tion. The pulverulent precipitate formed was washed many times by the decantation method and dried at 110° for analysis.

The specimen weighed 0.4754 g. Six-tenths gave 0.1258 g. CaO and 0.1735 g. KCl. Two-tenths gave 0.0300 g. N.

	Calc. for CaNK.2NH₃.	Found.		
		I.	II.	III.
Ca.............	31.5	30.6	31.5	31.5
N.............	33.1	32.0	32.5	31.6
K.............	30.8	33.4	31.4	31.8

Although the analytical results are distinctly unsatisfactory there can scarcely be a doubt of the formation of a potassium ammonocalciate of the formula $CaNK.2NH_3$, first, by the action of potassium amide on metallic calcium as represented by the equation

$$Ca + KNH_2 = CaNK + 2H,$$

and second, by the action of excess of potassium amide on a solution of a salt of calcium as represented by the equation

$$Ca(SCN)_2 + 3KNH_2 = CaNK + 2KSCN + 2NH_3.$$
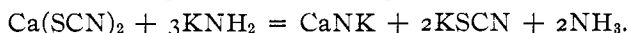
The salt is apparently amorphous, but settles well to a fairly dense, granular precipitate which is easily washed. It dissolves readily in liquid ammonia solution of ammonium nitrate. In contact with water it is energetically hydrolyzed to calcium hydroxide, potassium hydroxide and ammonia.

Summary.

It has been shown in this paper that just as the amides of zinc and magnesium are acted upon by potassium amide in liquid ammonia solution to form an ammonozincate and an ammonomagnesate of potassium, so the amides of barium, strontium and calcium, when submitted to the action of solutions of the ammono base, are similarly converted into an ammonobarate, an ammonostrontiate and an ammono calciate of potassium, respectively.

General formulas for the compounds obtained are the following: $MeNK.2NH_3$, $NH_2MeNHK.NH_3$, $Me(NH_2)_2.KNH_2$ or following Werner, $[Me(NH_2)_3]K$.

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LIQUID JUNCTION POTENTIALS.

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A concentration cell with transference, consisting of two similar reversible electrodes in contact with two differently concentrated solutions

of the same salt, will give an electromotive force which is the algebraic sum of three potentials: the voltages at the two electrodes and the potential at the junction of the solutions. Since, for many theoretical purposes, the potential at the electrodes alone is desired, many attempts have been made to evaluate the potential at the liquid junction. Formulas have been proposed for this purpose by Nernst,[1] Planck,[2] Henderson,[3] Cumming,[4] and others. Bjerrum,[5] Cumming[6] and Sackur[7] have studied the effect of interposing strong salt solutions on the electromotive force of the cell with a view of eliminating the effect of the liquid junction.

It has been usual to test the correctness of the value of the potential assigned to the junction, or the efficacy of the artifice employed in eliminating it, by seeing whether the resulting voltage at the electrodes can be calculated from the Nernst equation in its kinetic form:

$$E = \frac{RT}{F} \ln \frac{C_i}{C_i'} \tag{1}$$

where C_i and C_i' are the concentrations of the ions in the two solutions as calculated from conductance measurements. (E = electromotive force, R the gas constant, T the absolute temperature, and F the faraday, respectively.) As the substitution of values of ion concentrations determined from conductance measurements into the partially thermodynamic equations

$$E = \frac{2n_cRT}{F} \ln \frac{C_i}{C_i'} \quad \text{and} \quad E = \frac{2RT}{F} \ln \frac{C_i}{C_i'}$$

for cells with and without transference, has been shown[8] to give higher values of the electromotive force than are found by direct measurement, it is altogether probable that Equation 1 will also give too high values for the voltages at the electrodes of a cell with diffusion. For this reason the potentials of the liquid junctions, adopted on the assumption that Equation 1 gives the correct values for the voltage at the electrodes, will probably be too small. It is also very evident that the early workers in this field did not require very close accord of their predicted values of the electromotive force with those found by experiment in order to conclude that their theoretical premises were established. It therefore

[1] Z. physik. Chem., 2, 613 (1888).

[2] Wied. Ann., 40, 561 (1890).

[3] Z. physik. Chem., 59, 118 (1906), and 63, 325 (1908).

[4] Trans. Faraday Soc., 8, 86 (1912).

[5] Z. physik. Chem., 53, 428 (1905).

[6] Trans. Faraday Soc., 2, 213 (1907).

