[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA.]

THE HYDROGEN- AND HYDROXYL-ION ACTIVITIES OF SOLUTIONS OF HYDROCHLORIC ACID, SODIUM AND POTASSIUM HYDROXIDES IN THE PRESENCE OF NEUTRAL SALTS.

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If the law of mass action, as usually formulated, holds for solutions containing more than one electrolyte, the addition of a salt should decrease the hydrogen-ion concentration of a solution of an acid and the hydroxyl-ion concentration of a solution of a base. There is evidence, however, which seems to indicate that these hydrogen- and hydroxyl-ion concentrations are not decreased but increased by the additions of neutral salts.

From the conductance of solutions of acetic acid containing varying quantities of neutral salts, Arrhenius[1] concluded that the dissociation of the acid was increased. This evidence is not convincing, since so many disturbing factors may influence the results obtained by this method. Arrhenius further found that the addition of potassium chloride to a solution of hydrochloric acid increased its power of inverting cane sugar solutions. He pointed out that this was probably due to the increase in dissociation of the acid. The cause of this phenomenon has not been explained satisfactorily, but the suggestion that the undissociated molecules exert an influence on the velocity of the transformation has afforded the best explanation yet offered.[2]

If accurate data could be obtained on the hydrogen-ion concentrations of such solutions, a decided advance would be made toward a more complete solution of the problem. In view of the fact that none of the above-mentioned evidence is direct, Loomis and Acree[3] attempted to measure the hydrogen-ion concentrations of solutions of acetic acid containing potassium chloride by means of the hydrogen electrode. From the electromotive force of the cells:

$$(1)\ \text{Hg} \mid \text{HgCl} \mid \text{KCl}\ (0.1\ M) \mid \begin{array}{c}\text{saturated}\\ \text{NH}_4\text{NO}_3\end{array} \mid \begin{array}{c}\text{acetic acid}\ (0.25\ M)\\ +\ \text{KCl}\end{array} \mid \text{H}_2$$

and

$$(2)\ \text{Hg} \mid \text{HgCl} \mid \text{KCl}\ (0.1\ M) \mid \begin{array}{c}\text{saturated}\\ \text{KCl}\end{array} \mid \begin{array}{c}\text{acetic acid}\ (0.25\ M)\\ +\ \text{KCl}\end{array} \mid \text{H}_2$$

they obtain the following results:

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[1] *Z. physik. Chem.*, **31**, 197 (1899).

[2] Taylor, THIS JOURNAL, **37**, 551 (1915).

[3] *Am. Chem. J.*, 46, 632 (1911).

Mols of KCl per liter	0.000	0.05	0.1	0.5	2.06
E. m. f. of (1)	0.4907	0.4919	0.4927	0.4944	0.4984
E. m. f. of (2)	0.4930	0.4928	0.4918	0.4894	0.4857

According to the theory of this cell, an increase in electromotive force indicates a decrease in the hydrogen-ion concentration, if the change in electromotive force is produced solely at the contact of the molecular hydrogen and its ions. There is, however, an electromotive force produced at the boundary of the acetic acid and contact solutions, which, as shown by the above results, changes on the addition of potassium chloride. When ammonium nitrate is used as a contact substance, the electromotive force rises on the addition of potassium chloride; when a saturated solution of potassium chloride is used, the electromotive force falls. Of the two series of results obtained by Loomis and Acree, the one in which potassium chloride was used as a contact substance is the more reliable, for the reason that saturated potassium chloride was shown by them to be a better solution for the elimination of liquid potential than saturated ammonium nitrate.[1] If this second series be taken to represent approximately the change in electromotive force of the hydrogen electrode, the hydrogen-ion concentration of the acid has been increased considerably by the addition of potassium chloride.

In these measurements it is obvious that, under all conditions, there will be an effect due to mass action which will tend to decrease the hydrogen-ion concentration; secondly, liquid potential at the solution surfaces will influence the electromotive force of the cell; and thirdly, there may be an increase in hydrogen-ion concentration independent of mass action and liquid potential.

In this investigation, the hydrogen electrode was used in determining the change in hydrogen-ion concentration in solutions of hydrochloric acid, potassium and sodium hydroxides on the addition of different quantities of neutral salts. It was known that the change in liquid potential would be a troublesome factor in these determinations, but it was thought that some light might possibly be thrown on this source of error.

General Theory.

The original formula for the electromotive force of a cell of the type

$$\mathrm{Hg} \mid \mathrm{HgCl} \mid \mathrm{KCl}\ (M) \ \|^{2}\ \mathrm{HCl}\ (c_1) \mid \mathrm{H_2},$$

as given by Nernst was

$$\mathrm{E} = \mathrm{E_0} + 0.0591 \log 1/c_1, \qquad (1)$$

where E is the observed electromotive force, E_0 is the electromotive force of the cell

$$\mathrm{Hg} \mid \mathrm{HgCl} \mid \mathrm{KCl}\ (M) \ \|\ \mathrm{H^+}\ (M) \mid \mathrm{H_2} \qquad (2)$$

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[1] See also Bjerrum, *Z. physik. Chem.*, 53, 428 (1905).

[2] Double line indicates that liquid potential has been eliminated.

and c_1 is the concentration of the hydrogen ions at the hydrogen surface in (1). Lewis[1] has pointed out that the function c_1, calculated according to this formula, is not equal to the concentration of the ion in solutions which are at all concentrated. For this reason he differentiates this function from the concentration, uses the term activity, and designates it by the symbol a_1. This function equals the concentration in infinitely dilute solution. Since this investigation is a study of the variation of the value of this function, the term activity of the hydrogen ion will be used. The formula for the cell becomes

$$E = E_0 - 0.0591 \log a_1. \tag{3}$$

Now, suppose that on the addition of salt to the acid, the electromotive force of the cell changes from E to E_1, then the activity must have changed from a_1 to a_2, and, for the second cell, the following relation holds:

$$E_1 = E_0 - 0.0591 \log a_2 \tag{4}$$

Subtracting (4) from (3), the following equation is obtained:

$$E - E_1 = -0.0591 \log a_1 + 0.0591 \log a_2 = -0.0591 \log a_1/a_2 \tag{5}$$

Thus, if the activity of the hydrogen ion in the solution of the acid is known, then from the change in electromotive force, if liquid potential has been eliminated, the activity in the presence of the neutral salt can be calculated.

Preparation of Materials.

It is particularly important in making measurements with cells of this type to have the mercury and the calomel in the calomel electrode pure. In order to insure this, mercury, after having been washed ten times by dropping through a solution of nitric acid containing mercurous nitrate, was four times distilled. Samples from two successive distillations gave no difference in electromotive force when tested by the method proposed by Hulett.[2]

To prepare the calomel, this mercury was dissolved in distilled nitric acid, and, after dilution, the solution was precipitated by redistilled hydrochloric acid and washed free from acid by conductivity water.

The sodium, potassium and calcium chlorides were prepared by three reprecipitations of "analyzed" materials by passing hydrochloric acid gas over the aqueous solutions contained in platinum dishes in the apparatus designed by Lukens.[3] The sodium and potassium chlorides were fused in platinum, the calcium chloride was dried at 300°. These were kept in tightly stoppered bottles in a desiccator.

The strontium and barium chlorides were purified by recrystallization from redistilled water. The hydrated salts were used.

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[1] THIS JOURNAL, **35**, 1 (1913).

[2] *Phys. Rev.*, 21, 388 (1905).

[3] THIS JOURNAL, **35**, 1472 (1913).

Lithium chloride was dissolved in water and the carbonate was precipitated by a solution of ammonium carbonate. The carbonate was washed with a solution of ammonium carbonate until free from chlorides, then dissolved in nitric acid. The solution was evaporated until a large portion of the nitrate separated. The latter was three times recrystallized and finally converted to the chloride by passing hydrochloric acid gas over its solution in a quartz dish. The precipitated chloride was centrifuged out, redissolved, then reprecipitated by hydrochloric acid gas. The fused salt was used.

A pure grade of potassium and sodium hydroxide was used as purchased.

