ACTIVITY OF HYDROCHLORIC ACID IN THE PRESENCE OF ADDED SALTS

Thesis by

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I. INTRODUCTION

The effect of added salts upon the activity of hydrochloric acid has been studied by a number of investigators.[1] All of these, however, have used chlorides for the added salt; that is, both the total ion concentration and the concentration of one of the ions of hydrochloric acid itself have been varied simultaneously. This investigation was undertaken since it would appear that certain information valuable from the standpoint of the ion attraction theory could be obtained by investigating the effect upon the activity of hydrochloric acid of added salts which have no common ion.

The activity of hydrochloric acid and hence the mean activity of its ions in salt mixtures may be readily computed from measurements of cells of the type[2]

$$H_2(1\ \text{atm}),\ HCl\ c_1f_1 + \text{salt}\ c_2f_1,\ \underline{AgCl}+\underline{Ag}.$$

The quantities concerned are related by the equations:

$$E - E_0 = \frac{-RT}{F} \ln A_H + A_{Cl^-} = \frac{-2RT}{F} \ln C_1 \alpha_{\pm}$$

Here E is the measured electromotive force, E_0 the molal electrode potential, A_{H^+} and A_{Cl^-} the activities of the hydrogen and chloride ions respectively and $\alpha_{\pm}$ the mean activity coefficient of the ions of hydrochloric acid.**

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[2] The calomel half cell might be used instead of the silver chloride-silver half cell. The former, however, has been shown by Randall and Young (J.Am.Chem.Soc.,50,989 (1928)) to be subject to errors due to dissolved oxygen.

**More briefly the activity of hydrochloric acid.

There are two general methods of procedure which may be followed in making measurements on a series of solutions containing both hydrochloric acid and an added salt. Either the total concentration may be kept constant and the ratio of acid to salt varied, or the total acid concentration may be kept constant and different amounts of salt added. Each method has certain advantages. The method employed in this investigation was to keep the hydrochloric acid concentration constant and to vary the salt concentration. If a sufficient number of such measurements are made at suitable acid concentrations it is possible to interpolate to the other case, i.e., to compare the activity in various solutions in which the total concentration is constant.

A salt to be suitable for experiments of this kind must not react chemically with any of the essential constituents of the cell and must possess certain other properties. That is:

(1) It should be the salt of a strong acid.

(2) The silver salt of its acidic constituent should be soluble.

(3) It should not be the salt of an acid such as nitric acid which acts as a strong oxidizing agent.

(4) It should be readily soluble.

(5) It is preferable to start with univalent salts.

(6) It should not "poison" the electrodes.

These conditions greatly restrict the choice of salts. However, sodium perchlorate appears to fulfill the conditions admirably. In order to compare the effects of sodium and potassium in this case some measurements were made with potassium perchlorate even tho it does not fulfill condition (4) in a very satisfactory manner.

II. EXPERIMENTAL

The cell used consisted of three silver-silver chloride half cells and two hydrogen half cells,each containing two hydrogen electrodes, connected to the silver-silver chloride half cells thru two stopcocks. Hydrogen, prepared by electrolysis of a sodium hydroxide solution, was admitted to the hydrogen half cells by means of glass tubes, which extended almost to the bottom of the electrode vessels, and escaped thru a bubbler. The electrical contacts in the case of the silver-silver chloride electrodes were made by platinum wires which extended thru the bottom of the electrode vessel. The stoppers on the electrode vessels were glass, ground to fit tightly.

The silver crystals for the silver-silver chloride electrodes were prepared by the electrolysis of 0.01 M silver nitrate solution, following the procedure of Randall and Young.[2] A platinum wire was used for the cathode and a bar of pure silver for the anode. The solution was heated to about 90°C and a current of approximately five amperes was passed thru the solution. It is difficult to give exact specifications as to current density as the mass of minute crystals on the cathode increases and hence the current density is not constant. Prepared in this manner the crystals were dark grey in color and so finely divided that the individual crystals were invisible to the naked eye. The silver chloride was prepared by precipitation from a 0.01 M solution of silver nitrate. The silver crystals were washed until they gave no test for the silver ion and the silver chloride until it gave no test for chloride ion.

The hydrogen electrodes were of platinum foil. This was first covered electrolytically with a thin coating of gold and then with a coating of platinum black. The electrodes were washed with concentrated nitric acid and finally with many changes of water, in which they were allowed to stand until placed in the cell. A thin rather than a mediumly thick[3] coating of platinum black was found necessary when the acid concentration was low and the salt concentration high, otherwise the results were somewhat irregular.

The behavior of the hydrogen electrodes prepared in this manner was quite satisfactory. As a rule they checked to 0.02 or 0.03 millivolts. The three silver-silver chloride electrodes were not quite as satisfactory, the largest differences were seldom greater than 0.1 millivolt. The average deviation of the final results at various series of concentrations from the smooth curves is about 0.1 millivolt.

The cell was placed in an oil thermostat regulated to five hundredths of a degree. The electromotive force was measured by a type K potentiometer using as a standard a Weston cell that was frequently checked against a cell recently certified by the Bureau of Standards.

The sodium perchlorate used in these experiments was prepared by the addition of 60% c.p. perchloric acid to c.p. sodium carbonate, the product being recrystallized twice from water and dried at 120°C for thirty-six hours. The potassium perchlorate was purified by three crystallizations from water. Neither salt gave a test for chloride or sulfate. The hydrochloric acid used was obtained by distilling the c.p. acid diluted to a density of 1.1 in an all glass still, the middle portion alone being retained. It was then diluted to the desired concentration and standardized by the silver chloride gravimetric method.

In order to obtain as accurately as possible the effect of added salts upon the activity coefficient of hydrochloric acid, the electromotive forces of cells containing pure acid solutions were first determined and then to weighed amounts of these same solutions were added weighed amounts of the pure salt. The values for the pure acid solutions thus obtained differ from the mean of the values of other investigators by about the same amount as do those of others. However to determine the differential effect of the added salt, the values for pure solutions here obtained were used in the computations in preference to the presumably more accurate mean values, because thus any peculiarities of procedure or effects due to traces of impurities are cancelled out to a large extent. The method of procedure of making a series of solutions by adding crystalline salt to a stock solution of acid has the advantage that the concentration (expressed in mols per 1000 grams of water) of the acid which largely determines the electromotive force and hence the computed activity coefficients is identical thruout the series. Any error in the concentration of the added salt is of relatively small importance.

