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ELECTROMOTIVE FORCE OF ELECTROLYTIC THERMOCOUPLES AND THERMOCELLS AND THE ENTROPY OF TRANSFER AND ABSOLUTE ENTROPY OF IONS

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Systems of the type represented schematically as follows are often referred to as electrolytic thermocouples

$$\underset{T_1}{\text{Electrode}},\ \text{Solution I},\ \underset{T_1}{\ }\ \text{Solution II},\ \underset{T_2}{\ }\ \text{Solution I},\ \underset{T_1}{\ }\ \text{Electrode} \qquad \text{(I)}$$

The two electrodes in this arrangement are identical and are kept at the same temperature. Solutions I and II, the junctions of which are at different temperatures, may contain the same electrolyte at different concentrations, or different electrolytes.

Other arrangements consisting of two similar electrodes, at different temperatures, and a single solution in which the temperature gradient lies, are also occasionally given this name. The latter type may be represented as follows:

$$\underset{T_2}{\text{Electrode}},\ \text{Solution},\ \underset{T_1}{\text{Electrode}} \qquad \text{(II)}$$

In a previous paper[1] arrangements like (II) were referred to as thermocells. To distinguish them from the first class, this designation will be continued here.

The electromotive force of these cells is related to the entropy of transfer[2] and partial molal entropy of the ions of the electrolytes. Of the latter quantities, the first is of interest in connection with the Soret effect and the second is capable of many applications in the thermodynamics of solutions. It is the purpose in this paper to show the thermodynamic relations between these quantities and to employ certain of the existing data in illustrative calculations in order to determine to what extent it may prove possible to utilize these methods in numerical evaluations.

Thermodynamic Relations

Electrolytic Thermocouples.—The cells of Type I to be utilized in the later calculations all involve solutions of uni-univalent electrolytes having a common anion. The theory outlined will, therefore, be restricted to this case, though it is readily generalized. It is also convenient to consider cells in which the temperature difference is infinitesimal, T_1 and T_2 of Arrangement I being replaced by T and $T + \mathrm{d}T$.

When one faraday of electricity is passed through systems of this kind, the direction of positive current being from left to right through the cell,

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[1] Eastman, THIS JOURNAL, **48**, 1482 (1926).

[2] For a discussion of this quantity, see the preceding paper.

the change in state produced may be considered in the following parts: A, the electrode reaction at the first electrode, occurring at temperature T; B, the change, or "reaction" at the liquid junction, at T; C (1), the transfer of t_{C_2} equivalent of the cation of solution II from T to $T + \mathrm{d}T$ and (2) the corresponding transfer at t_{A_2} equivalent of anion from $T + \mathrm{d}T$ to T (t with the appropriate subscripts being used to represent the transference numbers of the ions in the two solutions); D, the reaction at the liquid junction at $T + \mathrm{d}T$; E (1), the transfer of t_{C_1} equivalent of positive ion in Solution I from $T + \mathrm{d}T$ to T; and (2), the transfer of t_{A_1} equivalent of negative ion from T to $T + \mathrm{d}T$; F, the electrode reaction, reversing (A) above, at T.

The electromotive force, $\mathrm{d}E$, corresponding to this series of changes, may be shown by the methods of the earlier paper to depend upon the heat transferred by reversible absorption at the upper temperature and evolution at the lower. The relation is

$$F\mathrm{d}E/\mathrm{d}T = L/T = \Delta S \tag{1}$$

Here F is the equivalent of electricity, and L and ΔS are the heat absorbed from and entropy lost by the surroundings of the system at the upper temperature and transferred to the lower when one faraday is passed reversibly from left to right through the cell.

Regarded from the standpoint of heat transfer in the cell processes, it is obvious that the electrode reactions, items A and F above, are without effect. The liquid boundary reactions, B and D, do, however, produce a heat transfer. The attendant entropy effect (loss by surroundings or gain by system due to the reaction at the upper temperature) will be called ΔS_B.

There is also an entropy effect due to the transfer (items C and E) of the ions between the two temperatures. The net entropy of transfer of the ions (loss of entropy by the surroundings at $T + \mathrm{d}T$ and gain at T) will be called ΔS^*.

