the electrolysis, the transference numbers hitherto obtained for the more concentrated solutions of these chlorides are erroneous, since the calculation involved the assumption that the water remained stationary. The true transference numbers, derived by reference to the non-electrolyte, are found to vary with the concentration much less than the apparent ones previously computed. In the case of potassium chloride, there is no variation whatever up to a concentration of 1.2 molal.

6. A mathematical relation between the true transference number and the ordinary one as obtained by the Hittorf method is derived. It is also pointed out that the method of moving boundaries gives the true transference number. The results of Denison and Steele obtained by this method are compared with the true transference numbers obtained in the present investigation and shown to agree. Attention is called to the fact that the combination of transference numbers obtained by the Hittorf method with those obtained by the method of moving boundaries furnishes a promising method for further investigating the hydration of ions.

THE POTENTIAL OF THE FERRO-FERRICYANIDE ELECTRODE.

BY GILBERT N. LEWIS AND LEDYARD W. SARGENT.

An electrode of platinum or other noble metal, in a solution containing potassium ferrocyanide and potassium ferricyanide, gives an extremely well defined potential.[1] In order to employ a method, which will be described in another paper, for determining accurately the potential between two liquids, it became necessary to study the properties of this ferro-ferricyanide electrode under varying conditions and especially in the presence of other salts. The results of the investigation not only acquaint us with a unique kind of oxidation and reduction electrode,

[1] Fredenhagen, Z. anorg. Chem., **29,** 396 (1902). Schoch, THIS JOURNAL, **26,** 1422 (1904).

but also throw some interesting light on the ionization of a little studied type of electrolyte.

The strengths of the stock solutions of potassium ferro- and ferricyanide employed throughout this work were determined by several independent methods. The results were not altogether concordant, especially in the case of the ferricyanide, for the determination of which it seems that no entirely satisfactory method exists. Still the concentrations of both solutions were certainly known to within 0.5 per cent., a sufficient accuracy for the present purpose. The solution of potassium ferrocyanide contained 0.408 mol per liter. For the sake of brevity this will be referred to as solution (o). The ferricyanide solution contained 0.542 mol per liter. It will be referred to as solution (i).

The electrodes first used were of plain platinum foil, later they were platinized, iridized, or gold-plated. The gold electrodes gave by far the most constant and reproducible results and were used in all the experiments which will be here described.

The electrode solution was made in each case by adding with an accurate pipette several tenths of a cubic centimeter of each of the stock solutions (o) and (i) to 100 cc. of a solution of potassium chloride. The concentration of the latter was varied between normal and 0.05 normal. In all cases, therefore, the concentrations of ferro- and ferricyanide were small compared with that of the potassium chloride.

The solution together with the gold electrode was placed in a tube of the form commonly used for "half-cells,"[1] and the potential was measured against a normal calomel electrode.[2] Immediately after being set up the electrode gives its true potential, which remains constant to within a few hundredths of a millivolt for an hour or two, after which time the potential changes slowly, probably because of a slight catalytic decomposition of one of the solutions by the electrode metal.

TABLE I.

0.25 cc. of solution (o) }
0.25 cc. of solution (i) } to 100 cc. 0.1 N KCl.

E.

a.	0.1409
b.	0.1409 +
c.	0.1408 +
d.	0.1409 —
e.	0.1409 --

In order to avoid any error that might arise from some peculiarity in a single electrode, the potential of each solution was measured independently with at least four different electrodes. The values thus obtained differed in the extreme by 0.0001 or rarely by 0.0002 volt. The above table

[1] See Ostwald-Luther, *Phys. Chem. Messungen*, Fig. 276.

[2] See note appended to this paper.

shows a typical set of measurements with five different electrodes. E represents the potential against a normal electrode. This and all the following series of measurements were made at $25°$.

Table II contains the results of measurements with varying quantities of ferro- and ferricyanides and different concentrations of potassium chloride. The second column gives the latter concentrations in equivalents per liter. The third and fourth columns give respectively the number of cc. of stock ferro- and ferricyanide solutions added to 100 cc. of the potassium chloride solution. The fifth column gives the numerical values of the potentials measured against the normal electrode. Each of these figures is the mean of several concordant results obtained with separate electrodes. In all cases the positive current tends to flow, through the electrolyte, from the calomel electrode to the ferro-ferricyanide electrode.

