[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Junction Potentials between Glass and Salts in Fusion

BY HERVEY B. ELKINS AND GEORGE S. FORBES

Solutions consisting of two or more salts in fusion have hitherto been studied by varying the concentrations in cells of two types. The first, exemplified by Ag | AgBr + $PbBr_2$ | Br_2, has proved reproducible, at least when bromides and bromine were used.[1] The second, such as Ag | $AgNO_3$ + KNO_3 | $AgNO_3$ + KNO_3 | Ag, is complicated by an unknown junction potential.[2,3,4]

Glass partitions have previously been used to separate fused salts from other fused salts or from gases containing ions or electrons,[5,6] but not, to our knowledge, in concentration cells involving salts in fusion. To eliminate experimental and theoretical difficulties due to diffusion at liquid junctions we investigated cells such as Ag_1 | AgCl + LiCl (+ KCl . . .) | glass | KNO_3 + $NaNO_3$ | glass | AgCl + LiCl (+ KCl . . .) | Ag_2. Problems connected with the electrochemistry of glass and the activity coefficients of salts in fusion could thus be attacked in a rather novel fashion, and we feel that our results have contributed in some measure toward their solution. We assumed that transference occurs when current runs through such a system. Following Warburg, Kraus and others,[7,8] we assumed also that cations, only, cross boundaries between glass and fused salts, movement of anions being negligible.

To calculate in the first approximation the e. m. f. in volts, consider a very large cell as defined above. The mole fractions of silver chloride are $(N_{AgCl})_1$ and $(N_{AgCl})_2$. If both solutions are ideal and uniformly dissociated, the amounts of current I_{Ag^+} and I_{Li^+} carried across a glass–salt boundary by Ag^+ and Li^+ should conform to an equation such as

$$I_{Ag^+}/I_{Li^+} = K_{Ag^+}{\cdot}N_{AgCl}/K_{Li^+}{\cdot}N_{LiCl}$$

The constants K_{Ag^+} and K_{Li^+} which involve the relative probabilities that two ions Ag^+ and Li^+ will cross the boundary, we shall term "transference constants." Similar comparisons can be instituted between Ag^+ and K^+, also between Li^+ and K^+ and so on, if additional salts are present. By combination

$$I_{Ag^+}/I_{total} = K_{Ag^+}N_{AgCl}/(K_{Ag^+}N_{AgCl} + K_{Li^+}N_{LiCl} + K_{K^+}N_{KCl}\ldots) = K_{Ag^+}N_{AgCl}/\Sigma KN$$

If one gram atom of silver is dissolved from electrode (1) and deposited on electrode (2), $1 - K_{Ag^+}N_{AgCl}/\Sigma KN$ moles of silver chloride pass from

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(1) Salstrom and Hildebrand, THIS JOURNAL, **52**, 4641 (1930).

(2) Gordon, *Z. physik. Chem.*, **28**, 302 (1899).

(3) Suchy, *Z. anorg. Chem.*, **27**, 192 (1901).

(4) Goodwin, *Trans. Am. Electrochem. Soc.*, **21**, 105 (1912).

(5) Tammann, *Z. anorg. Chem.*, **133**, 267 (1924).

(6) Haber and Moser, *Z. Elektrochem.*, **11**, 593 (1905).

(7) E. Warburg, *Ann. Physik*, **21**, 622 (1884).

(8) Kraus and Darby, THIS JOURNAL, **44**, 2783 (1922).

solution (2) to solution (1) while $K_{Li^+}N_{LiCl}/\Sigma KN$ moles of lithium chloride pass from (1) to (2). Still assuming the solutions to be ideal, the work required to replace the silver chloride removed in the previous step is

$$\int_{N_1}^{N_2} dW_{Ag^+} = \int_{N_1}^{N_2} RT\,(1 - K_{Ag^+}N_{AgCl}/\Sigma KN)\ dN/N_{AgCl}$$

where N_1 and N_2 refer to silver chloride. To replace the lithium chloride displaced in the transfer of one gram atom of silver, the work is

$$\int_{N_1}^{N_2} dW_{Li^+} = \int_{N_1}^{N_2} RT\,(K_{Li^+}N_{LiCl}/\Sigma KN)\ dN/N_{LiCl}$$

where N_1 and N_2 refer to lithium chloride. Noting that $-dN_{AgCl} = (dN_{LiCl} + dN_{KCl}\ \ldots)$, it comes out that

$$E = (RT/F)\ [\ln\,(N_1/N_2)_{AgCl} + \ln\,(\Sigma KN)_2/(\Sigma KN)_1] \qquad (1)$$

