in this reaction is not the stoichiometric equivalent in the most concentrated solution used and a greater amount is required in more dilute solutions although the concentration required then is less. Thus the amount of cupric chloride required depends on both the actual weight of silver present and the concentration of the salt.

From the time required for the reaction to take place, it is clear that 0.6% of gum arabic is a much better protector for silver than a 0.3% solution, and this is also true with various dilutions of the original sol.

Summary

1.   A silver sol can be prepared by heating a dispersion of silver hydroxide containing gum arabic, or by allowing the mixture to stand.

2.   A method is given for the preparation of a reversible silver sol protected with gum arabic, that is stable within wide limits of concentration and in the presence of high concentrations of electrolytes.

3.   Silver sols protected with gum arabic react with chlorides of antimony, bismuth, copper, gold and mercury to give other sols.

4.   The rate of the reaction between cupric chloride and a protected silver sol may be used to measure the extent of the protection.

5.   The bactericidal activity of silver sols protected with agar agar or gum arabic is of the same order as that of a commercial preparation protected with protein.

NEW BRUNSWICK, NEW JERSEY

THE ACTIVITIES OF STRONG ELECTROLYTES. III. THE USE OF THE FLOWING JUNCTION TO STUDY THE LIQUID-JUNCTION POTENTIAL BETWEEN DILUTE HYDROCHLORIC ACID AND SATURATED POTASSIUM CHLORIDE SOLUTIONS; AND THE REVISION OF SOME SINGLE-ELECTRODE POTENTIALS

BY GEORGE SCATCHARD[1]

Introduction

One of the outstanding problems in the theory of electrolytic solutions is the determination of the activity of individual ions, in particular that of the hydrogen ion. Individual ion activities have usually been calculated through one of the three following assumptions: (a) that, for a uni-univalent electrolyte, the activities of the two ions are equal; (b) that Assumption (a) holds in the particular case of potassium chloride, and

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that the activity of any ion depends only upon the total molality (or ionic strength) and not upon the ions with which it is associated; (c) that the saturated potassium chloride bridge eliminates liquid-junction potentials. Practically it is unnecessary that the potential be zero if only it is the same for the reference and unknown solutions.

Assumption (a) follows from the simple Arrhenius theory, which assumes that the ions, in so far as they exist as such, are perfect solutes. Assumption (b) was first made by MacInnes.[2] The assumption of equal activities for the potassium and chloride ions rests on their similarity in mass, mobility and atomic structure; the assumption of an individual activity independent of the other ions follows, though not as a necessary conclusion, from the consideration of the ions as distinct entities. Assumption (c) would follow from Planck's theory of liquid-junction potentials if the conductivity of the potassium chloride solution were infinitely large compared to that of the other solution, and the mobilities of potassium and chloride ions were exactly equal.[3] The general acceptance of this assumption is based largely upon the experimental work of Fales and Vosburgh.[4]

Assumptions (a) and (b) are in general incompatible. But the bases of Assumption (c) are entirely distinct from those of the other two, and it is possible to compare it with the others experimentally. Such a comparison from the existing experimental data has been given in an earlier paper.[5] The present paper describes a more detailed and accurate comparison.

To obtain the desired accuracy it seemed necessary to use the flowing junction,[6,7] which cannot be used directly with a hydrogen electrode since the change in the pressure due to the changing liquid level affects the potential at the hydrogen electrode, and since the junction is disturbed by the rocking or gas bubbling at the hydrogen electrode. Therefore the two cells, $Pt,H_2 \mid HCl,AgCl \mid Ag$ and $Hg \mid HgCl,KCl(sat.) \mid\mid^8 HCl,AgCl \mid Ag$, were used. The first, the data for which are given in the first paper of this series,[9] gives the mean activity of the hydrogen and chloride ions; the second gives the activity of the chloride ion if we assume that the liquid-junction potential is constant; with the same assumption the difference between the two gives the activity of the hydrogen ion. This method has the further advantage that, in the use of Assumption (b), it is the activity of the chloride ion which is directly measured as the mean activity of the ions of potassium chloride. Some supplementary measurements

[2] MacInnes, THIS JOURNAL, 41, 1086 (1919).

[3] Bjerrum, Z. physik. Chem., 53, 428 (1905).

[4] Fales and Vosburgh, THIS JOURNAL, 40, 1291 (1918). See, however, Ref. 5.

[5] Scatchard, ibid., 45, 1716 (1923).

[6] Lamb and Larson, ibid., 42, 229 (1920).

[7] MacInnes and Yeh, ibid., 43, 2563 (1921).

