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LIQUID-JUNCTION POTENTIALS, AND RELATIVE ACTIVITY COEFFICIENTS OF CHLORIDE IONS, IN CONCENTRATED MIXED CHLORIDES AND NITRATES AT 25° C

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ABSTRACT

Measurements are reported of the electromotive forces at 25° C of pairs of calomel half-cells in which portions of the saturated potassium chloride had been replaced at constant ionic strength (4.831) by hydrochloric acid and potassium nitrate. The method of cells with liquid junctions was used.

Data are given for the stability of half-cells prepared with these electrolytes, for the reproducibility of the liquid junction and the calculated value of its potential, and for the activity coefficient of the chloride ion in these mixtures relative to that of saturated potassium chloride solution. The addition of hydrochloric acid raises and the addition of potassium nitrate lowers the mean activity coefficient of chloride ion in potassium chloride solutions. Because the difference between the effective ionic mobilities for the cations and the anions in these solutions is smaller than in saturated potassium chloride alone, such cells are useful as reference electrodes in the reduction of the error caused by the neglect of the liquid-junction potential in the determination of pH by electrometric methods.

CONTENTS

I. INTRODUCTION

Calomel reference half-cells in combination with hydrogen, glass, or other electrodes are very convenient and are widely used for the determination of pH values by electrometric methods. The ideal reference half-cell is one with a stable, reversible electrode (AgCl, Hg_2Cl_2), without hysteresis, with a low emf-temperature coefficient, and whose electrolyte is very concentrated and isoelectric, that is, of such composition that equal numbers of positive and negative charges diffuse into its junction with another liquid whose pH is to be determined. The saturated (4.831 *m*) potassium chloride-calomel half-cell fulfills most of those requirements, but the chloride ion has a mobility slightly greater than that of the potassium ion and the liquid is approximately 1.1 mv (0.02 pH unit) positive toward its sharp junction with an isoelectric solution. A source of error, therefore, arises from the potential at the liquid junction between the two solutions surrounding the reference and hydrogen electrodes, respectively. This potential is a variable because of the differences in the rates of diffusion of the ions which compose the various solutions forming the liquid junctions in pH measurements. This uncertainty of the liquid-junction potential may cause large errors in extreme cases [1][1] when the buffer solution used to calibrate the pH meter is replaced by a highly acid or alkaline solution whose ionic constituents and pH value are not known.[2] For work within 0.01 pH, therefore, it is desirable to know how to reduce the liquid-junction potential to less than 1 mv toward average and specific types of solutions. This can be done by changing the composition of the solution in the reference-electrode compartment. The error caused by the liquid-junction potential can be further diminished by the selection of a standardizing buffer, which approximates the pH and the composition of the unknown solution.

The existence of these potentials has long been known, and the problem of their reduction has been studied for more than 50 years.[3] The equations developed by Planck [4] and by Henderson [5] constitute the most important theoretical advances in the field, and are regarded as being the two most practical methods for the calculation of the potential at the liquid junction.

In 1931 Murray and Acree [6] proposed the use of potassium chloride and nitrate in a molal ratio of 3:1 alone and the use of this mixture with dilute hydrochloric acid for the electrolyte in the calomel half-cell. For such a mixture, the effective anion and cation mobilities are very nearly equal. Consequently the contribution to the contact potential by this electrolyte should be lower than for saturated potassium chloride alone.

The present investigation was made to obtain data on the stabilities and the differences in the potentials at 25° C of calomel half-cells in which potassium nitrate and hydrochloric acid replaced a part of the saturated potassium chloride in the electrolyte at constant ionic strength, 4.831. Three mixtures of these electrolytes in calomel half-cells made stable reference electrodes and were better than potassium chloride alone in reducing liquid-junction potentials. A further purpose of this investigation was to determine the relative activity coefficients of chloride ion in these mixed electrolytes, and the variation of the liquid-junction potentials of these solutions for fixed and flowing junctions of the "pig-tail" type [3].

II. EXPERIMENTAL METHODS

1. SOLUTIONS, EQUIPMENT, AND ELECTRODES

The solutions were prepared from weighed quantities of conductivity water and reagent-grade chemicals conforming to the specifications of the American Chemical Society. The densities of the solutions were determined at 25° C by means of a Westphal balance and were used for converting the molal to the molar scales of concentration. The data are given in table 1.

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] Although pH values can be measured by means of cells without liquid junctions [2], a more detailed knowledge of the composition of the solution is required than is usually available.

[3] A review of the literature up to 1932 has been given by Kline, Meacham, and Acree [3].

Table 1.—*Composition and density of solutions used as electrolytes in cells with liquid junctions*

Solution	HCl	KCl	KNO_3	Total	Density at 25° C
	Moles per thousand grams of water				
					g/ml
A	----------	4.831	----------	4.831	1.1783
B	----------	3.623	1.208	4.831	1.1924
C	0.050	3.573	1.208	4.831	1.1910
D	.050	4.781	----------	4.831	1.1780
	Moles per liter of solution				
A	----------	4.185	----------	4.185	----------
B	----------	3.103	1.035	4.138	----------
C	0.043	3.061	1.035	4.139	----------
D	.043	4.147	----------	4.190	----------

The electromotive forces were measured by means of a precision type of potentiometer and a standard cell, both calibrated at this Bureau. All measurements were made in an air bath at 25°±0.1° C.

