2. The presence of dissolved air as a source of error has been eliminated by a new method of preparing the solutions.

3. A mean deviation from Raoult's law of only 0.0006 mm. is observed up to 0.8 *M* concentration.

4. By comparison with freezing-point lowerings it is found that $ln\ p_0/p_1$ decreases with the temperature or, the heat of dilution is a small negative value for concentrations up to 0.5 *M*. Comparisons with boiling-point determinations show that this changes to a positive quantity in the higher concentrations.

BALTIMORE, MD.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA.]

THE THERMODYNAMIC PROPERTIES OF THE IONS OF SOME STRONG ELECTROLYTES AND OF THE HYDROGEN ION IN SOLUTIONS OF TENTH MOLAL HYDROCHLORIC ACID CONTAINING UNI-UNIVALENT SALTS.

BY HERBERT S. HARNED.

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Introduction.

In two earlier communications[1] from measurements of the electromotive forces of cells of the types

$H_2 \mid MeCl(c)$ in $HCl\ (0.1) \mid$ saturated $KCl \mid$ calomel electrode and

$Hg \mid HgCl \mid KCl\ (c + 0.1) \mid KCl\ (0.1) \mid HgCl \mid Hg$

$H_2 \mid KCl\ (c)$ in $HCl\ (0.1) \mid HgCl \mid Hg$,

the author has shown that the hydrogen ion activity of 0.1 *M* hydrochloric acid as measured by this method is increased by the addition of salts to the acid. On account of the difficulties attending the calculation of the electromotive forces of the cells

$$H_2 \mid MeCl\ (c) \text{ in } HCl\ (0.1) \parallel^2 HCl\ (0.1) \mid H_2$$

from the above data, due largely to the present incomplete knowledge of liquid junction potentials, and a distrust of some of the earlier interpretations of the results, this investigation has been extended with the object of obtaining the complete thermodynamic data at 25° for the last mentioned series of cells containing potassium, sodium, and lithium chlorides. In this manner, the so-called "neutral salt effect" has been studied in a more searching manner from the thermodynamic point of view.

From the point of view of the theory of solutions a number of important contributions have been made comparatively recently. The first in importance of these is the hypothesis of complete dissociation of strong

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[1] THIS JOURNAL, 37, 2460 (1915); 38, 1986 (1916).

[2] Double bar indicates that liquid potential has been eliminated.

electrolytes as developed by Milner,[1] Ghosh,[2] Bjerrum,[3] Brönsted,[4] and others. A second, which may be looked upon as a corollary of the first, is the hypothesis of the independent activities of ions, first clearly proposed and used by MacInnes.[5] During the course of the present investigation, a large quantity of data have been obtained which, along with the data recently obtained by others, will contribute evidence of the validity of both of these hypotheses within narrow limits of error, and, for this reason, Part II of this paper will consist in the proof and application of these principles to the calculation of the activity coefficients of the ions of single electrolytes. Since the greater part of this investigation consists of complicated numerical calculations, a more detailed discussion of these hypotheses will be reserved until later sections.

PART I. GENERAL THEORY AND MEASUREMENTS.

(1) General Theory and Nomenclature.

Throughout this work, the system and nomenclature of G. N. Lewis[6] have been employed. The activity ξ can be defined by the equation

$$\overline{\mathrm{F}} = \delta \mathrm{F}/\delta n = RT\ ln\ \xi + i \qquad (1)$$

where $\overline{\mathrm{F}}$ is the partial molal free energy, (Gibb's chemical potential. See Brönsted)[7] or the partial derivative of the free energy with respect to mass, F is the free energy, i a constant, R the gas constant, and T the absolute temperature.

If we refer $\overline{\mathrm{F}}$ in any state to its value in some chosen standard state, $\overline{\mathrm{F}}_0$, we have

$$\overline{\mathrm{F}} - \overline{\mathrm{F}}_0 = RT\ ln\ \xi/\xi_0 = RT\ ln\ a \qquad (2)$$

where ξ_0 is the activity in the standard state, and a is "the relative activity," a term used by Lewis. If the arbitrary state is so chosen that $\overline{\mathrm{F}}_0 = 0$ and $\xi_0 = 1$, then

$$\overline{\mathrm{F}} = RT\ ln\ a \quad \text{and} \quad \mathrm{F} = RT\ ln\ a \qquad (3)$$

and

$$\Delta\mathrm{F} = \mathrm{F}_2 - \mathrm{F}_1 = RT\ ln\ a_2/a_1 \qquad (4)$$

$$\Delta\mathrm{F} = \mathrm{F}_2 - \mathrm{F}_1 = RT\ ln\ \xi_2/\xi_1 \qquad (5)$$

Where ΔF is the increase in free energy.[8]

In a similar manner, we may relate $\overline{\mathrm{F}}$ to the partial molal heat content function $\overline{\mathrm{H}}$ by the equation

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[1] Milner, *Phil. Mag.*, [6] **23**, 551 (1912); **25**, 743 (1913); **35**, 352 (1918).

[2] Ghosh, *J. Chem. Soc.*, **113**, 449 (1918); **113**, 627 (1918); **113**, 707 (1918).

[3] Bjerrum, *Z. Elektrochem.*, **24**, 321 (1918); *Z. anorg. Chem.*, **109**, 275 (1920).

[4] Brönsted, *ibid.*, **42**, 761 (1920).

[5] MacInnes, *ibid.*, **41**, 1086 (1919).

[6] Lewis, THIS JOURNAL, **35**, 1 (1913).

[7] *Loc. cit.*

[8] The function F in Lewis' system always equals the Gibb's function ξ: that is, $\xi = e - t\eta + pv$.

$$\bar{\bar{F}} = -RT \ln w + \bar{\bar{H}} + i \qquad (6)$$

where w is the probability.[1] By the same reasoning as the above

$$\Delta F = -RT \ln w_2/w_1 + \Delta H \qquad (7)$$

where ΔH is the increase in heat content function. ΔH can be computed from the ξ and w functions by

$$\Delta H = RT \ln \xi_2/\xi_1 + RT \ln w_2/w_1. \qquad (8)$$

In very dilute solutions ΔH is small, and hence the probability ratio will approach the reciprocal of the activity ratio.

In order to evaluate ΔH from measurements of ΔF, it is necessary to determine ΔF at different temperatures and express ΔF as a function of T, then substitute this value in the fundamental thermodynamic equation

$$\frac{d\,(\Delta F/T)}{dT} = -\frac{\Delta H}{T^2} \qquad (9)$$

or the equivalent expression

$$\Delta H = \Delta F - T\,d\Delta F/dT, \qquad (10)$$

perform the differentiation, and, from the numerical equation thus obtained, make the required calculations. In cases where ΔF cannot be conveniently expressed as a function of T, an approximation can be made by determining the temperature coefficient of free energy at the desired temperature and substituting this value for $d\Delta F/dT$ in Equation 10.

For the sake of brevity, the following system of nomenclature has been adopted for the 5 cells most frequently referred to in the calculations. The cells are

Type 1. $H_2 \mid MeCl\ (c)$ in $HCl\ (0.1) \mid HgCl \mid Hg$.

Type 2. $Hg \mid HgCl \mid MeCl\ (0.1) \parallel$[2] $MeCl\ (c_1) \mid HgCl \mid Hg$ (where $c_1 = c + 0.1$).

Type 3. $Hg \mid HgCl \mid MeCl\ (0.1) \mid Me$ in $Hg \mid MeCl(c_1) \mid HgCl \mid Hg$.

Type 4. $H_2 \mid MeCl\ (c)$ in $HCl\ (0.1) \parallel HCl\ (0.1) \mid H_2$.

Type 5. $H_2 \mid MeCl\ (c)$ in $HCl\ (0.1) \mid$ sat. $KCl \mid HgCl \mid Hg$.

The electromotive forces of the above cells are denoted $\mathbf{E}(1)$, $\mathbf{E}(2)$, $\mathbf{E}(3)$, $\mathbf{E}(4)$, and $\mathbf{E}(5)$, respectively. Also, let $\mathbf{E}_0(1)$ equal $\mathbf{E}(1)$ when $c = 0$; $\mathbf{E}_0(4)$ equal $\mathbf{E}(4)$ when $c = 0$ and so on.

The relation between the decrease in free energy $(-\Delta F)$ of transfer of ions, the activities of the ions and the electromotive forces of the above cells can be obtained from Equations 4 and 5, and the well known equation $(-\Delta F) = n\mathbf{EF}$, where $\mathbf{E}$ is the electromotive force in volts, $\mathbf{F}$ is 96,500 coulombs, and n is the number of Faraday equivalents transferred. The following equations are of importance and will be referred to frequently throughout this work:

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[1] H is the Gibb's function ξ that is, $\xi = e + pv$.

