It has been currently supposed that the electrode potential of lithium would prove to be smaller even than that of sodium;[1] but as a matter of fact the heats of formation of the three ions might have led us to expect the order in which the electrode potentials actually occur, for the heat of formation of lithium ion is nearly 1000 calories higher than that of potassium ion, and the latter is in turn about 5000 calories higher than the heat of formation of sodium ion.

ON A NEW KIND OF ELECTROMOTIVE FORCE AND SOME POSSIBLE APPLICATIONS TO PHYSICO-CHEMICAL PROBLEMS.

[PRELIMINARY COMMUNICATION.]

By Reinhard Beutner.

Received December 2, 1912.

The phenomena which are described in this paper relate to *galvanic cells composed of water-insoluble organic liquids and aqueous solutions. These cells have e. m. fs.* nearly equal to the well-known galvanic cells composed of metals and aqueous solutions and exhibit many interesting properties.

1. The well-known investigations of Nernst have shown that the single potential differences which compose the e. m. f. of whole cells depend on the concentration of the aqueous solution.

A concentration cell is, *e. g.*,

$$- \mathrm{Ag} \mid \mathrm{AgNO_3} \ldots\ldots\ldots\ldots \mathrm{AgNO_3} \mid \mathrm{Ag} +$$

diluted solution. concentrated solution.

which may also be arranged with one single piece of Ag as a middle conductor.

$$+ \mathrm{AgNO_3} \mid \mathrm{Ag} \mid \mathrm{AgNO_3} -$$

diluted sol. concentr. sol.

In order to make an electrical connection with the two silver solutions to the poles of a measuring instrument we have to use electrodes which do not introduce any new e. m. f. by themselves, *i. e.*, calomel electrodes.

In some experimental work, carried out by Dr. Jacques Loeb and myself,[2] it was found that certain vegetable and animal skins exhibited a change of potential difference with concentrations of the same kind as metals; but the question was, to what peculiar property or composition of the membrane this effect was due.

I have now found that a number of water-insoluble substances act in the same way. For instance, with *salicylic aldehyde* as a middle conductor we can build up a cell perfectly analogous to the last one above.

$$- m/10\ \mathrm{NaCl} \mid \text{salicylic aldehyde} \mid m/1250\ \mathrm{NaCl} + \quad \text{e. m. f. } 0.075 \text{ volt.}$$

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[1] See, for example, Patten and Mott, *J. physik. Chem.*, 8, 153 (1904); Abegg, *Handbuch der anorg. Chem.*, Vol. I, p. 116.

[2] *Science*, **34**, 886; also in *Biochem. Z.*, **41**, 1.

2. We may call the salicylic aldehyde therefore reversible for Na-ions. There is, however, no exclusive reversibility for Na-ions because the cell

$$- m/10 \text{ KCl} \mid \text{salicylic aldehyde} \mid m/1250 \text{ KCl} +$$

exhibits a similar e. m. f. (0.083 volt). In fact, with aqueous solutions of nearly every salt such concentration cells may be built up, as the following examples prove:

$- m/10$ Na_2SO_4 | salicylic ald. | $m/1250$ Na_2SO_4 + 0.060 volt.
$- m/10$ $CaCl_2$ | salicylic ald. | $m/1250$ $CaCl_2$ + 0.064 volt.
$- m/10$ $AlCl_3$ | salicylic ald. | $m/1250$ $AlCl_3$ + 0.070 volt.
$- m/10$ $CuSO_4$ | salicylic ald. | $m/1250$ $CuSO_4$ + 0.042 volt.
$- m/10$ NH_4Cl | salicylic ald. | $m/1250$ NH_4Cl + 0.055 volt.

As is well known, a metallic electrode is reversible for its own ions only, *i. e.*, the potential difference Ag | $AgNO_3$ is not affected by the presence of another salt. A reversibility for any cation, or for a great number of them, at least, is, therefore, a peculiar property of the new potential differences described here. On the other hand, the biological potential differences which I mentioned above exhibit this reversibility for any cation in the same way.

3. I now wish to show how these new phenomena may be explained from a theoretical standpoint. It has been pointed out by Nernst[1] that a phase junction is the seat of an e. m. f. which depends on the ionic concentrations, according to the formula

$$RT/nF \ln c_1/c_2 = \text{const.}$$

where c_1 is the concentration of a certain ion in one phase, *i. e.*, water, c_2 the concentration of the same ion in the other phase, *i. e.*, salicylic aldehyde. As is well known, a similar formula holds for metallic electrode potentials. This formula applies to a single potential difference located at the junction of two immiscible electrolytic phases; there can be no doubt that the electric conduction in salicylic aldehyde as well as in water is of an electrolytic nature. The application of the formula to our case involves, however, further difficult questions.

