The authors intend to study the application of the "Galvanometric" method to other reactions than those studied.

Summary

This paper describes a simple, direct reading and inexpensive system for determining end-points of oxidation-reduction reactions. The method depends upon the sudden change at the end-point in the potential difference between a platinum and a tungsten electrode which are immersed in the solution.

[Contribution from the Chemical Laboratory of the University of California]

THEORY OF THE SORET EFFECT

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In a previous paper[1] a thermodynamic theory of the reversible Soret effect was given. It was there shown that the effect is related in magnitude to the heat of transfer of the constituents of the solutions in which it is manifested. Consideration of the nature of the latter quantity leads to a number of conclusions concerning general questions not yet experimentally settled. These inferences, and the views on which they are based, render intelligible many obscure features in this very uncertain field and offer guidance to further progress in it. They will, therefore, be outlined in this paper.

Definitions and Thermodynamic Relations

When a portion of one of the constituents of a solution is transferred by diffusion, or in the case of ions by an applied electric field, from one region to another within the solution, there is in general an accompanying absorption of heat from the surroundings of one region and evolution in those of the other. The quantity of heat absorbed from the surroundings of the region (of infinite extent) from which one mole of constituent A is transferred will be denoted by Q^*_A.[2] The entropy lost by the surroundings of the region from which the transfer is made is then $Q^*_A/T = S^*_A$. These quantities will be referred to as the heat and entropy of transfer, respectively. Their nature will be discussed in detail later.

In the former paper it was shown that in a binary solution placed in a temperature gradient the equilibrium compositions due to reversible effects are governed by the equation

$$(\partial \overline{F}_A/\partial N_A)_T \, dN_A = - S^*_A \, dT \tag{1a}$$

or

$$(\partial \overline{F}_A/\partial \ln N_A)_T \, d \ln N_A = - S^*_A \, dT \tag{1b}$$

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[1] Eastman, This Journal, 48, 1482 (1926).

[2] In the previous paper, ref. 1, $\overline{Q}_A$ was used as the symbol for the heat of transfer. To avoid confusion with the partial molal quantities in the case of entropy it seems better to adopt the symbols above.

Here $\bar{F}$ and N represent partial molal free energy and mole fraction, respectively. These equations are correct if the composition change is the only effect produced by the gradient in temperature.

The first members of Equations 1 are each equal to the change in partial molal free energy of constituent A corresponding to an isothermal composition change of the same magnitude as that produced by the temperature gradient. It was this quantity which it was found desirable to use in defining a Soret coefficient for use in theoretical work. Calling the latter s_A, and writing $\mathrm{d}F_A^*$ in place of the first member of (1) a defining equation may be written

$$s_A = \mathrm{d}F_A^*/\mathrm{d}T = -S_A^* \qquad (2)$$

In numerical comparisons of the effect in different solutions it is also desirable to employ where possible the coefficient defined by (2) rather than the ordinary ones ($\mathrm{d} \ln N_A/\mathrm{d}T$ or $d \ln c_A/\mathrm{d}T$) resulting from direct determinations. The latter coefficients are proportional to the former in sufficiently dilute solutions, but in more concentrated imperfect solutions this proportionality fails. The magnitude of the composition change is then of lessened significance. As an extreme illustration of this the case of a metal, regarded as a "solution" of ions and electrons, may be cited. Ordinary temperature gradients can scarcely produce appreciable composition changes in such systems. Yet it would be a mistake to assume the Soret effect to be negligible, since an appreciable potential gradient and free energy difference are still possible. This is an example in which a large rate of change of free energy with composition is coupled with a small actual or fractional change in concentration. The reverse of this might be illustrated by substances forming a two-phase mixture. A solution near one of the equilibrium compositions would show very small values of $(\partial\bar{F}/\partial N)$ and correspondingly large values of $\mathrm{d}N$, even though the free energy change and therefore the true Soret effect were small.