TABLE II.

	Conc. KCl.	cc. (o).	cc. (i).	E.
(1)............	0.8	0.25	0.25	0.1855
(2)............	0.4	0.25	0.25	0.1690
(3)............	0.4	0.25	0.75	0.1970
(4)............	0.2	0.25	0.25	0.1538
(5)............	0.2	0.375	0.375	0.1539
(6)............	0.2	0.50	0.50	0.1540
(7)............	0.2	0.125	0.375	0.1820
(8)............	0.2	0.25	0.50	0.1719
(9)............	0.2	0.25	0.75	0.1824
(10)............	0.2	0.50	0.25	0.1362
(11)............	0.1	0.25	0.25	0.1409
(12)............	0.1	0.25	0.75	0.1694
(13)............	0.05	0.25	0.25	0.1293
(14)............	0.05	0.25	0.75	0.1587

The Heat of the Reaction in the Cell.—For two solutions the temperature coefficients of the potentials were accurately determined. The first, A, contained 0.25 cc. (o) and 0.25 cc. (i) in 100 cc. 0.2 N KCl. The second, B, contained 0.25 cc. (o) and 0.75 cc. (i) in 100 cc. 0.05 N KCl. These electrodes were connected with a fifth-normal calomel electrode which happened to be in use at the time as a working electrode. The e. m. f. of the cells thus constructed was found to vary linearly with the temperature between $18°$ and $40°$ according to the equations:

(A) $E = 0.1176 - 0.00229 (t - 25)$
(B) $E = 0.1221 - 0.00230 (t - 25)$

The reaction occurring in both cells may be written

$$Hg + Cl^- + Fe(CN)_6^{---} = HgCl + Fe(CN)_6^{----}.$$
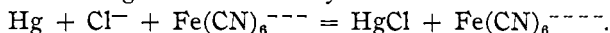
The heat, Q, evolved in this reaction can be found at once by the application of the Helmholtz equation

$$E - Q/F = T \, dE/dT.$$

From this equation and the above data we find for (A) $Q = 18500$ cal., and for (B) $Q = 18600$ cal. The difference between these two values is hardly greater than the possible experimental error. We shall see that the ferro- and ferricyanides had very different degrees of dissociation in the two solutions, the degree of dissociation of each being indeed several times as great in B as in A. We may conclude therefore that for these salts, as for salts of simpler type, the heat of ionization is very small.

From existing data the value of Q for the above reaction may be obtained by combining certain calorimetric determinations of Joannis[1] on the oxidation of ferrocyanide and of Varet[2] on the formation of mercury halides. The result is $Q = 17600$. The difference between this result and the above is almost undoubtedly to be ascribed to an error in the calorimetric data.

This calculation illustrates the fact, not generally recognized, that by the application of the Helmholtz formula it is possible to determine heats of reaction more easily and often much more accurately, than by calorimetric methods. It is very desirable that this method should be applied to the determination of the quantity of heat evolved in a number of the more important reactions.

The Degree of Ionization of Potassium Ferrocyanide and Ferricyanide.— From the data given in Table II. we can draw some interesting conclusions concerning the degree of dissociation of potassium ferro- and ferricyanides. It is a well-known fact that the degrees of dissociation of different electrolytes under corresponding conditions depend upon the type to which they belong, this type being determined by the product of the valences of the two ions of the electrolyte. Thus at equivalent concentrations potassium chloride (product $= 1$) is more dissociated than potassium sulphate (product $= 2$), and this in turn we should expect to be more highly dissociated than potassium ferricyanide (3) or potassium ferrocyanide (4). In fact we find, for example, that in tenth-normal solutions potassium chloride is 85 per cent. dissociated, potassium ferrocyanide only about 50 per cent.[3]

The reaction occurring at the ferro-ferricyanide electrode is most simply written

$$Fe(CN)_6^{---} + (-) = Fe(CN)_6^{----}.$$
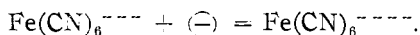
Hence the exact equation for the electrode potential is[4]

$$E = RT/F \, ln \, \xi_i / \xi_0 + \text{const.} \qquad (1)$$

where R, T, and F have their customary significance, *ln* denotes natural

[1] *Ann. chim. phys.* [5], 26, 520 (1882).

