

INDIVIDUAL THERMODYNAMIC BEHAVIORS OF IONS IN CONCENTRATED SOLUTIONS INCLUDING A DISCUSSION OF THE THERMODYNAMIC METHOD OF COMPUTING LIQUID JUNCTION POTENTIALS*

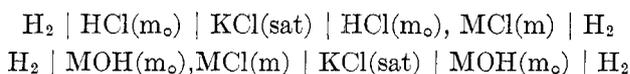
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As a result of earlier experimental investigations¹, some tentative conclusions were reached regarding the individual activity coefficients of the ions of some simple electrolytes, and the hydrogen ion in certain chloride solutions. From the electromotive force data then available, an attempt was made to compute the individual ion activity coefficients of the hydrogen, lithium, sodium, and potassium ions in solutions of their chlorides, and the hydrogen and hydroxyl ions in solutions of chlorides. More recently, further data² have been obtained which complete this experimental study, and which will be assembled in this paper.

Since the difficulty in estimating liquid junction potentials is the only cause of our not being able to estimate exactly the individual activity coefficients of the ions, an analysis of the problem of liquid junction potentials will be made.

Hückel³ has computed the individual ion activity coefficients of solutions of hydrochloric acid and sodium chloride by means of the general theory of Debye and Hückel and has found a qualitative but not quantitative agreement with our earlier conclusions. This, indeed, is to be expected since our conclusions have been considered to be but a rough approximation and not an exact solution of the problem, and since, on account of the theoretical complexity of the problem, it is not to be expected that the theory of Debye and Hückel is exact in the very concentrated solutions. In the following discussion, we shall consider these matters more fully.

(1) *Electromotive Forces of the Cells:*



Throughout these studies, we have employed cells containing a saturated potassium chloride solution for the purpose of reducing the liquid junction potentials as far as possible experimentally. In all cases stationary junctions were employed. These were made by having a capillary tube from one electrode compartment dip into a cup containing the other electrode solution. A

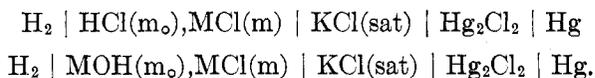
* Contribution from the John Harrison Laboratory of Chemistry of the University of Pennsylvania.

¹ J. Am. Chem. Soc., **37**, 2460 (1915); **38**, 1986 (1916); **42**, 180 (1920).

² J. Am. Chem. Soc., **47**, 684, 689 (1925); Harned and Swindells: **48**, 126 (1926).

³ Physik. Z., **26**, 93 (1925).

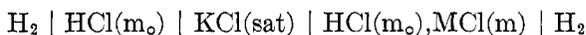
mixing of the two solutions across the boundary was therefore allowed to take place. The more recent results were obtained from cells of the types



All these data are compiled in Table I. The standard calomel electrode has been eliminated, and the electromotive forces corresponding to the transfer of the hydrogen or hydroxyl ions plus the liquid junction potentials have been given. At the end of the table, the values of the reference cells have been tabulated. These data come from three sources. Those denoted (1) were taken from our earlier study¹; those denoted (2) have been recently determined; and those denoted (3) have been recently obtained in this laboratory by Dr. Swindells. Molal concentrations have been employed. All measurements were carried out at 25°. The agreement between the more recent results and those previously determined was found to be good.

TABLE I

(1) Electromotive Forces of Cells:

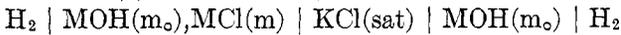
 $m_o = 0.1$

KCl		NaCl		LiCl	
m	E_H	m	E_H	m	E_H
	(1)		(1)		(3)
0.1380	0.0003	0.1867	0.0011	0.0705	0.0012
0.2775	0.0005	0.569	0.0041	0.1101	0.0017
0.560	0.0012	0.614	0.0041	0.2004	0.0021
0.848	0.0021	1.536	0.0128	0.3693	0.0041
			(2)		
1.141	0.0036	0.0959	0.0012	0.704	0.0083
1.441	0.0052	0.1779	0.0014	1.007	0.0120
3.473	0.0169	0.3456	0.0024	2.198	0.0283
	(2)				
1.341	0.0045	0.857	0.0063	3.695	0.0492
2.006	0.0082	1.707	0.0153	-----	-----
2.696	0.0123	2.130	0.0198	-----	-----
3.346	0.0161	2.599	0.0246	-----	-----
-----	-----	2.978	0.0285	-----	-----
-----	-----	3.424	0.0328	-----	-----

¹ Harned: J. Am. Chem. Soc., 37, 2460 (1915).

$m_0 = 0.01$					
KCl		NaCl		LiCl	
m	E_H	m	E_H	m	E_H
	(2)		(2)		(3)
0.02	-0.0003	0.02	-0.0002	0.0077	-0.0003
0.05	-0.0008	0.05	-0.0007	0.0103	-0.0003
0.1	-0.0015	0.1	-0.0005	0.0194	0.0001
0.2	-0.0021	0.2	0.0000	0.0422	0.0005
0.5	-0.0015	0.5	0.0014	0.0727	0.0011
1.	0.0016	1.	0.0058	0.1989	0.0020
2.	0.0071	2.	0.0152	0.402	0.0035
3.	0.0126	3.	0.0254	0.699	0.0072
-----	-----	-----	-----	1.004	0.0104
-----	-----	-----	-----	2.189	0.0260
-----	-----	-----	-----	3.989	0.0526

(2) Electromotive Forces of Cells:



$m_0 = 0.1$					
KOH,KCl		NaOH,NaCl		LiOH,LiCl	
m	E_{OH}	m	E_{OH}	m	E_{OH}
	(1)		(1)		(3)
0.262	-0.0013	0.472	-0.0044	0.1512	-0.0051
0.527	-0.0015	0.943	-0.0071	0.2908	-0.0082
1.357	-0.0009	1.445	-0.0094	0.432	-0.0108
2.167	0.0004	1.946	-0.0107	1.071	-0.0201
3.280	0.0044	2.458	-0.0120	1.709	-0.0284
	(2)		(2)		
0.1285	-0.0004	0.1704	-0.0029	2.675	-0.0384
0.2645	-0.0009	0.336	-0.0041	3.521	-0.0461
0.647	-0.0016	0.841	-0.0075	-----	-----
-----	-----	1.696	-0.0108	-----	-----
-----	-----	2.500	-0.0135	-----	-----
-----	-----	4.14	-0.0149	-----	-----

$m_0 = 0.01$					
KOH,KCl		NaOH,NaCl		LiOH,LiCl	
m	E_{OH}	m	E_{OH}	m	E_{OH}
	(2)		(2)		(3)
0.0496	-0.0036	0.0621	-0.0054	0.0078	-0.0005
0.1026	-0.0048	0.1462	-0.0076	0.0221	-0.0020
0.1928	-0.0067	0.302	-0.0094	0.0423	-0.0036
0.4889	-0.0081	0.362	-0.0096	0.0864	-0.0070
1.051	-0.0081	0.572	-0.0117	0.844	-0.0217
1.830	-0.0071	0.853	-0.0133	1.854	-0.0360
2.446	-0.0050	1.288	-0.0157	2.746	-0.0469
-----	-----	1.724	-0.0172	3.810	-0.0573
-----	-----	2.835	-0.0202	-----	-----
-----	-----	3.575	-0.0217	-----	-----

(3) Reference Cells:

H ₂ HCl(0.1) KCl(sat) Hg ₂ Cl ₂ Hg;	<i>E</i> = 0.3102
H ₂ HCl(0.01) " ;	<i>E</i> = 0.3679
H ₂ KOH(0.1) " ;	<i>E</i> = 1.0040
H ₂ KOH(0.01) " ;	<i>E</i> = 0.9491
H ₂ NaOH(0.1) " ;	<i>E</i> = 1.0031
H ₂ NaOH(0.01) " ;	<i>E</i> = 0.9485
H ₂ LiOH(0.1) " ;	<i>E</i> = 1.0028
H ₂ LiOH(0.01) " ;	<i>E</i> = 0.9483

(2) Discussion of Experimental Results

According to the dissociation theory of Arrhenius and van't Hoff, it was assumed that the thermodynamic coefficients of the two ions of a uniunivalent electrolyte in a given solution were identical. Both ions were assumed to have the same van't Hoff coefficient as long as this quantity was taken as a measurement of the degree of dissociation. More recently, many investigators have come to the conclusion that the thermodynamic coefficients such as the activity, osmotic, or van't Hoff coefficients¹ are not the same for the two ions of a given electrolyte but that each ion is characterized by an individual value for this thermodynamic property.