Sodium bromide was three times recrystallized from redistilled water.

All the water used was redistilled, first, from a solution of alkaline permanganate; secondly, from sulfuric acid, through a block tin condenser.

Apparatus.

For the measurements in which a saturated potassium chloride solution was used as a contact between the hydrogen and calomel electrodes, the cell (Fig. 1), a modified form of that used by Wilsmore,[1] was found to be easily reproducible to within a few tenths of a millivolt. The hydrogen, prepared electrolytically, was bubbled regularly through the solution contained in A, and thence through the hydrogen electrode vessel B. It was allowed to escape through the trap F which was open to the atmosphere. By passing the gas through the same solution in A as in B, it becomes saturated with the vapor of the solution, thus preventing evaporation of the solution in B.

A number of electrodes made of sheet platinum covered with a thick coating of platinum black, were employed, prepared according to Loomis and Acree.[2] All the precautions on preparing and cleaning the electrodes were taken.

The hydrogen electrode was connected with the calomel electrode through a saturated solution of potassium chloride contained in C. Between measurements, C was lowered after the stopcocks K and L were closed. In this way, the solution in C was kept separated from the solutions in the hydrogen and calomel electrodes. After each measurement the tubes TT were washed out by means of the solutions contained in DD. In this way any contact solution was prevented from entering the hydrogen electrode and fresh surfaces of contact between all the solutions were maintained.

Connection with the mercury in the calomel electrode was made by means of a platinum wire sealed in the end of tube M. The calomel paste, washed with a solution of potassium chloride of the desired strength,

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[1] *Z. physik. Chem.*, 35, 296 (1900).

[2] *Am. Chem. J.*, 46, 585 (1911).

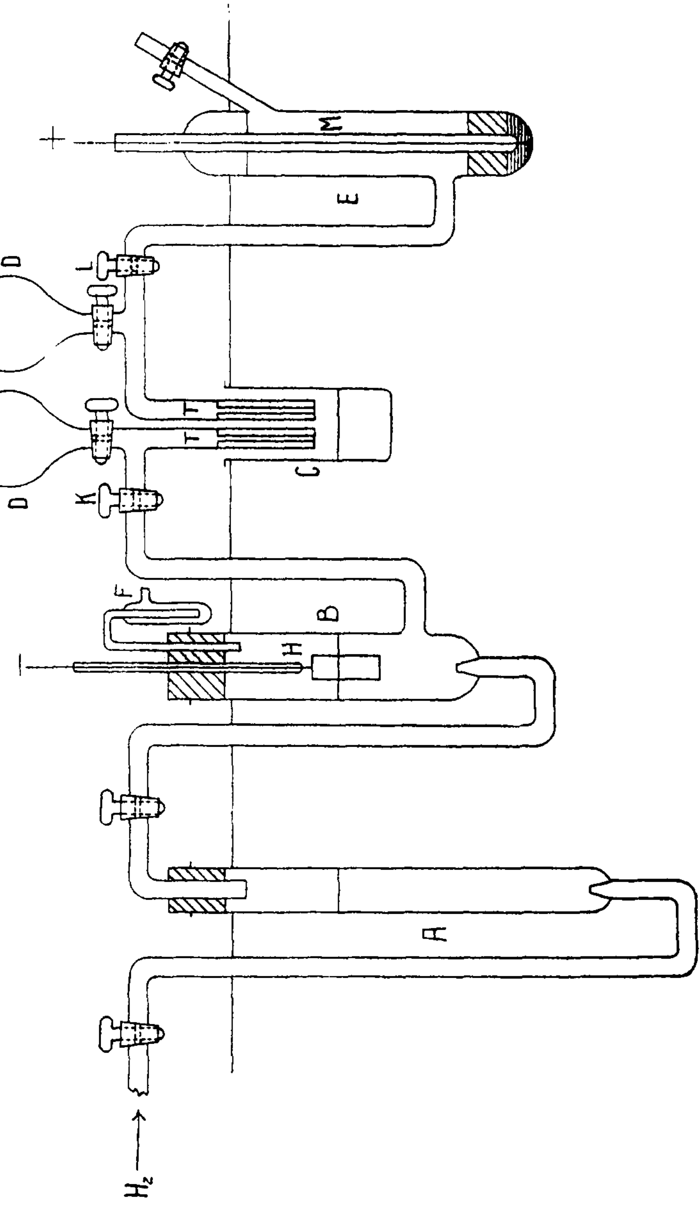

Fig. 1.

was introduced and simply shaken with the mercury as directed by Lewis.[1]

The whole cell was immersed in a thermostat up to the level P. All the measurements were carried out at a temperature of 25.00 ± 0.01°.

The electromotive force of this cell was obtained by means of a Wolff 15,000 ohm potentiometer and a suitable galvanometer.

Measurements of the Acid-Salt System.

Each observation required from four to five hours before constancy was assured. The following results made with the cell

$$\text{Hg} \mid \text{HgCl} \mid \text{KCl } (M) \mid \text{saturated KCl} \mid \text{HCl } (0.1\ M) \mid H_2$$

will show the constancy obtainable with the apparatus used. These particular measurements were made to test the reproducibility of the platinized sheet platinum electrodes. To each measurement it is necessary to apply the correction, $RT/(2F \ln 1/p)$ for the pressure of the hydrogen, where p equals the pressure of the gas in atmospheres. This is less than the atmospheric pressure by the vapor pressure of the solution. At 25°, the vapor pressure of water is 23.5 mm. This, expressed in atmospheres, subtracted from the barometric pressure, gave the value of p which was used in the above formula. Although the vapor pressure of the solutions in the hydrogen electrode were less than that of water, the error introduced by this substitution was less than the error of experiment.

TABLE I.—COMPARISON OF ELECTRODES.

Time. (Hours.)	E. M. F. (Obs.)	Corr. for the pressure of H.	E. M. F. (Corr.)
No. 1			
2	0.34893	.....	.....
3	0.34912	.....	.....
4	0.34916	0.00032	0.34948
No. 2			
2	0.34899	.....	.....
3	0.34907	.....	.....
4	0.34904	0.00036	0.34940
No. 3			
4	0.34921	0.00040	0.34961
No. 4			
4	0.34920	0.00040	0.34960
		Mean,	0.34952

From the first two of these results it is seen that the cell reaches a value constant within 0.05 of a millivolt in four hours. All observations were carried out in the same manner and were only accepted when this constancy was obtained. The final results are seen to vary in the fourth place. Therefore, in what follows, they will be expressed to 0.1 millivolt only.

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[1] THIS JOURNAL, 31, 355 (1909).

The variations in the electromotive force of this cell on the addition of neutral salts to the hydrochloric acid in the hydrogen electrode are given in Table II.

TABLE II.