Considering the two effects above, Equation 1 may be rewritten as

$$F\mathrm{d}E/\mathrm{d}T = \Delta S_B + \Delta S^* \tag{2}$$

The temperature coefficient of the whole cell as given by (2) may therefore be considered in the separate parts indicated. The part which may be designated $\mathrm{d}E_B/\mathrm{d}T = \Delta S_B/F$, due to the liquid junctions, may be calculated (exactly at infinite dilution and approximately at finite concentrations) by the methods due to Nernst and Planck. The remaining part, $\mathrm{d}E^*/\mathrm{d}T = \Delta S^*/F$, due to the transfer of the ions between different temperatures, may then be obtained from the measured e.m.f. of the cell and the calculated change in junction potential. This corrected e.m.f. may then be related to the entropies of transfer of the individual ions, since ΔS^* is expressible in terms of them. Thus, if S^* is the molal entropy of transfer of a single ion,

$$\Delta S^* = t_{C_1}S^*_{C_1} - t_{C_2}S^*_{C_2} + (t_{A_2} - t_{A_1})S^*_A \tag{3}$$

It will also be observed that dE^*/dT is the potential gradient accompanying the thermal one, and is due no doubt to partial separation of positive and negative ions in the solution lying in the temperature gradient, as first suggested by Nernst.[3]

Throughout the preceding discussion the composition of the electrolytes in the temperature gradient has been assumed to be uniform. Equations 1, 2 and 3 are exactly valid only if this condition is fulfilled, and do not apply, therefore, to cells in which Soret equilibrium has been established. Other equations covering the latter case can be deduced. The Soret equilibrium is, however, established very slowly as compared with the other cell processes, and it is possible therefore to avoid its effects by proper experimental precautions. It is then permissible to apply the equations in the forms given above.

Thermocells.—Cells of Type II were specifically treated in the former paper.[1] The entropy of transfer of the ions was neglected, however, in the development given there. When this is included, the equation (19 of the former paper) becomes

$$F\mathrm{d}E/\mathrm{d}T = \Delta S_R + \Delta S^* \tag{4}$$

In this equation ΔS_R is the entropy gained by the system at the higher temperature in the electrode reaction caused by one faraday passing from left to right through the cell. ΔS^*, again the net entropy of transfer of ions, is now given by

$$\Delta S^* = t_C S_C^* - t_A S_A^* \tag{5}$$

The Soret effect is again neglected, since the measurements may be made so as to exclude its influence in the solution, and it is assumed to be negligible for the electrons in the wire in the temperature gradient.

By opposing two cells of this second type having the same electrodes, and electrolytes with a common negative ion but with different positive ions, a change in state is produced on operation which is the same as that in the Type I cells, except for the liquid junction reactions. These combinations without liquid junction obviously offer many advantages over the first type for the determination of entropy sums such as that in Equation 3.

Approximate Calculation of Entropy of Transfer of Ions

Of the existing data applicable in Equations 2 and 3 for the determination of entropy of transfer of ions, the most satisfactory are those of Podzus,[4] since they relate to dilute solutions and were obtained under conditions designed to eliminate the effect of the Soret phenomenon. The observations to be used here were obtained from a series of cells of Type I (and a few combinations of Type II) in which the first and second electrolytes

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[3] Nernst, *Z. physik. Chem.*, **4**, 129 (1889).

[4] Podzus, *Ann. Physik*, [4] **27**, 859 (1908).

were different members of a group comprising the chlorides of hydrogen, ammonium and four of the alkali metals. They may be cast in the form of five independent equations, based upon Equation 3, as follows

