

# THE USE OF SATURATED AMMONIUM CHLORIDE<sup>1</sup> IN THE ELIMINATION OF CONTACT POTENTIALS

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## ABSTRACT

In the electrometric measurement of the concentrations of various ions in plant extracts and other organic mixtures the potential of the junction between two electrode liquids is a source of error unless this contact potential is calculated, measured, or eliminated. The study of various concentrations of ammonium chloride up to saturated (5.66 *N*) gives a practical method for annulling the contact potential to within  $\pm 1.0$  m. v.

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## I. INTRODUCTION

In the use of e. m. f. measurements for the determination of *H*-ion and other ionic concentrations or more exactly the ionic activities in xylan, lignin and other plant extracts, a source of serious error may be found in the potential of the junction between electrode liquids of different composition.<sup>2</sup> This potential may at times amount to 35 m. v. or more, and failure to correct for it would then cause an error of at least 0.5 pH.

There are three types of methods available for treating contact potentials. Of these, the first is that of calculation by formulas devised by Planck<sup>3</sup> and simplified later by Henderson,<sup>4</sup> Abegg and Cumming,<sup>5</sup> Lewis,<sup>6</sup> and more recently from newer points of view by MacInnes,<sup>7</sup> and Smith.<sup>8</sup> These formulas can be applied to specified simple cases for which they have been verified experimentally but can not be used with complex unknown mixtures, such as plant extracts and culture media.

<sup>1</sup> Presented in part at the Baltimore meeting of the American Chemical Society, April, 1925.

<sup>2</sup> Desha, L. J., and Acree, S. F., On Difficulties in the Use of the Hydrogen Electrode in the Measurement of the Concentration of Hydrogen Ions in the Presence of Organic Compounds, presented at Baltimore Meeting of the Am. Chem. Soc., 1908; Science, vol. 30, p. 624; 1909. Am. Chem. J., vol. 46, p. 638; 1911.

<sup>3</sup> Planck, M., On the Potential Difference between Two Dilute Solutions of a Binary Electrolyte, Wied. Ann., vol. 39, p. 178; vol. 40, p. 561; 1890. Ann. Physik, vol. 4, p. 581; 1890.

<sup>4</sup> Henderson, P., Thermodynamics of Liquid Chains, Z. Physik. Chem., vol. 59, p. 118; 1907; vol. 63, p. 325; 1908.

<sup>5</sup> Cumming, A. C., The Elimination of Potential Due to Liquid Contact, Trans. Faraday Soc., vol. 2, p. 213; 1906; vol. 8, p. 86; 1912; vol. 9, p. 174; 1913; Zt. Elektrochem, vol. 13, p. 17; 1907.

<sup>6</sup> Lewis, G. N., and Sargent, L. W., Potentials Between Liquids, J. Am. Chem. Soc. vol. 31, p. 363; 1909.

<sup>7</sup> MacInnes, D. A., and Parker, Karr, Potassium Chloride Concentration Cells, J. Am. Chem. Soc., vol. 37, p. 1445; 1915; MacInnes, D. A., Liquid Junction Potentials, Ibid., vol. 37, p. 2301; 1915; MacInnes, D. A., and Yeh, Y. L., The Potentials at the Junctions of Monovalent Chloride Solutions, Ibid; vol. 43, p. 2652; 1921.

<sup>8</sup> Smith, E. R., Potential Differences across the Boundaries between Solutions of Mixed Univalent Chlorides, B. S. Jour. Research, vol. 2, p. 1137; 1929.

