

ON ELIMINATION OF LIQUID CONTACT POTENTIALS WITH POTASSIUM CHLORIDE AND AMMONIUM CHLORIDE

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ABSTRACT

The method of employing 4.1 *N* potassium-chloride solution for annulling contact potentials between hydrochloric-acid and potassium-chloride solutions gives results within the present routine experimental errors and uncertainties regarding the contact potentials. The Bjerrum extrapolation correction is over three times as large as it should be, especially if used outside the limit of about 2 mv set by him. The use of the so-called "saturated" 3.5 *N* instead of the 4.1 *N* potassium-chloride solution may often leave an error of 1 to 3 mv, or more. In view of (1) the approximately correct, experimentally verified results given by the Loomis-Acree method, (2) its simplicity and rapidity, and (3) the avoidance of uncertain extrapolations, its adoption for general use is recommended for annulling contact potentials between (a) hydrochloric acid and especially organic salts and buffers on the one hand and (b) potassium-chloride or sodium-acid phthalate solutions used in standard or reference electrodes. An approximately isoelectric eliminator, such as 3 *N* KCl + *N* KNO₃ should be used between solutions with pH values between 3 and 10.

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I. INTRODUCTION

Contact potential is the source of greatest uncertainty, other than the purity of the water,¹ in comparative studies of the electrometric and isohydric colorimetric methods for measuring accurately the concentration or activity of hydrogen and other ions, and salt effects.² Such a potential is set up when the liquid of a standard reference electrode is brought into contact with complex solutions of xylans and lignins from cornstalk and other cellulosic wastes, and with paper,³ pulp, soils,⁴ tannin,⁵ and other extracts, especially when very acid⁶

¹ Fawcett, E. H., and Acree, S. F., The Problem of Dilution in Colorimetric H-ion Measurements. I. Isohydric Indicator Methods for Accurate Determination of pH in Very Dilute Solutions, *J. Bact.*, vol. 17, p. 168; 1929. Isohydric Indicators and Superpure Water, *Ind. Eng. Chem., Anal. ed.*, vol. 2, p. 78; 1930. Aeration of Buffers, *B. S. Jour. Research*, vol. 6, p. 757; 1931.

² Acree, S. F., and Fawcett, E. H., The Problem of Dilution in Colorimetric H-ion Measurements, *Ind. Eng. Chem., Anal. ed.*, vol. 2, p. 78; 1930.

³ Shaw, M. B., Hydrogen Ion Concentration in the Paper Mill, *Paper Trade J.*, vol. 81, p. 59; 1929.

⁴ Snyder, E. F., Methods for Determining the Hydrogen Ion Concentration of Soils, Circular No. 56, U. S. Dept. of Agriculture; 1928. The Application of the Antimony Electrode to the Determination of the pH Values of Soils, *Soil Science*, vol. 26, p. 107; 1928.

⁵ Wallace, E. L., and Beek, J., A Comparison of the Quinhydrone and Hydrogen Electrodes in Solutions Containing Tannin. *B. S. Jour. Research*, vol. 4, p. 737; 1930.

⁶ Blum, W. C., and Bekkedahl, N., The Measurement of pH in Nickel Plating Solutions, *Trans. Am. Electrochem. Soc.*, vol. 56, p. 287; 1929.

or alkaline. This liquid junction potential or contact potential may easily vary from 5 to 35 or more millivolts and failure to account for it properly may cause errors of tenths of pH units.

Formulas devised by Nernst,⁷ Planck,⁸ Negbaur,⁹ Johnson,¹⁰ Henderson,¹¹ Cumming,¹² Lewis,¹³ and especially the recent important developments by MacInnes¹⁴ and his students, and E. R. Smith¹⁵ for calculating the contact potential can be applied at present only in comparatively simple cases. The one absolute method of measuring simultaneously contact potentials and electrode potentials devised by MacInnes and the three by Acree¹⁶ are limited in application. The only general method available is that of approximate elimination of the contact potential.

II. EXTRAPOLATION METHOD FOR CORRECTING FOR CONTACT POTENTIAL

Tower¹⁷ used several concentrations ($N/128$ to $N/1$) of potassium chloride and of potassium nitrate and other salts in the study of the elimination of contact potentials. As the highest concentration of the potassium chloride was $N/1$ and the experimental error of their time was 2 to 3 mv, the magnitude of the contact potential was not as accurately measured as their excellent ideas merited.