$$\begin{array}{lllll}
0.497\,S^*_{\mathrm{K^+}} - 0.822\,S^*_{\mathrm{H^+}} & - 0.325\,S^*_{\mathrm{Cl^-}} & = & -7.15 \pm 0.15 & (6)\ \mathrm{a} \\
0.497\,S^*_{\mathrm{K^+}} - 0.343\,S^*_{\mathrm{Li^+}} & + 0.154\,S^*_{\mathrm{Cl^-}} & = & 0.57 \pm 0.15 & \mathrm{b} \\
0.497\,S^*_{\mathrm{K^+}} - 0.402\,S^*_{\mathrm{Na^+}} & + 0.095\,S^*_{\mathrm{Cl^-}} & = & 0.08 \pm 0.1 & \mathrm{c} \\
0.497\,S^*_{\mathrm{K^+}} - 0.508\,S^*_{\mathrm{Rb^+}} & - 0.011\,S^*_{\mathrm{Cl^-}} & = & -0.07 & \mathrm{d} \\
0.497\,S^*_{\mathrm{K^+}} - 0.498\,S^*_{\mathrm{NH_4^+}} & - 0.001\,S^*_{\mathrm{Cl^-}} & = & 0.60 \pm 0.1 & \mathrm{e}
\end{array}$$

The directly observed data upon which these equations depend are average temperature coefficients of electromotive force, dE/dT, over intervals of about 20°, the mid-point being 25°. The concentration of the solutions was 0.02 *N*. Podzus' calculations from the Planck equation of the junction e.m.f.'s were used to correct the direct observations to give the values of ΔS^*. The numerical values of ΔS^* in Equations 6 are averages obtained from several combinations. The average deviation of separate values from the mean is indicated in the equation when more than one value is obtainable.

From thermodynamics alone these relations are all that can be obtained. To calculate the entropies of transfer of the individual ions some further relation between them is required. At the present time no such relation is known. In the paper preceding, however, certain general deductions of a qualitative character were made concerning the magnitudes of these quantities. Thus it was concluded that they are independent of each other in dilute solution and that they are always positive in sign. It also appears probable that in a series of closely related ions, such as those of the alkali metals, the entropies of transfer vary in the same order as the mobilities. Utilizing these ideas in connection with Equations 6, the magnitudes may be roughly fixed for each ion. Thus from Equation 6e the minimum value of $S^*_{\mathrm{K^+}}$ is determined to be about 1.2 ± 0.2, since neither $S^*_{\mathrm{NH_4^+}}$ nor $S^*_{\mathrm{Cl^-}}$ may be less than 0. From Equation 6c, the maximum value of $S^*_{\mathrm{K^+}}$ is fixed as 0.9 ± 1, since $S^*_{\mathrm{Na^+}}$ cannot (according to the above ideas), exceed $S^*_{\mathrm{K^+}}$ and $S^*_{\mathrm{Cl^-}}$ cannot be less than 0. Adopting 1.0 as a probable value of $S^*_{\mathrm{K^+}}$, that for $S^*_{\mathrm{Cl^-}}$ must be about 0.0 if $\mathrm{Na^+}$ is to fall between $\mathrm{Li^+}$ and $\mathrm{K^+}$ in the series. With these values fixed, the others follow from the equations. The experimental errors in ΔS^+ in Equation 6 are large enough to render these values rather uncertain. Within the limits of error, however, the values shown in Table I agree with the experimental data, and with the general properties enumerated above, and no large changes in them are possible without some departure from this agreement.

TABLE I

ENTROPY OF TRANSFER, IN CALORIES PER DEGREE PER MOLE, OF IONS IN 0.02 *N* SOLUTIONS AT 25°

Ion	$\mathrm{H^+}$	$\mathrm{Li^+}$	$\mathrm{Na^+}$	$\mathrm{K^+}$	$\mathrm{Rb^+}$	$\mathrm{NH_4^+}$	$\mathrm{Cl^-}$
Entropy of transfer	9.3	0.1	0.9	1.0	1.1	0.0	0.0

The values in Table I can scarcely be said to have been calculated. Rather, they have been selected to agree with the known data and probable laws. Nevertheless, they can hardly fail to be correct in order of magnitude and the probability is high that the relative and absolute values are roughly correct also. Due in part to experimental uncertainties and partly to the approximate character of the assumptions made, nothing more than this rough correspondence can be claimed. The results of these estimates make it appear probable that experiments more expressly designed for the purpose would lead to a fairly close limitation of the values of the entropies of transfer, even though a sufficient number of quantitative relations for their exact determination be not available.

The results of the application of the values in Table I to the calculation of Soret coefficients are discussed in the preceding paper.