To illustrate the difference in the two coefficients in solutions of some representative electrolytes, the following examples may be given. According to Arrhenius[3] $\mathrm{d} \ln c/\mathrm{d}T$ in 0.05 M copper sulfate is -2.2×10^{-3}, and in 0.5 M -9.3×10^{-3} deg.$^{-1}$ Using Lewis and Randall's[4] activity data, the corresponding values of s (Equation 2) are found to be -1.5 and -4.6, cal./deg., respectively. Chipman[5] gives -2.1×10^{-3} and -0.33×10^{-3} for the ordinary coefficient in 0.1 M and 10 M hydrochloric acid, while the values of s are 2.3 and 1.4 cal./deg. For most strong electrolytes in concentrations up to 0.1 M, however, the relative values of the two coefficients are constant within the present rather wide limits of error.

One further point concerning the application of Equation 2 to solutions

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[3] Arrhenius, *Z. physik. Chem.*, **26**, 18 (1898).

[4] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**.

[5] Chipman, THIS JOURNAL, **48**, 2577 (1926).

of electrolytes should be mentioned at this stage. Solutions of binary electrolytes are really to be regarded in the present connection as systems of three components. This follows because of the partially independent distribution of the ions in the temperature gradient which manifests itself in the accompanying potential gradient[6] in the solution. It might, therefore, be supposed that the total Soret effect should be considered in two parts. These parts would be associated, respectively, with the free energy change due to the concentration gradient and that due to the electrical gradient. The latter part of the effect may, however, be seen to be negligible compared to the first. Owing to the very strong forces between ions of opposite charges, the gradient in ionic composition must be extremely small. The number of equivalents of positive ion transferred in establishing equilibrium, or in returning to the normal condition after removal of the temperature gradient, is therefore almost exactly the same as that of the negative ion. The free energy difference per mole of either ion transferred in such diffusion, which is the product of the difference in number of equivalents of oppositely charged ions, and the potential difference between which they are moved, must be negligibly small even though the potential difference itself is not. This being the case, the Soret free energy difference is due mainly to the concentration difference of the electrolyte and is governed by an equation like (2) in which the entropy term is the sum of the entropies of transfer of the ions corresponding to one mole of electrolyte. That is, the system may still be treated as one of two components.

The Nature of Heats of Transfer in Solutions of Electrolytes

For the purposes of the present discussion the space in the vicinity of an ion in an undissociated polar solvent may be divided, roughly, into three concentric regions of gradually differing properties. First, there is the "ion-cavity,"[7] within which there are no solvent molecules. This space varies in size from case to case and appears to be large compared to the volumes defined by the outer electron orbits of the ion. Immediately outside of the ion cavity the (polar) molecules of solvent are strongly attracted and oriented. The inner layers of solvent molecules in this second region, and those extending out from it to varying distances in different cases, are held so strongly by the central ion as to form a complex with it, acting in processes of diffusion, as a single molecule. The third region comprises all the rest of the outer space. In this sphere the solvent molecules are still subject to forces of compression and orientation, diminishing with distance from the center of the complex, and not sufficiently strong to bind these molecules to the ion. The second and third

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[6] Potential gradients of this kind are discussed in the paper following this.

[7] Webb, This Journal, **48**, 2589 (1926).

of these regions obviously merge into each other in such a way as to prevent sharp boundaries from being drawn between them.

When a solvated ion of the kind described is transferred by diffusion from one region to another of the solvent, the aggregate comprising the first and second regions above remains mostly intact and takes part in no internal energy or entropy changes. But as the ion moves it leaves behind material which had been under its influence in the third sphere, and brings under its influence solvent molecules not previously so strongly affected. A relaxation occurs, therefore, in the region from which it goes, with an attendant increase in entropy and absorption of heat. The reverse effects appear in the region into which it moves. It is, therefore, these changes in the third sphere that give rise to the heats of transfer that determine the reversible Soret effects in solutions of ionized substances.