<table>
<tr><th>Conc. of salt in mols per l.</th><th>E. M. F. (Obs.)</th><th>Corr. for pressure of H.</th><th>E. M. F. (Corr.)</th></tr>
<tr><td colspan="4">No. 1. Hg | HgCl | KCl (<i>M</i>) | sat. KCl | KCl in HCl (0.1 <i>M</i>) | H_2.</td></tr>
<tr><td>0.000</td><td>....</td><td>....</td><td>0.3495</td></tr>
<tr><td>0.1375</td><td>0.3488</td><td>0.0004</td><td>0.3492</td></tr>
<tr><td>0.275</td><td>0.3487</td><td>0.0003</td><td>0.3490</td></tr>
<tr><td>0.550</td><td>0.3479</td><td>0.0004</td><td>0.3483</td></tr>
<tr><td>0.825</td><td>0.3470</td><td>0.0004</td><td>0.3474</td></tr>
<tr><td>1.100</td><td>0.3455</td><td>0.0004</td><td>0.3459</td></tr>
<tr><td>1.376</td><td>0.3439</td><td>0.0004</td><td>0.3443</td></tr>
<tr><td>3.134</td><td>0.3322</td><td>0.0004</td><td>0.3326</td></tr>
<tr><td colspan="4">No. 2. Hg | HgCl | KCl (<i>M</i>) | sat. KCl | NaCl in HCl (0.1 <i>M</i>) | H_2.</td></tr>
<tr><td>0.000</td><td>....</td><td>....</td><td>0.3495</td></tr>
<tr><td>0.186</td><td>0.3480</td><td>0.0004</td><td>0.3484</td></tr>
<tr><td>0.562</td><td>0.3451</td><td>0.0003</td><td>0.3454</td></tr>
<tr><td>0.606</td><td>0.3450</td><td>0.0004</td><td>0.3454</td></tr>
<tr><td>1.488</td><td>0.3363</td><td>0.0004</td><td>0.3367</td></tr>
<tr><td colspan="4">No. 3. Hg | HgCl | KCl (<i>M</i>) | sat. KCl | $BaCl_2.2H_2O$ in HCl (0.1 <i>M</i>) | H_2.</td></tr>
<tr><td>0.000</td><td>....</td><td>....</td><td>0.3495</td></tr>
<tr><td>0.092</td><td>0.3479</td><td>0.0004</td><td>0.3483</td></tr>
<tr><td>0.185</td><td>0.3464</td><td>0.0003</td><td>0.3467</td></tr>
<tr><td>0.277</td><td>0.3448</td><td>0.0003</td><td>0.3451</td></tr>
<tr><td>0.461</td><td>0.3410</td><td>0.0004</td><td>0.3414</td></tr>
<tr><td>0.500</td><td>0.3402</td><td>0.0004</td><td>0.3406</td></tr>
<tr><td colspan="4">No. 4. Hg | HgCl | KCl (<i>M</i>) | saturated KCl | $SrCl_2.6H_2O$.in HCl (0.1 <i>M</i>) | H_2</td></tr>
<tr><td>0.000</td><td>....</td><td>....</td><td>0.3495</td></tr>
<tr><td>0.185</td><td>0.3464</td><td>0.0003</td><td>0.3467</td></tr>
<tr><td>0.093</td><td>0.3482</td><td>0.0003</td><td>0.3485</td></tr>
<tr><td>0.278</td><td>0.3453</td><td>0.0004</td><td>0.3457</td></tr>
<tr><td>0.324</td><td>0.3440</td><td>0.0004</td><td>0.3444</td></tr>
<tr><td>0.463</td><td>0.3413</td><td>0.0004</td><td>0.3417</td></tr>
<tr><td colspan="4">No. 5. Hg | HgCl | KCl (<i>M</i>) | saturated KCl | $CaCl_2$ in HCl (0.1 <i>M</i>) | H_2.</td></tr>
<tr><td>0.000</td><td>....</td><td>....</td><td>0.3495</td></tr>
<tr><td>0.132</td><td>0.3464</td><td>0.0004</td><td>0.3468</td></tr>
<tr><td>0.260</td><td>0.3442</td><td>0.0004</td><td>0.3446</td></tr>
<tr><td>0.396</td><td>0.3413</td><td>0.0004</td><td>0.3417</td></tr>
<tr><td>0.530</td><td>0.3385</td><td>0.0004</td><td>0.3389</td></tr>
<tr><td>0.795</td><td>0.3322</td><td>0.0003</td><td>0.3325</td></tr>
<tr><td colspan="4">No. 6. Hg | HgCl | KCl (0.1 <i>M</i>) | saturated KCl | LiCl in HCl (0.1 <i>M</i>) | H_2.</td></tr>
<tr><td>0.000</td><td>....</td><td>....</td><td>0.4004</td></tr>
<tr><td>0.359</td><td>0.3962</td><td>0.0006</td><td>0.3968</td></tr>
<tr><td>0.717</td><td>0.3931</td><td>0.0003</td><td>0.3934</td></tr>
<tr><td>1.077</td><td>0.3876</td><td>0.0006</td><td>0.3882</td></tr>
<tr><td>1.435</td><td>0.3834</td><td>0.0004</td><td>0.3838</td></tr>
</table>

TABLE II (*continued*).

Conc. of salt in mols per l.	E. M. F. (Obs.)	Corr. for pressure of H.	E. M. F. (Corr.)
No. 7. Hg | HgCl | KCl (0.1 *M*) | saturated KCl | NaBr in HCl (0.1 *M*) | H_2.			
0.000	....	....	0.4004
0.285	0.3980	0.0004	0.3984
0.855	0.3942	0.0003	0.3945
1.426	0.3897	0.0003	0.3900
No. 8. Hg | HgCl | KCl (0.1 *M*) | saturated KCl | mannite in HCl (0.1 *M*) | H_2.			
0.000	....	....	0.4004
0.116	0.4000	0.0004	0.4004
0.232	0.3998	0.0004	0.4002
0.464	0.3995	0.0004	0.3999
0.580	0.3997	0.0004	0.4001

When the solution of lithium chloride in hydrochloric acid was measured, a 0.1 *M* calomel electrode was used in order to compare the results obtained by this cell with those obtained by Loomis and Acree. For the cell

Hg | HgCl | KCl (0.1 *M*) | saturated KCl | HCl (0.1 *M*) | H_2

three different electrodes gave the following values:

E. M. F. (Obs.)	Corr. for pressure of H.	E. M. F. (Corr.)
0.3999	0.0003	0.4002
0.4001	0.0003	0.4004
0.4001	0.0004	0.4005
	Mean,	0.4004

As a mean of four measurements of the same cell, Loomis and Acree obtained 0.4001. This concordance is good confirmation of the accuracy of the apparatus employed in this series of measurements.

In Experiments 1 to 6, all the salts introduced into the acid possess an ion common with the anion of the acid. To introduce a salt which did not possess a common ion, sodium nitrate was tried, but this was found to be reduced to ammonia by molecular hydrogen in the presence of platinum black. Sodium bromide gave values under No. 7.

Finally, in order to have an example of the action of a nonelectrolyte, mannite was introduced into the acid. The results are given under No. 8.

These results can best be interpreted from the plots (Fig. 2). Here, change in electromotive force in volts is plotted against the concentration of the salt in the acid expressed in gram equivalents per liter. A drop in the plot indicates a drop of potential.

The first fact of importance to be observed from these results is that in every case there is a fall in electromotive force while the mass-action effect[1] would tend to increase the electromotive force of the cell owing

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[1] As ordinarily understood, where the equilibrium under consideration is assumed to be between the ions and the undissociated molecules and the equilibrium between these and the solvent is not taken into account.

to a decrease in hydrogen-ion activity. Secondly, since in every case the mobility of the anion of the salt is greater than that of the cation, addition of salt will change the liquid potential between the saturated potassium chloride solution and the hydrochloric acid-salt solution in a direction which will decrease the electromotive force of the cell. The question thus arises whether this drop in potential is entirely due to liquid potential.

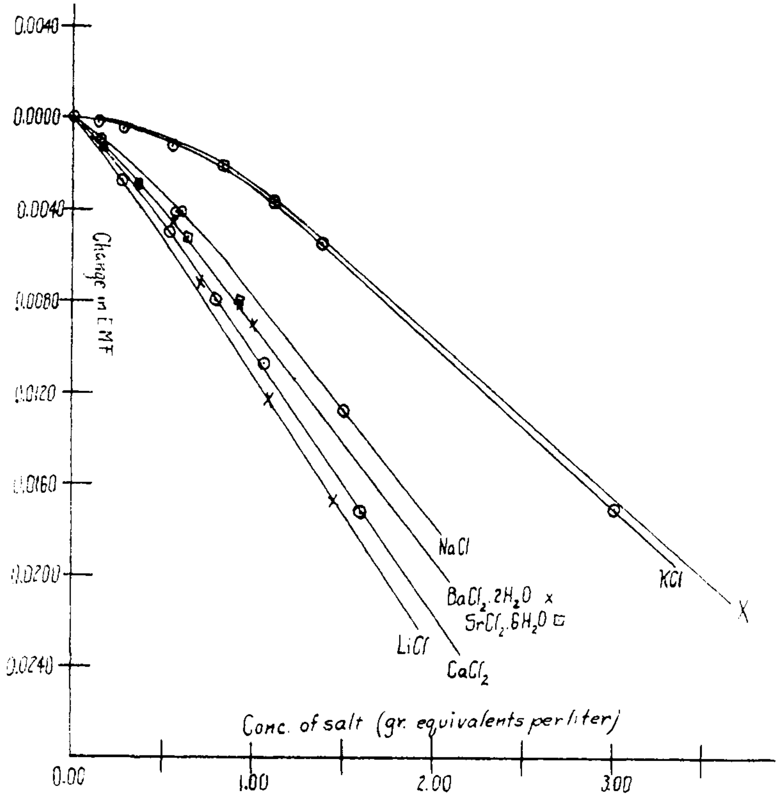

Fig. 2.—HCl-salt solution mixtures.

