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.

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(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.

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

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

[3] 14th Edition, Berlin, 1910.

The study of aqueous solutions has shown that such diffusion potentials depend on the velocity of migration of positive and negative ions; the theory of Nernst and Planck which makes their calculation possible, is well understood. At the junction of two electrolytes of different concentrations the potential difference (according to this theory) equals

$$E = \frac{u - v}{u + v} \frac{RT}{nF} \ln \frac{c_1}{c_2}.$$

An appreciable diffusion potential can therefore occur in such cases only where the velocities of the negative ion (v) and the positive ion (u) are so different that the quantity $u - v/u + v$ is of considerable magnitude; such is not the case in aqueous solutions (with the exception of acids and bases only). It will be shown in this paper that electrolytic solutions in nitrobenzene exhibit a behavior similar to aqueous solutions. The e. m. f. of systems composed of aqueous and water-immiscible electrolytes is, therefore, primarily due to the potential differences existing at the junction of the immiscible phases.

I. Objections to Ostwald's Theory of Selected Ionic Permeability and to Cremer's Experiments.

(2) This fact is contradictory to the conception of some physiologists who, recognizing the possible importance of water-immiscible layers (or membranes) for the production of electric currents by tissues, have tried to explain their action by assuming that the positive and negative ions have a very different mobility in these membranes, thus producing diffusion potentials. This view is based upon a hypothesis, put forward in a preliminary form by Ostwald,[1] according to which a selective ionic permeability of membranes is the cause of physiological currents. This hypothesis was not, however, accepted by most physical chemists and was disproved by Walden[2] working in Ostwald's own laboratory.

The observation, which Ostwald quotes in support of his hypothesis, can be easily explained in some other way, *i. e.*, the precipitation of Cu metal which he describes may be a kind of stenolysis, also the polarization observed is not necessarily due to an impermeability for kations. The one-sided passage of current observed on the boundary of coagulated protein and a precipitating aqueous solution may simply be due to a high specific resistance of the layer of precipitate or membrane, which is formed or dissolved according to the direction of current.

Nevertheless, the theory was accepted by some physiologists.[3]

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[1] *Z. physik. Chem.*, 6, 71 (1890).

[2] Walden, *Ibid.*, 10, 699 (1892). Compare also Tammann, *Göttingen Nachrichten*, 6, 213 (1891). Nernst objects to the theory of selective ionic permeability from a theoretical standpoint (Pflüger's *Archiv.*, 122, 307 (1908)).

[3] Compare Höber, *Physikalische Chemie der Zelle und Gewebe, Liepzig*, 1911 (page 477 f.f.) (Bernstein's membrane theory).

M. Cremer[1] tried to make Ostwald's conception of a selective ionic permeability of the "membranes" clearer by means of the assumption described, according to which the mobility of the positive and negative ions in the membrane is largely different. In order to find an experimental proof for this view he experimented on solutions of picric acid in nitrobenzene and measured the e. m. f. of the following arrangement:

+ $M/8$ NaCl solution	*Nitrobenzene*		$M/8$ NaCl aqueous solution—
	saturated with picric acid	without picric acid	

obs.: 0.1 volt (not constant)

If really the change of the concentration of the picric acid in the nitrobenzene causes this e. m. f. (diffusion potential) the conclusion would seem necessary that the anion of the picric acid has a very much larger mobility than the $H^{\cdot}$. This result would certainly be most striking, for in aqueous solutions the velocity of the $H^{\cdot}$ ion far exceeds that of all anions, as is well known. Therefore, all arrangements

— concentrated acid (aq.) — diluted acid (aq.) +
or
— concentrated acid (aq.) — pure water +

produce e. m. f. of the opposite direction.[2]

It is possible, however, to show that diffusion potentials and ionic mobilities have nothing, or very little, to do with the e. m. f. produced by Cremer's nitrobenzene cell, but that the junction of the aqueous solutions and the nitrobenzene produces nearly the total e. m. f. of the system, *for the nitrobenzene saturated with picric acid takes up sodium salts to a much larger extent than nitrobenzene containing no picric acid; and large interphase potential differences must be produced in this way, which account for the e. m. f. observed.*