As a first step towards evaluating the individual ion activity coefficients of highly polar electrolytes, we have made the very simple assumption that at a given concentration the relative partial free energies of the ions of the alkaline chlorides are additive. This assumption was first adopted by MacInnes for moderately dilute solutions. MacInnes² also assumed that in a solution of potassium chloride the activity coefficients of the potassium and chloride ions are equal. On account of the complicated nature of this problem, and the consideration of the numerous factors which may influence activity coefficients, these too simple assumptions are not to be expected to be more than a first rough approximation when applied to the very concentrated solutions. Our first step, however, in the following discussion will be to apply these assumptions to the completed data in hand.

If \bar{F}_1 , a_1 , and \bar{F}_2 , a_2 are the relative partial free energies and activities of an electrolyte or an ion in two solutions of concentrations m_1 and m_2 , respectively, then

$$\bar{F}_2 - \bar{F}_1 = RT \ln a_2/a_1 \quad (1)$$

The electromotive force of a concentration cell, $E_1 - E_2$, or ΔE at constant temperature and pressure is given by

$$NF\Delta E = NF(E_1 - E_2) = \bar{F}_2 - \bar{F}_1 = (-\Delta F) \quad (2)$$

From these two equations, it is seen that a change in partial free energy of an ion or electrolyte in passing from one concentration to another is pro-

¹ For definitions of these quantities, see Taylor: "Treatise on Physical Chemistry", pp. 728, 753, 754 (1924).

² J. Am. Chem. Soc., 41, 1086 (1919).

portional to the electromotive force of a concentration cell containing the electrolyte at these two concentrations, which in turn is proportional to the logarithm of the ratio of the activities at the two concentrations. With these relations in mind, we shall state the above postulates as follows:

(1) The relative partial free energies, or electromotive forces of the ions of potassium, sodium, and lithium chlorides in aqueous solution at a given concentration and referred to a given concentration are additive,

(2) E_K equals E_{Cl} (referred to a given concentration) in an aqueous potassium chloride solution of a given strength, and follow the consequences of their adoption.

In this discussion, the nomenclature and conventions regarding the signs of electromotive forces employed by Lewis and Randall¹ will be adopted. Let us first consider the cells:

Type (1): $H_2 | HCl(m_o) | Hg_2Cl_2 | Hg$; (E' has a positive value)

Type (2): $H_2 | HCl(m_o), MCl(m) | Hg_2Cl_2 | Hg$; (E'' has a less positive value than E'). If the second be subtracted from the first, we obtain

Type (3): $Hg | Hg_2Cl_2 | HCl(m_o), MCl(m) | H_2 | HCl(m_o) | Hg_2Cl_2 | Hg$; (E_{HCl} has a positive value). The equation which relates E_{HCl} to the activities is at 25°

$$E_{HCl} = 0.05915 \log \frac{a_{H(s)} a_{Cl(s)}}{a_{H(m_o)} a_{Cl(m_o)}}$$

$$E_H + E_{Cl} = 0.05915 \log \frac{a_{H(s)}}{a_{H(m_o)}} + 0.05915 \log \frac{a_{Cl(s)}}{a_{Cl(m_o)}} \quad (3)$$

where a_H etc. are the activities of the ions denoted by subscript, (s) refers to the solution containing the salt, and E_H and E_{Cl} are the electromotive forces corresponding to the relative partial free energies of the hydrogen and chloride ions, respectively. E_H would be the electromotive forces of the cells

Type (4): $H_2 | HCl(m_o) | HCl(m_o), MCl(m) | H_2$

where the liquid junction potential has been eliminated by some means (indicated by italic letter E). The electromotive forces of cells of this type, we shall denote $E_{H(MCl)}$. The nearest approach which has been made to an experimental realization of such cells has been obtained by interposing a saturated potassium chloride solution between the two electrode solutions. Thus, we obtain the cells

Type (5): $H_2 | HCl(m_o) | KCl(sat) | HCl(m_o), MCl(m) | H_2$

and, the smaller the difference between the two liquid junction potentials, the nearer its electromotive force will be to the E_H . Their electromotive forces we denote $E_{H(s)}$ where the (s) refers to the saturated potassium chloride.

Our procedure will be as follows. We shall first calculate E_{Cl} according to postulate (2). Values of E_{KCl} have been given in another place² which when divided by 2 give the values of E_K or E_{Cl} in Table II. By subtracting these

¹ "Thermodynamics", (1923).

² J. Am. Chem. Soc. 47, 930 (1925).

from the revised values of E_{HCl} obtained at round concentrations from the plots of electromotive computed from the results in Table III of a recent paper¹ we obtain $E_{\text{H}(\text{MCl})}$ which we compare with the values of $E_{\text{H}(\text{s})}$ read off curves of the results in Table I of this paper. This has been done for the cells containing acid at concentrations 0.01 and 0.1 M and potassium, sodium, and lithium chlorides at concentrations (m). The results are given in Part I, Table II.

In Part II, the data of the hydroxide cell electromotive forces have been compiled in a similar manner. In this case, for sake of convenience, we consider the cells

Type (6): $\text{H}_2 \mid \text{MOH}(\text{m}_o), \text{MCl}(\text{m}) \mid \text{M}_x\text{Hg} \mid \text{MOH}(\text{m}_o) \mid \text{H}_2$; (E_{MOH} has a positive value) where M may be either lithium, sodium, or potassium. The electromotive forces of these cells are given by

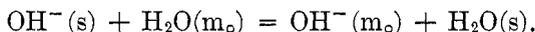
$$E_{\text{MOH}} = 0.05915 \log \frac{a_{\text{M}(\text{s})} a_{\text{OH}(\text{s})} a_{\text{H}_2\text{O}(\text{m}_o)}}{a_{\text{M}(\text{m}_o)} a_{\text{OH}(\text{m}_o)} a_{\text{H}_2\text{O}(\text{s})}}$$

$$E_{\text{M}} + E_{\text{OH}} = 0.05915 \log \frac{a_{\text{M}(\text{s})}}{a_{\text{M}(\text{m}_o)}} + 0.05915 \log \frac{a_{\text{OH}(\text{s})} a_{\text{H}_2\text{O}(\text{m}_o)}}{a_{\text{OH}(\text{m}_o)} a_{\text{H}_2\text{O}(\text{s})}} \quad (4)$$

E_{M} for the sodium and lithium ions have been calculated by subtracting E_{Cl} from E_{NaCl} and E_{LiCl} and the values are given in second and third columns in Part II, Table II. E_{NaCl} were obtained from the data compiled by Harned² and E_{LiCl} from the data of Harned and Swindells³. If E_{M} be subtracted from E_{MOH} , we obtain E_{OH} which corresponds to the cells

Type (7): $\text{H}_2 \mid \text{MOH}(\text{m}_o), \text{MCl}(\text{m}) \mid \text{MOH}(\text{m}_o) \mid \text{H}_2$

and the cell reaction



Thus, if E_{OH} is negative, $a_{\text{OH}(\text{m}_o)}$ will be greater than $a_{\text{OH}(\text{s})}$ and the reaction will tend to take place from right to left. The values of E_{OH} calculated by the above method in the cases of the three chlorides are given in the table and there compared with the values of $E_{\text{OH}(\text{s})}$, or the electromotive forces of the cells

Type (8): $\text{H}_2 \mid \text{MOH}(\text{m}_o), \text{MCl}(\text{m}) \mid \text{KCl}(\text{sat}) \mid \text{MOH}(\text{m}_o) \mid \text{H}_2$

These latter results were read off plots of the results in Table I.

In Fig. 1, the values of E_{H} and E_{OH} of the solutions containing 0.1 M acid and hydroxide calculated by means of our postulates are plotted against m. $E_{\text{H}(\text{s})}$ and $E_{\text{OH}(\text{s})}$ are similarly plotted and represented by the dashed lines. The maximum difference between the two sets of curves occurs at 3M lithium chloride in the acid solution and amounts to 5 millivolts. In general, the curves separate rapidly upon the first addition of salt and then become approximately parallel with a slowly widening difference. E_{OH} coincides with

¹ J. Am. Chem. Soc., **48**, 326 (1926).

² J. Am. Chem. Soc., **47**, 930 (1925), Table III, E_s in Part I and II, B.

³ J. Am. Chem. Soc., **48**, 126 (1926).