III. RESULTS

In Table I are given the results for the activity of hydrochloric acid in the presence of sodium perchlorate and potassium perchlorate. The electromotive forces have been corrected to one atmosphere of hydrogen. The activity coefficients, $\alpha_{\pm}$, are the square roots of the product of the activities of the separate ions, calculated on the basis of $E_0 = 0.2221$[2] at 25°. All concentrations are expressed as mols per thousand grams of water.

Table I

Molality of $NaClO_4$	Total Molality	E.M.F.	Activity Coefficient
		HCl=0.2480 Molal.	
0	0.2480	0.30781	0.7607
0.1450	0.3930	0.30862	0.7489
0.2428	0.4908	0.30891	0.7446
0.2459	0.4939	0.30880	0.7459
0.5484	0.7961	0.30793	0.7591
0.7208	0.9688	0.30701	0.7725
		HCl=0.1015 Molal.	
0	0.1050	0.351~~4~~50	0.7960
0.0887	0.1907	0.35367	0.7621
0.1684	0.2699	0.35429	0.7516
0.3069	0.4084	0.35482	0.7444
0.5059	0.6074	0.35480	0.7440
0.6985	0.8000	0.35422	0.7534
0.8567	0.9582	0.35339	0.7656
0.8902	0.9917	0.35320	0.7692
		HCl=0.04639 Molal.	
0.0	0.04639	0.38999	0.8223
0.01357	0.05996	0.39071	0.8098
0.03989	0.08628	0.39205	0.7881
0.06428	0.1107	0.39312	0.7729
0.09871	0.1451	0.39385	0.7610
0.1241	0.1705	0.39441	0.7532
0.2150	0.2614	0.39530	0.7404
0.2625	0.3089	0.39569	0.7355
0.2633	0.3097	0.39558	0.7344
0.2771	0.3235	0.39576	0.7333
0.3722	0.4385	0.39591 0	0.7318
0.4446	0.4909	0.39606	0.7291 ✓
0.4635	0.5098	0.39611	0.7291
0.4886	0.5350	0.39606	0.7291
0.6230	0.6690	0.39551	0.7376
0.8460	0.8924	0.39456 8	0.7506

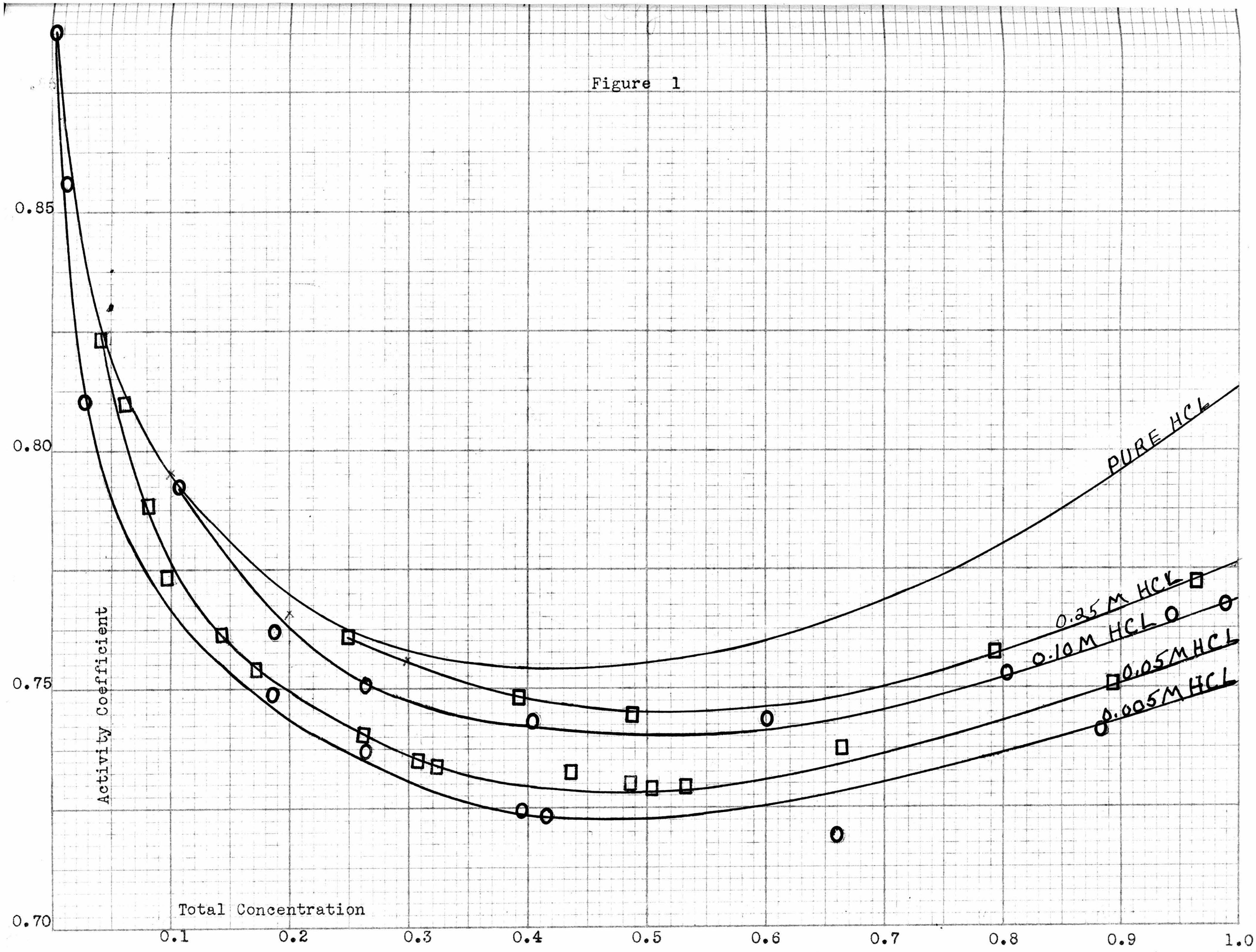
HCl=0.005143 Molal.