[8] The sign $\mid\mid$ is here used to signify a flowing junction.

[9] Scatchard, THIS JOURNAL, 47, 641 (1925).

were also made of the saturated calomel electrode against silver chloride electrodes in 0.1 N potassium chloride.

Apparatus and Materials

It was necessary to make some changes in the flowing-junction apparatus of MacInnes and Yeh[7] for use with solutions of widely different densities, in order that the rate of flow of the two solutions might be approximately equal. This was accomplished by replacing the conical reservoirs with cylindrical ones, which were graduated in millimeters above the level of the liquid junction to facilitate regulating the heights of the liquid columns to inverse proportionality to the densities (which gives equal weight to the two columns). This apparatus has the further advantages
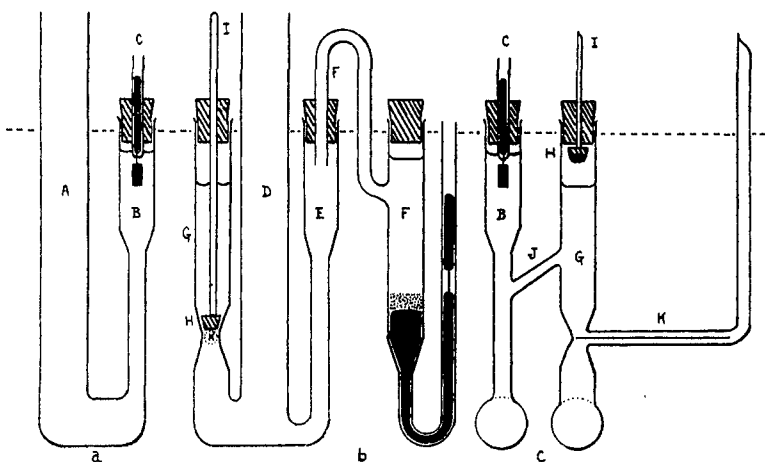

Fig. 1.

that almost all of the liquid is always in the thermostat, and that the elimination of stopcocks simplifies the washing and drying. Since two liquids of unequal densities mix turbulently as soon as they turn to the vertical, the horizontal section of the outlet tube was lengthened so that the resistance of a longer column of liquid might lessen any disturbing effect of the turbulent mixing. No disturbance from this effect was noticed in the experiments.

The apparatus is shown in Fig. 1, whose scale is 1:4; a represents the acid side with reservoir A, electrode vessel B, and electrode C; b is the potassium chloride side, with D the reservoir and E the tube connecting to the siphon of the calomel electrode vessel F, which is a simple form but with adequate precautions against the calomel coming into contact with the platinum wire. The liquid junction is made at the junction of tubes G and K. The two solutions are kept separated during the filling of the apparatus by the stopper H, which is later raised to the top of the apparatus by the glass rod I. In c is shown the joining of the two parts through the tube J which connects B and G. The liquid junction persists throughout the horizontal part of tube K.

The top of this tube is connected with a glass siphon, not shown in the figure, which leads outside the bath and which includes a glass stopcock and a pinchcock to regulate the rate of flow.   The thermostat and potentiometer set-up were the same as those described in the previous paper.[9]

The operation of this apparatus was entirely satisfactory.   Even with molal hydrochloric acid the electromotive force was constant and reproducible within a few hundredths of a millivolt.

The hydrochloric acid solutions were the same as those used in the first article of this series.[9]   The potassium chloride for the salt bridge was Kahlbaum's c. p. material, recrystallized once from distilled water.   For use in the electrode vessels this was further crystallized twice from distilled water.   The mercury was purified by passing eight or ten times in a fine spray through a 1.5-meter column containing a dil. nitric acid solution of mercurous nitrate and was then distilled twice in a current of air under reduced pressure.[10]   The calomel was prepared electrolytically from this mercury and molar hydrochloric acid,[11] and the resulting mercury-calomel paste was shaken several times with fresh portions of a saturated solution of potassium chloride.   A solution saturated with both calomel and potassium chloride was prepared by long agitation of the purified paste with a saturated solution of potassium chloride.

The silver chloride electrodes were taken from the batches described in the former paper[9] and their value was corrected to the average of the batch as there described.   Those used in the potassium chloride solutions were treated in the same way.   Two saturated calomel electrodes were used.   Their electromotive force never differed by more than 0.1 mv. and generally agreed to 0.05 mv.   All values were corrected to their average.