[2] The double bar indicates that the liquid junction potential has been eliminated.

$$(-\Delta F)_1 = F(E_0(1) - E(1)) = RT\, ln\, \frac{a_{H(s)}a_{Cl(c+0.1)}}{a_{H(0.1)}a_{Cl(0.1)}}\text{[1]} \qquad (11)$$

$$(-\Delta F)_2 = F(E(2)) = RT\, ln\, \frac{\sqrt{a_{Cl(c_1)}a_{Me(c_1)}}}{\sqrt{a_{Cl(0.1)}a_{Me(0.1)}}} \qquad (12)$$

$$(-\Delta F)_3 = F(E(3)) = RT\, ln\, \frac{a_{Cl(c_1)}a_{Me(c_1)}}{a_{Cl(0.1)}a_{Me(0.1)}} \qquad (13)$$

$$(-\Delta F)_4 = F(E(4)) = RT\, ln\, \frac{a_{H(s)}}{a_{H(0.1)}} \qquad (14)$$

$(-\Delta F)$ is the decrease in free energy attending the ionic transfers indicated in the right-hand members of these equations. In other words, the transfer of an ion from the more concentrated to the more dilute solution is accompanied by a decrease in free energy. Formula 12 is true for a cell of Type 2 if the liquid junction potentials have been computed by a thermodynamic formula such as $E_l = E_t(1 - 1/2n_c)$.[2]

Besides the above, there will be occasion to refer to the independent free energies and electromotive forces of transfer of the individual ions. The following equations and nomenclature will be adopted:

$$\left.\begin{aligned}(-\Delta F)_{Na} &= FE_{Na} = RT\, ln\, \frac{a_{Na(c_1)}}{a_{Na(0.1)}}\\ (-\Delta F)_{Li} &= FE_{Li} = RT\, ln\, \frac{a_{Li(c_1)}}{a_{Li(0.1)}}\end{aligned}\right\} \qquad (15)$$

An other function which will be employed frequently is the activity coefficient F_a, which is defined by the equation

$$F_a = a/c \qquad (16)$$

where c is the concentration of the electrolyte in equivalents per 1000 g. of solvent.

(2) Measurements of the Cells.

H_2 | MeCl (c) in HCl (0.1) | HgCl | Hg.[3]

These measurements are similar to those reported by the author in one of the earlier papers[4] where MeCl was potassium chloride; but since, in the present instance, the temperature coefficients are desired, all the results are new. The technique of the hydrogen and calomel half-cells and their combinations has been carefully described by many recent

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[1] $a_{H(s)}$ refers to the activity of the hydrogen ion in HCl (0.1) + MeCl (c) solutions.

[2] This formula has been used in the earlier papers by the author (*loc. cit.*).

[3] As far as the author is aware, these results are the only ones on this type of cell in which the acid concentration has been kept constant and the salt concentration varied. Loomis, Essex and Meacham (THIS JOURNAL, **39**, 1133 (1917)), and Ming Chow (*ibid.*, **42**, 497 (1920)) have measured cells of the same type in which the total ion concentration was kept constant but not the concentration of the acid.

[4] *Loc. cit.*

workers, including Acree,[1] Harned,[2] Ellis,[3] Lewis, Brighton and Sebastian,[4] and others and need not be described in great detail in this paper. Considerable care was exercized throughout the work. All the materials employed were carefully purified. Four times distilled mercury was used. The calomel paste was made from this mercury. The solutions of salt in the acid were made up at 25° by weighing both the salt and a carefully analyzed portion of the constant-boiling-point hydrochloric acid distillate and diluting to the mark on a carefully calibrated flask.[5] In the following table of data, concentrations are expressed in both mols of salt per liter and mols per 1000 g. of water.

The design of the cell employed was similar to that described by Ellis and previously used by the author. The calomel paste for the calomel half-cell was washed by decantation 7 or 8 times with the solution to be employed, then stirred by rotation in a thermostat at 25° for one or two hours, and finally allowed to stand 3 or more days in a thermostat at 25° before being introduced in the cell. For further details, the earlier papers may be consulted. When made up, each cell was kept in a thermostat for one week and measurements taken from time to time at the different temperatures employed. When made up in this manner, excellent constancy was maintained throughout this period of time. The final values were the mean of the readings taken at the temperatures designated. The deviations from this mean were rarely more than 0.01 of a millivolt. Table I contains the final data at 18, 25 and 30°. The values of the complete cell are believed to be reproducible to within ±0.2 of a millivolt throughout the entire series; and the temperature coefficients to within ±0.005 millivolt. Column 1 contains salt concentration in mols per liter, and Column 2 salt concentration in mols per 1000 g. of water. The column headed p contains the actual pressures of the hydrogen in the hydrogen half-cell, computed from the barometric pressure and the vapor pressure of the solution at the concentration and temperature designated. The values under $\mathbf{E}$ are the observed electromotive forces at the temperature designated, and $\mathbf{E}(cr)$ are these electromotive forces corrected so that they equal the electromotive forces of the cells at just one atmosphere hydrogen pressure at the temperature indicated. The method of making this correction is described in detail in the earlier papers. The concen-

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[1] Acree, *Am. Chem. J.*, **46**, 632 (1911).

[2] Harned, This Journal, **37**, 2460 (1915).

[3] Ellis, *ibid.*, **38**, 737 (1916).

[4] Lewis, Brighton and Sebastian, *ibid.*, **39**, 2245 (1917).

[5] In the earlier communication, the salt was dissolved in HCl (0.1) and diluted to the mark with same. No correction was made at that time for the acid dilution due to the volume occupied by the salt. In cases of the higher concentrations of salt, this correction is considerable.

tration of the acid used was 0.1000 mol per liter, or 0.1004 mol per 1000 g. of water.

TABLE I.

Cells, H_2 | KCl (c) in HCl (0.1) | HgCl | Hg.

(1).	(2).	p_{18}.	E_{18}.	$E_{18}(cr)$.	p_{25}.	E_{25}.	$E_{25}(cr)$.	p_{30}.	E_{30}.	$E_{30}(cr)$.
0.0000[a]	0.0000	738	0.39749	0.39785	732	0.39851	0.39898	737	0.39923	0.39963
0.2000	0.2018	737	0.37329	0.37357	727	0.37366	0.37424	718	0.37374	0.37446
0.2000	0.2018	...	...	...	728	0.37366	0.37421	...	...	...
0.5000	0.5086	746	0.35697	0.35722	735	0.35697	0.35736	729	0.35671	0.35734
1.0000	1.0346	751	0.34043	0.34057	750	0.34012	0.34029	740	0.33968	0.34001
1.0000	1.0346	759	0.34056	0.34058	750	0.34014	0.34032	741	0.33972	0.34004
2.0000	2.134	757	0.31680	0.31686	748	0.31580	0.31618	739	0.31530	0.31566
2.0000	2.134	746	0.31665	0.31690	739	0.31588	0.31624	730	0.31519	0.31571
3.0000	3.309	744	0.29702	0.29727	737	0.29591	0.29631	728	0.29503	0.29557
3.0000	3.309	750	0.29738	0.29751	732	0.29606	0.29651	730	0.29534	0.29576
Cells, H_2 | NaCl (c) in HCl (0.1) | HgCl | Hg.										
0.1000	0.1003	751	0.38207	0.38222	743	0.38273	0.38298	743	0.38298	0.38338
0.2000	0.2014	746	0.37297	0.37319	739	0.37341	0.37379	730	0.37354	0.37408
0.3600	0.3636	...	...	...	740	0.36208	0.36243	...	...	...
0.5000	0.5061	750	0.35556	0.35570	741	0.35555	0.35587	730	0.35531	0.35585
0.6000	0.6085	...	...	...	745	0.35118	0.35142	...	...	...
0.9000	0.9183	752	0.34046	0.34062	749	0.34024	0.34044	732	0.33973	0.34018
1.000	1.023	752	0.33736	0.33745	745	0.33690	0.33716	736	0.33649	0.33688
1.200	1.243	...	...	...	743	0.33089	0.33119	...	...	...
1.800	1.871	750	0.31567	0.31581	743	0.31491	0.31521	734	0.31428	0.31473
1.985	2.078	...	...	...	748	0.31055	0.31079	...	...	...
2.000	2.094	755	0.31082	0.31088	749	0.31001	0.31021	736	0.30923	0.30962
2.565	2.711	754	0.29774	0.29794	736	0.29671	0.29696	738	0.29599	0.29635
3.000	3.202	732	0.28744	0.28789	743	0.28658	0.28688	716	0.28537	0.28612
3.452	3.726	760	0.27814	0.27814	750	0.27691	0.27709	738	0.27593	0.27630
Cells, H_2 | LiCl (c) in HCl (0.1) | HgCl | Hg.										
0.4165	0.4203	...	...	...	729	0.35814	0.35867	...	...	...
0.8342	0.8485	745	0.33906	0.33929	738	0.33881	0.33919	734	0.33854	0.33898
1.668	1.727	738	0.31203	0.31241	730	0.31144	0.31196	720	0.31084	0.31152
2.503	2.636	755	0.28858	0.28865	748	0.28773	0.28795	739	0.28693	0.28730
3.336	3.579	747	0.26559	0.26579	741	0.26452	0.26485	738	0.26369	0.26407
4.171	4.556	742	0.24238	0.24269	733	0.24107	0.24154	726	0.24003	0.24061

[a] The value of the cell without salt (c equals 0.0000) is the mean of 4 determinations.