[2] *Compt. rend.*, 120, 620 and 921 (1893).

[3] For this value I am indebted to Dr. John Johnston, whose measurements of the conductivity of ferrocyanide solutions are about to be published.

[4] See Lewis, *Z. physik. Chem.*, 61, 129 (1907), equation (28).

logarithm, and ξ_i and ξ_o represent the activities of the ferri- and ferro-cyanide ions. Assuming that a solution of each of these ions obeys the laws of the perefect solution, the activities are proportional to the concentrations, and we may write

$$E = E_o + RT/F \; ln \; C_i/C_o, \qquad (II)$$

where E_o is a constant and C_i and C_o are the concentrations of the two ions. For any series of measurements in which the degree of dissociation is constant for both potassium ferrocyanide and potassium ferricyanide, C_i and C_o will be proportional to C'_i and C'_o, the total concentrations of ferri- and ferrocyanide. Hence for such cases we may write,

$$E = E'_o + RT/F \; ln \; C'_i/C'_o. \qquad (III)$$

All the existing evidence concerning mixtures of two or more salts having a common ion indicates that the *degree of dissociation of each salt depends solely upon the concentration of the common ion.*[1] We have in Table II material for testing this rule much more accurately than has been possible hitherto. Since in the above solutions the potassium chloride is present in large enough amounts, so that the potassium ion concentration is not materially changed by the small quantities of potassium ferro- and ferricyanide, the degree of dissociation of each of these salts in a given potassium chloride solution should be constant. The ion concentrations of ferro- and ferricyanide should therefore be proportional to the total concentrations of these salts, and equation III should be valid.

In the cases of (4), (5) and (6), all in 0.2 N KCl, the ratio of (i) to (o) added is constant and the potentials should be the same. They lie, in fact, within 0.2 millivolt. This difference is greater than the experimental error and was repeatedly observed, but it is a difference of about the order which might be expected from the small change in potassium ion due to the addition of the ferro- and ferri-cyanides. Even this small error has in Table III been avoided as far as possible by comparing solutions to which the same total amount of potassium ferro- and ferricyanides was added.

The theory may be more thoroughly tested by comparing solutions in which the ratio of (o) to (i) is changed in a given potassium chloride solution. The results are given in Table III which shows the differences found between various pairs of electrodes and the differences calculated by Equation III.

It is obvious that in the next to the last and especially in the last case the concentration of potassium chloride is too low to justify our assumption that the addition of the potassium ferro- and ferricyanides does not

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[1] See A. A. Noyes, Address at St. Louis, before the Congress of Arts and Sciences, *Technology Quarterly,* **17,** 293 (1904).

change the potassium ion concentration. In other cases the agreement between the observed and calculated potentials is extremely satisfactory, the average difference being only 0.00014 volt. This shows that the above rule for the degree of dissociation in mixed salts holds true in the present case within one-half of one per cent. This is the most severe test to which this rule has been subjected.

TABLE III.

	Conc. KCl.	E (obs.).	E (calc.).
(3)– (2)	0.4	0.0280	0.0282
(7)– (4)	0.2	0.0282	0.0282
(8)– (5)	0.2	0.0180	0.0178
(9)– (6)	0.2	0.0284	0.0282
(5)–(10)	0.2	0.0177	0.0178
(12)–(11)	0.1	0.0285	0.0282
(14)–(13)	0.05	0.0294	(0.0282)

The exact influence of the potassium ion concentration on the potential could hardly be calculated. It would have no influence if the ferro- and ferricyanides were completely dissociated, for then in all cases Equation III would hold. On the other hand, if they were completely undissociated the reaction at the electrode would best be written

$$K_3Fe(CN)_6 + K^+ + (\ominus) = K_4FeCN_6,$$
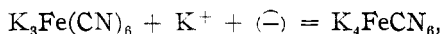
and the concentration of the potassium ion would obviously be an important factor in determining the potential. In Table IV are compared the potentials of several solutions all containing the same amounts of ferro- and of ferricyanide, and differing therefore only in the concentration of potassium chloride. It will be noted that the effect of doubling the potassium chloride solution is greatest in the concentrated solutions where the ferro- and ferricyanides are least dissociated.