Measurements and Results

It is essential that the two solutions should not mix before the junction is formed.   The stopper H is moistened with the acid solution before being put in place.   As the potassium chloride solution is poured in, it leaves a bubble of air below this stopper, and so does not come into contact with it. At the start the exit tube is entirely filled with this solution.   The acid solution is allowed to enter the tube G, by loosening the stopper at the top for a sufficient time, only when the pressure on the two sides is nearly equalized.

The stock solution of saturated potassium chloride is kept in contact with the solid salt in the thermostat.   To ensure saturation, a stick of fused potassium chloride, 6 cm. long and with cross section about half as great as that of the tube, stands in the bottom of reservoir D.   This stick is made by pouring the molten salt into a quartz combustion boat.   The cotton thread used to remove this stick from the aqueous solution soon becomes covered with potassium chloride crystals and aids in maintaining saturation.   This precaution is particularly necessary with the more concentrated acid solutions, with which a slight difference in the concentration of potassium chloride makes an appreciable difference in the potential.   In the reservoir A is placed a counter-volume of glass weighted with mercury which has the same length and cross section as the salt stick,

[10] Hulett, *Z. physik. Chem.*, **33**, 611 (1900).
[11] Ellis, THIS JOURNAL, **38**, 740 (1916).

After the apparatus has been filled and left in the thermostat for 30 minutes to attain the temperature of 25°, the stopper H is raised entirely out of the liquid. The flow is started immediately. After a few seconds of rapid flow to eliminate the liquid turbulently mixed by the withdrawal of the stopper, the flow is adjusted to 3 to 7 drops per minute. The electromotive force of the cell is then read every five minutes. After it has become constant within a few hundredths of a millivolt for half an hour the flow is stopped for one to three hours to study the behavior on stopping. During this time the electromotive force changes about three millivolts. Then the flow is started again and readings taken every five minutes until the value becomes constant once more. Then a second study is made of the effect of stopping the flow. On the second day the whole procedure is repeated.

This gives for each solution four measurements of the electromotive force with flowing junction and four determinations of the effect of stopping the flow. In Table I is given in the first column the molality of the solution, in the second the average of the four readings, and in the third column the mean deviation of the individual values from this average. In those cases in which the number of determinations was other than four, the number follows the third column in parenthesis. All values are in millivolts. The agreement between the different measurements on a single solution is very good. The two cases in which the mean deviation is as great as 0.1 mv. are early determinations made before the method of keeping the potassium chloride solution saturated was perfected.

TABLE I

ELECTROMOTIVE FORCE IN MILLIVOLTS OF CELLS Hg | HgCl, KCl(SAT.) || HCl, AgCl | Ag

Molality of acid	E	Deviation from average	E_0'	Deviation from curve
0.01000	+97.83	0.03	−20.47	−0.39
.01002	98.01	.07	20.22	− .14
.01010	97.50	.04	20.55	− .58
.01031	96.86	.02 (3)	20.66	− .94
.04986	59.65	.03	17.37	+ .01
.05005	59.54	.03 (3)	17.39	− .01
.09642	44.21	.01	15.87	+ .02
.09772	43.87	.10	15.87	± .00
.09834	43.78	.. (1)	15.80	+ .05
.2030	26.69	.00	14.27	− .02
.3063	16.75	.01 (2)	13.65	+ .01
.3981	10.18	.03	13.48	+ .03
.5009	3.99	.05	13.77	− .15
.5013	4.09	.02	13.65	− .03
.6367	− 2.37	.01	13.97	+ .06
.9377	−13.93	.01	15.59	± .00
1.0008	−16.02	.02	16.00	± .00
1.5346	−31.00	.13 (5)	20.00	± .00

The data were treated as were those on cells without transference in the previous paper[9] except that the numerical coefficients are taken half as large for the single electrode. E_0' was calculated from the equation $E_0' = E + 59.15 \log m$, where E is the electromotive force of the cell and m the molality. The values of E_0' are given in the fourth column of Table I. These values were plotted against $\sqrt{m}$ and a smooth curve drawn through them which approached asymptotically the line with slope $29.575 \sqrt{m}$. Values taken from this curve at rounded molalities were tested to see if the deviation from the linear asymptote was proportional to m, and the extrapolated value at zero concentration was shifted until such proportionality was attained. The final curve is fitted by the equation $E_0' - E_0 = 29.575\sqrt{m} - Bm$, $(B = 23.6)$ through a wider range than any of the curves for the cells without transference. The value of E_0, the extrapolated value of E_0' at zero concentration, is -22.80 millivolts.