If the solutions depart appreciably from ideality, we must write

$$E = (RT/F)\ [\ln\,(a_1/a_2)_{AgCl} + \ln\,(\Sigma K'a)_2/(\Sigma K'a)_1] \qquad (2)$$

where activities appear in place of mole fractions, and "transference constants" K' are correspondingly modified. We undertook the calculation of K and a from E, using these equations.

Materials.—Silver halides were precipitated from water solutions of silver nitrate with hydrochloric acid or hydrobromic acid or sodium bromide or barium bromide, and were well washed and dried at 120° or higher. The best obtainable commercial grades of the other salts required were dried at 120° and not further purified. The rubidium chloride while free from sodium and cesium was found to contain about 10% of potassium chloride, for which suitable correction was made. In some cases silver chloride was recovered from residues by extraction with ammonia, filtration, acidification or evaporation, filtration, washing with dilute hydrochloric acid and drying.

Apparatus and Method.—A clay cylinder was wound with Chromel A ribbon, using asbestos and alundum cement for insulation, and set upon an electric hot plate. Inside was a porcelain beaker containing about 150 cc. of fused $KNO_3 + NaNO_3$ with centrifugal stirrer and a thermocouple. The voltmeter which was graduated in degrees was calibrated at the boiling point of sulfur. Into the salt-bath were lowered two Pyrex tubes 8–12 mm. in internal diameter with closed ends (not bulbs) to contain the salt mixtures under investigation. The electrodes were made by igniting silver oxide in loops of fairly stout platinum wire[9] sealed into smaller Pyrex tubes, the glass being squeezed around the wire for about 4 mm. from the end to discourage leakage. Above the seal was a silver wire, welded to the platinum. A Leeds and Northrup Type K potentiometer and a sensitive d'Arsonval galvanometer served to record E well within a millivolt.

The best electrodes gave an electromotive force of less than a millivolt when two were immersed in identical mixtures of fused silver and alkali chlorides. When such electrodes were interchanged with suitable pre-

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[9] Compare G. N. Lewis, THIS JOURNAL, **28**, 166 (1906).

cautions between given mixtures of different composition, E was constant within the same limit. If discrepancies in such cases, or after substitution of additional electrodes, reached two or three millivolts, mean or average values were recorded. In cases still less favorable, both readings and electrodes were rejected and new electrodes were taken. Other irregularities in E of corresponding orders of magnitude were traced to peculiarities of individual Pyrex tubes and dealt with in similar fashion. It was found that a value of E reproducible to the extent noted above was attained within five minutes, and remained constant within a millivolt for several hours except in the case, noted below, where alkali halide was absent.

Data and Interpretation.—For orientation, cells were first studied in which silver chloride was dissolved in a low-melting "solvent" of lithium chloride and potassium choride in constant proportions. Weighed portions of the salts were melted with agitation in porcelain dishes or directly in the Pyrex tubes. If not used immediately, mixtures were preserved in desiccators. In Table I, N_{LiCl} gives the mole fraction of lithium chloride in the original *solvent* and N_{AgCl} the mole fraction in the *final* mixture. E was read in volts from the potentiometer and $E_{\text{calcd.}} = (RT/F) \ln (N_{\text{AgCl}})_1/(N_{\text{AgCl}})_2$, that is, for the moment assuming ideal solutions and negligible junction potentials. Temperatures averaged 490°.