PART II. ACTIVITY COEFFICIENTS.

Throughout the entire discussion and all the calculations which follow, the assumption has been made that all the electrolytes employed are completely dissociated over the entire concentration range.

(1) **The Hypothesis of the Independent Activities of Ions.**—MacInnes[1] first clearly proposed and used the following hypothesis which may be summed up in a general way by the two postulates.

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[1] *Loc. cit.*

1. The activities of the cation and anion of a solution of an electrolyte may differ from one another at a given concentration and temperature.

2. In solutions of the same strength (weight normal) and at the same temperature of different electrolytes possessing a common ion, the common ion will have the same activity independent of the ion or ions associated with it.[1]

If Postulate 2 is true, Postulate 1 will be true because the square roots of the activity products of different strong uni-univalent electrolytes have been observed to be different.

Postulate 1 has been suspected by numerous workers,[2] but had not been directly postulated and used before MacInnes' calculations; Postulate 2 as far as the author is aware, is entirely original with MacInnes.

The data obtained by the author in the earlier investigations along with the data presented in this paper can be used to test the validity of both of these postulates. Equations 11 and 14 are

$$\mathbf{E}_o(1) - \mathbf{E}(1) = \frac{RT}{\mathbf{F}}\, ln\, \frac{a_{\mathrm{H(s)}}}{a_{\mathrm{H(0.1)}}} + \frac{RT}{\mathbf{F}}\, ln\, \frac{a_{\mathrm{Cl}(c+0.1)}}{a_{\mathrm{Cl(0.1)}}}$$

and

$$\mathbf{E}(4) = \frac{RT}{\mathbf{F}}\, ln\, \frac{a_{\mathrm{H(s)}}}{a_{\mathrm{H(0.1)}}},$$

respectively.

By subtracting (14) from (11), the relation

$$\mathbf{E}_o(1) - \mathbf{E}(1) - \mathbf{E}(4) = \frac{RT}{\mathbf{F}}\, ln\, \frac{a_{\mathrm{Cl}(c+0.1)}}{a_{\mathrm{Cl(0.1)}}} \qquad (17)$$

is obtained. If Postulate 2 is correct, $\frac{RT}{\mathbf{F}}\, ln\, \frac{a_{\mathrm{Cl}(c+0.1)}}{a_{\mathrm{Cl(0.1)}}}$ should be the same at a given concentration in solutions containing each of the different salts; that is to say, the chlorine ion activity will be the same at a given salt concentration notwithstanding the fact that the cations differ.

In the earlier communication, an extended series of measurements was made of cells of Type 5 which contained potassium, sodium and lithium chlorides along with the 0.1 *M* hydrochloric acid in the hydrogen half-cell. At that time, it was thought that the potential between a solution of hydrochloric acid containing lithium chloride or sodium chloride and a saturated potassium chloride solution would be considerable. More recent work, particularly by Fales and Vosburgh,[3] show that the previous contentions are not true; nor are these liquid junction potentials calculable

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[1] This is a generalized statement of the hypothesis of MacInnes, who assumed that it was true of the chlorine ion in solutions of hydrochloric acid and potassium chloride.

[2] *E. g.*, Lewis, THIS JOURNAL, 34, 1640 (1912).

[3] Fales and Vosburgh, *ibid.*, 40, 1291 (1918).

by either Planck's or Henderson's formulas. Fales and Vosburgh find that the liquid potential between saturated potassium chloride and 0.1 *M* hydrochloric acid is 0.0000 volt; between saturated potassium chloride and 1 *M* hydrochloric acid is 0.0000 volt. Planck's formula gives 0.0046 and Henderson's formula 0.0048 volt for the first of the above liquid potentials. On the other hand, in all cases, the liquid potentials are much smaller than those predicted in the previous communication, probably in no case amounting to over one millivolt. For the present, let the approximation assumption be made that the liquid potentials at the saturated potassium chloride salt in acid boundary are zero for all concentrations of salt. Then it is possible to compute $E(4)$ from measurements of cells of Type 5 by using the expression $E(4) = E_o(5) - E(5)$. In Table II, Column 1 contains concentration of salt in mols per liter; Column 2, $E_o(1) - E(1)$ calculated from the data in Table I; Column 3, $E_o(5) - E(5) = E(4)$; and Column 4, $E_o(1) - E(1) - E(4)$, which by Equation 17 equals $\frac{RT}{F} \ln \frac{a_{Cl(c+0.1)}}{a_{Cl(0.1)}}$. The values of $E(4)$ have been read off the electromotive force—salt concentration plots of the earlier results supplemented by some more recent observations at the higher salt concentrations. These results are thought to be reproducible to within ±0.2 of a millivolt.

TABLE II.

	(1). c(mols)liter.	(2). $E_o(1) - E(1)$.	(3). $E(4)$.	(4). $\frac{RT}{F} \ln \frac{a_{Cl(c+0.1)}}{a_{Cl(0.1)}}$.
KCl................	0.2000	0.0247	0.0003	0.0244
	0.5000	0.0416	0.0012	0.0404
	1.0000	0.0587	0.0033	0.0554
	2.000	0.0828	0.0104	0.0724
	3.000	0.1026	0.0192	0.0834
NaCl................	0.2000	0.0252	0.0011	0.0241
	0.5000	0.0431	0.0030	0.0401
	1.000	0.0618	0.0070	0.0548
	2.000	0.0888	0.0176	0.0712
	3.000	0.1121	0.0300	0.0821
LiCl................	0.2000	0.0264	0.0020	0.0244
	0.5000	0.0452	0.0052	0.0400
	1.000	0.0661	0.0106	0.0555
	2.000	0.0966	0.0248	0.0718
	2.503	0.1110	0.0337	0.0773[a]

[a] Falls on the e. m. f., c plot of the potassium chloride and sodium chloride results.

There is excellent agreement, considering the sources of error due to the small liquid potentials, and to the quantity and nature of the data, between the values in Column 4 for the different salts at the same concentration. Throughout the entire range of concentration, the deviation is never greater than 1.3 millivolts. Hence, it may be said that the activity of the chlorine ion in these solutions is always the same within narrow limits at the same salt concentration and is not appreciably different when different ions are associated with the chlorine ion. This proves that Postulate 2 is correct to within narrow limits up to a concentration of 3.1 *N* chlorine ion, and confirms the truth of Postulate 1.

Postulate 3.—Another assumption made by MacInnes[1] is that at any given concentration of potassium chloride, the activities of the potassium and chlorine ions are the same. This assumption can be readily tested by the data in hand. In Table II, Column 4, $\frac{RT}{\mathbf{F}} ln \frac{a_{\mathrm{Cl}(c+0.1)}}{a_{\mathrm{Cl}(0.1)}}$ will correspond to electromotive forces of cells of Type 2 containing potassium chloride if the activities of the potassium and chlorine ions are the same at a given concentration. This can readily be seen from Equation 12. Table III shows this correspondence. Column 1 gives the concentration of salt in mols per liter plus 0.1, the acid concentration; Column (2) gives

$$\frac{RT}{\mathbf{F}} ln \frac{a_{\mathrm{Cl}(c+0.1)}}{a_{\mathrm{Cl}(0.1)}}.$$

taken from Table II, Column 4; Column 3 gives $\mathbf{E}_2$ (Equation 12) for potassium chloride, obtained from the data of Harned;[1] and Column 4 gives the differences between the values in Columns 3 and 2.

TABLE III.