TABLE II
Comparison of E_H and E_{OH} to $E_{H(s)}$ and $E_{OH(s)}$
Part I. The Acid System

$m + 0.1$	$m_0 = 0.1$						
	$E_K = E_{Cl}$	E_H	KCl $E_{H(s)}$	E_H	NaCl $E_{H(s)}$	E_H	LiCl $E_{H(s)}$
0.1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.2	0.0154	-0.0003	0.0002	0.0004	0.0012	0.0006	0.0017
0.4	0.0316	-0.0002	0.0004	0.0008	0.0018	0.0015	0.0030
0.6	0.0410	0.0002	0.0010	0.0016	0.0032	0.0031	0.0050
0.8	0.0473	0.0007	0.0017	0.0034	0.0050	0.0054	0.0077
1.1	0.0546	0.0022	0.0030	0.0060	0.0078	0.0086	0.0116
2.1	0.0705	0.0074	0.0082	0.0159	0.0182	0.0207	0.0256
3.1	0.0804	0.0132	0.0140	0.0250	0.0285	0.0344	0.0396

$m + 0.1$	$m_0 = 0.01$						
	$E_K = E_{Cl}$	E_H	KCl $E_{H(s)}$	E_H	NaCl $E_{H(s)}$	E_H	LiCl $E_{H(s)}$
0.01	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.02	0.0169	-0.0014	-0.0003	-0.0013	-0.0003	-0.0013	-0.0003
0.05	0.0389	-0.0028	-0.0006	-0.0025	-0.0007	-0.0023	0.0005
0.1	0.0552	-0.0036	-0.0014	-0.0032	-0.0006	-0.0030	0.0012
0.2	0.0711	-0.0040	-0.0021	-0.0035	-0.0002	-0.0029	0.0020
0.5	0.0921	-0.0037	-0.0015	-0.0022	0.0014	-0.0010	0.0045
1.	0.1078	-0.0013	0.0016	0.0022	0.0058	0.0048	0.0104
2.	0.1243	0.0044	0.0073	0.0115	0.0154	0.0171	0.0231
3.	0.1349	0.0091	0.0126	0.0211	0.0254	0.0303	0.0368

PART II. Hydroxide System

 $m_0 = 0.1$

$m + 0.1$	E_{Na}	E_{Li}	E_{OH}	KCl	$E_{OH(s)}$	E_{OH}	NaCl	$E_{OH(s)}$	E_{OH}	LiCl	$E_{OH(s)}$
0.1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.2	0.0164	0.0182	-0.0012	-0.0012	-0.0007	-0.0022	-0.0022	-0.0022	-0.0040	-0.0040	-0.0040
0.4	0.0328	0.0364	-0.0023	-0.0023	-0.0015	-0.0035	-0.0035	-0.0038	-0.0080	-0.0080	-0.0085
0.6	0.0429	0.0480	-0.0027	-0.0027	-0.0018	-0.0045	-0.0045	-0.0050	-0.0105	-0.0105	-0.0116
0.8	0.0500	0.0572	-0.0027	-0.0027	-0.0016	-0.0054	-0.0054	-0.0063	-0.0135	-0.0135	-0.0144
1.1	0.0587	0.0675	-0.0027	-0.0027	-0.0016	-0.0065	-0.0065	-0.0077	-0.0167	-0.0167	-0.0188
2.1	0.0783	0.0948	-0.0012	-0.0012	0.0000	-0.0098	-0.0098	-0.0112	-0.0284	-0.0284	-0.0316
3.1	0.0957	0.1176	0.0017	0.0017	0.0030	-0.0148	-0.0148	-0.0145	-0.0398	-0.0398	-0.0420

 $m_0 = 0.01$

$m + 0.1$	E_{Na}	E_{Li}	E_{OH}	KCl	$E_{OH(s)}$	E_{OH}	NaCl	$E_{OH(s)}$	E_{OH}	LiCl	$E_{OH(s)}$
0.01	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.02	0.0169	0.0169	-0.0020	-0.0020	-0.0018	-0.0020	-0.0020	-0.0020	-0.0020	-0.0020	-0.0020
0.05	0.0392	0.0392	-0.0042	-0.0042	-0.0036	-0.0045	-0.0045	-0.0045	-0.0045	-0.0045	-0.0045
0.1	0.0560	0.0561	-0.0054	-0.0054	-0.0050	-0.0065	-0.0065	-0.0065	-0.0079	-0.0079	-0.0071
0.2	0.0725	0.0738	-0.0065	-0.0065	-0.0065	-0.0083	-0.0083	-0.0083	-0.0117	-0.0117	-0.0114
0.5	0.0943	0.0985	-0.0097	-0.0097	-0.0097	-0.0105	-0.0105	-0.0108	-0.0175	-0.0175	-0.0185
1.	0.1119	0.1199	-0.0080	-0.0080	-0.0080	-0.0126	-0.0126	-0.0141	-0.0244	-0.0244	-0.0244
2.	0.1326	0.1487	-0.0065	-0.0065	-0.0065	-0.0162	-0.0162	-0.0180	-0.0376	-0.0376	-0.0376
3.	0.1465	0.1717	-0.0037	-0.0037	-0.0037	-0.0189	-0.0189	-0.0206	-0.0500	-0.0500	-0.0500

$E_{\text{OH(s)}}$ in sodium chloride solutions up to 0.3 M above which concentration it is less negative. It is important to note that E_{OH} is more negative than $E_{\text{OH(s)}}$ in potassium chloride solutions but less so in sodium and lithium chloride solutions. This interesting behavior will be explained later.

The results in 0.01 M acid are similar to these except that the differences between E_{H} and $E_{\text{H(s)}}$ are about 1.5 millivolts greater in the concentrated

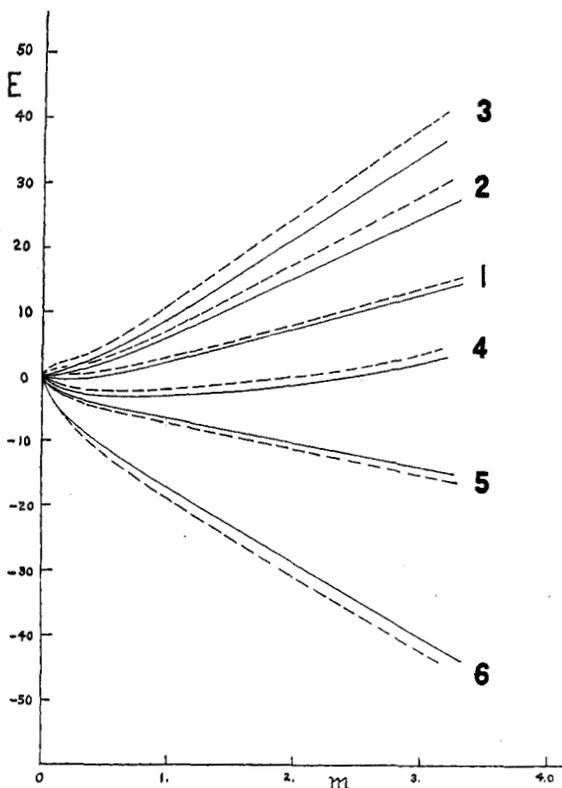


FIG. 1

Electromotive Forces of the Hydrogen and Hydroxyl Ions in Univalent Chloride Solutions.

1. $E_{\text{H}}(\text{HCl}(0.1), \text{KCl}(m))$
2. $E_{\text{H}}(\text{HCl}(0.1), \text{NaCl}(m))$
3. $E_{\text{H}}(\text{HCl}(0.1), \text{LiCl}(m))$
4. $E_{\text{OH}}(\text{KOH}(0.1), \text{KCl}(m))$
5. $E_{\text{OH}}(\text{NaOH}(0.1), \text{NaCl}(m))$,
6. $E_{\text{OH}}(\text{LiOH}(0.1), \text{LiCl}(m))$

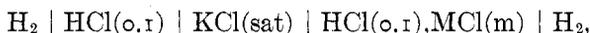
solutions. E_{OH} and $E_{\text{OH(s)}}$ of the 0.01 M potassium hydroxide—chloride series are identical. The 0.01 M sodium hydroxide—chloride series are similar to the 0.1 M series. On the other hand, E_{OH} and $E_{\text{OH(s)}}$ in the case of the 0.01 M lithium hydroxide chloride series are identical. This apparent inconsistency may be due to an error in the results of Harned and Swindells with amalgam cells containing these mixtures, and therefore at present we shall attach no significance to this coincidence.

On account of the difficulties inherent in judging the magnitudes of the liquid junction potentials, and the nature of liquid junction potential calculations by means of thermodynamics, it would be wrong to regard this uniformity of behavior as an exact proof but rather as a qualitative indication. It is improbable, on the other hand, that such a distribution of curves is purely fortuitous. In our previous articles on this subject, these postulates have been regarded as an approximation in the more concentrated solutions and as becoming more exact as the salt concentration is decreased.

