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THE INFLUENCE OF GELATIN ON TRANSFERENCE NUMBERS

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"The Influence of Gelatin on the Transference Numbers of Sulfuric Acid" by Ferguson and France[2] and "The Influence of Gelatin on the Transference Numbers of Hydrochloric Acid" by France and Moran[3] afford striking examples of the danger involved in the application of a physicochemical formula to conditions other than those of its derivation. Since these papers are of interest to biologists and others who cannot be expected to examine critically the validity of the formulas, it seems advisable to point out that the values which these authors give for transference numbers and for liquid-junction potentials cannot be interpreted as such quantities.

The formula used for the electromotive force of a concentration cell with transference is the ordinary one—for a uni-univalent electrolyte it is $E_- = t_+E = 2t_+ \frac{RT}{F} ln \frac{a_\pm'}{a_\pm}$, where E_- is the electromotive force of a cell with transference with electrodes reversible to the anion, E that of a cell without transference, t_+ is the transference number of the cation, and the $a_\pm$'s are the mean activities of the ions at the two concentrations.[4] It is derived through the assumption that, when an electric current passes through the cell, no matter is carried from one solution to the other except

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[2] Ferguson and France, THIS JOURNAL, **43**, 2161 (1921).

[3] France and Moran, *ibid.*, **46**, 19 (1924).

[4] The symbols of this paper are generally not the same as in the papers discussed. To facilitate comparison the following table is given.

This paper	E_-	E_+	E	E_b	E_x	E_z	t_+	a
Ferguson, France and Moran	E_{Cl}, E_{SO_4}	E_H	E	E_b	E_x	E_z	n_k	C

the ions under consideration. Whenever a second solute, such as gelatin, is present this assumption is contrary to fact because the water is certainly transferred and there will be changes in the concentration of the second solute which may lead to an appreciable error.[5]

In case the second solute is capable of producing ions, those ions will certainly be transferred, so that the error in the calculation of transference numbers may become enormous. From the work of other observers[6] there is little question but that gelatin and hydrochloric acid form a complex which ionizes largely to give chloride ion and a complex gelatin-hydrogen ion. Thermodynamically it makes no difference, of course, whether the mechanism of the reaction is as described or the gelatin reacts with the hydrogen ion to form a complex ion, a part of which combines with the chloride ion.

The cell will be still more complicated and different from the simple one postulated in the derivation of the formula if the concentration of the second electrolyte varies in the different parts of the cell. Such are the cells described in these papers. An example is,

$$\mathrm{Pt,\ H_2}\,|\,\underset{a_{\pm}'}{\mathrm{HCl}\ (0.1\,M)}\ \underset{\overrightarrow{E_{\mathrm{x}}}}{|}\ \underset{a_{\pm}''}{\mathrm{HCl}\ (0.1\,M),\ \mathrm{gel}\ (c)}\ \underset{\overrightarrow{E_{\mathrm{b}}}}{|}\ \underset{a_{\pm}'''}{\mathrm{HCl}\ (0.01\,M),\ \mathrm{gel}\ (c)}\ \underset{\overleftarrow{E_{\mathrm{z}}}}{|}\ \underset{a_{\pm}}{\mathrm{HCl}\ (0.01\,M)}\ |\ \mathrm{H_2,Pt} \qquad (1)$$

Taking into account the chemical reaction, this becomes:

$$\mathrm{Pt,\ H_2}\,|\,\mathrm{HCl}\ (0.1\,M)\,|\,\mathrm{HCl}\ (0.1\,M-x),\ \mathrm{GelCl}\ (x),\ \mathrm{gel}\ (c-x)\,|\,\mathrm{HCl}\ (0.01\,M-z),\ \mathrm{GelCl}\ (z)\ \mathrm{gel}\ (c-z)\,|\,\mathrm{HCl}\ (0.01\,M)\,|\,\mathrm{H_2,\ Pt} \qquad (1')$$

where z is either slightly less than x or slightly less than 0.01 M. Perhaps the discussion will be clearer if we set up an analogous cell entirely of inorganic solutes, neglecting the unchanged gelatin even though its effect must be greater than that of the neutral solute mentioned in the second paragraph because its concentration is different in the different parts of the cell. Such a cell would be,

$$\mathrm{Pt,\ H_2}\,|\,\mathrm{HCl}\ (0.1\ M)\,|\,\mathrm{HCl}\ (0.1\ M-x),\ \mathrm{LiCl}\ (x)\,|\,\mathrm{HCl}\ (0.01\ M-z),\ \mathrm{LiCl}\ (z)\,|\,\mathrm{HCl}\ (0.01\ M)\,|\,\mathrm{H_2,\ Pt} \qquad (2)$$

