which they exert, may throw light on the important questions of solutions. Qualitative results obtained with lithium chloride, sodium nitrate, sodium acetate, cupric chloride, sodium chloride, ethyl alcohol and acetic acid are promising and though no successful quantitative results with concentrated solutions have as yet been obtained, experiments on the more dilute solutions are now in progress, the results with phenol having already been published.

Summary

1. The method of experimentally determining osmotic pressures has been improved by filling with various silicates the cells on which the membrane is precipitated.

2. Such cells are efficient supporters of the membrane, allow but a minimal leakage, a rapid attainment of equilibrium, and do not require long seasoning.

3. An interferometer cell has been devised which is capable of acting as an accurate and rapid pressure gage.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF AMHERST COLLEGE]

ELECTROMOTIVE-FORCE MEASUREMENTS WITH A SATURATED POTASSIUM CHLORIDE BRIDGE OR WITH CONCENTRATION CELLS WITH A LIQUID JUNCTION

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Received May 17, 1923

The determination of the activities of individual ion species is a very interesting and important problem of physical chemistry. The measurement of hydrogen-ion activity, often under the name of hydrogen-ion concentration or P_H, is being applied to so many varied problems that a consideration of all the possible evidence as to the validity of the procedure becomes important. The applications themselves present a considerable body of evidence.

The electromotive force of a cell of the type, Pt, $H_2 \mid HCl, AgCl \mid Ag$, can be derived rigorously from thermodynamics alone. At constant temperature and pressure it is $E_1 = E'_1 - RT/F\, ln(a_H \times a_{Cl})$, where E'_1 is the corresponding electromotive force when the activities are unity, and the other symbols have their usual significance. This electromotive force is divided between the two electrodes; we will assume that it is so divided that the electromotive force at the hydrogen electrode is $E_2 = E'_2 - RT/F\ ln\, a_H$ and that at the silver-silver chloride electrode is $E_3 = E'_3 - RT/F\ ln\, a_{Cl}$. Although this generally accepted assumption is apparently incapable of direct proof there seems little reason to question it, for it is difficult to imagine a mechanism of the reaction in which the chloride ion could affect the electromotive force of the hydrogen electrode except by changing the activity of the hydrogen ion. Without such an assumption any attempt to determine the activity of individual ions by electromotive-force measurements is hopeless.

The customary procedure for measuring the activity of a single ionic species is to use a single electrode in combination with a saturated potassium chloride bridge and a standard electrode, which involves the assumption that the potential drop is zero at the liquid junction: saturated potassium chloride, unknown. Then, since the electromotive forces at the standard electrode and at the junction of the electrode solution with the bridge are constant and may be included in E', the electromotive force of the whole cell is given by E_2 or E_3. Corran and Lewis[1] have presented what they consider to be a proof of this equation for the hydrogen electrode in solutions of hydrochloric acid and sucrose in water. However, their proof contains the assumption that the electromotive force of the silver-silver chloride electrode is given by the equation, $E_4 = E'_4 RT/F \, ln\sqrt{a_{\mathrm{H}} \times a_{\mathrm{Cl}}}$, which differs from E_3. Since the value of E_3 follows necessarily from those of E_1 and E_2, the result proved is incompatible with the assumption made to prove it, and the proof is invalid.[2]

The assumption that a saturated potassium chloride bridge eliminates liquid-junction potentials is usually based on the extension to solutions in general of the proof of Fales and Vosburgh[3] for solutions of N and 0.1 N hydrochloric acid. The argument of Fales and Vosburgh depends upon the proof that the electromotive force at the liquid junction with saturated potassium chloride is the same for 0.1 N as for N acid, and that the most reasonable explanation is that both are zero. The authors recognize that this proof depends upon the assumption that "the combinations represented by Hg-HgCl x MHCl − x MHCl-H_2 (1 atmos.) Pt change their pole potential differences by the same amount, but in an opposite direction, as we vary x."[4] However, this assumption is not substantiated by the consistency of their results, for there are too many arbitrary variables. It is equivalent to assuming that the hydrogen and calomel electrodes each measure the mean activity of hydrogen and chloride ions, or that the ratios of the activities of the two ions are equal in these two solutions. The extension to all concentrations would require that the activities themselves be equal.