[7] Z. physik. Chem., 48, 129 (1904).

[8] See, for instance, Jahn, Z. physik. Chem., 33, 545 (1900); Tolman and Ferguson, THIS JOURNAL, 34, 232 (1912); MacInnes and Parker, Ibid., 37, 1445 (1915).

seems desirable to investigate the subject of the liquid junction connecting two solutions of the same salt with a view to finding an expression, involving the fewest possible assumptions, for its electromotive force.

If we allow the cell

| Ag | AgCl, KCl | KCl, AgCl | Ag |
| | solid, 0.1 N | 0.01 N, solid | |

to operate reversibly until one faraday has passed through it, one equivalent of chloride ions will enter the dilute solution and a similar amount will be electrolyzed out of the more concentrated solution. The current will be carried across the liquid junction by the movement of n_c equivalents of potassium ion in direction of the current and by the migration of $(1 - n_c)$ equivalents of chloride ion in the reverse direction, n_c being the transference number of the cathion. The total effect of the passage of the faraday of electricity will be the transference of n_c equivalents of salt from the more concentrated to the dilute solution. Now the osmotic work at the liquid junction will depend on the algebraic sum of the number of equivalents of ion that have been carried across it from the concentrated to the dilute solution, in this case equal to $n_c - (1 - n_c) = 2n_c - 1$. This, of course, involves the assumption that the osmotic work involved in the transferring of a gram equivalent positive ion from a dilute to a concentrated solution is the same as the work necessary for the transfer of a corresponding amount of negative ion. Now in order to obtain the electrical work, and with it the voltage, by which this osmotic work is accomplished, let us consider the cell without transference:

| Ag | AgCl, KCl | K(Hg)$_x$ — K(Hg)$_x$ | KCl, AgCl | Ag |
| | solid, 0.1 N | . | 0.01 N, solid | |
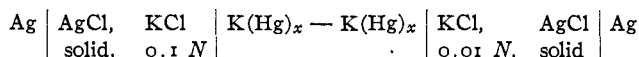
The operation of this cell consists in the formation of one equivalent each of potassium ion and chloride ion in the dilute solution during the passage of one faraday of electricity, and at the same time the removal of one equivalent of each ion from the more concentrated solution. The electrical energy accompanying the transfer of the two equivalents of ion from one solution to the other will be the electromotive force of the cell, E, multiplied by the value of the faraday, F.

The electromotive force of the liquid junction, E_L, can now be obtained by the simple proportion:

$$EF : E_L F = 2 : 2n_c - 1 \quad \text{or} \quad E_L = E (2n_c - 1)/2 \qquad (2)$$

Since our problem is that of apportioning the total voltage of a cell with transference between the electrode potentials and the liquid junction, we may replace the E. M. F. of the cell without transference, E, by that of the cell with transference, E_t, with the aid of the relation: $E_t = En_c$.[1] This formula, the derivation of which involves only the two

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[1] See MacInnes and Parker, THIS JOURNAL, **37**, 1445 (1915).

laws of thermodynamics, has been tested experimentally for cells of both types involving solutions of KCl and HCl. Making the substitution, (2) becomes

$$E_u = (E_t/2n_c)(2n_c - 1) = E_t(1 - 1/2n_c), \qquad (3)$$

an equation which contains no assumption regarding the concentration of the ions of the two solutions.

A direct test of this simple equation is, of course, not possible, but an indirect one is afforded by the following considerations: The electrode potential, i. e., the E. M. F. of the cell minus the potential of the liquid junction, for cells of the type

$$\text{Ag} \mid \text{AgCl, MCl} \mid \text{MCl, AgCl} \mid \text{Ag}$$
$$\qquad c_1 \qquad c_2$$
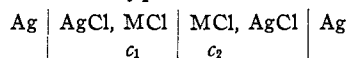
will be expected to be the same whether hydrogen or any one of the alkali metals is chosen for the radical M, if the concentrations c_1 and c_2 are the same in each case and below about 0.05 N. The potential at each electrode is, of course, the result of the tendency of the electrode material to form chloride ions and the opposing tendency of the osmotic pressure of the chloride ions already in solution. The sum of the electrode potentials will thus be determined by the difference of the osmotic pressures of the chloride ions in the two solutions. This difference of osmotic pressure will, in all probability, be very nearly the same for dilute solutions of chlorides of univalent metals at corresponding concentrations, since the degrees of dissociation in dilute solution as determined by the conductivity method have been found to be the same for these substances. The correct expression for the potential of the liquid junction in cells of the above type is, therefore, one which will yield values for the sum of the electrode potentials which are independent of the nature of the cation. Jahn's[1] accurate work on concentration cells of hydrochloric acid, potassium chloride and sodium chloride is, fortunately, well adapted to a test of these conclusions.