To prove this, nitrobenzene with and without addition of picric acid was shaken for 15 hours with $M/8$ sodium chloride solution, resp., with water and the increase of conductivity was measured. It was found that the conductivity of pure nitrobenzene was approximately the same whether it was shaken with water or with sodium chloride solution; the conductivity observed was very small in both cases and difficult to determine accurately (about 0.015 rec. megohms). A 20% solution of picric acid in nitrobenzene however, showed a marked increase in conductivity:

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[1] *Z. Biol.*, 47, 1 (1906).

[2] It must be said that Cremer himself seems doubtful as to whether really the ionic mobilities of positive and negative ions are reversed in nitrobenzene. He proposes his explanation as a working hypothesis only; his interesting investigation does not become less valuable therefor by the modified explanation given here.

20 cc. 20% picric acid in nitrobenzene shaken for 15 hours at room temperature with 100 cc. distilled water: 3.26 rec. megohms (at 25°).

20 cc. 20% picric acid in nitrobenzene shaken under the same conditions of temperature with 100 cc. $M/8$ NaCl solution: 4.73 rec. megohms (at 25°).

This difference of conductivity is likely to be due to formation of sodium ions in the nitrobenzene in the second experiment, or to the formation of a sodium picrate. This is supported by the observation that pure nitrobenzene shows an increase of conductivity of the same order of magnitude after shaking with a very dilute sodium picrate solution:

20 cc. nitrobenzene shaken under the same conditions as above with 100 cc. of a $M/100$ sodium picrate solution: 3.7 rec. megohms (at 25°).

Another proof for this formation of sodium picrate is found in the fact that the solution of picric acid behaves similarly to salicylic aldehyde; in contact with aqueous sodium chloride solutions of different concentrations the potential difference changes in the same direction; the conclusions mentioned on page 2043 tend to show that this phenomenon also is due to a formation of sodium picrate, dissolved in the nitrobenzene to some extent when equilibrium at the phase junction is established.

Cremer's cell arrangement is therefore a concentration cell with respect to $Na^{\cdot}$ ions:

+ aqueous $M/8$ NaCl	*Nitrobenzene*		aqueous $M/8$ NaCl—
	high $Na^{\cdot}$ concentration due to picric acid	low $Na^{\cdot}$ concentration	

The direction of the e. m. f. of this system would be such as indicated, a quantitative calculation is scarcely possible as the system is not well defined.

Since, in this case, the junction of the aqueous and the nitrobenzene solutions produces the e. m. f., and not the junction of the two different nitrobenzene solutions, no conclusions concerning a largely different mobility of *positive and negative ions* in nitrobenzene can be drawn.

II. Ionization in Nitrobenzene.

(3) The starting point of the experiments described in this paper are measurements which make a direct application of the fundamental formula

$$E = \frac{RT}{nF} \ln \frac{c_1}{c_2}.$$

const. at phase junctions possible, and allow the deduction of clear conclusions. Something about the ionization in the nonaqueous solvent must be known for this purpose.[1]

Although we are very well informed concerning ionic concentrations of aqueous solutions, very little is known concerning ionic concentrations in

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[1] Nitrobenzene is chosen as the water-immiscible solvent in most of the experiments, as it may be secured at low cost in large quantities and produces a sufficient conductivity to make measurements of the e. m. f. possible.

all organic solvents which mix incompletely with water. The reason is that the methods and laws established for aqueous electrolytes are not always otherwise applicable, as investigations on conductivity of nonaqueous solutions have demonstrated. Some preliminary tests were, therefore, undertaken for the purpose of determining which substances would produce a particularly high electric conductivity if dissolved in a water-immiscible organic fluid. *It was found that all bases and acids, even those* which are the best conductors in aqueous solutions (like picric acid), never produce any appreciable conductivity in substances like phenol, nitrobenzene or benzaldehyde; mixtures of acids and bases, however, have a conductivity which, in a 1/1 g. molecular solution is about one hundred or one thousand times larger; this is without doubt due to the formation of a salt-like compound, just as in aqueous solutions salts may have a higher conductivity than the (weak) acids and bases from which they are formed. It seems, therefore, as if all acids and bases are "weak" electrolytes in water-immiscible solvents. The comparatively high conductivity of salts exists in both cases in a qualitatively similar fashion.