(1).	(2).	(3).	(4).
$c_1 = c + 0.1$.	$\frac{\mathrm{RT}}{\mathbf{F}} ln \frac{a_{\mathrm{Cl}(c+0.1)}}{a_{\mathrm{Cl}(0.1)}}$.	$\mathbf{E}_2$(KCl)	Diff.
0.3000	0.0244	0.0250	0.0006
0.6000	0.0404	0.0412	0.0008
1.1000	0.0554	0.0557	0.0003
2.100	0.0724	0.0720	—0.0004
3.100	0.0834	0.0825	—0.0009

The small magnitude of the differences in Column 4 is good evidence that in solutions of potassium chloride the activities of the potassium and chlorine ions are very nearly the same, if not identical, at any given concentration, and that this is true up to 3 *N* concentration. The differences in Column 4 might be very easily due to the error caused by the assumption made above, regarding the liquid potentials between the solutions and the saturated potassium chloride solution. The fact that this difference changes in sign with the concentration is evidence that the error is experimental, or caused by liquid potentials.

This evidence of the validity of the above 3 postulates, along with the evidence previously obtained by MacInnes, Ming Chow[1] and others, is considered sufficient for their adoption; and, in all the calculations which follow, these assumptions are employed.

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[1] *Loc. cit.*

(2) Calculation of the Individual Activity Coefficients of a Few Univalent Ions.

By use of Postulates 2 and 3, it becomes possible to calculate the individual ion activities from available accurate electromotive force measurements on cells with and without transference. The following table of the individual electromotive forces of transfer of the chlorine, potassium, sodium, lithium and hydrogen ions in concentrated solutions has been compiled from the data of the author[1] on cells of Type 2 with transference containing potassium chloride and sodium chloride, respectively; on cells without transference, Type 3, containing lithium chloride[2] and from cells of the type

$$H_2 \mid HCl\ (c) \mid HgCl \mid Hg,$$

measured by Ellis.[1] Thus, from Equation 12,

$$\mathbf{E}_{Cl} = \mathbf{E}_K = \mathbf{E}(2)_{KCl} \qquad (18)$$

$$\mathbf{E}_{Na} = 2\mathbf{E}(2)_{NaCl} - \mathbf{E}_{Cl} \qquad (19)$$

and, from Equation 13,

$$\mathbf{E}_{Li} = \mathbf{E}(3)_{LiCl} - \mathbf{E}_{Cl} \qquad (20)$$

$$\mathbf{E}_H = \mathbf{E}(3)_{HCl} - \mathbf{E}_{Cl}. \qquad (21)$$

In order to calculate the activity coefficients at concentrations from 0.1 to 3.1 from the electromotive force data by means of Equations 15 and 16, it is necessary to obtain the values of the activity coefficients in 0.1 *M* solutions. The best values available for the square root of the ion activity products of the electrolytes potassium chloride, lithium chloride and hydrochloric acid are given by Noyes and MacInnes[3] as 0.754, 0.779 and 0.823 at 0.1 *M*, respectively. The value of the same for sodium chloride has been taken to be 0.765. These values have been obtained from electromotive forces of concentration cells without transference at low concentrations on the assumption that at 0.001 *M* concentration, the activity coefficient and conductance viscosity ratio are equal. From the above, the activity coefficients, F_a, at 0.1 *M* of the potassium and chlorine ions will be equal to 0.754; $F_{a(0.1)}$ of the sodium ion may be obtained from $0.765 = \sqrt{0.754\ F_{a(0.1)}}$, and equals 0.775; likewise $F_{a(0.1)}$ of the lithium ion can be obtained from $0.779 = \sqrt{0.754 F_{a(0.1)}}$, and equals 0.815; and $F_{a(0.1)}$ of the hydrogen ion can be obtained from $0.823 = \sqrt{0.754\ F_{a(0.1)}}$, and equals 0.899. The results of the electromotive forces of transfer of the individual ions are given at round concentrations (mols per 1000 g. water) and have been read off the electromotive force-concentration plots of the electromotive forces $\mathbf{E}_{Cl}$, $\mathbf{E}_K$, $\mathbf{E}_{Na}$, $\mathbf{E}_{Li}$ and $\mathbf{E}_H$, calculated by Equations 18, 19, 20 and 21. Corresponding to each electro-

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[1] *Loc. cit.*

[2] MacInnes and Beattie, THIS JOURNAL, 42, 1117 (1920).

[3] Noyes and MacInnes, *ibid.*, 42, 239 (1920).

motive force is given the value of F_a, calculated by Equations 15 and 16. The temperature is 25 ± 0.01°.

TABLE IV.

(c_1).	$E_K = E_{Cl}$.	$F_K = F_{Cl}$.	E_{Na}.	F_{Na}.	E_{Li}.	F_{Li}.	E_H.	F_H.
0.1000	0.0000	0.754	0.0000	0.775	0.0000	0.815	0.0000	0.899
0.300	0.0250	0.665	0.0260	0.711	0.0274	0.771	0.0228	0.920
0.500	0.0365	0.639	0.0389	0.712	0.0427	0.860	0.0431	0.964
0.750	0.0459	0.599	0.0497	0.715	0.0541	0.894	0.0553	1.030
1.000	0.0524	0.578	0.0572	0.719	0.0640	0.980	0.0662	1.181
1.500	0.0619	0.556	0.0707	0.806	0.0795	1.192	0.0825	1.483
2.000	0.0689	0.547	0.0801	0.876	0.0931	1.519	0.0971	1.960
2.500	0.0747	0.550	0.0893	1.000	0.1048	1.880	0.1098	2.583
3.000	0.0796	0.556	0.0977	1.150	0.1168	2.540	0.1228	3.546

(3) The Calculation of the Activity Coefficients of the Hydrogen Ion at 25° in 0.1 *M* Hydrochloric Acid Containing Potassium, Sodium, and Lithium Chlorides at Concentrations up to 3 *M*.

The values of the electromotive forces E(4), of cells of Type 4 containing potassium chloride, sodium chloride, or lithium chloride, and the activity coefficient $F_a/0.1$ of the hydrogen ion of 0.1 *M* hydrochloric acid in the presence of the above 3 salts at the concentrations designated are given in Table V. This calculation was made using the accurate data obtainable on cells of Type 1 and Type 2. From Equations 11 and 14, we obtain

$$E_o - E(1)_c = RT\, ln \frac{a_{H(s)}}{a_{H(0.1)}} + E_{Cl(c+0.1)}.$$

Thus

$$E_o - E(1)_c - E_{Cl(c+0.1)} = E(4).$$

The values under E(4) in Table V were obtained at round concentrations by reading the values of $E_o(1) - E(1)_c$, calculated from the data in Table I, from the electromotive force-concentration plots, and subtracting from these $E_{Cl(c+0.1)} = E_{Cl(c_1)}$, obtained from Table IV.

TABLE V.

c.	E(4)KCl.	F_H(KCl).	E(4)NaCl.	F_H(NaCl.)	E(4)LiCl.	F_H(LiCl).
0.000	0.0000	0.899	0.0000	0.899	0.0000	0.899
0.300	—0.0001	0.895	0.0013	0.948	0.0023	0.985
0.500	0.0008	0.929	0.0025	0.989	0.0044	1.066
0.750	0.0015	0.953	0.0041	1.053	0.0073	1.191
1.000	0.0032	1.018	0.0064	1.152	0.0107	1.362
1.500	0.0062	1.144	0.0107	1.362	0.0171	1.748
2.000	0.0100	1.326	0.0167	1.681	0.0240	2.29
2.500	0.0139	1.542	0.0224	2.145	0.0311	3.02
3.000	0.0176	1.785	0.0279	2.66	0.0390	4.10

It is important at this juncture to note that the activity of the hydrogen ion in these solutions is different, depending on the added salt. Although the activity of the common ion has been shown to be identical in solutions of equivalent normality, this is not true of the hydrogen ion which is not common to both electrolytes. A further discussion of this so-called "neutral salt effect" will be reserved until a later section in which the increments of the heat content function of transfer of the hydrogen ion will be discussed.

(4) A General Formula for the Calculation of the Activity Coefficients of the Individual Ions of a Single Electrolyte.

The formula here used in calculating the individual ion activity coefficients is partly empirical and depends on the combination of the 2 equations

$$-\log f_a = \beta c^m \tag{22}$$

and

$$\log F_a/f_a = \alpha c \tag{23}$$

where f_a is the "ideal activity coefficient," F_a the observed activity coefficient computed from electromotive force data, c is the concentration in mols per 1000 g. of water, and α, β and m are constants.

Bjerrum[1] has deduced a particular form of Equation 22 for uni-univalent electrolytes, namely

$$-\log f_a = \beta\sqrt[3]{c} \tag{24}$$

from the following considerations and equations.

1. The hypothesis of complete dissociation.

2. The empirical equation relating the osmotic coefficient, f_o, with the concentration, namely

$$f_o = 1 - k\sqrt[3]{c} \tag{25}$$

obtained from the empirical equation of Noyes and Falk[2]

$$2 - i = k\sqrt[3]{c} \tag{26}$$

where i is the Van't Hoff factor.