The second type is the direct measurement of the contact potential by a more or less absolute procedure which gives both the contact potential and the electrode potential. Only four of these methods are available, and they are limited to special cases. One used by MacInnes and Yeh with simple solutions and by Smith with mixtures is cited above. Another by Elliott, Duschak and Acree<sup>9</sup> depends upon the use of negative (calomel or silver chloride) electrodes, and of positive (hydrogen or quinhydrone) electrodes in two different concentrations of a solute (such as hydrochloric acid), whose anions and cations, respectively, are in equilibrium with the electrodes. The e. m. f. across the negative (calomel) electrodes is the algebraic sum of the contact potential and the electrode potentials,  $cp + E = a$ . The e. m. f. across the positive (hydrogen) electrodes is the algebraic difference between the contact potential and the electrode potentials,  $cp - E = b$ . These two equations give the values of  $cp$  and  $E$ . The ratios  $a/(a+b)$  and  $b/(a+b)$  are the transference numbers  $Nc$  and  $Na$ . A third method of this type involves the two e. m. f. readings given by the two contacted solutions containing two pairs of electrodes, one set giving an e. m. f. corresponding to the known  $a$  power of the ratio of the activities of an ion common to the two solutions and the other set giving an e. m. f. involving the known  $b$  power of the same ratio of the activities of that or another ion. In both cases the e. m. f. involves also the contact potentials and the equations may be written as follows for hydrogen-ion activities:

$$E = cp + (RT/F) \log (H/H')^a \quad (1)$$

and

$$E' = cp + (RT/F) \log (H/H')^b \quad (2)$$

By difference we get

$$E' - E = (b - a) (RT/F) \log (H/H').$$

From this equation  $(H/H')$ , the ratio of the hydrogen-ion activities may be calculated and substituted in either (1) or (2) to give  $cp$ . The hydrogen electrode functions through the first power of the ratio of the hydrogen-ion activities and the manganese dioxide electrode<sup>10</sup> involves the second power of the same ratio of the hydrogen-ion activities in the presence of  $M/1,000 Mn$  salts in both acid solutions. Within the experimental errors of about 1 m. v. the hydrogen and manganese dioxide electrodes have been found to give the contact potentials and electrode potentials calculated and observed by other methods for solutions of  $HNO_3$  and  $HCl$ . They may prove to be generally useful below pH 7.0 in complex organic solutions when the necessary salt errors are taken into consideration. By the addition of  $M/1,000 Mn$  salt to any unknown solution surrounding both a manganese dioxide electrode and a hydrogen (or other equivalent) electrode, the measured e. m. f. can be employed to calculate the pH without directly involving  $H$ -ion standards and contact potentials. A fourth method applicable to two different

<sup>9</sup> Article presented by Elliott, F., Duschak, E., and Acree, S. F., at the St. Louis meeting of the Amer. Chem. Soc., 1920.

<sup>10</sup> Tower, O. F., Studies of Superoxide Electrodes, *Zt. physik. chem.*, vol. 18, p. 17; 1895, on the Potential Differences at the Junctions of Dilute Solutions, *Ibid.*, vol. 20, p. 198; 1896. Hill, J. R., The Oxidation-Reduction Potential of the Manganese Dioxide Mangan Ion Electrode, *Diss.*, Catholic University of America; 1929.

concentrations of a uni-univalent electrolyte in contact, such as dilute (0.1*N*–0.001*N*) solutions of potassium chloride or hydrochloric acid, is the use of two pairs of electrodes reversible to both ions (for example, AgCl or HgCl electrodes for chloride ions), and measurement of the e. m. f. values with and without transference. The electrode potential is just one-half of the e. m. f. without transference. As the e. m. f. with transference is equal to the algebraic sum of the electrode potential and the contact potential, the subtraction of the electrode potential (obtained as above) therefrom gives the contact potential. The transference numbers can be calculated from the value of *cp*. This method can be modified for other types of electrolytes and complex solutions.

The third type is a practical general method of elimination or reduction of the contact potential to very small values by inserting between the electrode liquids concentrated solutions of salts whose ions have nearly equal mobilities. This method may be advantageously used in connection with the four preceding ones to see whether the elimination is complete. It may be said in advance that the efficiency of each respective contact potential eliminator varies with the junction liquids and hence that the method is only approximate. The following abstracts <sup>11</sup> give a résumé of the previous work on elimination of contact potentials.