Partial Molal Entropy of Chloride Ion

Richards[5] measured dE/dT in cells of Type II exemplified by

$$\underset{T_2}{\mathrm{Hg}},\ \underset{T_2}{\mathrm{HgCl}},\ \mathrm{HCl}(0.1\ M),\ \underset{T_1}{\mathrm{HgCl}},\ \underset{T_1}{\mathrm{Hg}}$$

Applying Equation 4 to this cell, it is seen that ΔS_{R} is the entropy change in the reaction

$$\mathrm{Hg} + \mathrm{Cl}^-(0.1\ M) = \mathrm{HgCl} + \mathrm{E}^-_{(\mathrm{Hg})}$$

Further

$$\Delta S^* = t_{\mathrm{H}} S^*_{\mathrm{H}} - t_{\mathrm{Cl}} S^*_{\mathrm{Cl}} \tag{7}$$

Using the measured values of dE/dT, with the entropy of transfer of H^+ and Cl^- from Table I, the entropy change in the calomel electrode half reaction may be calculated. From the known entropy of calomel and mercury that of chloride ion may then be obtained.

Richards's best experiments were made with the chlorides of hydrogen, lithium, sodium and potassium as electrolytes. Data pertaining to each of these cells are collected in Table II. The total entropy change of the cells as calculated from dE/dT is shown in the second column of the table. The temperature to which it corresponds is 15°, and the concentration of electrolyte is 0.01 M. The third column gives ΔS^* as calculated by Equation 7 from the data of Table I. The latter apply to 0.02 M solution at 25°. In calculating ΔS_R in the fourth column, the errors due to these differences in concentration and temperature are assumed to be no larger than the other errors. It is also assumed that the Soret equilibrium was not established in the cells, though this assumption is difficult to verify from Richards's descriptions. The entropies of Hg and HgCl used, with ΔS_R, in calculating $\overline{S}_{\mathrm{Cl}^-}$ in the fifth column of the table are 17.8 and 23.2, respectively.[6]

[5] Richards, *Z. physik. Chem.*, **24**, 39 (1897).

[6] See Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, and Gerke, THIS JOURNAL, **44**, 1684 (1922).

TABLE II

PARTIAL MOLAL ENTROPY, IN CALORIES PER DEGREE, OF CHLORIDE ION IN 0.01 M SOLUTION AT 15°

Electrolyte	$F dE/dT$	ΔS^*	ΔS_R	$\bar{S}_{Cl^-}$	Deviation from av.
HCl	−15.2	7.6	−22.8	28.2	0.2
LiCl	−23.1	0.0	−23.1	28.5	.5
NaCl	−21.9	.4	−22.3	27.7	.3
KCl	−21.7	.5	−22.2	27.6	.4
Average			−22.6	28.0	.4

A set of observations similar to those of Table II but with 0.1 M electrolytes gives 24.5 as the average entropy of chloride ion, at this concentration and 15°, the average deviation of individual results from the mean being 0.5. These values of $\bar{S}_{Cl^-}$ are in close agreement with those calculated by Chipman.[7]

In spite of the lack of correspondence of temperature, concentration and other experimental conditions in the various measurements on which these calculations are based, they appear to be of sufficient reliability to indicate the possibilities of this method of determination of partial molal entropies of ions. Absolute values for individual ions, as obtained here, are unnecessary in ordinary thermodynamic work, yet their use would agree with usual practice when pure substances are concerned. Comparison of these values with those calculated in other ways[8] is also of some interest. For these reasons this field seems worthy of further experimental development.

Summary

Thermodynamic equations are given connecting the entropy of transfer of ions and entropy changes in single electrode reactions with the e.m.f.'s of certain thermo-electric cells. Application of them is made to the calculation of the entropy of transfer of six of the common univalent cations, and chloride ion. As an illustration of the possibilities of the method in the field of ionic entropies, the partial molal entropy of chloride ion is calculated.

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[7] Chipman, *Thesis*, University of California, **1926**. Chipman made the assumption in his work that the potential gradient (corresponding to ΔS^*) in solutions of lithium chloride and ammonium chloride is negligibly small. This was based in turn on an assumed connection between the potential gradient and the Soret effect, the measured values of the latter being very small in the solutions in question. These ideas are supported by the present calculations.

[8] See, for example, Latimer, THIS JOURNAL, **48**, 1234 (1926).