0	0.005143	0.35221	0.8892
0.009538	0.01468	0.35244	0.8552
0.03565	0.04071	0.35288	0.8099
0.07544	0.08058	0.35322	0.7973
0.1848	0.1899	0.35330	0.7492
0.2618	0.2669	0.35412	0.7376
0.4912	0.4963	0.35485	0.7248
0.6571	0.6622	0.35496	0.7218
0.9943	0.9994	0.35536	0.7729

Molality of K~~Na~~ClO_4	Total Molality	E.M.F.	Activity Coefficient
	HCl=0.09942 Molal .		
0	0.1000	0.35221	0.796
0.007144	0.1066	0.35244	0.795
0.01308	0.1125	0.35288	0.788
0.01720	0.1166	0.35322	0.787
0.02476	0.1242	0.35330	0.784
0.05864	0.1580	0.35412	0.771
0.08836	0.1878	0.35485	0.760
0.09812	0.1975	0.35496	0.759
0.1219	0.2213	0.35536	0.755
	HCl=0.01162 Molal.		
0.004364	0.01618	0.45767	0.861
0.007164	0.01925	0.45838	0.863
0.008217	0.02004	0.45809	0.855
0.009897	0.02172	0.45846	0.847
0.01305	0.02514	0.45896	0.855
0.02407	0.03236	0.46062	0.830
0.02462	0.03624	0.46095	0.824
0.04397	0.05559	0.46188	0.809
0.04658	0.05820	0.46264	0.798
0.06377	0.07539	0.46121	0.820
0.06691	0.07853	0.46364	0.783
0.1053	0.1171	0.46410	0.762
0.1056	0.1172	0.46477	0.766
0.1097	0.1215	0.46411	0.760
0.1340	0.1458	0.46457	0.753

In Figure 1 the activity coefficients for hydrochloric acid at the different concentrations are plotted as ordinates against the total concentration as the abscissa. The upper curve corresponds to pure hydrochloric acid and, at concentrations greater than 0.25 molal, is based upon the data of Scatchard.[4]

Figure 1



PURE HCL
0.25 M HCL
0.10M HCL
0.05M HCL
0.005M HCL
Activity Coefficient
Total Concentration
0.85
0.80
0.75
0.70
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

IV. DISCUSSION

During the past few years many investigators and interpretations of the properties of solutions of strong electrolytes have demonstrated that in sufficiently dilute solutions the ion attraction theory[5] quantitatively accounts for the activity of strong electrolytes as determined from measurements of the electromotive forces of appropriate cells, of freezing point lowerings and of the effect of added salts upon the solubility of relatively insoluble salts.

In dilute solutions the physical basis for the ion attraction theory is relatively simple. The electrostatic forces acting between the ions are determined by the magnitude of their charges, their distribution and distances from one another and the dielectric constant of the medium. In the case of aqueous solutions the theory gives the following expression for the activity coefficient of the ion A of valence Z_A at the concentration C mols per liter

$$\log_{10} \alpha = \frac{-1.283 \times 10^6 Z_A^2 \sqrt{2CZ^2}}{(KT)^{1.5}} \qquad (1)$$

Here K is the dielectric constant of water and T the absolute temperature. In the present discussion solutions of uniunivalent electrolytes at 25° are chiefly concerned. For these conditions equation (1) reduces to

$$\log_{10} \alpha = -0.505 \sqrt{C} \qquad (2)$$

where C is the total salt concentration in mols per liter.

In a moderately concentrated solution a great many additional effects, many of them undoubtedly related to one another, come into play to influence the activity coefficient. Thus the distribution of the ions will be modified in solutions in which the average effective diameter of the ions is comparable with the average distances of the ions from one another in the solution.* Then at high concentrations ionization may no longer be complete. Hydration of the ions removes an appreciable part of the water from its normal state thus changing the effective mol fraction of the ions and also the dielectric constant of the medium, since the degree of association of the water will be affected. In addition the dielectric constant may be changed by the mere presence of a high ion concentration, the ions themselves having a dielectric constant different from that of the solvent.

The force between ions is subject to modification in concentrated solutions for a somewhat different reason. In the intense electric fields there prevailing the electron orbits of the ions may be deformed, and hence the ions cannot be considered as rigid spheres with the charge uniformly distributed over the surface. Those ions which resist this deformation will experience a repulsive force as well as the normal attractive force, that is they will tend to be salted out or to have their activity coefficients increased.

Of these effects one of the simplest physically is that due to the sizes of the ions themselves. When this is taken into account a complicated expression is deduced which however is approximately equivalent to dividing the right hand side of the above equations by the factor $1 + 3.3 \times 10^{-9} b \sqrt{c}$. Here b is the effective average diameter of the ions or the mean least distance of approach between the centers of the ions. From a consideration of the effect of the various influences which may be summed up in the term the "salting out" effect Huckel[5b]

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*At a concentration of 1 molal, for example, the average distances apart are but 3 to 10 times those of the usual molecular dimensions.

showed that this could be taken account of by adding the term B2C to equation (2). The resulting equation is then

$$\log \alpha_x = \frac{-0.505 \sqrt{c}}{1+3.3\times10^{-9} b\sqrt{c}} + B\,2\,c.$$

In this equation α_x has been written instead of α . The theoretical derivation of equation (2) and (3) give the ratio (α_x) of the activity of the ion to its mol fraction, rather than the more commonly used ratio (α) of the activity of the ion to its concentration (m) in mols per 1000 grams of solvent.

In dilute solution the difference* is insignificant, but in concentrated solutions it may not be neglected. The relation between the two is given by

$$\log \alpha_x - \log \alpha = \log(1 + 0.036\ m)$$

or

$$\frac{\alpha_x}{\alpha} = 1 + 0.036\ m$$

Thus they differ by 3.6 percent at one molal.

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[*] In dilute solutions the distinction between concentration expressed as mols per liter (c) and as mols per 1000 grams of water (m) is of no consequence. At the higher concentrations involved in the present discussion the difference is small and since the equations and solutions are to a very great extent empirical, there is no need to make this somewhat unusual correction. The densities of a number of the solutions employed are given in an appendix. The change of units to mols per liter may be made by the aid of this data.