The calomel half-cells (fig. 1) were Pyrex cylinders, *A*, approximately 2 cm in diameter and 7 cm tall, with a glass partition, *B*, extending 2.5 cm upward from the bottom of the cylinder and dividing the latter into two separate compartments, or half-cells. Tungsten leads, *C*, were introduced through the bottom of each half-cell. Two such units were connected by means of a tube approximately 1 cm in diameter. A stopcock, *D*, admitted the electrolyte to the cell. The hollow ground-glass stopper, *E*, was weighted with mercury.

The liquid-junction chamber, *A* in figure 2, was of the same general type used previously [3] but was separate from the half-cells and could be removed without disturbing them. The functions of stopcocks *H*, *I*, and *J* in figures 2 and 3 are explained later.

The mercury for use in the half-cells was washed repeatedly with 10-percent nitric acid and then twice distilled. The calomel electrodes were prepared in accordance with the recommendations of Wingfield and Acree [7]. The emf of new and aged cells of the same type differed at first by approximately 0.2 mv, but after approximately 12 hours this difference was reduced to 0.03 mv or less.[4]

No further change greater than ±0.02 mv was observed over a test period of 26 days. The aging period did not vary significantly for cells prepared with the different electrolytes listed in table 1.

The assembled apparatus is shown in figure 3. *A* and *B* are the calomel half-cells, and bulbs *C* and *D* are the corresponding reservoirs. Each was filled with one of the particular solutions under investigation; bulb *E* contained the less dense solution (generally the same as in *D*) to which had been added a small amount of an indicator (solid methyl orange) or a dye (alpha azurine *G*) to render the liquid junction more easily visible. Because the denser solution was always introduced through the "pig-tail", two such liquid junction chambers, *L* and *L'* were provided to facilitate the emf measurements on different pairs of solutions in any sequence.

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[4] In a detailed study of the preparation of calomel electrodes, Clarke, Myers, and Acree [8] found that an aging period of 2 days was necessary to attain an agreement of ±0.03 mv between new and aged electrodes. The shorter period of time observed in the present work may be attributed to technical advances in the manufacture of intimate mixtures of mercurous chloride and mercury. A variation of ±0.03 mv in emf corresponds to ±0.0005 in pH.

The solutions were admitted to the calomel half-cells and then to the liquid-junction chambers through stopcocks *F*, *G*, and *H*, and the entrapped air removed through stopcock *I*. Stopcock *I* was then closed, and stopcock *J* opened. The relative quantities of the heavier and of the lighter solutions entering the liquid-junction chamber were governed by the positions of stopcocks *F* and *G*, respectively, and the position of the boundary in the liquid-junction chamber could therefore be varied at will. Sharp junctions were obtained even when the rates of flow were varied widely. The combined solutions were discarded through the tip *K* into a graduated cylinder, which was used to measure the rates of flow.

2. ELECTROMOTIVE FORCES OF CELLS WITH LIQUID JUNCTIONS

In table 2 are given the data obtained for the cell

$$-\mathrm{Hg}\,|\,\mathrm{Hg_2Cl_2}\,|\,\mathrm{KCl}(4.831\ \mathrm{m})\|\mathrm{KCl}(3.623\ \mathrm{m})+\mathrm{KNO_3}(1.208\ \mathrm{m})\,|\,\mathrm{Hg_2Cl_2}|\mathrm{Hg}+ \tag{1}$$

When current is withdrawn from this cell, the reaction[5] is

$$\mathrm{Cl^-}(\text{in KCl})\|\mathrm{Cl^-}(\text{in KCl}+\mathrm{KNO_3});E_t=+8.74\ \mathrm{mv}, \tag{2}$$

where the symbol $\|$ indicates the presence of a liquid-junction potential, and E_t is the measured emf of the cell. The over-all electromotive force of any given cell combination was found to be independent to within ±0.01 mv of the total and the relative rates of flow of the two electrolytes, the position of the liquid junction in the pig-tail chamber, the order in which the electrolytes were admitted, and of the indicator or dye added. The emf of duplicate pairs of cells checked to within ±0.03 mv.

TABLE 2.—*Observed electromotive force at 25° C of a typical cell*

[Electrolyte *A*: 4.831 moles of KCl per 1,000 g of water. Electrolyte *B*: 3.623 moles of KCl and 1.208 moles of KNO_3 per 1,000 g of water]

Rate of flow of electrolyte			Electromotive force of cell	Junction
A	*B*	*A*+*B*		
ml/min	*ml/min*	*ml/min*	*mv* [a]	
¼	0	¼	8.72	Rising.
¼	¼	½	8.73	Steady.
½	35½	36	8.74	Falling rapidly.
35½	½	36	8.73	Rising rapidly.
0	0	0	8.73	Fixed.
0	25	25	8.74	Rising rapidly.
25	0	25	8.74	Falling rapidly.
25	25	50	8.74	Steady.
0	0	0	8.74	Fixed.
Average			8.74	

[a] Measurements made with a small amount of dye added to solution *B* showed the same degree of constancy.

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[5] In tables 2, 3, and 5 the sign of the total emf or of the liquid-junction potential is that of the electrode in the second solution, designated as *A*, *B*, etc., in table 1. The liquid-junction potential of the cell described in eq 2, for example, is −0.22 mv.