In 1905 Bjerrum¹⁸ developed a method for correcting for liquid contact potential, which consisted in placing between the two electrode solutions a 3.5 N solution of KCl, which he called a "saturated" solution, and measuring the potential of the system, and then replacing the 3.5 N KCl solution with his so-called "half-saturated" or 1.75 N KCl solution and measuring the potential of this resulting system. He subtracted the difference between the potentials of these two systems from that of the system containing the 3.5 N solution and called the resulting extrapolated emf. practically the correct one of the system in which there is no contact potential. In certain cases he thought that the difference to be subtracted should be even larger than the value found experimentally.

⁷ Nernst, W., The Electromotive Activity of Ions, *Z. physik. Chem.* vol. 4, p. 165; 1889.

⁸ Planck, M., On the Potential Difference Between Two Dilute Solutions of a Binary Electrolyte, *Wied. Ann.*, vol. 39, p. 178; vol. 40, p. 551; 1890. *Ann. Physik. Chem.* vol. 4, 551; 1890.

⁹ Negbaur, W., Experimental Investigations on Potential Differences at the Liquid Junctions of Very Dilute Solutions, *Ann. Physik. Chem.*, vol. 44, p. 737; 1891.

¹⁰ Johnson, K. R., On the Nernst-Planck Theory of the Potential Difference Between Solutions, *Ann. der Physik.*, vol. 14, p. 995; 1904.

¹¹ Henderson, P., On the Thermodynamics of Liquid Potentials. *Z. physik. Chem.*, vol. 59, p. 118; 1907; vol. 63, p. 325; 1908.

¹² 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.

¹³ Lewis, G. N., and Sargent, L. W., Potentials Between Liquids. *J. Am. Chem. Soc.*, vol. 31, p. 363; 1909.

¹⁴ MacInnes, D. A., and Parker, K., Potassium Chloride Concentration Cells, *J. Am. Chem. Soc.*, vol. 37, p. 1445; 1915. MacInnes, D. A., Liquid Junction Potentials, *J. Am. Chem. Soc.*, vol. 37, p. 2301; 1915.

MacInnes, D. A., and Yeh, Y. L., The Potentials at the Junctions of Monovalent Chloride Solutions, *J. Am. Chem. Soc.*, vol. 43, p. 2563; 1921.

¹⁵ Smith, E. R., Potential Differences Across the Boundaries Between Solutions of Mixed Univalent Chlorides, *B. S. Jour. Research*, vol. 2, p. 1137; 1929.

¹⁶ Duschak, E., Elliott, F., and Acree, S. F., Report at St. Louis Meeting of Am. Chem. Soc.; 1920; Address Bureau of Standards; Dec. 14, 1929; Murray and Acree, *B. S. Jour. Research*, vol. 7, p. 713; 1931.

¹⁷ Tower, O. F., Studies of Superoxide Electrodes, *Z. physik. Chem.*, vol. 18, p. 17; 1895.

¹⁸ 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. 428; 1905; vol. 59, pp. 336, 581; 1907. *Z. Elektrochem.*, vol. 17, pp. 58, 389; 1911.

III. ELIMINATION OF CONTACT POTENTIAL WITH SATURATED POTASSIUM CHLORIDE

With the idea of finding a single solution which is generally efficient as a contact potential eliminator, Loomis and Acree¹⁹ tried 11 *N* ammonium nitrate, 4.12 *N* potassium chloride, 7.7 *N* potassium iodide, 5.7 *N* potassium bromide, and 4.3 *N* calcium nitrate, and showed that the 4.12 *N* or completely saturated solution of potassium chloride at 25° C. practically annuls the contact potential between 0.1 *N* KCl and various concentrations of HCl from 1 *N* down to 0.001 *N*. In other words, the contact potentials between the 4.1 *N* KCl and the more dilute solutions on either side of it must be nearly zero and nearly cancel one another, the total emf. then corresponding to the algebraic sum of the two electrode potentials within about ± 1.0 mv. As we have found that the different types of liquid junctions used in routine work vary in emf. by ± 1.0 mv and that another error of 1 to 2 mv is caused by hysteresis in solubilities and emf. when saturated calomel electrodes containing solid potassium or ammonium chloride are used in open air instead of in thermostats, we may safely rely upon the 4.1 *N* KCl eliminator within these emf. limits. This method has since been nearly universally adopted, especially in combination with mercury and calomel as an electrode as suggested by Michaelis and Davidoff²⁰ and its value has been substantiated by Harned,²¹ by Fales and Vosburgh²² in studies of the Planck formula for contact potential, and by Hitchcock,²³ although criticized by Seatchard.²⁴