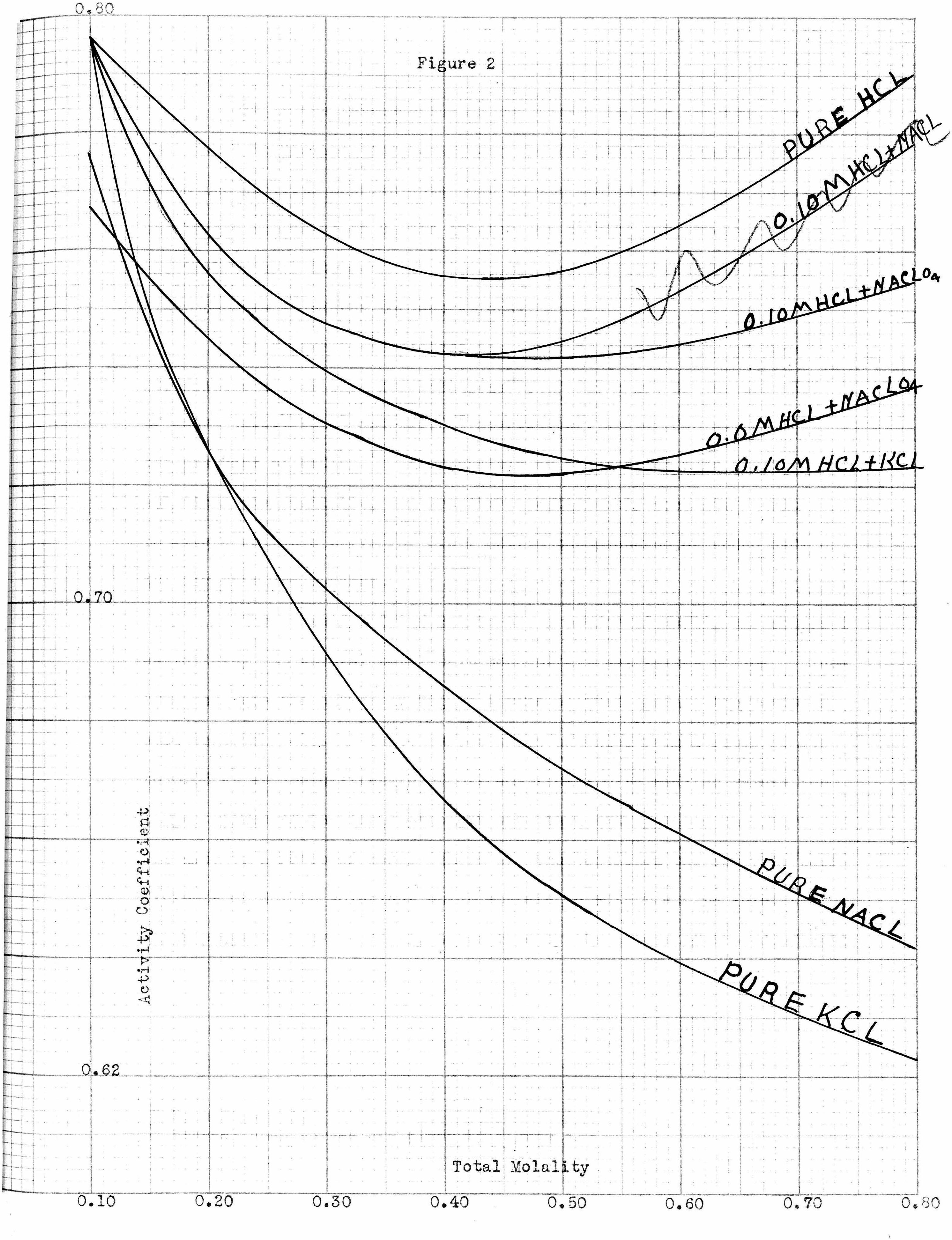
From equation (3) there is hence obtained the following relation:

$$\log \alpha = \frac{-0.505 \sqrt{c}}{1+3.3 \times 10^{-9}\, b\sqrt{c}} + B\, 2\, c - \log(1+0.036\, m) \qquad (5)$$

Huckel showed that by a proper choice of b and B it was possible to obtain good agreement between the calculated and observed activity coefficients for HCl, LiCl, NaCl and KCl up to about three molal. The values thus obtained for b are of the order of magnitude to be expected from molecular dimensions, namely 2-3 x 10^8 cm., but there is no satisfactory independent way of computing b. Similarly B must be obtained from a consideration of activity data itself, but here again there seems to be no means of determining whether or not the values determined for B are those to be expected from the fundamental physical concept.

In view of the large number of factors which equations (3) and (5) do not take into account,[6] of the mathematical approximations which it contains,[7] and of the fact that in a few cases it yields values of b which are susprisingly small or even negative,[8] it is to be doubted whether these equations may be looked upon as much more than empirical relations. In spite of this it may be that the significance of the constants b and B is substantially that originally assumed by Huckel, or at least that they take account of a number of closely related and undoubtedly overlapping effects. Thus B ame be related to the hydration of the ion salted out, to its deformability in intense electric fields, to the change in dielectric constant, to incomplete ionization, to the change in association of the water, etc.

Figure 2


0.80
0.70
0.62
Activity Coefficient
Total Molality
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
PURE HCL
0.10MHCL+NACL
0.10MHCL+NACLO4
0.0MHCL+NACLO4
0.10MHCL+KCL
PURE NACL
PURE KCL

It is the introduction of the term B 2c into the equation that makes it possible to account for the fact that in a number of cases the activity coefficients pass thru a minimum and then increase; the larger the value of B, the greater the salting out effect of an electrolyte upon its own ions, i.e., the greater its activity coefficient becomes at higher concentrations.

In Figure 2 are plotted the activity coefficients of pure HCl solutions*, of pure KCl solutions[5e], of 0.1 m HCl in the presence of added NaCl,[3] KCl,[3] and $NaClO_4$* respectively and of 0.0 m. HCl in the presence of $NaClO_4$.* Unfortunately no figures for pure $NaClO_4$ solutions are available, nor are there sufficiently accurate results to give a reliable curve for 0.0 M HCl in the presence of added NaCl or KCl for this whole range.

The curve for 0.0 M HCl in the presence of $NaCl)_4$ was obtained as follows. At several total salt concentrations, values of log determined from the curves of Figure 1 were plotted against the ratio of acid to total salt.** These curves which extended from a ratio of 1.0 to 0.05 at an ionic strength of 0.1 and from 1.0 to smaller values for larger values of the ionic strength were then extrapolated the short distance to a ratio of zero. There are thus obtained the activity coefficients of HCl in solutions which contain no HCl, i.e., in solutions whose properties are entirely determined by the nature of the added salt.

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* From Figure 1.

** Several such curves are given in Figure 3.

The relations between the curves in Figure 2 bring out clearly the fact that the position of the minimum and the subsequent rapid increase in the activity coefficient is primarily a property of the salt, here hydrochloric acid, whose activity coefficient is concerned and of the ionic strength and depends to only a limited extent upon the character of the added salt, which in the limiting case of solutions which contain no hydrochloric acid, entirely determines the properties of the solution. In this respect there appears to be no significant difference whether the added salt is a chloride or a salt without this common ion.

The facts that the activity coefficient of hydrochloric acid whether in its own pure solution or in mixtures shows this rise much more prominently than do the coefficients for sodium chloride or potassium chloride, and that the activity coefficient of thallous chloride[8] in the presence of added salts even at an ionic strength of one shows no signs of a minimum, indicates that this increase in the activity coefficient with increasing ionic strength is primarily a property of the hydrogen ion. It is not surprising that this ion is rather unique in its behaviour, especially if it is but slightly hydrated[9] for the unhydrated ion is of the simplest possible type and has no electron orbits to be deformed or polarized, and hence it might be expected that it would be salted out readily.