TABLE I

Solvent LiCl + KCl. $N_{\text{LiCl}} = 0.508$				Solvent LiCl + KCl, $N_{\text{LiCl}} = 0.396$			
$(N_{\text{AgCl}})_1$	$(N_{\text{AgCl}})_2$	E	$E/E_{\text{calcd.}}$	$(N_{\text{AgCl}})_1$	$(N_{\text{AgCl}})_2$	E	$E/E_{\text{calcd.}}$
0.0147	0.00468	0.0714	0.958	0.206	0.0898	0.0557	0.892
.0745	.0147	.0970	.922	.444	.1515	.0705	.840
.174	.0745	.0475	.862	.497	.206	.0588	.827
.249	.121	.0381	.808	.582	.240	.580	.914
.500	.249	.0345	.763	.872	.294	.71	1.34

The approach of $E/E_{\text{calcd.}}$ to unity when $(N_{\text{AgCl}})_1$ and $(N_{\text{AgCl}})_2$ both become small would be expected on the ground that the activity coefficients on both sides of the cell would become nearly equal as the two melts approached identity, and that all junction potentials would nearly cancel out. For values of N_{AgCl} of the same order of magnitude, $E/E_{\text{calcd.}}$ is greater when $N_{\text{KCl}} > N_{\text{LiCl}}$. $E/E_{\text{calcd.}}$ decreases with increasing N_{AgCl}, but in our second series (and in a third, not given) it passes through a minimum and then increases beyond unity. This last case invites one or both of two explanations: (1) the activity, a_{AgCl}, increases faster than N_{AgCl}; (2) large junction potentials prevail at the boundary glass–fused salt, conditioned by the three "transference constants" K_{Ag^+}, K_{Li^+}, K_{K^+} properly weighted for variations in γ and in N.

As we were unable at the outset to resolve the complexities of the cells just described, we next obtained data for cells of the type Ag | 0.952 mole % AgCl + 0.048 mole % NaCl | glass | KNO_3 + $NaNO_3$ | glass | AgCl +

one alkali chloride of variable concentration | Ag to discover what effects properties of the ions such as ionic diameter would have upon the results. Just after initial fusion of silver chloride, the electrode Ag | AgCl gave a reproducible maximum reading of E, but this fell off on standing. Therefore we made six cells of the type Ag | 0.952 mole % AgCl + 0.048 mole % NaCl | - - - | AgCl | Ag^+. The average initial maximum reading, 0.381 ± 0.0035, was added to the e. m. f. of all cells having a reference electrode containing 4.8 mole per cent. of sodium chloride to correct for the presence of the sodium chloride in the reference electrode.

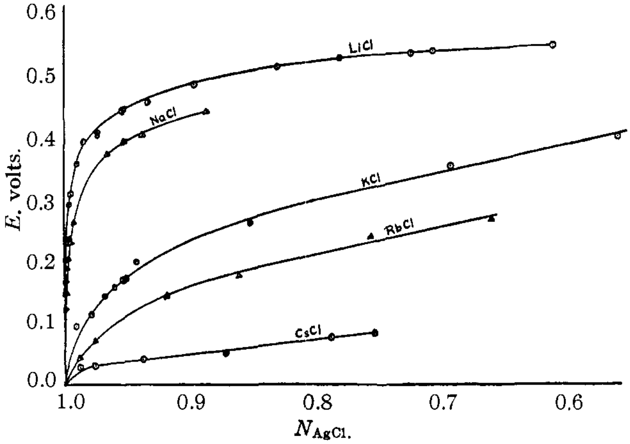

Fig. 1.

In Fig. 1, E thus found is plotted against N for each of five alkali chlorides. The rubidium values were corrected for the potassium content mentioned above. Effects increase in the order Cs^+, Rb^+, K^+, Na^+, Li^+, *i. e.*, as ionic diameter falls off, although the spacing is uneven. The term $RT/F \ln (N_1/N_2)_{AgCl}$ calculated provisionally for ideal solutions can contribute at most 0.05 volt to E. If one assumed that silver chloride is feebly dissociated, succesive increments of alkali chlorides would indeed increase the term $(RT/F) \ln ([Ag^+]_1/[Ag^+]_2)$, but the effect should be about the same for all alkali chlorides unless these in turn differ enormously in degree of dissociation. It seems more probable that the junction potentials are large so that E depends mainly upon $(RT/F) \ln (\Sigma KN)_2/(\Sigma KN)_1$ where K_{Ag^+} is much smaller than those of alkali ions. In Table II these transference constants are referred by use of Equation 1 to K_{Ag^+} taken as unity. The biggest percentage jump in K comes in passing from K^+ to Na^+, that is, where the ionic diameter ceases to be greater than that of the sodium in the glass.

