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THE POTENTIALS AT THE JUNCTIONS OF MONOVALENT CHLORIDE SOLUTIONS.

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1. Introductory.

The importance of the measurement and estimation of the potentials at the junctions of salt solutions does not need to be emphasized. Many investigations involving determinations of ion activities and of the free energies of reactions are rendered difficult or uncertain because of the necessity of correcting for these troublesome points of contact. The research to be described in the following pages was made with the purpose of finding the conditions for constant and reproducible junctions and with the hope of adding to our theoretical knowledge of the subject. The investigation was restricted to an examination of junctions of the type $MCl | M'Cl$ in which M and M' represent hydrogen or one of the alkali metals. The same electrolyte concentration was maintained on both sides of each boundary. These junctions were studied because (a) electrodes reversible to the chloride ion are easily made and are reproducible, and (b) certain simplifying assumptions regarding the chloride ion have resulted from recent work. Further, as one of the authors has shown, connection between any two solutions of univalent ions, with one ion in common, can be made by combining a junction of the type just mentioned with one in which the concentration, but not the salt, changes. The formation and computation of the potentials of the latter type of junctions is now well understood.¹

A large bibliography on liquid junctions could be collected, but the following references will be sufficient for our purpose. Apparently the first experimental work in connection with the evaluation of liquid junction was carried out by Nernst.² Further studies have been made by Lewis and Sargent,³ by Cumming and Gilchrist,⁴ by Meyers and Acree,⁵ and by Lewis, Brighton and Sebastian.⁶ In all but one of the articles mentioned the authors point out that the potentials of junctions connecting two different salts are variable. It seems to be tacitly assumed that the highest voltage, if moderately constant, is the "correct" value.

¹ See MacInnes, *THIS JOURNAL*, **37**, 2301 (1915); and MacInnes and Beattie, *ibid.*, **42**, 1117 (1920).

² Nernst, *Z. physik. Chem.*, **4**, 129 (1889).

³ Lewis and Sargent, *THIS JOURNAL*, **31**, 363 (1909).

⁴ Cumming and Gilchrist, *Trans. Faraday Soc.*, **9**, 174 (1913).

⁵ Meyers and Acree, *Am. Chem. J.*, **50**, 396 (1913).

⁶ Lewis, Brighton and Sebastian, *THIS JOURNAL*, **39**, 2245 (1917).

A method of renewing the surface between the two salt solutions, at intervals, is described by Lewis, Brighton, and Sebastian.⁶ Walpole⁷ has found that constant potentials can be obtained by forming the junctions with tapes, along which the solutions are flowed. The most decided advance, however, in the direction of the formation of reproducible potentials was made by Lamb and Larson⁸ who used a device which produces a junction which is constantly renewed. The following investigation was made with an apparatus which in most respects resembles that of the authors just mentioned, although it was, to an extent at least, developed independently.

2. The Apparatus.

The apparatus used in our experiments on the more dilute solutions (0.01 *N*) is shown in Fig. 1.

The boundary which formed at A, resulted from the meeting of two slowly moving streams of solution from the reservoirs B and C. The flow was regulated by a screw pinchcock on a rubber tube attached to the tube F.

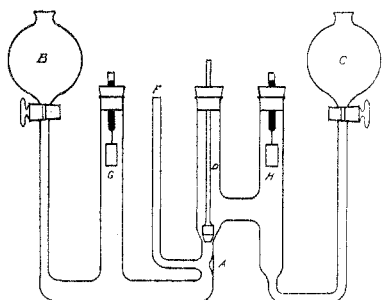


Fig. 1.

An addition to the apparatus as described by Lamb and Larson is the glass rod D which is tipped with rubber. When lowered this rubber tip fits into a constriction in the tube and temporarily separates the two halves of the apparatus containing the different solutions, making it possible to fill the reservoir without mixing the liquids. Unless this device is used it is very difficult to sweep out the resulting mixed solutions in the apparatus and obtain constant potentials. The tubes between the electrodes G and H were, as far as possible,

made wide, so as to cut down the resistance and increase the sensitivity of the potential measurements. A similar apparatus but made of narrower tubing was used for the experiments with 0.1 *N* solutions.