Other evidence showing that the Loomis-Acree method is approximately correct is found in the fact that Bjerrum, Loomis and Acree, Myers and Acree,²⁵ Harned, Lewis and his coworkers, and Fales and Vosburgh, cited above, have found the values 0.4273, 0.4269 and 0.4272, 0.4273, 0.4270 to 0.4274, 0.4267, 0.4272 (to 0.4257), 0.4274, and 0.4268 volts, or an average of about 0.4271 to 0.4272 volts for the potential of the system Pt-H₂-0.1 *N* HCl-0.1 *N* KCl-HgCl-Hg. The contact potential between the 0.1 *N* HCl and the 0.1 *N* KCl has been found by Bjerrum, by Myers and Acree, Murray and Acree, and by Lewis and his coworkers to average about 0.0278 volt. When this is subtracted from the 0.4271 to 0.4272 volt, it leaves 0.3993 to 0.3994 volt as the potential of this system with the contact potential eliminated. This value, 0.3994 volt, is very close to the values 0.3992, 0.3988, 0.3989, 0.3988, 0.3991, 0.3989, and 0.3990, or an

¹⁹ Loomis, N. E., and Acree, S. F., A Study of the Hydrogen Electrode and of Contact Potential, *Am. Chem. J.*, vol. 46, pp. 585, 621; 1911. Loomis, N. E., *J. Phys. Chem.*, vol. 19, p. 660; 1915. Loomis, N. E., and Acree, S. F., *J. Am. Chem. Soc.*, vol. 38, p. 2391; 1916. Loomis, N. E., and Meacham, M. R., *J. Am. Chem. Soc.*, vol. 38, p. 2310; 1916. Loomis, N. E., Essex, J. L., and Meacham, M. R., *J. Am. Chem. Soc.*, vol. 39, p. 1133; 1917.

²⁰ Michaelis, L., *Die Wasserstoffionem-Konzentration*, p. 150; 1914.

²¹ Harned, H. S., The Hydrogen and Hydroxyl-Ion Activities of Solutions of Hydrochloric Acid, Sodium, and Potassium Hydroxides in the Presence of Neutral Salts, *J. Am. Chem. Soc.*, vol. 37, p. 2460; 1915. The Hydrogen and Chlorine Activities of Solutions of Potassium Chloride in 0.1 Molal Hydrochloric Acid, *J. Am. Chem. Soc.*, vol. 38, p. 1986; 1916.

²² Fales, H. A., and Vosburgh, W. C., Planck's Formula for the Potential Difference Between Solutions and the Values of Certain Important Cells, *J. Am. Chem. Soc.*, vol. 40, p. 1291; 1918.

²³ Hitchcock, D. I., The Ionization of Protein Chlorides, *J. Gen. Phys.*, vol. 5, p. 383; 1922.

²⁴ Seatchard, G., Emf. Measurements with a Saturated Potassium Chloride Bridge or with Concentration Cells with a Liquid Junction, *J. Am. Chem. Soc.*, vol. 45, p. 1716; 1923. Use of Flowing Junction to Study the Liquid Junction Potential Between Dilute Hydrochloric Acid and Saturated Potassium Chloride Solutions, *J. Am. Chem. Soc.*, vol. 47, p. 696; 1925.

²⁵ Myers, C. N., Clarke, W. F., and Acree, S. F., A study of the Hydrogen Electrode, of the Calomel Electrode, and of Contact Potential, *J. Phys. Chem.*, vol. 20, p. 243; 1916. Myers, C. N., and Acree, S. F., *J. Phys. Chem.*, vol. 21, p. 334; 1917.

average of 0.3990, obtained in the laboratories of Noyes,²⁶ Lewis, Loomis, Harned, Fales and Vosburgh, and Acree, for the system Pt-H₂-0.1 *N* HCl-HgCl-Hg. Although there is some doubt regarding minor points, such as the relation of the electrode potential to the relative solubility of calomel²⁷ in 0.1 *N* KCl and 0.1 *N* HCl, and the method of making sharp or mixed liquid junctions, both of which should be studied more carefully by independent experimental methods, it can at present be assumed that the emf. of the system Pt-H₂-0.1 *N* HCl-0.1 *N* KCl-HgCl-Hg with contact potential eliminated is between 0.3990 and 0.3994.