Planck, cited above, and Nernst <sup>12</sup> proved in 1889 that two solutions of a substance with nearly equal ionic mobilities have low contact potentials. In 1895, Tower, cited above, discovered that the insertion of potassium chloride (*N*/128 to *N*/1) or of other salts between solutions of acids tends to eliminate contact potentials. In 1905, Bjerrum <sup>13</sup> measured the two e. m. f. produced when he interposed first 1.75 *N* KCl, which he called "half saturated," and then 3.5 *N* KCl, called "saturated," between two solutions of a given chloride containing calomel electrodes. He subtracted the difference between these two e. m. f. values from that found with the 3.5 *N* KCl solution, and called the resulting extrapolated e. m. f. the correct value for the electrode potentials. Although he clearly pointed out that the extrapolation must not amount to more than 1 or 2 m. v. his method has frequently been used incorrectly by other workers having larger corrections in their *H*-ion investigations. Confusion also arises because saturated KCl at 25° C. is 4.1 *N* and not 3.5 *N*.

The use of varying concentrations of ammonium nitrate up to saturated by Cumming <sup>14</sup> and Abegg in 1906 nearly completely eliminated the contact potential between different solutions of silver nitrate or of other salts. Desha, Loomis, Myers, Clarke, and Acree found in 1907–1914 that ammonium nitrate is not so efficient for hydrochloric acid, <sup>15</sup> and showed that 4.1 *N* KCl nearly completely

<sup>11</sup> All of the above methods and the data were discussed in a lecture before the chemical staff of the National Bureau of Standards on December 14, 1929.

<sup>12</sup> Nernst, W., The Electromotive Activity of Ions. *Z. physik. Chem.*, vol. 4, p. 165, 1889.

<sup>13</sup> Bjerrum, N., Elimination of Contact Potential Between Two Dilute Aqueous Solutions by Interposition of a Concentrated Solution of Potassium Chloride. *Z. physik. Chem.*, vol. 53, p. 423, 1905; vol. 59, pp. 336, 581, 1907. *Z. Elektroch.*, vol. 17, pp. 58, 389, 1911.

<sup>14</sup> Cumming, A. C., The Elimination of Potential Due to Liquid Contact, *Trans. Far. Soc.*, vol. 2, p. 213, 1906; vol. 8, p. 86, 1912; vol. 9, p. 174, 1913. *Z. Electrochem.*, vol. 13, p. 18, 1907.

<sup>15</sup> Desha, loc. cit.; Loomis, N. E., and Acree, S. F. A study of the Hydrogen Electrode and of Contact Potential, *Amer. Chem. J.*, vol. 46, pp. 585, 621; 1911. Loomis, J. Phys. Chem., vol. 19, p. 660; 1915. Loomis and Acree, *J. Am. Ch. Soc.*, vol. 38, p. 2391; 1916. Loomis and Meacham, *Ibid.*, vol. 38, p. 2310; 1916. Loomis, Essex, and Meacham, *Ibid.*, vol. 39, p. 1193; 1917. Myers, C. N., Clark, W. F., and Acree, S. F. A study of the Hydrogen Electrode, of the Calomel Electrode, and of Contact Potential, *V., J. Phys. Chem.*, vol. 20, 243; 1916. Myers and Acree, *J. Phys. Chem.*, vol. 21, p. 334; 1917.

eliminates the usual contact potentials. This method is now widely used.

Meacham and Acree<sup>16</sup> used 0.1 *N*, 1.75 *N*, 3.5 *N*, and 4.1 *N* KCl between 0.1 *N* KCl-HgCl and 0.1 *N* HCl-H<sub>2</sub> electrodes in 1916 and found the Bjerrum extrapolation too large in this case.

Fales and Vosburgh<sup>17</sup> in 1918 used various concentrations of KCl from 0.1 *N* to 4.1 *N* between KCl-HgCl and HCl-H<sub>2</sub> electrodes, proved Planck's formula inadequate, and confirmed the conclusion of Loomis, Myers, and Acree that 4.1 *N* KCl substantially eliminates contact potentials.