In making a measurement the procedure was as follows. The apparatus was first dried and cleaned, then the rubber tip on D was pushed into the constriction near A, and the two solutions were poured into the appropriate portions of the vessel. The electrodes G and H and stoppers were next inserted, the pinchcock on F closed, the reservoirs B and C partly filled and the stopcocks closed. The whole apparatus was then placed in a thermostat where it was rigidly supported. Adjustment was then made so that the tops of the reservoirs B and C were accurately in the same horizontal plane, after which these reservoirs were completely filled. The system was then ready for lifting of the plug D, opening the stopcocks and the pinchcock on F, after which a boundary soon formed at A and measurements of the potential

⁷ Walpole, *J. Chem. Soc.*, **105**, 2521 (1914).

⁸ Lamb and Larson, *THIS JOURNAL*, **42**, 229 (1920).

between G and H were determined with the potentiometer. It is evident that if the precaution of leveling of the tops of the two reservoirs is not observed there will be an initial surge of liquid through the apparatus and mixing of the solutions at A will result. It was found that if such mixing occurred that no amount of flowing would produce constant potentials and that the experiment had to be started, with a dry vessel, from the beginning. It was also found that for a steady flow, and to avoid entrapping air, the stopcocks should be made of large bore, (about 2.5 mm.).

The nature of the boundary between the two solutions was made clearly visible by operating the apparatus with two solutions, one of which contained a few drops of phenolphthalein and the other a small amount of sodium hydroxide, the pink color of the indicator showing only at the surface of the solutions and in the region in which they had mixed or diffused. A surface of almost microscopic thinness started at A and persisted, with a slight thickening, throughout the length of tube F. If the flow is stopped the colored area thickens at A, if too rapid there is evidence of turbulence. The depression at A (also present in Lamb and Larson's apparatus) prevented mixing due to a "dead space."

3. The Reversible Electrodes.

Following Lewis and Sargent⁹ some experiments were made with gold electrodes surrounded by the salt solutions under investigation, to which definite small amounts of ferro- and ferri-cyanides were added. Our experiments with these electrodes were, however, not successful. Calomel electrodes, although carefully made, were not very satisfactory, particularly with hydrochloric acid as electrolyte.

The final experiments were all carried out with silver-silver chloride electrodes formed on a platinum gauze, as described by MacInnes and Parker,¹⁰ with the additional precaution, recommended by MacInnes and Beattie,¹ of forming the layer of chloride in a solution of the same concentration and composition as that in which the electrodes are to be used. Such electrodes agreed with each other, when placed in the same solution, to 0.03 mv. or less.

The electromotive-force measurements were made with a Leeds and Northrup potentiometer which was calibrated during the investigation. The standard cell used was compared at intervals with a cell which had been recently standardized by the Bureau of Standards. The apparatus was placed in a thermostat which was regulated to $25^{\circ} \pm 0.03^{\circ}$, the latter being measured on a thermometer calibrated by the Bureau mentioned.

4. Preparation of Solutions.

Hydrochloric Acid.—The hydrochloric acid solutions were prepared by diluting

⁹ Ref. 3, p. 355.

¹⁰ MacInnes and Parker, *THIS JOURNAL*, 37, 1445 (1915).

the constant-boiling mixture prepared as directed by Hulett.¹¹ The concentration of this acid was checked by analysis.

Sodium and Potassium Chlorides.—The "c. p." salts furnished by a well-known manufacturer were recrystallized 5 times from conductivity water and then fused. The solutions were then prepared by weighing out the requisite amount of dry salt.

Ammonium Chloride.—A good commercial grade of the salt was sublimed. A concentrated solution was then prepared and analyzed, after which solutions of desired concentrations were obtained by dilution.