Table I, which is self-explanatory, gives the result of the author's calculations, based on Jahn's data. The transference numbers are from Noyes and Falk's[2] compilation. It will be observed that in each group of cells, in which the solutions of electrolytes have the same concentrations, the calculated sums of the electrode potentials have the same value within a few tenths of a millivolt. This is true even though the liquid junction correction in the case of the hydrochloric acid cells is 40% of the total voltage and of opposite sign to that necessary for the sodium chloride solutions. The agreement is as close as can be expected from our present knowledge of the transference numbers. A similar agreement of the values of the sum of the electrode potentials when the salt

[1] *Loc. cit.*, p. 2286.
[2] THIS JOURNAL, **33**, 1454 (1911).

TABLE I.—CALCULATION OF THE LIQUID JUNCTION AND ELECTRODE POTENTIALS OF CHLORIDE CONCENTRATION CELLS. (SILVER-SILVER CHLORIDE ELECTRODES.)

Substance.	Concentrations. Mols per liter.	Transference number of cathion.	E. M. F. of cell.	Liquid junction potential.	"Electrode potential" = E. M. F. — liquid junction potential.	Average deviation from mean, millivolts.
HCl........	0.01665	0.833	—0.09235	—0.03694	—0.05541	
	0.001665					
NaCl.......	0.01673	0.396	—0.04360	+0.01146	—0.05506	0.22
	0.001674					
KCl........	0.01670	0.496	—0.05424	+0.00044	—0.05468	
	0.001674					
HCl........	0.03330	0.833	—0.09162	—0.03664	—0.05498	
	0.003329					0.25
KCl........	0.03347	0.496	—0.05403	+0.00043	—0.05447	
	0.003347					
HCl........	0.008315	0.833	—0.06487	—0.02595	—0.03892	
	0.001665					
NaCl.......	0.008364	0.396	—0.03073	+0.00808	—0.03881	0.04
	0.001674					
KCl........	0.008329	0.495	—0.03844	+0.00039	—0.03883	
	0.001670					
HCl........	0.006686	0.833	—0.05614	—0.02245	—0.03369	
	0.001665					
NaCl.......	0.006686	0.396	—0.02652	+0.00697	—0.03349	0.08
	0.001674					
KCl........	0.006700	0.495	—0.03330	+0.00034	—0.03364	
	0.001670					

TABLE II.—CALCULATION OF THE LIQUID JUNCTION AND ELECTRODE POTENTIALS OF CHLORIDE CONCENTRATION CELLS. (CALOMEL ELECTRODES.)

Substance.	Concentrations. Mols pei liter.	Transference number of cathion.	E. M. F. of cell.	Liquid junction potential.	"Electrode potential" = E. M. F. — liquid junction potential.	Average deviation from mean millivolts.
KCl........	0.01999	0.496	—0.01608	+0.00013	—0.01621	
	0.01000					0.06
NaCl.......	0.02000	0.395	—0.01293	+0.00339	—0.01632	
	0.01000					
KCl........	0.03000	0.496	—0.02561	+0.00020	—0.02581	
	0.01000					0.07
NaCl.......	0.03003	0.396	—0.02056	+0.00538	—0.02594	
	0.01000					
KCl........	0.05009	0.496	—0.02125	+0.00017	—0.02142	
	0.02000					0.17
NaCl.......	0.05007	0.396	—0.01670	+0.00437	—0.02108	
	0.02000					

concentrations in the different cells are the same is shown in Table II, also based on Jahn's[1] work.

Although the foregoing test of the validity of Equations 2 and 3 can only be made using the results of measurements on cells containing dilute solutions, the equations are equally valid at higher concentrations. As has been mentioned, the equations involve no assumption concerning the concentrations of the ions in the solutions, a knowledge of which is necessary for the use of any of the formulas hitherto proposed. The uncertainty as to the correct method of calculating ion concentrations in moderately concentrated solutions is particularly great when, as is the case with hydrochloric acid and lithium chloride solutions, the transference number changes as the concentration increases. Formulas 2 and 3 require only that the value of the transference number shall remain constant within the concentration range included by the two solutions in contact at the liquid junction.