This article deals with further work on the elimination of contact potentials by means of ammonium chloride.

## II. EXPERIMENTAL WORK ON CONTACT POTENTIALS AND THEIR ELIMINATION

In order to learn more about the magnitude and cause of various contact potentials, especially in systems which may also give data on the individual electrode potentials, and to study the actual reversal or over-annulment of contact potentials by the interposition of salts with highly mobile cations between solutions with very mobile anions and vice versa,<sup>18</sup> we have undertaken further studies with potassium and ammonium chlorides and other very soluble salts with nearly equal ionic mobilities. It was believed that the higher solubility of ammonium chloride, and the nearly equal ionic mobilities would make its saturated solution perhaps a better practical contact potential eliminator than potassium chloride. Its use with hydrochloric acid was tried with the idea that if it effectively annuls the contact potential of about 28 m. v. for 0.1 *N* HCl, the saturated ammonium chloride should certainly eliminate the 5 to 10 m. v. formed at junctions between the usual well buffered organic solutions and standard calomel electrodes.

In order to make a comparison of the relative merits of KCl and NH<sub>4</sub>Cl as contact potential eliminators in such potentiometric *H*-ion measurements, NH<sub>4</sub>Cl solutions having about the same concentrations as the KCl solutions used by Tower, Bjerrum, Fales and Vosburgh, Meacham and Acree, and Duschak, Elliott, and Acree, cited above, were prepared, a dye being added to make the junctions easily observable. This series of concentrations makes possible an extension of the curve secured by Meacham and Acree in their attempt to approach asymptotically the maximum elimination of contact potentials by these salts. The solutions of NH<sub>4</sub>Cl used were 0.1 *N*, 0.5 *N*, 1 *N*, 1.75 *N*, 2.5 *N*, 3.5 *N*, 4.1 *N* (corresponding to saturated KCl) and saturated (about 5.66 *N*). Only 4.1 *N* KCl was employed in this series of experiments.

The double hydrogen electrode (fig. 1), without the traps *T* and *T'*, was used to form either fixed or flowing sharp liquid junctions. The gold electrodes were coated with palladium black. All readings were taken in an air bath at 25° C. The electrodes were first standardized with 0.1 *N* sodium acid phthalate in both electrode chambers.

<sup>16</sup> Meacham, M. R., Dissertation, Syracuse University; 1918. Work presented at the St. Louis meeting of the American Chemical Society, 1920.

<sup>17</sup> Fales, H. A., and Vosburgh, W. C., Planck's Formula for the Potential Difference Between Solutions and the Values of Certain Important Cells. *J. Amer. Chem. Soc.*, vol. 40, p. 1291; 1918.

<sup>18</sup> Cumming, loc. cit. p. 215, vol. 16.

Measurements were then taken directly between 0.1 *N* sodium acid phthalate and 0.1 *N* HCl, without a contact potential eliminator. The barrel or U tube *B* of the apparatus was filled with the sodium acid phthalate solution, which usually contained a dye to facilitate the observation of the junctions *J* and *J'*. In some cases no dye was used, but a satisfactory liquid junction was nevertheless formed

