

THE ACTION OF SALTS UPON THE pH  
OF SOME  $V_2O_5$  SOLS

BY

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1937

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## ABSTRACT

A study was made of the effect of the addition of salts to  $V_2O_5$  sols. The changes in pH were the item of chief interest and were observed in detail for a number of salts over the concentration range 0-0.05 cation molar.

The results obtained showed a wide variation of behavior, but may be divided into two classes as follows:

(a) Salts with buffer action.

Some of the salts studied showed such large changes due to buffer effect from one of the ions that it was considered unsafe to draw any conclusions as to their action on the sol, except that the system behaved like a mixture of two buffering substances.

(b) Salts without buffer action.

This class consists of salts of strong acids and bases. The salt alone will affect the pH only slightly, but by interaction with the sol causes liberation of  $OH^-$  or  $H^+$  from the micelles. This interaction may take place either by chemical combination (formation of an ionic or coordinate linkage), or by electrostatic adsorption.

Evidence appears for both types of behavior.

The precipitation behavior of the sols was also studied, but no direct connection with the pH changes could be established. Precipitation values seem to be of the same order of magnitude, as those reported for other sols in the literature. Incidentally, these sols form gels

with great readiness when salts are added, even at the low concentrations studied (0.035 to 0.15 %).

Thermal effects were investigated by refluxing the sols and it appeared that although some change in structure occurred, the sols were in equilibrium with the dissolved phase at their respective pH values.

All EMF determinations were made with the glass electrode and a full description is given of the apparatus and of the measures adopted to eliminate sources of error.

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## I. INTRODUCTION

During the last six or seven years, Thomas and his co-workers (1-10) at Columbia University have carried out a number of studies on the change of pH in various hydrous oxide sols on the addition of salts, chiefly those of potassium.

The results obtained showed a definite interaction between colloid and salt and were explained on the basis of the Werner complex theory.

Its application may be summarized briefly. If we consider almost any of the oxides of groups III-VI, there is ample evidence of the formation of polymers when hydrated.

Werner explains the formation of these substances by the assumed coordination of two metal atoms with an  $H_2O$ ,  $OH$ , or  $O^{2-}$  in common. Each of these metal atoms may coordinate in common with a third, and so on. It is then apparent that we need only continue this process to reach "giant molecules" of the size of colloid particles or of the organic resins and proteins.

In the case of the hydrous oxides, their low stability as compared to the carbon linkage allows interchange of groups in solution. Thomas, working with positive sols, was chiefly interested in the displacement of hydroxyl, since this effect was most readily observed due to the consequent change in pH.

Weiser attacked his work on the basis of X-ray data showing that the X-radiogram of  $\text{Al}_2\text{O}_3$  (fused) was quite different from that of flocculent  $\text{Al}(\text{OH})_3$ . This is not conclusive, however, as it is not evident why they should be similar. Such a quality as hardness, which is an intimate function of crystal structure, is certainly quite different as well. It is possible that as water is eliminated from the molecule and we approach the limiting case of a crystal with only  $\text{O}^{2-}$  linkages that profound changes in the crystal properties occur. All evidence seems to point to this, at any rate.

Another article by Weiser<sup>(16)</sup> includes a study of  $\text{Al}_2\text{O}_3$  sols under conditions similar to the following ones. None of the results, however, are considered as incapable of explanation by the theory to be set forth.

In any case, examination of Thomas' work showed that he had experimented with positively charged sols only. It was therefore decided to investigate some negatively charged hydrous oxide sol. Choice was made of the very interesting  $\text{V}_2\text{O}_5$  sol.

This sol, whose optical properties have been much studied, has long been known to show changes on aging which have been attributed to change of crystal structure. It should therefore exhibit effects similar to those sols studied by Thomas if his theory is independent of the charge on the sol, as should be the case.

## II. SOLS STUDIED

### Method of Preparation.

There are two general methods of preparing  $V_2O_5$  sols, one by hydrolysis and the other by pyrolysis. Four sols were prepared, two of each type, all data on which is given in the table at the end of this section.

The hydrolytic type of sol which is commonly known as the Biltz-type sol after the originator of the method, was made as follows: (12)

A known quantity of the C. P. grade of  $NH_4VO_3$  was mixed with a slight excess of dilute HCl. The stoichiometric equation is



The red paste obtained is ground in a mortar to ensure thorough mixing and complete reaction and filtered. The precipitate is washed until it starts to run thru the filter and then placed in 700-800 ml. of distilled water in which it disperses in colloid suspension, and the colloid dialyzed 8-10 days with slowly running distilled water at room temperature. Sol A, as shown below, was dialyzed 10 days with a short length of sausage skin (viscose) membrane (about 18 inches). Sol D was dialyzed 8 days with a greater length (six feet). At a rate of about 1 drop per second this was sufficient to bring the dialysate to equilibrium. Considerable  $V_2O_5$  was lost as the membrane was permeable to the smaller particles which

was shown by a distinct yellow color in the dialysate. Although about 8 times as much  $\text{NH}_4\text{VO}_3$  was used to prepare Sol D as Sol A, the greater efficiency of dialysis reduced the final concentration to nearly the same.

After dialysis was completed the sol was filtered thru asbestos and diluted to about three liters. The pyrolytic sol was prepared by the method of Muller, who first reported this process of preparation. (13) A known quantity of C. P.  $\text{NH}_4\text{VO}_3$  was evaporated to dryness after mixing with a considerable excess of  $\text{HNO}_3$ . This was done in a platinum crucible. The resulting oxide was then fused and kept molten 5-10 minutes to drive off all volatile material.

While still liquid, it was poured in distilled water, allowed to stand overnight to complete dispersion and then filtered thru asbestos to remove sediment and undispersed oxide.

Sol B was prepared as is shown, with a concentration about 4.5 times that of Sol C.

No dialysis was carried out on this sol as the final purity depends only on the absence of non-volatile impurities from the original  $\text{NH}_4\text{VO}_3$ .

#### Analysis.

The sols were then analyzed for  $\text{V}_2\text{O}_5$  content by the Jones reductor method. This consists in dissolving the sol in  $\text{H}_2\text{SO}_4$  by addition of sufficient acid to

decolorize it, passing thru the reductor and catching it under  $\text{Fe}_2(\text{SO}_4)_3$  solution and titrating with  $\text{KMnO}_4$ . Full details are given in Scott. (11)

Sols A and D were analyzed for N and for  $\text{Cl}^-$ . The first test was made by the Kjeldahl method by courtesy of Mr. Daniel Beady of the Department of Agriculture. Results were as tabulated.

Chloride was tested for by decolorizing with  $\text{HNO}_3$  and addition of  $\text{AgNO}_3$ .

TABLE NO. I

Sol	% $\text{V}_2\text{O}_5$	N(ppm.) (as nitrogen)	Cl
A	0.068	23.6	Trace (doubtful)
B	0.308	-	-
C	0.110	-	-
D	0.078	18.6	No test

Sol	Color reflected	Color transmitted
A	Brown-red	Wine-red
B	Black	Red-brown
C	Black	Red-brown
D	Brown-red	Wine-red

### III. MEASUREMENT OF pH

#### Instruments Used.

Only the glass electrode can be used for measurement of the pH of these sols. An attempt was made to use the quinhydrone electrode, but the sol set to a gel nearly instantly, turned a dark green and gave non-reproducible potentials, which averaged 1-1.5 pH different from the highly reproducible potentials obtained with the glass electrode.

The further use of the quinhydrone electrode was therefore not attempted. The hydrogen electrode cannot be employed with strong oxidants, as is well known, and as  $V_2O_5$  is a powerful oxidizing agent ( $E^0$  ca. 1.2 volts) no trial of it was made.

A Leeds and Northrup Type K potentiometer was used, with Weston standard cell and a special type low discharge lead storage cell as working battery.

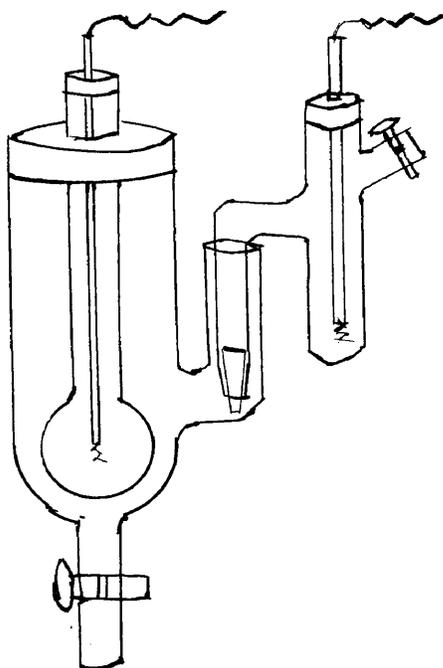
On some of the early measurements, a Leeds and Northrup Type R galvanometer (B suspension) was used as the null-point instrument, but this was of low sensitivity, allowing a precision of but  $\pm 2$  mv.

For the later work, which is shown on the curves below, a Hellige vacuum tube galvanometer was employed. This instrument had a sensitivity of better than 0.1 mv. but as the reproducibility of the system was over ten times this, no attempt was made to set or read it more closely,

though on certain test runs with buffers a sensitivity of 20-30 microvolts was indicated with the electrodes used.

The electrodes were made from 8 mm. tubing of Corning 015 glass. Bulbs were blown of 2-2.5 cm. diameter with the glass thin enough so that it readily dimpled under light pressure with a sharp point.

The bulbs were filled with 1.000 pH HCl (standardized by the quinhydrone electrode) and a small amount of quinhydrone added. A platinum electrode was immersed and the whole electrode placed in its mounting (see drawing).



The solution, whether standard or unknown, was poured in the side arm and leveled off with the HCl inside the electrode. A saturated calomel electrode with ground glass joint was placed in the side arm as shown and the leads attached to the potentiometer.

The 1.000 pH HCl used was prepared about 3 liters at a time by use of the quinhydrone-saturated calomel electrodes. One saturated calomel was kept in a thermostat and used for this alone as standard. The other calomels were frequently checked against it.

In making measurements, the zero point of the

electrode system (at pH = 1.000) was determined daily before and after other measurements by substituting quinhydrone-Pt in place of the glass electrode. This eliminated any error in the calomel. The glass electrode was then measured against the 1.000 pH acid, determining its asymmetry potential by subtracting this reading from the first. By this means the absolute pH could be determined, using the equations

$$E = E_{\text{observed}} + E_{\text{asym.}} \quad (1)$$

$$\text{pH} = \frac{0.4534 - E}{0.0591} \quad (2)$$

These are readily derived as follows. The system used was

Pt, Quinhydrone & solution ( $a_{\text{H}^+} = 1.000$ ), glass membrane, solution ( $a_{\text{H}^+} = x$ ), Sat. Cal.

If, as has been done, we eliminate the asymmetry potential we may consider this as the following cell without junction potential

Pt, Qh<sub>2</sub>, sol'n. ( $a_{\text{H}^+} = 0.1000$ ) // sol'n. ( $a_{\text{H}^+} = x$ ), Sat. Cal.

The asymmetry potentials as determined were seldom larger than 1-2 mv. Where this was the case the electrode was discarded.

Slow oxidation of the quinhydrone necessitated re-filling with fresh acid and quinhydrone every 2-3 days. Freshly filled electrodes gave small and reproducible asymmetry potentials.

Occasional difficulty was experienced with the vacuum tube galvanometer, such as variation of the end-point with the setting of the galvanometer needle.

When this occurred, frequent standard readings were made and the needle set to a definite point at which all determinations were carried out. All measurements were carried out in an air thermostat, controllable to  $\pm 0.01^\circ$  and the electrodes and all solutions were kept at least 1/2 hour in a water thermostat at  $25^\circ \pm 0.03$  before making a reading.

#### Preparation of solutions.

In studying the effect of salts on the various sols the factor of variability of concentration of salt or sol in successive or duplicate readings was eliminated as far as possible. The procedure was as follows:

A stock solution of a given salt was made up 0.1 molar in the metal cation of the salt for reasons which will appear below. This concentration expression will be hereafter termed cation molar (c.-m.). Thus the master solutions of  $\text{Tl}_2\text{SO}_4$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{K}_2\text{HPO}_4$  and  $\text{KH}_2\text{PO}_4$  all contained 0.1 mol per liter of Tl, Ba, or K respectively. Solutions were prepared gravimetrically.

To 10 ml. of the stock colloid there was added sufficient salt solution to give it the desired concentration of salt after adding enough water to make the final volume 20 ml. The water was always added first.

The concentration ranges 0.05 to 0.0005 c.-m. were studied with zero determinations of 10 ml. sol and 10 ml. water. This was necessary as simple dilution of the sol (1:1) with water caused a variation of 5-10 mv. in the potential.

After shaking, the sol-salt mixtures were kept in a thermostat at 30° C. for 3-4 days in stoppered flasks. Due to a shortage of glass stoppered flasks some cork stoppered ones were used, but no significant difference was shown on comparing with the results using glass stoppered ware.

As is noted above, the salted sols were brought to 25° C. in a thermostat before measuring the EMF.

Summing up, the following factors were taken into consideration.

The concentration of colloid was always the same even at zero salt concentration. Any EMF increment was then due to the action of the salt.

The concentration of salt was good to at least 1% (gravimetric preparation) and the concentration precision on duplicate measurements was limited only by the precision of the glassware.

Temperature effects were eliminated by rigid control of the temperature before measurement.

Variation of the electrodes and asymmetry potential were eliminated by the process of intercomparison with standards given above.

#### IV. PRECISION OF MEASUREMENTS

Analysis was made of the measurements from the basis of the theory of probability to determine the precision with which the various points plotted were known.

