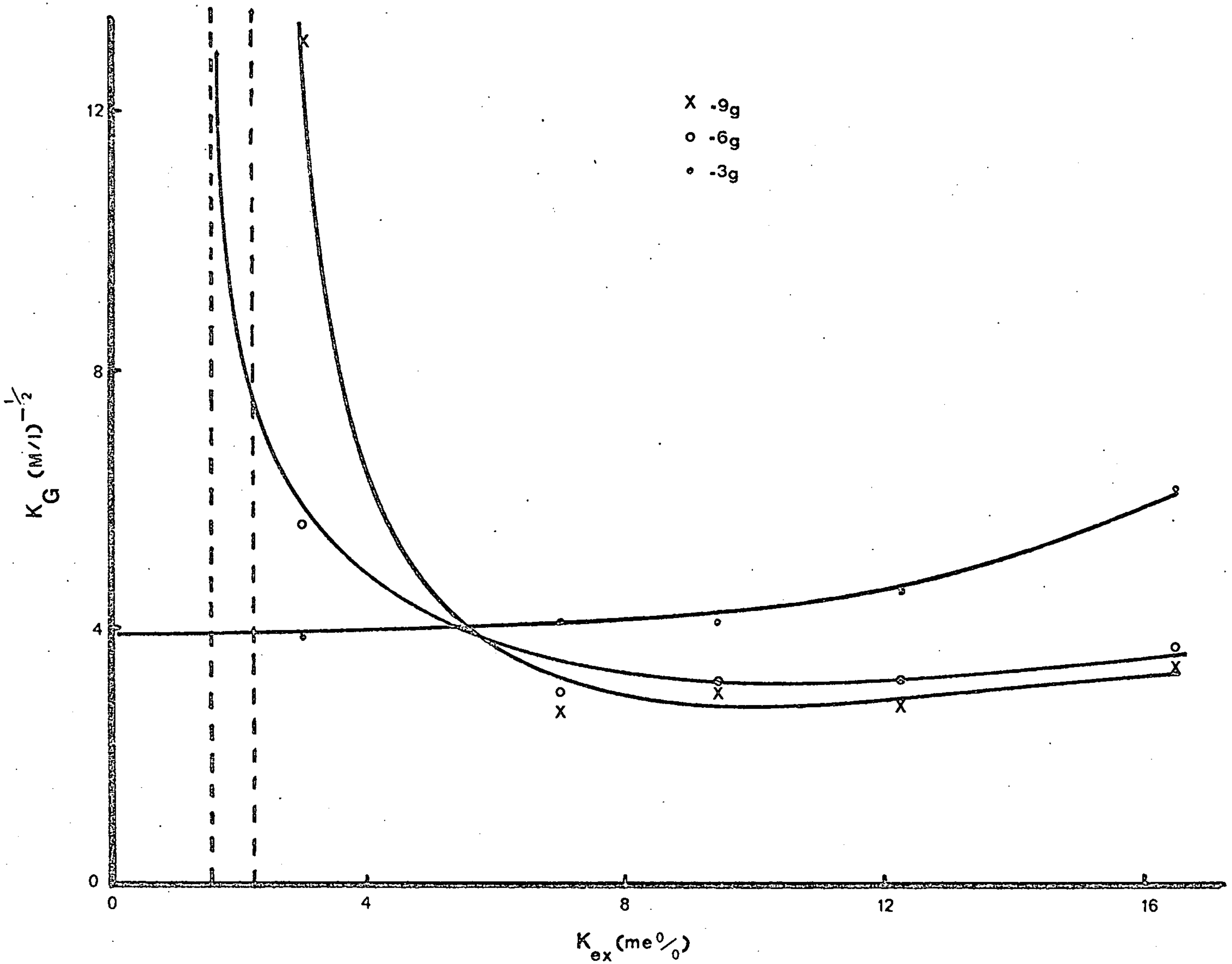

FIG. 91 Relationship between K_G and K_{ex} for different quantities of bentonite.

mixture E was nearer to EK^o and K_G was significantly higher (5.6 against a mean of 3.3 for the other mixtures) which is an indication of the start of an upward curve. For 0.9g clay the K_{ex} of mixture E is still nearer to EK^o and its K_G value is much higher (13.1) than the mean for the other mixtures (3.0) at this quantity.

The results for the relationships between indirect ER and AR^K for all three quantities of clay and at all initial K_{ex} levels are given in Table 55 and illustrated in Figures 92 to 106. The data again fitted the linear Gapon-like equation well, although not as good as in the case of the soils. The slopes of the lines decreased with increasing clay content. At the higher initial K_{ex} levels the intercepts remained fairly constant for the three quantities of clay, but at the lowest initial K_{ex} level (3.00me per 100g) the intercepts increased markedly with increasing quantity of clay. For each quantity of clay the intercept for 3.00me K_{ex} per 100g was also markedly higher than for the other initial K_{ex} levels. For 0.9g clay the intercept for mixture E, the K_{ex} of which is near to EK^o, was very similar to that for the line of ER versus AR_e^K (0.0404 against 0.042).

7.6 THE EFFECT OF HIGH POTASSIUM LEVELS ON THE GAPON RELATIONS OF BENTONITE

For 0.9g of clay the relationship between ER and AR_e^K consisted of two curved parts (Figure 107). For 2.7g of clay it consisted of a curved part for the four lower levels of K_{ex} and a linear part for the four higher levels. For both quantities of clay AR_e^K was higher relative to ER at the higher levels of K_{ex}, in other words K_G was lower at the higher levels.

The results for the relationships between indirect ER and AR^K for both quantities of clay and at all initial K_{ex} levels are given in Table 56 and Figures 108 to 123. The slopes of the lines were higher and the intercepts lower for 0.9g clay than for 2.7g clay. For 0.9g clay the slopes of the lines/tended to be lower at the higher than at the lower K_{ex} levels. The intercepts showed large variations, but showed

no/......................

TABLE 55 - Equations for lines relating indirect ER and AR^K at different initial K_{ex} levels for bentonite

Quantity of clay per 100 ml	Initial K_{ex} me %	Regression equation
0.3g	16.50	$ER=8.5939AR^K-0.1939$
	12.25	$ER=5.6894AR^K-0.0794$
	9.45	$ER=6.4650AR^K-0.0936$
	7.00	$ER=7.6087AR^K-0.0914$
	3.00	$ER=8.1862AR^K-0.0276$
0.6g	16.50	$ER=4.3693AR^K-0.0871$
	12.25	$ER=4.0621AR^K-0.0984$
	9.45	$ER=5.1368AR^K-0.1120$
	7.00	$ER=5.1065AR^K-0.0865$
	3.00	$ER=4.8212AR^K+0.0090$
0.9g	16.50	$ER=3.3718AR^K-0.0576$
	12.25	$ER=3.3720AR^K-0.0717$
	9.45	$ER=4.8612AR^K-0.1217$
	7.00	$ER=4.5964AR^K-0.0911$
	3.00	$ER=2.9734AR^K+0.0404$

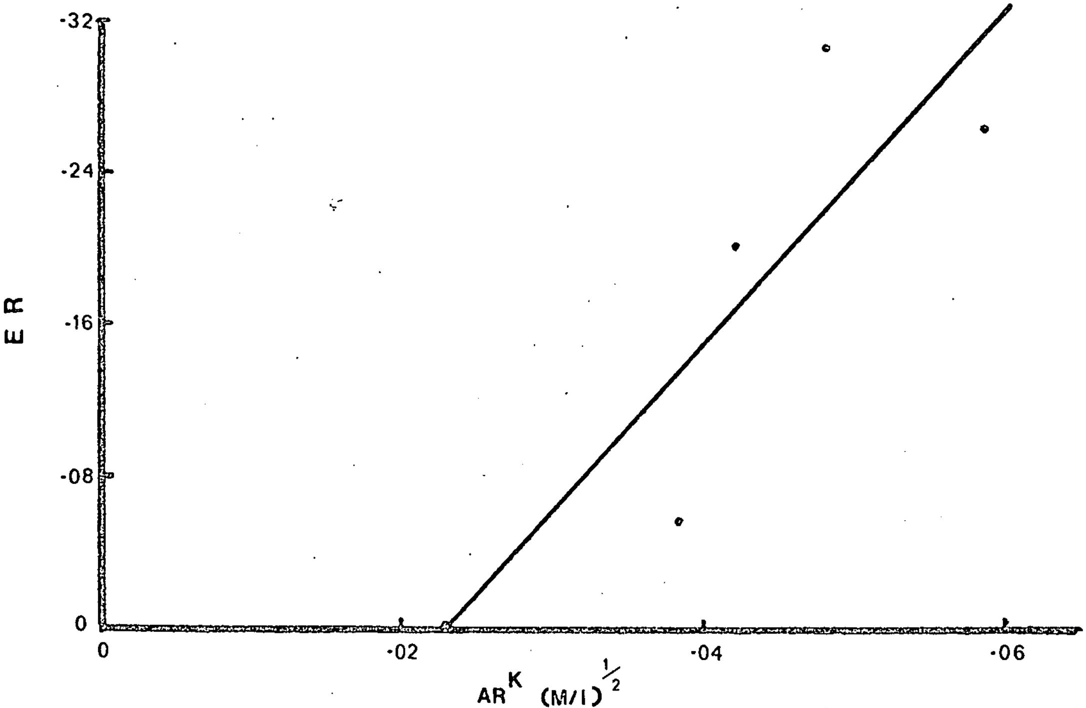

FIG. 92 Relationship between indirect ER and AR^K at an initial K_{ex} level of 16.5 me % for bentonite (.3g).

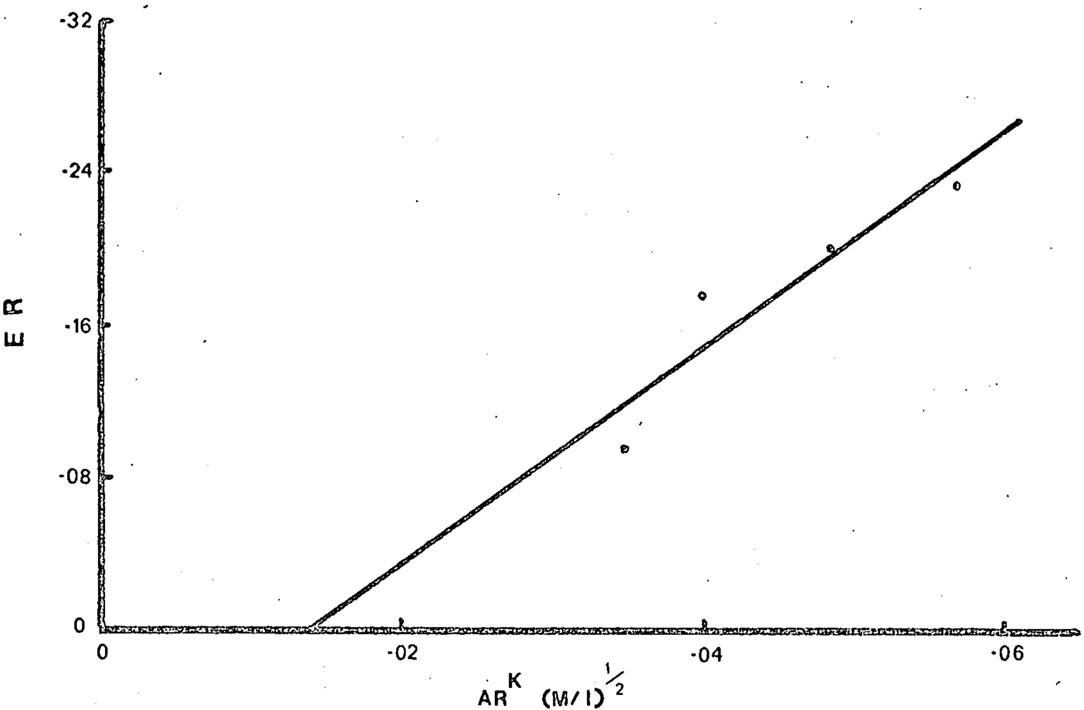

FIG. 93 Relationship between indirect ER and AR^K at an initial K_{ex} level of 12.25 me % for bentonite (.3g).

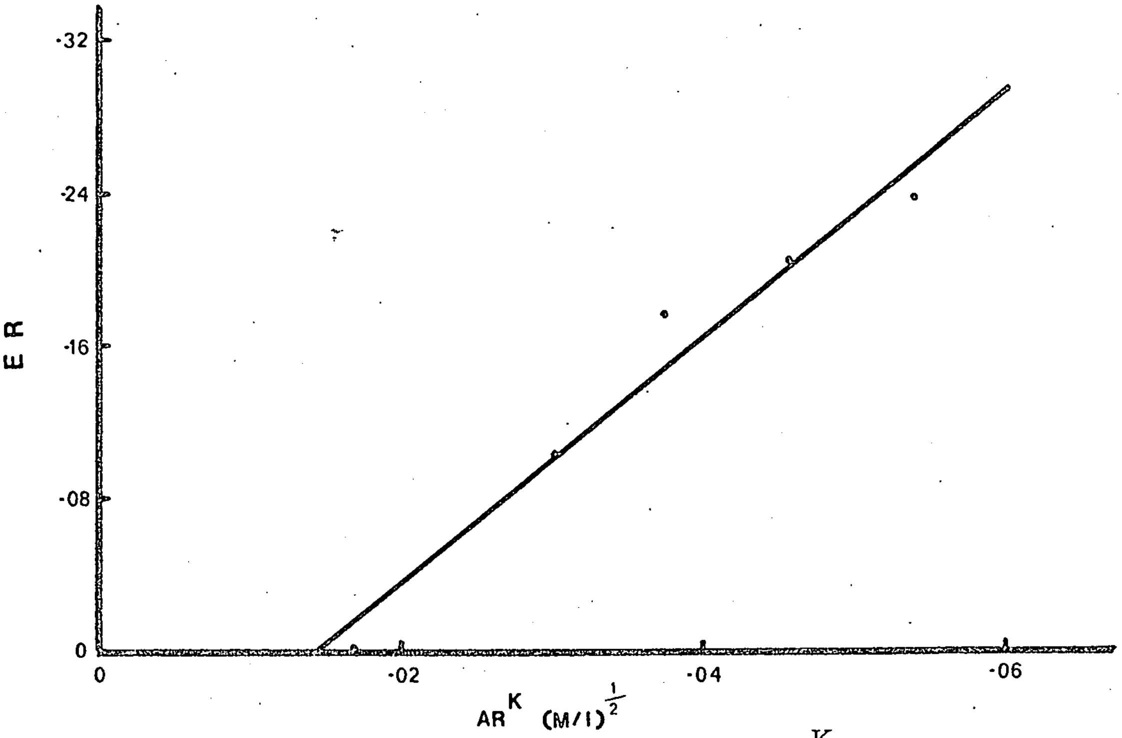

FIG. 94 Relationship between indirect ER and AR^K at an initial K_{ex} level of 9.45 me % for bentonite (.3g).