We shall take as an example the potential difference at the junction

salicylic aldehyde | KCl aqueous solution.

According to the formula of Nernst, cited above, the potential difference at the junction of salicylic aldehyde and the aqueous solution (of KCl) depends on the ratio

$$\frac{C_K \text{ in water}}{C_K \text{ in sal. ald.}}$$

If the ordinary law of partition were valid for the distribution of KCl between water and salicylic aldehyde, this ratio would be constant, and

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[1] *Z. physik. Chem.*, 9, 137 (1892).

therefore the potential difference would not depend on the concentration of the aqueous solution, as is clearly shown to be the case in the cells referred to above.

It is equally impossible to explain these phenomena on the assumption that the rate of electrolytic dissociation in salicylic aldehyde is smaller than in water. Even if this be so, it can easily be shown that $\frac{C_K \text{ water}}{C_K \text{ sal. ald.}}$ is constant as long as the simple law of partition is valid.

On the other hand, it is not very well possible to assume that the salicylic aldehyde possesses a certain unchangeable content of K-ions (perhaps as an impurity from which it can not be easily separated), for, as was said above, the reversibility of the potential difference does not apply to K^+ solutions exclusively, but to practically every other ion, and it is not probable that all these salts should be present in a preparation specified as "purissimum."

However, a satisfactory explanation is reached if it be assumed that the K^+ concentration of the salicylic aldehyde is determined by a reaction taking place between the salicylic acid (which is always formed by oxidation) and potassium chloride.

$$\underset{\text{salic. acid.}}{C_7H_5O_3.H} + KCl = C_7H_5O_3.K + HCl.$$

The compounds formed by this reaction—potassium salicylate and hydrochloric acid—are probably not equally distributed between the two phases (salicylic aldehyde and water); potassium salicylate is very likely more soluble in salicylic aldehyde than hydrochloric acid is. The effect of this unequal distribution appears to be such that *the concentrations of K^+ in water and in salicylic aldehyde are not proportional*, as the K^+ ions contained in water are those formed by the potassium chloride, while the K^+ ions contained in the salicylic aldehyde are formed by dissociation of potassium salicylate and of traces of potassium chloride. Under such circumstances the thermodynamic formula of Nernst (as mentioned on page 345) may explain the electromotive function of a water immiscible liquid like salicylic aldehyde.

The application of the formula of Nernst, as cited above, would be very simple, if the K^+-concentration in the salicylic aldehyde was constant and independent of the K^+-concentration of the aqueous solution; the potential difference should, in this case, depend on the concentration—in the same way as the potential difference at a metallic electrode:

$$\text{pot. diff.} = \frac{RT}{nF} \ln \frac{c_K \text{ water}}{c_K \text{ sal. ald.}} \cdot \text{const.}$$

$$\text{as } c_{K\text{ s. a.}} = \text{const.}$$

$$\text{pot. diff.} = RT/nF \ln c_K \text{ water-const.}$$

This, however, is not the case in general, nor could it be expected from the explanations given above, as $c_{\mathrm{K}\ (\text{sal. ald.})}$, though not proportional to c_{K} water, yet depends on c_{K} (water) according to a complicated function.

The writer has worked out a mathematical theory, which is based on the well-known physico-chemical laws of mass action and of distribution and on the explanation given above, and which made it possible to predict the nature of the function between c_{K} in water and c_{K} in sal. ald. A full account of this theory will be published later. It may be said here, that according to this theory, the change of the potential difference with the concentration must become more like that at a metal electrode *the smaller* the concentration.