This was necessary, as in developing the theory to cover the phenomena observed we must be able to determine whether a bend or concavity in a curve is significant or a mere fluctuation within the margin of error.

This was done by two methods. In the first case, a large number of observations (15-20) were available, determining for each sol the EMF of a 1:1 mixture of the sol and water.

These were averaged and the sum of the deviations from this average without regard to sign obtained. Division of this quantity by the number of observations gives us the average deviation. This, for the more than seventy observations on the zero points of the sols, was found to be  $\pm 0.8$  mv.

On the various concentrations observed, an equivalent process was carried out. Two to four observations were made on each concentration with each salt and each sol. At every point the average was taken and the deviation for each observation calculated. This was totalled and then divided by the total number of observations and the result found to be  $\pm 0.8$  mv. As is seen, this is identical with the result found from the first process.

This quantity was taken arbitrarily, as the margin of error. It is to be noted that such an assumption is quite conservative. The general practice is to divide by the square root of the number of observations or use the root mean square as divided by that quantity and so on. Such a procedure reduces the quantity considered as the error by a third to a half, or more.

In drawing the curves below, this precision is taken as the radius of the circles marking the points determined.

## V. COORDINATES OF THE GRAPHS

We come now to the consideration of the effects of the salts on the sols whose preparation was given above.

In the study of the graphs which follow, it is first necessary to deal with the quantities chosen as coordinates, their significance and the reasons for their choice.

On the y-axis, the dependent variable  $\Delta E$  is the increment of EMF stated in millivolts. This is related to the change of hydrogen ion activity (which it must be pointed out, is not the change in hydrogen ion concentration) by the simple equation

$$\frac{\Delta E}{59.1} = -\Delta \text{pH}$$

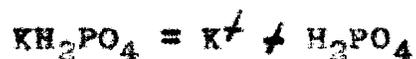
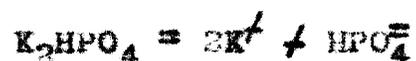
where  $\text{pH} = \log \frac{1}{a_{\text{H}^+}}$

This variable was chosen because it provides a unit of convenient size and in keeping with the precision obtained, and also because modern thought in the field of physics tends to the use and development of observed quantities or measurables rather than the secondary quantities which are given physical significance by the theory or model in use at the time. For a development of this theme, the work of Bridgman<sup>(14)</sup> is recommended.

This quantity further allows direct intercomparison of the sols which was the reason for using it rather than the E values actually read. As is seen, all curves then possess a common zero.

On the x-axis a variable was chosen which, so far as is known, has not hitherto been used, namely, cation molarity.

This refers to the number of metal ions yielded by the salt in question assuming complete ionization. Consider, for example, the salts  $K_2HPO_4$  and  $KH_2PO_4$ . These ionize for all practical purposes as follows (as a study of ionization constants of their acids will show):



This, at least, is assumed to be their primary action and the important secondary effects will be dealt with later.

Since the sols are negative (as proved by electrophoresis) they will adsorb and interact with the cation present.

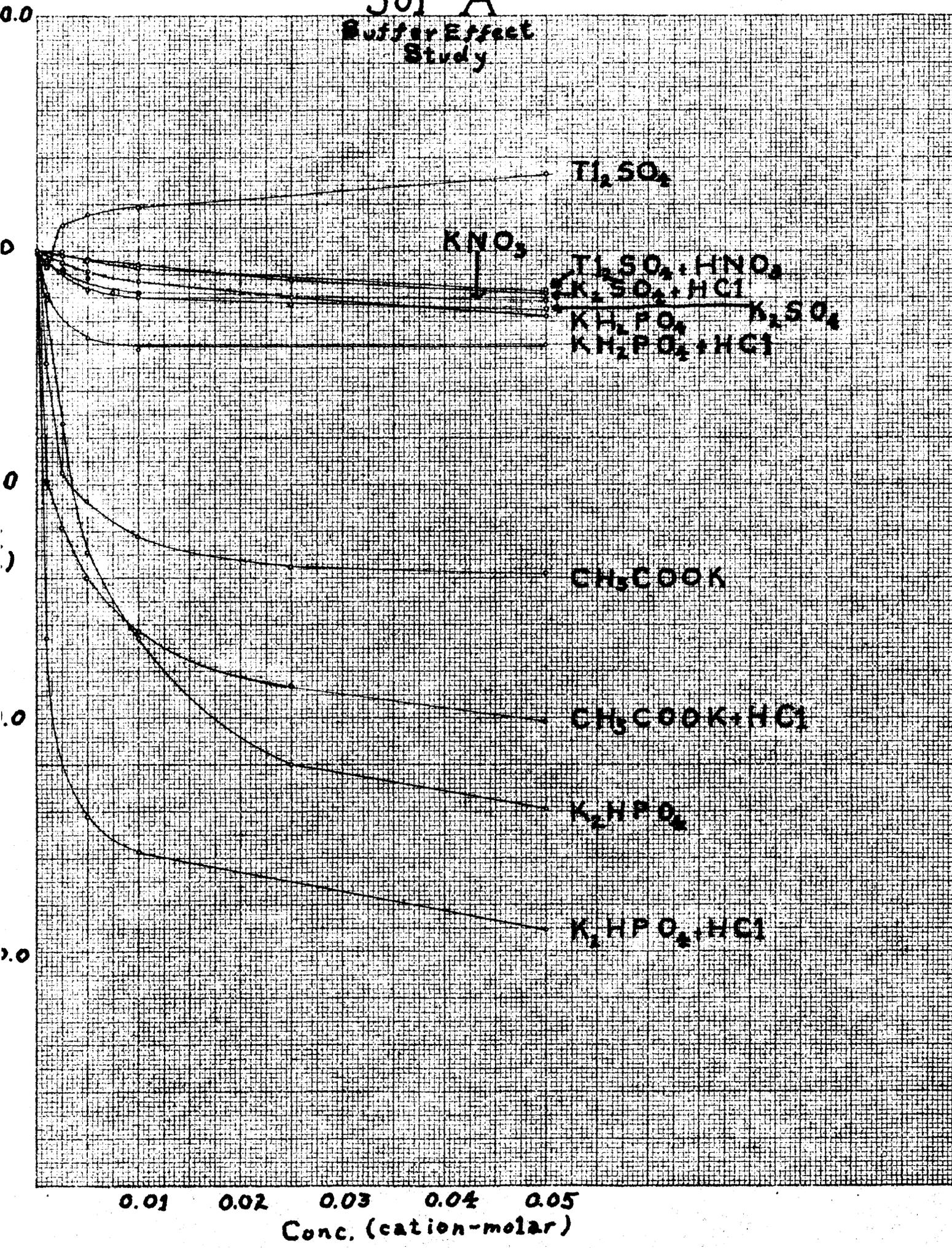
It is assumed that this interaction is largely by means of coordination and since the bases used are monatomic, that their coordination number is the same. This is a point which has not been carefully considered in the work of Thomas, who uses the normality or equivalent weight as a measure. That this latter assumption may not be safe is seen when we consider that the sulfate ion which is known to coordinate singly or doubly is given the same value as the oxalate ion which is nearly always double and the tartrate ion which has no less than four groups (2 hydroxyl

and 2 carboxyl) which may coordinate. In some cases, as is well known (eg. Fehling's solution), the hydroxyl groups coordinate preferentially to the carboxyl groups.

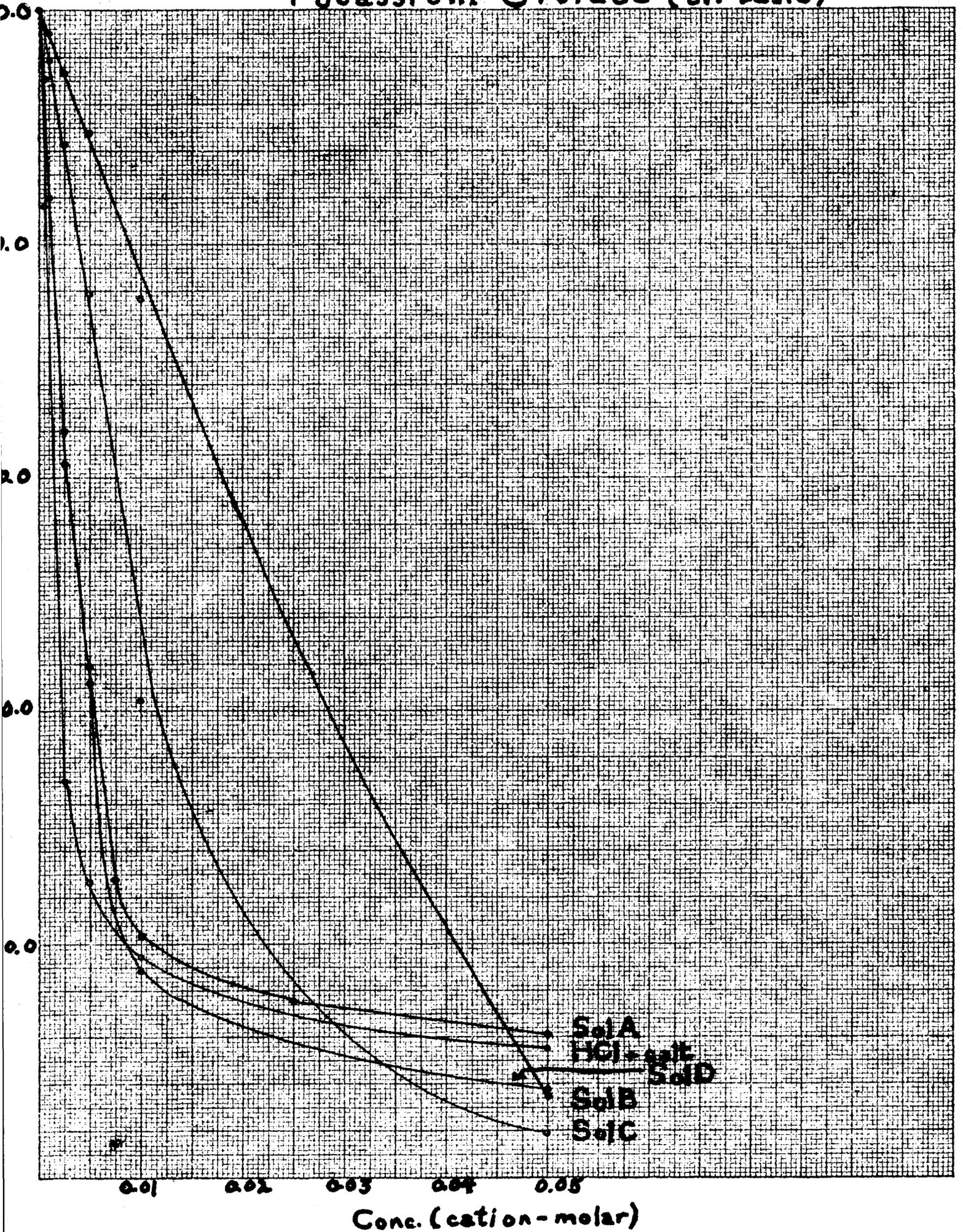
While the assumption of similar coordinative action on the part of all metal ions used may not be correct, it rests on the known tendency of the great majority of such ions to seek similar coordination numbers and upon their monatomic nature, rendering chelation improbable.

# Sol A

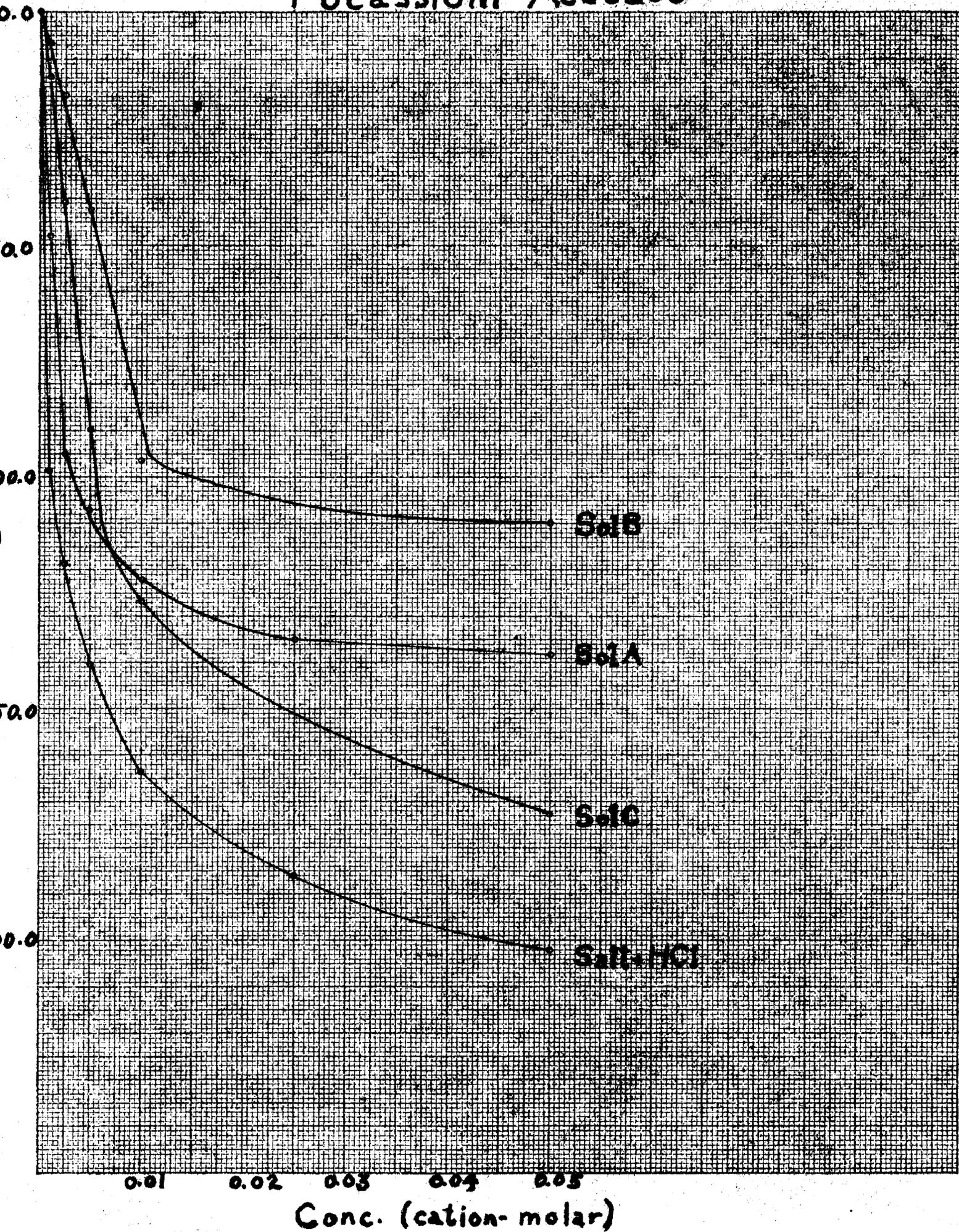
## Buffer Effect Study



# Potassium Citrate (tri-basic)



# Potassium Acetate



## VI. BUFFER ACTION

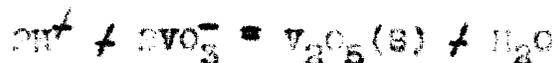
In the study of the action of salts on the sols, we deal with the changes of pH effected by their interaction.