These electrical properties of nonaqueous solutions can best be demonstrated with substituted anilines as bases; a strong acid like salicylic acid or picric acid must also be employed.

The following approximate measurements may serve as an example: The nitrobenzene employed without additions had a specific conductivity of 0.01 rec. megohms at 30°; dissolving dimethyl-*o*-toluidine in a molecular concentration (135 g. in a liter) increased the conductivity up to 0.09 rec. megohms ($t = 30°$); dissolving salicylic acid (molecular concentration) alone increased up to 3.5 rec. megohms ($t = 65°$).[1] A nitrobenzene solution, however, which contained both dimethyl toluidine and salicylic acid in a molecular solution showed a conductivity of *450* reciprocal megohms. This very large increase in conductivity is certainly due to a formation of a salt-like combination (dimethyl toluidine salicylate) which dissociates into dimethyl toluidine kations and salicylic acid anions. Nothing definite concerning the degree of ionization can, however, be determined by means of measurements of conductivity.

(4) Another proof for the presence of dimethyl toluidine kations and salicylic acid anions in this mixture can be found by means of electrometric measurements. The potential difference at the junction

Nitrobenzene containing dimethyl toluidine and salicylic acid in a mol. concentration	Sodium salicylate in water (concentration varied)

was measured by means of the apparatus described in Fig. 1. Instead

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[1] At 30°, salicylic acid is not sufficiently soluble for a molecular solution; it may be supposed, however, that the conductivity at 30° would be even smaller.

of salicylic aldehyde the nitrobenzene solution was filled in the U-tube. Using solutions of sodium salicylate the following e. m. f. were observed (constant, at room temperature).

	Concentration of sodium salicylate solution.		
	1/1 n.	1/2 n.	1/4 n.
E. m. f.	+0.0705 volt	+0.053 volt	+0.0355 volt

This change of the e. m. f. is exactly what would be expected according to the interphase formula if salicylic acid anions were present in the nitrobenzene:

$$E = \frac{RT}{F} \ln \frac{c_{\text{sal.}'\text{ in nitrobenzol}}}{c_{\text{sal.}'\text{ in water}}} \cdot \text{const.}$$

If the concentration in nitrobenzene is kept constant, and the aqueous concentration doubled, the potential difference should increase (the water becomes more positive). 58 ln 2 = 17.5 Milli-volt, which is exactly the value observed.[1]

It is seen that by changing the aqueous concentration in this system, not only the potential difference at the nitrobenzene-water interphase[2] might vary but also the diffusion potential between the 1/1 KCl calomel electrode and the sodium salicylate, the change of the latter, however, can be practically neglected, since $K^{\cdot}$ and Cl' and also $Na^{\cdot}$ and salicylic anion have very nearly the same migration velocity in aqueous solutions.

The total change of the e. m. f. observed, therefore, should be located at the nitrobenzene-water interphase and can be calculated according to the formula cited above.

If, however, the concentration of the sodium salicylate solution is decreased still further the e. m. f. decreases to a smaller amount:

Change of the concentration from:	Change of e. m. f.[2]
1/4 to 1/8	0.015 volt
1/8 to 1/16	0.014 volt
1/16 to 1/32	0.010 volt
1/32 to 1/64	0.006 volt
1/64 to pure water	0.006 volt (not constant)

This apparently is due to the fact that also pure water in contact with our nitrobenzene solution must contain salicylic acid anions owing to partition of dimethyl toluidine salicylate or salicylic acid alone between water and nitrobenzene; the concentration of the salicylic anion in water cannot be decreased below this value and therefore the potential difference does not decrease steadily but reaches a minimum value, which is determined by the distribution of the salicylic acid in the equilibrium.