Variation of transference constants with changes in mole fraction of alkali chloride might be expected if the solutions are non-ideal. The

TABLE II

N_{Ag}	K_{Li}	K_{Na}	K_K	K_{Rb}	K_{Cs}
0.999	14,700	5560			
.995	14,300	5350			
.990	14,400	5930	175		
.95	13,750	6160	215	70	
.90	10,500	5010	245	77	
.80	8,500		300	96	7.5
.70	6,700		340	99	
.60	4,900		420		
.50			550		

apparent trend of the activity of silver chloride in lithium chloride suggests a positive deviation from Raoult's law, that of silver chloride in potassium chloride a negative deviation.

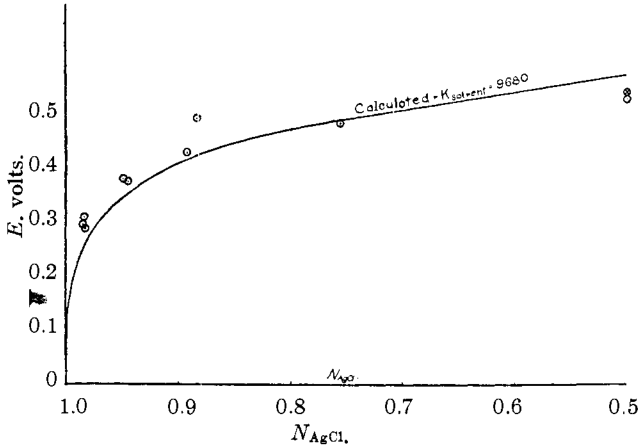

Fig. 2.

Before following up these possibilities, E was calculated by simple substitution of representative values of the "transference constant" K taken from Table II in the ideal equation (1) for several ternary systems. Figure 2 plots $E_{\text{calcd.}}$, for the cell Ag|AgCl|glass|KNO_3 + $NaNO_3$|AgCl + KCl + LiCl|Ag in which N_{KCl}/N_{LiCl} was uniformly 8.3, also ten experimental values of E. In Fig. 3, lithium chloride and sodium chloride, respectively, are added to a eutectic mixture for which $N_{AgCl} = 0.695$ and $N_{KCl} = 0.305$. The discrepancies are no greater than might be expected from neglect of activity coefficients, which seem to vary most in the presence of lithium chloride. The usefulness of the transference constants, thus indicated, justifies an attempt to work out the activity coefficients involved.

The application to the data of equation (2) should be exact, given complete information regarding activities. Thanks to Salstrom and Hildebrand,[10,11,12] data on activities of silver and alkali bromides became available during the progress of our work. Accordingly we measured (Table III) glass cells of the type above described, but containing bromides instead of chlorides. Reproducible results were obtained using sodium bromide and lithium bromide, but not in the case of potassium bromide. It will be noted that E referred to pure silver bromide, or E of cells having different alkali bromides on opposite sides, exceeded E in otherwise comparable cells containing silver chloride. This might be attributed to differences in free energy of silver chloride and bromide as against the corresponding halide ion, or to corresponding differences involving alkali chlorides and bromides.

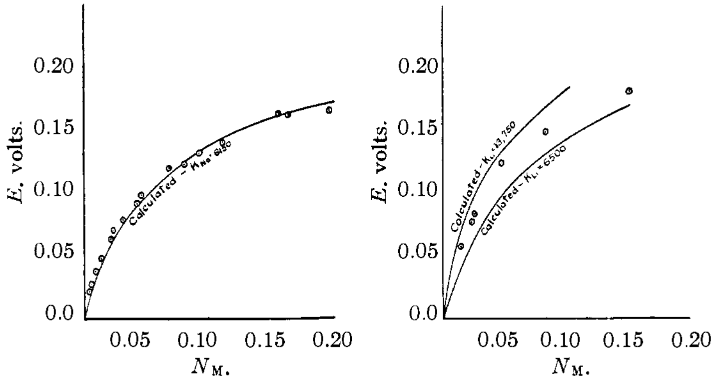

Fig. 3.