In table 3 a summary is given of the measured emf of each of the six possible cells that can be formed by the combination in pairs of the half-cells containing electrolytes *A* to *D*, inclusive. The statements made regarding the constancy of the emf, etc. of the cell described in eq 1 apply equally well to each of the additional measurements listed in this table.

TABLE 3.—*Summary of electromotive force measurements at 25° C*

Solutions	Electrolytes	Electromotive force
		mv
A, *B*	KCl versus KCl+KNO$_3$	8.74 ±0.02
A, *C*	KCl versus KCl+KNO$_3$+HCl	8.16 ±0.02
A, *D*	KCl versus KCl+HCl	−0.61 ±0.03
B, *C*	KCl+KNO$_3$ versus KCl+KNO$_3$+HCl	−.61 ±0.02
B, *D*	KCl+KNO$_3$ versus KCl+HCl	−9.29 ±0.02
C, *D*	KCl+KNO$_3$+HCl versus KCl+HCl	−8.73 ±0.02

III. CALCULATION OF THE LIQUID-JUNCTION POTENTIAL

The potential E_j at the junction of two different solutions, I and II, is given by the equation

$$E_j = -(RT/\mathbf{F})\sum\int_{\mathrm{I}}^{\mathrm{II}}(t_k/z_k)(d\; ln\; \mathbf{a}_k) \tag{3}$$

where t_k, z_k, and $\mathbf{A}_k$ are, respectively, the transference number, valence, and activity of a particular ion k, and R, T, and $\mathbf{F}$ are recognized constants. The integrations are made separately for each of the ions of which the boundary is composed. With the aid of certain simplifying assumptions, Planck [4] and Henderson [5] have integrated this equation for the "constrained diffusion" and the "continuous mixture" types of boundaries. The former type does not apply to the experimental work reported here and has not been considered further. For the case in which the ions are all univalent, the integration of eq 3 by Henderson reduces to

$$E_j = \frac{RT}{\mathbf{F}}\,\frac{(U_1-V_1)-(U_2-V_2)}{(U_1+V_1)-(U_2+V_2)}\ln\frac{U_1+V_1}{U_2+V_2}, \tag{4}$$

where

$$U_1 = C_k^{+\prime}U_k^{+\prime},\; V_1 = C_k^{-\prime}U_k^{-\prime},\; U_2 = C_k^{+\prime\prime}U_k^{+\prime\prime},\text{ and } V_2 = C_k^{-\prime\prime}U_k^{-\prime\prime}.$$

The single and double primes in the superscripts refer to the ions in the two solutions which form the boundary. C_k and U_k are, respectively, the concentration in moles per liter and the mobility of the ion k. The positive and negative signs refer to the charges on the ions.

The Henderson integration (eq 4) involves three assumptions: the mobility of an ion (a) does not change with concentration and (b) is not affected by the presence of other ions, and (c) the electrolytes are completely dissociated and the activity coefficient of each ion is unity in mixtures of ions at all concentrations. Each of these assumptions is questionable.

Measurements of the changes of ionic mobilities and of transference numbers with concentration have been made for simple solutions such as potassium chloride, but the corresponding data for mixtures of electrolytes are meager. None are available for the mixtures studied here. Longsworth [9] measured at 25° C the mobilities of the ions in mixtures of hydrochloric acid and potassium chloride in which the total molality was 0.1. The equivalent conductance of the chloride ion, for example, was found to vary linearly between the limits 65.98 and 65.79, respectively, with the mole fraction in mixtures of 0.1-m hydrochloric acid and 0.1-m potassium chloride. It is wholly speculative to assume that this linear relationship is valid for concentrations as high as 4.831 m, and until the data become available there is no choice other than to use the first two assumptions employed by Henderson. Additional conductance and transference measurements for mixtures of ions are needed.

The assumption regarding the activity coefficient is amenable to correction, but for the solutions studied here the entire effect is negligible. With the customary definition

$$a_k = m_k f_k, \tag{5}$$

where f_k is the activity coefficient of the ion k, eq 3 may be integrated to give

$$E_j = E_{\text{Henderson}} - \frac{RT}{F} \sum \int_{\mathrm{I}}^{\mathrm{II}} \frac{t_k}{z_k} (d \text{ in } f_k) = E_{\text{Henderson}} + E_f. \tag{6}$$

The activity coefficient, f_k, can be expressed by the modified Debye-Hückel equation

$$\log f_k = \frac{-A\mu^{1/2}}{1 + Ba_i\mu^{1/2}} + D\mu + E\mu^2. \tag{7}$$

The values of D and E can be obtained empirically or can be estimated from the co-volume effect [10]. In theory, the integral in eq 6 could be evaluated by use of eq 7 and the dependence of t_k upon C, but in practice it is found that the new integrals thus obtained are so complex that the effort is not warranted.

The graphical integration can be performed quite readily in the manner suggested by Harned [11].[6] The details of the procedure for the calculation of the integral in eq 6 for each ion in the junction

$$\mathrm{KCl}(4.831\ m) \| \mathrm{HCl}(0.05\ m) + \mathrm{KCl}(4.781\ m) \tag{8}$$

are as follows. First the transference numbers of H^+, K^+, and Cl^- are computed from the ionic mobilities [7] and the concentrations for mixtures of x parts of hydrochloric acid and potassium chloride (solution D) and $(1-x)$ parts of potassium chloride (solution A). Then values of $\log f$ must be computed for each ion. Hawkins [15] has measured at 25° C the emf of the cell

$$-\mathrm{H_2}|\mathrm{HCl}\ m_1,\ \mathrm{KCl}\ m_2|\mathrm{AgCl}|\mathrm{Ag}^+, \tag{9}$$

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[6] The method has been applied to electrometric titrations by Hamer and Acree [12] and to halide cells in general by Hamer [13].