It is vital, therefore, to remember that we have two factors which may change the pH, (a) the sol and (b) the salt. If, therefore, addition of a salt would effect a considerable pH change in the absence of the sol, it is evident that studies on that salt as to its effect on the pH of the sol are of doubtful significance.

This is shown conclusively by the graph covering buffer effect studies on sol A.

Like any  $V_2O_5$  sol, this consists of hydrated  $V_2O_5$  in equilibrium with the dissolved acid.

This acid, which we may denote  $HVO_3$  for convenience, is probably a strong acid in spite of the tendency of the oxide to be amphoteric.  $HPO_3$  is another example of such behavior. We then have the equilibrium



It is seen that the sol functions as a buffer. This is not important, however, as this action produces only a small error by tending to oppose the change of pH in either direction.

What we may be concerned with is the action of the salt on the solution. Solutions of HCl and  $KNO_3$  were prepared which, when diluted 1:1 with water, possessed pH

values close to that of the sols. This is shown by the following table:

TABLE NO. II

Solution	E	pH
Sol A / H <sub>2</sub> O (1:1)	0.2498	3.44
" B "	0.3027	3.55
" C "	0.2916	3.74
" D "	0.2638	3.21
HNO <sub>3</sub> "	0.2667	3.16
HCl	0.2520	3.40

To these solutions were added the salts used over the concentration range studied. In other words, the technique of the studies on the sols was duplicated, substituting the above mentioned acids for the sols.

The results are as plotted. Where the salt alone is given, it was mixed with sol A. We then have a series of curve pairs, showing the effect of the salt on the pH in an acid solution and the effect in conjunction with the sol.

No data is given for KNO<sub>3</sub>, as the A E for this salt was zero, within the error of measurement at all concentrations. It was measured with the HCl solution.

It is of interest to note that H<sub>2</sub>SO<sub>4</sub> is a distinctly weaker acid than HNO<sub>3</sub> or HCl. The close coincidence of the buffer effect curves for K<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> shows this, since

both cations are strong bases.

The validity of the effect of  $Tl_2SO_4$  is well shown by the fact that a negative error is incurred by buffer action of the salt. The slightly increased action of  $K_2SO_4$  over  $KNO_3$  is probably due to this factor.

Conversely, let us consider the phosphate and acetate pairs. The lesser  $\Delta E$  of the acetate sol curve is probably due to the buffer action of the sol as shown above. This is supported by the observation of disintegration and decolorizing of the sol, which was explained as due to the disintegration of the colored oxide to form the colorless ionic form.

The phosphate pairs are perhaps the best example of the danger of buffer action. The primary phosphate is the salt of a fairly strong acid, but the secondary phosphate is the salt of a weak one. In solutions of the pH given above (Ca. 2.5-3.5) it is probable that the phosphate equilibrium given above proceeds further for the secondary.



The ionization constant shows the equilibrium to lie far to the right. Thus we have a tremendous difference in the action of two salts which in solution yield identical ions.

The two curve pairs show precisely the action which we would expect from the above hypothesis, namely, a large change for the secondary phosphate with a much

smaller for the primary, with the change less for the sol-salt than for the salt-acid mixture. Inspection of the series of curves for all four sols with potassium acetate shows that the most concentrated sol (namely sol B) showed the greatest buffer effect and largest difference between the sol-salt and acid-salt curves.

The potassium citrate curves are somewhat different. Here the salt was sufficiently strong a buffer to completely disintegrate the sol and bring all four sols to a nearly identical pH value at a concentration of 0.05 c.-m.

Sols A, D, and C show a final value of  $\Delta E$  according to their variation in pH at the start. Sol B, owing to the greater concentration, shows a marked buffer effect but its high initial acidity gives it an intermediate final increment.

As with the acetate and phosphates, the effect due to buffer action of the salt is so large that it is unsafe to try to interpret any pH change in terms of coordination effect.

Thomas attempted to obviate this by adding some of the free acid to his salt solutions until the pH was close to 7.

This procedure cannot be supported, as may be easily shown. To prepare a buffer of a given pH the general procedure is to mix an acid with the appropriate ionization constant with its salt, which is what has been

done here. Considerable quantities of acid or base may be added to such a mixture without appreciably altering the pH. Similarly, it must be evident that addition of such a mixture to a dilute solution of acid or base would cause a large change in the pH of the latter solution.

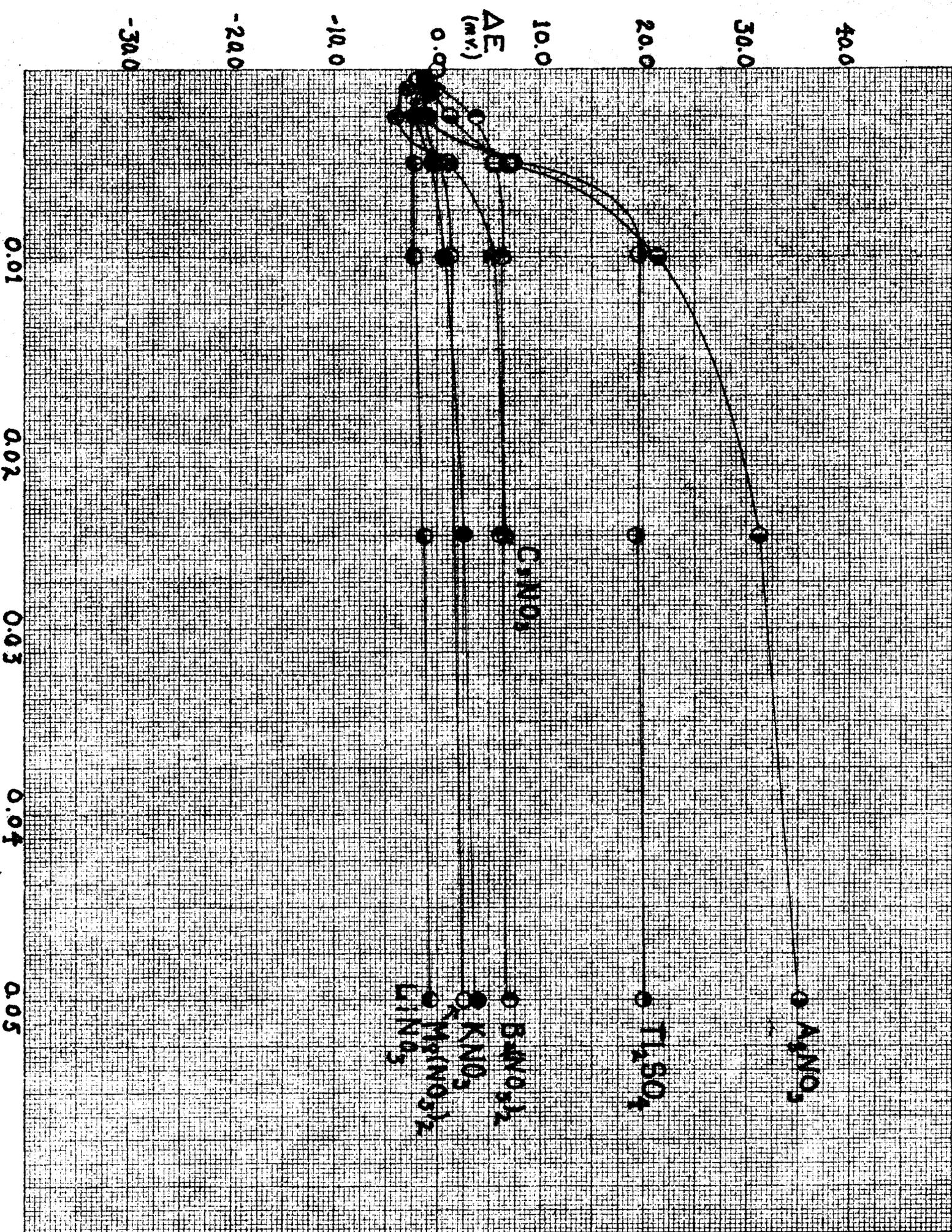
There remains only one method of eliminating such an effect. This is to restrict the investigation to the salts of strong acids and bases, whose only effect on the pH, other than by interaction with the sol, is through the change of ionic strength. This gives a pH change of a different order of magnitude and may be neglected.

It may be further urged that even these ions show measurable variations in strength and some buffer action, but the magnitude of this was determined by the method given for all salts and shown to be either smaller than the effect produced or, in one case, in the opposite sense.

