suffer less from irregularities in surface energy of the electrode and the presence of traces of oxygen.

The potentials of mixtures of stannic and stannous chlorides containing one-quarter of a gram-atom of tin per liter in hydrochloric acid of three concentrations were measured at mercury electrodes at 25°. The probable error is about two millivolts.

Halving the total tin concentration makes the potential very slightly more electronegative; it seems to be nearly independent of the total tin concentration, other things being equal.

By extrapolation to zero concentration of acid, results are obtained which should be largely unaffected by uncertainties due to hydrolysis and to the single potential at the boundary between the cell liquid and the indifferent electrolyte.

Up to two moles of hydrochloric acid per liter, the potentials are quite accurately expressed by the formula

$$\pi = 0.426 + 0.030 \log \frac{Sn^{IV}}{Sn^{II}} - 0.011 \times \text{conc. HCl},$$

provided sufficient acid is added to check hydrolysis.

Curves showing the relations existing among the several variables are discussed in the light of present knowledge of solutions of stannic and stannous chlorides.

CAMBRIDGE, MASS.

STUDIES ON A NEW KIND OF E. M. F.

BY REINHARD BEUTNER.
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I. Introductory Remarks.

1. It was shown by the author[1] in previous communications that it is possible to compose galvanic cells of water-immiscible organic substances and aqueous solutions without metals, which, in certain points, exhibit properties like the well-known galvanic cells of which metals are the most essential component. The most important aim of a systematic study of these phenomena is the artificial reproduction and the explanation of the electrical properties of living tissues, since it is well known that these also produce e. m. f. resembling e. m. f. of metals. This fact was well established by electrophysiologists long ago, for the magnitude of the e. m. f. produced by tissues resembles that of ordinary galvanic cells; the same is found to hold for the cell-systems described here.

An experimental investigation undertaken at the suggestion of Dr. J. Loeb by the author[2] had shown this similarity of e. m. f. produced by

[1] THIS JOURNAL, **35**, 344 (1913); Z. Electrochem., **19**, 467 (1913).
[2] Science, **34**, 884 (1911); Biochem. Z., **41**, 1 (1912).

tissues and metals in a still more striking form, for it was found that a quantitative law especially characteristic for metals (Nernst's formula) could be applied to tissues. The experimental method used for this purpose may briefly be described as follows: A leaf or the fruit of a plant is brought in contact on two points with two solutions of the same salt (*i. e.*, KCl) in different concentrations; the two salt solutions are connected by means of impolarizable electrodes to a measuring instrument and the e. m. f. observed. This e. m. f. depends on the ratio of the two concentrations according to Nernst's formula. *The observation that a similar e. m. f. can be produced without metals or without tissues by means of a pure organic substance (salicylic aldehyde) was the first step which led the author to a systematic study of cell combinations with immiscible substances.* Naturally not all of these combinations have a direct bearing on electrophysiological problems, but they serve to give a more complete knowledge of the fundamental phenomena upon which electrophysiology is ultimately based.

These investigations may also interest the organic chemist since it is found that the chemical constitution of the organic substances plays a most important role in their action in such cell systems. Such a combined application of organic and physical chemistry is able to solve problems which hitherto have been looked at as strictly vital.

2. Since cell combinations of the kind described have been very rarely investigated by previous authors it[1] may be well to describe first the experimental method. The apparatus used is sketched in Fig. 1. An S-shaped
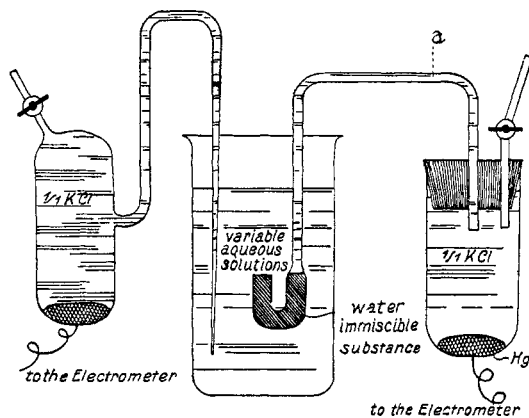

Fig. 1.

tube (*a*) is connected on one side with a calomel electrode; it is filled in the upper part with 1/1KCl solution and in the lower broader part with salicylic aldehyde which is saturated with salicylic acid. This lower part is then immersed in a series of beakers containing various solutions. Another calomel electrode is connected by means of a syphon

[1] Among these investigations I wish to mention here those by M. Cremer, "On Nitrobenzene Diphasic Cells" [*Z. Biol.*, **47**, 1 (1906)] and those by Haber and Klemersiewig's "On Benzene (and Toluene) Cells" [*Z. physik. Chem.*, **47**, 385 (1908)]. Some hypotheses put forward by these authors will be discussed in the following papers.

with this beaker and the e. m. f. of the arrangement is observed with various solutions successively.