[7] The values of the mobilities at infinite dilution taken from the compilation of MacInnes [14] are for hydrogen, potassium, chloride, and nitrate ions, respectively, 349.82, 73,52, 76.34, and 71.44.

in which m_1+m_2 was kept constant in any one series of experiments over the range 0.1 to 6.0 in ionic strength. The results have been put into algebraic form by Harned [16]:

$$\log f_1=\alpha_1 m_1+\log f_1^\circ=\log f_{1(0)}-\alpha_1 m_1, \tag{10}$$

and

$$\log f_2=\alpha_2 m_2+\log f_2^\circ=\log f_{2(0)}-\alpha_2 m_2, \tag{11}$$

where the subscripts 1 and 2 refer to the acid and to the salt in the same mixture; $f_{1(0)}$ and $f_{2(0)}$ are the activity coefficients of pure hydrochloric acid and potassium chloride solutions; f_1° and f_2° are the activity coefficients of vanishingly small quantities of hydrochloric acid in solutions of potassium chloride and of potassium chloride in solutions of hydrochloric acid; and α_1 and α_2 are constants. For values of $m_1+m_2=4.831$, and at a temperature of 25° C, $\log f_1^\circ=0.3485$, $\log f_2^\circ=-0.2273$, $\alpha_1=0.0710$, and $\alpha_2=-0.032$. Values of $\log f_{\mathrm{HCl}}$ and $\log f_{\mathrm{KCl}}$ at an ionic strength of 4.831 were then obtained for these mixtures which are predominantly KCl.

Two procedures are commonly used to estimate individual activity coefficients in mixtures of electrolytes. In the first of these, that of MacInnes [17], it was assumed that for pure solutions of potassium chloride, $f_{\mathrm{K}}=f_{\mathrm{KCl}}=f_{\mathrm{Cl}}$, where f_{KCl} is the mean activity coefficient of this salt, and that these individual activity coefficients are not altered as a result of partial substitution by other ions at constant ionic strength. From the definition of the mean activity coefficient it follows that for these mixtures $f_{\mathrm{H}}=(f_{\mathrm{HCl}})^2/f_{\mathrm{Cl}}$. This may be designated as procedure 1. The second procedure is that of Guggenheim [18], in which the activity coefficient of an ion is assumed equal to the mean activity coefficient of the electrolyte of which it is a part. For this case, $f_{\mathrm{H}}=f_{\mathrm{HCl}}$ and $f_{\mathrm{K}}=f_{\mathrm{KCl}}$, but no information is made available concerning the activity coefficient of chloride ion in these mixed chloride solutions. One may assume that $f_{\mathrm{Cl}}=f_{\mathrm{KCl}}$, as before (procedure 2a). Another assumption would be that $\log f_{\mathrm{Cl}}$ varies linearly with the mixing fraction x between the limits of the averages of $\log f_{\mathrm{HCl}}+\log f_{\mathrm{KCl}}$ for these solutions. This is equivalent to the assumption that (in mixture) $f_{\mathrm{Cl}}=[(f_{\mathrm{HCl}})(f_{\mathrm{KCl}})]^{1/2}$ (procedure 2b). Other postulates that might be made of the relations between the activity coefficients of the ions would lead to other sets of values for f_{H}, f_{K}, f_{Cl} and E_f. The values of $\log f_{\mathrm{H}}$, $\log f_{\mathrm{K}}$, and $\log f_{\mathrm{Cl}}$, respectively, which are needed for the graphical integration of $(\mathrm{RT}/\boldsymbol{F})(t_k/z_k)(d\ln f_k)$ in eq 6 by procedures 1, 2a, and 2b, are identical with those given in columns 7, 6, and 5; 5, 6, and 6; and 5, 6, and 8 of table 4 and are represented graphically in figure 4. The integrations yield, respectively, −0.004, −0.002, and −0.002 mv for hydrogen ion, −0.043 mv (identical for all three methods) for potassium ion, and −0.045, −0.045, and −0.075 mv for chloride ion.