Harned[3], assuming that the "apparent ionic diameters" of the ions in a mixture are the same, obtained from the ion attraction theory the following equation for the activity coefficient of hydrochloric acid in a mixture of uniunivalent electrolytes at constant total molality:

$$\log \alpha = \frac{-0.35\sqrt{2c_T}}{1 + A\sqrt{2c_T}} + B(2c_{,}) + B'(2c_T - 2c_{,}) - \tfrac{1}{2}\log(1 + 0.002\ w\ M') - \tfrac{1}{2}\log(1 + 0.002\ w\ M_T) \qquad (6)$$

Here C_T and M_T are the total normal and molal concentrations, $c_{,}$ and $M_{,}$ are the normal and molal concentrations of acid, and w is the molecular weight of water.

The last two terms of this equation presumably take account of the change from α_x to α and follow from the relation between mol fraction and molal concentration. However, since for the cases for which this equation is given, the total concentration is constant, the ratio between the mol fraction and the molal concentration of acid will be independent of the concentration of acid, the relation between and will be simply that given by equation (4). Making this correction and employing the notation of equation (5) we have then:

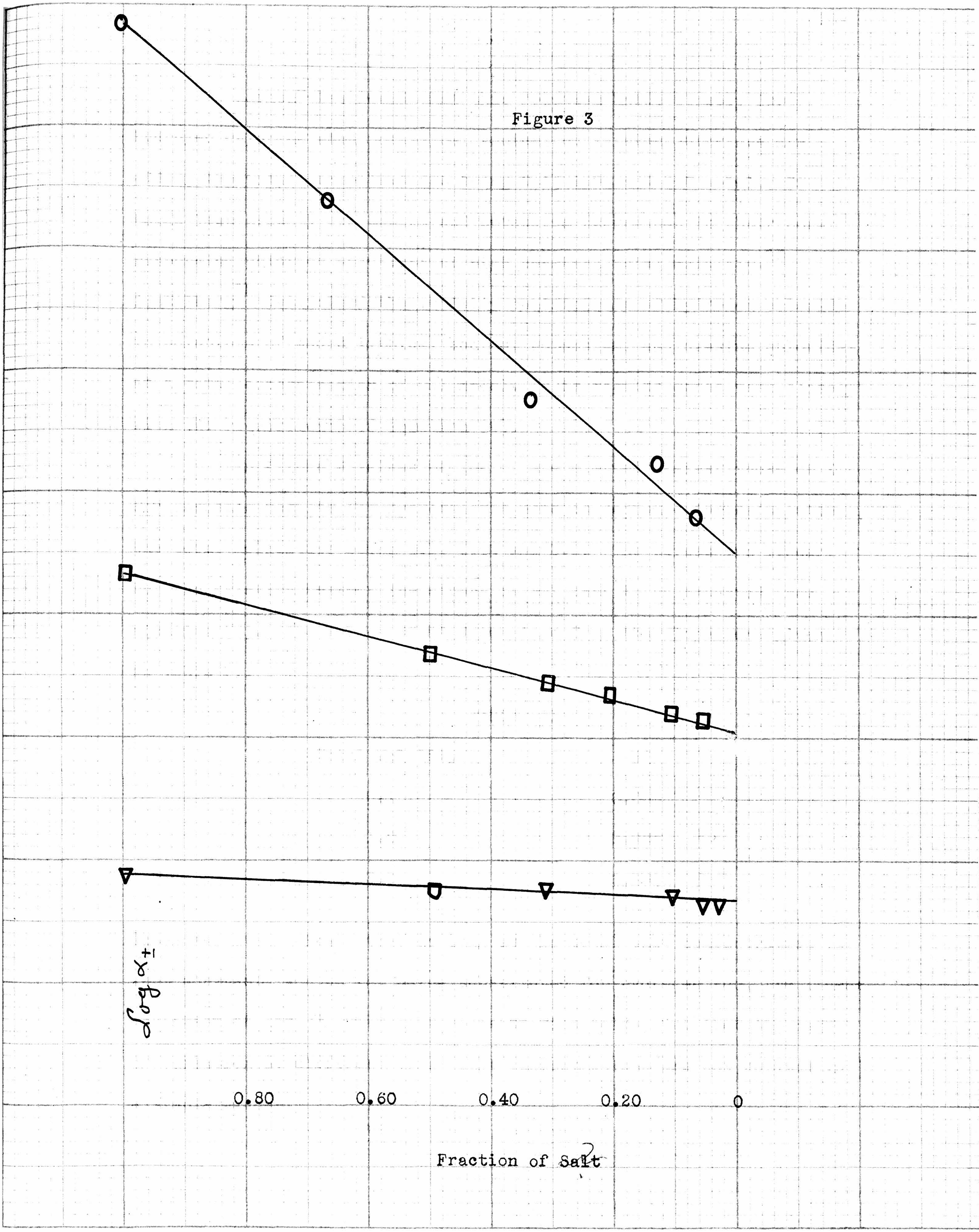
$$\log \alpha = \frac{-0.505\sqrt{c}}{1 + 3.3\text{x}10^{-9}\ b\sqrt{c}} + B\ 2c_{,} + B'(2c_T - 2c_{,}) - \log(1+0.036M_T). \qquad (7)$$

If α' is the activity coefficient of hydrogen chloride when present alone at the concentration M_T, then from equations (5) and (7) there follows the relation:

$$\begin{aligned} \log \alpha &= \log \alpha' + B'(2c_T - 2c_{,}) \\ &= \log \alpha' + B'2c_T\ X \qquad (8) \end{aligned}$$

where X is the ratio of the concentration of the added salt to the total salt concentration.

Figure 3



Harned[3] has found that this relation holds closely for hydrogen chloride when potassium, sodium, or lithium chlorides are added, the total concentrations being 0.1, 1.0, and 3.0 molal. It holds less closely for sodium and potassium hydroxides in their corresponding chloride solutions at high constant total molality.[10] Guntelberg[1b] determined the activity coefficients of hydrogen chloride in solutions of added lithium, sodium, potassium, and caesium chlorides at a total concentration of 0.1 molal. H is results agree very closely with the requirements of equation (8).