Hildebrand and Salstrom[13] showed that $\log \gamma_{\mathrm{AgBr}} = KN^2_{\mathrm{NaBr}}$, etc., thus facilitating the integration of the Gibbs–Duhem–Margules equation $N_1 \mathrm{~d} \ln a^1 + N_2 \mathrm{~d} \ln a_2 = 0$. Writing $\log \gamma_{\mathrm{MBr}} = -\int \frac{N_{\mathrm{Ag}}}{N_{\mathrm{M}}} \mathrm{~d}\,(\log \gamma_{\mathrm{AgBr}})$,

TABLE III

Solvent	$N_{\mathrm{Ag}}(1)$	$N_{\mathrm{Ag}}(2)$	Temp., °C.	E. m. f., volts
(1) (2) LiBr	1.000	0.594	495	0.738
	.955	.594	495	.125
	.978	.418	500	.187
	.978	.480	510	.177
	.978	.460	510	.175
(1) (2) NaBr	.955	.807	500	.098
	.953	.705	525	.128
(1) NaBr (2) LiBr	.955	.955	480	.128
	.807	.978	500	.015
	.807	.216	540	.238
(1) LiCl (2) LiBr	.952	.955	490	.286

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[10] Salstrom and Hildebrand, THIS JOURNAL, **52**, 4650 (1930).

[11] Salstrom, *ibid.*, **53**, 1794, 3385 (1931).

[12] Salstrom, *ibid.*, **54**, 4252 (1932).

[13] Hildebrand and Salstrom, *ibid.*, **54**, 4257 (1932).

where $\gamma = a/N$, and noting that $d\,(\log \gamma_{\mathrm{AgBr}}) = B\,d\,(N_{\mathrm{M^+}})^2 = 2\,B\,N_{\mathrm{M}}\,d\,N_{\mathrm{M}}$, where B is a constant; also noting that $N_{\mathrm{Ag}} = (1 - N_{\mathrm{M^+}})$ for a binary system, we have $\log \gamma_{\mathrm{MBr}} = -2\,B \int (d\,N_{\mathrm{M}} - \frac{1}{2}\,N_{\mathrm{M}}\,d\,N_{\mathrm{M}})$.

This equation was used to calculate the relative values of a_{MX} and a_{AgX} for equation (2). For cells involving sodium or lithium salts, however, it was possible to use a simpler expression, since the transference by silver ion was negligibly small and the second term could be written as $\ln\,[(a_{\mathrm{MX}})_2/(a_{\mathrm{MX}})_1]$. Calculations were made by trial, the value of B giving the observed electromotive force being obtained by interpolation. In Fig. 4 $\log \gamma_{\mathrm{AgX}}$ is shown as a function of the square of the mole fraction of the alkali salt. Both the glass cell data and those of Salstrom are shown. In both cases we have shown (details omitted) that B is independent of the concentration of silver salt. We inferred from this that the linear relationship between $\log \gamma_{\mathrm{AgX}}$ and N^2_{M} holds within the experimental error. This was true of chlorides as well as bromides.