Lithium Chloride.—This salt was kindly furnished, after careful purification, by J. A. Beattie of this laboratory. Solutions were made by diluting an analyzed concentrated solution.

Cesium Chloride.—Cesium chloro-iodide, which was prepared from an impure cesium salt, was recrystallized several times, after which the chloride was formed by heating. A 0.01 *N* solution was made by diluting an analyzed concentrated solution.

5. Theoretical Discussion.

A simple derivation, (similar in a number of respects to that given by Henderson,¹²) of an expression for the potential at a junction of the type $\text{HCl} | \text{KCl}$, in which the same concentration of electrolyte exists on both sides of the boundary, is given below. It differs from that of Planck in detail and in generality, but it has the advantage of indicating clearly the nature of the necessary assumptions, which can be compared with those of the more modern theory of strong electrolytes. For the sake of concreteness the derivation will be carried out with reference to solutions of the two substances given above.

At the surface where the two solutions meet there will be a layer in which the concentrations change continuously from pure hydrochloric acid to pure potassium chloride. Let us consider an intermediate plane in this layer. If the total concentration is c and that of the hydrochloric acid at all points in this plane is x then the concentration of potassium chloride is $c - x$. We are assuming that the boundary is formed by mixing and that appreciable diffusion has not occurred. Points on another plane a short distance, dl , away will have concentrations of $x + dx$, and $c - (x + dx)$, respectively. Let us consider the potential difference, dE_1 , between two such planes. The passage of one faraday, F , of current across these planes will be attended by the change of free energy

$$FdE_1 = RT(T_K d \ln a_K + T_H d \ln a_H - T_{Cl} d \ln a_{Cl}) \quad (1)$$

in which E_1 is the liquid junction potential, a_K , a_H and a_{Cl} are the activities of the potassium, hydrogen and chloride ions and T_K , T_H and T_{Cl} are the transference numbers of the ions in the mixture at this particular point. In this connection some recent work by Chow¹³ and Harned¹⁴ have shown that, for moderate concentrations, we can safely assume,

¹¹ Hulett, *THIS JOURNAL*, **31**, 390 (1902).

¹² Henderson, *Z. physik. Chem.*, **59**, 118 (1907).

¹³ Chow, *THIS JOURNAL*, **42**, 497 (1920).

¹⁴ Harned, *ibid.*, **42**, 1808 (1920).

for potassium chloride and hydrochloric acid solutions at least, that the activity of the chloride ion is the same in both solutions and throughout the boundary, *i. e.*, that $d \ln a_{\text{Cl}} = 0$.

The transference numbers T_{K} and T_{H} at points on the plane referred to above will be

$$T_{\text{H}} = \frac{x/c \cdot \Lambda_{\text{H}}}{x/c \cdot \Lambda_{\text{H}} + (c-x)/c \cdot \Lambda_{\text{K}} + \Lambda_{\text{Cl}}} \text{ and } T_{\text{K}} = \frac{(c-x)/c \cdot \Lambda_{\text{K}}}{x/c \cdot \Lambda_{\text{H}} + (c-x)/c \cdot \Lambda_{\text{K}} + \Lambda_{\text{Cl}}} \quad (2)$$

in which Λ_{H} , Λ_{K} and Λ_{Cl} are the equivalent conductances of the ions at the concentrations involved. If $x/c = l$ and $\frac{c-x}{c} = (1-l)$ Equations 2 become

$$T_{\text{H}} = \frac{l\Lambda_{\text{H}}}{l\Lambda_{\text{H}} + (1-l)\Lambda_{\text{K}} + \Lambda_{\text{Cl}}} \text{ and } T_{\text{K}} = \frac{(1-l)\Lambda_{\text{K}}}{l\Lambda_{\text{H}} + (1-l)\Lambda_{\text{K}} + \Lambda_{\text{Cl}}} \quad (3)$$