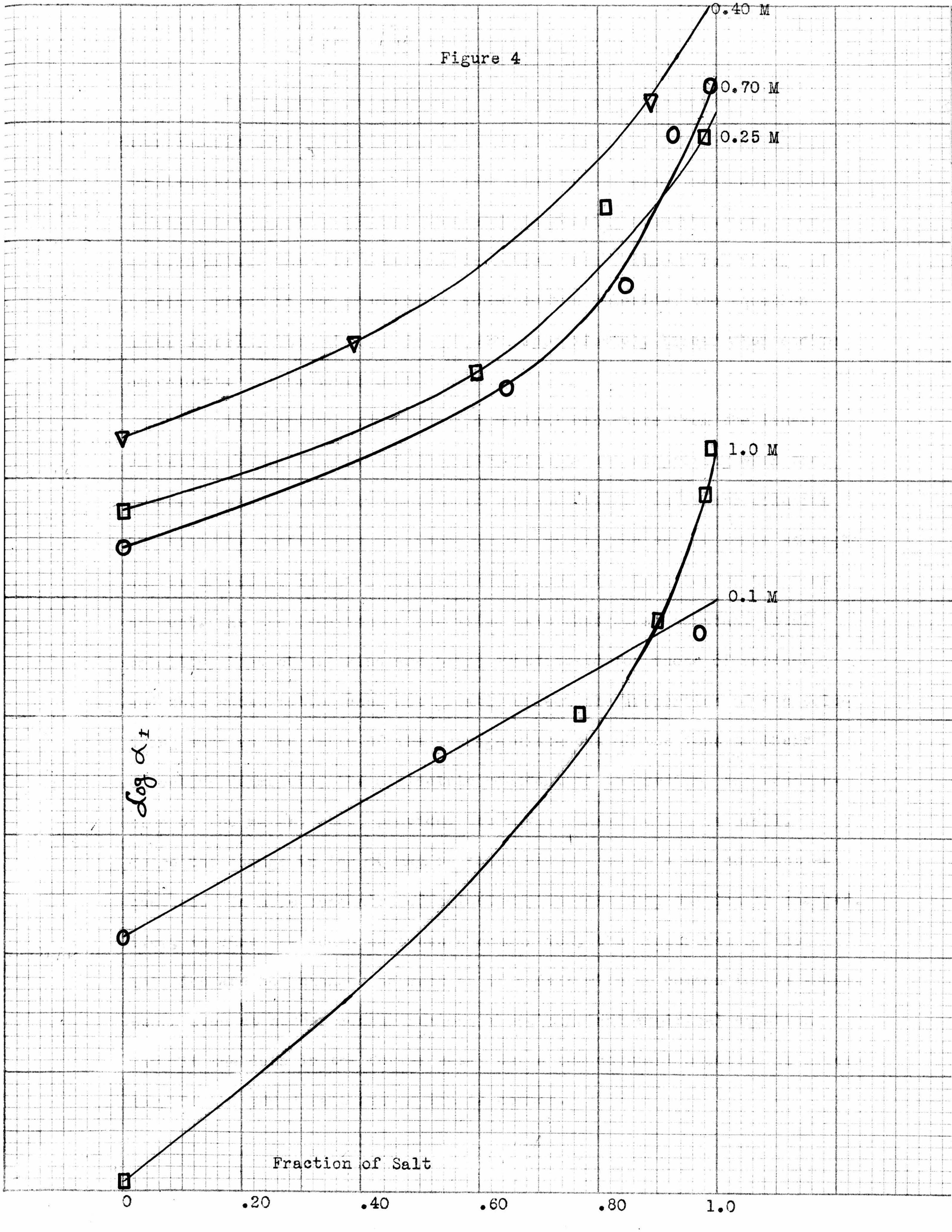
In Figure 3 values of log are plotted against those of X for Harned's results for hydrochloric acid in sodium chloride solutions, the total molalities being 0.1, 1.0, and 3.0. The curves are linear, but the relation between the slopes is not that to be expected from equation (8). The values of B' determined from the slopes are given in Table II.

TABLE II

Total Molality	B'
0.1	0.038
1.0	0~~.025~~ 24
3.0	0~~.035~~ 27

These results indicate that as long as the total salt concentration is kept constant, sodium ion being substituted for hydrogen ion, the linear variation of log α with acid concentration holds, but that the rates of variation at different total salt concentrations are not related in a simple manner.

Figure 4



In Figure 4 are plotted in a similar way the results for hydrochloric acid in the presence of added sodium perchlorate at various constant total molalities. It is seen that at 0.1 molal the data agrees closely with equation (8) but that with increasing concentration, even at 0.25 molal, there is a decided deviation from a linear relation. At 1 molal, where in the presence of added sodium chloride, the equation holds closely, the relation is not even approximately linear when sodium perchlorate is the added salt.

This general behaviour and radical departure from the linear variation of log α with acid concentration is not surprising when the general physical basis is considered qualitatively. In dilute solution the activity coefficient is almost wholly determined by the ionic strength and is dependent to but a limited extent upon the character of the ions present. As the fraction of the added salt changes at constant total molality, ions of one kind are being substituted for those of another, and this substitution does not greatly affect the properties of the solution, such as the ratio of the average distances of the ions to their effective diameters, the dielectric constant of the medium, the association of the water, etc., provided the total concentration is small. Hence the change in log α may be taken account of by a one constant equation. In more concentrated solutions, in case only one ion is changed, i.e., in case the added salt has a common ion, the properties of the solution are not changed as much as if a salt with no common ion is added. Hence even at higher concentrations a one constant empirical equation may fit the data in the former case, but a two constant equation is necessary if the added salt has no ion in common.

Over the comparatively small range in which the limited solubility of potassium perchlorate permits a comparison, this salt and sodium perchlorate have the same effect on the activity of hydrochloric acid. This is somewhat surprising in view of the fact that Guntelberg's very careful work shows that potassium chloride has a much greater effect than has sodium chloride, and that in general the effect of added potassium salts on the activity coefficients of relatively insoluble salts is greater than that due to added sodium salts.[11] However in case of thallous chloride there is no certain difference between the effect of added sodium and potassium chlorides.[12]

Guntelberg, partly theoretically and partly empirically, showed that the effect of added salts on the activity of hydrochloric acid could be related to the freezing point lowering of the electrolytes involved. The fact that sodium and potassium perchlorate have the same effect on hydrochloric acid would indicate that these two salts have the same freezing point lowerings at equivalent concentrations. In general they have larger lowerings than have potassium salts, but in a few cases as in those of the iodates there is no certain difference. This may well be the case for the two perchlorates also.