TABLE IV.

	Conc. KCl.	E.
(1)– (2)	0.8–0.4	0.0165
(2)– (4)	0.4–0.2	0.0152
(4)–(11)	0.2–0.1	0.0129
(11)–(13)	0.1–0.05	0.0116

A comparison of the data of Table IV with Equation II enables us to see how the relative degrees of ionization of the ferro- and ferricyanide are affected by a change in the concentration of potassium ion. If both were affected equally the ionic concentrations would remain proportional to the total concentrations of ferro- and ferricyanide and the potentials (1), (2), (4), (11), and (13) would all be alike. This is very far from being the case. Increasing the concentration of potassium ion evidently pushes back the dissociation of ferrocyanide more than that of ferricyanide, and this we should expect since the ferrocyanide is a salt of higher valence product. Equation II does not enable us to state how much

each degree of dissociation is changed but the ratio only. If we should provisionally assume the degree of dissociation of the ferricyanide to be not at all affected, and if we estimate on the basis of the conductivity measurements that in the most dilute potassium chloride solution the ferrocyanide is 50 per cent. dissociated, a value which is certainly not too low, then from the potential measurements we should calculate the degree of dissociation of potassium ferrocyanide in 0.8 N potassium chloride as 5.5 per cent. This, however, must still be regarded as much too high a value, for unquestionably the degree of dissociation of the ferricyanide is also lowered by the potassium ion very considerably. We are therefore led to the interesting conclusion that potassium ferrocyanide, although a typical strong electrolyte, in the presence of 0.8 N potassium chloride is not dissociated more than two or three per cent. into its normal quadrivalent ion. This is a very much smaller degree of dissociation than was to be predicted from the conductivity measurements. Hence we have a very strong indication that in the process of conduction intermediate ions are playing an important part.

We have seen that with a given ratio of ferro- and ferricyanide the potentials depend upon the concentration of potassium ion. It is important to show that they depend only on this concentration and not upon chloride ion, which was present in all the above solutions. Similar experiments were therefore made with the potassium chloride replaced by potassium bromide. 0.25 cc. each of solution (o) and of solution (i) were added to 100 cc. of 0.2 N KCl and also to 100 cc. of 0.2 N KBr; these two solutions, with electrodes, were connected with the normal electrode (N. E.) as follows:

$$\text{N. E.; } 0.2 \, N \text{ KCl} + (o) + (i). \tag{a}$$

$$\text{N. E.; } 0.2 \, N \text{ KCl; } 0.2 \, N \text{ KBr} + (o) + (i). \tag{b}$$
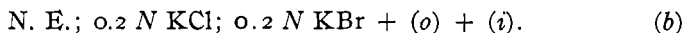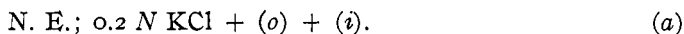
Since potassium bromide and chloride are equally dissociated the concentration of potassium ion is the same in both solutions. If this is the sole determining factor the potentials of the two solutions will be the same. There is, however, an additional liquid potential in (b) between 0.2 N KCl and 0.2 N KBr which, calculated from the Planck theory, amounts to 0.0004 volt. The e. m. f. of (b) should be larger than (a), therefore, by 0.0004 volt. In fact, (a) gave 0.1538, (b) gave 0.1542 volt. The potential is therefore independent of the nature of the anion.

Summary.

A gold electrode in a solution of potassium chloride containing potassium ferro- and ferricyanide gives a potential reproducible to 0.0001 volt. This potential was measured with varying concentrations of the three salts.

The temperature coefficient of electromotive force was measured at

two different concentrations and the heat of the reaction in the cell was determined. The results showed that the heat of ionization of potassium ferro- and ferricyanide is very small.