The assumption that Λ_{Cl} is the same on both sides of the boundary is justified by the computations of Lewis¹⁵ and of MacInnes,¹⁶ except for solutions whose viscosities are appreciably different. Chow¹³ and Harned¹⁴ have shown that the individual activities of the ions of hydrochloric acid and potassium chloride are the same at one concentration in solutions of the pure substances and in mixtures of the same total electrolyte concentration. Under these conditions then the ratios of the ion activities a_{H} and a'_{H} at two planes in the junction will be proportional to the corresponding concentrations x and x' , and the activities of the other positive ion will be proportional to values of $c-x$. (This does not involve the assumption that the activities of the hydrogen and potassium ions are equal.) We, therefore, have the relations

$$d \ln a_{\text{H}} = d \ln x/c = d \ln l = dl/l \quad (4)$$

$$d \ln a_{\text{K}} = d \ln (c-x)/c = -d \ln (1-l) = -dl/(1-l). \quad (4a)$$

Substituting 3, 4, and 4a in 1:

$$F dE_1 = RT \frac{(\Lambda_{\text{H}} - \Lambda_{\text{K}}) dl}{l(\Lambda_{\text{H}} - \Lambda_{\text{K}}) + \Lambda_{\text{K}} + \Lambda_{\text{Cl}}}. \quad (5)$$

Integrating between $l = 0$ and $l = 1$ we have

$$E_1 = \frac{RT}{F} \ln \frac{\Lambda_{\text{K}} + \Lambda_{\text{Cl}}}{\Lambda_{\text{H}} + \Lambda_{\text{Cl}}}. \quad (6)$$

This equation, in which the conductances refer to the concentration under consideration rather than to the limiting values, is a modification of the original Planck equation recommended by Lewis and Sargent.⁸

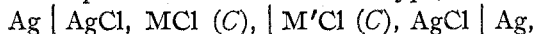
To summarize, the assumptions involved in this derivation are: (a) that the electrolyte concentration is constant throughout the boundary, *i. e.*, that the boundary is formed by mixture and not by diffusion; (b)

¹⁵ Lewis, *THIS JOURNAL*, **34**, 1640 (1912).

¹⁶ MacInnes, *ibid.*, **41**, 1086 (1919), and **43**, 1217 (1921).

the ion activities are independent, at each concentration, of the nature of the (monovalent) oppositely charged ions in solution; and (c) the ion conductances are also independent, at each concentration, of the accompanying ions. The validity of (b) has been tested, as already mentioned, by Chow and by Harned, for solutions of the pure substances and for mixtures; assumption (c) at moderate concentrations holds for many, if not most of the univalent salts,¹⁷ and is a close approximation for such mixtures as have been investigated. (Work on the conductances of mixtures of electrolytes is in progress in this laboratory.) Assumption (a) will be discussed in the next section.

It should also be noted that if the activity of the chloride ion at any one concentration is the same in two alkali chloride solutions or in hydrochloric acid the measured potential of a cell of the type,



is the potential of the liquid junction, since equal electrode potentials oppose each other.

6. Experiments on Rates of Flow.

With the apparatus described in the previous sections it was, of course, important to determine the effect of the rate of flow upon the potential

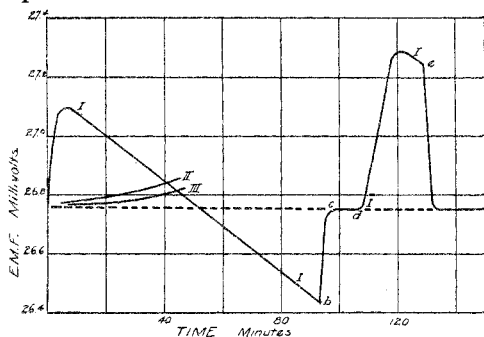


Fig. 2.