This is also found to be the case by experiment. As an example, the following measurements may be cited:

$m/6250$ KCl	sal. ald.	$m/1250$ KCl	31	millivolts.
$m/1250$ KCl	sal. ald.	$m/250$ KCl	29	"
$m/250$ KCl	sal. ald.	$m/50$ KCl	26	"
$m/50$ KCl	sal. ald.	$m/10$ KCl	24	"
$m/10$ KCl	sal. ald.	$m/2$ KCl	13	"
$^1/_2$ KCl	sal. ald.	$5m/2$ KCl	5	"

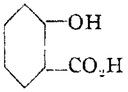
The ratio of the concentrations of the potassium chloride solutions is 5 in all these cells; at a metallic electrode this change of concentration would cause a constant change of the potential difference of 58 by 5 = *40 millivolts.* It is seen that the change observed approaches this value at small concentrations. It may be added that the change of the potential difference in a series of measurements like those cited is reproducible within the errors of the experiment and perfectly reversible. Calomel electrodes filled with $m/10$ KCl solution were used in order to make electrical connections to the measuring instrument (electrometer) in the above measurements. No "liquid potentials" could thus intervene (on account of the equality of migration velocity of K^+ and Cl^-). In similar measurements in which different salts were used instead of potassium chloride a slight change of the well-known "liquid potentials" with the concentration intervenes; this is by far too small, however, to account for the total change observed.

4. In another regard these theoretical considerations prove of distinct value, as they make it *possible to predict which water-insoluble substances, besides salicylic aldehyde, may show a like change in the potential difference with the concentration of the aqueous solution.* Apparently there are two conditions:

a. That the water-insoluble substance contains a strong acid, so that a reaction between this acid and the salt of the aqueous solution can take place.

b. That the concentration of the salt generated by this reaction in the water-insoluble substance, *i. e.*, salicylate, is far greater than the potassium chloride concentration, or, in other words, the coefficient of partition $\frac{c_{\text{KCl}}\text{ in water-insoluble substance}}{c_{\text{KCl}}\text{ in water}}$ is small.

The first condition is the most important one. Salicylic acid, which is contained in the salicylic aldehyde, is a very strong acid according to its constitution,



If instead we take benzoic acid, which does not contain an OH group, besides the COOH group, the effect of the concentration upon the potential difference should be less marked. This was found to be the case.

— $m/10$ KCl | salicylic aldehyde saturat. with salic. acid | $m/6250$ KCl$^+$ + 0.125 volt.

— $m/10$ KCl | benz. aldehyde saturat. with benz. acid | $m/6250$ KCl$^+$ + 0.091 volt.

If we take benzyl alcohol instead of benzaldehyde no e. m. f. at all is observed, as this substance does not possess any acid properties.

Other experiments which account for the same fact are the following: The cell

$m/10$ KCl | phenol | $m/1250$ KCl +

was found to have only a very slight e. m. f. (of 0.007 volt). Apparently the acid functions of the phenol are too small to effect a reaction with potassium chloride. If, however, a mixture of phenol and benzoic acid was used, the following was observed:

I. —$m/10$ KCl | 10 g. benz. ac. + 20 g. phenol liquid mixture | $m/1250$ KCl + 0.70 volt at 55°.

II. —$m/10$ KCl | the above mixture diluted 25 times with phenol | $m/1250$ KCl + 0.052 volt at 55°. 0.044 volt at room temperature.

III. —$m/10$ KCl | mixture of cell II diluted 10 times with phenol | $m/1250$ KCl + 0.030 volt at room temp.

These experiments prove very clearly that for the same change of the aqueous concentration (1/10 : 1/1250 m KCl) the change of the e. m. f. is greater the higher the acid concentration of the water-insoluble phase (*i. e.*, phenol).

5. What e. m. f. is observed if instead of an acid in the water-insoluble phase we use a strong base such as aniline, toluidine, or similar substituted compounds? The theory predicts that in this case a change of the potential difference with the aqueous solution should occur in an opposite

sense to that observed with salicylic aldehyde. As water is soluble in aniline to a small extent, a compound $C_6H_5NH_3OH$ may be supposed to be formed in the aniline, which dissociates into the ions $C_6H_5NH_3^+$ and OH^-.

This would react with KCl according to the equation

$$C_6H_5NH_3OH + KCl = C_6H_5NH_3Cl + KOH.$$

The Cl^- concentration in the aniline is therefore mainly determined by aniline-hydrochloride and is to a large extent independent of the aqueous Cl^- concentration. *This means that the aniline behaves like a reversible Cl^- electrode.*

In this regard the theory was found to hold in a most striking manner. The e. m. f. of a cell,

+ *m*/10 KCl | aniline | *m*/1000 KCl —,

was only 0.020 volt, but on substituting toluidine a considerable e. m. f. was observed,

+ *m*/10 KCl | toluidine | *m*/1000 KCl — 0.105 volt.