This shows that the error involved in assuming that the 4.1 *N* KCl completely eliminates the contact potential of this system is not over ± 1.0 mv which is less than 4 per cent of the contact potential involved.

It thus seems that of these two methods proposed by Bjerrum and by Loomis and Acree for eliminating contact potentials by the use of potassium chloride solutions as a connecting link, the latter has the advantages of (1) simplicity and rapidity; (2) direct experimental proof that the 4.1 *N* KCl actually eliminates, within the present routine experimental errors and uncertainties of ± 1 mv, the contact potential between different concentrations of HCl and KCl and other solutions containing salts; and of (3) the avoidance of any extrapolations. It should be pointed out, however, that data on which such a conclusion is based are extremely meager, and a comparison of these and other methods involving different types of junctions and solutions, especially of organic compounds, is highly desirable. This is especially the case since the 3.5 *N* potassium chloride was used by Bjerrum and others as saturated and gives emf. readings distinctly different from those obtained with the really saturated 4.1 *N* solution.

IV. COMPARISON OF THESE METHODS WITH THE SYSTEM HgCl-0.1 *N* KCl-*x* KCl-0.1 *N* HCl-H₂-Pt

In connection with the study of the growth of fungi on regulated culture media in 1916 we undertook a comparison of the two methods and the calculation of the contact potentials of the systems involving 0.1 *N* to 4.1 *N* and intermediate concentrations of KCl as the connecting solutions between the 0.1 *N* HCl-hydrogen electrode and the 0.1 *N* KCl-calomel electrode. Table 1 gives some of the values obtained. The general technique has been described before in papers by Loomis, Myers, Clark and Acree, Loomis and Meacham, and Loomis, Essex, and Meacham referred to above. Sharp liquid junctions were made before each emf. reading. The results show clearly (1) that the 4.1 *N* KCl solution practically completely annuls the contact potential of the system, (2) that the Bjerrum extrapolation correction is about 3 mv too large for 0.1 *N* KCl-0.1 *N* HCl, and (3) that the contact potentials of the systems containing the links 1.75 *N*, 3.5 *N*, and 4.1 *N* solutions and intermediate concentrations,

²⁶ Noyes, A. A., and Ellis, J. H., The Free Energy of Hydrochloric Acid in Aqueous Solution, *J. Am. Chem. Soc.*, vol. 39, p. 2532; 1917.

²⁷ Calomel is more soluble in *N*/1 HCl than in *N*/1 NaCl, but it might well be that in very dilute solutions, say from *N*/10 to *N*/10,000, the same solubility and emf. will be found for equivalent concentrations of sodium, potassium, lithium, hydrogen, and other chlorides. The facts should be established experimentally first, however, instead of making the assumption found in nearly every paper published recently that the electrode potential is the same for calomel in *N*/10 HCl and *N*/10 KCl.

a , although asymptotic are nearly linear and equal to $(4.1-a) \times 2.3$ mv for 0.1 *N* KCl-0.1 *N* HCl. We have also calculated the value $(4.1-a) \times 5.6$ mv for 0.1 *N* KCl-*N* HCl from data by Fales and Vosburgh. Some data were also secured with mixtures of KCl and KNO₃ as connecting links. All of these results show that the Bjerrum extrapolation correction is over three times as large as it ought to be; and it should be stated that Professor Bjerrum himself pointed out that his method should be applied only when the extrapolation is less than 2 mv, a fact overlooked by others using it when the extrapolation is several millivolts, and the error therefore large.

TABLE 1.—Change in emf. of the system HgCl-0.1 *N* KCl= x KCl-0.1 *N* HCl-H₂ with variation in x KCl

Difference between potentials with 1.75 <i>N</i> and 4.1 <i>N</i> KCl	Difference between potentials with 1.75 <i>N</i> and 3.5 <i>N</i> KCl	Difference between potentials with 3.5 <i>N</i> and 4.1 <i>N</i> KCl	
		First set (old calomel electrodes)	Second set (new calomel electrodes)
Volts	Volts	Volts	Volts
0.00541	0.0041	0.00139	0.00123
.00546	.0042	.00126	.00120
.00552	.0045	.00122	.00120
.00538	.0041	.00132	.00121
.00561	.0043	.00129	.00135
-----	-----	.00136	.00140
		.00105	-----
Average. .0055±2	.0042±2	.00127	.00127
Average.-----	-----	0.0013±1	