of the liquid junction. Fig. 2, in which the ordinates are potentials in millivolts and the abscissas times in minutes, summarizes, graphically, the results of the experiments on the junction between 0.1 *N* hydrochloric acid and 0.1 *N* potassium chloride. Curve I shows the effect of stopping the flow of a properly formed junction. The potential rises rapidly through a millivolt or more, and this is followed by a slow decrease of potential. It is the top of this curve that has, apparently, been considered to be the "correct" potential of the junction. At *b* on this curve the flow was started again and the original potential was quickly regained at *c*. At *d* the flow was again stopped and the potential rose to a different maximum, after which it slowly decreased. This time, at *e*, the original potential was almost instantly obtained from the higher value by starting the flowing. Curve II and III show the effect of too slow flowing, 1 and 2 drops a minute respectively dripping from the outlet tube. The

¹⁷ See MacInnes, *THIS JOURNAL*, 43, 1217 (1921).

dotted line represents the constant potential of the junction procured by the passage of from 3 to 7 drops a minute. Above the latter rate (from 8 drops per minute to rapid streaming) there was a perceptible decrease in the potential, but of the order of a few hundredths of a millivolt only. This was possibly due to drawing cool solutions from the reservoirs B and C into the boundary.

The phenomena underlying the curious rise of potential when the junction flow is stopped are obscure, but they are undoubtedly related to the fact that the moving junction tends to give a "mixture" boundary, *i. e.*, one in which the electrolyte concentration is constant throughout, whereas if time for diffusion is allowed there will be, immediately after stopping the flow at least, planes in the boundary at which the total concentration is greater than on either side, due to the fact that one electrolyte, in general, will have a greater diffusion constant than the other.

7. Experimental Results and Discussion.

The potentials at the junctions of solutions of hydrochloric acid with solutions of the alkali chlorides and of pairs of the alkali chlorides with each other, are given in Table I for 0.1 *N* solutions and in Table II for 0.01 *N* solutions. The different figures for each pair of electrolytes in the column headed "measured e. m. f." are the results of independent measurements, starting, in many cases, from freshly prepared solutions. The combination HCl | KCl at 0.1 *N* was, however, measured at least ten times with results that agreed within a few hundredths of a millivolt.

In the last column of each table the results of computations based on Lewis and Sargent's formula: $E_j = RT/F \ln \Delta c/\Delta'c$, are given.¹⁸ It is clear, on comparing this column of figures with that giving the directly measured values, that the Lewis and Sargent formula is remarkably successful in giving the order of magnitude of the liquid junction potential, but distinct variations are however to be observed. The junctions involving the potassium ion are, it will be noted, particularly far from agreement, the differences between the observed and computed values

¹⁸ The following values for Δ at 25° were used in this computation:

Substance.	0.01 <i>N</i> .	0.1 <i>N</i> .
HCl	411.6	390.4
KCl	141.4	129.0
NaCl	118.7	106.8
LiCl	108.6	96.7
NH ₄ Cl	147.7	128.1
CsCl	144.6	...

Of these the values for the first three substances were taken from Noyes and Falk's compilation. (*THIS JOURNAL*, **34**, 454 (1912)). The other values are computed from Kohlraush and Maltby's values at 18° and the temperature coefficients of Kohlraush and of Arrhenius, (Landoldt and Börnstein, "Tabellen").

being close to 1.7 mv. at 0.1 *N* and 1.5 mv. for 0.01 *N* for each junction involving this ion. Since the mobilities of the potassium and ammonium ions are nearly equal the junction $\text{KCl} \mid \text{NH}_4\text{Cl}$ would, according to any theory thus far advanced, be expected to be very low. The formula stated above gives 0.2 mv. for this junction whereas the measured potential is ¹⁰ten times that value. The difference between the observed and computed potentials is, however, nearly the same as that found for other combinations involving the potassium ion.

TABLE I.

POTENTIALS AT THE JUNCTIONS OF 0.1 *N* SOLUTIONS OF UNIVALENT CHLORIDES, AT 25°.