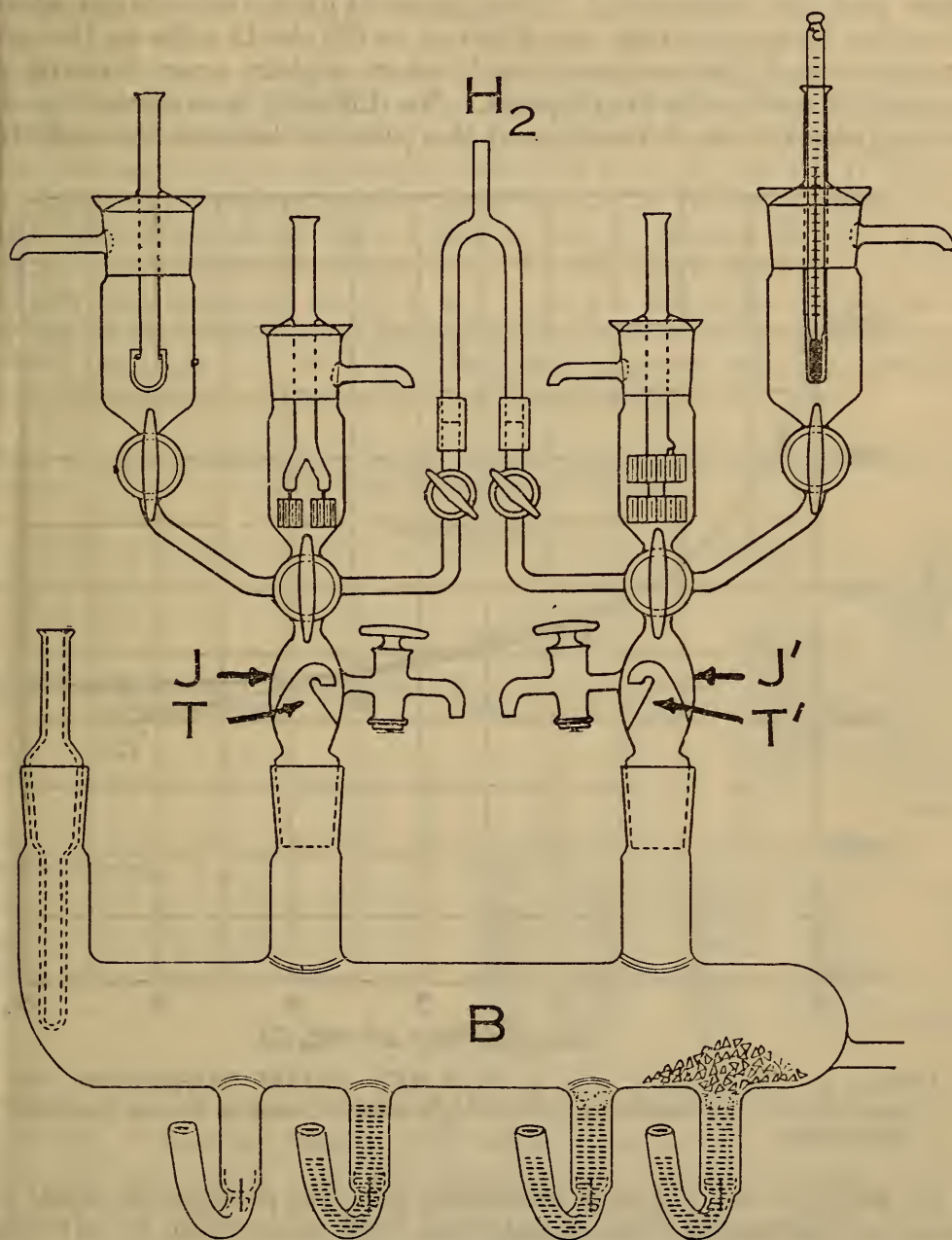


FIGURE 1.—Double hydrogen electrode

without difficulty. The barrel was then filled successively with the different solutions of the ammonium or potassium chloride as "bridges" or "links," junctions were made with the 0.1 *N* sodium acid phthalate and 0.1 *N* HCl, and the e. m. f. values measured for each "bridge." The liquid junctions are very sharp with links whose concentrations are above  $N/1$  ammonium or potassium chloride. Other accessories to this apparatus involving the principle of the

traps  $T$  and  $T'$  for joining (heavier or) lighter liquids, such as the very dilute ammonium chloride solution, and (lighter or) heavier solutions, such as 0.1  $N$  sodium acid phthalate, to form good junctions were not available in this work. Consequently, at the lower concentrations of  $\text{NH}_4\text{Cl}$  (normal and below) difficulty was experienced in making the liquid junction between the lighter bridge solution below and the heavier 0.1  $N$  sodium acid phthalate solution above. The dyed bridge solution was allowed to fill the U tube to the main left stopcock 2, the stopcock itself when slightly open forming the boundary between the two liquids. No difficulty was encountered in securing steady e. m. f. readings at this junction because the mobilities