The deviations of the individual points from this curve are given in the fifth column of Table I. The agreement is very good except at $0.01\ M$, and there the deviation of the individual points is not larger than might be expected from the differences between the various determinations. The direction of the deviation is the same as for other electromotive-force determinations in dilute solutions. Probably these solutions are too dilute for accurate measurements with the technique used in this work.

TABLE II

ACTIVITY COEFFICIENTS OF THE IONS OF HYDROCHLORIC ACID

Molality	γ_{Cl^-} F. J.	γ_{Cl^-} MacInnes	$\gamma \sqrt{\overline{H^+ \times Cl^-}}$	γ_{H^+} F. J.	γ_{H^+} MacInnes
0.001	0.965	0.965	0.966	0.967	0.967
.002	.952	.951	.954	.956	.956
.005	.926	.926	.932	.937	.937
.01	.899	.899	.910	.921	.921
.02	.866	.865	.881	.887	.888
.05	.809	.809	.836	.863	.863
.1	.762	.762	.801	.841	.842
.2	.718	.715	.774	.834	.838
.3	.701	.688	.763	.829	.845
.4	.696	.669	.760	.829	.863
.5	.700	.654	.763	.833	.890
.6	.707	.642	.770	.838	.923
.75	.725	.627	.783	.845	.978
1.0	.767	.605	.817	.871	1.103

The values for the activity coefficient of the chloride ion, assuming that the liquid-junction potential is constant with the flowing junction (γ_{Cl^-}, F. J.), are calculated from the equation $E_0 - E_0' = 59.15 \log \gamma$. They are given for rounded molalities in the second column of Table II. The third column contains the mean activity coefficient of the ions of potassium chloride, which is equal to the activity coefficient of the chloride ion in

hydrochloric acid (γ_{Cl^-}, MacInnes) according to assumption (b)—that the activities of the chloride and potassium ions are equal and also independent of the ions with which they are associated. The fourth column gives the mean activity coefficient of the hydrogen and chloride ions ($\gamma_{\sqrt{H^+ \times Cl^-}}$), which is also the activity coefficient of the chloride or hydrogen ion according to Assumption (a)—that the two activities are equal. The fifth and sixth columns give the activity coefficients of the hydrogen ion according to Assumptions (c) and (b). These values are obtained by dividing the square of the quantity in the fourth column by the quantity in the second and third columns, respectively. The logarithms of these activity coefficients are plotted against $\sqrt{m}$ in Fig. 2.
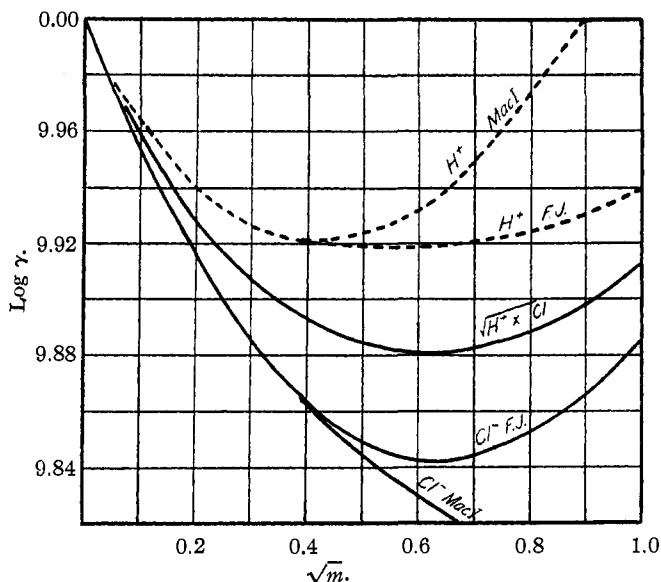

Fig. 2.—Log γ. Hydrochloric acid.

The comparison of these assumptions may be made more clear by determining the electromotive force which must exist at the liquid junction if either of the first two assumptions is true. The values of this potential are plotted against the molality in Fig. 3. The liquid-junction potential is arbitrarily taken as zero when the molality is zero, without assuming, however, that its value actually is zero. The upper curve refers to Assumption (a) and the corresponding ordinates are given on the right side. The lower curve, whose ordinates are given on the left, refers to Assumption (b).

It is highly probable that liquid-junction potentials are due to the different mobilities of the ions. Since the hydrogen ion has a greater mobility than the chloride ion, there should be a potential increasing with the

concentration and negative as the cell is written. This is fulfilled by the curve representing the MacInnes assumptions. On the other hand, the curve for the liquid-junction potential assuming equal activities for the hydrogen and chloride ions passes through a minimum. In the more dilute solutions the change with changing acid concentration is in the opposite direction to that predicted from the mobilities of the ions. This alone appears to me to be sufficient evidence to disprove the hypothesis that the ions of hydrochloric acid have equal activities.

