This compound ($CuFe_2O_4$) was prepared by List[1] and its strongly magnetic properties described in 1878. I prepared it by heating mixtures of cupric and ferric oxides in several different proportions and separating the product from the excess of uncombined simple oxide by gravity and magnetism. Analyses for copper gave 25.60 and 25.83 per cent. of copper Calculated for $CuFe_2O_4$, 26.57.

My work on this magnetic material led me to believe that there is at least one other magnetic double oxide of iron and copper not yet described. Work on this and other similar substances is now in progress in this laboratory.

The fact that Koch obtained the same substance although he used cuprous oxide in a covered crucible is easily understood when it is recalled that cuprous oxide is not stable in the air at temperatures below 1025°[2] and that the change to cupric oxide is probably rapid enough at 750° to give an appreciable quantity of that compound in fifteen minutes. Even though the crucible cover was perfectly tight, which is not probable, the oxygen inside the crucible must have been completely absorbed with the formation of cupric oxide.

SHEFFIELD LABORATORY, YALE UNIVERSITY,
June, 1908.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 35.]

THE DETERMINATION OF IONIC HYDRATION FROM ELECTROMOTIVE FORCE.

BY GILBERT N. LEWIS.

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In the theory of concentration cells an important point seems to have been hitherto overlooked. It has been supposed that the electromotive force is a true measure of the change of free energy in the transfer of salt from the higher to the lower concentration. This is only true if the transfer of salt is the only process that takes place when a current passes through the cell. This is not always the case. If the ions present in solution are *hydrated*, water will be carried in both directions when the current passes, and if the cation carries more or less water than the anion, a definite transfer of water in one direction or the other will result from the passage of the current. Since the activity[3] of the water is not the same in the concentrated and the dilute solution, this transfer will be accompanied by a change in free energy.

The electrical work which can be obtained from such a cell, when one

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[1] *Ber.*, 11, 1512.

[2] Foote and Smith, THIS JOURNAL, 30, 1345.

[3] For the definition of the term activity see Lewis, *Z. physik Chem.*, 61, 129 (1907).

equivalent of electricity passes, is therefore the sum of two quantities, one of which is due to the transfer of ions from one activity to another, the other to the transfer of water from one activity to another. Hence[1]

$$EF = \Sigma nRT ln \frac{\xi_1}{\xi_2} + n'RT ln \frac{\xi'_1}{\xi'_2},$$

where E is the electromotive force; F, Faraday's equivalent; R, the gas constant; T, the absolute temperature; n is the number of mols of a given ion carried from the first solution where its activity is ξ_1 to the second where its activity is ξ_2; n' is the number of mols of water carried from the first solution where its activity is ξ'_1 to the second where its activity is ξ'_2.

If we are dealing with a simple type of concentration cell, for example two calomel electrodes in solutions of potassium chloride of different concentration, and if we make the common assumption that the activity of each ion is proportional to its concentration, the above equation may be written

$$E = \frac{2t_cRT}{F} ln \frac{C_1}{C_2} + \frac{n'RT}{F} ln \frac{\xi'_1}{\xi'_2}.$$

Here tc is the *true* transference number of the cation. The equation, except for the last term, is identical with the well known equation of Nernst. This term is entirely negligible when, both solutions being dilute, ξ'_1 and ξ'_2 are nearly equal. If one of the solutions is normal, and the other tenth normal, the activity of water is about 3 per cent. less in the strong solution. The last term would then be equal to 0.0007 volt if $n' = 1$. E. W. Washburn[2] has determined directly the values of n' in solutions of potassium, sodium, and lithium chlorides and found 0.6, 0.8 and 1.5 respectively, the water moving in each case with the positive current. The term due to hydration in these cases is therefore of the order of one-half to one millivolt, a quantity which may be easily measured.

We could, therefore, calculate the important quantity n' from the observed electromotive force of a concentration cell, provided that the concentrations of the ions could be accurately determined and shown to be proportional to the activities. This is unfortunately not yet the case and this method cannot at present be employed, but it suggests another method which may be of considerable value in investigating the hydration of ions.

Let us consider a cell on one side of which is an electrode of thallium and a saturated solution of thallous chloride in water, on the other another thallium electrode and a saturated solution of thallous chloride in a molal sugar solution. When a current passes through this cell, four

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[1] Lewis, *loc. cit.*, equation 27.

[2] *Technology Quarterly*, Sept., 1908.

substances may be transferred from one side to the other, (1) metallic thallium, (2) thallous chloride, (3) water, (4) sugar. Let us assume that the sugar does not combine with the ions and is not carried by the current. Of the three remaining processes the first two are capable of doing no work, for the activity of the thallium, and of the thallous chloride is the same on both sides. The activity of the water, however, is about 2 per cent. lower in the sugar solution. Since the transfer of water is the only process which is accompanied by a change of free energy, the electromotive force of the cell will be a direct measure of the amount of water transferred. The general equation will obviously be

$$E = \frac{n'RT}{F} \ln \frac{\xi'_1}{\xi'_2},$$

when ξ'_1 and ξ'_2 are the activities of the water on the two sides and n' is the number of mols of water carried with one Faraday.

The successful application of this simple method of determining the relative hydration of the ions depends solely upon finding a suitable non-electrolyte which itself is not carried with the current. An experimental investigation of the method has already been begun in this laboratory.

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THE FREE ENERGY CHANGES ATTENDING THE FORMATION OF CERTAIN CARBONATES AND HYDROXIDES.

BY JOHN JOHNSTON.

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In recent years much attention has been directed to the measurement and calculation of the free energy changes attending chemical reactions. For the most part the equilibria studied for the purpose of determining the changes in free energy have been cases of homogeneous gaseous reactions, such as those studied by Haber and Nernst; in addition, certain heterogeneous equilibria have been investigated; for example, the decomposition of silver oxide by G. N. Lewis,[1] while calculations of free energy from electromotive force data have been made by M. de K. Thompson.[2]

It is the purpose of this article to present the results of such calculations from existing data in the cases of the hydroxides and carbonates of lithium, sodium, and alkaline-earth elements.

Unfortunately the various authors do not all define "free energy" in the same way. In the present calculations the increase in free energy, ΔF, is defined by the following equation:

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[1] THIS JOURNAL, 28, 158 (1906).

[2] *Ibid.*, 28, 731 (1906).