From inspection of these cells it is obvious that when an electric current passes through there must be a transfer of the ions of both the acid and the

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[5] I have already pointed out this danger in a previous paper [(a) THIS JOURNAL, **45**, 1719 (1923)]. I noted there that this formula had never been derived rigorously. Dr. R. H. Gerke has called my attention to the fact that the derivation of Lewis and Randall [(b) "Thermodynamics," McGraw-Hill Book Co., **1923**, p. 337] becomes rigorous if the differential elements are defined, not to have constant volume, but to contain constant amounts of water, and the transference number is defined in terms of molalities rather than concentrations. This latter definition is consistent with recent experimental practise. My previous statement must now be withdrawn for the case of a solution of a single electrolyte. When a second solute is present, however, any movement of the water relative to the ordinary space coördinates would appear as a movement of the solutes relative to these special coördinates, and the difficulty remains.

[6] J. Loeb, "Proteins and the Theory of Colloid Behavior," McGraw-Hill Book Co., **1922,** Chap. V. D. I. Hitchcock, *J. Gen. Physiol.*, **4,** 733 (1922); **5,** 383; **6,** 95, 201 (1923).

salt through all three of the liquid junctions, and that the mean activity of the ions of hydrochloric acid is not the same in either one of the end solutions as in the corresponding middle solution. The formula which assumes the same activities at the electrodes as at the middle liquid junction (*b*) and that the only transfer is that of the ions of hydrochloric acid across this junction is certainly not applicable. The cell is far too complicated to be interpreted from our present knowledge. Whatever the ratio of its electromotive force to that of a concentration cell without transference may be, it is not a transference number.

The authors justify the omission of gelatin from the electrode solutions by the statement, "the influence of gelatin on transference is due only to its effect on the boundary potential."[7] In the next paragraph, however, they describe difficulties due to the diffusion of the gelatin to the electrodes. Later[8] they give values for the electromotive force of the cell, H_2,Pt | HCl (0.1 *M*) | KCl (*M*) | HCl (0.1 *M*), gel (*c*) | H_2,Pt, which show an effect of the gelatin many times larger than a possible error in the assumption that the potassium chloride bridge eliminates liquid-junction potentials. In the paper of France and Moran the concentrations of hydrogen ion are calculated from the formula, $E' = 2RT/F\ ln\ a'_+/a_+$ instead of $E' = RT/F\ ln\ a'_+/a_+$, so that their calculated change in concentration is much too small. The values calculated from their measurements are given in Table I, in which the values for the solutions without gelatin are taken from their paper. It is clear that, unless the liquid-junction potential with potassium chloride changes enormously, the gelatin does have an important effect on the potential drop at the hydrogen electrode, and that the results would be quite different if gelatin were present in the electrode solutions.

TABLE I

CELLS WITH HYDROGEN ELECTRODE AND POTASSIUM CHLORIDE BRIDGE

Gelatin	0.1 *M*		0.01 *M*	
%	E'	a_+	E'	a_+
0	.....	0.0917	.....	0.00975
1	0.00217	.0843	0.03946	.00210
2	.00391	.0788	.09754	.00022
3	.00588	.0729	.12057	.00009
4	.00789	.0674	.12421	.00008

The customary formula for the liquid-junction potential in a concentration cell is for uni-univalent electrolytes: $E_b = (1-2t_-)\ \frac{RT}{F}\ ln\ \frac{a_\pm'}{a_\pm} = \frac{(1-2t_-)}{2}\ E = \frac{E_- - E_+}{2}$ where E_b is the liquid-junction potential. The first form is derived by subtracting the electrode potentials from the total electromotive force of the cell with transference; the others, by combining

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[7] Ref. 2, p. 2162.