3. The thermodynamic equation

$$f_o + c\,\frac{df_o}{dc} = 1 + c\,\frac{d\ ln\ f_a}{dc} \tag{27}$$

which relates the osmotic coefficient with the activity coefficient. Since a correct theoretical treatment of these relationships has been presented by Bjerrum[3] and Brönsted,[4] no further comments are necessary. Equation 26 was shown by Noyes and Falk to hold within the error of experiment with the results then available for dilute solutions of electrolytes (from 0.001 M to 0.05 M), and, hence, Equation 24 will hold in very dilute solutions where abnormalities due to heats of dilution, hydration, etc.,

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[1] Bjerrum, *Meddel. K. Vetenskapsakad. Nobelinst.*, **5**, No. 16; *Z. anorg. Chem.*, **109**, 275 (1920).

[2] Noyes and Falk, THIS JOURNAL, **32**, 1011 (1910).

[3] *Loc. cit.*

[4] Brönsted, THIS JOURNAL, **42**, 761 (1920).

are not great. For this reason, Equation 24 can be used in calculating what the activity coefficient would be in solutions of higher concentrations if these abnormalities did not occur. f_a has, therefore, been termed the "ideal activity coefficient." β computed from the values of K in Equation 26 will differ for different types of electrolytes.

By using a different method Lewis and Linhart[1] have deduced the equation

$$-\log f_a = \frac{\beta'(\alpha' + 1)c^{\alpha'}}{2.303\, n'\lambda\alpha'} \tag{28}$$

from the thermodynamic equation relating the activity and the freezing-point lowering, and an empirical equation relating the freezing-point lowering and concentration of electrolyte. α' and β' are constants, n' equals the total number of gram ions contributed by the electrolyte (thus, for NaCl, $n' = 2$; for $La_2(SO_4)_3$, $n' = 5$) and $\lambda = 1.858°$ or the molal lowering of the freezing-point. This equation for any given electrolyte can be reduced to the general form

$$-\log f_a = \beta c^m$$

since, for that electrolyte α', β', n', λ, in Equation 28 are constants.

Lewis and Linhart showed that electrolytes of similar type such as potassium chloride and sodium chloride or potassium iodate and sodium iodate would possess up to 0.01 M concentrations, identical f_a values, but that there would be large differences in f_a in these very dilute solutions between electrolytes of different types, such as sodium chloride, sodium iodate, copper sulfate, etc. From this consideration, the author has employed the general Equation 24.

The activity coefficients, F_a, as determined by the electromotive force method vary greatly from the values of f_a at the higher concentrations, and hence, it becomes necessary to seek a relation between F_a and f_a. Bjerrum[2] has made the only attempt to calculate on a theoretical basis the relation between the activity coefficients and the molal concentrations for single electrolytes. In Bjerrum's calculations, however, the hypothesis is made that the electromotive force method measures the activity of the non-hydrated ion. Since the effect of hydration on activity coefficients is at present little understood, since the ionic hydration values computed by this method are improbable (*e. g.*, for the lithium and hydrogen ion), and since thermodynamic data alone cannot decide the truth of such an hypothesis, it has been thought preferable to hold this idea in abeyance. In the second place, Bjerrum has employed the correction factor $\frac{55.5}{55.5 + 2c - (m_1 + m_2)c}$, for the volume correction due to hydra-

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[1] Lewis and Linhart, THIS JOURNAL, 41, 1951 (1919).

[2] *Loc. cit.*

tion. Here, m_1 and m_2 are the hydration values (the number of water molecules combined with an ion) of the 2 ions of an electrolyte, respectively, and c is the concentration. For a highly hydrated electrolyte, this correction is considerable, amounting, for example in the case of lithium chloride, to 25% at 3 *M* concentration. Further, this correction factor would affect both the ions in the solution, and, if true, the activity coefficient of the chlorine ion would not be the same in solutions of the same concentration, independent of the ions associated with it. This contradicts both the hypothesis of MacInnes, and the data of the author (Table II).

On the other hand, the equation $\log F_a/f_a = \alpha c$ has been employed to relate the functions F_a and f_a. By combining Equations 22 and 23, the equation

$$\log F_a = \alpha c - \beta c^m \tag{29}$$

is obtained, and in what follows this equation will be shown to express, within experimental errors, F_a as a function of the concentration in the concentration range 0.01 to 3.0 molal.

To determine the values of α, β, and m, from the observed results, an empirical method has been employed. By transposition of Equation 29, we obtain

$$-\log F_a/c + \alpha = \beta c^{m-1}$$

and, taking the logarithms of both members

$$\log [-\log F_a/c + \alpha] = \log \beta + (m - 1) \log c. \tag{30}$$

From Equation 30, it is clear that if α is known, the plot of $\log[-\log F_a/c + \alpha]$ against $\log c$ will be a straight line from which the values of β and

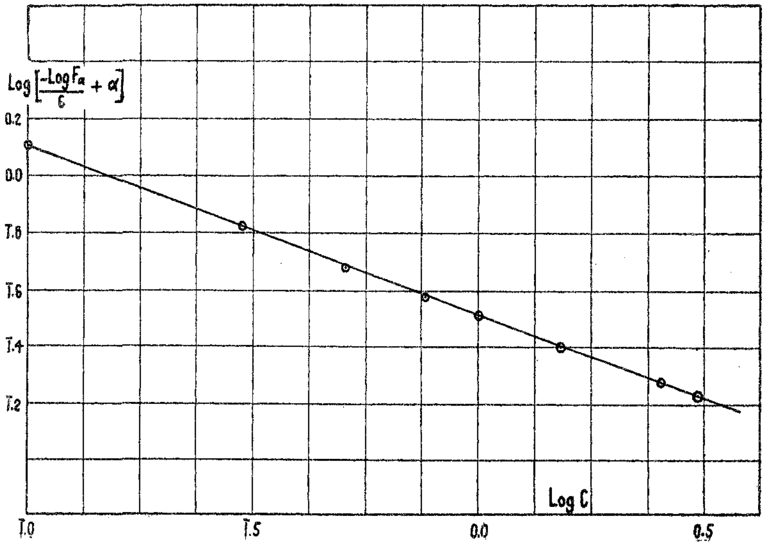

Fig. 1.

m can readily be read off. In order to determine these 3 constants, the above plot was made, using different values for α until a straight line could be drawn through the points. In all cases of the individual ions, Equation 29 can be shown to hold within experimental error throughout the concentration range under consideration. In Fig. 1, the plot of $\log [-\log F_a/c + \alpha]$ against $\log c$ of the potassium ion is shown, and in Table VI a comparison of the observed values of the activity coefficients and the values calculated by Equation 29 are given for the potassium, sodium, lithium, hydrogen, and chlorine ions, along with the respective values of α, β, and m for each ion. The results of this calculation are quite satisfactory; the observed lithium ion results exhibit the greatest inconsistency.

TABLE VI.

	K^+, Cl^-.		Na^+.		Li^+.		H^+.	
c.	F_a(obs.).	F_a(calc.).	F_a(obs.)	F_a(calc.).	F_a(obs.).	F_a(calc.).	F_a(obs.).	F_a(calc.).
0.001	0.979	0.955	...	...	0.973	0.965	...	...
0.010	0.890	0.892	...	...	0.920	0.910	0.975	0.963
0.100	0.754	0.766	0.775	0.770	0.815	0.813	0.899	0.906
0.300	0.665	0.666	0.711	0.715	0.771	0.790	0.920	0.904
0.500	0.639	0.629	0.712	0.703	0.860	0.814	0.964	0.950
0.750	0.599	0.598	0.715	0.716	0.894	0.875	1.030	1.051
1.000	0.578	0.578	0.719	0.735	0.980	0.955	1.181	1.175
1.500	0.556	0.557	0.806	0.795	1.192	1.175	1.483	1.496
2.000	0.547	0.550	0.876	0.885	1.519	1.500	1.960	1.964
2.500	0.550	0.551	1.000	1.005	1.880	1.919	2.583	2.624
3.000	0.556	0.558	1.150	1.160	2.540	2.500	3.546	3.557

	α.	β.	m.
K^+	0.080	0.318	0.397
Cl^-	0.080	0.318	0.397
Na^+	0.175	0.309	0.385
Li^+	0.309	0.329	0.435
H^+	0.390	0.322	0.596

By use of Equation 29, the activity coefficients of the potassium, lithium, hydrogen and chlorine ions can be computed with accuracy down to concentrations approaching 0.001 molal. The observed results for concentrations of 0.01 and 0.001 molal are taken from Noyes and MacInnes.[1] β and m for the potassium, chlorine and sodium ions are nearly identical as was found by Lewis and Linhart; β and m for the lithium ion are near but not identical with the same for the potassium and sodium ions. The values of these 2 constants for the hydrogen ion differ greatly from the values obtained for the alkali metal ions and the chlorine ion. The values of α for the potassium, sodium and lithium ions are approximately in the ratios of the relative ionic hydration values as determined by Washburn.[2]

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[1] *Loc. cit.*

[2] See Harned, THIS JOURNAL, **40**, 1462 (1918).