Another way of considering the results obtained in this investigation is to calculate them over into terms of the effect of added salt upon the "solubility" of hydrochloric acid. The change in "solubility" may then be compared with that observed in cases investigated by the usual solubility method. In the latter the activity of the slightly soluble salt is maintained constant by the presence of the solid salt and its concentration in solutions of other salts determined

Figure 5

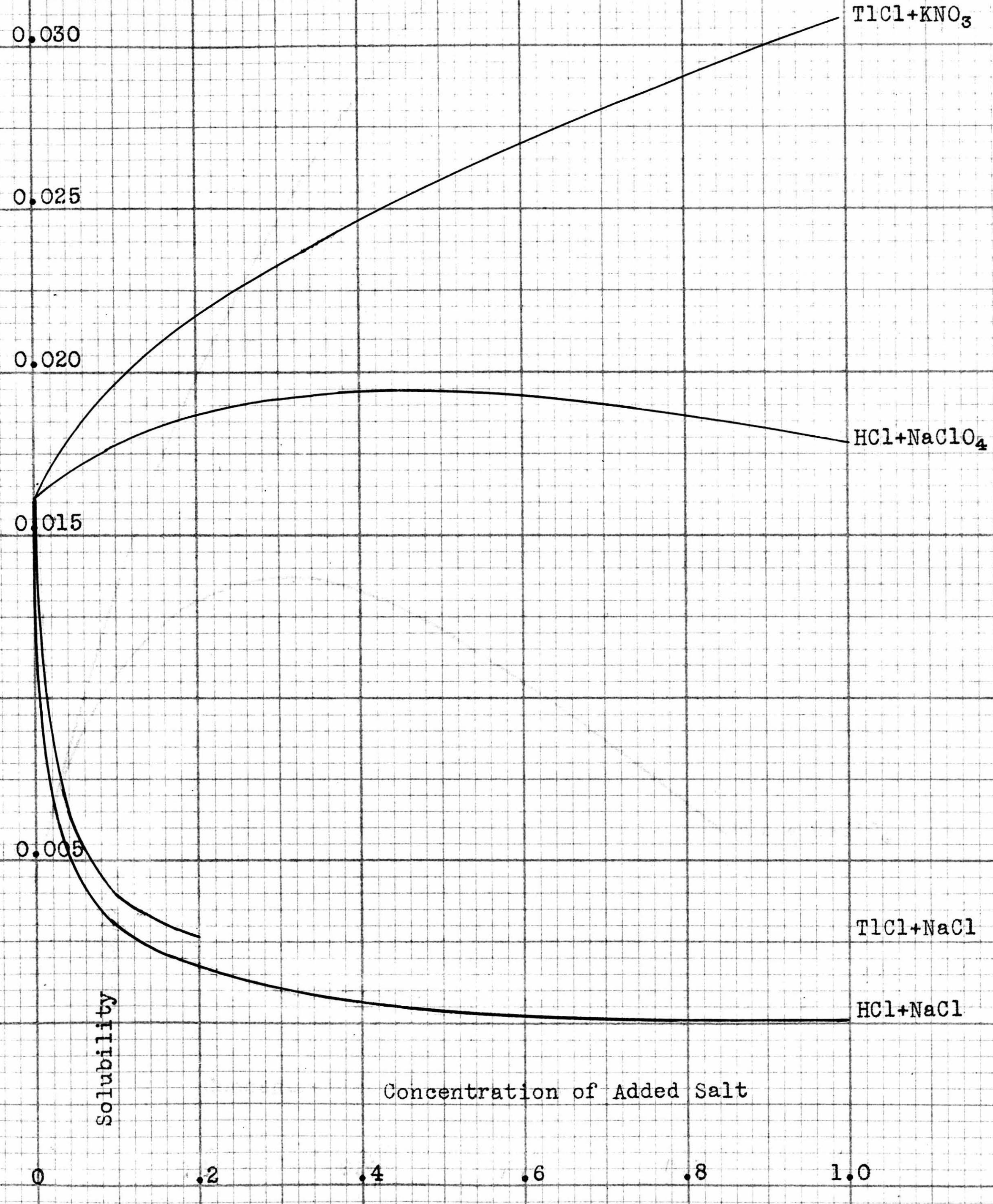
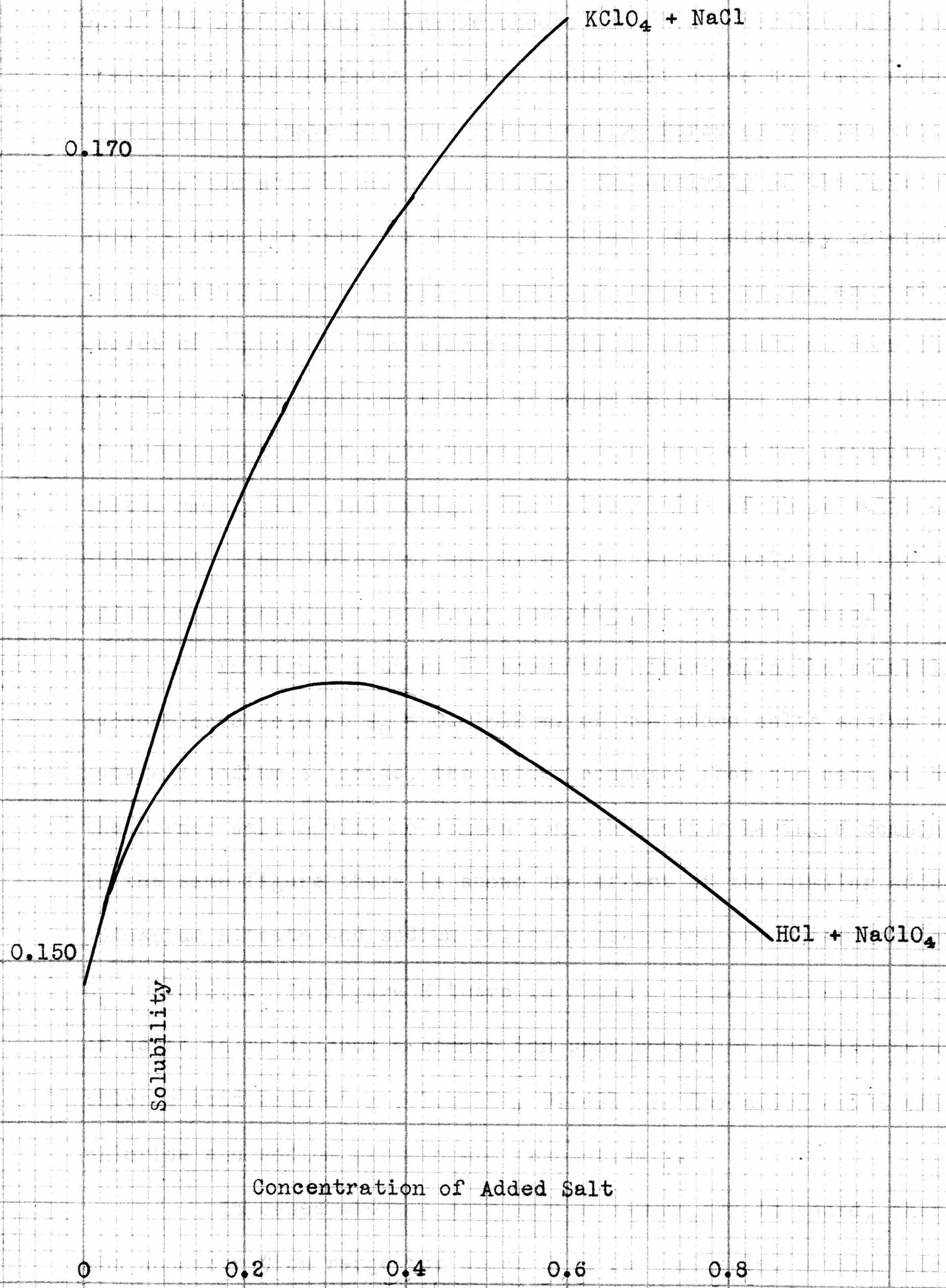