If the liquid-junction potential is due to mobility differences, and therefore must be negative as represented in Fig. 3, the values of γ_{Cl^-}, F. J. given in Table II must be maximum values. Those of γ_{Cl^-}, MacInnes are, on the other hand, minimum values unless the activity of the chloride ion is less than that of the potassium ion. For the more concentrated
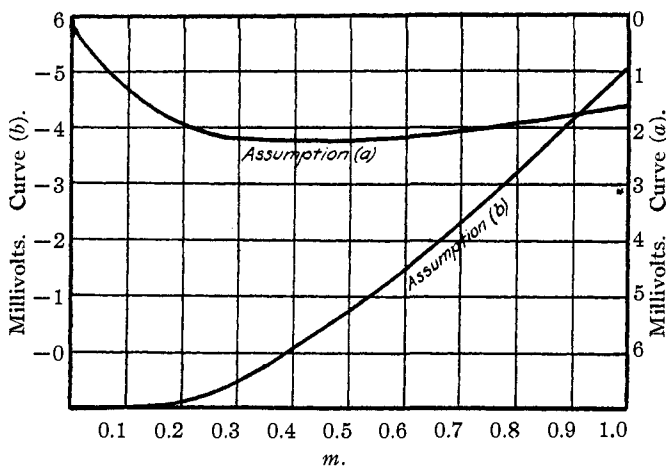

Fig. 3.—Liquid-junction potentials.

solutions, where there is a considerable difference between the two values, indirect evidence points to values of the activity of the chloride ion much nearer to the minimum than to the maximum, but the evidence is not very conclusive. At 0.2 M the difference between the two values is only 0.3% which corresponds to 0.1 mv. or about the experimental error; up to 0.1 M the two are identical. In the very dilute solutions this identity may be ascribed to the method of extrapolation but the experimental results themselves are entirely concordant at 0.05 and 0.1 M. Even at 0.01 M the agreement between the experimental measurements by the two methods is much better than the agreement of either with the smoothed curve.

Brönsted[12] has shown that the assumption that the activity of the choride ion is the same in solutions of hydrochloric acid and of potassium

[12] Private communication to Lewis and Randall. See their (a) "Thermodynamics," McGraw-Hill Book Co., 1923, p. 368.

chloride of the same molality is contrary to the laws of thermodynamics, since the activity of water in the two solutions is different.   His argument gives no indication of the magnitude of the difference demanded by thermodynamics.   The results of the present paper give evidence that it is so small up to 0.1 M that the activity of the chloride ion is given to a few tenths of a per cent. by either the MacInnes assumptions or the assumption that the saturated potassium chloride bridge with a flowing junction gives a liquid-junction potential independent of the acid concentration. The agreement between these two methods is even more striking when it is recalled that, not only do they give the maximum and probable minimum values, respectively, but the assumptions upon which they are based are independent and of entirely different natures.   The fact that they lead to the same results gives strong support to each.

Effect of Stopping the Flow

The flowing junction presumably gives a "mixture boundary,"—one in which the composition of each infinitesimal layer is the same as though it had been prepared by stirring together the two solutions in the proper proportions, and one which is extremely thin.   When the flow is stopped the junction changes to a "diffusion boundary,"—one whose composition is determined by the rates of diffusion of the various ions, which gradually increases in thickness.   Any change in the total electromotive force of the cell when the flow is stopped must be due to the difference between the potentials of these two types of liquid junction.   Then the effect on the electromotive force of stopping the flow should give some insight into the absolute magnitude of the liquid-junction potential.

When the flow is stopped the total electromotive force becomes more positive, indicating a decrease in the negative liquid-junction potential, at first rapidly and then more slowly.   For 0.2 M and more concentrated solutions it reaches a maximum in about two hours and then decreases almost linearly.   The maximum change is about 3.5 millivolts.   The 0.05 and 0.1 M solutions reach the same maximum but remain constant.   The 0.01 M solution increases slowly for at least six hours.   For a solution of any given concentration the change in any given time is reproducible within a few hundredths of a millivolt.   The fact that the electromotive force returns to the original value when the flow is started again proves that all the change is in the liquid junction potential.   In Fig. 4 is plotted the change with time of the electromotive force of 0.01, 0.1 and 1.0 M solutions, which are typical of the three classes.   Each curve is a slightly smoothed composite of four determinations.