Electrolytes.	Measured e. m. f. Millivolts.	Computed e. m. f. Millivolts.	
		By difference.	Lewis and Sargent's formula.
HCl, KCl.....	26.78	26.78	28.4
HCl, NaCl.....	33.07	33.08	33.3
	33.13		
	33.07		
HCl, LiCl.....	34.87	35.65	35.8
	34.87		
	34.83		
HCl, NH ₄ Cl.....	28.40	28.78	28.6
	28.39		
KCl, NaCl.....	6.45	6.30	4.9
	6.35		
	6.45		
KCl, LiCl.....	8.85	8.87	7.4
	8.63		
	8.89		
KCl, NH ₄ Cl.....	2.13	2.00	0.2
	2.16		
	2.20		
NaCl, LiCl.....	2.65	2.57	2.5
	2.65		
	2.57		
NaCl, NH ₄ Cl.....	-4.21	-4.30	-4.6
	-4.26		
	-4.15		
LiCl, NH ₄ Cl.....	-6.93	-6.87	-7.2
	-6.92		

Since this abnormality of the potassium ion is very surprising, it was considered desirable, after the work described above was completed, to get independent measurements of some of the potentials of junctions involving that ion. With the aid of a liberal grant from the Warren Fund of the American Academy of Arts and Sciences, Mr. E. R. Smith of this laboratory repeated a number of the determinations. To be sure

TABLE II.
 POTENTIALS AT THE JUNCTIONS OF 0.01 *N* SOLUTIONS OF UNIVALENT CHLORIDES AT 25°.

Electrolytes.	Measured e. m. f. Millivolts.	Computed e. m. f. Millivolts.	
		By difference.	Lewis and Sargent's formula.
HCl, KCl.....	25.70	25.62	27.4
	25.75		
	25.72		
	25.73		
HCl, NaCl.....	31.12	31.19	31.9
	31.19		
	31.18		
HCl, NH ₄ Cl.....	27.06	26.93	27.4
	27.00		
	27.00		
HCl, LiCl.....	33.77	33.82	34.2
	33.79		
	33.70		
KCl, NaCl.....	5.65	5.57	4.5
	5.65		
KCl, LiCl.....	8.25	8.20	6.8
	8.16		
	8.20		
KCl, NH ₄ Cl.....	1.30	1.31	0.05
	1.31		
KCl, CsCl.....	0.30	0.30	0.005
	0.32		
NaCl, LiCl.....	2.65	2.63	2.3
	2.57		
	2.67		
NaCl, NH ₄ Cl.....	-4.31	-4.26	-4.5
	-4.21		
NaCl, CsCl.....	5.40	-5.17	-5.1
	5.41		
	5.36		
LiCl, NH ₄ Cl.....	-6.89	-6.89	6.9
	-6.89		
LiCl, CsCl.....	-7.78	-7.80	-7.3
	-7.81		
CsCl, NH ₄ Cl.....	0.95	0.91	0.5

that the abnormality was not due to the sample of potassium chloride used, measurements were made with (a) the material used in the foregoing experiments, (b) another sample of German origin, and (c) an American product. The latter two samples were purified as described in Section 4. The potentials of 0.1 *N* potassium chloride solutions against a newly prepared 0.1 *N* hydrochloric acid solution were as follows: Sample (a) 26.70 mv., Sample (b), 26.90 mv. and Sample (c), 26.87 mv. which agree substan-

tially with the value (26.78 mv.) given in Table I. Independent determinations were also made of the potentials of the junctions: $\text{HCl}|\text{NaCl} = 33.11$ mv., and $\text{KCl}|\text{NaCl} = 6.38$ mv. both at 0.1 *N*, and of the junction $\text{HCl}|\text{KCl} = 25.74$ mv. at 0.01 *N*, all of which agree closely with the potentials given in the tables above. It would appear, therefore, that the deviation of the potentials of junctions involving the potassium ion from values predicted by the Lewis and Sargent formula are real and not due to experimental error or to impurities in the materials. This later work has also demonstrated that the apparatus, though apparently complex, will give correct results with but little practice in its use. Mr. Smith is now determining the potentials at the junctions of the alkali bromides. We wish, at this point, to express our gratitude to the Committee of the Warren Fund for its assistance.