0.030
0.025
0.020
0.015
0.005
$TlCl+KNO_3$
$HCl+NaClO_4$
$TlCl+NaCl$
$HCl+NaCl$
Solubility
Concentration of Added Salt
0
.2
.4
.6
.8
1.0

Figure 6


$KClO_4$ + NaCl
0.170
HCl + $NaClO_4$
0.150
Solubility
Concentration of Added Salt
0
0.2
0.4
0.6
0.8

In the case of hydrochloric acid one may arbitrarily fix the solubility S_0 of the acid at any value we choose and then determine what concentrations of hydrochloric acid and added salt cause the cell under investigation to have the same electromotive force as has the cell which contains the acid alone at S_0 molal. The activity of the hydrochloric acid is then the same for all such cells. The necessary interpolation is most readily carried out in terms of activity by the acid of the curves of Figure 4. The values 0.01612 m. and 0.1491 m. were chosen for S_0 in order that the effect of added salts upon the solubility of hydrochloric acid might becompared with that of two uniunivalent salts, namely $TlCl$ and $KClO_4$. The solubilities of these salts are quite different being 0.01612 m. and 0.1491 m. respectively, and the effect of added salts have been carefully investigated in both cases.[13]

In Figure 5 there is shown the effect upon the solubility of hydrochloric acid at $S_0 = 0.01612$ m. of the added salts sodium perchlorate and sodium chloride, the latter computed from the data of Harned,[3] the former salt having no common ion, the latter having a common ion. In the same figure there is shown the effect of the similar added salts potassium nitrate and sodium chloride upon thallous chloride, for which $S_0 = 0.01612$. In Figure 6 there is shown a comparison between the effect of added salts without a common ion upon potassium perchlorate and hydrochloric acid both at a solubility 0.1491 m. The added salts are sodium chloride and sodium perchlorate respectively.

In cases where a salt with a common ion is added, there is in the concentration range for which data is available, nothing striking. But in the case of hydrochloric acid in the presence of a salt without a common ion, a new phenomenon is observed, namely the solubility of the "insoluble" salt increases as usual with added salt but then it diminishes with further additions of salt. This effect is of course to be expected from the minimum of the curves for the activity coefficient, Figure 1. This method of comparing the activity coefficient of hydrochloric acid with that of relatively insoluble salts, emphasizes that that of this acid and possibly of other acids, is unique and quite different from that of other strong electrolytes.

V. SUMMARY

The effect of added salts without a common ion upon the activity of hydrochloric acid has been determined by measurements of the electromotive force of cells of the type

H_2, HCl c_1m + $NaClO_4$ c_2m, AgCl+Ag,

where c_1 = 0.25 m, 0.1 m, 0.05 m and 0.005 m, and for values of $c_1 + c_2$ up to 1 m.

Similar cells substituting $KClO_4$ for $NaClO_4$ were investigated over a concentration range which, however, was rather restricted due to the limited solubility of potassium perchlorate.

The results show that the activity coefficient of hydrochloric acid in the presence of the added salts without a common ion is, at similar ionic strengths, somewhat less than that of the pure acid, that is at a fixed concentration of acid the activity goes thru a minimum with increasing ionic strength and then increases in a manner which is roughly similar to that observed for pure acid solutions.

The ion attraction theory is discussed qualitatively. In dilute solutions it undoubtedly accounts for the facts upon a relatively simple physical basis, but its extension to more concentrated solutions resulting in a two constant equation and the application of this to mixtures of electrolytes is probably largely empirical in nature.

The fact that the activity coefficient of hydrochloric acid in its own pure solution, and in solution in the presence of a salt without a common ion including solutions which contain no acid, and whose properties therefore depend entirely upon those of the added salt goes thru a minimum with increasing ionic strength shows that this electrolyte is very readily "salted out". This behaviour is probably associated with the unique structure of the hydrogen ion in that it has no electron orbits to be deformed in the strong electrical field prevailing in concentrated solutions.

The principle of linear variation of log α with the concentration of acid at constant total molality applies to mixtures of the acid and sodium perchlorate in dilute solutions, but does not hold at concentrations from 0.25 m. to 1.0 m. In this last respect the behaviour is different from that observed when a chloride is the added salt.

The results of this investigation are discussed in terms of the effect of added salt upon the solubility of hydrochloric acid and its change in solubility with added salt is compared at similar initial solubilities with those of thallous chloride and potassium perchlorate. For hydrochloric acid in the presence of an added salt without a common ion, a solubility curve of a new type is disclosed, in that its solubility increases to a maximum and then decreases as the concentration of added salt is increased.

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Appendix

Molality of $NaClO_4$	Density of Solutions	Concentration of HCl	Concentration of $NaClO_4$
HCl=0.248 Molal			
0	1.002	0.2468	0
0.1450	1.011	0.2441	0.1427
0.2428	1.020	0.2433	0.2383
0.5480	1.043	0.2403	0.5314
0.7208	1.055	0.2380	0.6912
HCl=0.1015 Molal			
0	0.9987	0.1010	0
0.08887	1.006	0.1007	0.08808
0.1684	1.012	0.1003	0.1664
0.3069	1.025	0.09980	0.3021
0.5095	1.032	0.09826	0.4932
0.8567	1.066	0.09769	0.8245
0.8902	1.067	0.09732	0.8534
HCl=0.005143 Molal			
0.1848	1.014	0.005097	0.1831
0.2618	1.020	0.005082	0.2587
0.3278	1.032	0.005052	0.3220
0.4912	1.038	0.005037	0.4811
0.5662	1.043	0.005013	0.5519
0.6578	1.050	0.004993	0.6386
0.9943	1.067	0.004889	0.9452

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