A study of the distribution of these curves will afford evidence that the latter is not the case, but that a decrease in electromotive force of the hydrogen electrode (0.1 *M* HCl) is produced by the addition of neutral salts. Fig. 3 gives the conductance curves of the alkali and alkaline earth chlorides.[1] Here, equivalent conductance is plotted against the concentration in gram equivalents per liter. It is obvious that there is an analogy between the distribution of these plots with those given in Fig. 2. The molecular conductance is a function of the degree of ionization and

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[1] From the data of Kohlrausch (18°).

ionic mobilities. Therefore, the difference between these conductance plots for the different salts is a function of the degrees of dissociation and the difference of the mobilities of the cations, since in every case the anions are the same. In like manner, the differences in the electromotive force plots (Fig. 2) will be a function of the degrees of dissociation and the differences between mobilities of the cation. The meaning of these facts is obvious, for it is the difference in the ionic mobilities which gives rise to the production of a liquid potential between two solution surfaces. This interpretation is borne out by the experimental results. The mobility of the potassium ion[1] is 64.5, that of the chlorine ion 65.5. These are nearly the same, and, for this reason the addition of potassium chloride would be expected to produce only a slight change in

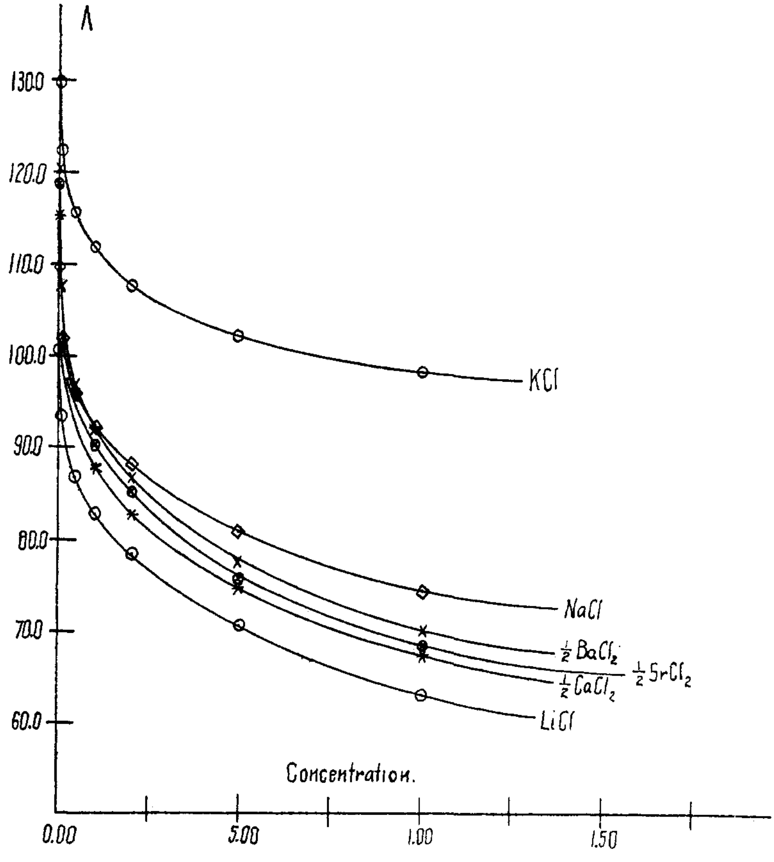

Fig. 3.—Conductance plots. 18°.

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[1] Noyes and Falk, THIS JOURNAL, 34, 479 (1912). The mobility of the lithium ion at 25° is not given by Noyes and Falk. For this reason, the values at 18° are used here. Since ratios are desired, these values are satisfactory for the present discussion.

liquid potential. The mobilities of the sodium and lithium ions, 43.45 and 33.3, respectively, are less than that of the potassium ion and hence should give a greater change in liquid potential than does potassium chloride. This is found to be the case. Furthermore, since from the conductance data the degrees of dissociation of these chlorides are nearly the same, the differences in change of liquid potential produced by them should be in the ratios of their ionic mobilities. Thus, the difference between the ionic mobilities of the potassium and sodium ions is 21.1, between the sodium and lithium 10.1. The ratio of the difference between the potassium chloride and sodium chloride plots and the sodium and lithium chloride plots (Fig. 2) is found by experiment to be approximately 2 to 1. Since this ratio holds, it seems that the mass-action effects of these chlorides are approximately identical.

As a result of this evidence there is fair reason to assume that the differences in the distribution of these curves are entirely due to differences in change of liquid potential. The curve for potassium chloride now becomes extremely interesting, for, since the ionic mobilities in this salt are so nearly the same, practically no change in liquid potential would be expected. This argues for the conclusion that there is a third influence operating here, opposite in its action to the effect of mass action as ordinarily understood and influencing the electromotive force of the cell in the same direction as the change of liquid potential. Furthermore, if the differences in the distribution of these plots is, as has been assumed above, due entirely to differences in liquid potential, a curve of zero liquid potential can be predicted. This would be a plot produced by a salt which would yield ions having identical mobilities. If the above assumptions are true, X will represent the change in electromotive force of the hydrogen electrode produced by the addition of salts to 0.1 *M* hydrochloric acid.

The following calculations made from plot X by means of Formula 5 will show the increase in activity of the hydrogen ion in a 0.1 *M* solution of hydrochloric acid on the addition of a neutral salt. First, however, it is necessary to determine the hydrogen-ion activity in 0.1 *M* hydrochloric acid. From the most recent and accurate work of the hydrogen electrode, Lewis[1] has obtained 0.3460 and 0.3980, respectively, for the electromotive forces of the following cells:

$$\mathrm{Hg} \mid \mathrm{HgCl} \mid \mathrm{KCl}\ (M) \parallel \mathrm{HCl}\ (0.1\ M) \mid \mathrm{H_2}$$

$$\mathrm{Hg} \mid \mathrm{HgCl} \mid \mathrm{KCl}\ (M) \parallel \mathrm{HCl}\ (0.01\ M) \mid \mathrm{H_2}$$

Furthermore, he gives 0.92 as the corrected value of the degree of dissociation of 0.01 *M* HCl. On the assumption that in 0.01 *M* solution the activity equals the concentration, the activity of the hydrogen ion

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[1] THIS JOURNAL, 36, 1969 (1914).

in 0.1 M solution can be calculated by Equation 5. From the above data, it is found that the cell

$$H_2 \mid HCl\ (0.1\ M) \parallel HCl\ (0.01\ M) \mid H_2$$

has an electromotive force of 0.0520 volt. Hence,

$$0.0520 = 0.0591 \log a/0.0092$$

and a becomes 0.0698.

TABLE III.—HYDROGEN-ION ACTIVITY FROM PLOT X.

Conc. of salt	0.000	0.500	1.000	1.500	2.000	2.500	3.000
a	0.0698	0.0720	0.0778	0.0882	0.1002	0.1149	0.1323

From these data it is seen that the hydrogen-ion activity has been nearly doubled by the presence of a salt of 3 M concentration. Observation of the calcium, strontium, and barium chloride plots will show that the effect of hydration is small. It is interesting to note that the excess of four molecules of water of crystallization of the strontium chloride over those of the barium chloride dilutes the solution sufficiently to render their plots identical. According to the conductance curves, the strontium chloride plot should lie between the calcium and barium chloride plots.