For the calculation of the potential of the liquid junction connecting two solutions of the same uni-univalent electrolyte it is, therefore, necessary to know the transference number of one of the ions and either E_i of Equation 3 or E of Equation 2. Both the latter quantities may be determined by direct experiment. E can also be calculated from any data which will give the free energy of dilution, $(E\,F)$, of the salt, $i.\,e.$, any of the colligative properties. Freezing point, or more exactly freezing point and heat of dilution, measurements will give accurate values of this quantity. Lewis[2] has calculated the free energy of dilution of various dilute salt solutions from cryoscopic measurements with the help of the Duhem-Margules equation. More and accurate experimental data are needed in this field, as it involves the whole question of the relation of the total salt concentration to the activity of the ions, without a knowledge of which the electromotive force methods for determining solubilities, small ion concentrations, etc., cannot be expected to yield accurate results, even if all the problems in connection with liquid junctions are successfully solved.

A modification of Planck's formula for the E. M. F. of a liquid junction connecting two *equally concentrated* solutions of salts having a common ion has been proposed by Lewis and Sargent.[3] This takes the form

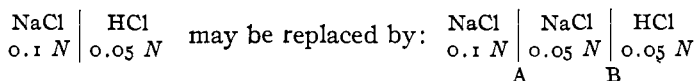$$E_L = \frac{RT}{F} \ln \frac{\Lambda_1}{\Lambda_2},\qquad(4)$$

where Λ_1 and Λ_2 are the equivalent conductances of the salts in the two solutions. Direct experiment shows that this formula may be relied

[1] *Z. physik. Chem.*, **41**, 288 (1902).
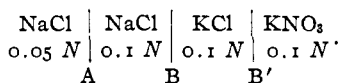
[2] THIS JOURNAL, **34**, 1631 (1912).

[3] *Ibid.*, **31**, 363 (1909).

upon to give values of the potential of this type of junction accurate within 0.1 or 0.2 millivolt. It will be noted that the junction connecting differently concentrated solutions of two salts with a common ion may be replaced by two junctions, one of which joins solutions of the same salt at different concentrations and the other connects solutions of different salts at the same concentration. For instance, the junction

$$\begin{array}{c|c} \text{NaCl} & \text{HCl} \\ \text{0.1 } N & \text{0.05 } N \end{array} \text{ may be replaced by: } \underset{\text{A} \qquad \text{B}}{\begin{array}{c|c|c} \text{NaCl} & \text{NaCl} & \text{HCl} \\ \text{0.1 } N & \text{0.05 } N & \text{0.05 } N \end{array}}$$

in which the potential of junction A may be calculated by Equations 2 or 3, and B by Equation 4. This method has been used by Lewis and Randall[1] and by Sammet[2] for junctions connecting KCl solutions with solutions of other chlorides.

The E. M. F. at the contact of differently concentrated uni-univalent salt solutions containing *no* common ion may, similarly, be made readily calculable by using three junctions. For example, 0.1 N KNO$_3$ and 0.05 N NaCl may be connected by

$$\underset{\text{A} \qquad \text{B} \qquad \text{B}'}{\begin{array}{c|c|c|c} \text{NaCl} & \text{NaCl} & \text{KCl} & \text{KNO}_3 \\ \text{0.05 } N & \text{0.1 } N & \text{0.1 } N & \text{0.1 } N \end{array}}.$$

As before, the E. M. F. of the junction marked A may be found by Equation 2 or 3 and the potentials of junctions B and B' by Equation 4.

Summary.

It is shown that the probable value of the electromotive force, E_L, of the liquid junction connecting differently concentrated solutions of the same salt, may be expressed by the equations

$$E_L = E(2n_c - 1)/2 \cdot \text{ and } E_L = E_t(1 - 1/2n_c),$$

in which E is the voltage of a concentration cell without transference and E_t that of the concentration cell with transference, each of the latter containing the solutions which are in contact at the liquid junction. These formulas are in accord with the most accurate work on the potentials of concentration cells.

By combining junctions to which the above equations apply with junctions the voltage of which may be computed by Lewis and Sargent's formula, the potential between any two uni-univalent salt solutions may be calculated to a few tenths of a millivolt.

URBANA, ILL.

[1] THIS JOURNAL, **36**, 1975 (1914).
[2] Z. physik. Chem., **53**, 641 (1905).