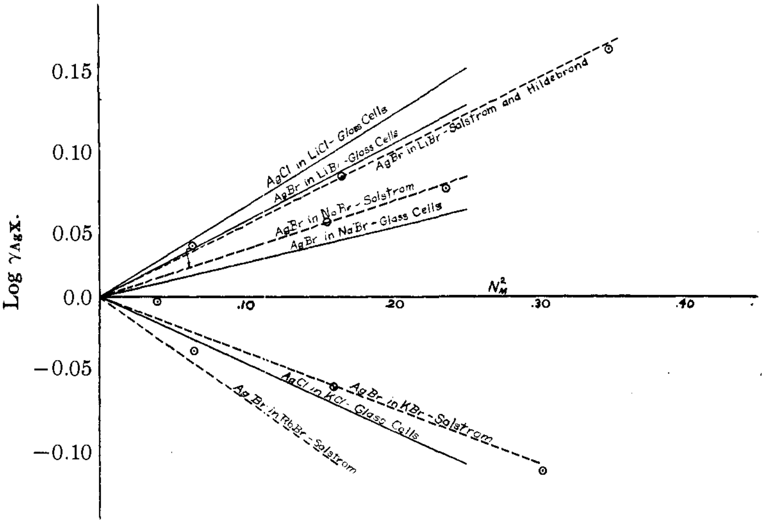

Fig. 4.

The agreement between the glass cell data and those of Salstrom is excellent in the case of lithium bromide, but not quite so satisfactory with sodium bromide, where we had to extrapolate Salstrom's data from 550 to 500°. Both lithium and potassium chlorides in solution with silver chloride appeared to be somewhat less ideal than the bromides.

It is clear that this method of determining γ for a salt in fusion presupposes only that the cation shall enter glass reversibly. The anion could be chosen at will if the salt (mixed with the corresponding silver salt) melts at a suitable temperature and does not attack glass. Though less direct, the method is more general in application than that of Hildebrand and Salstrom.

To observe over a wider range of cases the various factors influencing E, the experiments summarized in Fig. 5 were carried out. Each series started with a known weight of the same known mixture of silver chloride with one other chloride, either potassium chloride, lithium chloride or cadmium chloride, at both electrodes. (The cadmium chloride contained a trace of sodium.) Successive increments of a third chloride were then added at one electrode and E was read in each case. In Fig. 5 the formula of the chloride originally present is intersected by the corresponding curve; the chloride subsequently added is written in beside the curve.

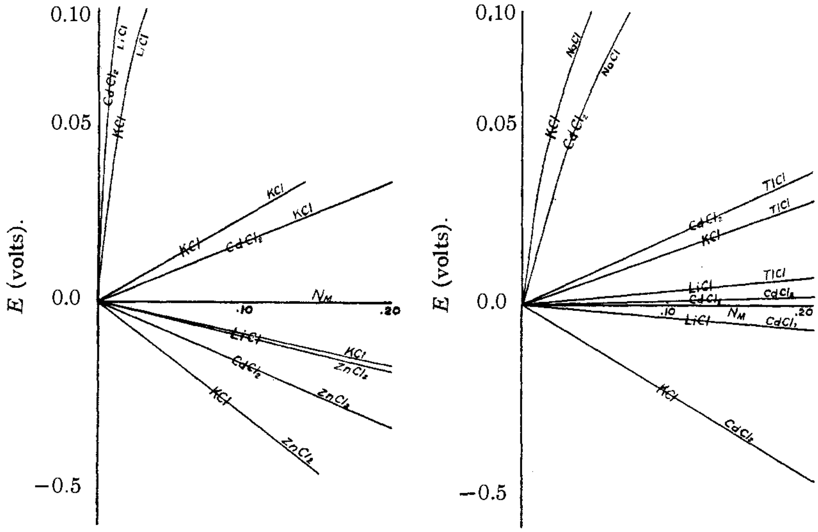

Fig. 5.

It will be noted that increments of sodium chloride and lithium chloride yielded solutions against which the original mixture containing potassium chloride or cadmium chloride became increasingly positive, while potassium chloride and thallous chloride had a smaller effect. Other relationships will be apparent from the study of the other curves.

Let us consider the application of equation (2) to a typical case, involving addition of potassium chloride to an original solution of silver chloride in lithium chloride. $E = (RT/F)[\ln (a_1/a_2)_{\text{AgCl}} + \ln (13{,}000\ a_{\text{LiCl}} + 1 \times a_{\text{AgCl}} + 300\ a_{\text{KCl}})_2/(13{,}000\ a_{\text{LiCl}} + 1 \times a_{\text{AgCl}})_1]$. It is obvious that the second term depends mainly upon the ratio $(a_{\text{LiCl}})_2/(a_{\text{LiCl}})_1$, which, as potassium chloride is added, decreases more rapidly than $(a_1/a_2)_{\text{AgCl}}$ increases and thus makes the original solution increasingly more negative against that containing potassium chloride. The other curves invite analogous interpretations.