The results on Pt-H₂-0.1 *N* HCl-KCl link-0.1 *N* KCl-HgCl-Hg show a drop of 22.3 mv in the contact potential for the 0.1 *N* KCl connecting link (about 27.8 mv), down to that of 1.75 *N* KCl (about 5.5 mv). The difference between the contact potentials when the 1.75 *N* and the 3.5 *N* KCl solutions are used as links is then about 4.3 mv which agrees within routine experimental errors with the 3.6 mv observed by Bjerrum, 4.1 mv observed by Fales and Vosburgh, and 4.9 mv observed by Sorensen,²⁸ and the 4.3 mv can be considered as the average, approximate value. The difference between the contact potentials observed when the 3.5 *N* and 4.1 *N* KCl are used as links is only 1.3 mv instead of the above-named average of about 4.3 mv, the latter being the correction to be applied if the Bjerrum extrapolation method is used outside the limits set by him. In such a case it is clear that the Bjerrum extrapolation correction would be 3.3 times the true value. That this conclusion is correct is further borne out by data of Fales and Vosburgh on contact potential differences observed when different concentrations of KCl are inserted between 0.1 *N* KCl and 1 *N* HCl at 25°. Their differences in the contact potentials for the 1.75 *N* and 3.5 *N* KCl connecting solutions is 14.5-3.1 or 11.4 mv, which is 3.6 times their difference of 3.1 mv between the contact potentials for the 3.5 *N* and 4.1 *N* KCl connecting links. In this case the error in the wrong use of the Bjerrum method is about 8 mv or many times the experimental error.

²⁸ Sorensen, S. P. L., *Enzyme Studies*, *Biochem. Zeit.*, vol. 21, p. 158; 1909.

V. ELIMINATION OF CONTACT POTENTIALS OF ORGANIC ACIDS AND ACID SALTS

Following the above measurements on the system 0.1 *N* HCl-0.1 *N* KCl, a considerable amount of work was carried on in which various buffered culture media replaced the 0.1 *N* HCl. The results clearly showed that such organic salts have very small contact potentials, less than 5 mv, toward 0.1 *N* KCl which can be estimated within ± 0.5 mv by the above formula based on the Loomis-Acree method. It was, therefore, thought desirable to extend the studies to organic acids, bases, and salts of known compositions and ionic mobilities in order to secure data which will be of both (a) practical use in determining the hydrogen ion activities and ionization constants of sugar acids and related organic acids and bases, and also of (b) theoretical value in devising the best methods of forming liquid junctions and studying the underlying cause, measurement and elimination of their potentials. It was thought to be especially desirable to supplement the method used above with that of Murray and Acree²⁹ to see the effect of increasing concentrations of both potassium and ammonium chlorides on the asymptotic approach to the maximum elimination of the contact potentials of acid solutions having various pH values from 1 to 4. A 0.1 *N* solution of sodium acid phthalate was chosen as a reference standard. Quinhydrone was added to it and also to the other solutions whose contact potentials against the sodium acid phthalate were to be determined. The measurements were made in the open air with observations of the temperature at regular intervals and correction of all readings to 28° C. Measurements were made to learn the values of the emf., including the contact potential between *N*/10 sodium acid phthalate (pH 3.95) as a reference standard combined in pairs with 0.1 *N* HCl (pH 1.04), 0.05 *M* universal buffer solution composed of 0.05 *M* citric acid and 0.05 *M* boric acid (pH 1.95), 0.1 *M* malic acid (pH 2.16), 0.1 *M* sodium acid malate (pH 4.01) and the standard mixture of 0.1 *N* sodium acetate-0.1 *N* acetic acid (pH 4.59). Then various concentrations of ammonium chloride and potassium chloride were interposed as contact potential eliminators between the above pairs of acid solutions, and the emf. again measured. These contact potential eliminators included 0.5 *N*, 1.75 *N*, 3.5 *N*, 4.1 *N*, 5.0 *N*, and 5.66 *N* (saturated) ammonium chloride and 0.5 *N*, 1.75 *N*, 3.5 *N*, and 4.1 *N* (saturated) potassium chloride.

TABLE 2.—Contact potentials referred to 3.5 *N* NH₄Cl and KCl at 28° C.