(3) *Analysis of the Liquid Junction Potentials.*

(a) Some Qualitative Considerations

Let us first consider the electromotive forces of the cells

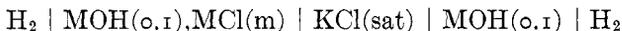


represented in Fig. 1 by the dotted lines. In the cases of potassium, sodium, and lithium chlorides, the anion has a greater mobility than the cations, although the difference is very small in case of potassium chloride. The addition of the salt will charge the saturated potassium chloride solution negatively to the acid-salt solutions, and small liquid junction potentials would be produced which would cause a positive electromotive force from left to right within the cell. Thus, in all cases, these electromotive forces would be greater than the calculated electromotive forces of the cells



From inspection in Fig. 1, we find that the values of the cells containing the saturated chloride are always somewhat more positive than the calculated values, and that the differences between $E_{\text{H}(s)}$ and E_{H} are greater in the order potassium, sodium, lithium chlorides as would be expected since the differences in mobilities of the anion and cation of these salts vary in the same order.

The electromotive forces of the cells



are given by the dotted lines 4, 5 and 6 in Fig. 1. In these cases, by similar reasoning, the addition of the salt should increase the negative electromotive force, and the dotted lines should lie below the calculated values. This is found to be true in the concentrated solutions for the sodium hydroxide—sodium chloride, lithium hydroxide—lithium chloride cells, but not for those containing potassium hydroxide—chloride mixtures. This would appear to be an inconsistency in the results but will be seen to disappear when we come to consider the situation more carefully. The negative increase in liquid junction potential is greater for lithium than for sodium than for potassium chloride which would be expected from the mobilities.

Another important point concerning the plots in Fig. 1 should be considered. The dotted and smooth curves diverge from one another up to about 0.5 M and then run nearly parallel to one another in all six cases. Since the liquid junction potential in any case will be a function of the logarithm of the ratios of two concentrations, it is obvious that it will change the least throughout the concentration ranges where the concentration ratio varies the least.

This fact is qualitatively in agreement with the calculations of liquid junction potentials by either Planck's equation¹ or Henderson's equation².

Exactly similar considerations hold for the 0.01 M acid-salt series in which case, however, the differences between $E_{H(s)}$ and E_H are somewhat greater. This behavior is also to be expected. $E_{OH(s)}$ is identical with E_{OH} for the 0.01 M potassium hydroxide—chloride series. This indicates a greater negative liquid potential change than in the case of the 0.1 M series. $E_{OH(s)}$ differs from E_{OH} by a slightly greater negative amount in the 0.01 M than in the 0.1 M sodium hydroxide—chloride series. These results, therefore, agree with the ordinary qualitative considerations of the liquid junction behaviors.

(b) Analysis of the Thermodynamic Method of computing
Liquid Junction Potentials.

Let us bring together two solutions containing ions of different kinds of which the ion i is of the i^{th} kind. Let us assume that between solution 1 and solution 2 there is a uniform mixing according to the assumption employed by Henderson. Across the boundary, the decrease in free energy accompanying the reversible transfer of 1 Faraday at constant temperature and pressure will be

$$(-dF) = NFdE_e = - \sum RTt_i d \ln a_i \quad (5)$$

where t_i and a_i are the transference number and activity of the ion of the i^{th} kind. The summation is to be taken for all the ions. The liquid junction potential, E_l , may then be evaluated by integrating each integral throughout the region of mixing or between the limits 1 and 2 where 1 refers to solution 1 and 2 to solution 2. Thus

$$E_l = - \sum \frac{RT}{NF} \int_1^2 t_i d \ln a_i \quad (6)$$

or for univalent ions which is the only case we shall consider,

$$E_l = - \sum 0.05915 \int_1^2 t_i d \log a_i \quad (7)$$

Now, since $\log a_i$ becomes minus infinity as m_i becomes zero, it is more convenient for our purposes to make use of the definition, $a_i = \gamma_i m_i$, and split equation (7) into two parts, one of which contains only the activity coefficients γ_i , and one which contains the molal concentrations, m_i . Thus, we obtain

$$E_l = - \left[\sum 0.05915 \int_1^2 t_i d \log \gamma_i + \sum 0.05915 \int_1^2 t_i d \log m_i \right] \quad (8)$$

The first integral may be more easily obtained than the integral of (7) since γ_i for a single electrolyte is defined so as to equal 1 when m_i equals zero. The second integral of equation (8) is recognized to be that which Henderson

¹ Wied. Ann., 39, 161 (1890); 40, 561 (1890).

² Z. physik. Chem., 59, 118 (1907); 63, 325 (1908).

evaluated except that we shall employ molal concentrations. Thus, the second part of E_1 which we shall denote E_m will be given by Henderson's equation, or

$$E_m = -0.05915 \frac{(U_1 - V_1) - (U_2 - V_2)}{(U_1' + V_1') - (U_2' + V_2')} \log \frac{U_1' + V_1'}{U_2' + V_2'}$$

where

$$\begin{aligned} U_1' &= U_1 = \bar{u}_1 \bar{m}_1 + \bar{u}_2 \bar{m}_2 + \bar{u}_3 \bar{m}_3 + \dots \\ V_1' &= V_1 = \bar{v}_1 \bar{m}_1 + \bar{v}_2 \bar{m}_2 + \bar{v}_3 \bar{m}_3 + \dots \\ U_2' &= U_2 = \bar{u}_1' \bar{m}_1' + \bar{u}_2' \bar{m}_2' + \bar{u}_3' \bar{m}_3' + \dots \\ V_2' &= V_2 = \bar{v}_1' \bar{m}_1' + \bar{v}_2' \bar{m}_2' + \bar{v}_3' \bar{m}_3' + \dots \end{aligned}$$

and where U_1 , etc. refer to solution 1, U_2 etc. to solution 2, u_1 and \bar{u}_1 etc. are the mobilities of the cations and anions in solution 1, and \bar{u}_1' and \bar{u}_1'' etc. are the mobilities of the same in solution 2. The second term on the right of (8) may be regarded as solved if our assumption concerning the mixing of the solutions is correct, and we may write

$$E_1 = - \left[\sum 0.05915 \int_1^2 t_i d \log \gamma_i + E_m \right] \quad (9)$$

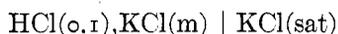
The summation of the integrals in this equation is the value which we must add to E_m in order to obtain E_1 .

Equation (9) contains a part which depends on the concentrations of the ions, but it also contains a part which is a function of the " γ_i 's" or the thermodynamic coefficients of each of the ions taken individually. Thus in order to obtain E_1 , we must know the " γ_i 's" but in order to evaluate the " γ_i 's" by this thermodynamic method, we must know E_1 . Thus, thermodynamics leads us into a circular situation from which it is at once clear that the above qualitative discussion cannot be regarded as a proof of our postulates. All we can say is that such a uniform distribution of the results for E_H , E_{OH} , and $E_{H(s)}$, $E_{OH(s)}$ would not be obtained if our postulates were not a first approximation. Further, any postulates which lead to the evaluation of the individual ion activities are equivalent to an evaluation of the liquid junction potentials. That is to say, if we should employ values of the activity coefficients of the individual ions calculated by our postulates in equation (9), we should obtain values of E_1 which should be just equal to the estimated liquid junctions if our experimental results are consistent and if we are measuring reversible electromotive forces. To illustrate, if from the values of the activity coefficients of the hydrogen, potassium and chloride ions throughout the mixtures HCl(o.1), MCl(m) to KCl(sat) were evaluated by means of our postulates and E_1 then calculated by equation (9), then E_1 would be found to equal $E_{H(s)} - E_H$. From this, we see that it is illegitimate to use equation (9) in order to verify our postulates.

Then, to what end may we employ this general thermodynamic equation? The answer is merely to test whether the estimated liquid junction potentials agree with the Henderson assumption regarding the mixing of the solutions, to test the consistency of the experimental results, and to show that such apparent anomalies as the distribution of curves of E_{OH} and $E_{OH(s)}$ for the

potassium and sodium chloride solutions (Fig. 1) are really not anomalies or caused by experimental error. Further, it is instructive to carry the thermodynamic analysis of liquid junction potentials further than Henderson, and thus show the approximate nature of Henderson's equation. To this end, we shall employ equation (9) in a further analysis of the simplest liquid junctions which we have to consider.

(c) Analysis of the Liquid Junction Potentials at the Boundaries:



where m is varied from 0 to 3.

Since we are dealing with ratios of ionic mobilities, we have employed the ionic conductances at 18° in place of the mobilities. The ratios of these quantities do not vary greatly between 18° and 25°. Thus, we have taken Λ_{H} , Λ_{K} , and Λ_{Cl} to be 314.5, 64.5, and 65.5, respectively, and employed these in calculating the transference numbers¹. We have also taken the mobilities to be invariant with respect to the total concentration. All concentrations are expressed in mols per 1000 gs. water.

E_m was calculated by Henderson's formula at 0, 0.3, 0.5, 1, 2, and 3M potassium chloride concentrations and the values obtained are given in the second column of Table V.