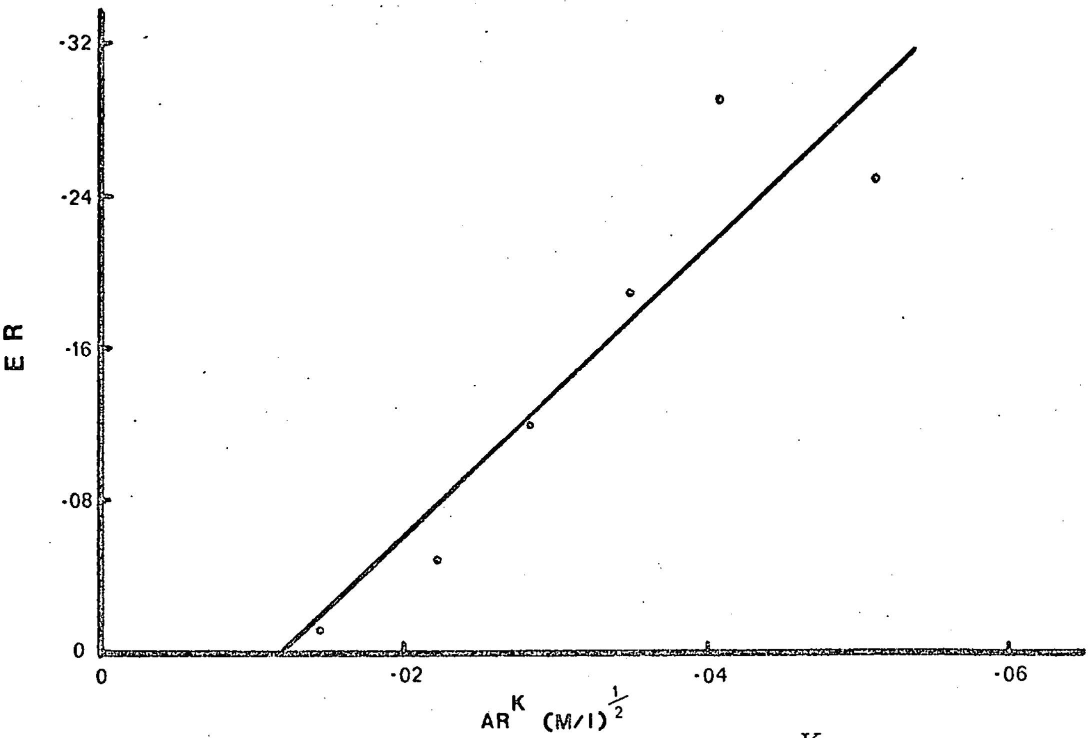

FIG. 95 Relationship between indirect ER and AR^K at an initial K_{ex} level of 7.00 me % for bentonite (.3g).

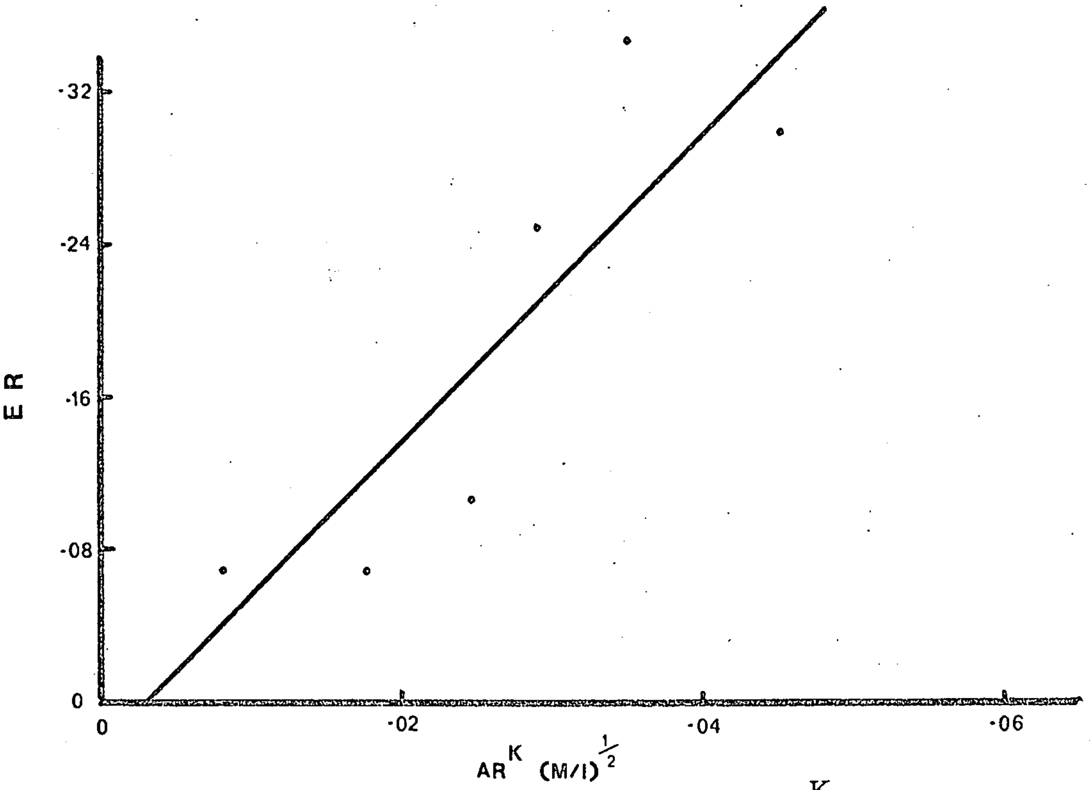

FIG. 96 Relationship between indirect ER and AR^K at an initial K_{ex} level of 3.00 me % for bentonite (.3g).

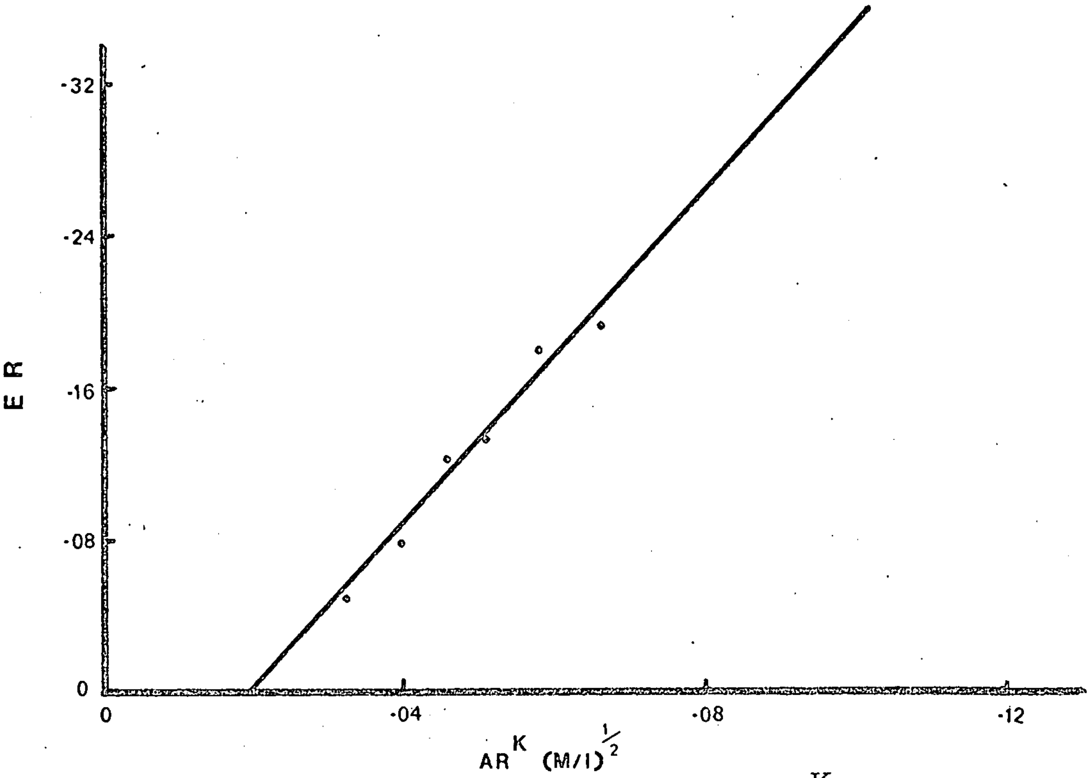

FIG. 97 Relationship between indirect ER and AR^K at an initial K_{ex} level of 16.5 me % for bentonite (.6g).

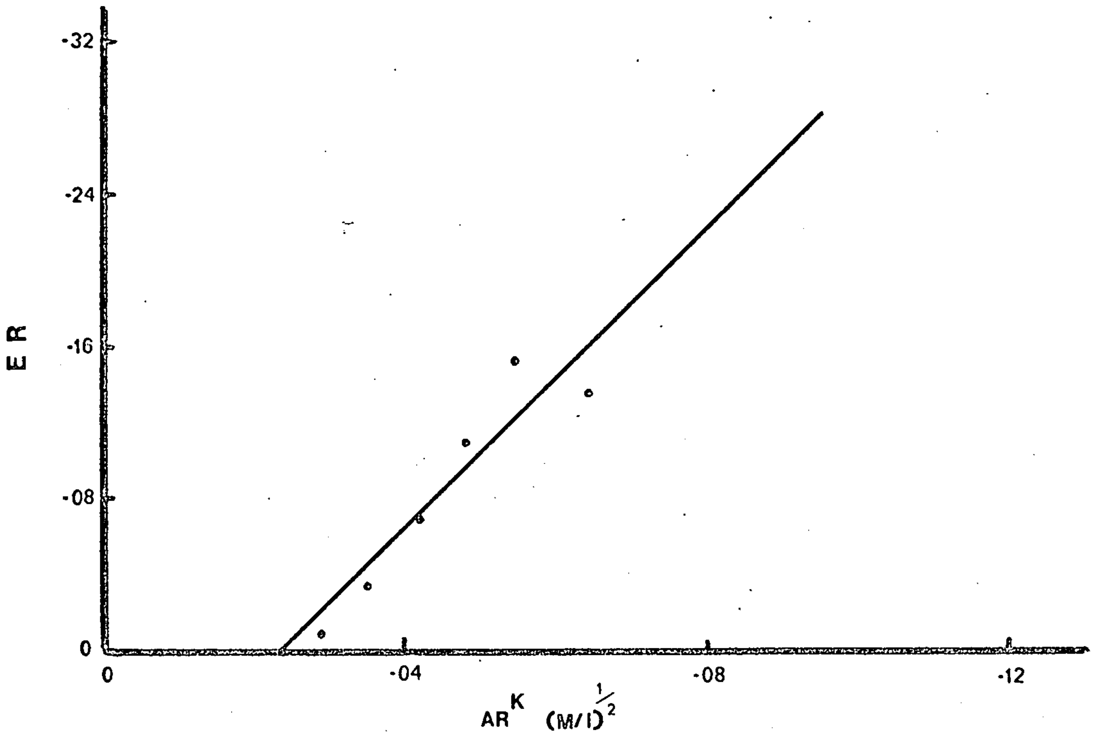

FIG. 98 Relationship between indirect ER and AR^K at an initial K_{ex} level of 12.25 me % for bentonite (.6g).

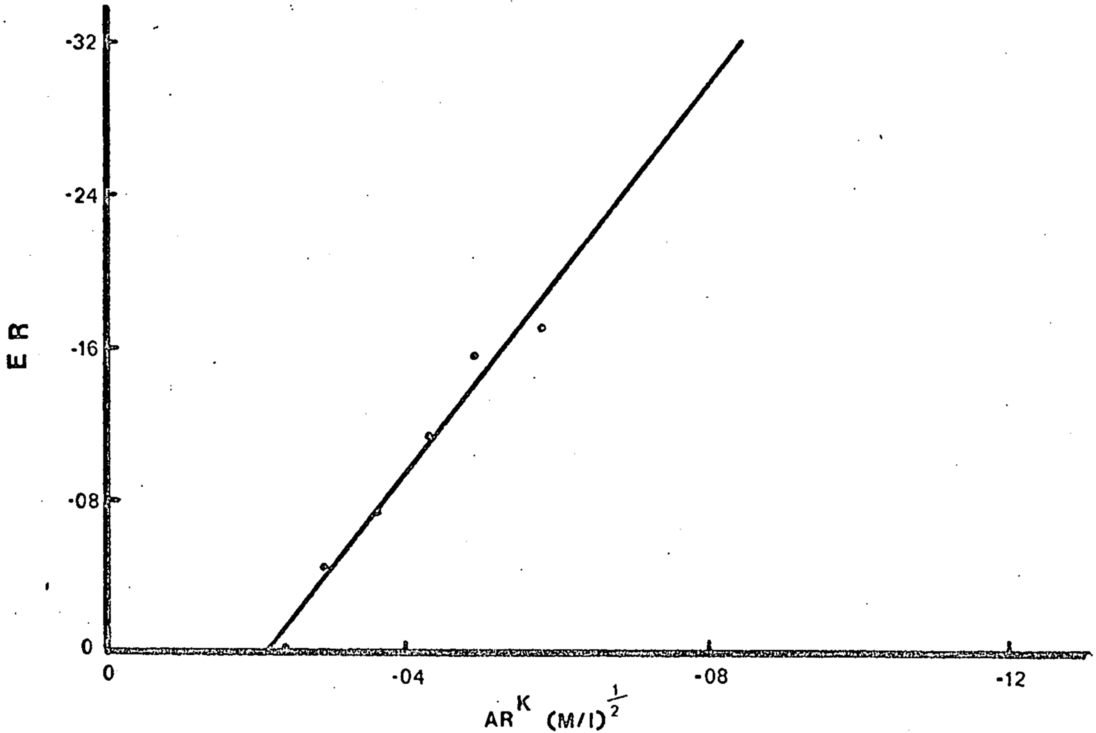

FIG. 99 Relationship between indirect ER and AR^K at an initial K_{ex} level of 9.45 me % for bentonite (.6g).