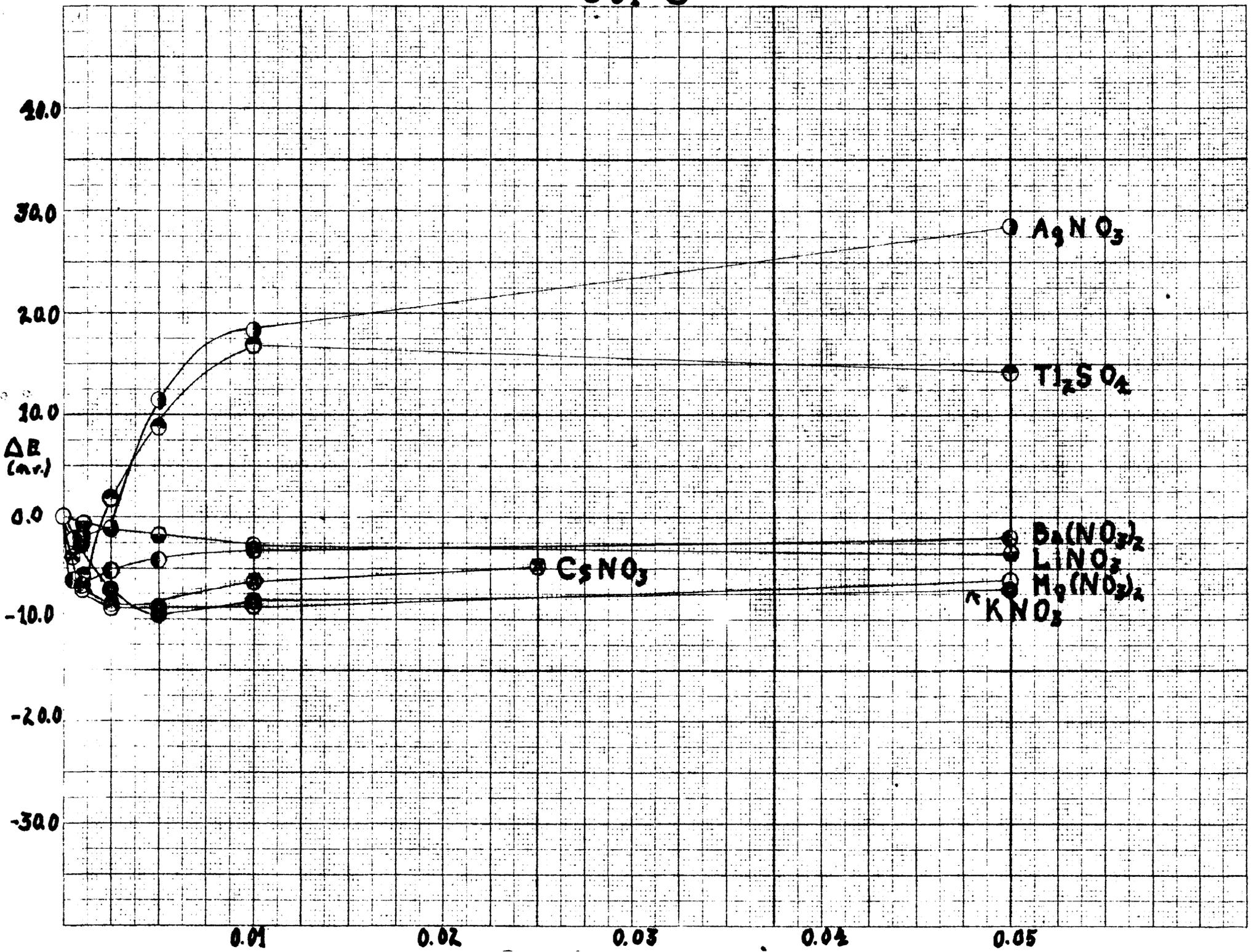


901 A

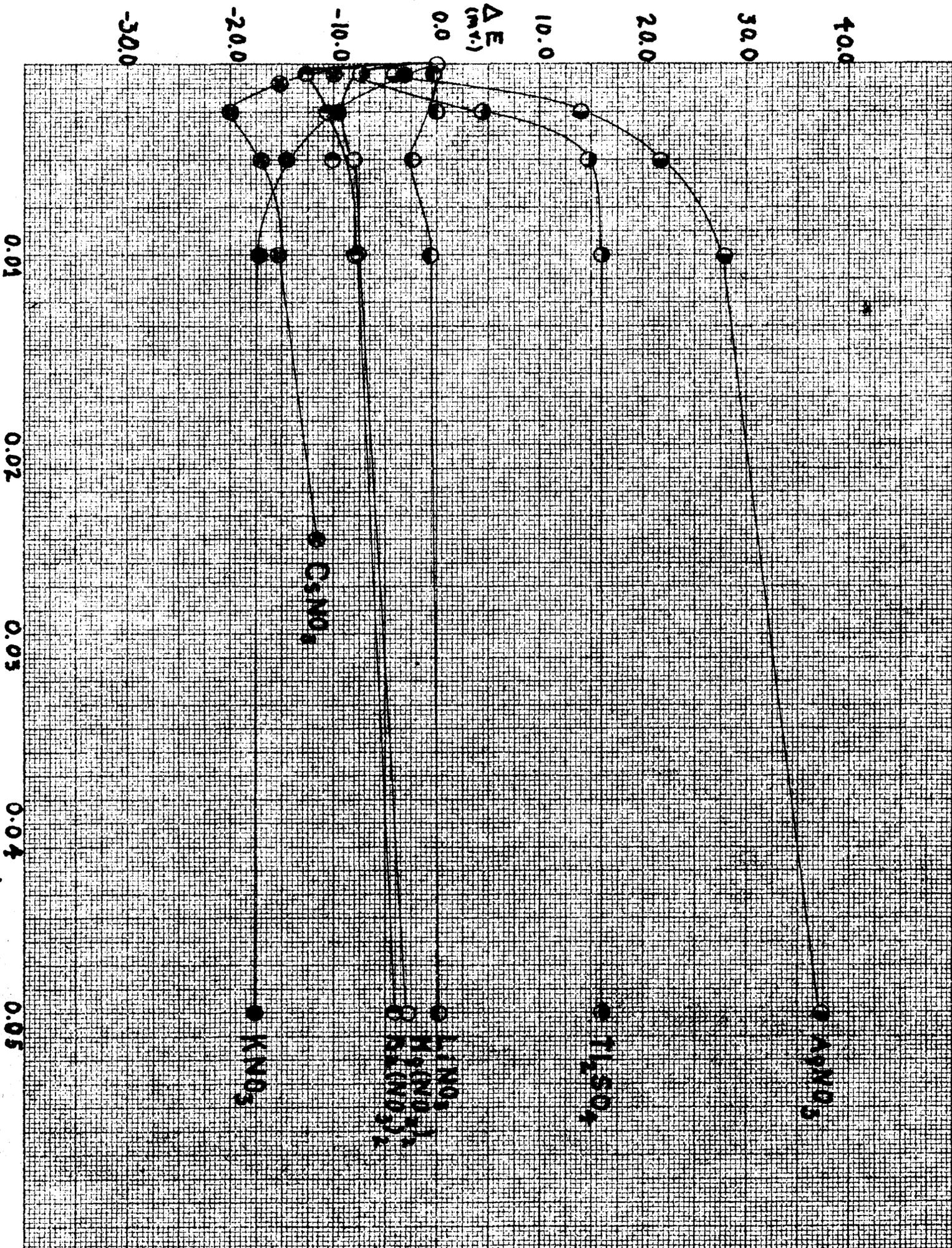
# Soil B



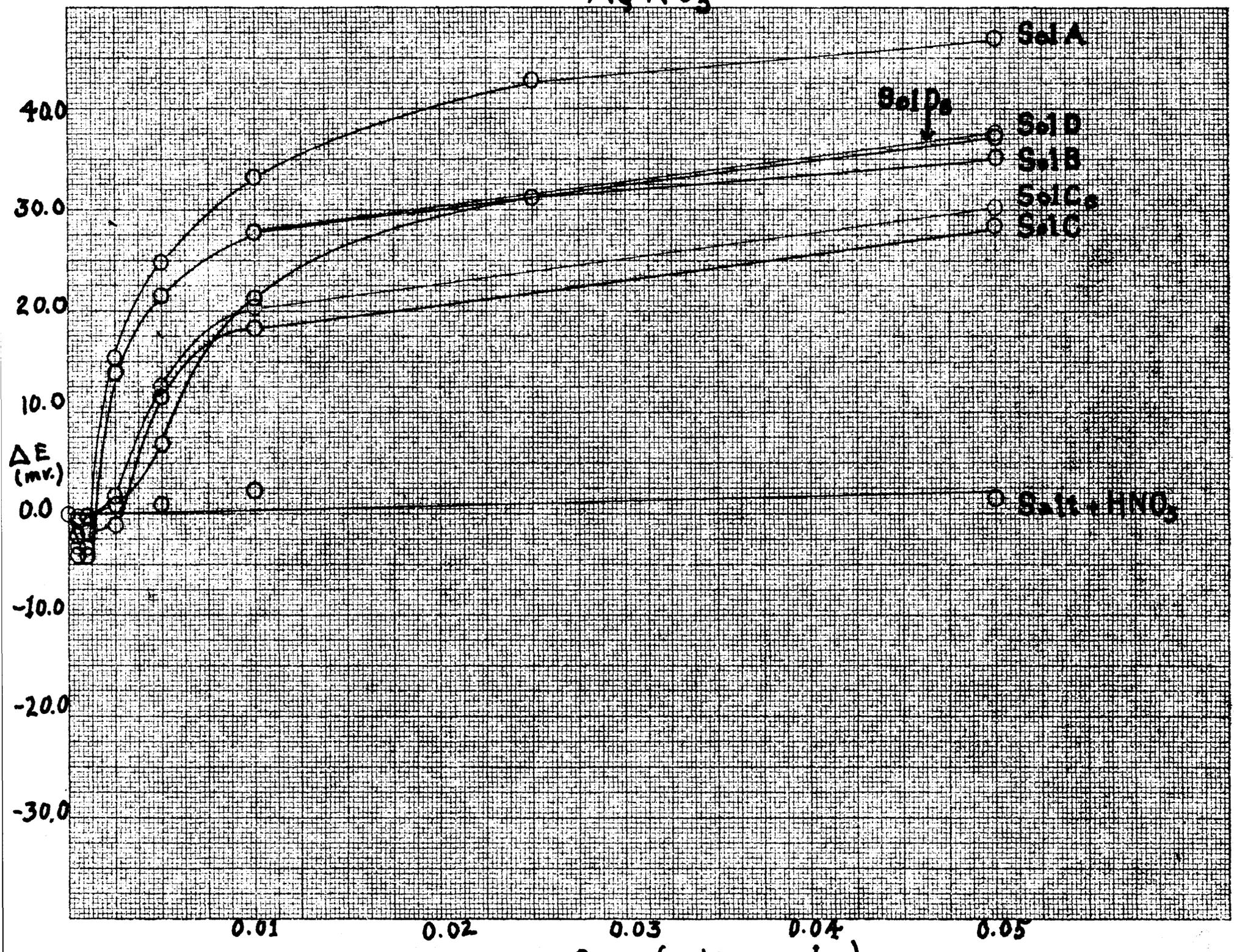
# Sol C



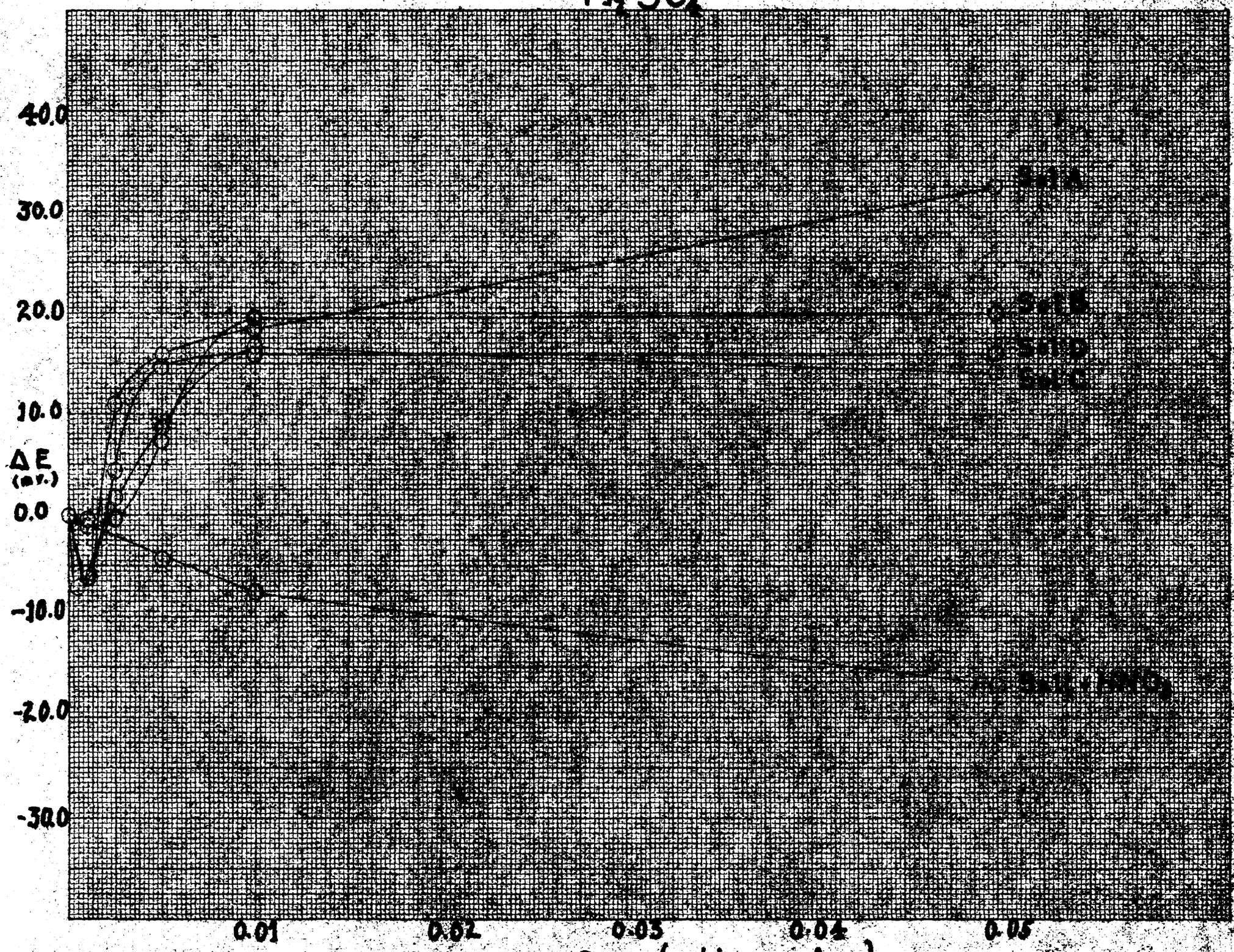
Solid