We have now to determine the value of the integrals, $E_{\gamma_i} = 0.05915 \int_1^2 t_i d \log \gamma_i$ for the hydrogen, potassium, and chloride ions and sum them up according to equation (9). Since the integration is to extend between solution 1 and solution 2, it is necessary to know $\log \gamma_i$ as a function of t_i throughout the intermediate solutions for each of these ions. Since we have no analytical expression for this variation, we have resorted to a graphical integration. That is, we have plotted t_i against $\log \gamma_i$ for the three ions and for values of m equal to 0.0, 0.3, 0.5, 1, 2, and 3, and determined the integrals by evaluating the corresponding areas.

Firstly, it is necessary to evaluate $\log \gamma_i$ at definite total concentrations between solution 1 and solution 2. Thus, if solution 1 is HCl(0.1),KCl(0.3), then in mixing all total concentrations between 0.4 and 4.8, or pure saturated potassium chloride will occur. Now, we make the following assumptions:

(1) γ_{H} throughout these mixtures of decreasing hydrochloric acid content is the same as in a mixture of 0.1 acid and potassium chloride at the same total concentration. This is known to be very nearly true as a result of the law of the linear variation of $\log \gamma$ at a given total concentration². According to this law, there is little difference between $\log \gamma_{\text{H}}$ in a 0.1 acid - (m) salt mixture and a 0.0 acid - (m + 0.1) salt mixture.

(2) γ_{K} equals γ_{Cl} at the same total concentration. Thus, γ_{K} in HCl(0.1), KCl(m) equals γ_{Cl} in this mixture. When m equals zero, γ_{K} will equal γ_{Cl} in 0.1 HCl. This is our postulate (2).

¹ Since the final values for E_1 are small, no great error is caused by these assumptions. All calculations were made with a 20-inch slide rule.

² Harned: J. Am. Chem. Soc., **48**, 326 (1926).

The values of γ_i and $\log \gamma_i$ obtained by the use of these assumptions are given in Table III.

TABLE III

Activity Coefficients of the Hydrogen, Potassium, and Chloride Ions

m	$E_{H^{(x)}}$	γ_H	$\log \gamma_H$	$\gamma_K = \gamma_{Cl}$	$\log \gamma_K = \log \gamma_{Cl}$
0.0	0.0000	0.842	9.925	0.779	9.891
0.3	-0.0002	0.835	9.922	0.675	9.829
0.5	0.0002	0.849	9.929	0.645	9.810
I.	0.0022	0.920	9.968	0.608	9.784
2.	0.0077	1.136	0.0555	0.566	9.756
3.	0.0128	1.385	0.141	0.577	9.761
4.8	0.0220	1.985	0.298	0.620	9.792

It is now necessary to calculate the "t_{i,s}" throughout the mixtures. In the present case

$$t_H = \frac{\Lambda_H m_{H^{(1)}} x}{\sum \Lambda_i m_{i^{(1)}} x + \sum \Lambda_i m_{i^{(2)}} (1-x)} = \frac{\Lambda_H m_{H^{(1)}} x}{S}$$

$$t_{Cl} = \frac{\Lambda_{Cl} m_{Cl^{(1)}} x + \Lambda_{Cl} m_{Cl^{(2)}} (1-x)}{S}$$

$$t_K = \frac{\Lambda_K m_{K^{(2)}} (1-x)}{S}$$

where x is the degree of mixing or the percentage of solution 1 in the mixed layer divided by 100 at the concentration in question. Thus, if we consider the boundary HCl(0.1) | KCl(4.8), we have all the intermediate mixtures between these concentrations. We select convenient total concentrations such as 0.4, 0.6, etc. and calculate x by assuming a uniform mixing law. Thus, we find that at 0.4 M, x equals 0.937, at 0.6 M, x equals 0.895 etc. These values are sufficient for calculating the "t_{i,s}" of our first integral. Then, in a similar manner, we consider the boundary HCl(0.1), KCl(m) | KCl(4.8), compute the degrees of mixing and calculate the "t_{i,s}" at 0.6 M, 1.1 M total concentrations etc, etc. All these results are given in Table IV. The first column contains the values of m at the intermediate concentrations. The columns with Roman numerals contain the values of the "t_{i,s}" at the total concentrations m . I, II, III, IV, V, and VI refer to the boundaries: HCl(0.1), KCl(m) | KCl(4.8) where the solutions 1 contain salt at concentrations 0.0, 0.3, 0.5, 1, 2, and 3, respectively. Thus, if we consider the boundary HCl(0.1), KCl(0.5) | KCl(4.8), in an intermediate solution at a total concentration of 2, t_H , t_K , t_{Cl} will be 0.073, 0.455, 0.473, respectively. I, II, etc. are the values which we shall employ in our integrals and which we shall designate integrals I, II, etc.

¹ This calculation was made before Table II in this paper was compiled. The values of E_H are somewhat different from those in Table II.

TABLE IV

Transference Numbers of the Hydrogen, Potassium, and Chloride Ions

m	I	II	t_H III	IV	V	VI
0.0	0.828	—	—	—	—	—
0.3	0.394	0.408	—	—	—	—
0.5	0.283	0.294	0.305	—	—	—
1.	0.154	0.161	0.170	0.187	—	—
2.	0.051	0.068	0.073	0.080	0.105	—
3.	0.029	0.030	0.032	0.036	0.049	0.073
4.8	0.0	0.0	0.0	0.0	0.0	0.0

m	I	II	t_K III	IV	V	VI
0.0	0.0	—	—	—	—	—
0.3	0.260	0.251	—	—	—	—
0.5	0.327	0.320	0.313	—	—	—
1.	0.404	0.400	0.394	0.384	—	—
2.	0.458	0.457	0.455	0.448	0.433	—
3.	0.479	0.478	0.477	0.475	0.467	0.452
4.8	0.496	0.496	0.496	0.496	0.496	0.496

m	I	II	t_{Cl} III	IV	V	VI
0.0	0.172	—	—	—	—	—
0.3	0.346	0.340	—	—	—	—
0.5	0.391	0.386	0.381	—	—	—
1.	0.442	0.438	0.436	0.429	—	—
2.	0.478	0.475	0.473	0.472	0.462	—
3.	0.499	0.491	0.491	0.489	0.484	0.476
4.8	0.504	0.504	0.504	0.504	0.504	0.504

In Figs. 2 and 3, the values of $\log \gamma_i$ in Table III have been plotted against the values of t_i in Table IV. Integral I refers to the boundary $HCl(0.1) | KCl(4.8)$, integral II to the junction $HCl(0.1), KCl(0.3) | KCl(4.8)$, etc., up to integral VI which corresponds to $HCl(0.1), KCl(3) | KCl(4.8)$. There are in all 18 integrals, six for each ion. The scale was chosen so that 100 sq. cm. equalled 0.000296 volt. Each integral is designated according to the ion considered. Thus H-I is the first integral of the hydrogen ion. 1 and 2 refer to solutions 1 and 2. The sign of the integral is also given. From these plots the values of the integrals were obtained by counting squares, and these in volts are given in Table V. These are added to E_m , and their negative according to equation (9) is E_i .