The question immediately presents itself: Why do the potassium, and to a lesser extent the lithium, ions yield potentials that cannot be computed by the Lewis and Sargent formula, when junctions involving pairs of the hydrogen, sodium, cesium, and ammonium ions can be obtained from it almost within experimental error? We have at present no answer to offer, but we hope that the matter will be cleared up by further work.

There is, however, a remarkably simple relation connecting the observed potentials in Tables I and II. At both concentrations a figure can be obtained, for each electrolyte, such that the difference between any two figures gives the corresponding liquid junction potential. A set of such figures for each concentration can be found in Table III and the results of each subtraction are given in the columns headed "by difference" in Tables I and II. The figures in Table III are, of course, averaged from the results themselves. It will be seen that, with one exception, the potentials can be found, almost within experimental error, from these figures. This relation appears to be another instance of the remarkable additivity of the properties of solutions of strong electrolytes. As is obvious from the properties of the logarithm, a similar relation would hold if all the potentials could be calculated from Lewis and Sargent's equation or from Planck's original equation. The potassium and lithium ions behave, however, as if, in this connection, they have different Λ values than those obtained from conductance measurements.

TABLE III.

CHARACTERISTIC POTENTIALS.		
Electrolyte.	0.1 <i>N</i> .	0.01 <i>N</i> .
LiCl.....	0.0	0.0
KCl.....	8.87	8.20
HCl.....	35.65	33.87
NaCl.....	2.57	2.63
NH ₄ Cl.....	6.92	6.89
CsCl.....	7.80

7. Summary.

Using a slightly modified form of Lamb and Larson's "flowing" junction apparatus, reproducible values were obtained, within a few hundredths of a millivolt, of the potentials of the liquid junctions between equi-concentrated solutions of a series of monovalent chlorides. The Lewis and Sargent form of Planck's original equation, $E_i = RT/F \ln \Lambda_c/\Lambda'_c$, expresses the results for junctions involving most of the ions studied, and gives qualitative agreement in all cases. The experimentally determined potentials can, however, be obtained from the differences between numbers, one for each ion at each concentration. This is equivalent to the expression given above, except that, for the potassium and lithium ion, values of Λ which are slightly different from those obtained from conductance measurements would have to be used.

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NOTES.

A Simple Method for the Preparation of Sodium Hydroxide free from Carbon Dioxide.—Having recently had occasion to prepare solutions of sodium hydroxide free from carbon dioxide, the method of preparation here described was evolved and in use found simpler than most methods commonly used.

Method.—Distilled water contained in an Erlenmeyer flask is boiled to remove any carbon dioxide present, after which, when the water is cooled enough, ethyl ether is added to form a layer 3 or 4 cm. in depth. Pieces of metallic sodium, not exceeding about 1 cm. in diameter are then dropped into the flask. They will fall no further than the ether layer where they remain suspended. The water contained in the ether layer causes the slow formation of sodium hydroxide, which readily passes below to the water layer. Meanwhile the ether prevents the results usually observed when metallic sodium is brought in contact with water in the presence of air. After the desired quantity of metallic sodium has reacted, the larger portion of ether is removed by a pipet, and the last traces by boiling the solution. Various modifications and adaptations will suggest themselves to the reader.

Fire Hazard.—It would seem that the above procedure is fraught with considerable danger from fire and explosions. Particular effort was made to cause explosions. As a result it was observed that none occurs so long as the depth of the ether layer is great enough so that the suspended sodium cannot simultaneously come in contact with both air and water. When the quantity of sodium to be dissolved is rather large in proportion to the quantity of ether present it sometimes happens that the heat evolved by the reaction is sufficient to evaporate the ether sufficiently to cause