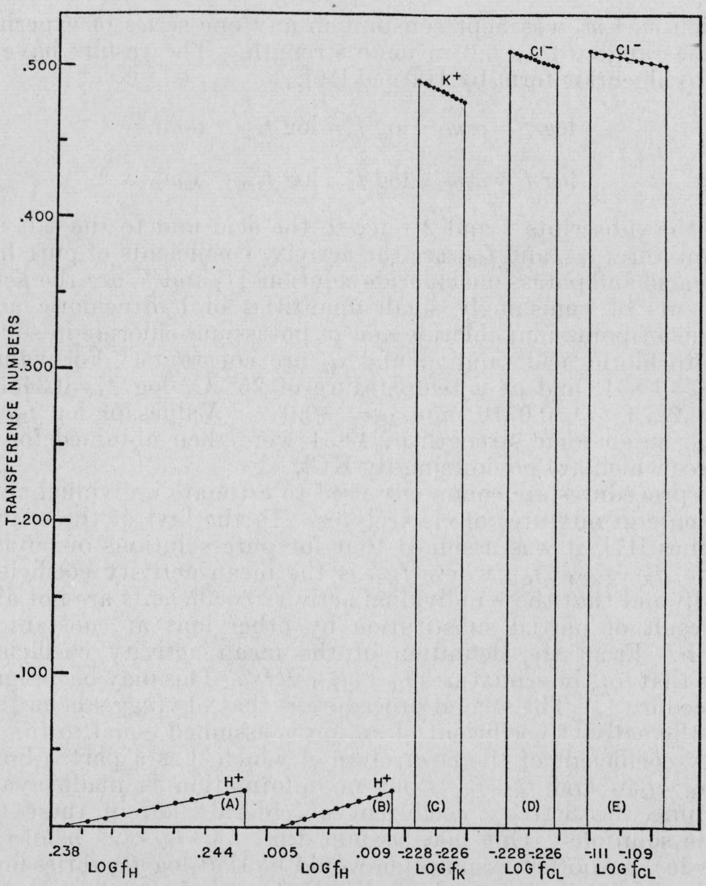

FIGURE 4.—*Evaluation of $\int t_k\, d \log f_k$ at 25° C for the ions of mixtures of potassium chloride and hydrochloric acid.*

Areas *A* and *B* correspond to procedures 1 and 2a, and 2b, respectively, for the hydrogen ion; *C*, for the potassium ion by all three procedures; *D* and *E*, for the chloride ion by procedures 1 and 2a, and 2b, respectively.

TABLE 4.—*Values of the quantities required for the computation of $\int_{\mathrm{I}}^{\mathrm{II}} t_k\, (d \log f_k)$ at 25° C for mixtures of potassium chloride and hydrochloric acid-potassium chloride solutions*

Mixing fraction, x	t_{H}	t_{K}	t_{Cl}	$\log f_{\mathrm{HCl}}$	$\log f_{\mathrm{KCl}}$	$\log f_{\mathrm{H}}$	$\log f_{\mathrm{Cl}}$
1	2	3	4	5	6	7	8
0.0	0.0000	0.4906	0.5094	0.0055	−0.2277	0.2385	−0.1111
.1	.0024	.4892	.5084	.0059	.2275	.2392	.1109
.2	.0048	.4877	.5075	.0062	.2274	.2398	.1106
.3	.0072	.4863	.5065	.0066	.2272	.2404	.1104
.4	.0096	.4849	.5055	.0069	.2271	.2409	.1101
.5	.0120	.4834	.5046	.0073	.2269	.2415	.1099
.6	.0143	.4820	.5036	.0076	.2268	.2420	.1096
.7	.0167	.4806	.5027	.0080	.2266	.2426	.1094
.8	.0190	.4793	.5018	.0083	.2265	.2432	.1091
.9	.0214	.4778	.5008	.0087	.2263	.2437	.1088
1.0	.0237	.4764	.5000	.0091	.2262	.2443	.1086

Values at 25° C of the integral in eq 6 for hydrogen, potassium, and chloride ions are totalled according to the equation

$$E_f = -\frac{RT}{F}\sum\int_{\text{I}}^{\text{II}}\frac{t_k}{z_k}(d\ln f_k)$$
$$= -2.303\frac{RT}{F}\left[\int_{\text{I}}^{\text{II}} t_{\text{H}}(d\log f_{\text{H}}) + \int_{\text{I}}^{\text{II}} t_{\text{K}}(d\log f_{\text{K}}) - \int_{\text{I}}^{\text{II}} t_{\text{Cl}}(d\log f_{\text{Cl}})\right] \quad (12)$$

and yield +0.002, +0.000, and +0.030 mv, respectively, by the three procedures for the value of E_f for the junction depicted in eq 8. There is no a priori reason for the preferential selection of any one of these procedures because of the assumptions common to all. The average correction $E_f = +0.011$ mv is within the experimental reproducibility of the emf of the cells. The above is proof of the statement made earlier in this paper that the inclusion of the terms involving the activity coefficients is a negligible correction to the simple Henderson equation for the solutions studied here. The consistent use of concentrations expressed in moles per kilogram of water instead of moles per liter of solution makes no difference in these conclusions, as values of E_j computed by these two procedures are identical within 0.01 mv. For those cases in which the numerator or the denominator becomes zero and eq 4 is indeterminate, the reduced form [18]

$$E_j = (RT/F)[(U_1 - V_1) - (U_2 - V_2)]/(U_1 + V_1) \quad (13)$$

should be used. The liquid-junction potentials have therefore been calculated by means of eqs 4 and 13 and are given in column 3 of table 5.

TABLE 5.—*Values of the liquid-junction potential* (E_j) *at 25° C calculated by the Henderson equation, and ratios of the activity coefficients of chloride ion in mixed chlorides*

Solutions in contact	E_{total}	E_j	$\frac{(E_{\text{total}} - E_j)}{59.14}$	$\log\frac{m_{\text{Cl}_\text{I}}}{m_{\text{Cl}_\text{II}}}$	$\log\frac{f_{\text{Cl}_\text{I}}}{f_{\text{Cl}_\text{II}}}$	$\frac{f_{\text{Cl}_\text{I}}}{f_{\text{Cl}_\text{II}}}$
A, B	8.74	−0.22	0.1515	0.1249	0.0266	1.0631
A, C	8.16	−.70	.1498	.1249	.0249	1.0590
A, D	−0.61	−.48	−.0022	.0000	−.0022	0.9950
B, C	−.61	−.49	−.0020	.0000	−.0020	.9953
B, D	−9.29	−.28	−.1523	−.1249	−.0274	.9388
C, D	−8.73	.21	−.1512	−.1249	−.0262	.9414