In order to determine the amount of salicylic acid anions present in water in equilibrium, the nitrobenzene solution was shaken with an equal volume of distilled water, and the conductivity of the water determined (= $2.7.10^{-3}$) (at t = 30°); assuming

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[1] This calculation is only correct if the diffusion potential of the aqueous solution is zero, as the system really measured is the following:

— calomel electrode	nitrobenzene cont. dimethyl toluidine and, salicylic acid (concentration)	aqueous solution containing sodium salicylate (varying concentrations)	calomel electrode +
	1	2	3

[2] All these values are constant and reversible with the exception of the last one, which is rather difficult to determine.

that the ionic mobility of the dimethyl toluidine kation and of salicylic acid anion equals 40, the order of magnitude of the ionic concentration may be estimated from this to equal about 0.03 m.[1]

This value must be added, therefore, to the concentration of the anion due to dissociation of sodium salicylate, which is practically equal to the total concentration of sodium salicylate. Therefore,

A change of the concentration.	Really corresponds to a change of the concentration.	Calculated change of e. m. f.
from 1/4 to 1/8	from 0.28 to 0.155	0.0148 volt
from 1/8 to 1/16	from 0.155 to 0.093	0.013 volt
from 1/16 to 1/32	from 0.093 to 0.061	0.010 volt
from 1/32 to 1/64	from 0.061 to 0.045	0.0065 volt
from 1/64 to pure water	from 0.045 to 0.030	0.010 volt

It is seen that these values agree with those observed.

The presence of dimethyl toluidine kations in our nitrobenzene solution can be proved in an analogous way by measuring the potential difference at the junction

Nitrobenzene containing dimethyl toluiline + salicylic acid, *const.*	Dimethyl toluidine hydrochloride[2] in aqueous solution

The common ion should be in this case the positive ion (dimethyl toluidine kation); therefore, by changing the aqueous concentration the change of the e. m. f. observed should be opposite to that observed with sodium salicylate in the aqueous solution, the magnitude of the change should be about the same. The result of the measurement confirmed this as the following data show:

Molecular concentration of the dimethyl toluidine hydrochloride.	E. M. F. observed.	Difference.
1/1	—0.068 volt	
		>0.0155 volt
1/2	—0.0525 volt	
		>0.0145 volt
1/4	—0.038 volt	
		>0.013 volt
1/8	—0.025 volt	
		>0.009 volt
1/16	—0.016 volt	
		>0.006 volt
1/32	—0.010 volt	
		>0.002 volt
1/64	—0.008 volt	

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[1] The total concentration of salicylic acid was found by means of titration with phenolphthalein to equal: 0.055 m. Only one-half of the total amount is, therefore, electrolytically dissociated. Since there must be, however, a slight hydrolytic splitting, producing free acid and free salt, both of which have a slow degree of ionization, the rather low degree of electrolytic dissociation *in toto* might be explained.

[2] The aqueous solution of dimethyltoluidine hydrochloride was prepared by shaking the calculated quantity of the base with hydrochloric acid. Owing to hydrolytic dissociation this salt partly decomposes and a part of the base is left undissolved.

The magnitude of the change of the e. m. f. observed is slightly smaller here than in each case with observations on sodium salicylate. This is difficult to account for by a quantitative theory as the equilibria in this system are also complicated through the hydrolytic splitting of dimethyl toluidine hydrochloride in aqueous solution, diffusion potentials may also be produced in the aqueous solution by this hydrolysis. In order of magnitude, the approach towards a limiting value at low concentrations and the direction of the change of the e. m. f. are a sufficient proof for the assertion.