If we immerse the tube containing salicylic aldehyde successively in series of KCl solutions of varying concentrations, the following is observed:

Concentration of the KCl in which the tube was immersed.	E. M. F. observed in millivolt.	Time in minutes allowed for observation.
$M/10$	$+12$ to 13	$0'$ to $1'$
$M/50$	$+37$	$3'$ to $4'$
$M/250$	$+62$	$7'$ to $9'$
$M/1250$	$+96$	$11'$ to $12'$
$M/6250$	$+137$	$17'$ to $19'$
$M/1250$	$+96$ to 95	$20'$ to $23'$
$M/250$	$+61$ to 60	$26'$ to $73'$
$M/50$	$+32$ to 31	$78'$ to $81'$
$M/10$	$+ 7$	$84'$ to $86'$
$M/2$	-14	$88'$ to $90'$
$2.5\ M$	-32 to 33	$95'$ to $97'$
$M/2$	-15	$103'$ to $104'$
$M/10$	$+ 7$	$107'$ to $108'$

(The sign signifies the polarity of left side in diagram.)

These figures show to which degree such measurements are accurate and reproducible.

The change of the e. m. f. of the system can only be due to the change of a potential difference located at the junction of the salicylic aldehyde and the aqueous solution; the potential difference located at the junction of the $1/1$ KCl solution of the calomel electrode and the variable KCl solution is practically zero and constant as the velocity of migration is practically equal for $K^{\cdot}$ and Cl'.[1]
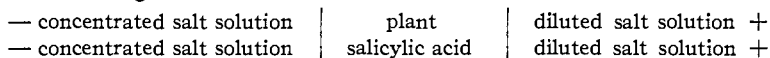
The magnitude of this change is as follows:

Between $2^1/_2\ M$	and $M/2$	18 Millivolt
$M/2$	and $M/10$	21 Millivolt
$M/10$	and $M/50$	24 Millivolt
$M/50$	and $M/250$	28 Millivolt
$M/250$	and $M/1250$	34 Millivolt
$M/1250$	and $M/6250$	41 Millivolt

As the ratio of the concentrations is $1 : 5$ in all cases, the value calculated from Nernst's formula would be $58 \ln 5 = 40$ millivolt; it is seen that the values observed gradually approach this value with decreasing concentrations. It is important that this observation can be explained on the basis of theoretical considerations as shall be explained later.

These observations on cells containing salicylic aldehyde as a middle conductor also were the first instance of the artificial imitation of the

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[1] A well-known theory of Nernst states that this diffusion potential equals $\dfrac{u - v}{u + v} \dfrac{RT}{F} \ln \dfrac{c_1}{c_2}$, since in our case u and v are practically equal, the diffusion potential is zero in all cases.

electrode-like potential differences between some living tissues and aqueous solutions, for the magnitude and direction of the e. m. f. is the same in both cell arrangements.

| — concentrated salt solution | plant | diluted salt solution + |
| — concentrated salt solution | salicylic acid | diluted salt solution + |

Further investigations have shown that a number of other water-immiscible liquids show a similar behavior, e. g., fatty acids mixed with substituted phenols.[1]

3. The theoretical explanation for these phenomena given in previous communications was based on a thermodynamic formula of Nernst and of Haber, stating that the potential difference at the junction of two immiscible electrolytic phases (such as an aqueous solution and salicylic aldehyde) equals $RT/nF \ln c_1/c_2$, const. where c_1 and c_2 signify the ionic concentrations of the *same* ion in the two respective phases, *i. e.*, the $K^{\cdot}$ concentration in water and in the salicylic aldehyde. The latter is due to a partition or slight solubility of the $K^{\cdot}$ salt in the salicylic aldehyde. The partition of KCl between water and salicylic aldehyde is, however, not satisfactorily explained by the simple well-known law of partition, according to which the $K^{\cdot}$ concentration in water and in salicylic aldehyde (c_1/c_2) should be constant. For if this were so, the potential difference should *not* change if the aqueous concentration is changed, according to the thermodynamic formula cited above. The fact that the potential difference does vary indicates that the partition is of a more complicated nature. The assumption was put forward in previous papers of the author that a chemical reaction between salicylic acid (in the aldehyde) and KCl was the cause of the complicated partition. This view was supported by other observations based upon measurements with various other water-immiscible electrolytic conductors.

In the following papers these theories will be also controlled by measurements of the conductivity in the non-aqueous phase, by measurements by distribution and various electromotive phenomena not described previously.

4. A brief review seems also justified concerning the thermodynamic derivation of the fundamental formula $E = RT/nF \ln c_1/c_2$ const. (cited above) at phase junctions.[1] In order to derive this formula we consider

[1] This formula was first put forward by Nernst (*Z. physik. Chem.*, 9, 385 (1892)). Haber, however, first described those experiments which showed the usefulness of this theory in a way which was not easy to predict from Nernst's theoretical explanations (*Ann. Physik.*, [4] 26, 947 (1908)). Compare also Beutner, *Trans. Am. Electrochem. Soc.*, 21, 2191 (1912).

a cell system of the following general type:

metal | phase I containing $M^{\cdot}$ | phase II containing $M^{\cdot}$ | metal (as before).
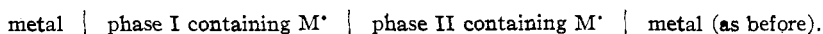
[1] J. Loeb and R. Beutner, *Biochem. Z.*, 51, 288 (1913).