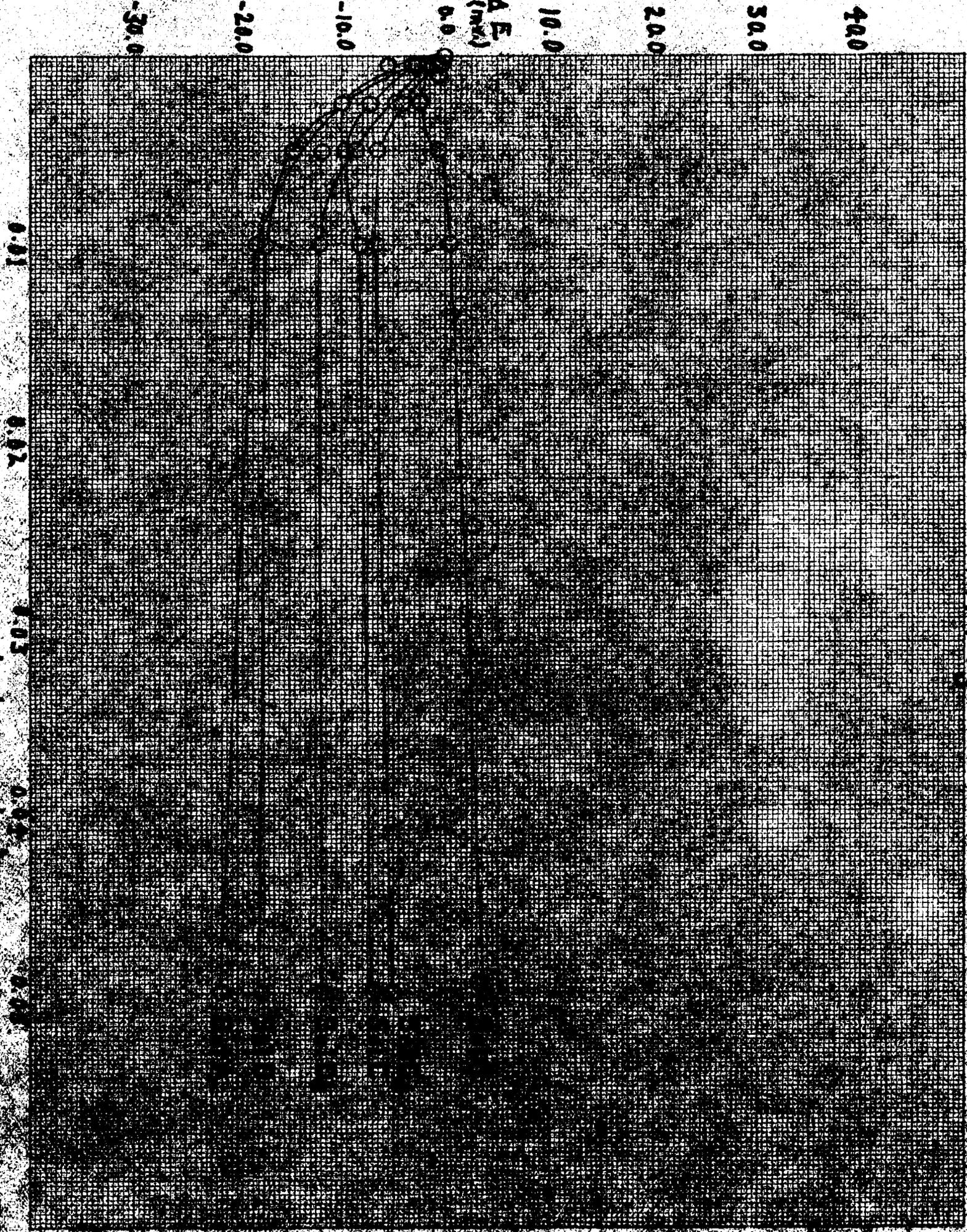
# AgNO<sub>3</sub>



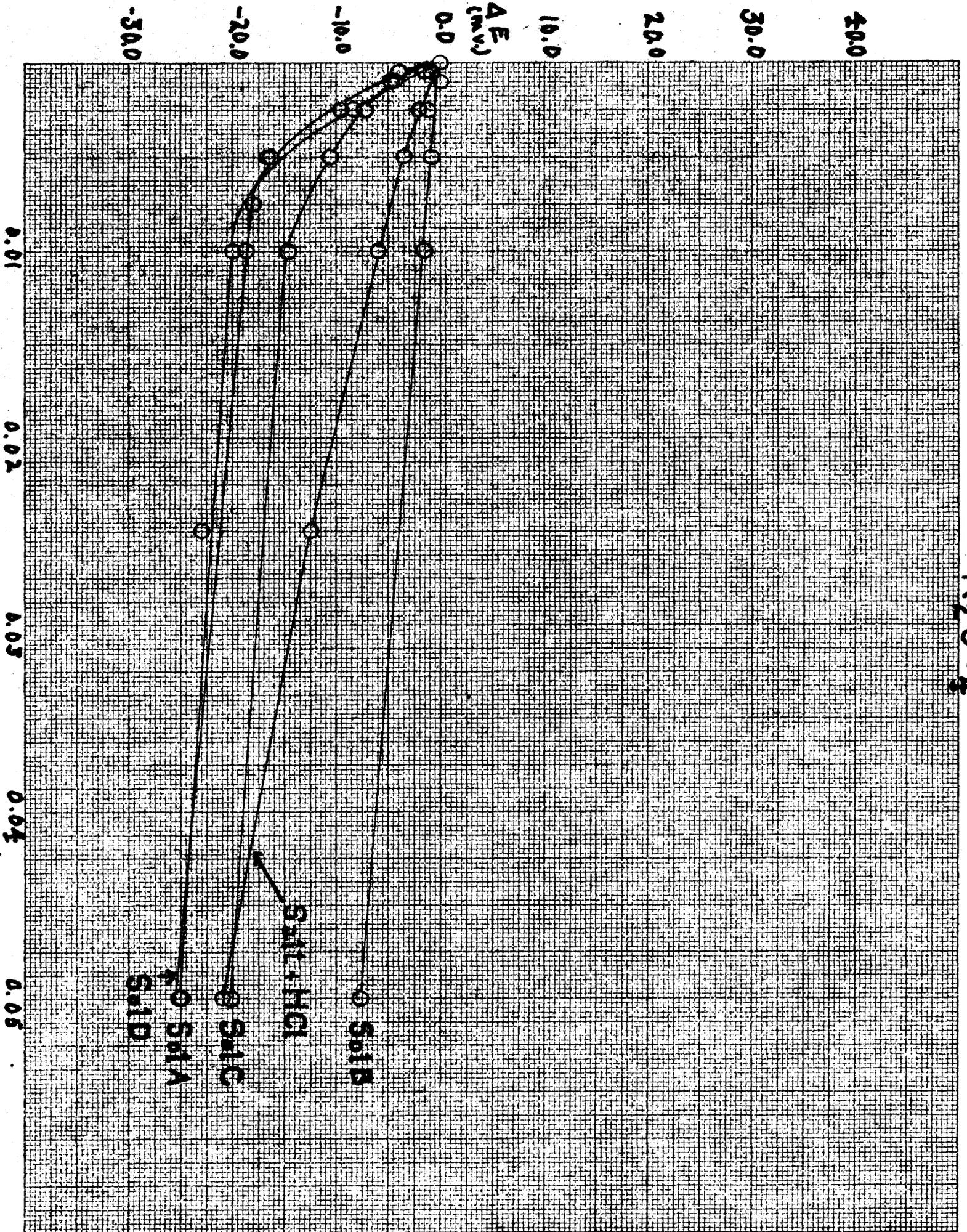
T1, SO



KNO<sub>3</sub>



$K_2SO_4$



11NO7

40.0

30.0

20.0

10.0

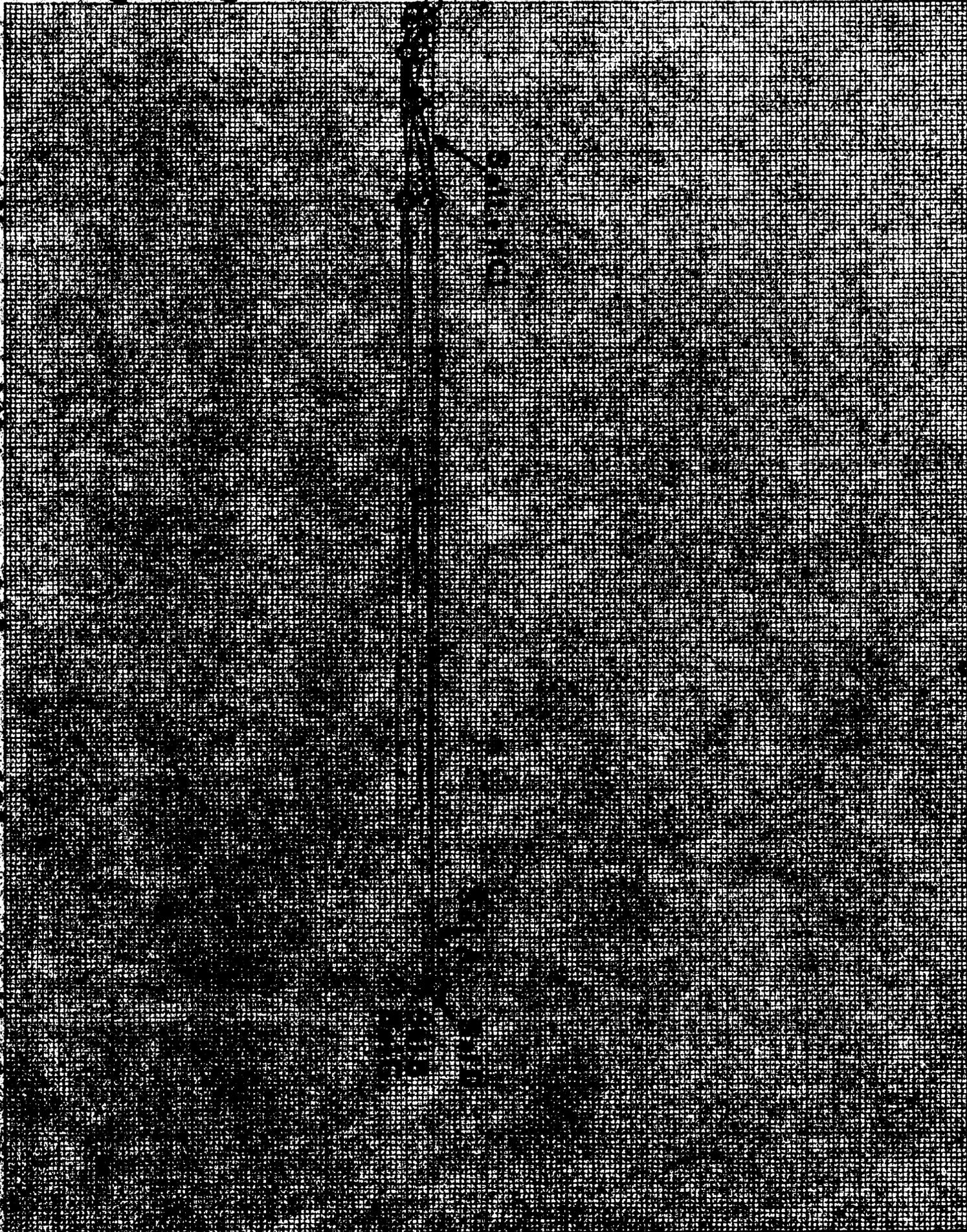
AE  
(mV)