It seems more reasonable to make the assumptions of MacInnes:[5] that (a) the activity of the chloride ion is the same in solutions of all uni-

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[1] Corran and Lewis, THIS JOURNAL, **44**, 1673 (1922).

[2] H. S. Harned [*ibid.*, **42**, 1808 (1920)] makes the same two contradictory assumptions, but uses them in only a few of his calculations.

[3] Fales and Vosburgh, *ibid.*, **40**, 1291 (1918).

[4] Ref. 3, p. 1299.

[5] D. A. MacInnes, *ibid.*, **41**, 1086 (1919).

valent chlorides at the same molality, and (b) equal to the activity of potassium ion in potassium chloride solutions. With these assumptions the difference between the 2 liquid-junction potentials is 6.4 mv.; both cannot be zero and there is no reason to suppose that either is.

From other results of Fales and Vosburgh it is possible to determine the electromotive force of the cell, Hg | HgCl, KCl (c_1) | KCl (sat.) | HCl (c_1), HgCl | Hg. A combination of Experiments 9, 18 and 23 gives 0.1 mv. when the solutions are 0.1 N. Expt. 1 give 8.3 mv. for 1 N solutions; corrected to equal molalities this becomes 8.9 mv. for 1.023 M solutions. By the MacInnes assumption (a), the electrode potentials cancel. The liquid-junction potentials between the solutions of potassium chloride are probably only a few tenths of a millivolt; the Nernst-Planck formula gives 0.6 and 0.4 mv. With this assumption the liquid-junction potential is small with 0.1 N solutions, but becomes large for N solutions.

A test of this assumption would be very simple by comparing the activity determined with a saturated potassium chloride bridge with that from cells without transport, but apparently the necessary measurements have never been made. The most direct comparison possible is one between the measurements of Fales and Morrell[6] with the bridge at 35° and the values given by Lewis and Randall[7] for cells without transport at 25°. The activities change with the temperature, but the general nature of the curves should be the same. Table I contains this comparison for the activity coefficients (activity divided by molality), and also for the activity coefficient of the hydrogen ion calculated by the MacInnes assumptions.

TABLE I

COMPARISON OF ACTIVITY COEFFICIENTS IN HYDROCHLORIC ACID

Molality	$\sqrt{a_{\mathrm{H}} \times a_{\mathrm{Cl}}}/m$	a_{H}/m Fales and Morrell	a_{H}/m MacInnes assumptions
0.0010	(1.00)	(1.00)	(1.00)
0.0100	0.94	0.94	0.94
0.1001	0.83	0.84	0.84
0.3017	0.78	0.84	0.83
0.6071	0.78	0.82	0.90
0.9161	0.82	0.82	1.02
1.229	(0.88)	0.87	(1.22)

The necessary change from moles per liter to molality is made by means of the density determinations of Fales and Morrell. Since their values are only relative, all coefficients are given on such a scale that the coefficient is unity for the 0.001 M solution. It is apparent that the cell with saturated potassium chloride bridge measures neither the mean activity nor that of the hydrogen ion calculated by the MacInnes assumptions. For solutions 0.1 M, or more dilute, the agreement with the MacInnes assumptions is

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[6] Fales and Morrell, THIS JOURNAL, **44**, 2071 (1922).

[7] Lewis and Randall, *ibid.*, **43**, 1112 (1921).

good, confirming our conclusions that the liquid-junction potential is very small with these solutions.

Hitchcock[8] has used a saturated potassium chloride bridge with both hydrogen and silver-silver chloride electrodes in hydrochloric acid through the concentration range 0.001–0.1 M, but his measurements were reproducible only to about 1 millivolt. His results show that the liquid-junction potential may be ignored within this range and within his experimental error.