The conception of solvated ions outlined above takes into account only the electrical effects produced by the charge of the ion upon the molecules of the solvent regarded as electric dipoles. The mechanism of the heat of transfer dependent upon it holds strictly therefore only in the simpler cases. Several factors that were neglected in its discussion may be of importance in certain cases. Any sort of chemical bonding in the ion aggregate may greatly affect the spheres of influence about the central charge, and so alter the heat effects attending its diffusion. This kind of thing may differentiate, for example, between positive and negative ions in their orienting and bonding effects on water molecules. The hydrogen nuclei of the solvent may form a sort of hydrogen bond[8] with electrons of the outer shell of negative ions, a type which is not possible between the oxygen atoms and most positive ions. The effect of such bonds, if extensively formed, would be to increase region two at the expense of three, with consequent lessening of the heat of transfer. The possibility that either ion of the solvent may be transferred, in effect, by a chain mechanism, must also be considered in solutions of acids and bases. For if this occurs, not only the energy represented in the third sphere above, but that of the second as well, a very much larger quantity, would be involved in the heat of transfer.

The simple mechanism pictured above would appear to afford a basis for quantitative theoretical treatment. The entropy effects in region three about the ion depend upon the degree of compression and orientation of the solvent molecules in it. Both are approximately calculable in any element of volume at a given distance from an ionic center by methods like those of Webb.[7] The dependence of the entropy of the solvent upon pressure is measurable, and the entropy change due to orientation might be calculated from the relative probabilities of the axial distributions

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[8] Rodebush and Latimer, THIS JOURNAL, **42**, 1419 (1920).

of the dipoles in the field of the ion and without it by methods like those of Langevin. Volume integrations throughout the sphere should result in the desired entropy. One of the limits in the integration is obviously infinity. The other, which is the boundary between regions two and three, is somewhat indefinite and variable from one ion to another. It could probably be fixed with enough exactness as the radius at which the equipartition amount of kinetic energy would be just sufficient to carry a solvent molecule against the force of attraction of the ion (known as a function of distance) to infinity. This would be, on the average, the dividing line between the "bound" and "unbound" solvent molecules, and would serve to define the third region above for the purpose of integration. The calculation outlined therefore appears theoretically feasible. Practically, however, several obstacles are encountered. Thus some of the essential data required in it, such as the electric moment of solvent molecules, are known only very inaccurately at present. Further refinements, taking into account the ion cavity, in calculations of the force field about ions, and some indication as to the influence of other factors than the purely electrostatic ones, are no doubt also necessary. This is particularly true since the effect in question is of the second order, as compared with the entire "entropy of solvation" of the ions. The actual application must therefore await these developments. It is, however, possible to draw a number of conclusions and suggest correlations from these ideas. Before proceeding to their discussion it is desired to present in the next section a comparison of certain indirectly measured entropies of transfer with those corresponding to measured Soret effects.

Comparison of Directly and Indirectly Determined Soret Effects

In the paper following this, approximate values are calculated for the entropy of transfer of the ions of a number of substances for which Soret coefficients have also been measured. The Soret coefficients corresponding to these, together with the experimentally determined values by several investigators, are shown in Table I.

TABLE I

SORET COEFFICIENTS, IN CALORIES PER DEGREE PER MOLE, OF CERTAIN ELECTROLYTES IN WATER

Observer	Av. temp., °C.	Av. concn., *M*	HCl	LiCl	NaCl	KCl	NH_4Cl
Soret[9]	47	±1.0	...	−0.10	−0.67	−1.1	..
Arrhenius[3]	47	0.02	−2.9	....	−1.3	....	..
Wereide[10]	50	.17	...	....	(−2.5)	....	..
Chipman[5]	25	.1	−2.3	−0.023	−0.15	−0.19	0.00
Calculated	25	.02	−9.3	−0.1	−0.9	−1.0	0.0

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[9] Soret, *Ann. chim. phys.*, [5] **22,** 293 (1881).

[10] Wereide, *Ann. Physik,* **2,** 55 (1914).