Calculations of the liquid-junction potentials of solutions *A*, *B*, *C*, and *D* against a hypothetical isoelectric solution of ionic strength 4.831 composed of univalent ions having mobilities equal to the average of those of the potassium and chloride ions yield −1.11, −0.27, +0.19, and +0.02 mv, respectively, for E_j. It is interesting to note that solution *D* is very nearly isoelectric, and that solutions *B*, *C*, and *D* are all better than pure saturated potassium chloride for the reference electrolyte. Because of the assumptions made in the use of the Henderson equation, it is questionable whether the values given for E_j in table 5 can be improved until an opportunity is had to investigate thoroughly the more rigorous procedure suggested by Murray and Acree [6]. The method involves using two buffer solutions of known pH and chloride concentrations and measuring the four possible emf between the hydrogen and the silver-silver-chloride or calomel electrodes which are immersed in each of the two solutions forming the liquid junction. A contact-potential eliminator is then interposed between the two buffer solutions and emf data again obtained. Both the electrode and liquid-junction potentials can be thus computed.

IV. RELATIVE ACTIVITY COEFFICIENTS OF CHLORIDE ION IN MIXED ELECTROLYTES

The over-all emf of a cell involving a liquid junction is the sum of three separate contributions: the emf generated at the two electrodes and that at the liquid junction. For a cell such as depicted in eq 1, the total electromotive force, E_t, is given by the equation

$$E_t = E_j + \frac{RT}{F} \ln \frac{a_{\mathrm{Cl}_\mathrm{I}}}{a_{\mathrm{Cl}_\mathrm{II}}}, \tag{14}$$

where a_{Cl} is the activity of the chloride ion and the subscripts I and II refer, respectively, to the solutions on the left and the right-hand members of eq 1. Combination of eq 5 and 14 yields

$$\log \frac{f_{\mathrm{Cl}_\mathrm{I}}}{f_{\mathrm{Cl}_\mathrm{II}}} = \left(\frac{E_t - E_j}{k}\right) - \log \frac{m_{\mathrm{Cl}_\mathrm{I}}}{m_{\mathrm{Cl}_\mathrm{II}}}, \tag{15}$$

where $k = 2.303\ RT/F$ and is equal to 0.05914 at 25° C. All of the quantities to the right of the equality sign in eq 15 are known, and hence the ratio of the activity coefficients of chloride ion in the two solutions can be obtained from the experimental data. The results are presented in table 5.

The activity coefficients of potassium chloride at 25° C have been measured by Robinson [19] and by Scatchard, Hamer, and Wood [20]. The results have been summarized by Robinson and Harned [21] and yield $f_{\mathrm{KCl}} = 0.592 \pm 0.002$ for the saturated solution. With this value as a basis, the activity coefficients of chloride in the mixtures may be calculated from the experimental values of $f_{\mathrm{Cl}_\mathrm{I}}/f_{\mathrm{Cl}_\mathrm{II}}$.

Emf measurements of the three cells *AB*, *AC*, and *AD* represent the direct comparison of saturated potassium chloride solution *A* with the mixtures. The use of $f_{\mathrm{KCl}} = f_{\mathrm{Cl}_A} = 0.592$ for solution *A* yields values of f_{Cl_B}, f_{Cl_C}, and f_{Cl_D}. For the sake of brevity, these symbols have been shortened to f_A, f_B, f_C, and f_D, respectively. Intercombinations are thus possible; the quantity f_B, for example, may be combined with the ratios f_B/f_C and with f_B/f_D, obtained from emf measurements on cells *BC* and *BD*, to calculate additional values of f_C and f_D. The process is repeated for all the nonrecurrent combinations of the six ratios of $f_{\mathrm{Cl}_\mathrm{I}}/f_{\mathrm{Cl}_\mathrm{II}}$ given in table 5. The notation *CD*, *C* for the last entry in table 6, for example, indicates that the ratio of the activity coefficients of the solutions in cell *CD* was combined with the value of f_C obtained from cell *AC*. The activity coefficients relative to saturated potassium chloride thus obtained are listed in table 6.

TABLE 6.—*Activity coefficient at 25° C of chloride ion in mixtures of concentrated electrolytes containing chloride*

[Basis: f_{KCl}=0.592]

KCl	KCl+KNO$_3$	KCl+KNO$_3$+HCl	KCl+HCl
0.592	0.5569 (*AB*, *A*) .5564 (*BC*, *C*) .5586 (*BD*, *D*)	0.5590 (*AC*, *A*) .5595 (*BC*, *B*) .5601 (*CD*, *D*)	0.5950 (*AD*, *A*) .5932 (*BD*, *B*) .5938 (*CD*, *C*)
Average	0.5573 ±0.0009	0.5595 ±0.0003	0.5940 ±0.0007

The averages of the values of the activity coefficients of the chloride ion in solutions *B*, *C*, and *D* are, respectively, 0.5573±0.0009, 0.5595 ±0.0003, and 0.5940±0.0007.[8] The deviations from the averages point to an internal consistency of ±0.0007 in the measurement of f, and when combined with an uncertainty of ±0.002 in f_{KCl} yield ±0.003 for the probable errors in the values of f_B, f_C, and f_D compared with saturated potassium chloride.