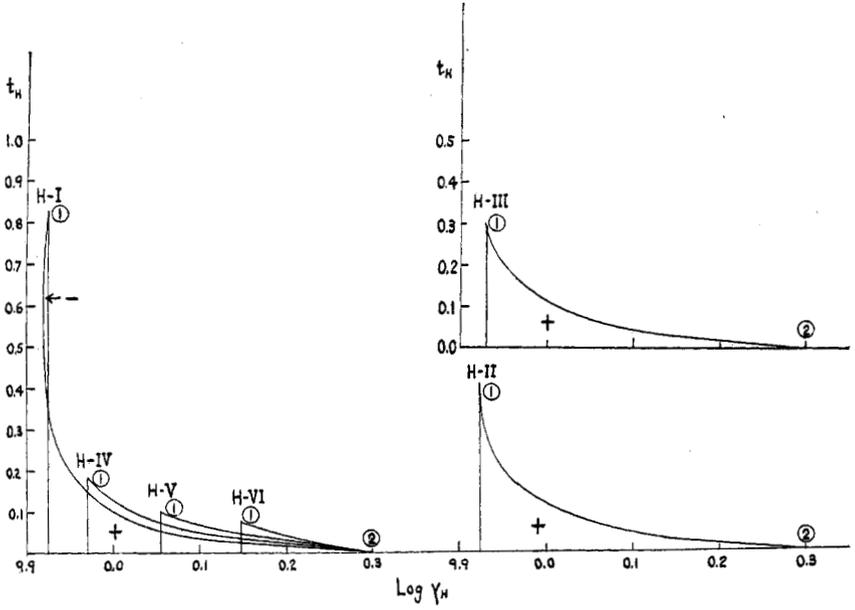


FIG. 2
Hydrogen Ion Integrals

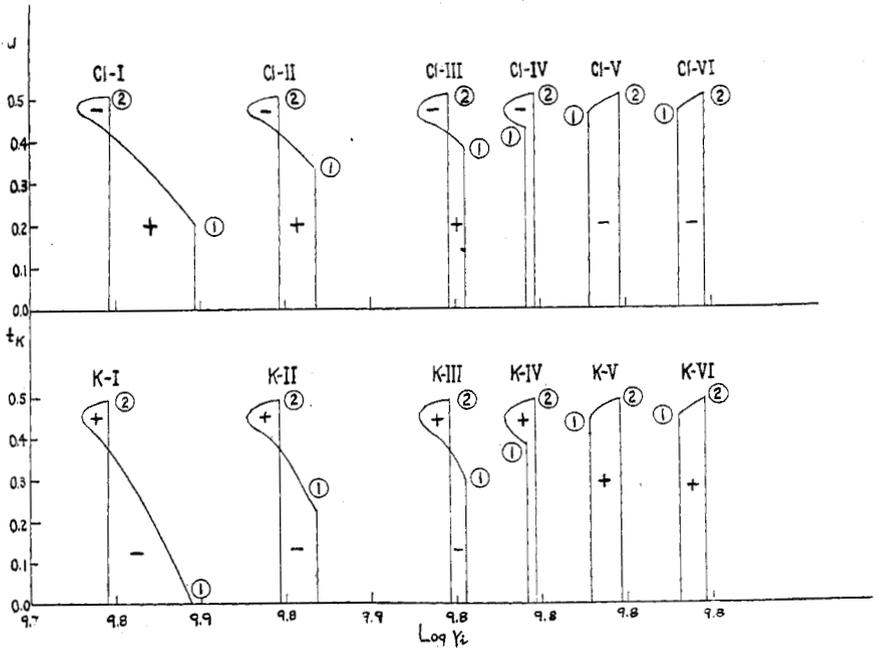


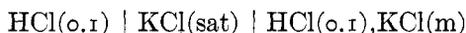
FIG. 3
Potassium and Chloride Ion Integrals

TABLE V

Liquid Junction Potentials by Equation (9)

m	E_m	$E\gamma_{(H)}$	$E\gamma_{(K)}$	$E\gamma_{(Cl)}$	E_1	ΔE_1	$E_{H(s)}-E$
0.0	-0.00363	0.00130	-0.00103	0.00178	0.00158	0.00000	0.0000
0.3	-0.00289	0.00152	-0.00053	0.00085	0.00105	0.00052	0.0006
0.5	-0.00258	0.00148	-0.00021	0.00042	0.00089	0.00069	0.0008
1.	-0.00192	0.00107	-0.00038	-0.00035	0.00082	0.00076	0.0008
2.	-0.00161	0.00060	0.00104	-0.00088	0.00085	0.00073	0.0008
3.	-0.00123	0.00027	0.00087	-0.00083	0.00082	0.00076	0.0008

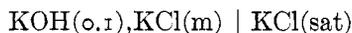
In the next to last column, the values of ΔE_1 or the calculated sum of the liquid junction potentials



are given. These are positive and agree very well as they should with the differences $E_{E(s)}-E_H$ computed from the results in Table II and given in the last column.

It is very important to emphasize at this juncture the fact previously mentioned that this does not constitute a proof of the second of our postulates. To illustrate this, another calculation was made in which we assumed that E_H was 0.0003, 0.0005, 0.001, 0.002, and 0.003 volts less than in our first calculation at 0.3, 0.5, 1, 2, and 3 M salt concentrations. With these new values, $\log \gamma_H$, $\log \gamma_K$, and $\log \gamma_{Cl}$ were calculated, and the above calculation of E_1 repeated. We obtained 0.0012, 0.0013, 0.0016, 0.0030, and 0.0035 for ΔE_1 which agree as well as could be expected with the new values of $E_{H(s)}-E_H$, namely, 0.0009, 0.0013, 0.0018, 0.0028, and 0.0038 volts at values of m equal to 0.3, 0.5, 1, 2, 3, respectively.

(d) Analysis of the Liquid Junction Potentials at the Boundaries:



In a similar manner, we have computed the liquid junction potentials at the boundaries between potassium hydroxide—chloride solutions and saturated potassium chloride. As in the first calculation we have assumed that $\log \gamma_K$ equals $\log \gamma_{Cl}$ at a given concentration. Δ_{OH} has been taken to be 174. In Fig. 4, the values of $\log \gamma_{OH}$ are shown plotted against t_{OH} . The plots for the potassium and chloride ions are similar to those in Fig. 3 so they have not been given. The integrals I-OH and II-OH differ considerably from the corresponding ones for the hydrogen ion in Fig. 2, and also from each other. Thus, as shown by Table VI, the first of these integrals equals 0.00106 and the second equals -0.00006 volts. This has an effect which causes the sign of ΔE_1 to be opposite to that which would be obtained by Henderson's equation, or which would be expected from the ordinary qualitative considerations. The values of E_m , $E\gamma_{(s)}$, E_1 , ΔE_1 and $E_{OH(s)} - E_{OH}$ are given in Table VI.

TABLE VI

Calculations according to Equation (9)

m	E_m	$E\gamma(\text{OH})$	$E\gamma(\text{K})$	$E\gamma(\text{Cl})$	E_1	ΔE_1	$E_{\text{OH}(s)} - E_{\text{OH}}$
0.0	0.00088	+0.00106	-0.00218	0.00130	-0.00106	0.00000	0.0000
0.3	0.00066	-0.00006	-0.00085	0.00070	-0.00045	0.00061	0.0007
0.5	0.00063	-0.00021	-0.00040	0.00029	-0.00031	0.00073	0.0009
1.	0.00056	-0.00024	0.00042	-0.00035	-0.00032	0.00079	0.0011
2.	0.00049	-0.00016	0.00104	-0.00119	-0.00033	0.00083	0.0012
3.	0.00046	-0.00006	0.00090	-0.00110	-0.00039	0.00087	0.0013

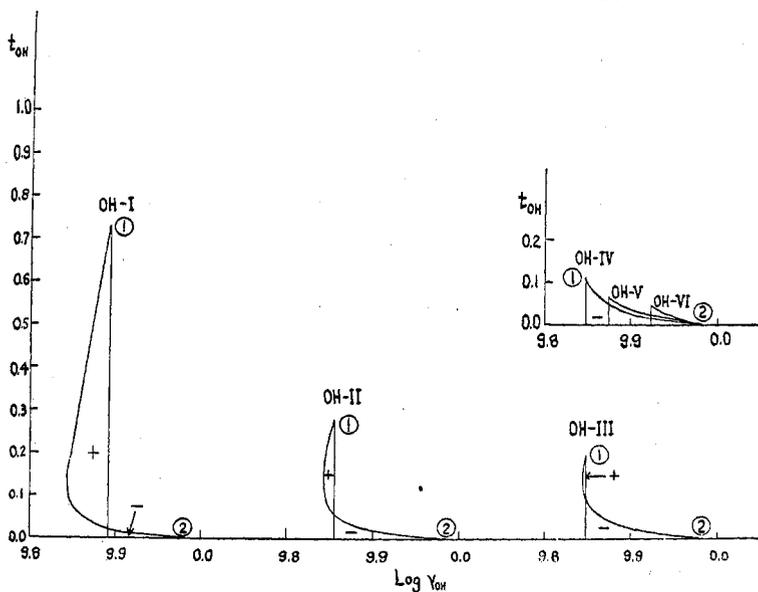


FIG. 4
Hydroxyl Ion Integrals

In order to fit the previous conventions, ΔE_1 is obtained by subtracting $E_{1(o)}$ from $E_{1(m)}$, is positive, and corresponds to the sum of the liquid junction potentials of the system



The agreement between ΔE_1 and $E_{\text{OH}(s)} - E_{\text{OH}}$ is again very good considering the complicated calculation. It is particularly interesting to note that the sign of $E_{\text{OH}(s)} - E_{\text{OH}}$ which at first glance appeared to be anomalous agrees with the calculated by the general equation.