Most applications of the saturated potassium chloride bridge involve the presence of a second solute. Some insight into the validity of assuming that the liquid-junction potential is eliminated in such cases may be obtained from the measurements of Corran and Lewis[1] on sucrose solutions if we recognize that the silver-silver chloride electrode measures the activity of the chloride ion and not the mean activity. These solutions have a particular interest in themselves on account of the importance of sucrose inversion to the study of reaction speed. The measurements on potassium chloride are made with a concentration cell with transport; those on hydrochloric acid with a saturated potassium chloride bridge.

Although a concentration cell with transport cannot be reversible on account of diffusion, it seems generally accepted that the derivation of the differential equation for its electromotive force rests only upon the two laws of thermodynamics.[9] The thermodynamic derivation, however, involves the assumption that the only matter transported when a current is passed through is the ions, and it must be recalled that the ions whose activity is measured are the anhydrous ions. Washburn[10] has definitely established that there is also a transport of water. If we follow the method of Lewis and Randall, taking this into account and changing at the end from free energies to activities, we obtain for the electromotive force of a cell with electrodes at which the anion reacts,

$$E = -\frac{RT}{F}\left[\int_{\mathrm{A}}^{\mathrm{B}} t_{+}\,\mathrm{d}\ln(a_{+} \times a_{-}) + \int_{\mathrm{A}}^{\mathrm{B}} t_{\mathrm{w}}\,\mathrm{d}\ln a_{\mathrm{w}}\right],$$

where the a's are activities, and the t's transport numbers, or the number of moles carried in the direction of the positive current when 1 faraday of electricity is passed through the solution. The subscript w refers to water, the others to the ions, and A and B to the two solutions.

An idea of the magnitude of the second term may be obtained from the measurements of MacInnes and Beattie[9] on lithium chloride solutions

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[8] Hitchcock, *J. Gen. Physiol.*, **5**, 383 (1923). I wish to acknowledge my gratitude to Dr. Hitchcock for the use of some unpublished calculations and for calling my attention to some results of Fales and Vosburgh.

[9] MacInnes and Parker, THIS JOURNAL, **37**, 1445 (1915). MacInnes, *ibid.*, **37**, 2301 (1915). MacInnes and Beattie, *ibid.*, **42**, 1117 (1920). Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923**, p. 337.

[10] Washburn, *ibid.*, **31**, 322 (1909).

if it is assumed that t_w is constant and equal to 1.5, the value found by Washburn for 1.28 *M* solution. The corresponding electromotive force is 0.14 mv. for a 0.1 *M*, and 5.35 mv. for a 3.0 *M* solution. The value of 308 for t_+ in 1.28 *M* solution agrees well with 306 and 301 found by Washburn for the true transport number. Since there is no reason to suppose that t_w is really constant, t_+ by this assumption should not equal the true transport number at other concentrations, and it does not seem worth while to publish the complicated calculations. Neglecting the transport of water, MacInnes and Beattie find excellent agreement between t_+ and the Hittorf transport number, but the above argument shows that no exact relationship between these two quantities is thermodynamically established.

The magnitude of the effect of the transport of water in the potassium chloride-sucrose solutions may be estimated by integrating the equation assuming that t_+ is constant, and that t_w is, first, zero or, second, constant and equal to the value 0.6 found by Washburn. The mean activities calculated by these two assumptions are given in the second and third columns of Table II, on such a scale that the activity is unity in the solution without sucrose. The neglect of t_w makes a difference of about 10% in the most concentrated solution. Since we know nothing of the effect of sucrose on either t_+ or t_w, and there is no reason to suppose that either is constant, we cannot even say that the activities lie between these two values.