The calculated values in the last line of Table I are approximate in character and subject to revision when more reliable measurements of the electromotive forces from which they were obtained are available. They are, however, thought not to be seriously in error. In comparing them with the experimental Soret coefficients of the table it is seen that they agree fairly well with the older determinations, but are much higher than the more recent results of Chipman. It should be borne in mind in this connection that for stable substances all of the systematic errors of measurement render the observed values too low. There is, moreover, much evidence that some unstudied source of error is present in some, at least, of the measurements. Thus, two observers of the same quantity seldom agree. Duplicate determinations by one observer show differences much larger than the apparent errors in either observation. The occasional occurrence of curves of Type C in Chipman's[5] observations of the approach to equilibrium points to the presence of convection, the effects of which may have been present but masked in his other experiments. The relative values obtained by a single observer for a series of substances are probably approximately correct. It is only to such relative values that much weight is given in the following discussion, since it appears to the writer that few actual magnitudes for individual substances are known at present with any degree of certainty. It is also thought that the indirect method of determination is capable of greater accuracy than the direct.

Effect of Concentration on Magnitude of Soret Coefficients

The mechanism outlined in the second section to explain the heat of transfer of ions obviously requires a finite value of this quantity for every ion at infinite dilution. As has been previously assumed, and will be discussed later, in strong electrolytes the total effect is the sum of the effects of the constituent ions. For this class of substance it follows that the Soret coefficient approaches a constant finite value with dilution.[11] The form of the curve chosen by Chipman[5] to represent his results for hydrochloric acid at small concentrations is therefore correct.

The heat and entropy of transfer have many of the properties of partial molal quantities. It is easy to show, for example, that for both quantities equations of the following type are valid.

$$N_AS_A^* + N_BS_B^* + \dots\dots = 0 \qquad (3)$$

It follows, therefore, that in the infinitely dilute solution the Soret effect (defined by Equation 2) is zero for the solvent though it is not for the solute; and dN/dT becomes zero for both.

In solutions of electrolytes each ion is surrounded mainly by ions of

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[11] This corrects a statement in the earlier paper. See also in this connection Rodebush, This Journal, **49**, 792 (1927), and Eastman, *ibid.*, **49**, 794 (1927).

opposite sign. The decrease in average distance between oppositely charged ions produced by increasing concentration from infinite dilution will, up to a certain limit at least, increase the field acting on the intervening molecules of the solvent and therefore increase the heat of transfer and Soret coefficient. With further approach of the oppositely charged centers, conditions become more complex and it is difficult to be sure without exact analysis how the third zone of the ions will be affected. If there is appreciable formation of ion pairs, with partial neutralization of the external fields of the ions, a decrease in heat of transfer may be looked for. This would lead to a maximum in the Soret coefficient at higher concentrations. In certain cases, as is pointed out in the following section, continued increase in concentration may lead to a reversal of sign of the effect, with the possibility of a minimum as well as maximum.

The Sign of the Soret Effect

As long as the charge of the ion is chiefly responsible for its solvation, the entropy of transfer of strong electrolytes predicted on the basis of the above mechanism will always be such as to produce an increased concentration of solute in the colder portions of the solution. This is found experimentally to be the case.

It would appear possible, however, to find solutions in which the role of ionized solute and polar (un-ionized) solvent might be reversed at different concentrations. For example, a small amount of water in hydrogen chloride might be ionized and solvated by the halide molecules. It should then be the water which would show increased concentration at the lower temperature. It might, of course, in this instance be necessary to go to very great dilution to secure much ionization of the water. Two constituents of more nearly equal ease of ionization in solution, and still ionized but little when pure, might more readily show this behavior.

Additivity of Soret Coefficients of Ions

The present theory requires, as does almost any other, that individual values be assignable to the Soret coefficients of all ions at infinite dilution, irrespective of the particular combination, and this idea has been used throughout. The theory also indicates many specific effects (such as the possibility of different geometrical packing of ions of different size ratios) which might destroy the additivity in more concentrated solutions. None of these effects would be thought, however, to be of great importance below about 0.1 *M*. That the additivity rule has not been approximately established experimentally at these concentrations is a further indication of uncertainty in the magnitude of the experimental values.