A like consistency was found for similar calculations of the potentials $\text{HCl}(o.o.I)$, $\text{KCl}(m) \mid \text{KCl}(\text{sat})$, and $\text{KOH}(o.o.I)$, $\text{KCl}(m) \mid \text{KCl}(\text{sat})$. Cases of the junctions such as $\text{HCl}(o.I)$, $\text{NaCl}(m) \mid \text{KCl}(\text{sat})$ are much more complicated involving as they do four ions, and a knowledge of the variation of γ_{Na} and γ_{K} in mixed potassium and sodium chloride solutions. A simple but

approximate mixture law was assumed, and a similar calculation was made for the junctions, $\text{HCl}(\text{o.1}), \text{NaCl}(\text{m}) \mid \text{KCl}(\text{sat}), \text{HCl}(\text{o.1}), \text{LiCl}(\text{m}) \mid \text{KCl}(\text{sat})$, etc. Suffice it to say that fairly good agreements between $E_{\text{H}(\text{s})} - E_{\text{H}}$ and ΔE_1 were obtained.

(e) A Summary of the Above Analysis of the Thermodynamic Calculation of Liquid Junction Potentials.

(1) It is shown that Henderson's equation does not give the liquid junction potential but only part of it. The other part can only be determined thermodynamically by the evaluation of the expression

$$\sum_{\text{I}} 0.05915 \int_1^2 t_i d \log \gamma_i.$$

To do this, a knowledge of the individual activity coefficients, the " γ_i 's", of all the ions involved must be known as a function of the transference numbers, the " t_i 's", throughout all mixtures between solutions 1 and 2.

(2) Henderson's assumption of uniform mixing of the two solutions leads to correct results as far as can be determined by the above data. In other words, the method of measuring the liquid junctions here employed seems to agree with Henderson's mixing assumption.

(3) The calculations prove that our experimental results are consistent. This is important since it is good evidence that we are measuring reversible electromotive forces in all cases.

(4) The "apparent anomaly" of the sign of the liquid potentials of the junctions, $\text{KOH}(\text{o.1}), \text{KCl}(\text{m}) \mid \text{KCl}(\text{sat}) \mid \text{KOH}(\text{o.1})$, is shown to be in accord with calculations by the general equation.

(5) It is shown that the thermodynamic liquid junction calculation cannot be used to prove or disprove the validity of postulates I and II. Our earlier conclusions on the question of the independent ion activities depend only on the conviction that unless these postulates are an approximation, the distribution of the curves in Fig. 1 would not be observed. This is a point which we have had in mind from the beginning of these investigations.

(4) *Comparison with the Results of the General Theory of Debye and Hückel:*

In a recent publication, Hückel¹ has considered the problem of the individual ion activity coefficients in the light of his extension of the theory of Debye and Hückel², and as a result has found a qualitative but not a quantitative agreement with the postulate of the additivity of the relative partial free energies of the ions of the alkaline chlorides and hydrochloric acid. In view of the difficulty in obtaining the individual activity coefficients by direct measurement which certainly has been made obvious by the preceding discussion of the liquid junction potentials, this qualitative agreement is encouraging. It will therefore be of considerable interest to compare the results obtainable

¹ Physik. Z., 26, 93 (1925).

² Physik. Z., 24, 185 (1923).

from Debye and Hückel's theory with those derived by means of our postulates. To do this, we shall calculate the chloride ion activity coefficients of the chlorides by Hückel's general equations.

Following Hückel's procedure, we let

$$\log f_{\text{Cl}} = \log f_{\text{Cl}}^{\circ} + \log f_{\text{Cl}}^{\times} \quad (10)$$

where f_{Cl} is equal to a_{Cl}^1/N where a_{Cl}^1 is the activity of the chloride ion and N is mol fraction. From f_{Cl} , γ_{Cl} or a_{Cl}^1/m may be obtained by the equation

$$\log \gamma_{\text{Cl}} = \log f_{\text{Cl}} - \frac{1}{2} \log (1 + 0.036m). \quad (11)^1$$

From equations (64), (68), and (85a) in Hückel's paper, we obtain

$$\begin{aligned} \log f_{\text{Cl}}^{\circ} = & -0.354 \sqrt{\Gamma}^2 \left[\frac{1}{2 x_{\text{Cl}}^{\circ}} - \frac{1}{x_{\text{Cl}}^{\circ 2}} + \frac{1}{x_{\text{Cl}}^{\circ 3}} \text{lu} (1 + x_{\text{Cl}}^{\circ}) \right] \\ & + \frac{3}{2} \left[\frac{1}{x_{\text{Cl}}^{\circ 2}} + \frac{1}{x_{\text{Cl}}^{\circ 2}} \frac{1}{1+x_{\text{Cl}}^{\circ}} - \frac{2}{x_{\text{Cl}}^{\circ 3}} \text{lu} (1 + x_{\text{Cl}}^{\circ}) \right] \\ & + \frac{3}{2} \left[\frac{1}{x_{\text{M}}^{\circ 2}} + \frac{1}{x_{\text{M}}^{\circ 2}} \frac{1}{1+x_{\text{M}}^{\circ}} - \frac{2}{x_{\text{M}}^{\circ 3}} \text{lu} (1 + x_{\text{M}}^{\circ}) \right] \quad (12)^* \end{aligned}$$

where Γ equals $2c$, and

$$x^{\circ} = 0.232 \times 10^8 a_i \sqrt{2c}$$

where a_i is the apparent ionic diameter of the ion and c is the normal concentration.

According to equation (85b) in Hückel's paper, we obtain

$$\begin{aligned} \log f_{\text{Cl}}^{\times} = & 0.0194 \times 10^{-8} \Gamma \left[\frac{1}{a_{\text{Cl}}} \frac{1}{1 + A_{\text{Cl}} \sqrt{2c}} \frac{\delta_{\text{M}} + \delta_{\text{Cl}}}{2} + \frac{\delta_{\text{Cl}}}{2} \left[\frac{1}{a_{\text{Cl}}} \right. \right. \\ & \left. \left. \frac{1}{1 + A \sqrt{2c}} + \frac{1}{a_{\text{M}}} \frac{1}{1 + A_{\text{M}} \sqrt{2c}} \right] \right] - 0.00225 \Gamma^{3/2} \frac{\delta_{\text{M}} + \delta_{\text{Cl}}}{2} \left[\frac{1}{2} \right. \\ & \left. \frac{1}{[1 + A_{\text{Cl}} \sqrt{2c}]^2} + \frac{1}{2} \frac{1}{[1 + A_{\text{M}} \sqrt{2c}]^2} \right] + 0.000246 \times 10^{-8} c^2 (\delta_{\text{M}} + \delta_{\text{Cl}}) \\ & \left\{ \frac{1}{a_{\text{Cl}}} \left[\frac{3}{4} \frac{1}{1 + A_{\text{Cl}} \sqrt{2c}} + \frac{1}{4} \frac{1}{[1 + A_{\text{Cl}} \sqrt{2c}]^2} \right] (\delta_{\text{M}} + \delta_{\text{Cl}}) + \frac{2\delta_{\text{Cl}}}{a_{\text{Cl}}} \left[\frac{3}{4} \right. \right. \\ & \left. \frac{1}{1 + A_{\text{Cl}} \sqrt{2c}} + \frac{1}{4} \frac{1}{[1 + A_{\text{Cl}} \sqrt{2c}]^2} \right] + \frac{2\delta_{\text{Cl}}}{a_{\text{M}}} \left[\frac{3}{4} \frac{1}{1 + A_{\text{M}} \sqrt{2c}} + \frac{1}{4} \right. \\ & \left. \left. \frac{1}{[1 + A_{\text{M}} \sqrt{2c}]^2} \right] \right\} \quad (13) \end{aligned}$$

¹ Scatchard: J. Am. Chem. Soc., 47, 2098 (1925); Harned: 48, 326 (1926).

* The second member on the right of Equation (68) in Hückel's paper should be positive.

In this equation, A_i equals $0.232 \times 10^8 a_i$, and δ_i is a constant characteristic of the effect of the ion on the dielectric constant of the medium.

In this calculation, we have employed the values of the constants obtained in another paper¹. We have assumed that both the apparent ionic diameters of the potassium and chloride ions and their δ values are identical according to the second of our postulates, and have calculated the values of a_i and δ_i for the other ions upon this assumption. The values of these constants are given in Table VII. By using these constants in equation (11), (12), and (13), the values of γ_{Cl} given in this table were calculated.