00.0

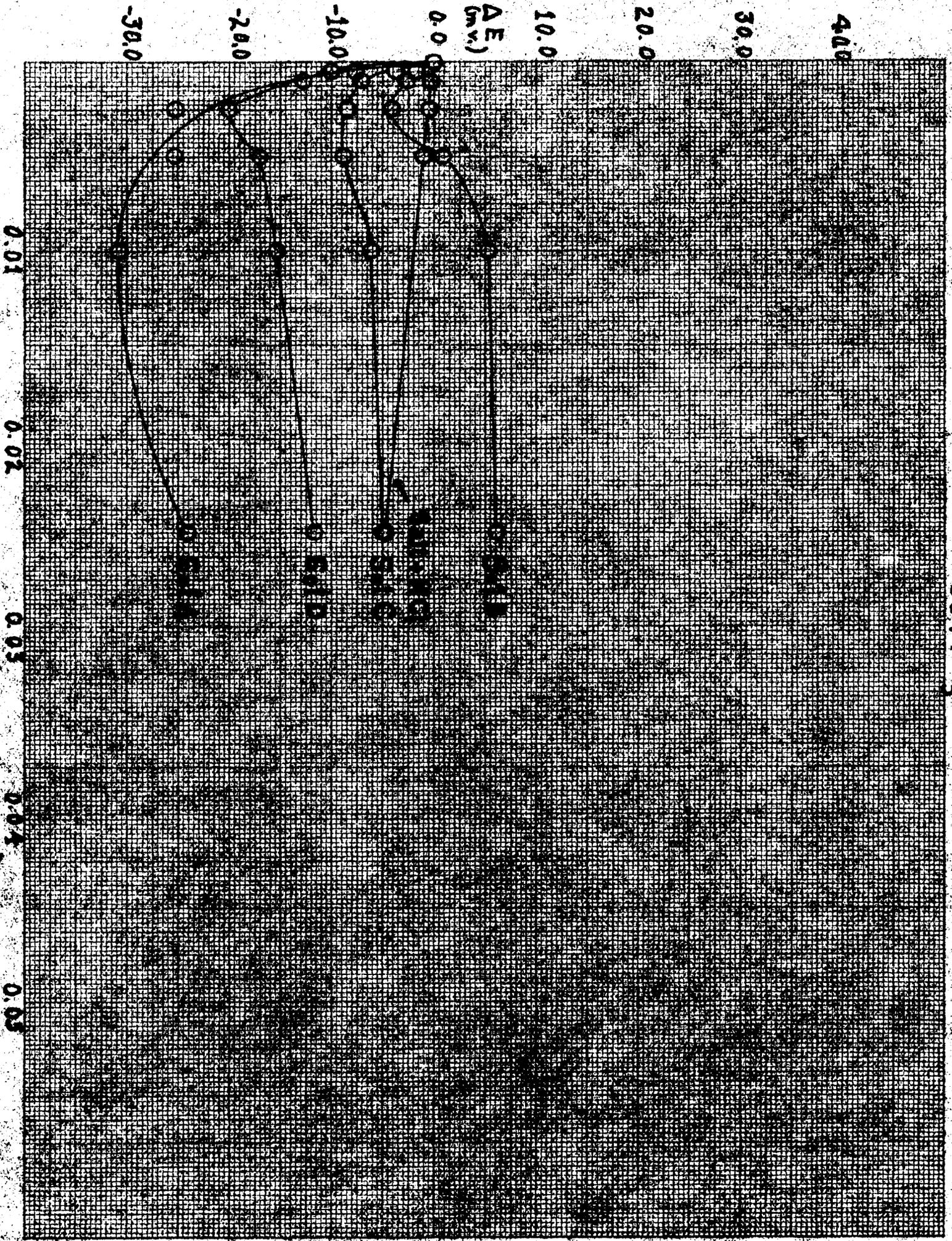
-10.0

-20.0

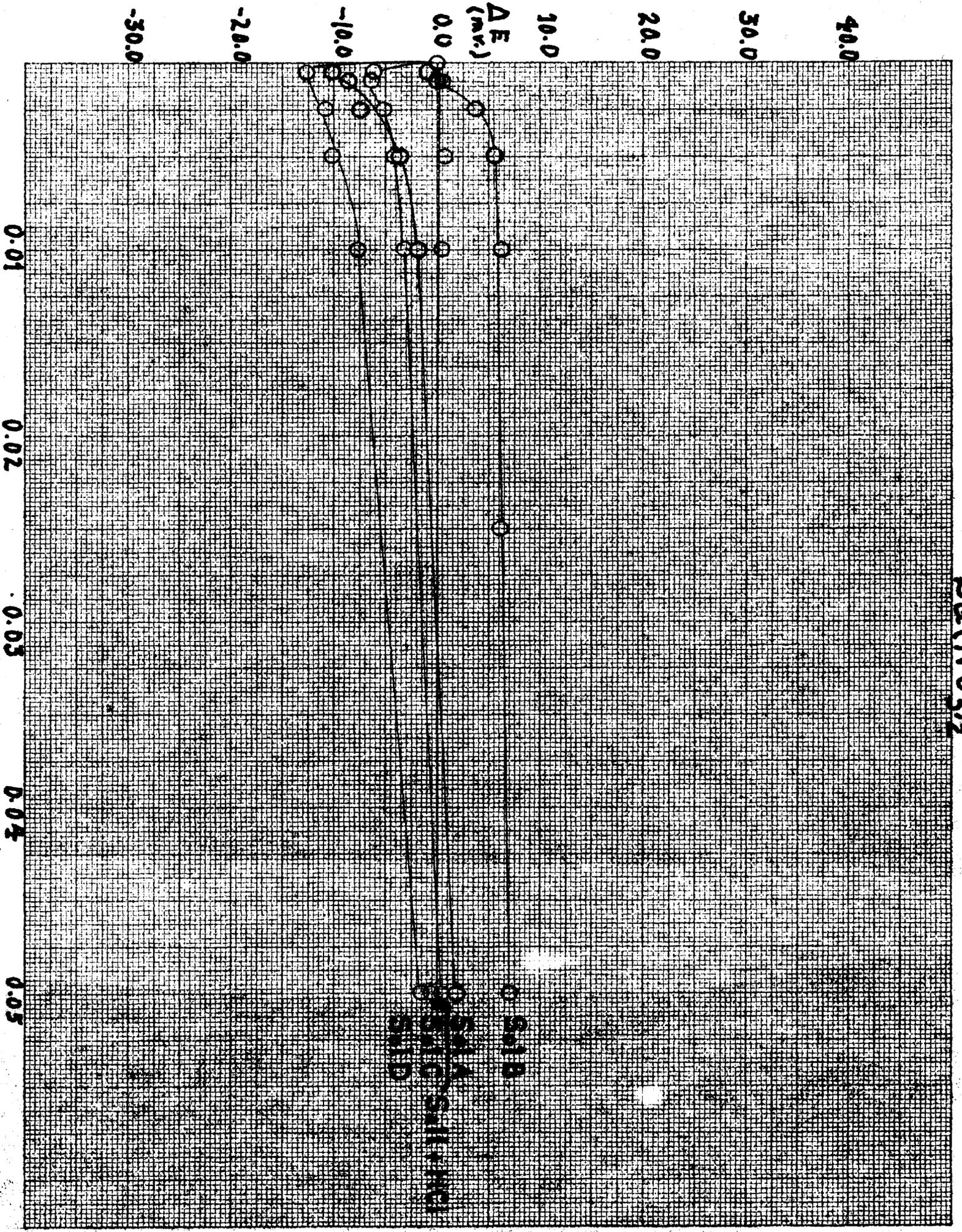
-30.0



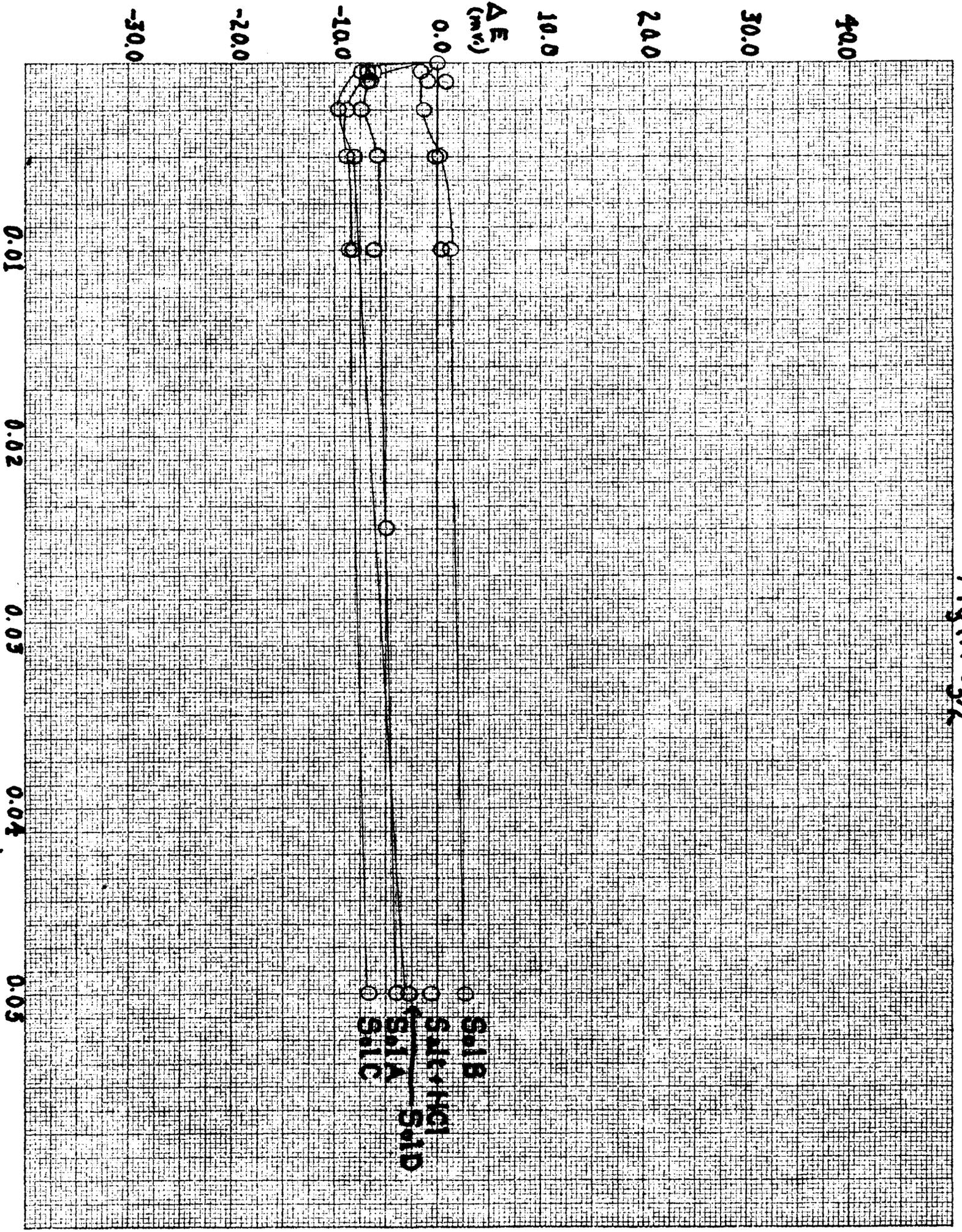
CsNO<sub>3</sub>



$Ba(NO_3)_2$



$Mg(NO_3)_2$



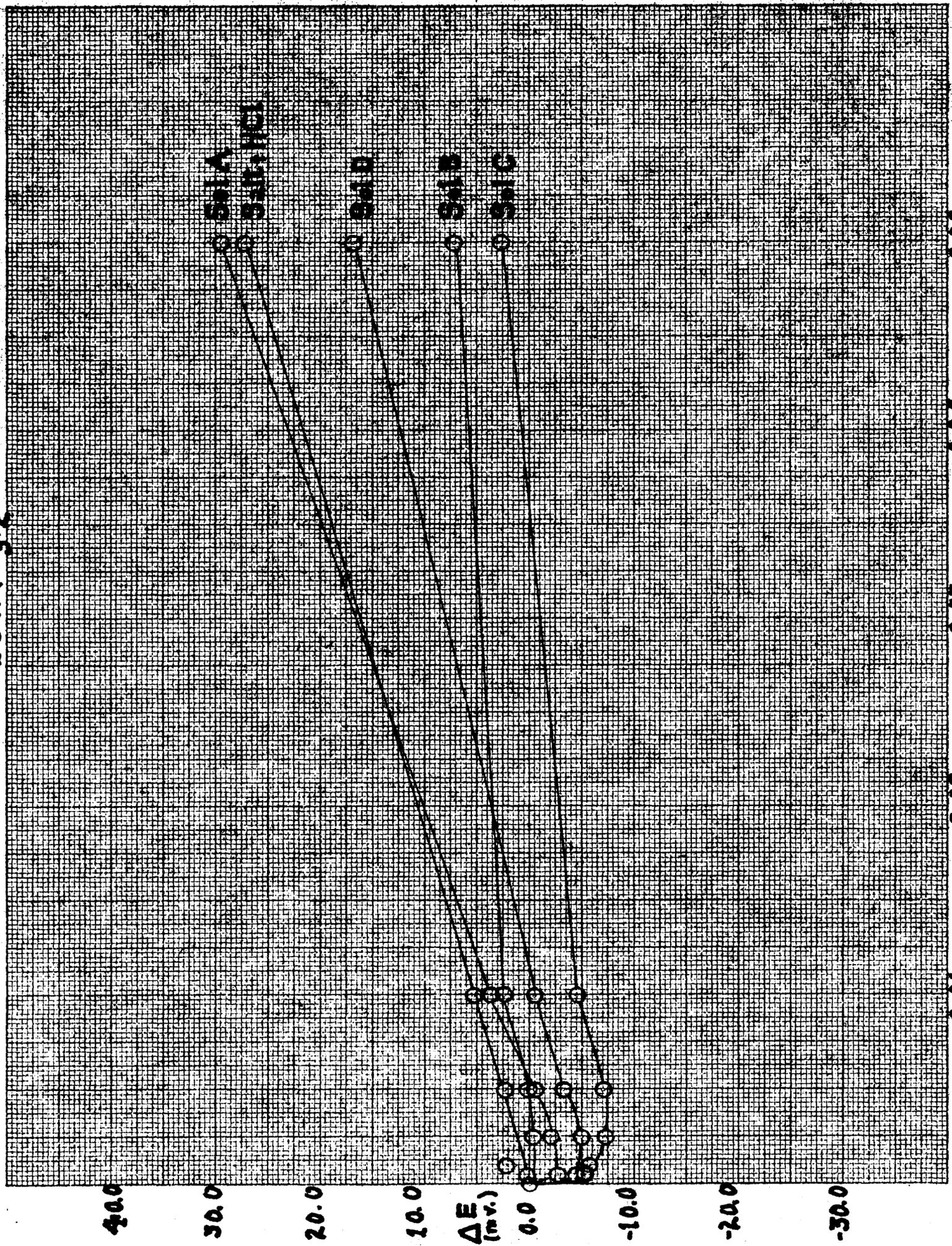
○ Salt B

○ Salt HCl

○ Salt A

○ Salt D

$\text{Be}(\text{NO}_3)_2$



## VII. NON-BUFFERING SALTS

Having laid down the necessary conditions to eliminate interfering effects, we may proceed to the consideration of the effects produced by neutral and non-buffering salts on the sols which have been studied, and to an attempt to explain these phenomena.

The salts which were studied, as is seen from the graphs on Sols A to D, fall roughly into two classes.

The first is exemplified by  $\text{AgNO}_3$  and  $\text{Tl}_2\text{SO}_4$  showing a large positive  $\Delta E$  or increase in acidity for higher concentrations. The second includes all the others. Decided variations in shape of curve, order of magnitude of  $\Delta E$ , sign of  $\Delta E$ , etc., occur, depending on the concentration and method of preparation of the sol.

Summarizing, then, it appears that the pH of these sols can be increased, decreased, or kept fairly constant on the addition of neutral salts, depending on the salt and the concentration and that these effects arise from some action of the salt upon the colloidal particles present. The action appears to be a function of the cation, since studies with  $\text{KNO}_3$  and  $\text{K}_2\text{SO}_4$  showed little difference and some early determinations with  $\text{KMnO}_4$  on Sol A gave a curve closely approaching that of  $\text{KNO}_3$ .

These results are much more complex than those of Thomas and his co-workers, since all their results showed large or small increases in pH.

It is therefore necessary to expand the theory

which he developed, while at the same time it is needful to take into account that part of his results to which the objections raised above do not apply.

Such a theory should also be consonant with the large amount of data available on adsorption and ion interchange of colloid surfaces, and if possible, it should be substantiated by use in other fields.

The fundamental postulate is therefore laid down that in dealing with the problem at hand and with colloid and surface forces in general, we deal with the same forces encountered in organic, inorganic, analytical, or any other type of chemistry. The apparent differences are not of kind but of degree due to the special conditions obtaining in colloidal solutions.

Another and perhaps simpler way of stating this is to say that modern theories of valence and chemical combination can be used to deal with the problems of colloid chemistry and will be used here.

It may well be objected that the theory of valence is in a confused state consequent to the modern work upon the nature and properties of valences, bonds, etc. It has indeed been stated that not only do we possess no complete and simple theory as to the nature of valence, but that the appearance of one seems increasingly improbable.