III. Nitrobenzene Concentration Cells and the Magnitude of Diffusion Potentials in Nitrobenzene.

(5) *Summarizing the results obtained so far, we have proved the existence of dimethyl toluidine kations and salicylic acid anions in a nitrobenzene solution of this base and this acid: (1) by measurements of conductivity, (2) by studying the electrode-like action of the nitrobenzene solution. Those experiments will now be described in which the ionic concentration of the nitrobenzene solution is changed while the aqueous concentration is kept constant. Nitrobenzene solutions, of the kind described, with considerable conductivity will be used for these concentration cells; it can be proved that no, or very small, diffusion potentials occur at the junction of two nitrobenzene solutions of different concentration.* The method used is as follows:

According to the theory the potential difference at the junction of the nitrobenzene solution and aqueous solution should change in opposite directions whether the ion common to both phases is an anion or a kation; the potential differences located at the phase junctions

(1) *Nitrobenzene* containing dimethyl toluidine + salicylic acid, | Aqueous solution of sodium salicylate

resp.

(2) *Nitrobenzene* containing dimethyl toluidine + salicylic acid | Aqueous solutions of dimethyl toluidine hydrochloride

should therefore react in an opposite sense to a dilution of the nitrobenzene solution.

This conclusion could be easily verified by measuring the cell arrangements

—$M/5$ sodium salicylate aq. solution	Nitrobenzene con toluidine $M/1$	taining dimethyl salicylate $M/10$	$M/5$ sodium salicylate + aq. solution
	a	*x*	*b*

obs.: *0.031* volt, (constant) at room temperature (20°)

and

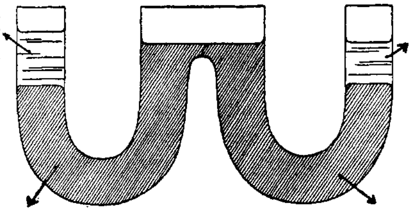
+ $M/5$ dimethyl toluidine hydrochloride aq. sol.	Nitrobenzene con toluidine $M/1$	taining dimethyl salicylate $M/10$	$M/5$ dimethyl toluidine hydrochloride aq. sol.
	a	*x*	*b*

obs.: *0.035* volt (constant), at room temperature (20°).

The apparatus used for these measurements is described in Fig. 2, which requires no further explanation. (The connection from both aqueous solutions to the measuring instrument electrometer was made by means of calomel electrodes which did not produce any new e. m. f., since diffusion potentials existing in the aqueous solutions must be equal and opposite.)

In the first cell the more concentrated nitrobenzene solution is on the negative pole (reversibility for anions), in the second on the positive (reversibility for kations).

Comparing these concentration cells with those known in earlier electrochemistry we may say that the metallic electrodes are replaced here by the aqueous solutions while the two nitrobenzene solutions replace the two aqueous solutions usually employed. *These observations furnish a striking contradiction to the theory that diffusion potentials of considerable magnitude exist at the junction of two different nitrobenzene solutions. If this were so, and if the interphase potential differences played no role, the direction of the e. m. f. would be the same in the two cell arrangements described, i. e., it would not be possible to reverse the direction of the e. m. f. by changing the aqueous solutions* (replacing sodium salicylate by dimethyl toluidine hydrochloride), *as is actually the case.*



M/5 aqueous solution of sodium salicylate (or of dimethyl toluidine hydrochloride).

M/5 aqueous solution of sodium salicylate (or of dimethyl toluidine hydrochloride).

M/10 nitrobenzene solution of dimethyl toluidine + salicylic acid.

M/1 nitrobenzene solution of the same.

Fig. 2.

The question, however, presents itself whether the total e. m. f. observed is located at the nitrobenzene-water interphases a, b, a' and b' exclusively or whether a small additional diffusion potential is also produced at the junction of the two nitrobenzene solutions of different concentration (x). This problem can be solved approximately in the following way:

The e. m. f. of the first cell (concentration cell with respect to salicylic acid anions) equals ($0.058 \lg c_1/c_2$) $+ x$ volts at room temperature, if c_1 and c_2 are the concentrations of the anions of salicylic acid in the two nitrobenzene solutions the e. m. f. of the second cell (concentration cell with respect to dimethyl toluidine kations) equals $0.058 \lg c_1'/c_2' - x$ volts if c_1' and c_2' are the concentrations of the kations in the two nitrobenzene solutions.