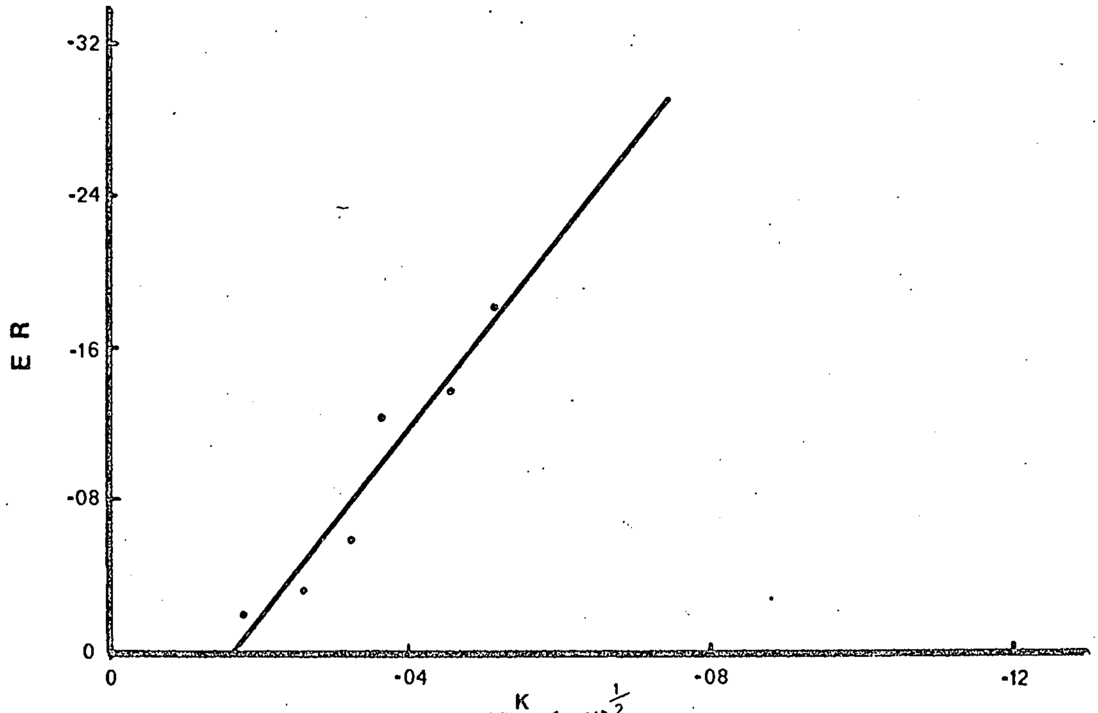

FIG. 100 Relationship between indirect ER and AR^K at an initial K_{ex} level for 7.00 me % for bentonite (.6g).

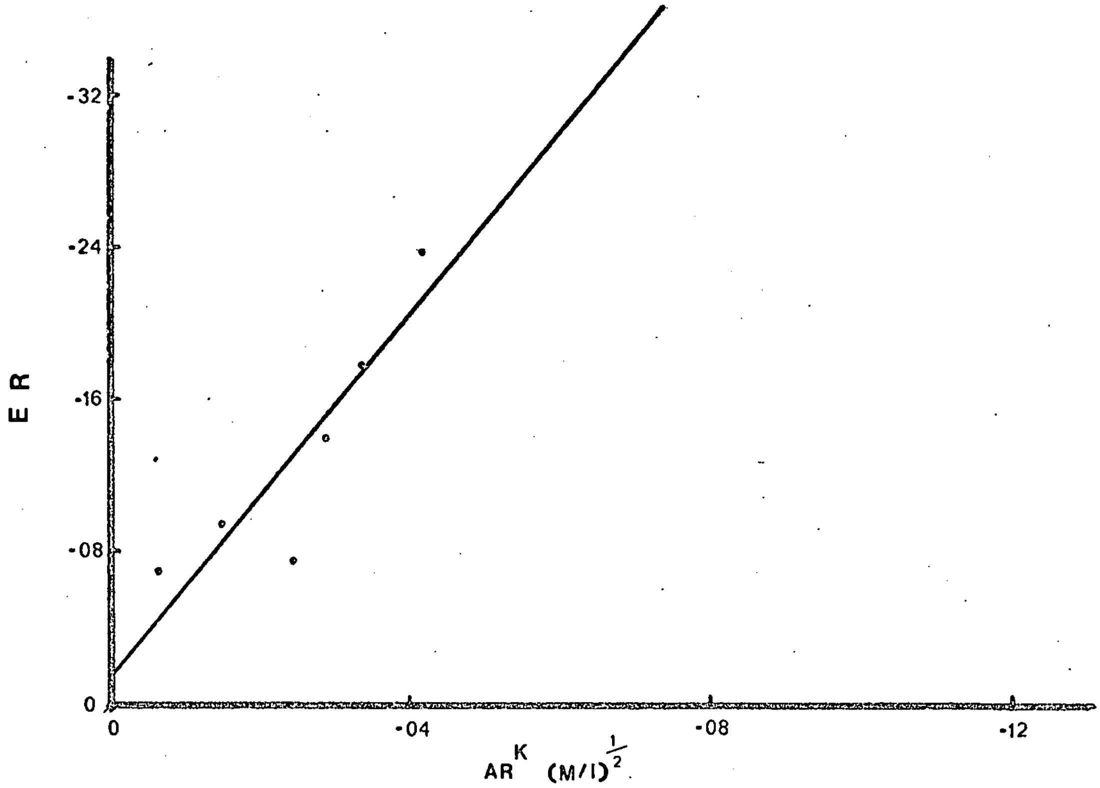

FIG. 101 Relationship between indirect ER and AR^K at an initial K_{ex} level of 3.00 me % for bentonite (.6g).

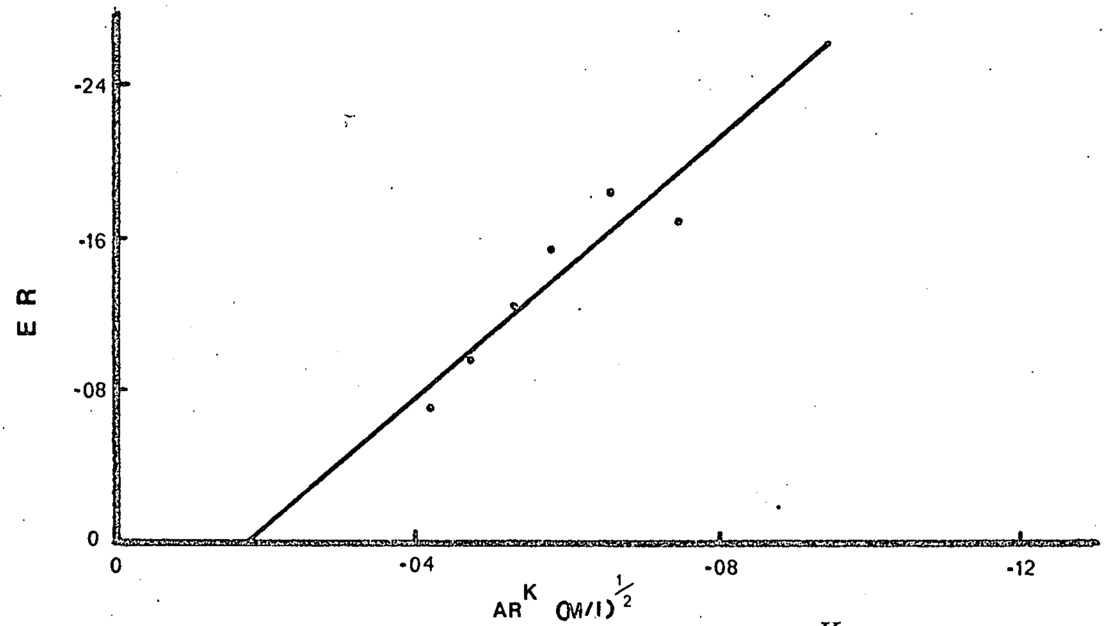

FIG. 102 Relationship between indirect ER and AR^K at an initial K_{ex} level of 16.5 me % for bentonite (.9g).

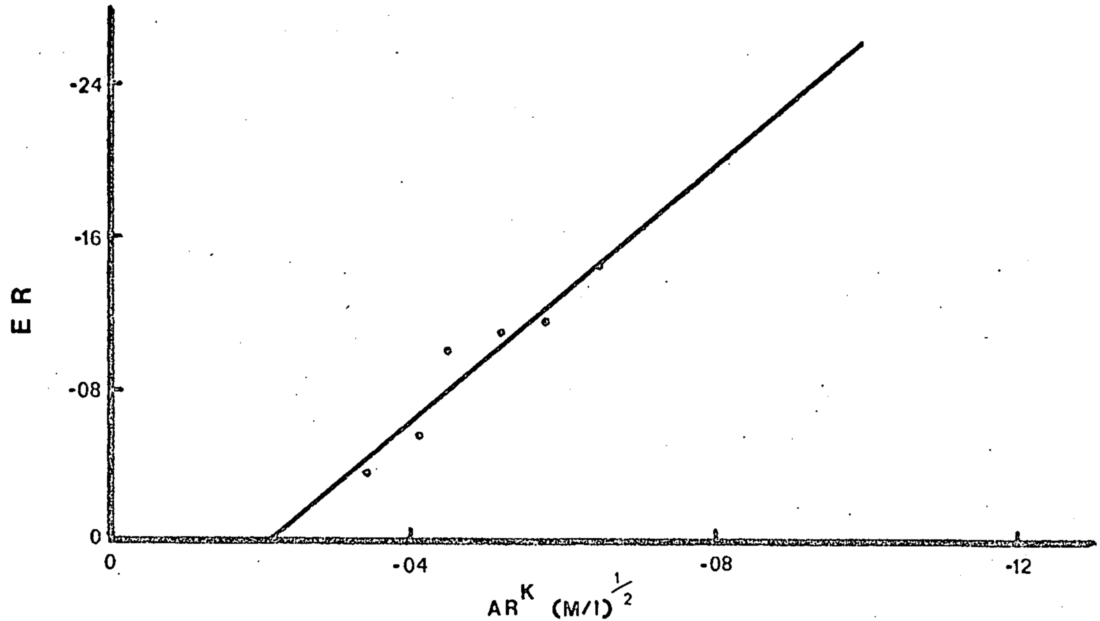

FIG. 103 Relationship between indirect ER and AR^K at an initial K_{ex} level of 12.25 me % for bentonite (.9g).

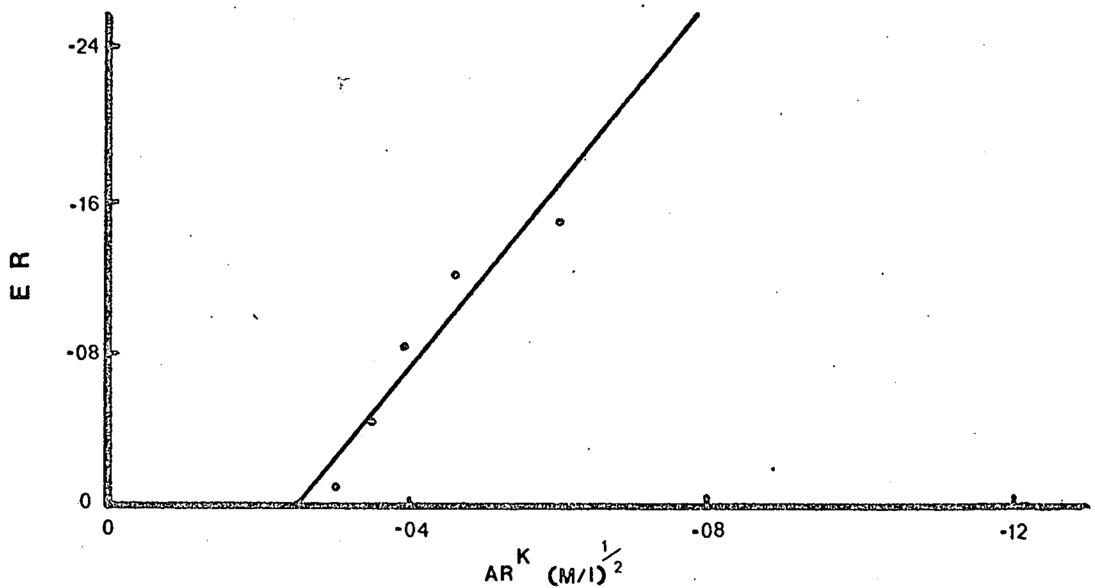

FIG. 104 Relationship between indirect ER and AR^K at an initial K_{ex} level of 9.45 me % for bentonite (.9g).

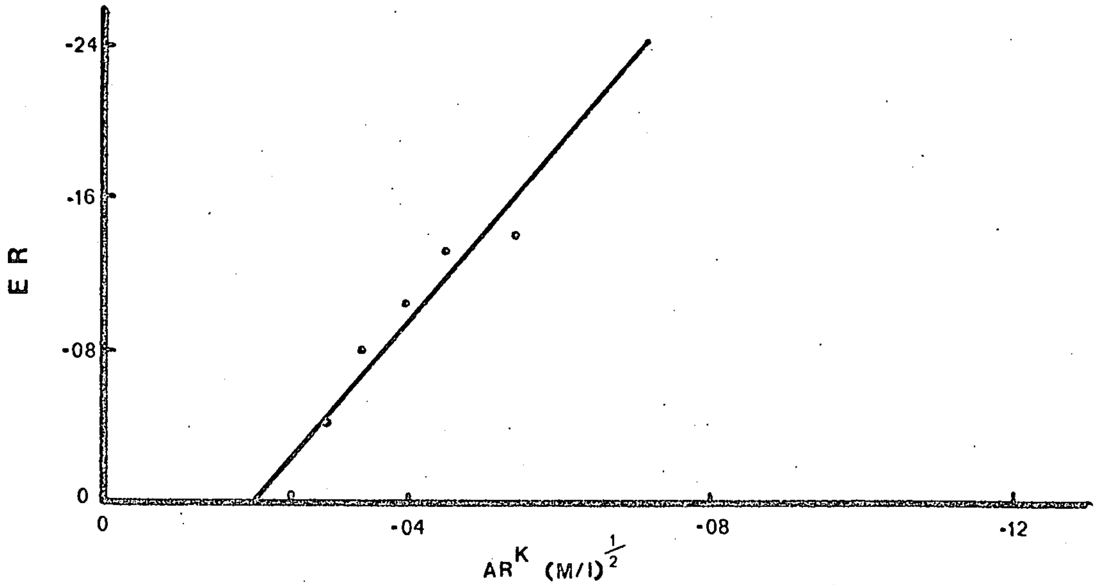

FIG. 105 Relationship between indirect ER and AR^K at an initial K_{ex} level of 7.00 me % for bentonite (.9g).