[8] Tables IV in both papers.

the first with the formulas for the total electromotive force of the various cells. They depend upon the same assumptions as the formula for the electromotive force of the cell with transference. Moreover, the electrode potentials are calculated on the assumption that in any solution the positive and negative ions have equal activities. This assumption is contrary to present day theories of the nature of electrolytic solutions. Probably the error is small for solutions of 0.1 and 0.01 *M* hydrochloric acid; it is 1.6 millivolt according to the values given by Lewis and Randall.[9] For sulfuric acid it may be somewhat larger. Moreover, it is obvious from inspection of the type cells given above that there are three liquid-junction potentials. The value given by the authors for the liquid-junction potential would be the sum of the three potentials if the assumptions were justified. All that can be obtained from these measurements without assumption is that the change in the total electromotive force on the addition of gelatin equals the sum of these three potentials minus the single liquid-junction potential when no gelatin is present.

Planck[10] and Henderson[11] have derived formulas for the potential at liquid junctions of this type, using two different assumptions as to the nature of the junction. They both assume that ionization is complete and that both the activity coefficients and the mobilities are independent of the concentration. The first assumption is incompatible with each of the other two for solutions of finite concentration, so that the formulas are certainly not accurate. Moreover, they require a knowledge of the concentration and mobility of each ion, so that they are not applicable to the present case even as approximations.

The papers of Ferguson, France and Moran also include a supposed proof that the change in liquid-junction potential cannot be due to a change in acid concentration because the algebraic sum of the three liquid-junction potentials, calculated on the assumption that the activity of the chloride ion is equal to that of the hydrogen ion as measured by the cell with potassium chloride bridge, is equal to the potential when no gelatin is present (E_0). The symbols for these potentials and for the activities in the four solutions are indicated in the first cell diagram (1). The check equation is $E_x + E_b - E_z = E_0$ or $E_z - E_x = E_b - E_0$. The formulas for the potentials used by the authors are,

$$E_z = [(1-2t_-)RT/F](ln\ a_\pm - ln\ a_\pm''') \quad E_x = [(1-2t_-)RT/F](ln\ a_\pm' - ln\ a_\pm'')$$
$$E_b = [(1-2t_-)RT/F](ln\ a_\pm'' - ln\ a_\pm''') \quad E_0 = [(1-2t_-)RT/F](ln\ a_\pm' - ln\ a_\pm)$$

Obviously $E_z - E_x = E_b - E_0 = [(1-2i_-)RT/F](ln\ a_\pm - ln\ a_\pm''' + ln\ a_\pm'' - ln\ a_\pm')$, and this equation must hold whatever values are given to the transference number and to the activities in the different solutions.

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[9] Ref. 5b, p. 382.

[10] Planck, *Ann. Physik*, **40**, 561 (1890).

[11] Henderson, *Z. physik. Chem.*, **59**, 117 (1907); **63**, 325 (1908).

The small discrepancies found by the authors must be due to inaccuracies in calculation rather than to slight experimental errors.

It is clear that this proof does not depend at all upon experiment. As a mathematical argument, it merely proves that, in a concentration cell containing but one solute, the electromotive force depends only on the concentrations at the electrodes, and not at all upon intermediate concentrations. This has been proved many times in the literature. Perhaps the simplest proof is that of Lewis and Randall.[5b]

It may be added that, even if the transference numbers and liquid-junction potentials were correct as given, there would be nothing in these papers which appears to me to be evidence bearing on any of the following questions which the authors discuss: Is the reaction of gelatin and hydrochloric acid a stoichiometrical chemical reaction or an adsorption? Is there a single compound, or several? Is the reaction one between gelatin and hydrochloric acid, or between gelatin and hydrogen ion? There does appear to be evidence in the work of others referred to above[6] that the authors' conclusions regarding the first two are correct.

Summary

1. The values given by Ferguson and France and by France and Moran for the transference numbers of sulfuric and hydrochloric acids in the presence of gelatin and for the liquid-junction potentials in concentration cells of these acids containing gelatin cannot be so interpreted.

2. The cells measured by these authors are too complicated for interpretation without supplementary experiments and without an extension of the theory of liquid junctions.

3. Their proof that the change in liquid-junction potential is not produced by a change in acid concentration is independent of the experimental measurements upon which it is apparently based.

4. The experimental results, however interpreted, do not give evidence either for or against many of the conclusions drawn by the authors.

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