TABLE VII
Activity Coefficients of the Chloride Ion in Uniunivalent Chlorides
according to Hückel's General Equations

(1) Constants				
Ion	$a_i \times 10^8$		δ_i	
H ⁺	3.38		20.6	
Li ⁺	3.84		19.8	
Na ⁺	3.82		8.6	
K ⁺	3.38		3.2	
Cl ⁻	3.38		3.2	
(2) γ_{Cl}				
c	γ_{Cl} (KCl)	γ_{Cl} (NaCl)	γ_{Cl} (LiCl)	γ_{Cl} (HCl)
0.5	0.654	0.665	0.695	0.700
1.0	0.607	0.629	0.686	0.698
2.0	0.578	0.613	0.747	0.775

As a result, we find that the activity coefficient of the chloride ion is greater in the solution of the electrolyte which has the greater activity coefficient. The differences between the results from Debye and Hückel's theory and our postulate (1) correspond to 0.4, 1.5, 1.8, millivolts at 0.5 N; 0.9, 3.1, and 3.7 millivolts at 1 N; and 1.5, 6.5, and 7.5 millivolts at 2 N in the cases of sodium and lithium chlorides and hydrochloric acid solutions, respectively. To make this comparison more clear, the values of E_H and E_{OH} in the 0.1 M hydrochloric acid-salt mixtures and the 0.1 M hydroxide salt series have been calculated from these values of γ_{Cl} and the results are shown plotted against the molal salt concentrations in Fig. 5. The dashed lines are the values obtained by our postulates and previously shown in Fig. 1. The full lines are those obtained by Hückel's equations.

A small difference in distribution of the curves of E_H and E_{OH} in the potassium and sodium chloride solutions as predicted by the two theories is noticeable. E_H in the lithium chloride solution as predicted by Hückel's equation lies considerably closer to E_H in the sodium chloride solutions than does the

¹ J. Am. Chem. Soc., 48, 0000 (1926).

dashed line of our earlier theory. The general similarity of distribution of these plots requires no further comment. Like calculations leading to a somewhat closer agreement were obtained for the activity coefficient of the chloride ion in the alkaline earth chloride solutions but this question need not be considered here.

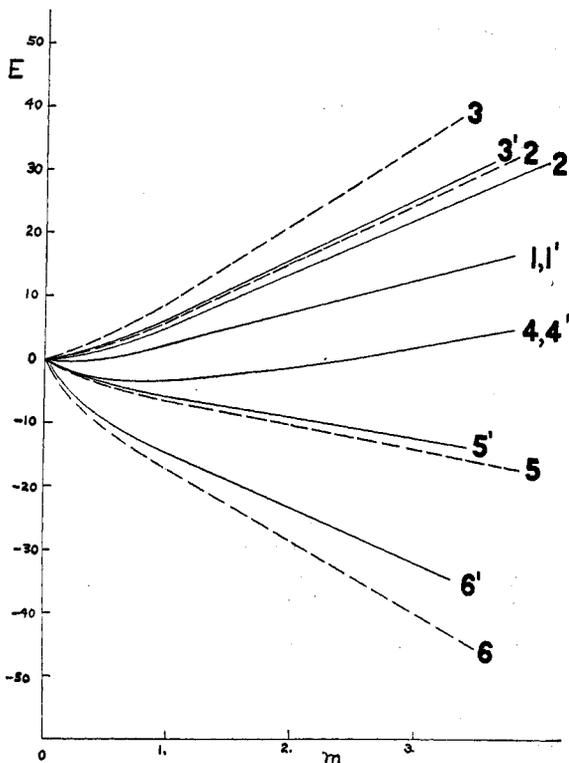


FIG. 5

Comparison of E_H and E_{OH} (Fig. 1) with the Values obtained by Hückel's General Equations.

1, 2, 3, 4, 5, and 6, are taken from Fig. 1.

1', 2', 3', 4', 5', and 6', are the curves obtained by Debye and Hückel's general theory.

1,1'	$E_H(\text{HCl}(0.1), \text{KCl}(m))$
2,2'	$E_H(\text{HCl}(0.1), \text{NaCl}(m))$
3,3'	$E_H(\text{HCl}(0.1), \text{LiCl}(m))$
4,4'	$E_{OH}(\text{KOH}(0.1), \text{KCl}(m))$
5,5'	$E_{OH}(\text{NaOH}(0.1), \text{NaCl}(m))$
6,6'	$E_{OH}(\text{LiOH}(0.1), \text{LiCl}(m))$

(5) Theoretical Considerations:

In the last section, two series of results were compared, one of which depends on a probable conclusion based on experimental behaviors, and the other derived from a theory. It is not to be expected that the results from either of these methods are exact.

According to Debye and Hückel's theory, the difference between the activity coefficients of univalent ions of different kinds is due, firstly, to the dif-

ference in apparent ionic diameters, and, secondly, to the difference in effects of the ions of different kinds on the dielectric constant of the medium. The first of these causes turns out to be small since we find a small difference in ionic diameters of the ions here considered, and therefore this factor will be omitted in the following discussion. Hückel assumes that the dielectric constant, D , of the medium varies according to the linear law

$$D = D_0 - \sum \delta_i c_i \quad (14)$$

where D_0 is the dielectric constant of the pure solvent, δ_i is a constant characteristic of an ion of the i^{th} kind, and c_i is its concentration. The introduction of this equation into the theory leads to an equation for the activity coefficient of a strong electrolyte containing an approximately linear term which is found to conform with the behavior of uniunivalent and biunivalent chlorides, and hydrochloric acid in chloride solutions. D is supposed to be uniform between all the ions. That is to say the medium is considered macroscopically. δ_i is greater for the ion which appears to cause the greatest electrostriction in its immediate neighborhood. Thus, $\delta_{\text{Li}} : \delta_{\text{Na}} : \delta_{\text{K}}$ as 19.8 : 8.6 : 3.2 which is the order of their hydration values¹, a possible measure of electrostriction. This fact would suggest that the change in dielectric constant of the medium is not uniform but is greater in the immediate environment of the ions, or in the regions where the greatest electrostriction would occur, and that when we consider the individual activities, it may be necessary to take a microscopic point of view. According to this theory the variation of these microscopic dielectric constants would be expressed by

$$D_1 = D_0 - \delta_1' c ; D_2 = D_0 - \delta_2' c,$$

and these should be employed separately in calculating the individual ion activities of a uniunivalent electrolyte. Such a theory would lead to a result in conformity with our postulates. But this theory is seen to be an extreme point of view since it requires a change in dielectric constant of the solvent in the immediate neighborhood of the ions while the intermediate solvent is not influenced. Further, in mixtures at the same total concentrations, or total chloride ion concentration, this theory would require that as the cation concentrations were varied, the values of the dielectric constants in the immediate neighborhood of the cations should vary with changing cationic concentrations while that in the neighborhood of the chloride ion would not be influenced. Such a condition would not be expected to be strictly valid.

There is another important consideration which indicates that the true values lie between those calculated by the postulate of additivity and those predicted by Hückel's theory. Equation (14) cannot be valid in very concentrated solutions of electrolytes such as hydrogen, lithium, or calcium chlorides because the calculated δ - values are so high for these electrolytes that the dielectric constant, D , would pass through 0 and become negative in the neighborhood of 4M lithium chloride and 2M calcium chloride, a condition

¹ Washburn: *J. Am. Chem. Soc.*, **31**, 322 (1909); **35**, 751 (1913); **37**, 694 (1915).

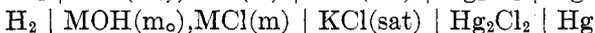
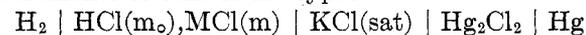
which is obviously an impossibility. If the general idea of the theory of Debye and Hückel is correct, that is to say that the dielectric constant change is the important factor in the concentrated solutions, then δ_i of the ions such as lithium, hydrogen and calcium ions and also the chloride ions must decrease with increasing concentration. Such a decrease would bring the results of Hückel's into closer agreement with those predicted by the postulate of additivity.

Looked at in this way, it would seem that both "the hypothesis of the independent ion activities" and Hückel's theory are extreme points of view. The first would require only a change in dielectric constant with changing electrolyte concentration in the immediate environment of the ion, the intermediate solvent not being influenced, and the second assumes a uniform dielectric between the ions. Such considerations would lead us to expect that the values of the individual ion activity coefficients should be somewhere between those predicted by these two theories. We have considered this question from the narrow point of view that the dielectric constant is the only factor to be considered. A similar argument could have been made if we had considered another factor or group of factors which would account numerically for the behaviors of these concentrated solutions.

Neither of these theories should be applied to solutions of ions other than the alkaline, alkaline earth metal, hydrogen and halide ions, which are characterized both by their simplicity and the symmetrical space distribution of electron orbits. The more complex ions such as NO_3^- , SO_4^{2-} or the unsymmetrical ions such as OH^- do not conform to the principle of additivity or to Debye and Hückel's theory unless some further factor be introduced.

Summary

- (1) Measurements of cells of the types



have been revised, completed, and tabulated.

- (2) These data have been considered from the point of view of "the hypothesis of the independent ion activity coefficients".

(3) A comprehensive study of the general thermodynamic method of computing liquid junction potentials has been made.

(4) The results from the "hypothesis of the independent ion activities" are compared with those obtained from Hückel's extension of the Debye and Hückel theory.

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