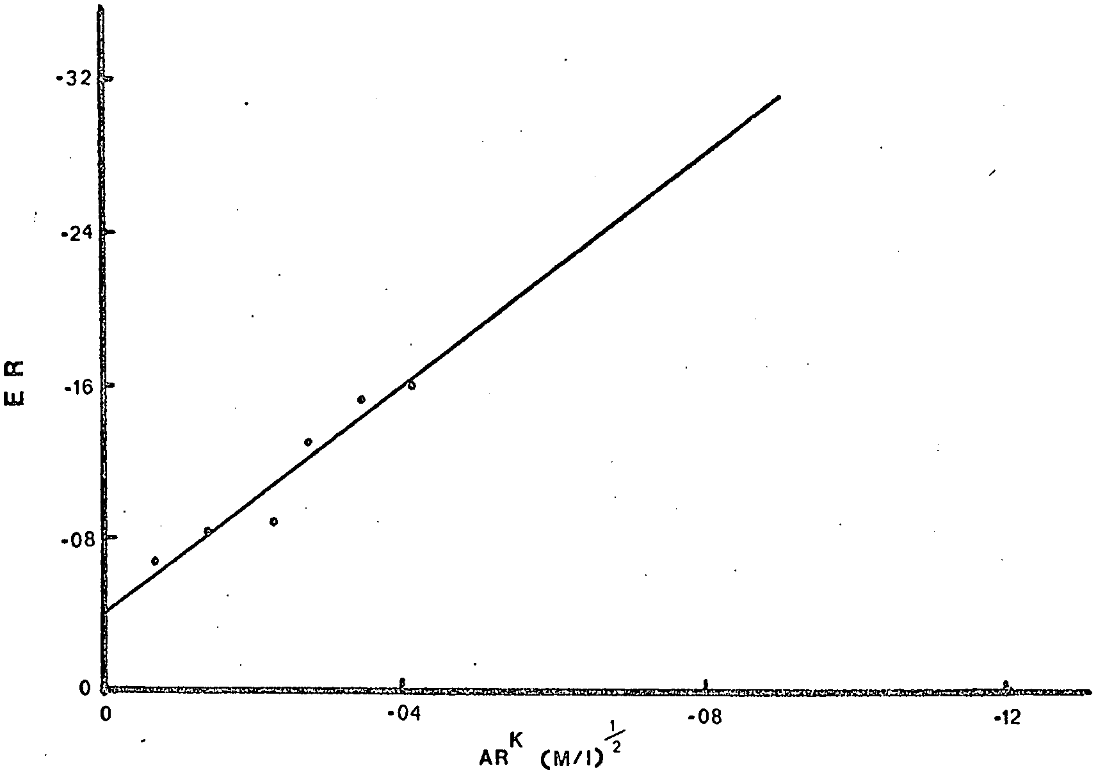

FIG. 106 Relationship between indirect ER and AR^K at an initial K_{ex} level of 3.00 me % for bentonite (.9g).

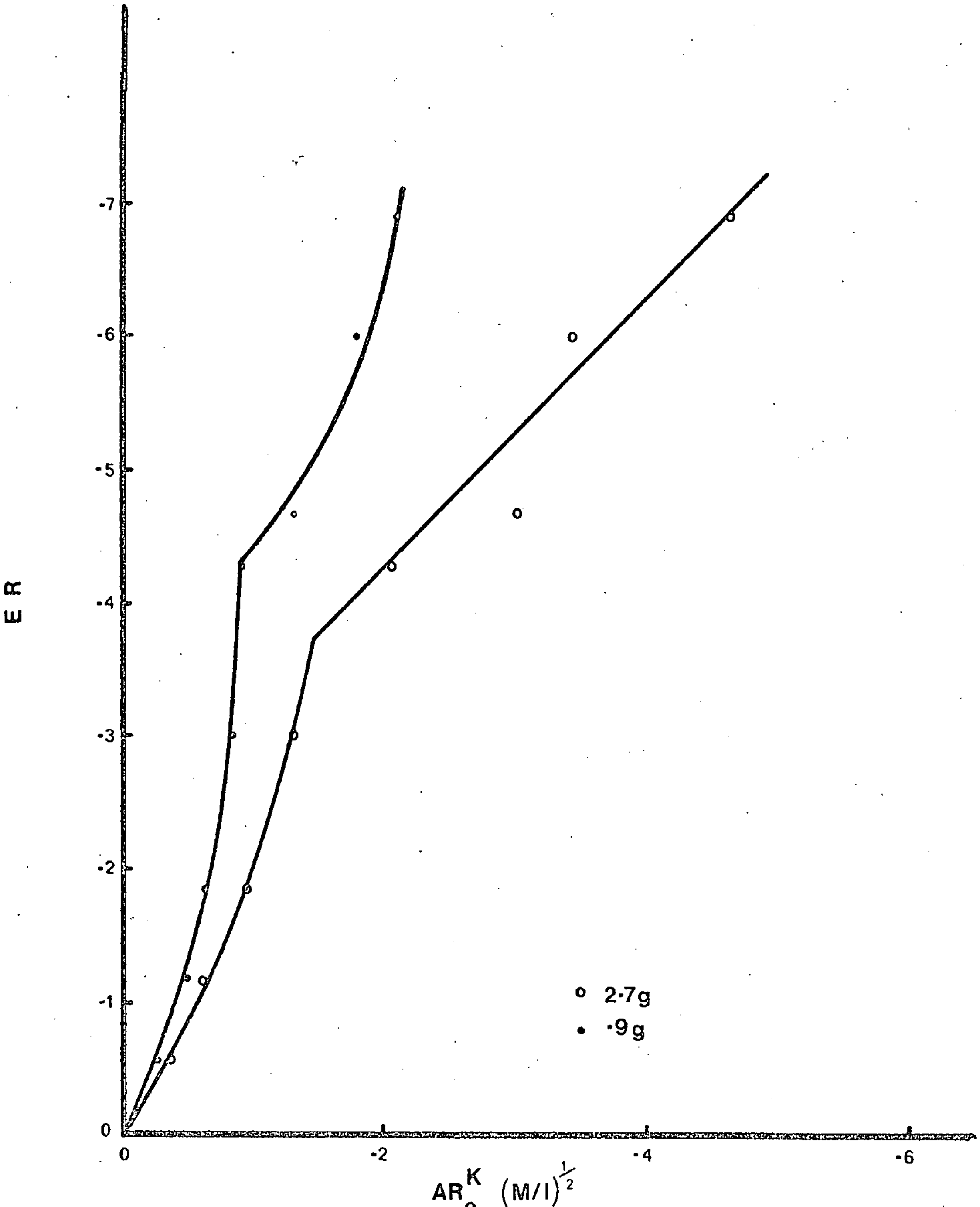

FIG. 107 Relationship between ER and AR_e^K for different quantities of bentonite per 100 ml shaking solution, including high potassium levels.

TABLE 56 - Equations for lines relating indirect ER and AR^K at different initial K_{ex} levels for bentonite, including high K_{ex} levels

Quantity of clay per 100 ml	Initial K_{ex} me %	Regression equation
0.9g	26.50	$ER=2.6167AR^K-0.0540$
	24.25	$ER=2.5702AR^K-0.0084$
	20.63	$ER=3.4428AR^K-0.0555$
	19.38	$ER=5.6410AR^K-0.1373$
	15.00	$ER=4.0191AR^K-0.0670$
	10.19	$ER=4.4528AR^K-0.1020$
	6.91	$ER=3.1557AR^K-0.0401$
	3.56	$ER=4.2540AR^K-0.0532$
2.7g	26.50	$ER=0.8633AR^K+0.1438$
	24.25	$ER=1.1559AR^K+0.0967$
	20.63	$ER=0.7974AR^K+0.1207$
	19.38	$ER=1.4558AR^K+0.0781$
	15.00	$ER=2.2081AR^K-0.0112$
	10.19	$ER=2.0738AR^K-0.0237$
	6.91	$ER=2.3798AR^K-0.0328$
	3.56	$ER=2.0317AR^K-0.0114$

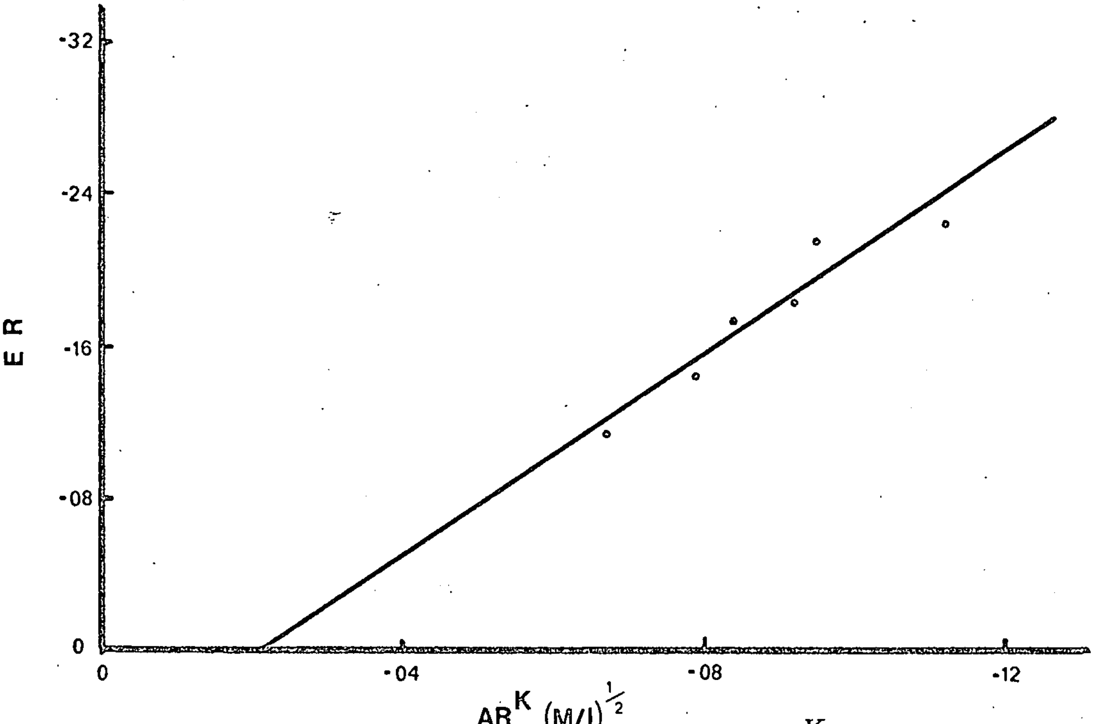

FIG. 108 Relationship between indirect ER and AR^K at an initial K_{ex} level of 26.5 me % for bentonite (.9g).

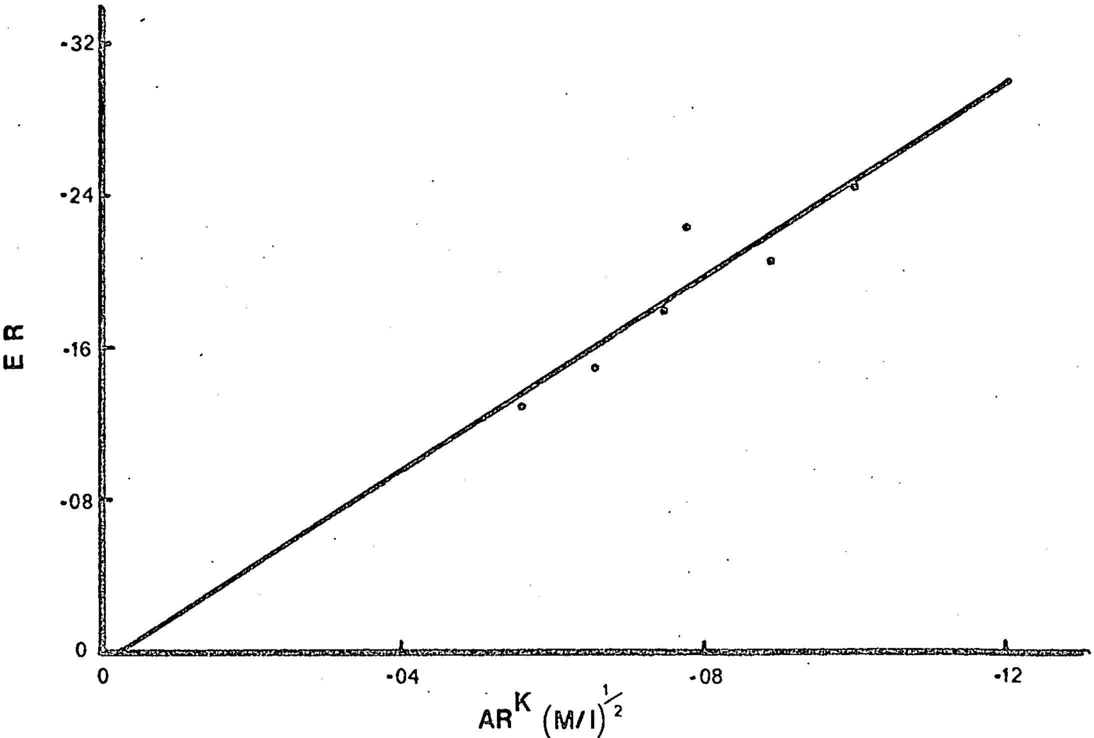

FIG. 109 Relationship between indirect ER and AR^K at an initial K_{ex} level of 24.25 me % for bentonite (.9g).

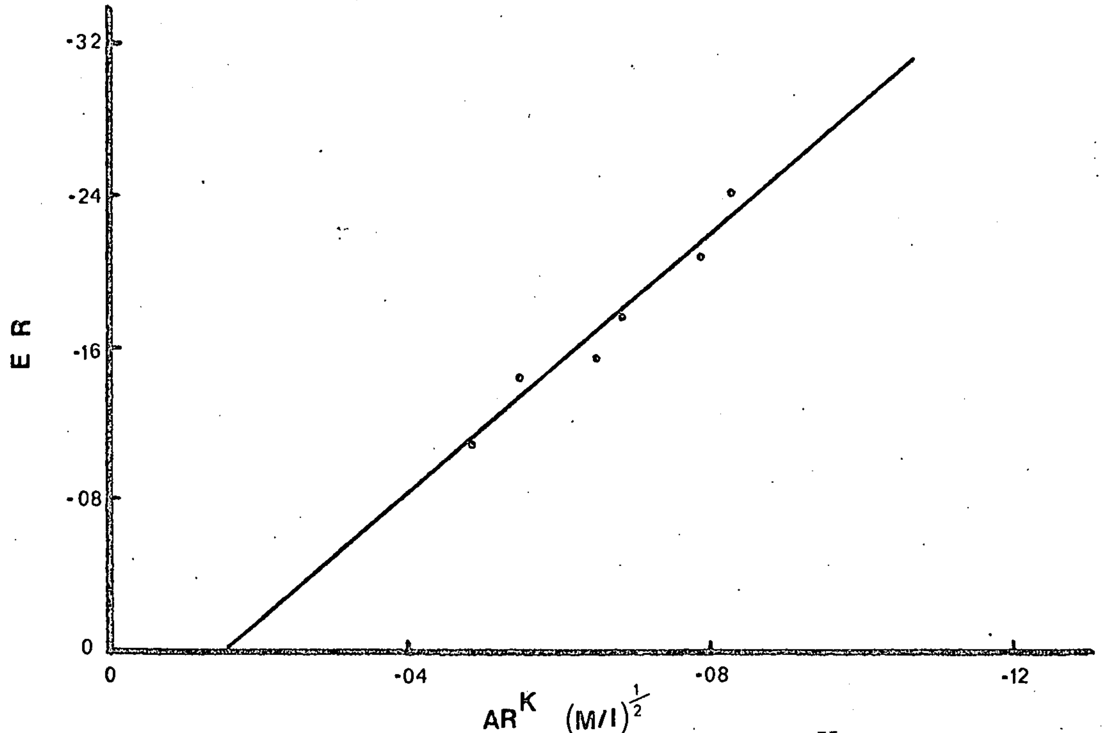

FIG. 110 Relationship between indirect ER and AR^K at an initial K$_{ex}$ level of 20.63 me K for bentonite (.9g).