Correspondence with Mobilities of Ions

The total entropy of hydration of ions is known[12] to be an approximately linear function of the inverse of the radius of the ion. The entropy located in the outer sphere of unbound solvent molecules probably is a similar function of the radius of the ion complex (second sphere). The mobility of the ion may also be expected to be a similar function of the latter quantity. If it is, the Soret coefficient of ions should form a series having about the same order as the mobilities. The experimental values again are too uncertain to permit sure conclusions. Yet it appears that in certain series of similar ions, alkalies and halides, the order is actually the same. Apparently the generalization cannot be extended to ions of dissimilar type. For example, ammonium ion and, if the calculations of the following paper are correct, chloride ion appear to have much lower Soret coefficients than potassium ion, though the mobilities are not greatly different. The former both belong to the class of ions in which the electrical effects are perhaps not the only ones determining the size of the ion complex, which may account for the discrepancy.

Effects in Solutions of Non-electrolytes

In considering non-electrolytes in the light of the discussion in the second section, it is apparent that any kind of a molecule that can influence the neighboring molecules of the solvent must give rise to a finite Soret effect, even at infinite dilution. The fields of molecules of non-electrolytes are very much more nearly closed or saturated than are those of ions. The reversible Soret coefficients of non-electrolytes in general should then be very much smaller than those of ions. Even in the latter the effect is often small. With all non-polar substances and many non-electrolytes the coefficient may then be expected to be in general very close to zero. This is found experimentally by Wereide[10] and others to be true for a number of typical substances. Those for which the values appeared not to be zero are almost without exception of an unstable type in which some reaction occurring at different speeds at different temperatures might cause spurious effects. As an example, the fermentation of unsterilized sugar solutions may be mentioned. It is, of course, possible that extremely polar molecules may give rise to effects comparable with actually dissociated ions. In the absence of such polar bonds the conclusion seems fairly sure that only very small reversible Soret coefficients are possible.

Reversibility of the Effect

In the former paper the question of the relative magnitude of the reversible and irreversible Soret coefficients was left open. It now seems

[12] Latimer and Buffington, THIS JOURNAL, 48, 2297 (1926).

likely that in liquid solutions only the reversible effect is of importance. The conditions favorable to a large irreversible effect would appear to have been met in several of the solutions of non-electrolytes which have been studied. The failure to obtain measurable effects (in cases where the source of error mentioned above was precluded) indicates that no large irreversible effect exists in these solutions.

Summary

In this paper the thermodynamic properties of the entropy of transfer of dissolved substances are discussed. This quantity is also considered in its relation to the effect on the solvent of the charge of the ions of electrolytic solutes. A comparison of indirectly determined entropies of transfer is made with measured Soret coefficients for certain substances. From these three sources a number of conclusions, often to be regarded as predictions for the guidance of further experimental investigation but all of a high degree of probability, are drawn. The following ideas are in this way developed.

Soret coefficients are best expressed, when possible, in terms of entropies of transfer. A solution of an electrolyte may be considered from the standpoint of the Soret effect as a two-component system in spite of the partial separation of positive and negative ions in the temperature gradient. Some unknown source of error probably affects seriously many of the existing measurements of Soret coefficients, and indirect determinations may prove more reliable. The Soret coefficient of the solute in imperfect solutions is finite at zero concentration and nearly constant over a certain range from zero. At higher concentrations of strong electrolytes an increase in magnitude of the effect is normally expected. The possibility, in some instances, of a change in sign with both a maximum and minimum in the curve against composition is indicated. The coefficients for all strong electrolytes at small concentrations in water are negative in sign. The Soret coefficients of ions are additive. There is a limited correspondence between the mobility of ions and their Soret coefficients. The Soret coefficient in solutions of non-polar substances is negligibly small, as is also the irreversible Soret effect in all liquid solutions.

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