Apparently the stronger effect of toluidine is due to the strengthening of its basic character by the CH_3 group.

Similar e. m. fs. were observed with xylidine and methylaniline. Both of these bases are reversible for any anion, just as the water-insoluble acids were found to be reversible for any cation.

To prove this, I wish to cite some measurements on toluidine cells:

+ *m*/10 KNO_3 | toluidine | *m*/1250 KNO_3 — 0.098 volt.
+ *m*/10 $CaCl_2$ | tol. | *m*/1290 $CaCl_2$ — 0.085 volt.
+ *m*/10 K_4FeCy_6 | tol. | *m*/1250 K_4FeCy_6 — 0.046 volt.
+ *m*/10 KSCN | tol. | *m*/1250 KSCN — 0.105 volt.

As with the "salicylic aldehyde" potential differences, the change of potential difference is also in these cases the higher the more dilute the solutions are. The same theoretical considerations can also be applied here. The following measurements may serve as an example that the change approaches the limit of 0.040 volts (for dilution 1 : 5) at very small concentrations:

— 1/6250 KSCN | toluidine | 1/1250 KSCN + 0.042 volt.
— 1/1250 KSCN | tol. | 1/250 KSCN + 0.042 volt.
— 1/250 KSCN | tol. | 1/50 KSCN + 0.037 "
— 1/50 KSCN | tol. | 1/10 KSCN + 0.035 "
— 1/10 KSCN | tol. | 1/2 KSCN + 0.030 "
— 1/2 KSCN | tol. | 5/2 KSCN + 0.027 "

6. All cells described above are mere concentration cells, the e. m. f. being due to the difference in concentration of two solutions of the same salt. The question presents itself, what e. m. f. will be observed with a

cell composed of equimolecular solutions of two different salts? The experiment shows that such cells may also produce considerable e. m. f., *i. e.*,

— 1/10 KCl | salicyl. ald. | 1/10 $CaCl_2$ + 0.060 volt.
— 1/10 KCl | salicyl. ald. | 1/10 $MgSO_4$ + 0.086 volt.
— 1/10 KCl | salicyl. ald. | 1/10 $BaCl_2$ + 0.040 volt.
— 1/10 KCl | salicyl. ald. | 1/10 $AlCl_3$ + 0.030 volt.
— 1/10 KCl | salicyl. ald. | 1/10 $HgCl_2$ + 0.140 volt.
+ 1/10 KCl | toluidine | 1/10 Na_2SO_4 — 0.120 volt.
1/10 KCl | toluidine | 1/10 NaCl 0.00 volt.
+ 1/10 KCl | toluidine | 1/10 $MgSO_4$ — 0.125 volt.
+ 1/10 KCl | toluidine | 1/10 Na_2HPO_4 — 0.116 volt.
+ 1/10 KCl | toluidine | 1/10 $K_4Fe(CN)_6$ — 0.100 volt.
— 1/10 KCl | toluidine | 1/10 KSCN + 0.130 volt.
+ 1/10 KCl | aniline | 1/10 Na_2SO_4 — 0.140 volt.

As is seen, the order of magnitude of these e. m. fs is nearly as large as that of cells with metal electrodes. "Liquid potentials" (at the junction of the aqueous solutions and the calomel electrodes) can amount to a few per cent. only of the values observed.

According to the well-known thermodynamic theory of Helmholtz, concentration cells as described in the first part of this paper exhibit an e. m. f. on account of a merely physical reaction (the equalizing of the different concentrations) which takes place, if an indefinitly small current passes through the system. In the last "cell" systems, however, a *chemical* reaction is the cause of the e. m. f. and the problem presents itself to determin the nature of this reaction. I have been able to find a method for this determination, which, however, can not very well be described in full in this preliminary communication on account of the space required. I wish to say only that the respective reaction, *i. e.*, for the first "cell" is found to be the following:

2KCl + Ca-salicylate = $CaCl_2$ + 2K salicylate
in water. in sal. ald. in water. in sal. ald.

for the second last "cell" the reaction is:

toluidine thiocyanate + KCl = toluidine chloride + KSCN.
in toluidine. in water. in toluidine. in water.

7. The description given here of these new galvanic phenomena is by no means complete. I have observed many more complicated phenomena which I shall not discuss here at length. I wish, however, to add a few words about the applications of these phenomena.