The α ratios are

$$0.080 : 0.175 : 0.309 \text{ or } 4 : 8.7 : 15.4.$$

Washburn's results give the ratio

$$5.4 : 8.4 : 14.0.$$

The departure of the values of F_a from f_a is due in great part, at least to the effect of hydration. Reasons for the abnormal behavior of the hydrogen ion will be discussed in Part III.

Further, Equation 29 shows the minimum in the F_a–c plots. The potassium and chlorine ions show a minimum at 2 *M*, the sodium ion at 0.50 *M*, and the lithium ion at 0.3 *M*. The observed hydrogen ion F_a–c plot does not show a minimum at concentrations above 0.1 *M*, although Equation 29 predicts one at about 0.2 *M* concentration. It can easily be seen that the position of this minimum depends on the magnitude of α.

PART III. THE FREE ENERGY AND HEAT CONTENT INCREMENTS.

(1). The Decrease in Free Energy and Heat Content of the Cell Reaction $H_2 + 2HgCl = 2HCl\ (0.1) + 2Hg$ in the Presence of Potassium, Sodium and Lithium Chlorides.

From the data in Table I, the decrease in free energy ($-\Delta F$) of the cell reaction at the temperature designated may be obtained by multiplying

TABLE VII.

c.	$(-\Delta F)_{18}$.	$(-\Delta F)_{25}$.	$(\Delta F)_{30}$.	$\left(\frac{d\Delta F}{dT}\right)_{25}$.	$(-\Delta H)_{25}$.
(1) KCl.					
0.0000	76785	77003	77129	29.0	68360
0.2018	72098	72228	72272	13.0	68354
0.5086	68943	68970	68967	1.5	68523
1.0346	65730	65678	65625	−8.5	68211
2.134	61157	61029	60929	−20.0	66989
3.309	57397	57207	57063	−28.0	65551
(2) NaCl.					
0.1003	73768	73917	73993	18.5	68404
0.2014	72027	72142	72199	13.5	68218
0.5061	68653	68683	68679	2.0	68087
0.9183	65740	65705	65656	−7.0	67791
1.023	65129	65072	65017	−8.5	67605
1.871	60952	60836	60744	−17.3	65987
2.094	60000	59870	59754	−20.5	65979
2.711	57503	57315	57197	−25.0	64765
3.202	55564	55369	55221	−28.0	63713
3.726	53680	53478	53326	−30.0	62418
(3) LiCl.					
0.4203	...	69223	...	..	...
0.8485	65483	65463	65423	−5.0	66953
1.7267	60294	60209	60124	−13.5	64232
2.636	55711	55575	55450	−21.0	61833
3.574	51297	51114	50966	−27.0	59160
4.556	46839	46618	46417	−34.0	56750

the electromotive force by 2 × 96,500. Only in a few cases was it possible to obtain $(\Delta H)_{25}$ by using the linear equation $(-\Delta F) = (\Delta F)_{25}(1 + \alpha(t - 25))$, substituting for $(-\Delta F)$ in Equation 9 and differentiating, because of the complicated nature of the variation of $(-\Delta F)$ with the temperature. For this reason, $\left(\frac{d\Delta F}{dT}\right)_{25}$ in the neighborhood of 25° was read off from a carefully drawn large scale $(-\Delta F)$, T plot and then $(\Delta H)_{25}$ was computed by Equation 10. The data is compiled in Table VII. $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ are given in joules. $\left(\frac{d\Delta F}{dT}\right)_{25}$ is given in joules per degree. An error of 0.01 of a millivolt in $\left(\frac{d\Delta F}{dT}\right)_{25}$ will cause an error of 596 joules. It is thought that the following values of $(\Delta H)_{25}$ are not in error by more than ±300 joules.

(2). $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ of Transfer of Two Gram Ions of Hydrogen and Two Gram Ions of Chlorine from (MeCl(c) in HCl(0.1)) to HCl(0.1).

By subtracting $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ at a salt concentration c from $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ at a zero salt concentration, $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ of transfer of 2 gram ions of hydrogen ion and 2 gram ions of chlorine ion from MeCl (c) in HCl (0.1) to HCl (0.1) will be obtained. (See Equation

Table VIII.

	c.	$(-\Delta F)_{25}$.	$(-\Delta H)_{25}$.
(1) KCl.			
	0.2018	4775	6
	0.5086	8033	37
	1.0346	11325	149
	2.134	15974	1371
	3.309	19796	2807
(2) NaCl.			
	0.1003	3086	—44
	0.2014	4861	142
	0.5061	8320	273
	0.9183	11298	569
	1.023	11931	755
	1.871	16167	2373
	2.094	17133	2381
	2.711	19688	3595
	3.202	21634	4647
	3.726	23525	5942
(3) LiCl.			
	0.4203	7780	...
	0.8485	11557	1407
	1.7267	16794	4128
	2.636	21428	6527
	3.574	25889	9200
	4.556	30385	11610

11). Table VIII contains these values of $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ of transfer in joules.

(3) General Considerations Regarding the Increment in Heat Content Function of Ionic Transfer.

The only accurate data available on $(-\Delta H)$ of transfer of an electrolyte from a solution of strength c_1 to a solution of strength c_2 by electromotive force measurements have been obtained by Ellis[1] on hydrochloric acid. It has been necessary, therefore, to calculate $(-\Delta H)$ of transfer of potassium chloride and sodium chloride from the heats of dilution, or the heat absorbed or evolved on changing the concentration from c_1 to c_2 and the partial molal heats of dilution of water at the concentrations c_1 and c_2.[2] This can be done as follows.

1. Start with infinite quantities of 2 solutions at concentrations c_1 and c_2, respectively, and let $c_1 > c_2$. Let x_1 equal the number of mols of water per mol of salt corresponding to c_1, and x_2 equal the number of mols of water per mol of salt corresponding to c_2. Let $\overline{H}$ equal the partial molal heat of dilution of water, $\overline{H}_{c_1}$ and $\overline{H}_{c_2}$, the partial molal heats of dilution of water at concentrations c_1 and c_2, respectively. Remove one mol of solute and x_1 mols of water from 1. $(-\Delta H) = 0$. Remove $(x_2 - x_1)$ mols of solvent from 2. $(-\Delta H)_1 = -(x_2 - x_1)\overline{H}_{c_2}$.

2. Dilute one mol of solute and x_1 mols of water with $(x_2 - x_1)$ mols of water. $(-\Delta H)_2 = Q = \int_{x_1}^{x_2} \overline{H}\,dx$ = heat of dilution from x_1 to x_2. Add one mol of solute and x_2 mols of solvent to 2. $(-\Delta H) = 0$.

3. Remove x_1 mols of solvent from 2. $(-\Delta H)_3 = -x_1\overline{H}_{c_2}$.

4. Add x_1 mols of solvent to solution 1. $(-\Delta H)_4 = x_1\overline{H}_{c_1}$. The total heat content change of transfer $(-\Delta H)$, will be the sum of the above heat content changes. This gives

$$(-\Delta H) = \int_{x_1}^{x_2} \overline{H}dx + x_1\overline{H}_{c_1} - x_2\overline{H}_{c_2}. \qquad (31)$$

In Table IX are given the values of $(-\Delta H)$ of transfer in joules at 25° for potassium chloride and sodium chloride from a solution of concentration c to 0.1 M, calculated by Equation 31. The heats of dilution of potassium chloride necessary for the calculation have been taken from the data of Bishop,[3] and the partial molal heats of dilution of water in potassium chloride solutions have been taken from Stearn and G. McP. Smith.[4] All data on the heats of dilution, etc. of sodium chloride have been taken

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[1] *Loc. cit.*

[2] This partial molal heat of dilution equals the change in heat content when one mol of water is added to an infinite amount of a solution of the designated concentration.

[3] Bishop, *Phys. Rev.*, **26**, 169 (1908).

[4] Stearn and Smith, THIS JOURNAL, **42**, 18 (1920).

from Randall and Bisson.[1] The data on hydrochloric acid in the last column have been obtained from Ellis' electromotive force measurements.

TABLE IX.