Solution	With 0.1 <i>M</i> NaH Ph	With NH ₄ Cl as contact potential eliminator					
		0.5 <i>N</i>	1.75 <i>N</i>	3.5 <i>N</i>	4.1 <i>N</i>	5.0 <i>N</i>	5.66 <i>N</i>
<i>N</i> /10 HCl (pH 1.04)-----	<i>mv</i> -26.6	<i>mv</i> -11.6	<i>mv</i> -3.1	<i>mv</i> 0	<i>mv</i> 0.4	<i>mv</i> 1.0	<i>mv</i> 2.6
<i>M</i> /20 universal buffer (pH 1.95)-----	-17.7	-----	-6.6	0	1.2	.7	1.6
<i>M</i> /10 malic acid (pH 2.16)-----	-7.9	-4.1	.6	0	.2	.6	1.2
<i>M</i> /10 NaH malate (pH 4.01)-----	-1.6	-----	-1.1	0	-1.1	-.2	-1.4
<i>N</i> /10 NaAc.HAc (pH 4.59)-----	-1.1	-----	1.0	0	0	-.4	-1.5
		With KCl as contact potential eliminator					
<i>N</i> /10 HCl-----	-26.6	-13.1	6.0	0	-0.3	-----	-----
<i>M</i> /10 malic acid-----	-7.9	-1.7	-.5	0	+1.2	-----	-----
<i>N</i> /10 NaAc.HAc-----	-1.1	-1.3	-.1	0	-.2	-----	-----

²⁹ Murray, C. N., and Acree, S. F., Elimination of Contact Potential by Means of Saturated Ammonium Chloride and Potassium Chloride. B. S. Jour. Research, vol. 7, p. 713; 1931.

Table 2 shows the magnitude of the changes in emf. produced by the insertion of each contact potential eliminator between the pairs of acids, all of the reductions of emf. being referred to that of the 3.5 *N* solution as a base line. The 4.1 *N* solution could also be used for reference. The difference between the residual contact potentials for 1.75 *N* and 3.5 *N* contact potential eliminators is not very large but can not be neglected for the very acid solutions. But eliminators varying from 3.5 *N* to 5.66 *N* produce nearly the same contact potential within the usual experimental error of about ± 1 mv in these routine methods. The more acid solutions seem to show a slight increase in contact potential with increase in concentration of the eliminator and this is being measured more accurately by precision work under way in a constant temperature bath under better-controlled conditions.

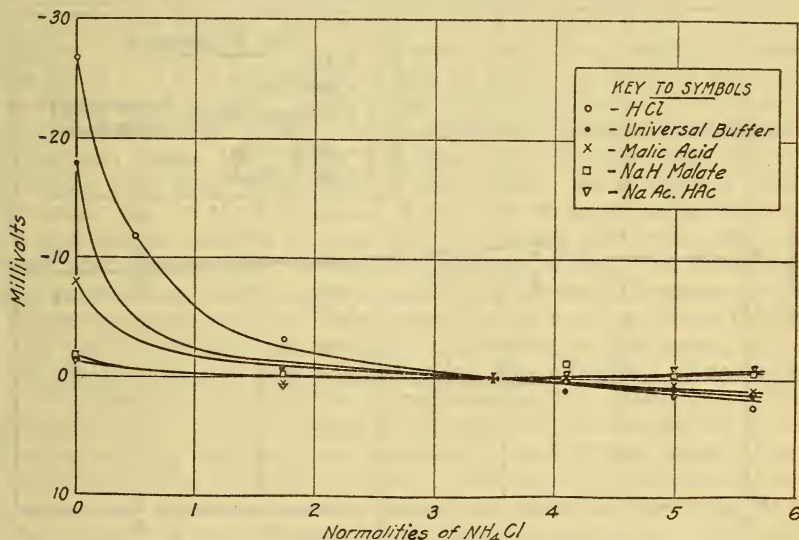


FIGURE 1.—Relation between concentration of contact potential eliminator and change in the contact potentials of *M*/10 sodium acid phthalate and several buffers with different pH values

Figure 1 gives some smooth curves for the above-named five acid solutions which show the wide divergence of the contact potentials with no eliminators and a gradual asymptotic approach or merging of all curves as the eliminator is increased in concentration. The 3.5 *N* concentration was chosen as a base line because of its historical significance and its position near the beginning of the series of concentrated eliminators which nearly annul the contact potentials. Figure 2 gives a composite graph which represents the best smooth curve for all the data on the assumption that it should be asymptotic and can represent a uniform effect of the contact potential eliminator on all solutions. Probably neither of these assumptions, especially the second one, is exactly true, but such a curve gives at least a first approximation, pending precision work, which shows that 4.1 *N* and higher concentrations of ammonium or potassium chloride certainly annul the contact potentials of all usual buffers, culture media, etc.,

to within about ± 0.5 to 1 mv. If the most concentrated eliminators under annul or even over annul the contact potential by a nearly fixed amount in certain cases, or asymptotically approach any such state, this excess emf. when known can be included as a part of the emf. of the standard electrode.