It is important to note that the addition of potassium nitrate to potassium chloride lowers the relative activity coefficient of the chloride ion (cell *AB*), whereas the opposite effect is observed when hydrochloric acid is added to potassium chloride (cell *AD*) or to potassium chloride containing potassium nitrate (cell *AC*). These observations are in qualitative agreement with the magnitude of the mean activity coefficients at 25° C for separate 4.831-*m* solutions of potassium chloride, 0.592 ±0.002, [21]; potassium nitrate, 0.196 ±0.003, [22] [9]; and of hydrochloric acid, 2.231 ±0.001, [23].

According to Brönsted [24], if two solutions with the same valence type and ionic strength are mixed in the proportions of x to $1-x$, the logarithm of the mean activity coefficient of an electrolyte in the mixture is a linear function of x.[10] In the present work, however, the ionic strength is too high for the successful application of this principle. Treating these cases as an extension of Brönsted's rule would yield $f_B=0.439$, $f_C=0.457$ and $f_D=0.600$. The deviations from the values given in table 6 are considerably greater than the probable experimental errors in the measurements.

The equation

$$\log f_C=\frac{-0.5059C^{1/2}}{1+0.3287a_iC^{1/2}}+2.2062\times10^{-3}a_i^3C+2.6269\times10^{-6}a_i^6C^2, \qquad (16)$$

has been proposed by Van Rysselberghe and Eisenberg [10] for rep-

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[8] Uncertainties of ±0.05 percent in concentration and of ±0.02 mv in emf correspond, respectively, to ±0.0005 and ±0.0003 in f. An uncertainty of ±0.02 percent in the equivalent conductance of the ions at infinite dilution alters the calculated value of the potential at the liquid junction by only ±0.002 mv. Because of the assumptions made in the integration of eq 3, especially that regarding the transference numbers at high concentrations, the uncertainties in the absolute values of the liquid junction potentials are unknown. The internal consistency obtained for the values of f_B, f_C, and f_D would indicate, however, that these uncertainties are either small or largely compensated internally by the symmetry of eq 4.

[9] The solubility of potassium nitrate in water at 25° C is given in the International Critical Tables as 3.74 *m*. The value of the activity coefficient at a hypothetical molality of 4.831 was determined by extrapolation.

[10] Güntelberg [25] proved this to be true for solutions 0.1 in ionic strength.

resenting the mean activity coefficient on the molar scale, f_C, of a uni-univalent electrolyte at 25° C in terms of a single parameter a_i and the concentration C in moles per liter of solution. Substitutions of the activity coefficients of individual solutions of potassium chloride [21] potassium nitrate [22], and of hydrochloric acid [23] of the concentration C corresponding to 4.831 m (on the weight basis) into eq 15 yield, respectively, 2.71, 0.91, and 3.79 A for a_i.[11]

The experimental values of log f given in table 6 correspond, respectively, to 2.64, 2.67, and 2.72 A for a_i for solutions B, C, and D. The hydrochloric acid in solution D contributes only 1 percent to the ionic strength of the mixture, and the value of a_i is therefore essentially the same as for pure potassium chloride. These values for a_i lie between those for the constituents of which the mixtures are composed, but they bear neither a linear nor a logarithmic relation to them. The activity coefficients obtained by the assumption of either linear or logarithmic relations are too low by 10 and 20 percent, respectively, and correspond to differences of 0.3 and 0.6 mv in emf, which are much larger than the experimental error.

Equations 10 and 11 on the other hand, yield $f_{HCl}=1.0212$ and $f_{KCl}=0.5940$ for a solution of composition D (in table 1). The latter is identical with the value of f_{Cl} obtained here for the same solution and reported in table 6. It is of interest to note that the value of 0.5940 is the same as obtained by procedure 2b, previously discussed, but many additional measurements on mixtures of hydrochloric acid and potassium chloride are necessary before any conclusions can be drawn regarding the relative merits of the assumptions of MacInnes and Guggenheim.

The method of cells with liquid junctions as employed here is well adapted to measurements of the ratios of the mean activity coefficient of chloride ion in two solutions, especially if the concentrations are high. The best conditions are those in which the liquid junction potentials are small or contribute only a small part to the total emf. The mixtures of electrolytes studied here, or modifications thereof, may be found useful in reference electrodes for the determination of pH by electrometric methods.

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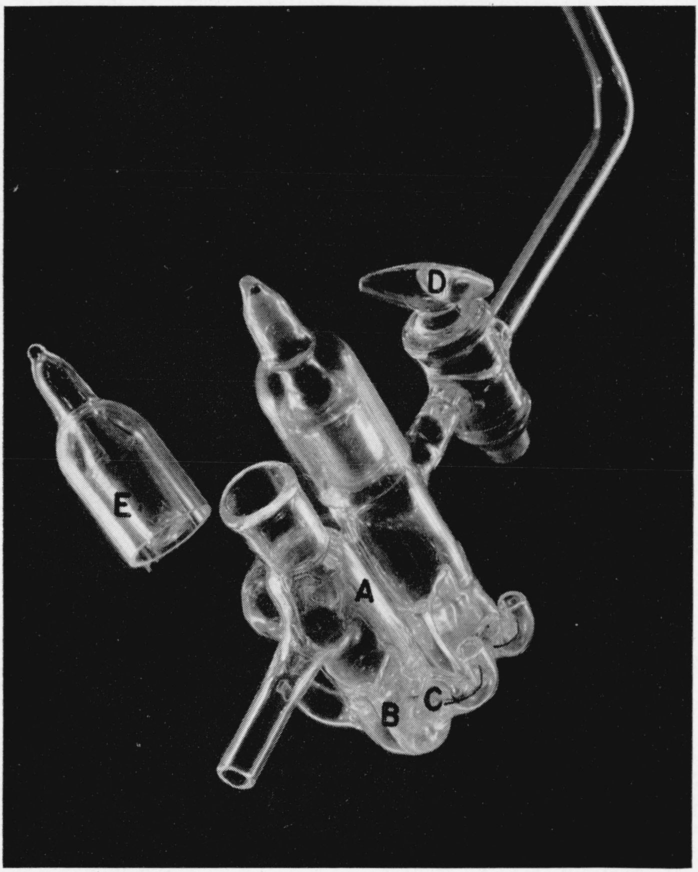