$(c + 0.1)$.	KCl. $(-\Delta H)_{25}$.	NaCl. $(-\Delta H)_{25}$.	HCl. $(-\Delta H)_{25}$.
0.1000	000	000	000
0.3000	— 355	— 300	420
0.5000	— 650	— 570	820
1.000	—1310	—1196	1820
1.500	—1900	—1780	2770
2.000	—2375	—2300	3720
2.500	—2810	—2690	4740
3.000	—3175	—3010	5710

No further reliable data sufficient for calculating $(-\Delta H)$ of transfer of other electrolytes were available.

In order to carry further the calculation of the thermodynamic data presented in this paper, another hypothesis will be necessary regarding $(-\Delta H)$ of transfer of the ions. If the heats of dilution from molal concentrations c_1 to c_2 of a number of electrolytes be compared,[2] the conclusion (at least approximate), may be drawn that the ions have a specific individual effect. Thus, hydrochloric acid has a high positive heat of dilution, and sodium and potassium chloride have negative heats of dilution. Further, solutions of other acids have a positive heat of dilution. Thus, wherever the hydrogen ion occurs, there is a positive heat of dilution. If, in the cases of sodium chloride, potassium chloride, and hydrochloric acid, the chlorine ion has the same heat of dilution irrespective of the cation associated with it, then the hydrogen ion will have a greater positive heat of dilution than either the sodium or potassium ion In a general qualitative way, this same principle is true for the heats of dilution of all electrolytes. A rough study of the data will arrange some of the common ions in the following order, those on the left having a positive heat of dilution and those on the right a negative heat of dilution.

$$H^+ > {}^1/_2Cu^{++},\ {}^1/_2Zn^{++},\ {}^1/_2Ca^{++} > {}^1/_2Sr^{++} > {}^1/_2Ba^{++} >$$
$$ {}^1/_2Mg^{++} > OH^- > NH_4^+,\ {}^1/_2SO_4^{--} > K^+,\ Na^+,\ Li^+,\ Cl^- > NO_3^-.$$

From these considerations, the following 2 hypotheses have for the time being been adopted.

1. The ions act independently of one another in respect to the heat content increment of transfer.
2. The potassium and chlorine ions produce identical heat content increments of transfer between the same concentration limits.

The first hypothesis is believed to be approximately true for all ions, and a very close approximation, at least, for the univalent ions of strong

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[1] Randall and Bisson, THIS JOURNAL, **42**, 347 (1920).

[2] *E. g.*, the data of Pratt, *J. Franklin Inst.*, **185**, 663 (1918).

electrolytes. The second hypothesis is probably true because the activity coefficients of the potassium and chlorine ions are identical or very nearly so, and because other evidence points to the conclusion that these ions behave alike as regards hydration.

By means of these 2 hypotheses, the values of (—ΔH) of transfer in joules at 25° of the potassium, sodium, hydrogen, and chlorine ions were calculated at round concentrations from the results in Table IX. The results of this computation are given in Table X.

TABLE X.

$c + 0.1$.	$(-\Delta H)_{25}(H^+)$.	$(-\Delta H)_{25}(Cl^-)$.	$(\Delta H)_{25}(K^+)$.	$(-\Delta H)_{25}(Na^+)$.
0.100	000	000	000	000
0.300	598	— 178	— 178	— 122
0.500	1145	— 325	— 325	— 245
1.000	2477	— 655	— 655	— 541
1.500	3670	— 950	— 950	— 830
2.000	4908	—1188	—1188	—1112
2.500	6095	—1405	—1405	—1285
3.000	7299	—1588	—1588	—1422

These results are approximations, and the error cannot be estimated. They will, suffice, however, to bring out the main points of the following discussion.

(4). $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ of Transfer of Two Gram Ions of Hydrogen Ion from a Solution of MeCl(*c*) in HCl(0.1 *M*) to HCl(0.1 *M*).

From the data in Table IV, the free energy of transfer of 2 gram ions of chlorine ion from a solution of concentration (c + 0.1) *M* to 0.1 *M* can be easily obtained by multiplying E_{Cl} at a concentration (c + 0.1) *M* by 2 × 96,500. $2(-\Delta H)_{25}$ for the chlorine ion at the proper concentration can be read off the heat content decrease-concentration plot of the results in Table X, Column 3. By subtraction of $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ of transfer of 2 gram ions of chlorine at a concentration (c + 0.1) *M*, thus obtained, from $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ of transfer of 2 gram ions of hydrogen ion and 2 gram ions of chlorine from MeCl (c) in HCl (0.1*M*) to HCl (0.1 *M*), given in Table VIII, $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ of transfer of 2 gram ions of the hydrogen ion from MeCl (c) in HCl (0.1 *M*) to HCl (0.1 *M*) will be obtained. This calculation has been made and the data compiled in Table XI. The last column gives $(-\Delta H)_{25}$ of transfer of one gram ion of the hydrogen ion.

In Fig. 2, the values of $(-\Delta H)_{25}$ of transfer of the hydrogen ion taken from the last column of Table XI are plotted against the concentration of added salt. The plot denoted hydrochloric acid is the $(-\Delta H)_{25}$ concentration of acid plot for the hydrogen ion in solutions of hydrochloric acid, taken from Table X, Column 2. These plots are straight lines within the error of experiment.

Table XI.

	c.	$(-\Delta F)_{25}$.	$(-\Delta H)_{25}$.	$(-\Delta H)_{25}$. (1 gram ion).
(1) KCl.				
	0.0000	000	000	000
	0.2018	—49	356	178
	0.5086	79	902	451
	1.0346	575	1519	759
	2.134	2097	3960	1980
	3.309	3886	6177	3088
(2) NaCl.				
	0.1003	40	131	66
	0.2014	37	492	246
	0.5061	366	1073	536
	0.9183	938	1899	949
	1.023	1181	2215	1108
	1.871	2827	4723	2361
	2.094	3256	4931	2465
	2.711	4615	6630	3315
	3.202	5718	8022	4011
	3.726	..	9582	4791
(3) LiCl.				
	0.8485	1579	2682	1341
	1.7267	3766	6353	3176
	2.636	6470	9507	4754
	3.574	..	12775	6388

It is first clear from the above plots that these increments of transfer are of the same order of magnitude whether the hydrogen ion is transferred from a solution of HCl (c + 0.1) to HCl (0.1), or from a solution

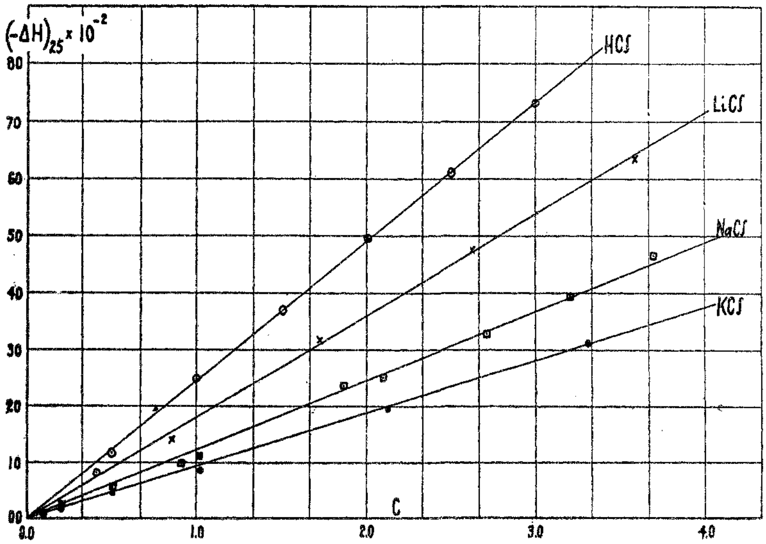

Fig. 2.

of HCl (0.1) + MeCl (c) to HCl (0.1). This points directly to the extremely important principle *that the decrease of heat content function of transfer of the hydrogen ion is a function of the total salt concentration or total ion activity, and not of the concentration or activity of the hydrogen ion.*

The following will clearly demonstrate this principle. In the first place

$$(-\Delta H)_{25} = Kc \qquad (32)$$

where c is the concentration of salt or hydrochloric acid added to 0.1 M hydrochloric acid, and K is a constant. Second, it is to be observed that, at a given concentration, the greater the activity of the ions of the single electrolyte added to the acid, the greater will be this decrease in heat content of transfer. The results tabulated in Table XII will roughly illustrate this relationship. Column 1 contains the values of K (Equation 32), or the slope of the plots in Fig. 2, Column 2, the sum $(\alpha_{Me} + \alpha_{Cl})$ of the values of the constant α of Equation 29 (Table VI) of both the ions added to the acid, and Column 3 contains the ratio $(\alpha_{Me} + \alpha_{Cl})/K$.