Now if $c_1 = c_1'$, resp., $c_2 = c_2'$, *i. e.*, if the concentration of the dimethyl toluidine kations equals the concentration of the salicylic acid anions in both nitrobenzene solutions at the junction of the aqueous solutions, we can calculate the magnitude of the diffusion potentials from the difference of the e. m. f. observed; the difference of the e. m. f. of the two cells (0.035–0.031 volts) would then equal $0.058 \lg c_1/c_2 - 0.058 \lg c_1'/c_2' + 2x$ or $x = 0.002$ volts.

Apparently the assumption of the equality of c_1 and c_1', resp., c_2 and c_2' is justified if the nitrobenzene contains no other electrolyte than dimethyl toluidine salicylate (no sodium salicylate, resp., no dimethyl toluidine HCl). A certain quantity of the electrolyte present in the *aqueous* solution will, however, penetrate into the nitrobenzene at the phase junction until equilibrium of distribution is established; but this amount must be so small that the ionic concentration in the nitrobenzene is not considerably changed. In the experiments described, all the concentrations were selected in such a way that this is actually the case. This can be proved by means of measurements of conductivity; the conductivity imparted to pure nitrobenzene after shaking with the aqueous solutions is so small that it can be neglected as compared with the own conductivity of the nitrobenzene solutions used (as the following figures show):

Conductivity of the mol. solution in nitrobenzene	450 rec. Megohms
Conductivity of the $M/10$ solution in nitrobenzene	84 rec. Megohms
Conductivity of nitrobenzene after shaking with a double volume of $M/5$ sodium salicylate (for six hours)	0.6 rec. Megohms
The same after shaking with $M/5$ dimethyl toluidine HCl	1.5 rec. Megohms

The highly conducting nitrobenzene solutions were also shaken with the two aqueous solutions. A slight decrease in conductivity was observed in this case [from 450 to 430 rec. megohms (sod. salic.), resp., 420 (dimethyl tol. HCl), and from 83.7 to 83 (sod. salic.), resp., 83 (dimethyl tol. HCl)]. The cause of this decrease is hard to define. We are certainly justified, however, to conclude from these measurements that the ionic concentrations in nitrobenzene are not changed considerably by distribution equilibrium at the phase junction in question, and that therefore *the calculation of the diffusion potential is correct.* *$x = 0.002$ volts* or only a small fraction of the total e. m. f. observed.[1]

Conductivity of $M/5$ dimethyl toluidine HCl	0.017 rec. ohms
Conductivity of $M/5$ sodium salicylate	0.012 rec. ohms
Conductivity of water after shaking with the mol. nitrobenzene sol.	0.0023 rec. ohms
The same after shaking with the $M/10$ nitrobenzene solution	0.0006 rec. ohms

This is of importance for quantitative calculation of the e. m. f. described below.

(6) Similar experiments were performed with other substances; for instance, the following arrangement was measured:

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[1] The ionic concentration of the two aqueous solutions in our experiments is not changed either by the electrolytes diffusing *from* the nitrobenzene solution *into* the aqueous phase at the phase junctions, as the following data show:

— $M/5$ sodium nitrobenzoate aq. sol.	Nitrobenzene containing di methyl aniline and *m*-nitrobenzoic acid $M/1$ $M/10$	$M/5$ sodium nitrobenzoate + aq. sol.

obs. 0.037 volt (constant)

+ $M/5$ dimethyl aniline hydrochloride aq. sol.	Nitrobenzene containing dimethyl aniline and *m*-nitrobenzoic acid $M/1$ $M/10$	$M/5$ dimethyl toluidine hydrochloride

obs.: 0.03 volt (constant).