FIGURE 1.—*Calomel half-cells, showing cylinder A, glass partition B, tungsten leads C, stopcock D, and weighted stopper, E.*

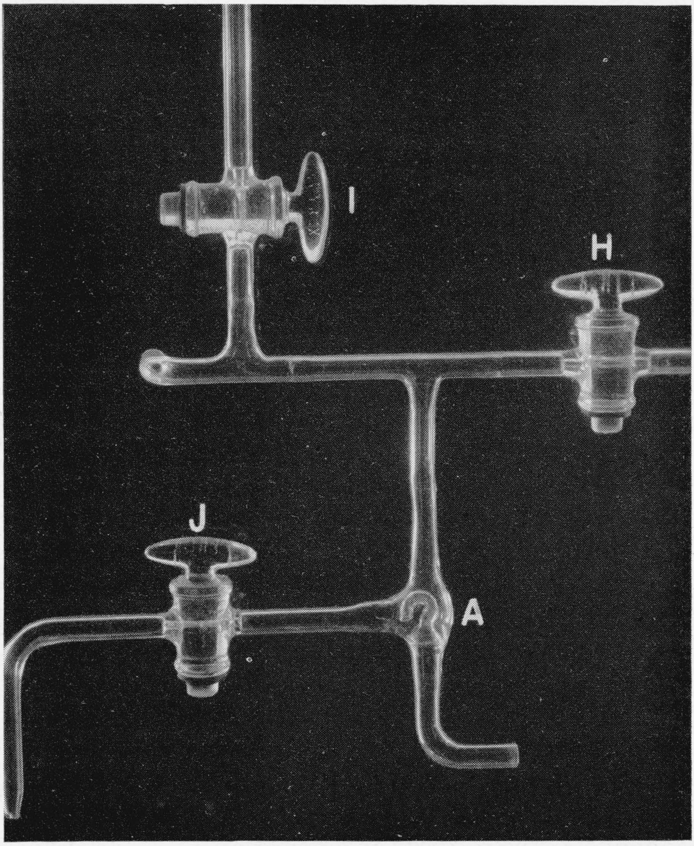

FIGURE 2.—*Details of the liquid junction, A, of the "pig-tail" type.*

See fig. 3 for a description of the functions of stopcocks *H*, *I*, and *J*.

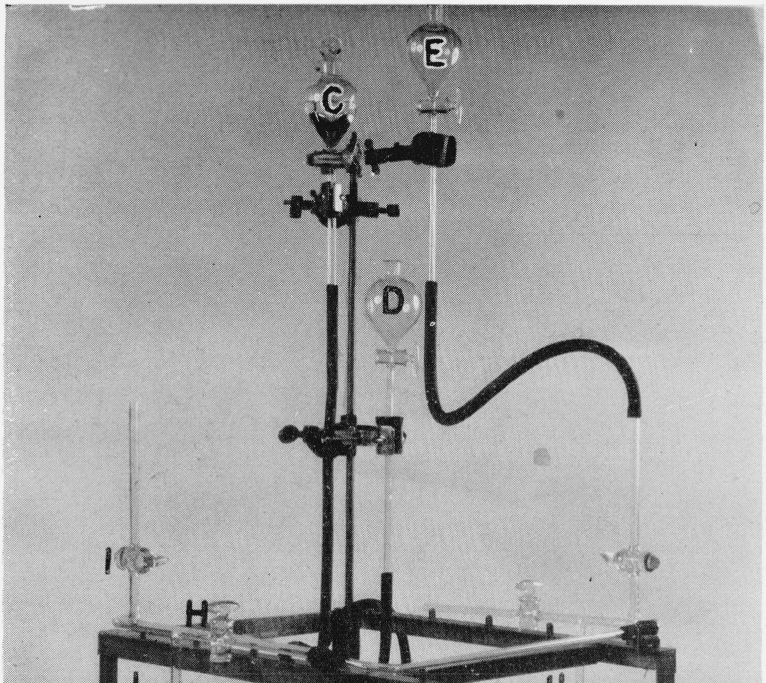

FIGURE 3.—*Liquid-junction and calomel cell assembly, showing half-cells A and B; reservoirs C (for the heavier solution), D and E (for the lighter solution); stopcocks F and G for controlling the rates of flow of the electrolytes to the cells; stopcock H for admitting the lighter solution to the liquid-junction chambers (L or L'), I for removal of entrapped air, and J for discarding the mixed solutions through tip K.*