These measurements show that, for some unknown reason, the potential drop at a diffusion boundary is independent of the thickness of that boundary in 0.05 and 0.1 M solutions.   Also, since there is a difference of about

3.5 mv. between the liquid-junction potentials at a "mixture boundary" and at a "diffusion boundary," both cannot be zero and it is probable that neither is. Since this difference is almost independent of the acid concentration, it appears that at least the order of magnitude of the potential must be the same in dilute as in concentrated solutions.
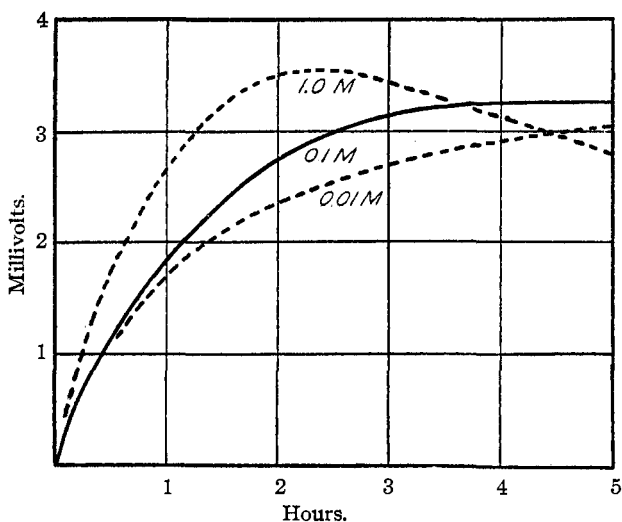

Fig. 4.—Effect of stopping flow.

The Absolute Value of the Liquid-Junction Potential

Using the MacInnes assumptions, it is possible to determine the absolute magnitude of this liquid-junction potential. If the activity of the chloride ion is the same in the two solutions, the only difference in electromotive force between the two cells Hg | HgCl,KCl(sat.) || HCl(c_1),AgCl | Ag and Hg | HgCl,KCl(sat.) || KCl(c_1),AgCl | Ag is in the liquid junction. If the activities of the potassium and chloride ions are equal, the liquid-junction potential between two solutions of potassium chloride is given by the equation, $E_b = \int (0.5 - t_+) d E = 59.15 \int (0.5 - t_+) d \log a_\pm$, where E_b is the liquid-junction potential, E is the electromotive force of the concentration cell without transference, t_+ is the transference number of the potassium ion, and $a_\pm$ is the mean activity of the ions.

For the graphic integration of this last equation, the activity of the ions of potassium chloride at 20°, determined from vapor-pressure measurements,[9] was used. The values of t_+ were determined from the equation $1 - 2t_+ = 0.005 + 0.028\sqrt{m}$, which fits the experimental determinations at 0.01, 0.1 and 1.25 M. The value of E_b between 0.1 M and saturated (4.1 M) potassium chloride is 2.7 mv. This involves a large extrapolation of the transference number, but even if t_+ is assumed to be constant in solu-

tions more concentrated than 1.25 M the value is reduced only to 2.4 mv. The greatest uncertainty probably lies in the extension of the assumption of equal activities even to the saturated solution. The final result may be in error as much as 1 mv., but it does give an approximate value for the liquid-junction potential.

To determine the difference in liquid-junction potential with potassium chloride and with hydrochloric acid three measurements were made on the cell, Hg | HgCl,KCl(sat.) || KCl(c_1),AgCl | Ag. The results are given in Table III. As predicted from the fact that the electromotive force of a concentration cell is independent of the nature of the junction, the electromotive force of these cells was unchanged when the flow was stopped.

TABLE III

ELECTROMOTIVE FORCE OF CELL Hg | HgCl, KCl (SAT.) || KCl (c_1), AgCl | Ag

Molality	E	E_0'	$E_0'_{HCl}$	Difference
0.09040	47.52	−14.22	−16.04	1.82
.10006	45.40	13.73	15.80	2.07
.10057	45.23	13.77	15.79	2.02
			Av.	1.97

The liquid-junction potential between 0.1 M hydrochloric acid and saturated potassium chloride is the sum of these two values, or 4.7 mv., the acid solution being negative. A glance at Fig. 3 shows that this potential is constant in more dilute solutions, but increases to about 11.0 mv. with molar hydrochloric acid. It must be remembered that this calculation of the liquid-junction potential depends upon the acceptance of the MacInnes assumptions as exact even in concentrated solutions.