While all of this is true, and even though any analytical chemist can testify to the difficulty of

proving the Law of Definite Proportions for most substances, it must be said that we gain little by setting up a separate class of phenomena shown by substances in the colloid state and attribute their behavior to some ill-defined and less understood force called "adsorption."

We proceed then by assuming that the forces between atoms and molecules in a colloid are fundamentally the same as those in the compounds, solutions, etc. generally met with.

Let us now deal with the question of what these forces are and what their behavior might be.

It may be said in general that the forces operating between atoms and giving rise to the phenomena of chemistry are electrostatic in nature, and dependent on sharing and interchange of electrons between atoms and ions.

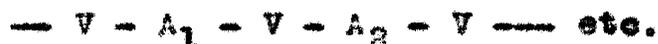
There are two extreme or limiting uses of atom binding or valence between which all others will lie, namely, purely ionic binding as in KCl, and purely covalent linkage as in the C-C linkage of ethane. In ionic or polar linkages, an electron is surrendered by one atom or group to another, while in coordinate linkages two electrons at least are shared, which may come from one or both of the groups coordinated.

Bindings of almost any given strength or character between the two cases cited above have been shown to exist. For example, we may pass in a fairly smooth series from

strong electrolytes to weak electrolytes to non-electrolytes. We generally, however, divide substances into the classes of electrolytes and non-electrolytes though no absolute line can be drawn.

It is also possible that, given a charged micelle, it may function as weak and moderately strong electrolytes do, and bind ions electrostatically. That is to say, colloids may function in the manner postulated by the Debye-Huckel theory, reducing the mobility of ions present by the action of the particle field and hence giving a decreased activity to them.

In the case of the hydrous  $V_2O_5$  sol, we may assume in the manner of Thomas, that the colloid particle is a large size Werner complex built up on the plan



$A_n$  may be any coordinating group or atom either negative or neutral in charge.

This is particularly probable with vanadium when we consider the ease of formation and stability of the polyvanadic acids of which a number have been reported. (15)

If, as is likely, the groups A are  $H_2O$ ,  $OH^-$ , or  $O^-$  ionization may occur from the first two. We would then have the giant ion or micelle  $(V_n O_m H_x \cdot xH_2O)^{n-} / nH^+$ .

If we add a salt to the sol, two possible types of action arise.

(a) The classical type of adsorption in which the

ion is drawn close to the inner wall of the Gouy double layer and there held by electrostatic attraction. A particle change may take place by release of some ion of similar sign which was previously bound in this manner.

We may better define this type of action as being analogous to the ionic restraint treated by the Debye-Huckel theory. The merging of fields cuts down the mobility and apparent charge of both ion and micelle.

(b) The type of adsorption or interchange postulated by Thomas which we may term Werner or displacement type adsorption. In this case the ion penetrates or is imbedded in the inner wall of the Gouy double layer expelling some particle, charged or otherwise, and replacing it as an integral part of the micellar complex.

Under this head come all the truly "chemical" types of reaction involving electron interchange or sharing.

If we add a salt dissociating to  $A^{n+}$  and  $B^{m-}$  to the negative colloid, three cases are encountered.

(1) The cation is adsorbed by the classical type of adsorption. Reduction of the wall charge with consequent flocculation occurs.

Lowering of the zeta potential may make the double layer more diffuse, thus releasing electrostatically bound hydrions. This will cause a drop in the pH.

(2) Chemical type adsorption of the cation occurs with displacement of a particle of some kind. This may be

positive, negative, or neutral. A displacement of a charged particle will give for a hydrous oxide sol either  $H^+$  or  $OH^-$ . The effect of these on the pH is evident.

(3) Adsorption of the anion by displacement and coordination. This, too, would give rise to the emission of a particle from the micelle and so might affect the pH.

The fourth case of electrostatic adsorption of the anion would not arise unless an irregular series occurred with change of sign of the colloid, when it would be equivalent to case (1).

We may now consider the curves more fully. Of great interest is the depression indicating a rise in pH which occurs at low concentrations for all salts with all the sols.

This can only take place through the liberation of hydroxyl ion from the sol. The single alternative is that on adsorption of the salt, hydrogen ion is removed from the intermicellar liquid which seems highly improbable. In a negative sol the cation would be adsorbed and (a) displace hydrogen ion (b) lower the zeta potential decreasing the probability of hydrogen ion adsorption.

We must now find a mechanism by which an adsorbed cation can displace hydroxyl ion. Let us assume a large differential between the coordination strengths of  $OH^-$  and  $O^{2-}$  but a small one between  $H_2O$  and  $OH^-$ . The differences in properties in the oxide series makes this a plausible

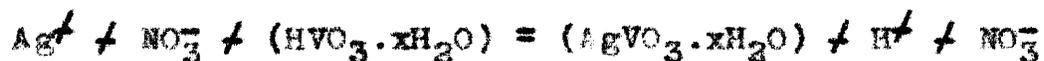
assumption. Thus  $Al(OH)_3$  is soft and does not become corundum ( $Al_2O_3$ ) until the last traces of water are driven off by fusion, as is the case with many other oxides.

All ions are hydrated to some degree in aqueous solution. If, then, the hydrated cation carries a shell, so to speak, of water molecules with it as it penetrates the micelle, it is possible that these in turn coordinate with some of the V atoms present. Some of these coordinate linkages may contain  $OH^-$  ions which are thus ejected into the solution causing the observed change.

We further notice that nearly all the graphs re-curve after an initial drop. This we may ascribe to action by the cation of a more direct sort, involving the displacement of hydrions. It has been indicated above that reduction of the particle charge might tend to release electrostatically adsorbed hydrions into the solution.

Direct displacement is also a possibility. Thus if we have  $V \text{---} OH$  or  $V \text{---} HOH$  coordinated and a cation  $Me^+$  enters, it may react with the oxygen, displacing  $H^+$ .

In the peculiar cases of Ag and Tl such a phenomenon probably occurs. Here the low solubility of silver and thallos vanadates causes these ions to react with what we may term the nascent acid, namely, the hydrated oxide of the colloid. Thus



It was noted that addition of Ag and Tl caused

striking color changes and in sufficient quantity caused precipitation of the sol as a crystalline yellow or orange material quite different from  $V_2O_5$ .

It may be argued that such a metathesis yielding a salt which, though insoluble, is highly ionized as to the traces which dissolve, does not involve coordination.

While this may be true, the point is that we have here explained an unusual phenomenon in terms of ordinary chemical theory, which is all that was attempted.

The theory of crystal structure and binding of ions in a lattice is beyond the scope of this paper. It must be stressed that our chief object is to explain the complex data obtained in terms of ordinary chemical concepts. In fact, it would be difficult to explain them otherwise.

The probability is that all processes occur and that the extent to which one or the other predominates depends upon the character and concentration of the sol, the concentration of salt, the nature of the cation, the pH of the sol, etc.

In the consideration of the graphs which follow, giving the behavior of the four sols with each individual salt, we shall deal with this question as far as the data allows.

We take up first the potassium salts  $KNO_3$  and  $K_2SO_4$ . The pyrolytic sols B and C show a smaller increase of pH than the hydrolytic A and D. To explain this, it

is only necessary to refer to the table of zero-point values. The higher initial acidity of the pyrolytes requires that a much larger quantity of hydroxyl ion be emitted for equal EMF increments, in fact, from five to ten times as much. Since, in most cases, the EMF drops for the pyrolytes are of the same order of size or greater than those for the hydrolytes, we may assume that they have more OH groups coordinated.

For  $\text{KNO}_3$  decided recurving occurs for the pyrolytes. This may be due to their greater acidity as more  $\text{H}^+$  is bound in the double layer which is released by electrostatic interchange.

Since  $\text{K}^+$  is not a strongly coordinative ion and does not form an insoluble vanadate, the alternative possibility of a  $\text{K}^+ - \text{H}^+$  metathesis is less likely.

With  $\text{K}_2\text{SO}_4$  we note that no recurving occurs. This may be due to the buffer effect of the sulfate ion. Since we have no proof that sulfuric is a weaker acid than vanadic, it is not safe to assume this. Thomas has shown that the coordinative and displacing effect of  $\text{SO}_4^{2-}$  is much greater than that for  $\text{NO}_3^-$ . It is possible that we have here behavior of the type mentioned in case (3) above, that is, that some of the  $\text{SO}_4^{2-}$  ions have sufficient energy to penetrate the potential barrier of the micelle and once there displace  $\text{OH}^-$  ion.

$\text{LiNO}_3$ , which comes next, displays almost the opposite type of behavior. The initial drop in EMF is small and is followed by a sharp rise for the hydrolytic sols, a slow one for Sol B and none at all for Sol C. We may further note that Sol C displays the slowest rate of fall at the start.

The explanation of this behavior may be found in the known high degree of hydration of the lithium ion. Such an ion would not show either of the types of adsorption mentioned above. Its water mantle would prevent close approach to the inner wall of the double layer and in a manner akin to steric hindrance would probably prevent penetration of the micelle.

It is probable that those  $\text{Li}^+$  ions which enter the complex undergo a metathesis with displacement of  $\text{H}^+$ . This is shown by the more rapid recurving of the hydrolytic sols (compare  $\text{KNO}_3$ ).

The slow rate of fall of Sol C may be due to its lower concentration of  $\text{V}_2\text{O}_5$  decreasing the number of micelles which react.

As before, when we speak of adsorbed hydrion we must remember that it may be held either electrostatically or by coordination to the oxygen of the complex. As more  $\text{H}^+$  is available in the more acid pyrolytic sols it is probable that more is adsorbed. Since the hydrolytic sols give off  $\text{H}^+$  more quickly, we may attribute this behavior

to a metathesis.

In the case of  $\text{CsNO}_3$  we encounter no new phenomena. The greater activity of the ion is due to its larger size and increased coordinating power. It loses water to the vanadium complex and displaces  $\text{OH}^\dagger$  more readily (note the larger drop at low concentration) but it also metathesizes more readily, as the greater tendency to recurve demonstrates. Owing to the expense of the salt the concentration range was carried only to 0.025 c.-m. but the curves seem to have flattened at this point.

The cases of  $\text{AgNO}_3$  and  $\text{Tl}_2\text{SO}_4$  were mentioned above. The distinct fall in E at low concentrations is followed by a large rise. The lesser drop for the pyrolytic sols is as before to be attributed to the scarcity of coordinated  $\text{OH}^-$ . The large rise at higher concentrations is due to the metathetic disintegration of the sol. This would liberate hydrogen ion independently of the nature of the coordinating groups whether  $\text{H}_2\text{O}$ ,  $\text{OH}^-$  or  $\text{C}^-$ .

We come now to the divalent ions Ba and Mg. While the curve shapes are the same, we note as before a much greater tendency on the part of Sol B to give off  $\text{H}^\dagger$ . This is to be attributed to its greater concentration and acidity. The greater number of micelles adsorb more  $\text{H}^\dagger$  from the more acid solution, and likewise adsorb more metal ion giving off  $\text{H}^\dagger$  more readily when salted.

Ba shows a distinctly stronger action than Mg. This

cannot be attributed to change of the zeta potential since the precipitation values are the same. It must then be due to a greater tendency to coordinate or metathesize. This is shown both by the larger drop in  $E$  near the origin and the larger rise further out. For all except Sol B, this is true and here the greater tendency to desorb  $H^+$  masks the initial action.

Finally, we may observe the behavior of  $Be(NO_3)_2$ . This cation is a weak base and shows a distinct buffer effect as might be expected. The initial drop of  $E$  appears for all sols, however. This would appear to validate this part of the curve beyond question when we see that on adding a salt which by itself tends to decrease the pH we have obtained definite increases in the pH.

The hydrolytic sols show the greatest rise in  $E$  which may be due either to their lower acidity, which would increase the buffer effect, or to their greater ability to metathesize. Probably both factors are involved when we observe that Sol C, the more dilute pyrolytic sol, shows the greatest initial drop of all, followed by a steeper slope than Sol B. Thus, although C has a larger tendency to give off  $OH^-$  than A or B, it also has less tendency to increase its pH by buffer effect. Sol B, on the contrary, gives off  $H^+$  very readily at low concentration, as observed above. Hence its very slight drop in  $E$ . As the concentration increases, buffer effect increases, along with the

emission of  $H^+$  from the complex. Both are larger for the less acid, A and D so that great increases of E are obtained.

B, on the contrary, is buffered most strongly in the reverse sense (most concentrated) and is most acid at the start. It therefore shows the smallest rise in E. C at the higher concentrations is intermediate in its properties.

TABLE NO. III

In the following table the units are the same as those used in the graphs, namely, cation molarity for the concentration and  $\Delta E$  for the abscissa. The  $\Delta E$  is expressed in millivolts. This  $\Delta E$  is the average for the several runs carried out on each sol with each salt. The number of runs in each case is given by the number in parenthesis following the heading naming the sol.