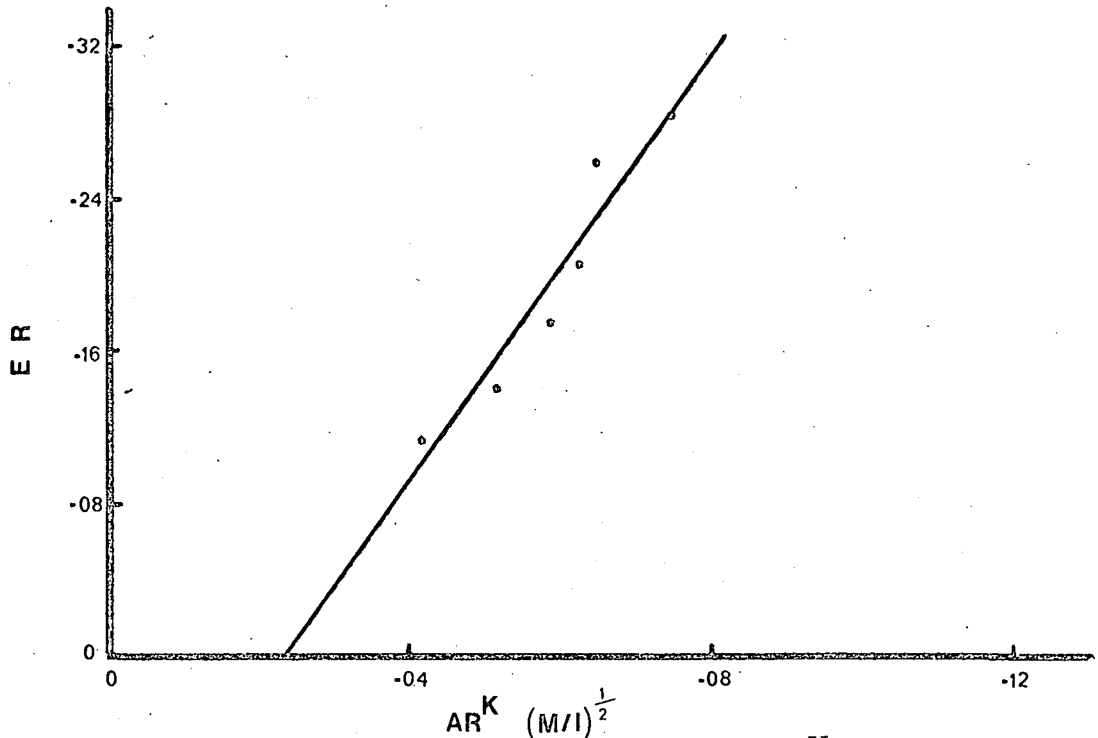

FIG. 111 Relationship between indirect ER and AR^K at an initial K$_{ex}$ level of 19.38 me % for bentonite (.9g).

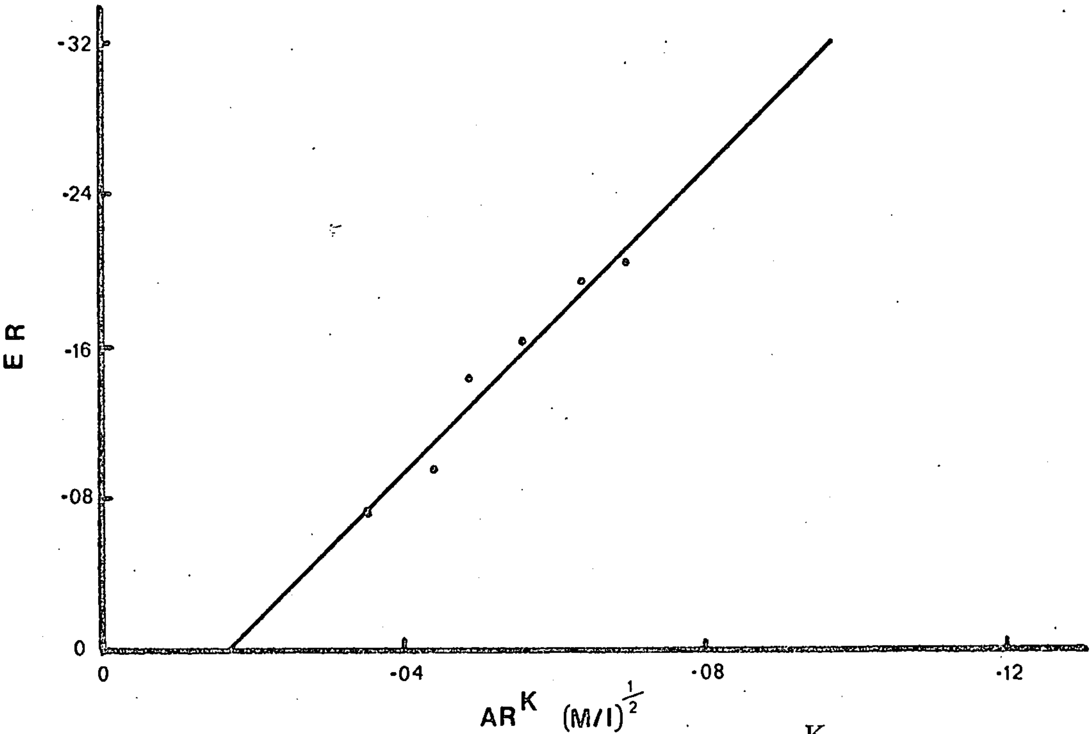

FIG. 112 Relationship between indirect ER and AR^K at an initial K_{ex} level of 15.00 me % for bentonite (.9g).

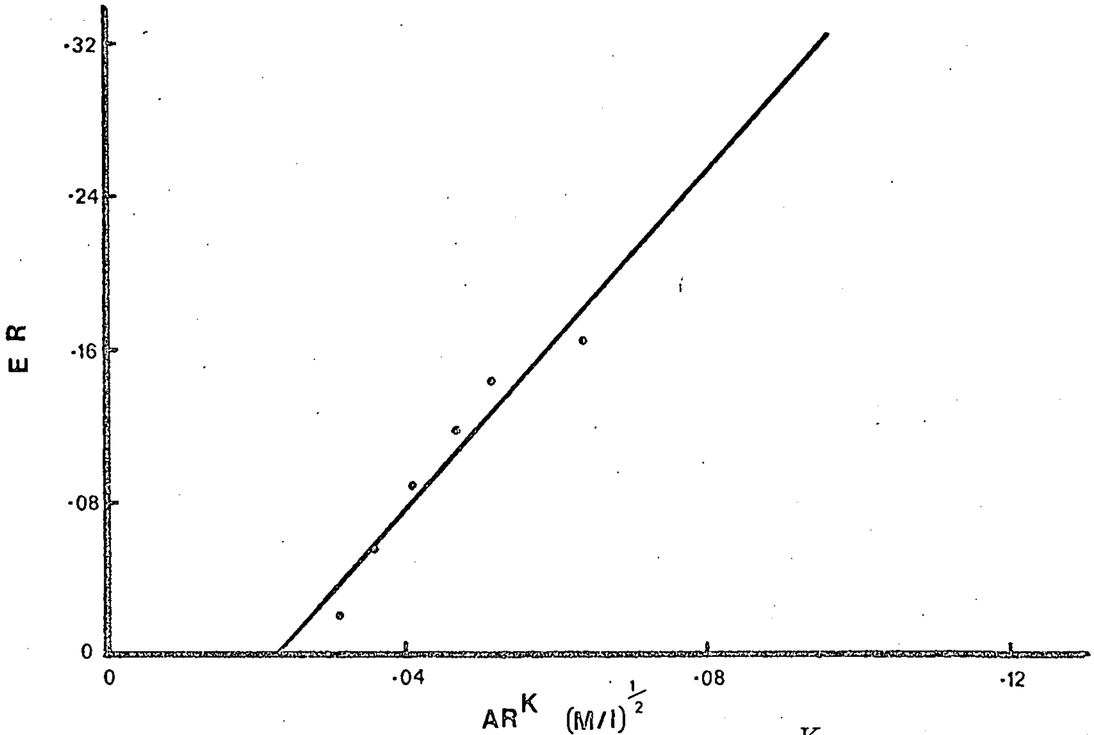

FIG. 113 Relationship between indirect ER and AR^K at an initial K_{ex} level of 10.19 me % for bentonite (.9g).

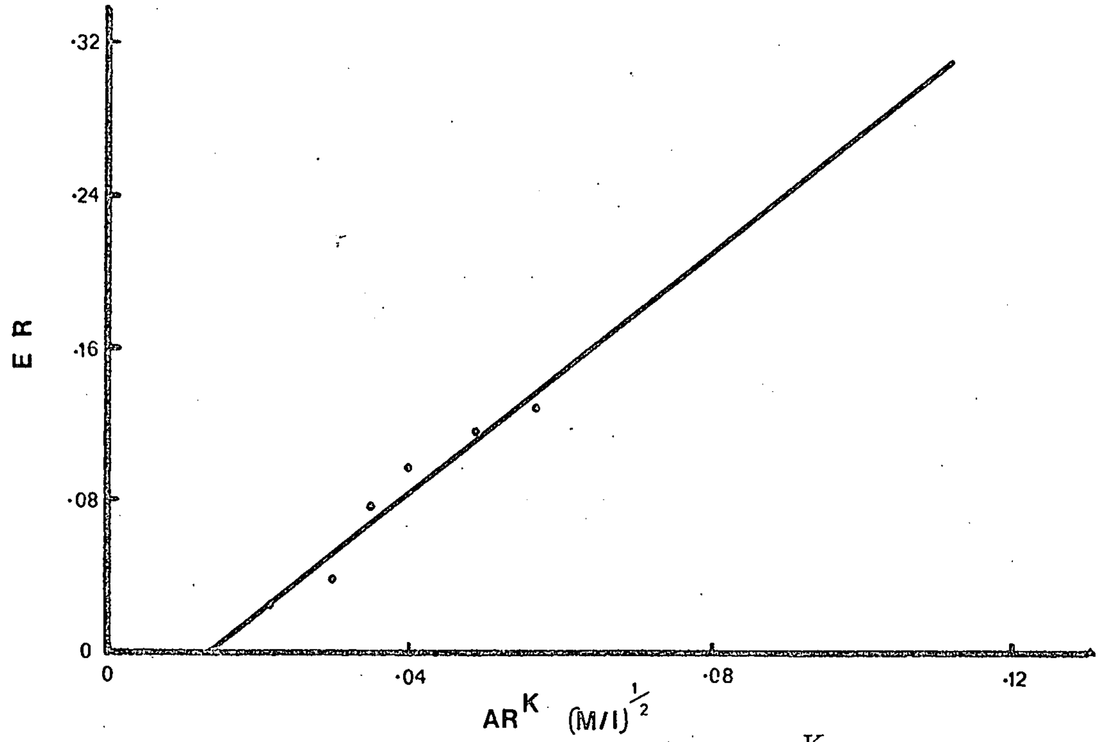

FIG. 114 Relationship between indirect ER and AR^K at an initial K_{ex} level of 6.91 me % for bentonite (.9g).

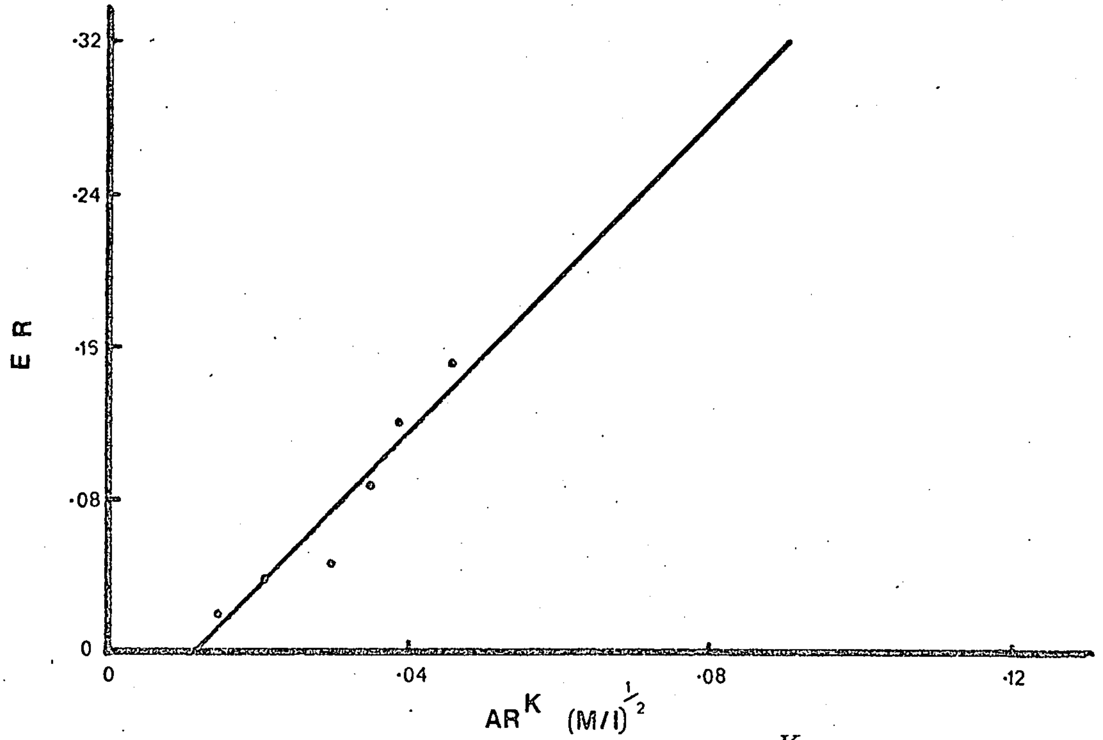

FIG. 115 Relationship between indirect ER and AR^K at an initial K_{ex} level of 3.56 me % for bentonite (.9g).