(M⋅ denotes electrolytic ions of the metal which acts as the electrode at both ends.) *It is supposed that the two electrolytic phases are in equilibrium with each other as well as with the metal. Then the e. m. f. of the whole cell must equal zero, since it is not possible to bring about any change in this system even with a current passing through it.* This simple fact makes it possible to calculate the potential difference located at the junctions of the electrolytic phases. The potential difference between the left-hand electrode and Phase I is, according to Nernst's theory, $RT/nF \ln c_1$. const.' (where c_1 is the ionic concentration of M'), and the potential difference between the right-hand electrode and Phase II is $RT/nF \ln c_2$. const."

As the total e. m. f. of the system must be zero, the difference of these two volumes must equal the e. m. f. located at the junctions of the two phases. This difference is $RT/nF \ln c_1/c_2$. const.$_1$/const.' or $RT/nF \ln c_1/c_2$ const., as stated above.

We therefore conclude that the potential difference at the junction of the two phases does not depend, in any way, on ionic mobility as does the potential difference between miscible solutions, but must have properties characteristic of potentials at metallic electrodes.

Haber[1] first devised a method for directly demonstrating this property of "phase potentials." The feature of the method is that one of the concentrations c_1 and c_2 is maintained constant, while the other is varied. This can be done, if the salt whose concentration is varied is soluble in one phase only.

To fulfil this condition he used as Phase I an aqueous solution of $HgNO_3$ and as Phase II an insoluble salt with the same ion, for instance, HgCl. The e. m. f. of the following combination is measured:

Calomel electrode | solid HgCl | $HgNO_3$ aqueous solution | Calomel electrode

If the concentration of the $HgNO_3$ solution in this cell is varied, the ionic concentration of the solid HgCl layer will not be affected. Nor will it have any considerable effect on the potential difference between the $HgNO_3$ solution and the right-hand calomel electrode, since no "phase potential" exists there. Hence the e. m. f. of the whole system must vary with the Hg⋅ concentration according to the logarithmic law, just as in the case of a metallic electrode.

This was shown by experiment to be very exactly true. The concentration of Hg⋅ was changed over a large range by employing NaCl solutions saturated with HgCl (instead of the $HgNO_3$) solution. As is well known the Hg⋅ concentration of such a NaCl solution is exceedingly small and yet very accurately defined.

Experiments of the same kind were made with other insoluble salts, like AgCl and $CaSO_4$, and their ions in aqueous solution, and the same results were obtained.

[1] *Loc. cit., Ann. Physik,* **26**, 947 (1908).

Further, Haber and Klemensiewics[1] made experiments on phase potentials of this kind varying the H˙ concentration. Both phases contained water in their experiments. For instance, if Phase I is ice, and Phase II is water, then only in Phase II acids and bases are soluble, permitting a variation of the H˙ concentration. For Phase I, instead of ice, such materials as glass or solutions of water in organic solvents (like benzene) were taken. Haber's hypothesis, however, that potential differences existing in living tissues are also reversible for H˙ ions could not be verified.

5. It may be remarked that another interesting investigation, which illustrates the similarity between e. m. f. at phase junctions and at metallic electrodes, relates to cell systems built up from solid salts.[2] By means of such cells it is possible to measure the free energy of reactions between solid salts without the aid of metals. Recently the author has carried this idea one step further by discussing the question whether definite chemical reactions could be subjected to a measurement of their e. m. f. by means of cell systems containing phase junctions. The result of this (theoretical) investigation is that even such reactions could be measured as the formation of a salt hydrate from a solid salt and water. Such electrometric measurements have never been carried out previously, because the electric function of the phase junction has been entirely disregarded, the usual electrochemical investigation bearing only on cells with aqueous electrolytes and metals.

It seems probable that the helpless condition of the electrophysiologist, when endeavoring to utilize the results of physical investigations in his own science, is also due to the restricted applicability of the older electrochemistry. The following sentence quoted from L. Herrmann's handbook of physiology[3] expresses the realization of what has till now been lacking. He says on page 170 "The hope of gaining an understanding for the physical nature of the potential differences mentioned has not so far been fulfilled."

NEW YORK. N. Y.

STUDIES ON A NEW KIND OF E. M. F.
II. Cell Arrangements of Aqueous and Nitrobenzene Solutions Containing One Common Ion in Both Phases.

BY REINHARD BEUTNER.

(1) The experiments and the theoretical considerations described above have proved the existence of interphase potential differences with properties resembling electrode potentials. The nature of (diffusion) potential differences existing in non-aqueous solutions at the contact of two different ionic concentrations will be discussed in this paper.

[1] Z. physik. Chem., 67, 385.

[2] Compare Beutner, Z. Electrochem., 15, 433 (1908).

[3] 14th Edition, Berlin, 1910.