The Hydroxide-Salt System.

From these experiments it follows that the addition of neutral salts to a 0.1 M hydrochloric acid solution increases the hydrogen-ion activity of the solution. Whether the hydroxyl-ion activity of solutions of sodium and potassium hydroxides is increased or decreased by the addition of neutral salts, is shown by the variations of the cells

$$Hg \mid HgCl \mid KCl\ (M) \mid \text{saturated } KCl \mid NaOH\ (0.1\ M) \mid H_2$$

$$Hg \mid HgCl \mid KCl\ (0.1\ M) \mid \text{saturated } KCl \mid KOH\ (0.1\ M) \mid H_2$$

on the addition of neutral salts to the hydroxides in the hydrogen electrode as can be seen in the results of Table IV.

TABLE IV.

Conc. of salt in mols per l.	E. M. F. (Obs.)	Corr. for pressure of H.	E. M. F. (Corr.)
No. 1. $Hg \mid HgCl \mid KCl\ (M) \mid$ saturated $KCl \mid KCl$ in $NaOH\ (0.1\ M) \mid H_2$.			
0.000	1.0412	0.0004	1.0416
0.386	1.0413	0.0003	1.0416
1.157	1.0409	0.0004	1.0413
1.928	1.0425	0.0004	1.0429
No. 2. $Hg \mid HgCl \mid KCl\ (M) \mid$ saturated $KCl \mid NaCl$ in $NaOH\ (0.1\ M) \mid H_2$.			
0.000	....	....	1.0416
0.467	1.0368	0.0004	1.0372
0.926	1.0341	0.0004	1.0345
1.402	1.0318	0.0004	1.0322
1.869	1.0305	0.0004	1.0309
2.337	1.0292	0.0004	1.0296

TABLE IV (*continued*).

Conc. of salt in mols per l.	E. M. F. (Obs.)	Corr. for pressure of H.	E. M. F. (Corr.)
No. 3. Hg | HgCl | KCl (0.1 *M*) | saturated KCl | KCl in KOH (0.1 *M*) | H_2.			
0.000[1]	1.0941	0.0004	1.0945
0.000[1]	1.0940	0.0003	1.0943
0.000[1]	1.0943	0.0003	1.0946
0.259	1.0929	0.0003	1.0932
0.518	1.0927	0.0003	1.0930
1.295	1.0933	0.0003	1.0936
2.027	1.0945	0.0004	1.0949
2.978	1.0986	0.0003	1.0989
No. 4. Hg | HgCl | KCl (0.1 *M*) | saturated KCl | NaCl in KOH (0.1 *M*) | H_2.			
0.000	....	....	1.0945
0.346	1.0879	0.0003	1.0882
0.692	1.0857	0.0004	1.0861
1.038	1.0838	0.0004	1.0842
1.728	1.0814	0.0004	1.0818
No. 5. Hg | HgCl | KCl (0.1 *M*) | saturated KCl | LiCl in KOH (0.1 *M*) | H_2.			
0.000	....	....	1.0945
0.661	1.0803	0.0003	1.0806
1.322	1.0709	0.0003	1.0712
1.983	1.0629	0.0004	1.0633

The plots of these observations are given in Fig. 4. Change in electromotive force of the cell is plotted against the concentration in mols per liter of the salts added. The electromotive forces of the cells when no salts are present in the hydroxides are zero on the scale of ordinates.

In the first place, in the case under immediate discussion, the change in liquid potential and mass-action effect increases the electromotive forces of the cells. The plots of potassium chloride in both the sodium and potassium hydroxides clearly show that there is an increase in electromotive force which indicates an increase in hydroxyl-ion concentration.

There is, however, a striking difference between the distribution of the plots in Fig. 2 and Fig. 4. In the acid system, the difference in the changes in electromotive force produced by the different salts is much less than the corresponding differences in the hydroxide system. This is due, in part at least, to the differences in magnitude of the liquid potentials. A comparison of the liquid surfaces under discussion will serve to explain this difference. In the acid system, the change in liquid potential will be produced at the liquid surface

MeX in HCl (0.1 *M*) | saturated KCl.

On the addition of salt, the acid solution will become positively charged to the saturated potassium chloride solution, owing to the fact that, in

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[1] Carried out with three different electrodes.

every case, the anion has a greater mobility than the cation. At the same time, we have found that the activity of the hydrogen ion has been increased. This will tend to charge the saturated potassium chloride solution positive to the acid solution, owing to the relatively high mobility of the hydrogen ion. Thus, there is set up a liquid potential which tends to oppose that set up by the salt. Therefore, the influence of this increase in hydrogen ion activity on the liquid potential in the acid system will cause the plots of the different salts to fall close together.

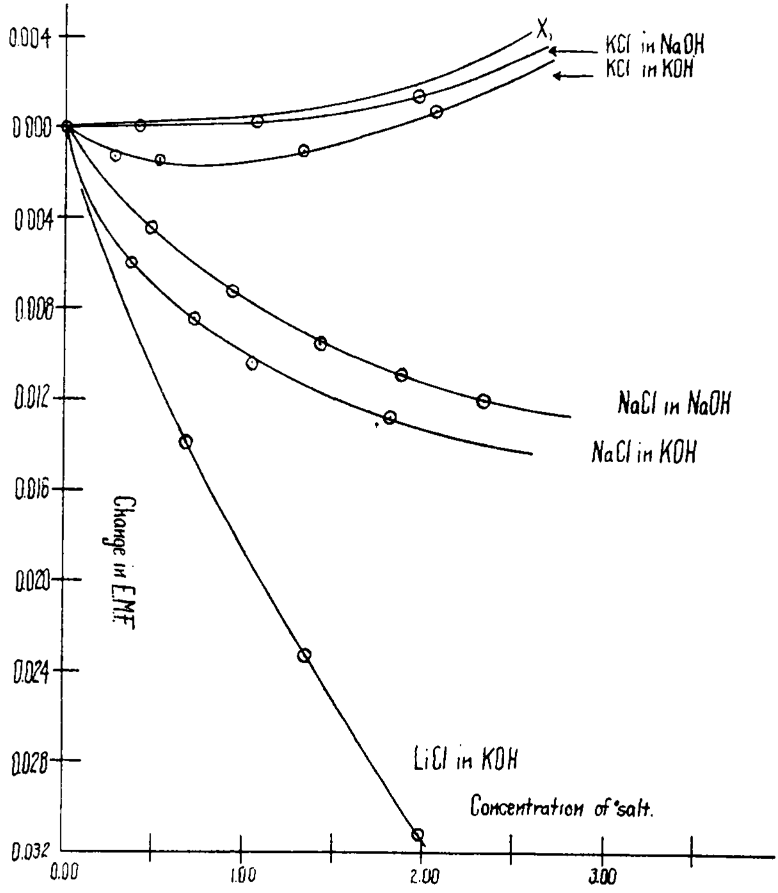

Fig. 4.

Now in the hydroxide system, the surface

MeX in MeOH (0.1 M) | saturated KCl

will produce the liquid potential. As before, the influence of the addition of salt will be to decrease the electromotive force of the cell. But the hydroxyl-ion concentration has increased, and this will change the liquid potential, and, like the salt, it will tend to increase the negative charge on the saturated potassium chloride solution, owing to the high mobility of the hydroxyl ion. The total effect will be to spread the plots in Fig. 4.

The wide differences between these plots are probably not entirely due to these differences in liquid potentials. Since, in a solution containing lithium chloride and potassium hydroxide, there will be an equilibrium between the ions and the undissociated molecules, and, since the best evidence shows that the degree of dissociation of lithium hydroxide is less than that of sodium or potassium hydroxides, a difference in mass-action effects would be expected. This may act in such a way as to cause the plots to spread.

These plots afford excellent evidence that there is an increase in electromotive force produced by the presence of neutral salts in hydroxide solutions, according to which the hydroxyl-ion activity of the solution will be increased.