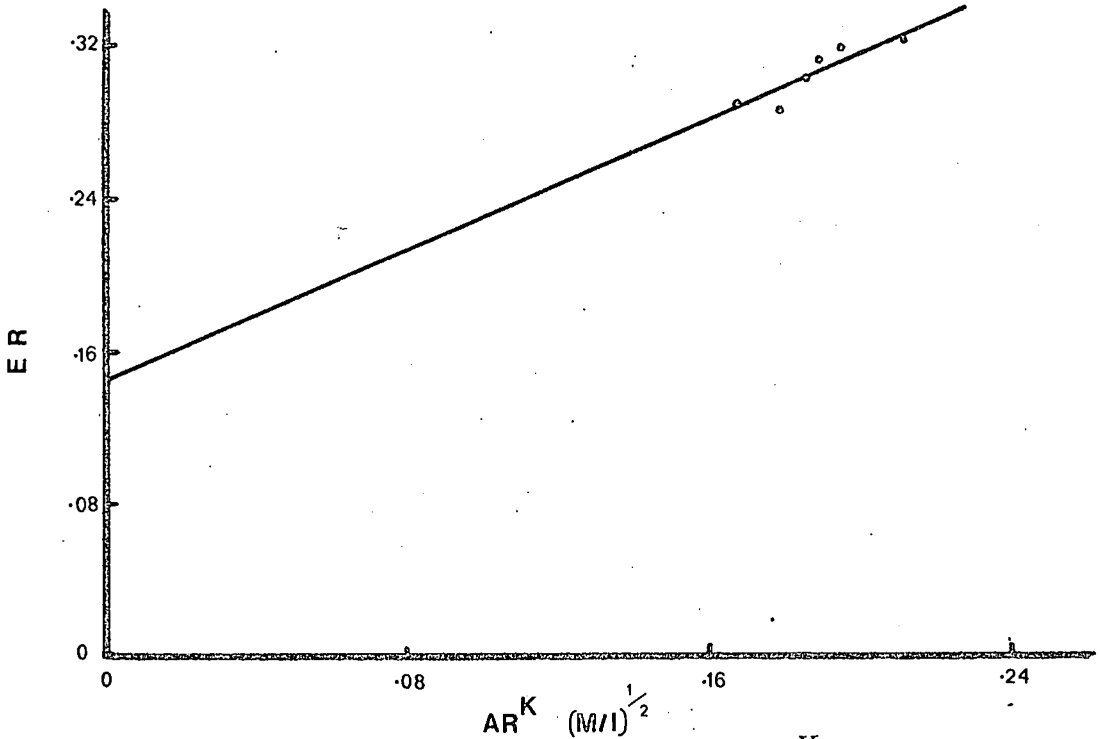

FIG. 116 Relationship between indirect ER and AR^K at an initial K_{ex} level of 26.5 me % for bentonite (2.7g).

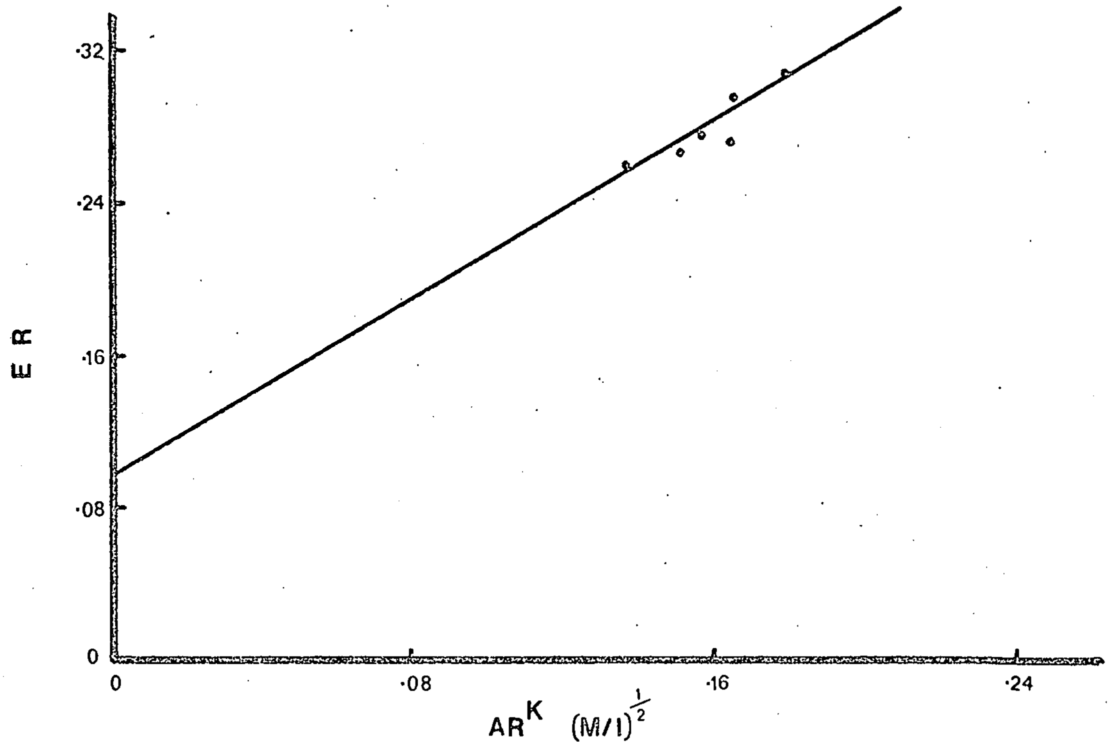

FIG. 117 Relationship between indirect ER and AR^K at an initial K_{ex} level of 24.25 me % for bentonite (2.7g).

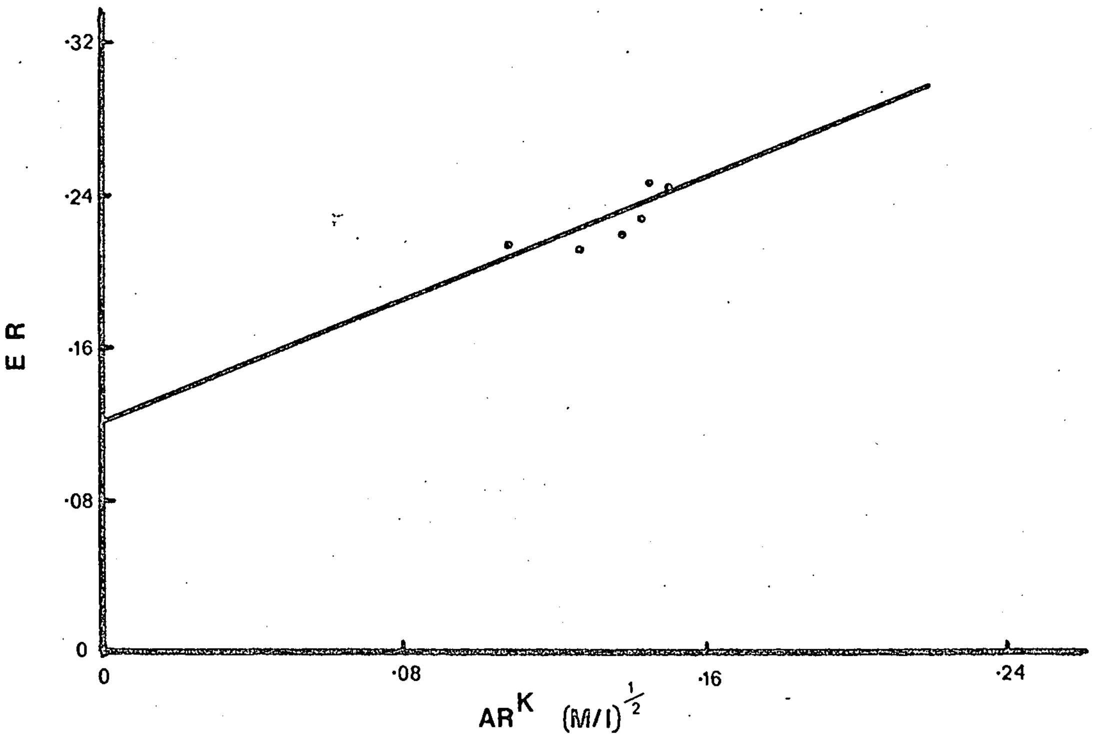

FIG. 118 Relationship between indirect ER and AR^K at an initial K_{ex} level of 20.63 me % for bentonite (2.7g).

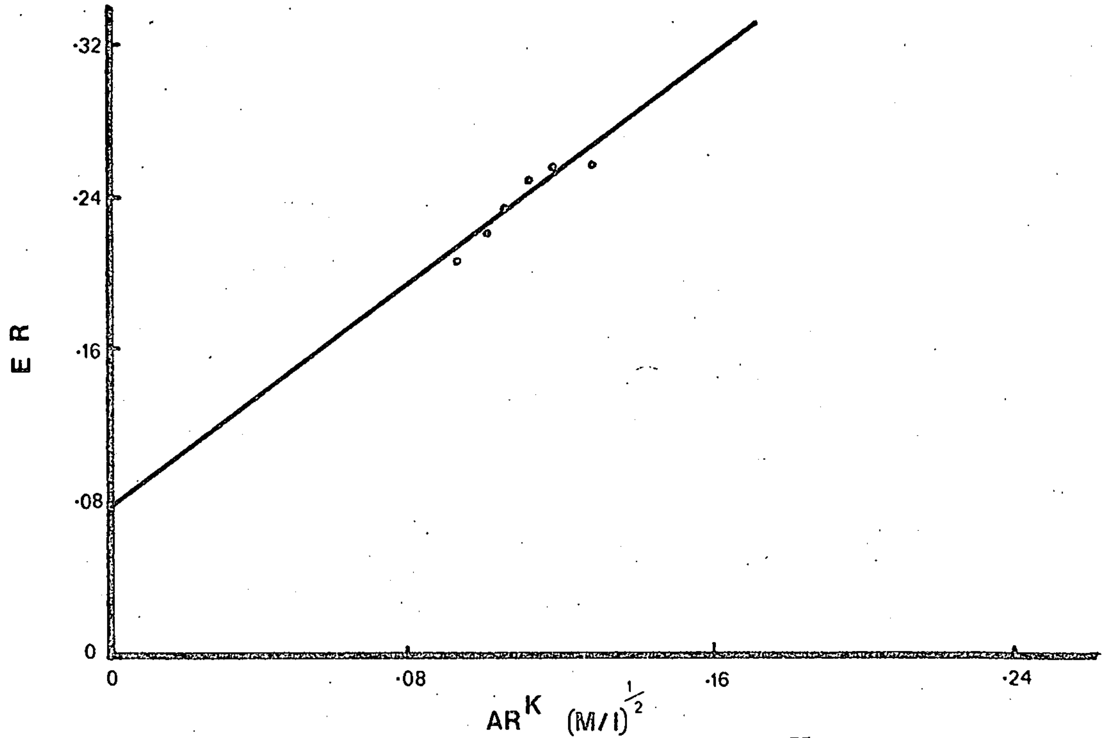

FIG. 119 Relationship between indirect ER and AR^K at an initial K_{ex} level of 19.38 me % for bentonite (2.7g).

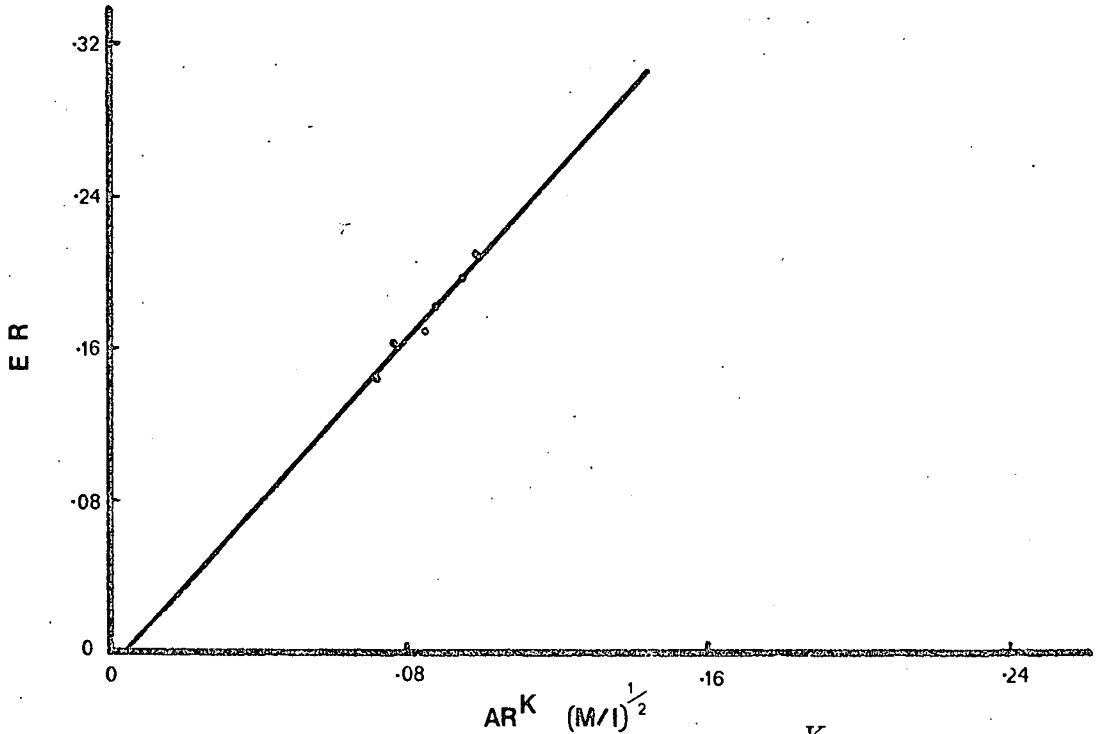

FIG. 120 Relationship between indirect ER and AR^K at an initial K_{ex} level of 15.00 me % for bentonite (2.7g).

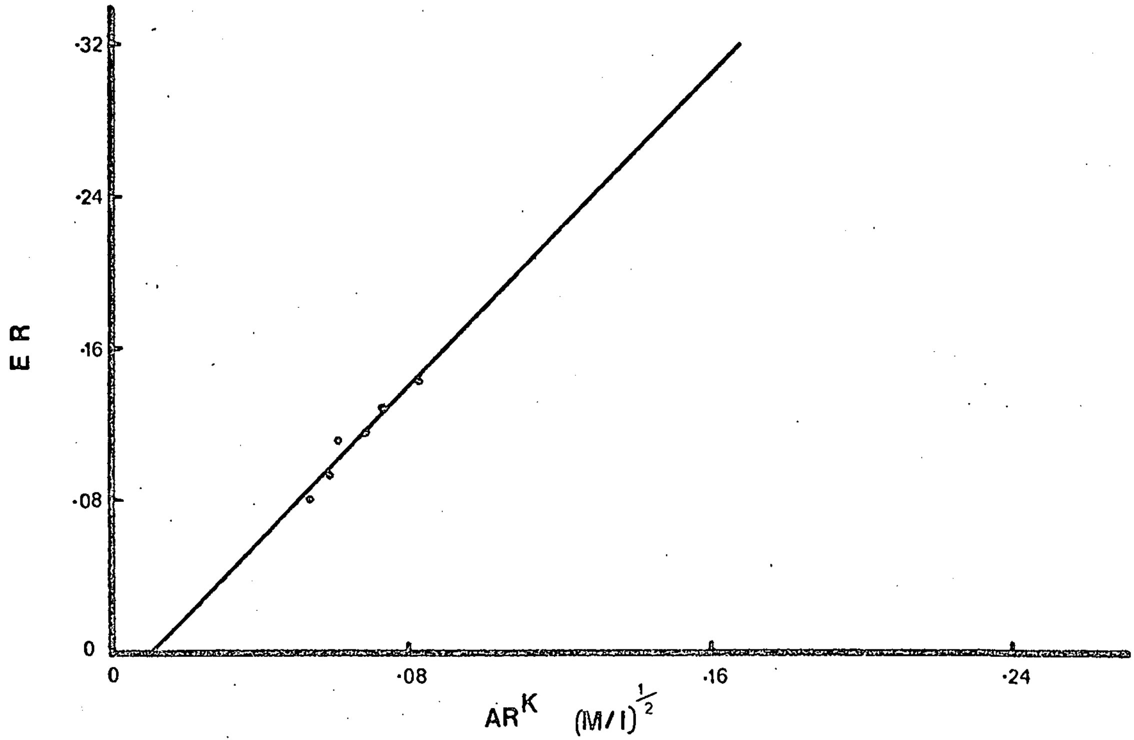

FIG. 121 Relationship between indirect ER and AR^K at an initial K_{ex} level of 10.19 me % for bentonite (2.7g).