If sufficient acid or alkali or a buffer is added to the eliminator to make its pH close to that of the solution studied, or if sufficient ammonium or potassium nitrate or sodium chloride is added to the eliminator to offset the effect of the difference in the mobilities of the ions of the eliminator and of the other solutions, a more nearly perfect elimination of contact potential will be effected. The compositions of ammonium chloride-ammonium nitrate mixtures necessary to annul the contact potentials of various concentrations of sodium acetate-acetic acid solutions have been calculated by use of the Hen-

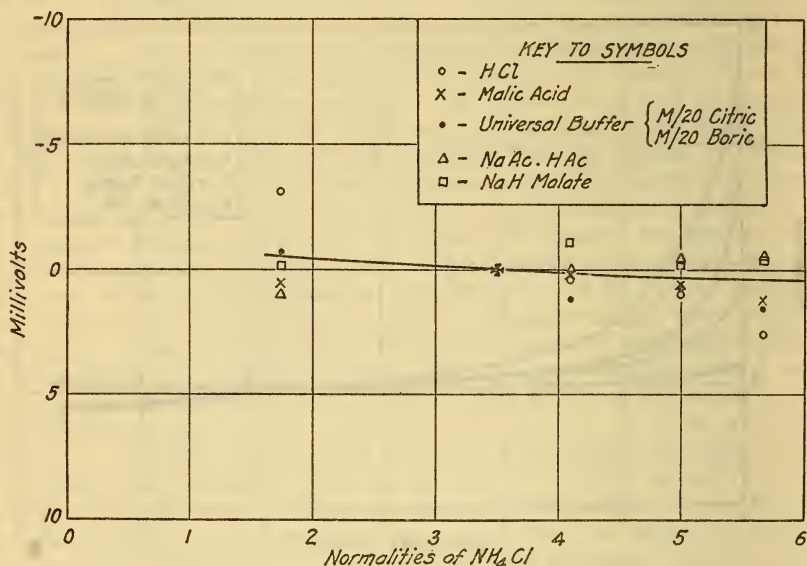


FIGURE 2.—Composite curve for the relation between the concentration of the contact potential eliminator and the deviation of the contact potentials from those found with 3.5 N NH_4Cl

erson equation. As the concentration of the sodium acetate-acetic acid solutions becomes less, the calculated ammonium chloride-ammonium nitrate ratios approach an isoelectric mixture; that is, one in which the mobility of the ammonium ions is exactly balanced by the joint effect of the mobilities of chloride and nitrate ions. Such isoelectric mixtures calculated from the transference numbers accepted for dilute solutions with various normalities of ammonium ion contain approximately 76.2 M per cent ammonium chloride and 23.8 M per cent ammonium nitrate. The use of these isoelectric mixtures for various normalities of eliminator from 0.1 to 0.001 N gives calculated contact potentials which are less than when ammonium chloride only is used and which approach zero as the concentration of the isoelectric mixture increases. Similar calculations have been made for hydrochloric acid solutions. These calculations and experimental studies based upon them will be reported in another article

of this series. We suggest the use of transference numbers measured at the respective higher concentrations instead of the corresponding ionic mobilities in the derivation and use of formulas similar to that of Henderson.