## TABULATION OF DATA

Conc.	KNO <sub>3</sub>					
	Sols					
	A(3)	B(2)	C(2)	C <sub>B</sub> (1)	D(2)	D <sub>B</sub> (1)
0.05	-21.5	∓ 3.9	- 7.0	- 5.0	-17.7	-11.7
0.025	-17	∓ 3.6				
0.010	-18.0	∓ 0.6	- 8.2	- 6.7	-17.2	-12.2
0.0075	-13					
0.0050	-21.7	- 0.5	- 9.6	- 6.5	-14.7	- 8.6
0.0025	- 9.8	- 2.2	- 7.1	- 4.1	- 9.6	- 4.7
0.0010		- 0.6				
0.0005	- 5.3	- 1.2	- 2.7	- 0.5	- 3.2	- 1.8

## TABULATION OF DATA (Cont'd.)



Conc.	Sols				Salt / HCl(1)
	A(3)	B(2)	C(2)	D(2)	
0.05	-35.0	- 7.7	-30.3	-28.4	-18.5
0.025	-23				-12.5
0.010	-20.0	- 1.5	-12.1	-18.6	- 6.0
0.0075	-18				
0.005	-16.7	- 0.9	-10.6	-13.3	- 3.5
0.0025	- 8.3	- 1.2	- 7.3	- 8.7	- 2.1
0.0010	- 4.4		- 4.7		
0.0005		- 0.8	- 1.0	- 2.9	

## POTASSIUM CITRATE

Conc.	Sols				Salt / HCl(1)
	A(3)	B(1)	C(1)	D(1)	
0.05	-219.1	-232.7	-240.6	-231.0	-222.2
0.025	-212				
0.010	-197	- 61.4	-147.9	-205.8	-202.4
0.0075	-186				
0.0050	-144	- 26.2	- 60.6	-140.6	-186.8
0.0025	- 97	- 13.0	- 28.8	- 90.3	-165.0
0.0010	- 40	- 4.7	- 10.6		
0.0005				- 14.3	- 41.7

## TABULATION OF DATA (Cont'd.)

## POTASSIUM ACETATE

Conc.	Sols			
	A(3)	B(1)	C(1)	Salt / HCl(1)
0.05	-138	-109.7	-172.6	-201.8
0.025	-135			-186.0
0.010	-122	- 96.5	-126.1	-163.3
0.0075	-122			
0.005	-107	- 42.2	- 89.5	-140.1
0.0025	- 95	- 17.8	- 40.6	-118.5
0.0010	- 48	- 6.9	- 13.3	- 96.4
0.0005				

 $Tl_2SO_4$ 

Conc.	Sols				Salt / HNO <sub>3</sub> (1)
	A(3)	B(4)	C(3)	D(2)	
0.05	/32.5	/20.0	/14.2	/16.0	-16.7
0.025		/19.2			
0.010	/18.5	/19.5	/16.8	/15.9	- 7.5
0.005	/15.9	/ 7.3	/ 8.7	/14.7	- 4.3
0.0025	/11.0	- 0.8	/ 1.7	/ 4.4	
0.0010	- 6.2	- 1.1	- 5.7		- 0.4
0.0005				- 7.2	

## TABULATION OF DATA (Cont'd.)

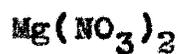
 $\text{AgNO}_3$ 

Conc.	Sols						Salt $\neq$ $\text{HNO}_3$
	A(4)	B(3)	C(3)	$C_B$ (1)	D(2)	$D_B$ (1)	
0.05	$\neq$ 46.9	$\neq$ 35.2	$\neq$ 28.5	$\neq$ 30.5	$\neq$ 37.1	$\neq$ 37.6	$\neq$ 1.5
0.025	$\neq$ 42.9	$\neq$ 31.2					
0.010	$\neq$ 33.2	$\neq$ 21.3	$\neq$ 18.3	$\neq$ 20.4	$\neq$ 27.7	$\neq$ 27.3	$\neq$ 2.3
0.005	$\neq$ 24.8	$\neq$ 6.8	$\neq$ 11.5	$\neq$ 13.6	$\neq$ 21.5	$\neq$ 21.2	$\neq$ 1.0
0.0025	$\neq$ 15.4	$\neq$ 0.9	- 1.1	$\neq$ 1.7	$\neq$ 13.9	$\neq$ 13.9	
0.0010	- 3.4	- 0.3	- 1.8				- 0.4
0.0005			- 2.1	- 0.3	- 4.1	- 3.3	

 $\text{Ba}(\text{NO}_3)_2$ 

Conc.	Sols				Salt $\neq$ HCl(1)
	A(2)	B(3)	C(3)	D(2)	
0.05	$\neq$ 1.8	$\neq$ 7.0	- 2.0	- 4.1	- 0.7
0.025		$\neq$ 6.1			
0.010	- 1.8	$\neq$ 6.2	- 3.2	- 7.7	$\neq$ 0.3
0.005	- 3.7	$\neq$ 5.5	- 4.2	-10.1	$\neq$ 0.7
0.0025	- 7.5	$\neq$ 3.7	- 5.2	-10.7	$\neq$ 0.6
0.0010	- 8.6	- 0.1	- 6.7		
0.0005	-10.2	- 1.0	- 6.2	-12.7	$\neq$ 0.4

## TABULATION OF DATA (Cont'd.)



Conc.	Sols				Salt $\neq$ HCl(1)
	A(3)	B(3)	C(3)	D(2)	
0.05	- 4.0	$\neq$ 2.6	- 6.6	- 2.8	- 0.6
0.025	- 5				
0.010	- 6.2	$\neq$ 1.3	- 8.6	- 8.1	$\neq$ 0.3
0.005	- 5.8	$\neq$ 0.2	- 8.8	- 8.0	- 0.2
0.0025	- 7.4	- 1.4	- 8.8	- 9.5	
0.0010	- 6.7	- 1.0	- 6.5		
0.0005	- 6.8	- 1.7	- 6.1	- 7.4	$\neq$ 0.8



Conc.	Sols				Salt $\neq$ HCl(1)
	A(2)	B(3)	C(3)	D(2)	
0.05	$\neq$ 0.5	- 0.7	- 3.5	$\neq$ 0.2	0.0
0.025		- 1.3			
0.010	$\neq$ 0.2	- 2.5	- 2.7	- 0.6	$\neq$ 0.6
0.005	- 1.5	- 2.3	- 1.7	- 2.4	$\neq$ 0.4
0.0025	- 2.2	- 2.6	- 1.1	$\neq$ 0.3	
0.0010	- 2.3	- 2.1	- 0.6	- 0.1	- 2.3
0.0005	- 2.0				

## TABULATION OF DATA (Cont'd.)



Conc.	Sols				Salt $\neq$ HCl(1)
	A(3)	B(2)	C(2)	D(2)	
0.05	$\neq$ 29.0	$\neq$ 7.1	$\neq$ 3.6	$\neq$ 16.7	$\neq$ 27.1
0.01	$\neq$ 3.5	$\neq$ 2.2	- 4.5	- 0.5	$\neq$ 5.2
0.005	- 0.5	$\neq$ 0.3	- 7.1	- 3.3	$\neq$ 2.4
0.0025	- 2.1	- 0.4	- 7.3	- 5.0	
0.0010		$\neq$ 1.3	- 5.8		$\neq$ 2.2
0.0005	- 2.8	$\neq$ 0.2	- 5.2	- 4.5	



Conc.	Sols				Salt $\neq$ HCl(1)
	A(3)	B(2)	C(2)	D(2)	
0.025	-24.1	$\neq$ 6.6	- 4.8	-11.7	- 5.0
0.010	-30.8	$\neq$ 5.2	- 6.2	-15.4	
0.005	-25.3	$\neq$ 0.9	- 8.8	-17.0	- 1.0
0.0025	-25.3	- 4.1	- 8.5	-20.0	- 0.5
0.0010		- 2.7	- 7.1	-15.3	- 0.3
0.0005	- 7.7	- 1.8	- 3.8	-10.0	

## TABULATION OF DATA (Cont'd.)

 $K_2HPO_4$ 

Conc.	Salt / HCl (l)	Sol A (l)
0.050	-290.7	-259
0.025		-220
0.010	-257.7	-166
0.0050	-242.2	-129
0.0025		- 74
0.0010	-165.7	- 21

 $KH_2PO_4$ 

Conc.	Salt / HCl (l)	Sol A (l)
0.050	-40.3	-26
0.025		-20
0.010	- 42.5	-13
0.0050	- 37.5	- 9
0.0025		- 5
0.0010	- 16.7	0

## VIII. THERMAL EFFECTS

It was thought to be of interest to see whether heating would cause any change in the pH of the sols or in their properties as regarded salt effect.

Such treatment might cause a change in the groups coordinated with V in the complex, altering the ratio of  $H_2O:OH^-:O^{2-}$ . Accordingly, portions of Sols C and D were refluxed one hour and the EMF of the pure sol determined.

Salt series were made up with  $KNO_3$  and  $AgNO_3$ . These curves are shown on the graphs for those salts and are marked  $C_B$  and  $D_B$  respectively.

The results indicate a lessening in the available  $OH^-$  groups as shown by the lesser drop in E at the start. The powerful metathetic action of  $AgNO_3$  masks this for the higher concentration for this salt and in the case of  $D_B$  throughout the curve.

Oddly enough, no sensible change in pH occurs with the pure sol as is shown in the following table.

TABLE NO. IV

Sol	E	pH
A	0.2556	3.35
B	0.3106	2.43
C	0.3007	2.58
$C_B$	0.3000	2.59 (boiled 1 hr.)
D	0.2722	3.07
$D_B$	0.2724	3.07 (boiled 1 hr.)
$D'_B$	0.2721	3.07 (boiled $6\frac{1}{2}$ hrs.)

This is what might be expected in the relatively simple system  $V_2O_5(s) + H_2O \rightleftharpoons 2HVO_3(\text{dissd.})$ . It is probable that at any given pH equilibrium is reached between the dissolved and colloid forms of the oxide. The structure of the polymers in the micelle and so on may influence this, but an equilibrium is clearly indicated.

## IX. PRECIPITATION EFFECTS

It is of interest to note the visible changes occurring in the sols when salts were added. Depending on the concentration and the specific cation, gels, flocculent precipitates or crystalline precipitates might be obtained. Some of these gels showed the phenomenon of thixotropy while nearly all were distinctly synergetic. This information is given in the accompanying set of four tables (one for each sol).

At this point, however, it must be stated that no correlation can be made between the pH changes and flocculation or gelation of the sols. As is usual, the divalent ions were most powerful flocculating agents with the heavy monovalent ions next and the lighter ones a poor third, especially Li which had a very high liminal value.

The points at which gelation or flocculation appeared over the 3 day storage period cannot be connected with any characteristic portion of the curves.

As is readily seen by comparison of the curves with the tables, these points may be on flat portions or on steep negative or positive slopes near minima or maxima.

The tendency of  $V_2O_5$  sols to form gels is well known. Though none of the gels appearing here contained less than 0.03%  $V_2O_5$ , gels of much lower concentrations have been reported. Some sort of mesh structure is probable as on shaking some quite firm gels nearly half their volume was

obtained as a clear solution with the residuum a gelatinous floc.

For this reason, it is believed that the distinction between a floc and a gel is more apparent than real, and that the former only appeared when the rate of precipitation was too great to allow building up a structure which would inclose all the water.

Thixotropy was observed for only one or two gels, and appeared to occur in a rather narrow concentration range, close to the gelation point. Decided increases in viscosity were noted on some occasions just below the gelation point.

TABLE NO. V  
Precipitation Effects

Salt	Gelation concentration	Flocculation concentration	Remarks
Sol A			
$KNO_3$	0.0075 c-m	0.050 c-m	
$K_2SO_4$	0.0075	0.050	
$LiNO_3$	Above 0.05		
$AgNO_3$	0.0025	0.025	Changes of color red to orange in floc. and gel.
$Tl_2SO_4$	0.0025	0.025	
$CsNO_3$	0.0025-0.005	0.025	
$Mg(NO_3)_2$	0.00075	0.005	
$Ba(NO_3)_2$	0.00075	0.005	
$Be(NO_3)_2$	0.00075	0.005	
Sol B			
$KNO_3$	0.0050	0.050	This gel was thixotropic.
$K_2SO_4$	0.0050	0.050	
$LiNO_3$	0.025		
$AgNO_3$	0.001	0.025	See Sol A
$Tl_2SO_4$	0.001-0.0025	0.025	
$CsNO_3$	0.0025	0.025	
$Mg(NO_3)_2$	0.00075	0.005	
$Ba(NO_3)_2$	0.00075	0.005	
$Be(NO_3)_2$	0.00075	0.005	

TABLE NO. V (Cont'd.)

Salt	Gelation concentration	Flocculation concentration	Remarks
Sol C			
$KNO_3$	0.0050	0.050	
$K_2SO_4$	0.0050	0.050	
$LiNO_3$	0.05		
$AgNO_3$	0.001	0.025	
$Tl_2SO_4$	0.001-0.0025	0.025	
$CeNO_3$	0.0025	0.025	See Sol A
$Mg(NO_3)_2$	0.00075	0.005	
$Ba(NO_3)_2$	0.00075	0.005	
$Be(NO_3)_2$	0.00075	0.005	
Sol D			
$KNO_3$	0.0075	0.050	
$K_2SO_4$	0.0075	0.050	
$LiNO_3$	Above 0.05		
$AgNO_3$	0.001	0.025	Change in color red to orange of flocc. and gel.
$Tl_2SO_4$	0.0025	0.025	
$CeNO_3$	0.0025-0.005	0.025	
$Mg(NO_3)_2$	0.00075	0.005	
$Ba(NO_3)_2$	0.00075	0.005	
$Be(NO_3)_2$	0.00075	0.005	

## X. CONCLUSIONS

1. The effect on the pH of the addition of salts to several  $V_2O_5$  sols has been studied, taking into account the effect of buffering salts, concentration of salt and sol, etc.

2. The results were complex, indicating the existence of several types of reaction, all of which processes may occur simultaneously, involving displacement of  $OH^-$  or  $H^+$  from the colloid and in some cases the disintegration of the sol.

3. The change of pH of the sol does not appear to be connected to the precipitation of the colloid.

4. An explanation of the results is offered, using as a basis ordinary chemical theory as to interaction of ions and their effects on each other in solution, together with the theory of chemical binding and valence in inorganic chemistry.

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