According to our interpretation, the data obtained indicate the change in activity of the silver halide (and alkali halide) and tell nothing of the silver ion (or alkali ion) itself. Now Günther-Schulze[14] some time ago obtained data on the diffusion of silver into glass from fused silver chloride and bromide which he interpreted in terms of concentration of silver ion. Since the addition of very small amounts of sodium salt diminished greatly the rate of diffusion of silver ion into the glass, he concluded that the silver halide behaved like a weak electrolyte, and that its dissociation was suppressed by the addition of completely dissociated alkali halide. Our data were of similar nature; but because of the specific effect of different alkali salts we rejected this hypothesis. A different explanation of Günther-Schulze's observations suggested itself. In the diffusion of silver ion into glass, the silver ion replaces the sodium ion in the glass. Now the assumption that the diffusion of sodium ions out of the glass occurs more readily than the diffusion of silver ion in is not the only possible one. Suppose, instead, that the rate of diffusion of metallic ions from the fused salt into the glass is dependent primarily on the rate at which the sodium ions come out of the glass. In this case the total number of ions diffusing into the glass in a given time will be nearly constant. If we denote the rate of diffusion of silver and of sodium ions into glass as V_{Ag} and V_{Na}, respectively, it follows that V_{Ag} (from pure AgCl) = $V_{Ag} + V_{Na}$ (from any solution). The relative rates of diffusion of any two ions should be proportional to the ratio of the mole fractions.

$$\frac{V_{Na}}{V_{Ag}} = p\,\frac{N_{Na}}{N_{Ag}} = \frac{V_{Ag}\text{ (pure AgCl)} - V_{Ag}\text{ (sol.)}}{V_{Ag}\text{ (sol.)}}$$

If this mechanism is correct, the values of p, calculated for solutions containing different concentrations of sodium chloride, should be constant. The degree of constancy obtained is shown in Table IV.

TABLE IV

V_{Ag} (mg./min.)	N_{NaCl}	p (Cl)	V_{Ag}	N_{NaBr}	p (Br)
0.380	0.00	...	0.085	0.00	..
.30	.00087	300	.06	.00016	2600
.15	.0029	525	.043	.00032	3000
.08	.0058	670	.026	.00064	3600
.045	.0116	670	.015	.0012	3800
		Av. 540			Av. 3250

The constancy of the value of p is probably within the limits of experimental error, although the tendency to increase as the concentration of NaX is increased is disturbing. These terms are similar to the transference constants of equation (1), but differ from them in that p is not made dependent upon mobility *in* the glass. Experimental agreement between

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(14) Günther-Schulze, *Z. Elektrochem.*, **19**, 122 (1913).

the two values would not be expected in any case, for Günther-Schulze worked with soft glass.

The ratio of $p_{(Br)}$ to $p_{(Cl)}$, however, should equal the corresponding ratio of transference constants for the sodium salts. The agreement $p_{Br}/p_{Cl} = 6.0$, $K_{NaBr}/K_{NaCl} = 5.1$, is easily within the experimental error.

A few experiments were made substituting other glasses for Pyrex. Of these, Scotch glass, Jena hard glass and Jena normal glass gave reproducible results. The hard glasses gave practically the same electromotive forces as Pyrex. A single measurement in Jena normal glass between pure silver chloride and its solution in sodium chloride gave an electromotive force much lower than the corresponding cell in Pyrex, which can be linked with the fact that p_{Na^+} calculated from Günther-Schulze's data on soft glass is lower than K_{Na^+}.

Table V contains data on temperature coefficients. It appears that $E \propto 0.000198\ T$ quite nearly in the case of cells dilute in silver chloride. At lower temperatures, for cells concentrated in silver chloride, $E < 0.000198\ T \log (N_1/N_2)$, but rapidly approaches this value as T increases, which may signify that the solutions tend to become ideal meanwhile.