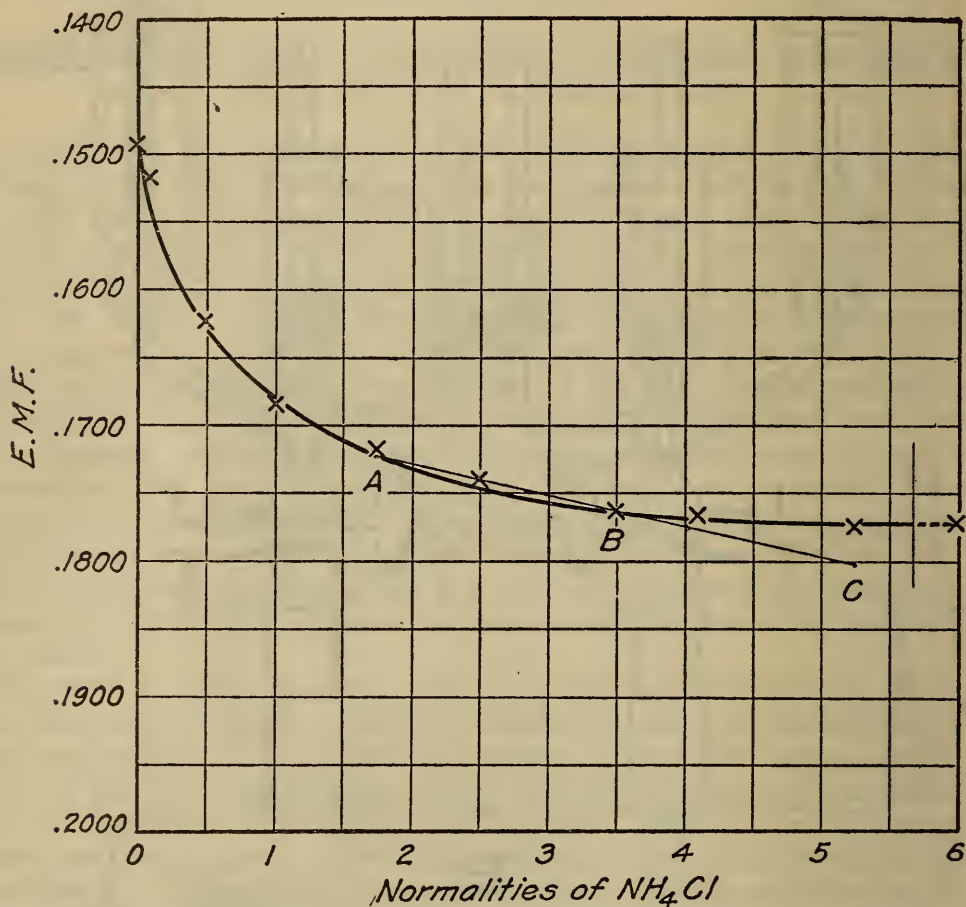


FIGURE 2.—Change in e. m. f. of  $N/10$   $\text{HCl}$ — $N/10M$   $\text{NaHphthalate}$  with variation in concentration of the  $\text{NH}_4\text{Cl}$  solution used as contact potential eliminator.

of the sodium and the acid phthalate ions are practically equal and cause no appreciable contact potential with ammonium or potassium chlorides in either sharp or mixed boundaries. On the other hand, the contact potential at the junction with the 0.1  $N$  hydrochloric acid drifted as much as one millivolt unless a sharp, new junction was made before each e. m. f. reading.