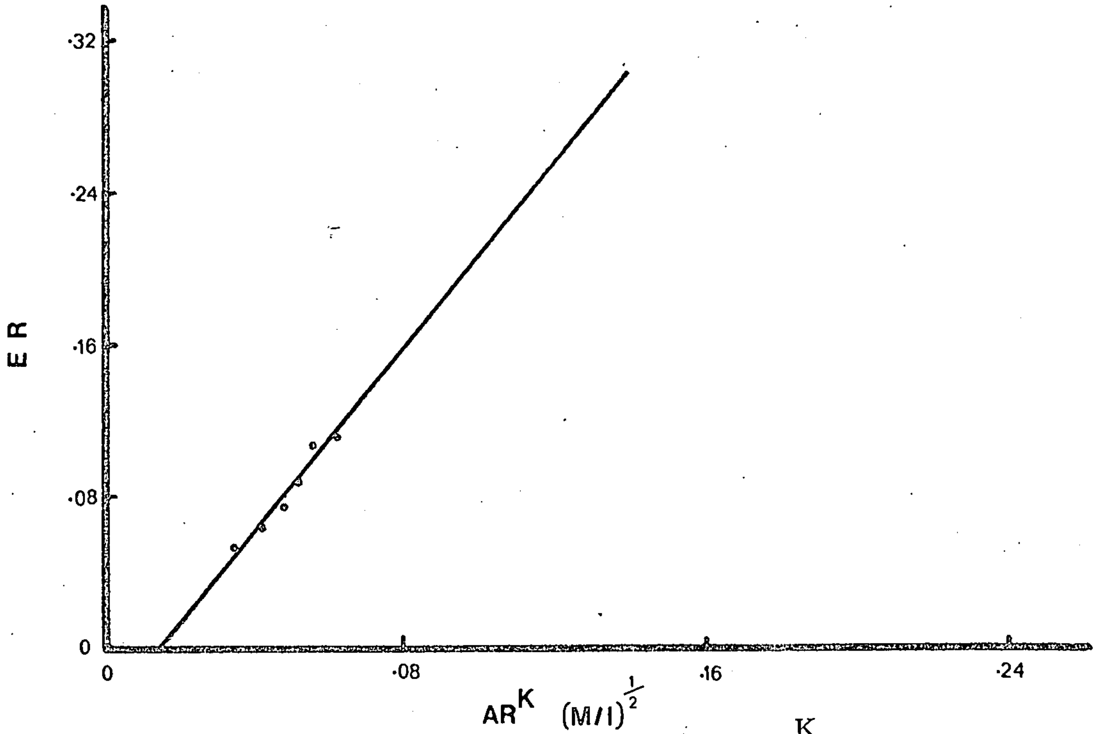

FIG. 122 Relationship between indirect ER and AR^K at an initial K_{ex} level of 6.91 me % for bentonite (2.7g).

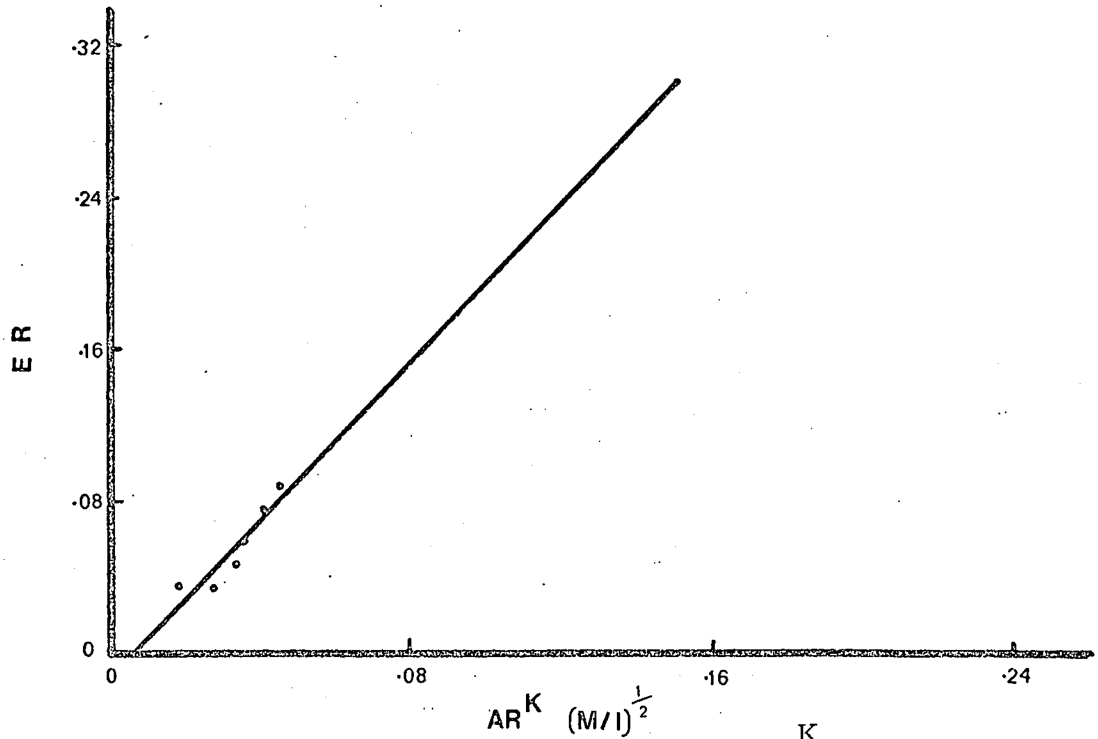

FIG. 123 Relationship between indirect ER and AR^K at an initial K_{ex} level of 3.56 me % for bentonite (2.7g).

TABLE 57 - Exchange ratios and K_G values for bentonite, including high potassium levels

Quantity of clay per 100ml	ER	K_G $(M/l)^{-\frac{1}{2}}$
0.9g	0.6919	3.3
	0.5980	3.3
	0.4671	3.5
	0.4267	4.7
	0.3012	3.5
	0.1866	3.0
	0.1194	2.4
	0.0584	2.2
2.7g	0.6919	1.5
	0.5980	1.7
	0.4671	1.5
	0.4267	2.1
	0.3012	2.3
	0.1866	1.9
	0.1194	1.9
	0.0584	1.7

no general trend of decrease or increase with decreasing initial K_{ex} level. For 2.7g clay the slopes of the lines were much lower at the four higher K_{ex} levels than at the four lower levels. On the other hand the intercepts of the lines for the four higher levels were much higher than those for the four lower levels.

The normal K_G values, obtained by dividing AR_e^K into ER, are given in Table 57. As in the previous experiment K_G was again lower for the larger quantity of clay used. For both quantities of clay there was no sharp increase in K_G at very low K_{ex} levels. This is not unexpected as EK^o was zero.

It is of interest to note that K_G tended to increase at the K_{ex} levels where the changes from one line for K_{ex} versus AR_e^K to the other line occurred. This was especially true for 0.9g clay (Table 57). This increase can be ascribed to the fact that, if there was no change in the graph, the K_G values would increase as K_{ex} decreased and become infinite at the EK^o values which would be obtained by extrapolating the lines relating K_{ex} and AR_e^K for the four higher levels of K_{ex}.

CHAPTER 8

GENERAL DISCUSSION

Before a fruitful critical analysis of a series of experiments can be made, all the experimental data must be known and sorted out. Only after this picture is filled in an overall impression can be obtained of the ways in which all the results fit in with each other and of the gaps which still remain unfilled. Then only an evaluation can be made of whether the results have contributed by filling in any gap in the overall picture of the subject as constructed by previous research. Should it fail in this requirement, it must be considered of no significance and that no contribution has been made.

In the foregoing chapters the results of the various experiments of the present study were merely given as actual facts which were found in the laboratory. Although experimental techniques are open to criticism the experimental data were presented here as found. In some instances remarks were made about possible practical and/or theoretical implications of certain results.

A general discussion, in which certain related data are grouped together and which provides for some speculation on certain of the trends obtained, is, however, needed in an attempt to fit the pieces together in a logical pattern.

In all the experiments with the soils and with the clays the patterns of the results indicated that the experimental techniques which were followed, were satisfactory. The Q/I determinations were essentially the same as carried out by Beckett (1964b). The main deviation, with the exception of the first experiment, was that the smaller quantities of soil and lowest level of potassium, which normally give the curved part of the Q/I graph, were omitted. By doing this more points could be obtained on the linear part of the graph without increasing the number of equilibrating solutions. No problems were expected and found in carrying out the procedure since it had been studied intensively by Beckett (1964a, b), Le Roux (1966) and others.

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The saturation of the soil and clay samples with potassium and calcium (and sodium in the one experiment) and preparation of the mixtures were also considered not to present any critical problems. The saturation and mixing procedures were done by accepted techniques. Since the main attention centered round the exchangeable potassium content of all samples, soil and clay alike, this cation was determined with great care throughout. Other cations (Ca^{++}, Mg^{++} and Na^{+}) were also determined where necessary. In the first experiment it was proved that the principle of pretreatment to obtain a range of K saturation levels of a soil was valid. The fact that the data of the untreated field sample were exactly in line with those of the samples with different K levels proved that the pretreatment and mixing presented no problems. Subsequent experiments could therefore be designed using this principle and they also confirmed the validity thereof.

Further to the principle of constructing Q/I graphs for a soil on samples pretreated to give a range of K levels, the thus obtained AR_e^K values for each soil or clay were then plotted against their respective K_{ex} values. This relationship proved to be linear for all samples of soils and pure clays. At extremely high levels of K saturation, not usually found in nature, there were, however, evidence of deviations in the linear character of these relationships. These deviations were only found in experiments with a pure bentonite clay. At levels above approximately 20% K saturation the graph sharply changed direction continuing again linearly, but with a smaller slope.

Although these graphs to some extent resemble Gapon relationships, it must be pointed out that they differ from the latter in a major respect, viz. only K_{ex}, and not the exchange ratio, figures in these graphs.

The quantity of exchangeable potassium in a soil is fairly generally accepted as the pool of labile potassium in a soil (e.g. Beckett, 1964 b). As was pointed out in the Introduction, Burger (1955) stated that this pool regulates short term potassium uptake by plants. Burger (1955) and Fariña (1970) found remarkably good correlations between exchangeable potassium and potassium uptake

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by plants in pot experiments. The results of Du Toit & Fölscher (1970) for a series of fertilizer experiments support this.

The linear relationship between K_{ex} and AR_e^K therefore is an indication of a linear relationship between the quantity of labile potassium in the soil and the relative intensity of potassium in the soil solution. The expression "relative intensity" is used because AR_e^K cannot be considered an indication of the actual activity of potassium in the soil solution, as was pointed out in the Introduction. The fact that the actual quantitative value of one of the two parameters which figure, is known, must be considered a good starting point. This may perhaps be an advantage over the normal Gapon relationship where both the exchange ratio and the activity ratio are relative values and not absolute values. Fariña (1970) for instance found no correlation between percentage K saturation of the soil's exchange complex and K uptake by plants. This was for one potassium level for each of a number of soil horizons.

It is practically impossible to determine the composition of the true soil solution. Schofield's (1947) Ratio Law, however, enables one to determine the relative composition of this solution. Beckett's (1964a, b) Q/I concept provides a simple and very good method for practically determining the true activity ratio (AR_e^K) of the soil solution. For any specific soil which conforms to the prerequisites stated by Schofield (1947) and Beckett (1964a) this activity ratio will be a good indication of the relative potassium activity in the soil solution because the cations against which it is measured (Ca+Mg) must be in large excess and consequently is considered as relatively constant.

From the results it is evident that a relatively high exchangeable potassium level in one soil may be associated with an extremely low AR_e^K value while the same, or a lower, K_{ex} value in another soil is associated with a high AR_e^K value. Although PBC_T^K has an effect in this respect the main factor responsible for this situation in most cases is the differences in EK^O, that value of exchangeable potassium where AR_e^K becomes zero. EK^O causes a large displacement of the whole graph.

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The fact that exchangeable potassium values widely different from zero are obtained where AR_e^K is zero cannot be ascribed to incorrect extrapolation of the lines as actual zero values for AR_e^K were obtained in some cases. Zero AR_e^K values are not uncommon in literature (e.g. Le Roux, 1966). It has also been pointed out that saturation extracts of soils of the Orange Free State often contain no detectable amounts of potassium, although they have significant (normal field) amounts of exchangeable potassium.

A zero AR_e^K value means that there actually must be no potassium in the soil solution irrespective of the actual concentrations of calcium and magnesium in the solution. As it is accepted that plant roots feed mainly from the soil solution, this means that under these conditions it will be very difficult for plants to obtain enough potassium for normal growth. EK^o must therefore be taken as a very critical value because this will indicate the exchangeable potassium level below which the activity of potassium in the soil solution becomes practically zero, and severe limitations with regards to potassium uptake may be expected.

The same conclusions are drawn when the Gapon relationships of the results are investigated. It is generally accepted that K_G indicates the power with which potassium is adsorbed relative to the adsorption power of calcium and magnesium. From this it can be seen that potassium was more tightly adsorbed than calcium and magnesium. This is in accordance with the results of Marques (1964) and others.

In all experiments with soils linear relationships between ER and AR_e^K were found. Most of the lines relating these two parameters had intercepts greater than zero. As actual zero AR_e^K values were found, these intercepts cannot be ascribed to incorrect extrapolation of the lines. The slopes of these lines indicate the retaining power of a soil for potassium relative to calcium and magnesium for all exchange sites in excess of EK^o. The linearity of the relationship for these sites is an indication that the relative retaining power of a soil for potassium on all these sites is constant. This relationship breaks down sharply at EK^o. At K_{ex} levels equal to or lower than EK^o, the retaining power of a soil for potassium relative to calcium and magnesium is infinite.

The occurrence of an intercept different from zero is responsible for the phenomenon that the normal K_G ratios, obtained by dividing AR_e^K into ER, are not constant over the whole range of K_{ex} levels. Although K_G is constant at K_{ex} levels much higher than EK^o, this constant value is higher than the constant given by the slope of the line relating ER to AR_e^K. The latter must be taken as a more correct indication of the relative retaining power for potassium on the planar sites. In discussing K_G obtained by a range of reduced activity ratios and their corresponding exchange ratios Marques (1964) reasoned along the same lines. His work was restricted, however, by the fact that Beckett's (1964a) method for determining AR_e^K was not available at that stage. The normal K_G value is an integral value, giving the overall relative retaining power for potassium for all exchange sites saturated with potassium.