The diffusion potential between the two nitrobenzene solutions would equal zero in this case, as the e. m. f. of the two systems is equal and opposite.

(7) We may conclude from these experiments that ionic mobilities and diffusion potentials exhibit similar properties in aqueous and nitrobenzene solutions and that there is no reason to suppose that a relatively excessive velocity of certain ions produces particular effects in systems of immiscible electrolytic conductors. Interphase potential differences determine the magnitude and the direction of the e. m. f. in all such systems.

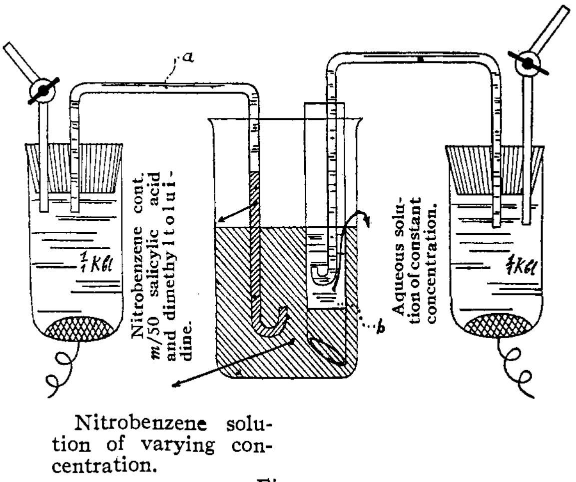

Fig. 3.

Concerning electrophysiological theories it can be said, that the results obtained are in direct contradiction to the theory of selective ionic permeability. This theory is applied by some physiological authors in rather vague theoretical considerations, explaining various visible changes in living cells through an invasion of positive and negative ions due to an alleged mobility or permeability of the ion in or through the cell membrane. The experiments described furnish proof against such theories by means of the evidence that no essential difference exists between + and — ions in water-immiscible solvents so far as the mobility is concerned.

(8)-*A quantitative calculation of the e. m. f. of our concentration cells from the ratio of the ionic concentrations* should be possible in the same way as with the ordinary concentration cell. If we assume that the ionic concentration in the nitrobenzene is proportional to conductivity, the e. m. f. calculated would be 0.058 lg c_1/c_2 volts, where c_1 and c_2 are the conductivities of the two nitrobenzene solutions: c_1 = 450 rec. megohms, c_2 = 83 rec. megohms; e. m. f. therefore should be 0.042 volt; this value is not identical, however, with the one observed (0.033 volt). Owing to our incomplete knowledge concerning ionization in nitrobenzene solutions, it is difficult to account, with certainty, for this deviation; the following observations, however, may have some bearing on the problem: The conductivity of the grammolecular nitrobenzene solution (of dimethyl toluidine + salicylic acid) equals 430 rec. megohms only if saturated with water; the same solution in dry nitrobenzene had only 340 rec. megohms; the conductivity of the $M/10$ nitrobenzene solution, however, did not change by saturating with water. If we assume that the conductivity of the dry nitrobenzene solutions is proportional to the concentrations of those ions which act in the concentration cells (dimethyl toluidine$^{\oplus}$ salic.$^{\ominus}$) we get, in fact, a much closer agreement: 0.058 lg 340/83 = 0.035 volt, which is identical within the experimental errors with the value observed. We may assume that the increase in conductivity observed, if the molecular nitrobenzene solution is saturated on water, is due to a chemical reaction of hydrolysis resulting in the formation of $H^{\cdot}$ ions or other ions.[1]

(9) Experiments of the same kind may be described at last with a somewhat modified experimental arrangement (see Fig. 4). By means of this arrangement the nitrobenzene-water interphase could be kept constant on one side (in the narrow tube *a*) while the other interphase (in broader tube *b*) could be changed; the change of the e. m. f. with the change of the solution then is the effect observed. This method is therefore quite analogous to the one described above (compare Fig. 1), with the difference that in this case the concentration of the nitrobenzene varied while the aqueous concentration is kept constant.