Some Single-Electrode Potentials

The experiments and calculations of this and the previous paper permit the calculation of some single-electrode potentials at 25° more accurately than has previously been possible. I shall follow Lewis and Randall[13] in arbitrarily fixing as zero the potential difference between hydrogen at atmospheric (partial) pressure and hydrogen ion with an activity of one, and also in their use of symbols.

Ag | AgCl(s), Cl⁻.—The e.m.f. of this electrode is given directly by —E_0 for the cell, Pt,H₂ | HCl,AgCl | Ag. Although Lewis and Randall find —0.2234 volt by this method, they prefer the value —0.2245 determined from their value for the calomel electrode and the difference between calomel and silver chloride electrodes. Since the measurements of Linhart permit an extrapolation for this cell more accurate than for any other, it is more reasonable to accept the direct determination of this e.m.f. and to determine that for the calomel electrode from the difference.

[13] Ref. 12 a. Chap. XXX.

Taking the more accurate extrapolation of my previous paper, we have: $Ag \mid AgCl(s), Cl^-$. $E^0 = -0.2226$ *volt*.[14]

Hg $\mid$ HgCl(s), Cl$^-$.—The cell Pt, $H_2 \mid$ HCl(0.1 M), HgCl $\mid$ Hg has been measured by many observers with the following results: 0.3991,[15] 0.3988,[16] 0.3988,[17] and 0.3989;[18] av., 0.3989.   Using 0.0814 for the mean activity of hydrogen and chloride ions in 0.1 M hydrochloric acid, Lewis and Randall find —0.2700 volt for E^0 of the calomel electrode.   Taking from my previous paper 0.0801 as the mean activity, we obtain $Hg \mid HgCl(s), Cl^-$. $E^0 = -0.2692$ *volt*.   This corresponds to a difference of 0.0466 volt between the calomel and silver chloride electrodes.

Saturated Calomel Electrode (S. E.), Flowing Junction.—The e.m.f. of this electrode is given by the difference in E_0 for the cells, Pt,$H_2 \mid$ HCl,-AgCl $\mid$ Ag and Hg $\mid$ HgCl,KCl(sat.) $\|$ HCl,AgCl $\mid$ Ag.   It must be remembered that this derivation assumes that the flowing junction is between the saturated potassium chloride and 0.1 M or more dilute hydrochloric acid.   The value would probably be approximately the same for any other electrolyte in concentration not greater than 0.1 M.   S. E., *Flowing Junction*. $E = -0.2454$ *volt*.

Tenth-Molal Calomel Electrode (D. E.) $\mid$ KCl(sat.), Flowing Junction.—Combining the value for the last electrode with 0.0453 volt, from Table III for the cell Hg $\mid$ HgCl,KCl(sat.) $\mid$ KCl(0.1 M),AgCl $\mid$ Ag, and 0.0466 volt for the difference between these silver chloride electrodes and calomel electrodes, we have $D. E. \mid KCl(sat.)$, *Flowing Junction*. $E = -0.3373$ *volt*.[19]   This is in fair agreement with the value —0.3376 volt given by Sörensen[20] and generally accepted for hydrogen-ion determinations using the saturated potassium chloride bridge.

D. E. (0.1 M Calomel Electrode without Liquid-Junction Potential).—Lewis and Randall calculate the e.m.f. of this electrode from E^0 for Hg $\mid$ HgCl(s),Cl$^-$ and from the activity of 0.1 M potassium chloride and with their values for these two they obtain —0.3351 volt.   The calculation assumes that the activities of potassium ion and chloride ion are equal.   Sörensen's value for the 0.1 N electrode,[19] corrected by using 0.0801 instead of 0.0917 for the mean activity of the ions of 0.1 M hydrochloric

[14] This value holds for the silver chloride electrodes prepared by three different methods by Linhart, by Noyes and Ellis and by me.   Gerke [THIS JOURNAL, **44,** 1684 (1922)] found 0.0455 volt for the difference between his silver chloride and calomel electrodes, which gives —0.2237 for E^0 for his silver chloride electrodes.

[15] Harned, THIS JOURNAL, **37,** 2475 (1915).

[16] Ellis, *ibid.*, **38,** 752 (1916).

[17] Loomis and Meacham, *ibid.*, **38,** 2315 (1916).

[18] Lewis, Brighton and Sebastian, *ibid.*, **39,** 2245 (1917).

[19] 0.1 N Potassium chloride is 0.1006 M, so the value (negative) of the 0.1 N electrode is 0.00015 volt less than that of the 0.1 M electrode.