It can be assumed, as in the case of the acid systems, that the differences in the plots of the different salts, with the exception of the lithium chloride plot, is due only to the differences in liquid potential and mass action, and from the above data, X_1 can be plotted, which represents the change in electromotive force of the hydrogen electrode produced by the addition of salts to 0.1 *M* sodium hydroxide.

Table V gives the increase in hydroxyl-ion activity due to the presence of neutral salts according to curve X_1. From the recent accurate investigations of Lewis and Lorentz, and Bohi,[1] the value of the cell

$$H_2 \mid KOH\ (0.1\ M) \parallel KOH\ (0.01\ M) \mid H_2$$

is 0.0562 volt. From the assumption that in 0.01 *M* potassium hydroxide, the hydroxyl-ion activity is 0.0092, the hydroxyl-ion activity in 0.1 *M* solution can be computed by Equation 5 as follows:

$$0.0562 = 0.05915 \log a/0.0092$$

Thus a equals 0.0822.

TABLE V.—HYDROXYL-ION ACTIVITY FROM PLOT X_1.

Conc. of salt	0.000	0.500	1.000	1.500	2.000	2.500	3.000
a	0.0822	0.0828	0.0835	0.0855	0.0892	0.0961	0.1071

The Liquid Potential Effect.

It was thought that a further investigation of the liquid potentials might contribute evidence in confirmation of the positions of the plots for zero liquid potential, namely, X and X_1 (Figs. 2 and 4). To this end, measurements of the cells

$$Hg \mid HgCl \mid KCl\ (0.1\ M) \mid KCl \text{ in } HCl\ (0.1\ M) \mid H_2$$
$$Hg \mid HgCl \mid HCl\ (0.1\ M) \mid NaCl \text{ in } HCl\ (0.1\ M) \mid H_2$$

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[1] *Z. physik. Chem.*, 66, 733 (1909).

were made. In this series of observations, it was found that the cell used in the previous experiments gave results which did not attain the desired constancy even after a period of ten hours. In order to overcome this difficulty, another cell was set up which differed only in the slightest particulars from that used by Loomis and Acree. Even then, the constancy obtained by using a saturated potassium chloride solution as a contact was not reached when the concentration of the salt in acid was greater than 0.5 *M*. In all cases, however, constancy was attained within 0.2 of a millivolt. Table VI shows the results.

TABLE VI.

Conc. of salt.	E. M. F. (Obs.)	Corr. for pressure of H.	E. M. F. (Corr.)
No. 1. $\mathrm{Hg} \mid \mathrm{HgCl} \mid \mathrm{KCl}\ (0.1\ M) \mid \mathrm{KCl\ in\ HCl}\ (0.1\ M) \mid \mathrm{H_2}$.			
0.000	0.42704[1]	0.00034	0.4274
0.095	0.4230	0.0003	0.4233
0.286	0.4161	0.0003	0.4164
0.477	0.4123	0.0003	0.4126
0.953	0.4085	0.0004	0.4089
2.358	0.3968	0.0003	0.3971
3.423	0.3861	0.0002	0.3863
No. 2. $\mathrm{Hg} \mid \mathrm{HgCl} \mid \mathrm{HCl}\ (0.1\ M) \mid \mathrm{NaCl\ in\ HCl}\ (0.1\ M) \mid \mathrm{H_2}$.			
0.000	0.3987	0.0004	0.3991[2]
0.014	0.3983	0.0003	0.3986
0.028	0.3975	0.0003	0.3978
0.070	0.3975	0.0003	0.3978
0.141	0.3963	0.0006	0.3969
0.423	0.3947	0.0003	0.3950
0.705	0.3922	0.0003	0.3925
1.062	0.3890	0.0002	0.3892
1.133	0.3879	0.0003	0.3882
1.416	0.3843	0.0004	0.3847

A comparison of the plots of these results with those obtained when a contact solution was used are given in Figs. 5 and 6. With Plot B (Fig. 5) there is a definite liquid potential at the start between the 0.1 *M* potassium chloride solution and the 0.1 *M* hydrochloric acid. This, according to Lewis and Sargent,[3] amounts to 0.0284 volt. On the addition of potassium chloride to the acid, this is decreased. The fact of most importance to be derived from Plots A and B (Fig. 5) is the large difference in the change in e. m. f. between them. This wide discrepancy affords an excellent means of testing the liquid potential formula.

The former experiments have indicated that the plots X and X_1 (Figs. 2 and 4) represent the changes in e. m. f. produced at the hydrogen elec-

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[1] This agrees with the value 0.4270 obtained by Bjerrum (*Z. physik. Chem.*, **53**, 428 (1905)).

[2] The latest value of Sebastian (Lewis, THIS JOURNAL, **36**, 1968 (1914)) is 0.3990.

[3] THIS JOURNAL, **33**, 306 (1911).

trode alone. In order to confirm the assumptions made in regard to these experiments, the values of a few of these liquid potentials were calculated and deducted from the original results. After the liquid potential has been eliminated by this method, the plots of the results may be compared to Plots X and X_1.

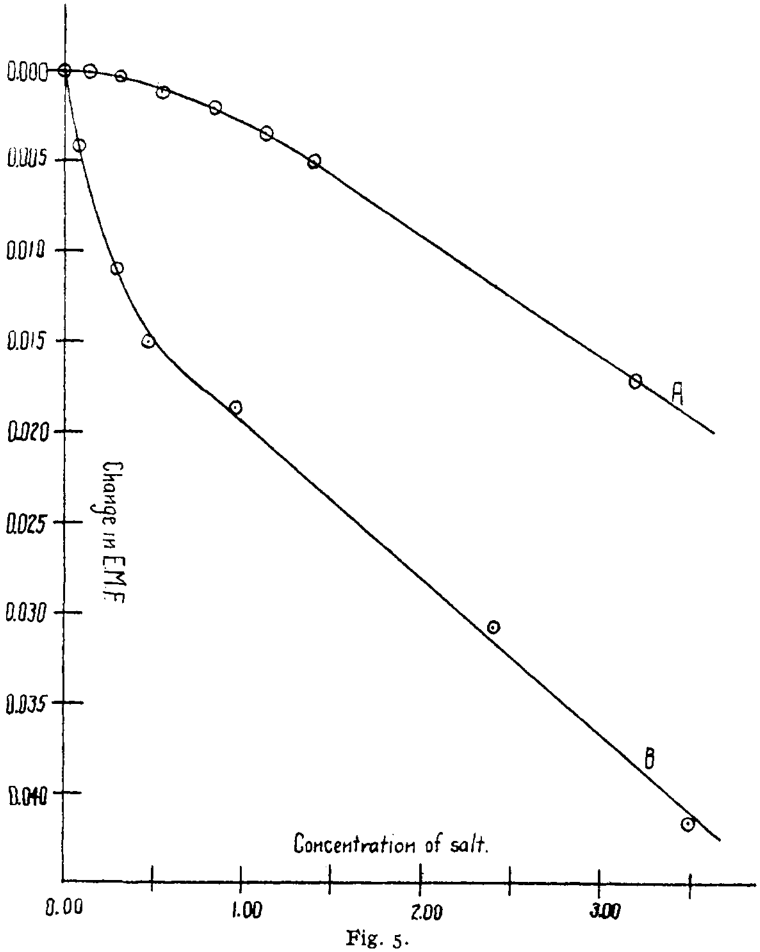

Fig. 5.

Planck[1] has deduced a general differential equation for the liquid potential between two solutions containing univalent ions. On the assumption that the simple gas equation holds for solutions, and that the ideal diffusion laws hold, this equation can be integrated, and gives the following:

$$\frac{\xi U_2 - U_1}{V_2 - \xi V_1} \times \frac{C_2 - \xi C_1}{\xi C_2 - C_1} = \frac{\log C_2/C_1 - \log \xi}{\log C_2/C_1 + \log \xi}$$

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[1] *Wied. Ann.*, 39, 161 (1890); 40, 561 (1890).

where U_1 equals the product of the mobilities of the cations in the dilute solution and the concentration of the ions; U_2 the same in the concentrated solution; V_1, the product of the mobility and the concentration of the anions in the dilute solution; V_2, the same for the anions in the concentrated solution. C_1 equals the total ionic concentration in the dilute solution; C_2 the total ionic concentration in the concentrated solution. From the function ξ, the liquid potential E can be calculated by the formula

$$E = 0.0591 \log \xi.$$

Although this equation was cumbersome, and could only be solved by a method of approximation, it was the only one which was general enough for the calculation of the complex liquid potentials under consideration. Furthermore, it was realized that it was only accurate to within a few millivolts when applied to solutions of concentration above 0.1 *M*. However, it was the best that could be found for the present purpose, and, as will be seen, affords interesting confirmation of the experimental results.