The rule that in a mixture of salts having a common ion the degree of dissociation depends solely upon the concentration of that ion, was subjected to a very severe test and found to be accurate within one-half of one per cent. The presence of other anions does not influence the potential.

In the presence of $0.8 N$ potassium chloride the degree of ionization of potassium ferrocyanide into its quadrivalent ion is not over 2 or 3 per cent. This fact can only be reconciled with the measurements of electrical conductivity by the assumption of intermediate ions.

Note on the Calomel Electrode.

All the above potentials were measured against calomel electrodes, a large number of which were constructed and studied with reference to constancy and reproducibility. In most points our results corroborate those of Sauer,[1] who has made a careful investigation of the normal and tenth-normal calomel electrodes. Sauer states that normal calomel electrodes give reproducible potentials within 0.1 millivolt, and tenth-normal within 0.2 millivolt. We find likewise that the tenth- and fifth-normal electrodes are a little less reproducible than the normal when all are made up according to the method of Luther.[2]

It is not difficult to construct a number of electrodes, all agreeing within the above limits if all are made from the same materials, but with different samples of calomel and potassium chloride more widely deviating results may be obtained, even if the materials are all of a fairly high grade. In order, therefore, to construct out of purchasable materials a normal electrode which will not only give a constant but also a correct potential, the materials must be purified with more care than Luther or Sauer prescribe. "C. P." potassium chloride should be at least twice recrystallized, better from water alone than with alcohol. Instead of using calomel that is in the market it is better to prepare it from pure mercury, dissolving the latter in dilute acid, precipitating with dilute hydrochloric acid, and washing carefully by decantation. In making up the electrode Luther recommends grinding or shaking together the calomel and mercury with the potassium chloride solution. We find through a number of experiments that there is a difference of several tenths of a millivolt when the materials are ground together in a mortar and when they are shaken together in a bottle. The electrodes prepared in the latter way are more negative. This agrees with the conclusion of Sauer that the potential depends upon the size of the calo-

[1] Z. physik. Chem., **47**, 146 (1904).
[2] Ostwald-Luther, Phys. Chem. Messungen, p. 381.

mel grains.   Since the size of particles produced by grinding will not always be the same, this method of preparing the electrode should be abandoned and the method of shaking should always be employed.   Sauer's further conclusion that the potential is different when mercury is pres-ent in small drops in the electrode paste we have not been able to cor-roborate.   Electrodes made in the usual way with finely divided mer-cury in the "paste" gave the same result as those in which this paste was replaced by pure calomel.   It is however advisable to use the paste, since the large surface of mercury which it offers enables the electrode to come to equilibrium more quickly when subjected to temperature changes or other disturbances.

POTENTIALS BETWEEN LIQUIDS.

BY GILBERT N. LEWIS AND LEDYARD W. SARGENT.

In conducting a series of investigations upon electrode potentials we have found it necessary to study also the potentials which exist at the boundary between two contiguous solutions, for these potentials almost invariably enter when another electrode is compared with the normal electrode.   These liquid potentials have been the subject of extensive theoretical treatment and the formulae which have been obtained by Nernst, Planck, and others have been frequently tested experimentally. The values found have usually agreed with those calculated from theory within a few millivolts,[1] that is, within the customary limits of experi-mental error.   It seems desirable, however, to subject the formulae to a severer test.

This paper will deal with a single type of potentials between liquids, namely, with the potential between equally concentrated solutions of two binary salts having one ion in common.   To such a case we may apply the familiar equation of Planck,

$$E = RT/Fln(u_1 + v_1)/(u_2 + v_2), \qquad (1)$$

where R, T, and F have their customary significance, ln stands for natural logarithm, E is the potential at the boundary between the two solutions, n the valence of all the ions, u_1 and u_2 the so-called mobilities (or equiva-lent conductivities at infinite dilution) of the cations; v_1 and v_2, of the anions.   If the ions are univalent and one ion is common to both solu-tions we have either,

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[1] Negbaur (*Ann. d. Phys.*, **44**, 731) found in several cases a more exact agree-ment between his observed potentials and those calculated from Planck's equation. But his experiments have not been corroborated by the later experiments of Jahn, Sauer, and others.