VI. DISCUSSION OF STANDARDIZATION ON ONE METHOD OF ELIMINATING CONTACT POTENTIAL

For the purposes of uniformity of published data one method should be adopted for the elimination of contact potential. The saturated (4.1 *N*) potassium chloride solution has been widely recommended and employed. In some instances, however, the extrapolation method is still used. In an excellent article Walpole³⁰ used the 4.1 *N* KCl solution in the measurement of the ionization of acetic acid,³¹ but he also measured the contact potential differences when the 1.75 *N* and 3.5 *N* KCl were inserted between the acetic acid and standard acetate solutions and subtracted this difference from the potential observed when the 4.1 *N* KCl solution was used to annul the contact potential. It is obvious that if the 4.1 *N* solution eliminates the contact potential within experimental errors, this additional Bjerrum extrapolation (correction) makes the results just that much in error and the total correction over four times what it should be. As Walpole's correction amounted to the calculated 3 to 5 mv in some cases involving HCl and acetic acid, it is clear that for these particular cases the results are considerably in error. Lubs and Clark³² in their work along bacteriological lines have stated that they used the same method of correction employed by Walpole and have in other places referred to the use of the Bjerrum method. However, in the recent edition of his book, Clark³³ has recommended the adoption of saturated (4.1 *N*) potassium chloride for the elimination of contact potential, predicting that "the Bjerrum extrapolation will be abandoned as contributing nothing definite," and has recalculated on that basis the data of Clark and Lubs referred to above. Sørensen³⁴ recommended and employed the Bjerrum method throughout most of his work. In a recent article³⁵ he has preferred to use the saturated potassium chloride solution method. Büllmann³⁶ in his well-known researches on the quinhydrone electrode has used the Bjerrum extrapolation method to eliminate liquid junction potentials. Schmidt and Hoagland³⁷ state that "for very accurate work the extrapolation method of Bjerrum gives the closest approximation." Prideaux³⁸ in his book on indicators refers repeatedly to the use of the Bjerrum method as being the correct one. Michaelis³⁹ recommends the Bjerrum method in his latest book on hydrogen-ion measurements. There are numerous

³⁰ Walpole, G. S., Hydrogen Potentials of Mixtures of Acetic Acid and Sodium Acetate, *J. Chem. Soc.*, vol. 105, pp. 2591, 2521; 1914.

³¹ Preliminary Measurements on Acetic Acid and Aniline had been reported by Loomis and Acree, *Am. Chem. J.*, vol. 46, p. 621; 1911, and Loomis, N. E., *J. Phys. Chem.*, vol. 19, p. 660; 1915.

³² Clark, W. M., and Lubs, H. A., Hydrogen Electrode Potentials of Phthalate, Phosphate, and Borate Buffer Mixtures, *J. Biol. Chem.*, vol. 25, p. 479; 1916.

³³ Clark, W. M., The Determination of Hydrogen Ions, p. 461; 1928.

³⁴ Sørensen, S. P. L., and Linderstrom-Lang, K., The Determination and Value of π_0 in Electrometric Measurements of Hydrogen-Ion Concentrations, *Compt. rend. trav. lab. Carlsberg*, vol. 15, p. 40; 1924.

³⁵ Sørensen, S. P. L., Linderstrom-Lang, K., and Lund, E., The Influence of Salts upon the Ionization of Egg Albumin, *J. Gen. Physiol.*, vol. 8, p. 543; 1927.

³⁶ Büllmann, E., The Quinhydrone Electrode and its Applications, *Bull. Soc. Chim. (4)*, vol. 41, p. 224; 1927.

³⁷ Schmidt, C. L. A., and Hoagland, D. R., University of California Publications in Physiology, vol. 5, p. 29.

³⁸ Prideaux, E. B. R., Theory and Use of Indicators, p. 46; 1917.

³⁹ Michaelis, L., and Perlzweig, W. A., Hydrogen Ion Concentration, pp. 174-182; 1926.

other instances in the literature where the authors state that they have employed the Bjerrum extrapolation to annul the contact potential. Even though in most work with buffered media the error is small, the use of a wrong principle will make the errors large in other cases. In the future there should be no doubt in the minds of workers in these fields that the use of the 4.1 *N* (saturated) potassium chloride solution or especially of (3 *N* KCl + *N* KNO₃) is both more reliable and much more convenient.

VII. SUMMARY

The Bjerrum method of correcting for contact potential by the use of an extrapolated value and the Loomis-Acree method of eliminating contact potential by the use of 4.1 *N* (saturated) potassium chloride solution are compared for the system HgCl-0.1 *N* KCl-*x* KCl-0.1 *N* HCl-H₂-Pt, and for systems in which organic acids and acid salts replace the highly ionized hydrochloric acid. In view of the greater accuracy, simplicity, and rapidity of the Loomis-Acree method and its avoidance of uncertain extrapolations, its adoption for general use is recommended in order to insure uniformity of published data. An approximately isoelectric eliminator, such as 3 *N* KCl + *N* KNO₃, should be used between solutions with pH values between 3 and 10,

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