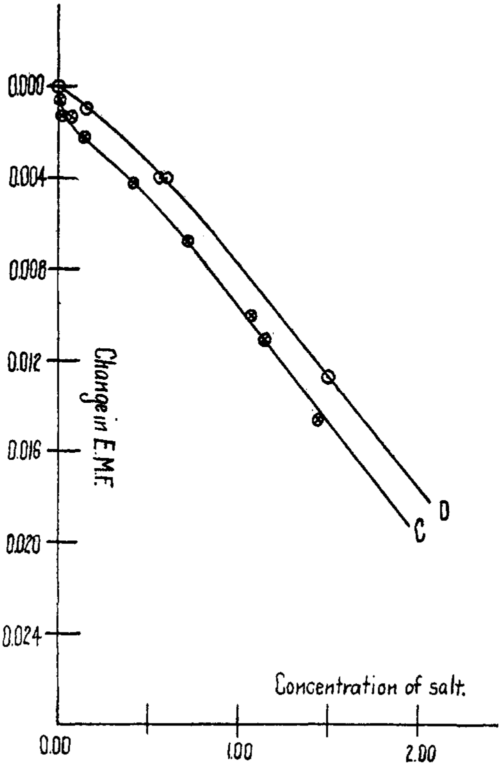

Fig. 6.

In the use of this equation, the following assumptions were made:

1. That the degree of dissociation, α, obtained from conductance measurements, represents the correct value.

2. That, in solutions containing both salt and acid or hydroxide, the ions act independently. U_2, V_2, U_1, V_1 represent, then, the mean mobility of the ions times their total concentration in the concentrated and dilute solutions, respectively.

In Table VII (1) is the liquid potential calculated by the Planck formula, (2) is the change in liquid potential produced by the addition of the salt to the solution.

These calculated changes in electromotive force are eliminated from those actually observed, and the resulting values are plotted in Fig. 7

TABLE VII.

Conc. of salt.	(1).	(2).	(1).	(2).
No. 1. KCl in HCl (0.1 *M*) | KCl (0.1 *M*).			No. 3. NaCl in HCl (0.1 *M*) | HCl (0.1 *M*).	
0.000	0.0267[1]	....	0.0000	....
0.10	0.0201	—0.0066	—0.0018	—0.0018
0.50	0.0105	—0.0162	—0.0059	—0.0059
1.00	0.0099	—0.0168	—0.0088	—0.0088
2.00	0.0095	—0.0172	—0.0092	—0.0092
No. 2. KCl in HCl (0.1 *M*) | KCl (4.16 *M*).			No. 4. KCl in NaOH (0.1 *M*) | KCl (4.16 *M*).	
0.000	0.0052	....	—0.0006	....
0.50	0.0025	—0.0027	—0.0009	—0.0003
1.00	0.0021	—0.0031	—0.0010	—0.0004
2.00	0.0019	—0.0033	—0.0011	—0.0005

along with the plots X and X_1.[2] First, it is to be noticed that the plots A and B (Fig. 5) have been brought close together and fall near Plot C in Fig. 6. For example, in the presence of 2 *M* salt, there is a difference of 0.005 volt. Before the correction for liquid potential was made, the difference was 0.019 volt. Furthermore, the acid curves fall around X. It is realized that the agreement between the calculated and the ob-

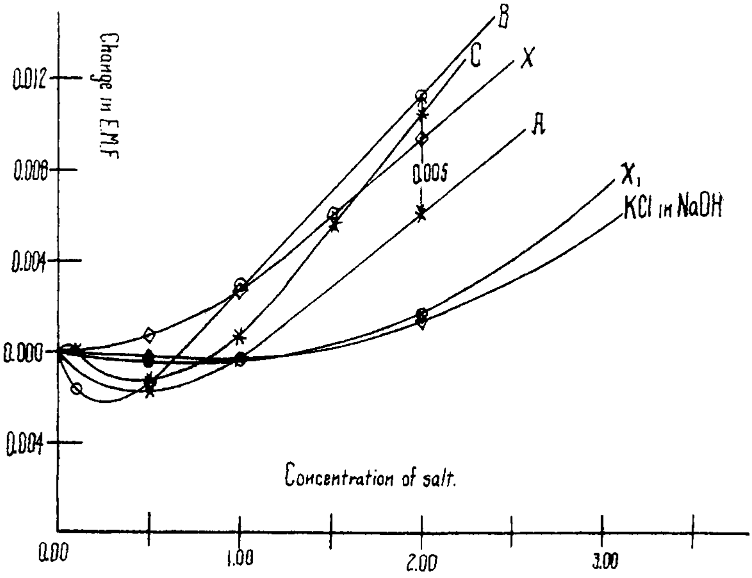

Fig. 7.

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[1] The value obtained by Lewis and Sargent's formula (*loc. cit.*) is 0.0284. The value calculated by Planck's formula is used in these calculations, for, since the change in e. m. f. is the important factor, it was thought best to use the same equation for all calculations.

[2] In Fig. 7, a drop in potential for the acid plots is indicated by a rise in the curve; a rise in potential for the hydroxide plots corresponds to a rise in the curve. In this way, the relative magnitudes of X and X_1 can be compared.

served results is not all that may be desired, but the evidence thus obtained contributes in confirming the position of X and X_1.

The Mass-Action Effect.

It is of interest to notice the similarity of the plots of sodium chloride and bromide in hydrochloric acid solution (Fig. 8). Up to the salt concentration of 0.65 *M*, these plots are almost identical; beyond this, there is a slight deviation. Since the mobilities of the chlorine ion and bromine ion only differ slightly, a very small difference in liquid potential would be expected. Also, the plots of potassium chloride in potassium amd sodium hydroxides are nearly identical, as are those of sodium chloride in these two hydroxides. It appears that the presence in the salt of an ion common with the acid or the base causes no greater mass-action effect than when no common ion is present. This raises the question as to whether this behavior is in full theoretical accord with the law of mass action as usually applied. In the following deductions, the action of sodium chloride and bromide on the hydrogen-ion concentration[1] of hydrochloric acid is investigated. These examples will serve as types:

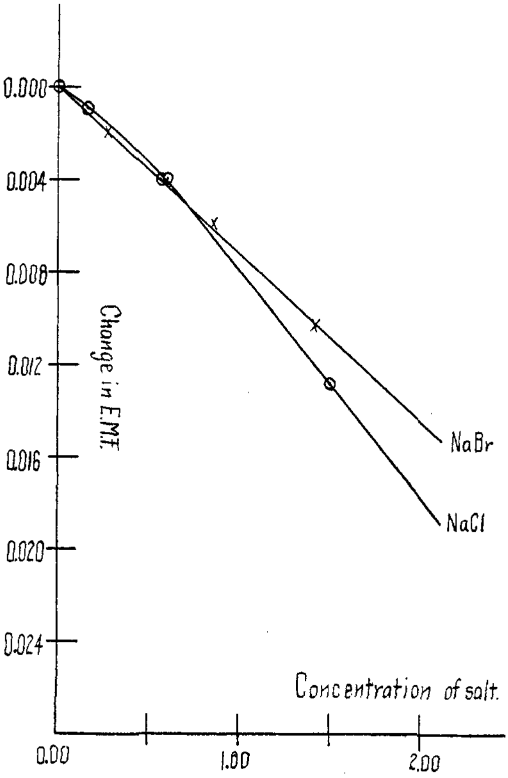

Fig. 8.