TABLE XII.

Electrolyte added.	(1).	(2).	(3).
KCl	920	0.160	1.74×10^{-4}
NaCl	1230	0.255	2.07×10^{-4}
LiCl	1800	0.389	2.16×10^{-4}
HCl	2420	0.430	1.98×10^{-4}

The approximate constancy of the values in Column 3 point to the conclusion that the decreases in heat content under consideration are functions of the total ion activities of the solutions.

This conclusion is also good indirect substantiation of the principle used by Bjerrum[1] and mentioned by Ming Chow[2] that "the activity coefficient, F_a/c, of uni-univalent ions of largely ionized substances is in general a function of the total salt or ion concentration, and not of its own concentration."

The above principles must have an important bearing on the phenomenon of the "neutral salt effect." In a previous communication,[3] the author has shown that the increase in velocity constant in hydrogen ion, and iodine ion catalysis, produced by the addition of a neutral salt (a chloride) is a function of the square root of the activity product of the ions of the added salt.[4] In other words, the "neutral salt effect" on catalysis in liquid systems was shown to be function of the total ion activity and not of the activity of the catalyzing ion.

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[1] *Loc. cit.*

[2] Ming Chow, THIS JOURNAL, **42**, 447 (1920).

[3] *Ibid.*, "Neutral Salt Catalysis," **40**, 1462 (1918).

[4] This was termed the chlorine ion activity at that time because the assumption of the individual activities of the ions was not known or used when that paper was written.

The question as to the underlying causes of this effect is an obscure one. The increase in activity of the hydrogen ion of hydrochloric acid by the addition of neutral salts has been assumed to be due, first, to the high hydration of the hydrogen ion,[1] second to the hydration of the ions of the added salts.[2] In view of the fact of the evidence in favor of the hypothesis of MacInnes, and the principle above relating to the decrease in heat content of transfer of the hydrogen ion, it is the belief of the author that these views will have to be modified or abandoned after a still deeper investigation of the phenomenon is made. The main point of interest is that the increase in activity coefficient of the hydrogen ion in solutions of hydrochloric acid on the addition of salts is probably due to this decrease in heat content function of transfer of the hydrogen ion caused by salt addition. Indirectly, ionic hydration will unquestionably have an effect. The fact that the hydrogen ion has a positive and the chlorine ion a negative decrease in heat content function of transfer indicates a fundamental difference in the behavior of these ions, and must receive an explanation before the problem of the "neutral salt effect" can be adequately solved.

Final Considerations.

The present investigation of the thermodynamic properties of concentrated solutions of strong uni-univalent electrolytes and their mixtures leads to verifications and conclusions which may be stated briefly as follows:

(1) The hypothesis of complete dissociation of strong electrolytes promulgated by Milner, Ghosh, Bjerrum and others is a good working hypothesis.

(2) The hypothesis of independent activity coefficients is also tenable.

(3) The hypothesis of MacInnes "that in solutions of the same strength of different electrolytes containing a common ion, the common ion will have the same activity independent of the ion or ions associated with it" is true or very nearly true for the chlorine ion in the solutions investigated in the present research.

(4) At a given concentration of a solution of potassium chloride, the potassium ion and the chlorine ion have the same activity.

(5) The activity coefficient of an ion is a function of the total ion concentration or activity, and not a function of its own concentration.[3]

(6) The hypothesis that the ions of strong electrolytes have independent heat content increments of transfer is probably a good approximation.

(7) It is also probable that the heat content increment of transfer of

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[1] Bjerrum, *loc. cit.*

[2] Poma, *Z. physik. Chem.*, **87**, 197 (1914); **88**, 671 (1914); Harned, *loc. cit.;* Thomas and Baldwin, THIS JOURNAL, **41**, 1981 (1919).

[3] Bjerrum, *loc. cit.;* Ming Chow, *loc. cit.*

the potassium ion is identical with the heat content increment of transfer of the chlorine ion.

(8) The increment in heat content of transfer of an ion is a function of the total ion concentration or activity and not of its own concentration.

(9) The so-called "neutral salt effect" in hydrochloric acid—uni-univalent salt mixtures is probably due to the large decrease in the heat content function of transfer of the hydrogen ion caused by the addition of the salt and not to the high hydration of the hydrogen ion.

Summary.

(1) Measurements of the electromotive forces of the cells

$$H_2 \mid \text{MeCl } (c) \text{ in HCl } (0.1) \mid \text{HgCl} \mid \text{Hg}$$

at 18°, 25°, and 30° containing potassium, sodium and lithium chlorides, respectively, have been made.

(2) Assuming the complete dissociation of the above electrolytes, it is shown that the hypothesis of the individual ion activities as postulated by MacInnes is true within narrow limits, and, that, at a given concentration of potassium chloride, the potassium and chlorine ion activities are identical within narrow limits.

(3) The individual ion activity coefficients of the hydrogen, potassium, sodium, lithium, and chlorine ions from concentrations 0.1 to 3 *M* have been computed.

(4) The activity coefficients of the hydrogen ion in solutions containing potassium, sodium, and lithium chloride up to 3 *M* concentration have been computed.

(5) It has been shown that the semi-empirical formula

$$\log F_a = \alpha c - \beta c^m$$

where F_a is the activity coefficient of the ion, c the concentration, and α, β, and m are constants, will express F_a as a function of c within experimental error from 0.01 to 3 *M* concentration.

(6) A table of the free energies and heat content decreases of the cell reaction

$$H_2 + 2\text{HgCl} = 2\text{HCl } (0.1) + 2\text{Hg}$$

in the presence of potassium, sodium, and lithium chlorides, respectively, has been compiled.

(7) On the assumptions that the ions have independent heat contents of transfer, and that, at a given concentration of potassium chloride, the potassium and chlorine ions possess identical heat contents of transfer from a solution of concentration c_1 to a solution of concentration c_2, it becomes possible to compute the decrease in heat content of transfer of the hydrogen ion from solutions of MeCl (c) in HCl (0.1) to HCl (0.1). The results of this calculation have been tabulated.

(8) The decrease in heat content of transfer of the hydrogen ion from MeCl (*c*) in HCl (0.1) to HCl (0.1) is shown to be a function of the total ion activity of the solution, and not of the activity of the hydrogen ion.

PHILADELPHIA, PA.

THE IONIZATION POTENTIAL OF HYDROCHLORIC ACID AND THE ELECTRON AFFINITY OF CHLORINE.[1]

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There are several means conceivable whereby a molecule of hydrogen chloride may be ionized.

1. The structure of the molecule might remain intact, the molecule as a whole losing an electron, as in the case of an atom of monatomic metal. This would require the existence of positively charged molecules of hydrogen chloride. The work of Aston[2] on positive ray analysis indicates that such *may be* the case. In discharge through phosgene containing hydrogen chloride, he found that ions were present of mass 35, 36, 37 and 38, and identified these as due to the 2 isotopes of chlorine and their corresponding acids.

2. We have shown[3] that in the case of hydrogen our experimental data lead to the conclusion that the hydrogen molecule may be ionized by dissociation into atoms and ionization of one atom. If hydrogen chloride were similar to hydrogen in this respect, the ionization might result in a positively charged hydrogen atom and a neutral chlorine atom. The work required to ionize thus a gram molecule of hydrogen chloride may be computed in the following manner.

Let Q_{HCl} = heat of formation of one gram mol. of HCl from the diatomic gases H_2 and Cl_2.

D_H = $^1/_2$ the heat of dissociation of a gram mol. of H_2 into monatomic hydrogen.

D_{Cl} = $^1/_2$ the heat of dissociation of a gram mol. of Cl_2 into monatomic chlorine.

Accordingly,

$$\begin{aligned} \mathrm{HCl} + Q_{HCl} &= {}^1/_2\mathrm{H}_2 + {}^1/_2\mathrm{Cl}_2 \\ {}^1/_2\mathrm{H}_2 + D_H &= \mathrm{H} \\ {}^1/_2\mathrm{Cl}_2 + D_{Cl} &= \mathrm{Cl} \end{aligned}$$

Adding $\mathrm{HCl} + Q_{HCl} + D_H + D_{Cl} = \mathrm{H} + \mathrm{Cl}.$

The quantity $Q_{HCl} + D_H + D_{Cl}$ is the work required to dissociate a gram mol of hydrogen chloride into neutral monatomic hydrogen and

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[1] Published by permission, Director Bureau of Standards.

[2] Aston, *Phil. Mag.*, **39**, 611 (1920).

[3] Mohler and Foote, *J. Opt. Soc. Am.*, 4, 49 (1920).