It is well known that living tissues produce considerable e. m. fs. Their physical nature has always been doubtful. The difficulty was so far to explain how e. m. fs. of this order of magnitude could originate without metals. Potential differences between two aqueous solutions (such as have often been studied by the German physico-chemical school) cannot fully account for it. Many explanations have been tried, but they have all lacked the possibility of an experimental imitation producing artificially e. m. fs. like those of living organs. I think that my experiments have solved this problem and it may be hoped that a careful study of the electrical properties of tissues on this basis may also lead to new facts regarding their physical and chemical properties.

Another application of these new phenomena relates to electric endosmosis and precipitation of colloidal solutions by electrolytes.

Helmholtz[1] has shown that the migration of particles suspended in an aqueous solution is due to a potential difference or a "charge" of these particles, and he devised a method for calculating the magnitude of this potential difference from the velocity of the migration. If it is assumed that the water-insoluble substance which forms the suspended particles possesses an electric conductivity one could conclude from my observations that the charge of the particles depends on the chemical nature and on the concentration of the salt in the aqueous solution. In fact, a change and even a reversal of the charge by addition of various electrolytes has often been observed.

The migration of a solution through a diaphragm or a narrow tube under the influence of the current is accounted for in the same way. Freundlich and Elissafoff,[2] in a recent experimental investigation on electric migration of solutions through tubes, found a distinct change of the charge with concentration of the aqueous solution. With decreasing concentration the solution was found to become more positive. Freundlich, trying to apply his theory of adsorption potential, admits himself that it cannot give a satisfactory explanation. If it is attempted to explain Freundlich's result on the basis of the above experiments, it is necessary to conclude that the material of the tube through which the current drives the solution was a water-insoluble acid. This was so in fact as a silica tube was used.

By means of such endosmotic measurements the absolute values of single potential differences may be determined, while the e. m. f. of cells, as described above, only determins the difference of two potential differences. I do now know, however, whether—if the size of the suspended particles is below a certain limit—the potential difference may not be affected by new forces which do not act as plain phase-junctions.

From ultra-microscopic investigation it has been established that the so-called "colloidal" solutions are really suspensions. The charge of the very small "colloidal" particles has a large influence on the stability of

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[1] *Wiedmann's Ann.*, 7, 337 (1879).

[2] *Z. physik. Chem.*, 79, 385.

the colloidal solution. Electrostatic repulsion keeps the particles apart if the charge is high, while with a small or no charge the Brownian movement agglutinates the particles into greater masses, thus causing precipitation. This explanation was first given by Hardy and has often been confirmed. As the chemical composition and the concentration of the solution affects the charge, according to my experiments, it is possible to explain the precipitating action of salts. If the change of the charge brought about by increasing the concentration is such that the charge becomes smaller, precipitation may occur. Pauli,[1] in his investigation on the precipitating action of salts on egg albumin, finds that with salts of the same bases the precipitating power increases according to the anion in the following series:

$$SCN > I > NO_3 > Cl > HPO_4 > SO_4 > Fl.$$

As seen from the data on page 350, salts of these anions create negative e. m. f. on toluidine, if a potassium thiocyanate solution is kept constant on the one pole; the magnitude of the e. m. f. increases in the same series. One should conclude, according to the theory proposed, that the colloidal albumin particle has a high positive charge. This is the case in an acid solution where, as a rule, the action of anions is clearly manifested.

A series of cations, according to precipitating strength, which is in accordance with the above experiments, has also been found.

[The experiments described in this paper were performed in the writer's private laboratory at Berlin, Germany, during summer 1912.]

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THE ACTION OF THIONYL CHLORIDE ON THE OXIDES OF METALS AND METALLOIDS.

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Received February 6, 1913.

The action of thionyl chloride on oxides of metals and metalloids has been studied but little. The first research of this nature appears to have been made by Lenher and North,[2] who investigated the reaction of thionyl chloride on selenium dioxide in 1907. This work was followed in 1908 by a study of the reaction on tellurium dioxide by Lenher and Hill.[3] In 1910 North[4] investigated the reaction of thionyl chloride on both the red and yellow varieties of mercuric oxide.

In each of the above-mentioned investigations reaction was found to proceed readily at elevated temperatures, with the formation of the

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[1] *Hofmeister's Beiträge*, 3, 225.

[2] THIS JOURNAL, 29, 33 (1907).

[3] *Ibid.*, 30, 738 (1908).

[4] *Ibid.*, 32, 184 (1910).