[20] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., **1923,** Chap. XIX.

acid, becomes —0.3342 volt. Using my value for E^0, and taking 0.0762 for the activity of the chloride ion in 0.1 M potassium chloride,[9] we have *D. E.   E = —0.3353 volt.* The differences between the values used for various quantities by Lewis and Randall and by myself have nearly canceled out in the calculation of the e.m.f. of this electrode.

A comparison of the last two electrode potentials gives 2.0 mv. as the difference between the liquid-junction potentials of saturated potassium chloride with 0.1 M potassium chloride and with 0.1 M hydrochloric acid, which is identical with the value determined in the last section. The determination in this section involves the extrapolation of the activity coefficients of both hydrochloric acid and potassium chloride and the assumption that the activity of the potassium ion equals that of the chloride ion. The previous determination involves only the assumption that the activity of the chloride ion is the same in 0.1 M hydrochloric acid as in 0.1 M potassium chloride. Although there is, of course, some possibility of compensating errors, the agreement between these two results is considered a valuable confirmation of the accuracy of the activity determinations, and of the assumptions of MacInnes applied to 0.1 M solutions.

In conclusion I wish to express my gratitude to the National Research Council for its financial assistance, and to Professor F. G. Keyes and the other members of the staff of this Laboratory, especially to Professor D. A. MacInnes, for the suggestions and help they have given.

Summary

1.   Using a flowing-junction apparatus which gives results constant and reproducible within a few hundredths of a millivolt, the electromotive force at 25° of the cell, Hg | HgCl,KCl(sat.) || HCl(c_1),AgCl | Ag, has been measured with acid concentration varying from 0.01 to 1.5 M.

2.   On stopping the flow the liquid-junction potential changes about 3.5 mv. The exact behavior depends upon the acid concentration.

3.   For 0.1 M solutions and those more dilute, the results give striking confirmation of the conclusion that the saturated potassium chloride bridge gives a liquid-junction potential that does not vary with the acid concentration, and of the assumptions of MacInnes regarding individual ion activities.

4.   For more concentrated solutions the results give a maximum value for the activity of the chloride ion, and a minimum value for the activity of the hydrogen ion.

5.   Making the MacInnes assumptions, the liquid-junction potential, with flowing junction, between saturated potassium chloride and dilute hydrochloric acid is calculated as 4.7 mv.

6.   From the data of this paper and of the first two of this series, the following are determined as the most probable values for some single electrode potentials at 25°: Ag | AgCl(s),Cl⁻, —0.2222 volt; Hg | HgCl(s),

Cl⁻, —0.2692 volt; S. E., flowing junction, —0.2454 volt; D. E. | KCl(sat.), flowing junction, —0.3373 volt; D. E. (without liquid-junction potential), —0.3353 volt.

CAMBRIDGE 39, MASSACHUSETTS

A LABORATORY VACUUM GAGE[1]

BY MARSTON LOVELL HAMLIN

The introduction into common laboratory use of moderately priced vacuum pumps producing vacua of 3 to 0.005 mm. of mercury has made desirable the design of a vacuum gage covering approximately this range.

The open or closed type of U-tube manometer cannot be read with sufficient precision at pressures in this range, and the McLeod gage and its modifications, while satisfactory in precision at high vacua, lack range
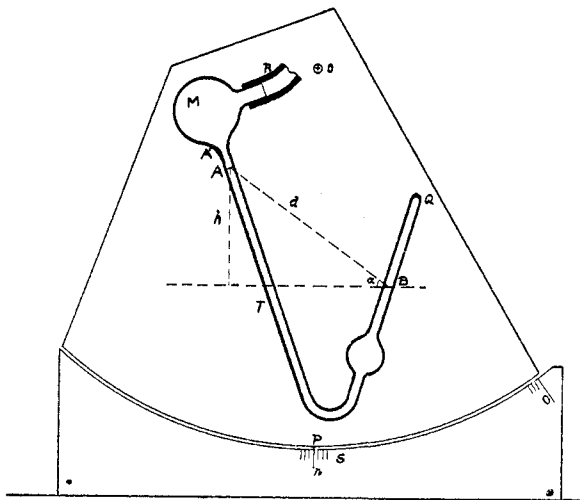

Fig. 1.

and convenience in manipulation, are somewhat difficult to construct and calibrate, and require considerable mercury.

A gage is described below that is simple to construct and calibrate and requires little mercury; it has a useful range of 10–0.05 mm., and may be constructed with a second range covering pressures one-fifth to one-tenth that covered by the first range; it is rapid in operation, only eight to ten seconds being required for a reading.

[1] Presented at the annual meeting of the North Carolina Academy of Sciences, Greensboro, N. C., May 5, 1923.