The accompanying Table 1 and Figure 2 show the change in e. m. f. readings obtained with the several concentrations of  $\text{NH}_4\text{Cl}$  used between 0.1  $N$   $\text{HCl}$  and 0.1  $N$  sodium acid phthalate ( $\text{NaHPh}$ ). These are compared in column 6 with some average values for the same concentrations of  $\text{KCl}$  used between 0.1  $N$   $\text{HCl}$  and 0.1  $N$

KCl-HgCl by Bjerrum, Sørensen, Lewis and Sargent, Fales and Vosburgh, Meacham and Acree, and Duschak, Elliott, and Acree, cited above. In Table 1 the first column gives the concentration of the ammonium or potassium chloride solution used as the contact potential eliminator between the electrode solutions; the second column gives the e. m. f. reading; the third column gives as "Δ values" the difference between the e. m. f. readings of column 2; the fourth column gives as "total Δ values" the differences between the e. m. f. reading with saturated ammonium chloride and the reading with any other solution of ammonium chloride; the fifth column gives the same data calculated from the e. m. f. for 4.1 *N* NH<sub>4</sub>Cl; the sixth column gives similar data for 4.1 *N* KCl and the systems *N*/10 KCl-*x*KCl-*N*/10 HCl. The e. m. f. values in the second column are uniformly about 6 m. v. too large because the *N*/10 NaHPh was adjusted about 6 m. v. or 0.1 pH high. This has no bearing on our conclusions, however, because we are really concerned with the change in e. m. f. or decrease in contact potential produced when the various concentrations of the eliminator are used.

TABLE 1.—*Electromotive force of the systems N/10 NaHPh-xNH<sub>4</sub>Cl-N/10 HCl and N/10 KCl-xKCl-N/10 HCl*

(Temperature 25° C.)

Concentration ( <i>x</i> ) of NH <sub>4</sub> Cl used as contact potential eliminator	E. m. f. volts	Δ Values	Total Δ values	Deviation from e. m. f. for 4.1 <i>N</i> NH <sub>4</sub> Cl as contact potential eliminator	Average difference between e. m. f. for <i>N</i> /10 KCl- <i>x</i> KCl- <i>N</i> /10 HCl and e. m. f. for <i>N</i> /10 KCl-4.1 <i>N</i> KCl- <i>N</i> /10 HCl observed by other workers
Saturated (5.66 <i>N</i> ).....	0.1773				
4.1.....	.1769	0.0004	0.0000	0.0000	0.0000
3.5.....	.1763	.0006	.0010	.0006	.0006
2.5.....	.1740	.0023	.0033	.0029	.0022
1.75.....	.1719	.0021	.0054	.0050	.0047
1.00.....	.1685	.0034	.0088	.0084	.0076
.50.....	.1625	.0060	.0148	.0144	
.10.....	.1518	.0107	.0255	.0251	
.00.....	.1493	.0025	.0280	.0276	0.0270-0.0284

Table 1 and Figure 2 show that the curve for the e. m. f. readings with NH<sub>4</sub>Cl starting from 0.1493 volts in the case of the direct junction with no contact potential eliminator, becomes less steep as saturation is approached, until the difference between 4.1 *N* and saturated NH<sub>4</sub>Cl is only 0.4 m. v., the curve at last approaching asymptotically a horizontal straight line in the neighborhood of 0.1774 volt. An average of five readings with 4.1 *N* KCl gave 0.1766 v. instead of 0.1769 v. with 4.1 *N* NH<sub>4</sub>Cl. This e. m. f. curve for NH<sub>4</sub>Cl may be taken either as showing complete elimination of contact potential or elimination of the same to the greatest extent possible by the saturated NH<sub>4</sub>Cl. The line *ABC* gives at *C* the electrode e. m. f. obtained by the Bjerrum method. These curves show that the wrong use of Bjerrum's extrapolation gives an e. m. f. postulating complete elimination of contact potential which is 3 m. v. too high in this type of case. As the figures for maximum elimination of contact potential in-