TABLE V

SOLVENT: LiCl·KCl, $N_{Li} = 0.597$

$N_{Ag}(1)$	$N_{Ag}(2)$	Temp., °C.	E, volts	$E/E_{calcd.}$
0.0504	0.00992	400	0.0865	0.92
.0504	.00992	570	.1115	.945
.654	.203	405	.051	.74
.654	.203	550	.0735	.89

Summary

1. The electromotive forces of cells of the type $Ag_1 | AgCl + LiCl (+ KCl \ldots) | glass | KNO_3 + NaNO_3 | glass | AgCl + LiCl (+ KCl \ldots) | Ag_2$ were measured at 500°. Some cells involving silver bromide were also measured.

2. Single alkali chlorides and low melting mixtures of lithium and potassium chlorides were used as "solvents." An alkali salt was found necessary to stabilize the electromotive force.

3. An equation derived on the assumption of a concentration cell with transference by cation alone seemed to describe the electromotive forces satisfactorily.

4. "Transference constants," dependent on the readiness with which the metallic ions entered the glass, were calculated and it was found that $K_{Li} > K_{Na} \gg K_K > K_{Rb} \gg K_{Cs} > K_{Ag}$. The order of the alkali ions was ascribed to higher mobility of the smaller ion, and the small value of K_{Ag} to the great stability of silver chloride.

5. Integration of the Gibbs–Duhem–Margules expression made possible the calculation of deviation from laws of perfect solution. Fair agreement

with Salstrom's data upon activities was obtained in the case of silver bromide in lithium bromide and sodium bromide. In the case of lithium and potassium salts the deviation from ideality seemed slightly greater for the chlorides than for the bromides.

6. The activity coefficients of various salts other than chlorides and bromides might be determined by measurements of e. m. f. in cells otherwise similar to those employed in this research.

7. An interpretation of Günther-Schulze's observations upon the diffusion of silver ion into glass from fused silver halides was offered.

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Ceric Sulfate as a Volumetric Oxidizing Agent. XIV. Indicator Methods for the Standardization and Use of Ceric Sulfate

BY HOBART H. WILLARD AND PHILENA YOUNG

Introduction

Accurate methods, already described, for the standardization of ceric sulfate include (1) the titration of sodium oxalate in a hot hydrochloric, sulfuric or perchloric acid solution. The end-point may be determined either potentiometrically[1,2] or visually.[1] If the titration is made in a hydrochloric acid solution at room temperature in the presence of iodine chloride as catalyst, the end-point is determined potentiometrically.[1] (2) The titration of ferrous ion from electrolytic iron in a sulfuric, hydrochloric, or perchloric acid solution. The end-point may be determined potentiometrically,[3] with diphenylamine sulfonic acid as an oxidation–reduction indicator,[4] with diphenylamine or diphenylbenzidine,[3] or with methyl red, erio glaucine, or erio green.[5] *o*-Phenanthroline ferrous complex has been suggested as an oxidation–reduction indicator for this titration[6] and because of its high oxidation potential it is more satisfactory than any of the indicators mentioned above. (3) The titration of arsenious oxide in a hydrochloric acid solution. If bromide or iodide ion or iodine chloride is present, the titration may be carried out at room temperature and the end-point determined potentiometrically[7] or by the use of chloroform if iodine chloride is the catalyst.[8]

[1] Willard and Young, THIS JOURNAL, **50**, 1322 (1928).

[2] Furman, *ibid.*, **50**, 755 (1928).

[3] Willard and Young, *ibid.*, **50**, 1334 (1928).

[4] Willard and Furman, "Elementary Quantitative Analysis," D. Van Nostrand Co., New York, 1933, p. 183.

[5] Furman and Wallace, THIS JOURNAL, **52**, 2347 (1930).

[6] Walden, Hammett and Chapman, *ibid.*, **53**, 3908 (1931).

[7] Willard and Young, *ibid.*, **50**, 1372 (1930).

[8] Swift and Gregory, *ibid.*, **52**, 901 (1930).