TABLE II

ION ACTIVITIES IN SUCROSE SOLUTIONS

G. of sucrose per liter	Mean activity KCl $t_w = 0$	Mean activity KCl $t_w = 0.6$	a_{Cl} in HCl	a_H in HCl	N/N_0
0	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)
100	1.06	1.07	1.12	1.20	1.08
200	1.14	1.16	1.26	1.44	1.19
300	1.21	1.24	1.41	1.74	1.33
400	1.31	1.36	1.59	2.09	1.49
500	1.41	1.49	1.80	2.50	1.71
600	1.52	1.64	2.07	3.00	1.97
700	1.66	1.84	2.38	3.60	2.31

The fourth and fifth columns of Table II give the activities of chloride ion and of hydrogen ion in hydrochloric acid determined with a saturated potassium chloride bridge. The chloride-ion activity increases much more rapidly than the mean activity of the ions of potassium chloride calculated upon the above assumptions, and the hydrogen-ion activity increases still more rapidly. It may be noted that, if we assume that the chloride-ion and hydrogen-ion activities are really equal, all the discrepancies between Cols. 4 and 5 must be attributed to the liquid-junction potential, which leads to a difference of 5.3 mv. between the liquid-junction potentials of saturated potassium chloride with 0.1 N hydrochloric acid when there is no sucrose present, and when there is 700 g. per liter.

The following argument indicates that it is at least reasonable to assume that the saturated potassium chloride bridge does give constant liquid-junction potentials with varying sucrose concentration. There are two important reasons for the deviation of the activities of the ions from proportionality to their mole fractions which, in dilute solutions of the univalent chlorides, seem to exceed greatly the total of other more specific effects. The first is the effect of the electrical charges upon each other, which depends upon the total ionic concentration (not mole fraction) and upon the dielectric constant of the medium. In these solutions the concentration of salt is constant and the dielectric constant probably varies but little. If we assume that it is constant, the concentration of the ions and the effect of this factor will be constant. The second factor arises from the fact that our measurements give the activities of the unhydrated ions. The fraction of ions not hydrated may be extremely small, but any change in this fraction will give a corresponding change in the activity coefficient. Since the ions probably vary both in the stability and the complexity of their hydrates this effect will be specific for the various ions. It will be a function of the activity of the water, and should not be measurable until that activity becomes appreciably less than that of pure water. It offers the simplest explanation of the unequal activities of ions and the increase of activity coefficients with concentration in concentrated solutions. The behavior of the metallic chlorides indicates that this factor is very small for the chloride ion. If it is zero, the activity of the chloride ion should be proportional to its mole fraction in these solutions. Any effect of this factor would be to make the activity increase more rapidly than the mole fraction as the concentration of sucrose is increased. The last column of Table II gives N/N_0 for either ion, calculated by the equation, $N/N_0 = [55.5 + 0.2]/[C_s/(1 - a_w) + 0.2]$, where N and N_0 are the mole fractions with and without sucrose, C_s is the concentration of sucrose in moles per liter, and a_w is the activity of water in a solution containing the same proportion of sucrose and water but not salt. The use of this formula assumes that the solution is ideal with respect to water except for the hydration of sucrose, and that no appreciable fraction of the water is used to hydrate the ions at such dilutions. The values are only a little smaller than the measured values of the chloride-ion activity in hydrochloric acid, indicating a small decrease in hydration and offering some confirmation of the assumption that the liquid-junction potential is independent of the sucrose concentration.

According to these hypotheses the increase in the ratio of activity to mole fraction for the hydrogen ion is due to an increase in the fraction of unhydrated ion with decreasing activity of the water, whether this decrease is due to high concentrations of sucrose or of the acid itself. Whatever the cause is, it is obvious that the activity of the hydrogen ion is not proportional to its mole fraction or molality, and that it cannot be used legitimately to calculate the extent of hydration.[11] The fact that the activity of hydrogen ion in acetic[11] and in sulfuric[12] acids increases less rapidly than in hydrochloric acid may be accounted for most simply by assuming that the dissociation of these acids decreases as the sugar concentration increases. This decrease may be explained, at least semiquantitatively, by the increase in the mole fraction without any variation in the ionizing power of the solvent.[13]

The confirmation of the elimination of liquid-junction potential with sucrose solutions is not too reassuring, but even this cannot be extended to the addition of another solute in general. Analysis of Planck's differential equation for liquid-junction potentials indicates that the potential depends upon both the activity and the conductivity of the ions, and probably also upon their concentration.[14] In these solutions the concentration remains constant, the activity increases, and the conductivity decreases still more rapidly. It is possible that these effects equalize one another in this particular case, but it is not probable that they would do so in general. The extension of the use of the saturated potassium chloride bridge to solutions in general seems very dangerous.