icated by this method agree within limits of usual experimental errors with those obtained by the Loomis-Acree 4.1 *N* KCl method in routine tests, it is reasonable to assume that  $\text{NH}_4\text{Cl}$  more nearly approaches an ideal contact potential eliminator for precision work than does KCl because of its greater (38 per cent larger) molar solubility. MacInnes and his coworkers showed furthermore that these two salts have nearly identical transference numbers in dilute solutions, and that in the case of KCl these values do not change appreciably between 0.005 *N* and 2 *N*. Comparative data are greatly needed for more concentrated solutions up to 4.1 *N* or 5.66 *N*, respectively, for KCl and  $\text{NH}_4\text{Cl}$ . The work of E. R. Smith<sup>19</sup> is a recent contribution in this field. It seems probable that  $\text{NH}_4\text{Cl}$  may conveniently replace KCl in potentiometric measurements of contact potentials of solutions of sufficiently low pH to avoid any possible errors due to the liberation of  $\text{NH}_3$ .

### III. DISCUSSION

We have carried on further experiments with various types of buffer solutions of known pH value for the purpose of determining: (a) The lowest and highest pH at which  $\text{NH}_4\text{Cl}$  can still be used to replace KCl as a contact potential eliminator; (b) the relative values of other salt bridges having nearly the same mobilities of anion and cation for the elimination of contact potential, such as rubidium bromide, lithium iodate, and ammonium perchlorate; and (c) the effect of the addition of sufficient amounts of ammonium and potassium nitrates, respectively, to saturated ammonium and potassium chlorides to counterbalance the effect of the slightly higher mobility of the chloride ion.

It seems that a molar ratio of 1:3 for these nitrate-chloride mixtures should form an approximately isoelectric contact potential eliminator capable of annulling liquid junction potentials of buffer solutions with pH values between 3 and 10. The molar ratio and the nature of the salt mixture can be changed for more acid and alkaline solutions, respectively. We have found that these mixed ammonium and potassium nitrates and chlorides form very stable standard calomel electrodes.

The possible practical advantage of using such chloride-nitrate mixtures as contact potential eliminators may be illustrated as follows. By use of the Henderson equation for mixed boundaries cited above and the accepted conductivity data we have made the following calculations. Whereas 4.0 *N* potassium or ammonium chloride gives the contact potentials 0.9, 1.1, and 1.4 m. v., respectively, with 0.1 *N*, 0.01 *N* and 0.001 *N*, sodium acetate-acetic acid standards, the corresponding 1:3 nitrate-chloride 4 *N* mixture gives the contact potentials 0.2, 0.03, and 0.01 m. v., respectively: Whereas 5 *N*  $\text{NH}_4\text{Cl}$  gives the contact potentials 4.4, 1.5, and 1.3 m. v., respectively, with 0.1 *N*, 0.01 *N*, and 0.001 *N* HCl, the corresponding 1:3 nitrate-chloride 5 *N* mixture gives the values 4.0, 0.7, and 0.1 m. v. Consequently, the calculated contact potentials for the 1:3 nitrate-chloride 4 *N* mixture in junctions with the usual well-buffered solutions with pH 3 to 10 are apparently less than 0.2 m. v., whereas the 4 *N* KCl or  $\text{NH}_4\text{Cl}$  may leave a residual error of around  $\pm 1$

<sup>19</sup> E. R. Smith, B. S. Jour. Research, vol. 6, p. 917; 1931.



m. v. Another error of 1 to 2 m. v. in saturated calomel electrodes may be caused by the customary use of potassium chloride crystals over the calomel and resulting hysteresis in solubilities and e. m. f. when the temperature fluctuates. The authors urge the use of 4 *N* KCl without any solid potassium chloride if the calomel electrode is used in the open room instead of in a thermostat. All these conclusions should be considered tentative pending further experimental work outlined above because of the uncertainties regarding the properties of the concentrated contact potential eliminators. The ionization, ionic mobilities, transference numbers, diffusion of the molecules, interionic effects, and other properties concerned with contact potentials need further investigation and new equations must be devised if errors and uncertainties are to be reduced to  $\pm 0.1$  m. v.

WASHINGTON, July 1, 1931.