Case I.—The acid and salt have no ion in common. In this the sodium bromide hydrochloric acid solution, four equilibria must be considered, namely, those between the ions and the undissociated hydrochloric acid, hydrobromic acid, sodium chloride and sodium bromide. The assumption that the equilibrium constants of these four substances are equal is in good accord with the experimental results. This leads to the following set of equations:

$$K = xy/a = xv/b = yz/c = zv/d \qquad (6)$$

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[1] Concentrations are used instead of activities in the following mass-action calculations.

where x = [H], y = [Cl], z = [Na], v = [Br], a = [HCl], b = [HBr], c = [NaCl], and d = [NaBr].

Now, let n equal the equivalent acidity, m the concentration of salt added in moles per liter. Then

$$\left.\begin{aligned} x + a + b &= n \\ y + a + c &= n \\ z + c + d &= m \\ v + b + d &= m \end{aligned}\right\} \qquad (7)$$

Eliminating a, b, c, d from Equations 6 and 7, the following set of equations is obtained:

$$\left.\begin{aligned} x + xy/\mathrm{K} + xv/\mathrm{K} &= n \quad (a) \\ y + xy/\mathrm{K} + yz/\mathrm{K} &= n \quad (b) \\ z + yz/\mathrm{K} + zv/\mathrm{K} &= m \quad (c) \\ v + xv/\mathrm{K} + zv/\mathrm{K} &= m \quad (d) \end{aligned}\right\} \qquad (8)$$

By dividing (b) by (d), we obtain $v/y = m/n$. (9)

By dividing (a) by (c), we obtain $z/x = m/n$. (10)

Furthermore, Equations 8 are symmetrical and hence

$$x = y \text{ and } z = v. \qquad (11)$$

Therefore, from (9), (10) and (11), we obtain

$$x^2 \,[(n + m)/\mathrm{K}n] + x - n = 0. \qquad (12)$$

When $m = 0$, α, the degree of dissociation of the acid, equals x/n or $x = \alpha n$. Hence,

$$\mathrm{K} = \alpha^2 n/(1 - \alpha).$$

This is the well-known dilution law.

Case II.—The acid and the salt have an ion in common. In this case, there will be present only two undissociated molecules, namely, hydrochloric acid and sodium chloride, and, on the assumption that the dissociation constants of these are the same, we obtain

$$\mathrm{K} = xy/a = yz/c. \qquad (13)$$

Furthermore,

$$\left.\begin{aligned} x + a &= n \quad (3) \\ z + c &= m \quad (2) \\ y + a + c &= m + n \quad (3) \end{aligned}\right\} \qquad (14)$$

Hence, $x + z = y$. (15)

Equations 13 and 14 give on the elimination of a and c

$$x + xy/\mathrm{K} = n; \quad z + yz/\mathrm{K} = m \qquad (16)$$

which with (15) give on elimination of y

$$x + x(x + z)/\mathrm{K} = n; \quad z + z(x + z)/\mathrm{K} = m. \qquad (17)$$

Solving for x by direct substitution, the same expression is obtained as in Case I, namely:

$$x^2\,[(n + m)/\mathrm{K}n] + x - n = 0 \qquad (12)$$

Thus, according to the law of mass action, the effects of sodium chloride and bromide on the hydrogen-ion concentration are identical, if the assumption is made that the dissociation constants of all the substances present are the same. In the same manner, the identity of the plots in the hydroxide–salt system could receive a theoretical explanation.

As a conclusion to this discussion, it is desirable to emphasize that a similar deviation from the mass-action law, as generally applied, is observed in solutions of salts in hydrochloric acid, in sodium and potassium hydroxides as in solutions of a single electrolyte. In order to bring out this point, Table VIII is appended, in which Column 1 represents the concentration of the salt in the acid, (2) the hydrogen-ion concentration calculated according to Equation 12, (3) the observed hydrogen-ion concentration calculated from Plot X, and (4) is the ratio of the calculated to the observed values. For potassium chloride, Kraus and Bray[1] concluded that K equals 0.08 at 18°. This value was used for both the dissociation constant of the acid and the salt. 0.092[2] was taken as the hydrogen-ion concentration of the acid. In obtaining the values in Column 3, it was assumed that the ratio of the activity to the concentration of the hydrogen ion was a constant.

Table VIII.

Conc.	Calc. H^+.	Obs. H^+.	Calc.: Obs.	Conc.	Calc. Cl^-.	Obs. Cl^-.	Calc.: Obs.
0.000	0.058	0.092	0.630	0.100	0.058	0.087	0.667
0.200	0.040	0.093	0.430	0.300	0.143	0.244	0.586
0.500	0.031	0.095	0.327	0.600	0.216	0.466	0.464
1.000	0.024	0.102	0.233	1.100	0.259	0.842	0.308
2.000	0.018	0.132	0.136	2.100	0.367	1.472	0.249
3.000	0.014	0.174	0.081	3.100	0.459	2.118	0.216

For comparison, the following calculations from the conductance data have been added: Column 5 gives the concentration of salt, (6) is the chlorine-ion concentration calculated by Equation 12, (7) is αC or the observed chlorine-ion concentration, and (8) is the ratio of the calculated and the observed values.

This is sufficient to show the increasing deviation from the mass-action law in the two cases under discussion.

Summary and Conclusion.

1. By measurements with the hydrogen electrode, evidence has been obtained which indicates that the hydrogen-ion activity and concentration of 0.1 *M* hydrochloric acid is increased by the presence of neutral salts.

2. Evidence has also been obtained that the hydroxyl-ion activities

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[1] This Journal, **35**, 1412 (1913).

[2] Noyes and Falk, This Journal, **34**, 485 (1912).

and concentrations of 0.1 *M* potassium and sodium hydroxides is increased by the addition of neutral salts.

3. Tables for the increase of the hydrogen-ion activity of hydrochloric acid solutions, and the hydroxyl-ion activity of potassium and sodium hydroxide solutions containing neutral salts have been appended.

4. The evidence thus far obtained in the acid-salt system indicates that the increase in activity of the hydrogen ion in the acid differs little for the different salts used in these experiments. This does not appear to hold in the hydroxide-salt system.

5. Calculations made by the Planck formula for liquid potential lend confirmation to the experimental results.

6. The experimental fact that sodium bromide produces the same effect on the hydrogen-ion activity of hydrochoric acid solutions as does sodium chloride has been proved to be in accord with the law of mass action. This is also true of similar cases in the hydroxide-salt systems.

7. If the interpretation of the experimental results as given above is correct, then, in a solution of 0.1 *M* hydrochloric acid, the hydrogen-ion concentration has been increased from 0.092 to 0.1765 *M* by the presence of 3 *M* potassium chloride. This points to the conclusion that the solution acts as if it were contracting, or that the volume of solvent has decreased.

PHILADELPHIA, PA.

[FROM THE LABORATORY OF GAS INVESTIGATION OF THE BUREAU OF MINES.]

THE VAPOR PRESSURES OF ACETYLENE, AMMONIA AND ISOBUTANE AT TEMPERATURES BELOW THEIR NORMAL BOILING POINTS.[1]

BY G. A. BURRELL AND I. W. ROBERTSON.

Received August 16, 1915.

In this report are shown the vapor pressures of acetylene, ammonia, and isobutane at temperatures below their normal boiling points. The method of procedure is the same as that detailed in previous communications to THIS JOURNAL by the authors.[2] The thermometers were calibrated at two additional points, other than those used by the authors in previous work. These points are the melting points of mercury and ice. Henning[3] gives for the melting point of mercury, —38.89°. In calibrating thermometers against this point, the authors carefully purified mercury by the method of Hulett.[4] About 15 cc. of mercury were placed in a test tube and immersed in the gasoline bath[5] maintained at a

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[1] Published by permission of the Director of the Bureau of Mines.

[2] THIS JOURNAL, **37**, 1893 (1915).

[3] *Ann. Phys.*, **43**, 294 (1913).

[4] *Phys. Rev.*, 34, 307 (1911).

[5] See THIS JOURNAL, **37**, 1893 (1915) (Fig. 1).