Summary

1. The proof of Fales and Vosburgh that the saturated potassium chloride bridge eliminates liquid-junction potentials depends upon the assumption that in a hydrochloric acid solution the activities of the 2 ions are equal. The proof of Corran and Lewis depends upon incompatible formulas for the electromotive forces at the 2 electrodes.

2. An analysis of experimental results indicates that the liquid-junction potential with saturated potassium chloride is not more than 1 millivolt for solutions less than 0.1 *M* but that it increases rapidly with the concentration for hydrochloric acid.

3. There is some theoretical confirmation for the assumption that the liquid-junction potential with a saturated potassium chloride bridge is independent of the sucrose concentration if the concentration of electrolyte remains constant. This substantiation cannot be extended to solutes in general.

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[11] Lewis, Merriman and Moran, THIS JOURNAL, **45**, 702 (1923).

[12] Jones and Lewis, *J. Chem. Soc.*, **117**, 1120 (1920).

[13] I must disclaim any credit given me in Ref. 12 for originating the hypothesis that the increase in hydrogen-ion activity on the addition of another solute is due to increased ionization, which dates back at least to Loomis and Acree [*Am. Chem. J.*, **46**, 621 (1911)]. My contribution was to show that, if this effect were attributed to increased ionization, the ionization need not be more than 100% for sulfuric acid.

[14] See also MacInnes and Yeh, THIS JOURNAL, **43**, 2563 (1921).

4. The ordinary thermodynamic formula for the electromotive force of a concentration cell with transport ignores the transport of water. If this be taken into account the transport number involved is the true and not the Hittorf number.

5. Emphasis is laid upon the fact that activity measurements give the activity of the unhydrated ion. An increase in the fraction of ions not hydrated gives the simplest explanation of the increase of activity coefficients in concentrated solutions.

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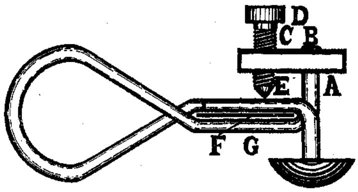
NOTES

A Screw Modification of the Mohr Pinch Clamp.—Although the use of a Mohr buret is often made imperative in volumetric work, no satisfactory pinch clamp has ever been devised to allow dropwise delivery of solutions from a buret of this type. The accompanying sketch shows the details of a pinch clamp designed to fill this need. It may easily be made from an ordinary Mohr clamp, and has an advantage over a screw clamp in that only one hand is required for its manipulation.



Into a brass plate 3 mm. thick, 1 cm. wide, and 2 cm. long 2 holes, B and C, are drilled and then tapped. The wire A leading up from the jaws of the clamp is threaded, screwed into the plate through B, and then brazed or soldered securely in the position shown in the figure. A large-headed brass screw D is then screwed through C until its pointed end E just touches the top of plate F when the clamp is pressed just hard enough to allow liquid to pass in drops through the rubber tube between plate F and wire G. Of course, by screwing D further it is possible to secure any other desired rate of flow.

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Received February 10, 1923

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Gas Electrode.—A convenient form of hydrogen or other gas electrode and one which attains the equilibrium value very quickly, may be made as follows. A piece of round graphite rod A of any convenient size (3 mm. diameter was used) is drilled axially to within 6 mm. of the bottom. This is attached to a similar sized copper tube B, for leading in the gas, by a short length of rubber tubing C as shown in the figure. A spiral of light