In the Gapon curve of normal K_G versus K_{ex} there was an increase in K_G as K_{ex} decreased to levels near to EK^o. EK^o was approached asymptotically, which means that K_G tended to become infinite at EK^o. These increases in K_G are always taken as an indication that potassium adsorption is increased relative to the adsorption of the other dominant cations (e.g. Skeen & Sumner, 1970). This means that the release of potassium into the soil solution will decrease sharply and this probably limits immediate plant uptake of potassium (see also Marques, 1964). The hyperbolic form of the graphs which leads to this conclusion is not theoretical, but was illustrated in practice by the experimental results. It is also in accordance with the experimental results of others, e.g. Marques (1964) and Skeen & Sumner (1970).

From both the graph of normal K_G versus K_{ex} and the graph of ER versus AR_e^K it is therefore concluded that the relative retaining power for potassium becomes infinite at EK^o. In this respect the interpretation of these two graphs thus leads to the same conclusion. Their interpretation differ widely, however, in two other respects. The first is that the constant normal K_G is higher than the slope of the line for ER versus AR_e^K, as was indicated. The other major difference is that there is a progressive increase in the normal K_G values at K_{ex} levels just above EK^o as K_{ex} decreases towards EK^o, while the slope of the line for ER versus AR_e^K remains constant over all K_{ex} levels down to EK^o, as was also indicated. The latter again must be taken as more correct.

Where EK^o is zero the hyperbolic type of increase in K_G will not occur. In this case ER wil become minimal too where AR_e^K is minimal and K_G will remain constant. Where AR_e^K is zero, ER is zero too so that there is no case of an infinite K_G value. The relative strength of adsorption of potassium will therefore be constant over the whole range of K_{ex} levels. In this special case K_G and the slope of the line for ER versus AR_e^K will also be numerically equal.

The Gapon-like equation (Marques, 1964) and the Q/I technique are combined in the sence that the Q/I technique is used to obtain the equilibrium activity ratio, AR_e^K. By plotting ER against this AR_e^K the Gapon-like relationsnip is found. In addition, by plotting AR_e^K against K_{ex}, EK^o is obtained. EK^o is an important parameter in Gapon studies because it indicates that K_{ex} value at which K_G becomes infinite.

Although the data for indirect ER versus AR^K fitted the Gapon-like linear equations well, the lines for different initial K_{ex} levels differed from each other. The lines for the lowest K_{ex} levels gave the best approximation to the line for ER versus AR_e^K for each given soil and in some cases resembled it remarkably well. The most important deviation at the higher initial K_{ex} levels was that the intercepts of these lines were too low.

It is unfortunately so that EK^o values for the same soil varied markedly between successive experiments. No explanation is attempted for this, but the apparent value of EK^o in potassium nutrition studies warrants further investigation to clarify this discrepancy.

With regards to the implications for the Orange Free State soils studied, it has already been pointed out that it is common experience to find no detectable dissolved potassium ions in the saturation extracts of field samples of these soils, even though they contained what were thought to be sufficient (though definitely not high) quantities of exchangeable K. The present studies proved, however, that some soils have EK^o values of considerable magnitude. The exchangeable potassium content of some of these field samples were actually practically equal to their EK^o values. From large numbers of field samples analysed in our laboratories during the past few seasons it is evident that the vast majority have exchangeable potassium levels very close to these EK^o values and often even lower. It is perhaps not irrelevant to suggest that such high EK^o values may be one of the reasons for the high incidence of potassium deficiencies in agricultural crops on soils of the western irrigated areas.

The former are only indications and suggestions and must be tested before any definite conclusions can be drawn. It is, however, felt that these indications are of such a nature that they warrant an intensive and systematic study of the relationship between exchangeable potassium and AR_e^K for the irrigated soils of these regions and also for other arable soils. As the data for the field samples fitted the curves for the specially prepared samples well, the tedious preparation method may be omitted and different K_{ex} levels can be effected by merely adding different quantities of potassium to a soil. This must also be correlated with plant studies. The author would suggest that these studies are done in such a way that groupings can be done on soil series basis. Although Le Roux (1966) and Beckett & Nafady (1968) found fairly large differences between the Q/I relations of soils in any specific series it is felt that certain refinements of techniques and the introduction of correction factors, especially for CEC, may improve these groupings within series.

Although some of the EK^o values may seem to be very high, they are quite normal when compared to the critical values suggested by Stanton (1958) and by Marques (1964) for a subtropical clay from Natal.

The effects of high exchangeable sodium levels on the Q/I relations of the two soils are of interest and importance. Although sodium had large effects on the Q/I relations of the soils, it did not cause poorer Q/I relations or poorer relations between K_{ex} and AR_e^K. Had the no sodium samples not been used, then the Q/I relations for the high sodium samples would seem quite normal and sodium might easily be regarded as without any effect.

The main effects of sodium were direct effects on the different Q/I parameters. Calculation effects by bringing sodium into the equation for the activity ratio were of somewhat lesser importance. Because the effect of sodium on the calculation is related to the amount of sodium in the soil and not to the percentage sodium saturation and as the amount of sodium at a certain saturation level is governed by the cation exchange capacity, this effect is of much importance for the finer textured soils. Within a certain soil with a specific exchange capacity the amount of sodium is of course directly related to the percentage sodium saturation. These effects of sodium content of the soil will have to be taken into account on some of the clayey alluvial irrigation soils in this Region in which significant amounts of sodium occur because of salinization and alkalization.

The most significant effect of high sodium levels was the lowering of EK^o, as manifested especially in the Riet River No. 2 soil with a relatively high cation exchange capacity. As mentioned in chapter 4, this may be seen as an opening up of some of the internal exchange sites. It may also, to some extent, contribute to the synergistic effect of relatively high sodium levels on potassium uptake sometimes experienced (e.g. Heimann, 1966). Within a certain range of K_{ex} levels for a specific soil the strength of adsorption of potassium relative to calcium and magnesium was decreased markedly by sodium (according to the accepted interpretation of the hyperbolic curve of K_G versus K_{ex}). Furthermore the activity of potassium ions in the soil solution was increased, as shown by increased AR_e^K

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values. Both these facts may be expected to provide improved potassium uptake by plants. This latter statement is in full agreement with the interpretation of graphs of this nature by Marques (1964) and others.

Although this study was based on the Q/I technique only one Q/I parameter, viz. AR_e^K, figures in the foregoing parts of the discussion. PBC^K, $-\Delta K^O$ and AR^K, the other Q/I parameters, cannot be ignored, however. Of these $-\Delta K^O$ and PBC^K are the most important ones.

In the Q/I concept $-\Delta K^O$ is described as the capacity factor of the labile pool and Beckett (1964b) stated that it is the same as the exchangeable potassium content of the soil. Tinker (1964a, b) determined $-\Delta K^O$ and then simply called it the "exchangeable potassium content" of the soil.

Le Roux (1966) found that $-\Delta K^O$ was seldom more than 50 per cent of K_{ex} for a number of field samples. Fariña (1970) found that $-\Delta K^O$ gave no indication of K_{ex} for a number of samples. Both these authors did not determine $-\Delta K^O$ at different levels of K saturation for the respective samples. Zandstra & MacKenzie (1968) on the other hand found good correlations between exchangeable K and $-\Delta K^O$.

For most field samples, such as those used by Le Roux (1966) and Fariña (1970), the values of $-\Delta K^O$ were much smaller than those of K_{ex} for specific soils. In order to compensate for this difference attempts were made by different workers to use extrapolation of the curved part of the normal Q/I relationship (that is of ΔK versus AR^K) for this purpose. This approach was found to be unsatisfactory, especially as the extrapolation of the curved part is subject to too much uncertainty, as pointed out by Beckett & Nafady (1967) and Fariña (1970).

For all the soils and clays used in the present study it was found that there was a relationship between K_{ex} and $-\Delta K^O$ at all relatively high levels of exchangeable potassium. In some cases the correlation was quite good. In some cases the numerical similarity between K_{ex} and $-\Delta K^O$ was notable. Where this similarity did not exist, $-\Delta K^O$ was mostly 50 - 100 per cent higher than K_{ex}.

Therefore no asymptotic extrapolation of the curved part of the Q/I relation is needed to supplement $-\Delta K^o$ to give total K_{ex}.

This relationship between $-\Delta K^o$ and K_{ex} breaks down when K_{ex} decreases to only just above EK^o. For values of K_{ex} near that of EK^o, $-\Delta K^o$ diminished relative to K_{ex} and the differences between the two parameters increased rapidly as EK^o was approached. Unfortunately the K_{ex} levels of many, or even most, field samples are apparently in the region near EK^o where $-\Delta K^o$ is much smaller than K_{ex} and where changes in K_{ex} are accompanied by relatively large changes in the ratio between $-\Delta K^o$ and K_{ex}. Therefore $-\Delta K^o$ cannot be considered identical to K_{ex} or even a fairly good indication of K_{ex} in such samples. For these field samples it will then also be irrelevant to use $-\Delta K^o$ as an indication of the capacity factor because K_{ex} is generally accepted as the capacity factor of the labile potassium pool. This is not contradictory to Beckett's statement that exchangeable potassium indicates the capacity of the labile pool (Beckett, 1964b). Regarding plant uptake of potassium this poor relationship may contribute to the fact that several workers (e.g. Zandstra & MacKenzie, 1968 and Fariña, 1970) found poor correlations between $-\Delta K^o$ and potassium uptake, but good correlations between K_{ex} and potassium uptake.

Furthermore it means that there is a correlation between K_{ex} and $-\Delta K^o$ for those K_{ex} levels where K_G is relatively constant, but not in the region of K_{ex} near EK^o where K_G varies considerably between different K_{ex} levels.

Mean PBC^K was found to be the most constant property of the soils. It varied the least of all parameters between different successive experiments, despite variations between individual PBC^K values for any specific soil. If it is remembered that these determinations were done on specially prepared samples from the same bulk sample, then it is not unexpected that others, e.g. Le Roux (1966) and Beckett & Nafady (1968) found fairly large variations between single determinations on various soils within any specific series. From the present results it seems as if

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the PBC^K of any soil will have to determined at least in triplicate.

As exchangeable potassium level had no definite effect on PBC^K the fact that different samples from the same series vary with respect to exchangeable potassium should not be a serious limitation. The clay content of various samples within a series can differ markedly, but clay content did not have a large influence on PBC^K (cf. the results for the two Riet River soils). The introduction of a correction factor for clay content or CEC may, however, be expected to improve the relation of PBC^K to series. From the studies with clay samples it can be expected that type of clay mineral will have a very large effect on PBC^K. No problem from this is expected on series basis as soils with widely different clay mineral suites are not generally grouped together in the same soil series.

Where the results for bentonite were expressed as me per 100 grams of clay, it was evident that PBC^K increased with decreasing clay:solution ratio. This increase was extremely large at the lowest quantity of clay used. This led to the conclusion that the curved part of the Q/I relation, found with smaller quantities of soil per 100 ml equilibrating solution, is at least partly due to the effect of the wider soil:solution ratio. It may be expected that each of these smaller quantities should also yield linear graphs with a full range of equilibrating solutions. Therefore each point on the lower part of the curved portion is representative of different linear graphs of varying slope through these points. The real value of PBC^K as a measure of soil fertility and in plant nutrition is still open to much speculation. PBC^K undoubtedly is of value in characterizing a soil within a series (see also Le Roux, 1966).

It must be pointed out here that once AR_e^K and $-\Delta K^o$ are obtained by interpolation and extrapolation, PBC^K can be calculated by simply dividing AR_e^K into $-\Delta K^o$. When this test is applied to some of the published results significant anomalies come to light, e.g. Beckett (1964b) and Le Roux (1966).

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The consistency of the relationship between mean PBC^K and PBC^K_T in the experiment with the four soils is quite remarkable. Although the same constant factor was not found in the following experiment, it is of interest to note that these relationships in each experiment for each soil or clay were notably constant.

A high PBC^K_T value means that AR^K_e changes relatively little when K_{ex} is changed. In other words the intensity factor is buffered well against changes resulting from changes in the capacity factor. A low PBC^K_T will have the opposite meaning. This is identical to the characteristics ascribed to PBC^K by Beckett (1964b).

As compared to results generally obtained from literature, the PBC^K values for the soils in the present study, were very low. In contrast to values of 55 to 340 found by Zandstra & MacKenzie (1968) the present PBC^K values ranged from 12.32 to 39.44. This means that severe decreases in the activities of potassium ions in these soil solutions are expected to occur upon potassium removal, e.g. by growing crops. This may further contribute to the poor potassium nutrition of crops, especially on the Mangano soil where the problem of poor potassium nutrition is extensively found.

Finally it may be stated that an intensive study of the relationship between K_{ex} and AR^K_e for soils of the Orange Free State Region is needed and may prove fruitful. It is evident that we are in the fortunate position that the field samples of these soils conform to the requirements for the application of the Q/I technique. Certain important results concerning the potassium relationships of these soils were obtained in the present study.

With regards to the Q/I technique it must again be emphasized that it is regarded as an extremely useful technique for determining certain cationic parameters, especially the equilibrium activity ratio of the soil solution (AR^K_e). The author cannot envisage any better or easier method for determining AR^K_e.

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It must be remembered that the sole initial object of the technique, which was later called the Q/I technique or concept, was to confirm Schofield's Ratio Law (Beckett, 1964a). To be even more correct: it was designed to obtain the true equilibrium activity ratio of the soil solution by interpolation. This is so very logical and simple that it is quite incredible that it took so long before someone thought of doing it. By doing this, Beckett made an extremely valuable contribution to the study of cationic equilibria in soils. By combining the AR_e^K obtained in this way with the exchange ratio, for instance, the true relationship between the activity ratio of a soil solution and the corresponding exchange ratio can be obtained. Beckett (1964b) quite obviously had the intention of this type of study, as pointed out in the Introduction. By some inexplicable misunderstanding this was not done and certain characteristics were ascribed to parameters within the Q/I curve. These characteristics could, however, only be obtained by combining several of these curves and further combining these with studies of exchangeable cations.

The most significant errors were (i) AR^K was used as the activity ratio of the soil solution, something for which only AR_e^K qualifies according to Beckett's (1964a, b) own definitions, and (ii) $-\Delta K^o$ was described as the exchangeable potassium content of a soil. Mention has been made of results from literature which indicate that the latter is not the case. The results of the present study showed that Beckett's statement is true for high K_{ex} levels, but not for relatively low levels. Unfortunately the K_{ex} of field samples often fall in the latter range.

These basic errors led to poorer results than could be expected and confused some people to such an extent that they unfortunately became antagonistic to the Q/I technique.

By concentrating on the Q/I technique mainly for the purpose of obtaining AR_e^K and by introducing these AR_e^K values into the various exchange equations like those of Gapon, Donnan, Krishnamoorthy-Overstreet, Kerr and Vanselow these equations may be studied to good effect. The square

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of AR_e^K will of course have to be used in the latter two equations.

The author is convinced too that a study of the relationship between exchangeable K and AR_e^K (with the introduction of EK^o and PBC_T^K) warrants some attention because this may prove important with regards to the practical problems of potassium uptake by plants.

It is the wish of the author that positive critical evaluation of the Q/I concept will lead to its refinement as it evidently has considerable potentialities, provided that it is used and developed correctly.

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