The narrow tube (*a*), connected with one electrode, is filled with 1/1 KCl (aq. sol.) in upper part and with a 0.02 M nitrobenzene solution of dimethyl toluidine and salicylic acid in the lower hook-shaped part; this is immersed into a beaker containing the same nitrobenzene solution in varying concentrations; an aqueous 0.5 M solution of sodium salicylate (or toluidine hydrochloride) supernates on the nitrobenzene in the beaker, in a broader tube (*b*), this is connected with the other calomel electrode by means of a hook-shaped tube.

With sodium salicylate as constant aqueous solution, the system really measured is:

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[1] In the experiments with nitrobenzene solutions of dimethyl aniline and *m*-nitrobenzoic acid the value calculated from the ratio of the conductivities of the dry solutions is 0.054 volt (obs. 0.037 volt). This deviation is due to a very complicated state of this nitrobenzene solution which we cannot fully account for so far; the molecular conductivity of this solution increases with increasing concentration.

— calomel electrode (1/1 KCl)	Nitrobenzene solution of salicylic acid and dimethyl toluidine 0.02 M (constant) variable concentration	0.5 M sodium salicylate in water	calomel electrode +

The following e. m. f. were observed:

Concentration of the variable solution.	E. M. F.	Change of the E. M. F.
$M/2$	0.060 volt	
		>0.028 volt
$M/10$	0.088 volt	
		>0.021 volt
$M/50$	0.109 volt	
		>0.024 volt
$M/250$	0.133 volt	
		>0.000 volt
$M/1250$	0.133 volt	

With dimethyl toluidine hydrochloride the system measured is:

+ calomel electrode	Nitrobenzene solution of salicylic acid and dimethyl toluidine 0.02 M (constant) variable concentration	0.5 M dimethyl toluidine in water	calomel electrode —

E. M. F. observed:

Concentration of the variable solution.	E. M. F.	Change of the E. M. F.
$M/12$	0.048 volt	
		>0.029 volt
$M/10$	0.077 volt	
		>0.029 volt
$M/50$	0.106 volt	
		>0.000 volt
$M/250$	0.135 volt	
		>0.000 volt
$M/1250$	0.135 volt	

It is seen that the direction of the change is opposite in both cases as the e. m. f. of the two systems are in opposite directions.

The conductivities of the dry nitrobenzene solutions were observed as follows ($t = 30°$):

$M/2$	243 rec. megohms
$M/10$	80.5 rec. megohms
$M/50$	15.3 rec. megohms
$M/250$	2.7 rec. megohms
$M/1250$	0.4 rec. megohms

In order to calculate the change of the e. m. f. from the ratio of conductivity, it must be considered that some sodium salicylate or dimethyl toluidine passes from the aqueous solution into the nitrobenzene; it was found that the pure nitrobenzene with a conductivity of 0.006 rec. megohm had 2.4 rec. megohms after shaking with 0.5 M sodium salicylate (aq. sol.); 2.3 rec. megohms after shaking dimethyl toluidine hydrochloride. The ionic concentration in the nitrobenzene can therefore not be lowered below a value corresponding to this conductivity, which is about $M/250$. A dilution of the nitrobenzene from *M*/250 to *M*/1250 can, therefore, produce no change of the e. m. f. as was really observed. With relatively concentrated nitrobenzene solutions the salts invading from the aqueous solution can be neglected, the change of the e. m. f. equals the one calculated from the ratio of conductivities 0.5 *M* to 0.1 *M* : 0.058 lg 80.5 = 0.028 volt; (obs. 0.029). For the intermediate concentrations the value observed is in each case smaller than the one calculated owing to the electrolytes penetrating into the nitrobenzene from the aqueous solution,

M/10 to *M*/50 0.058 lg 80.5/15.3 = 0.042 volt (obs. 0.021, 0.029 volt).
M/50 to *M*/250 0.058 lg 15.3/2.7 = 0.044 volt (obs. 0.029 volt).

A quantitative calculation similar to that described above for aqueous solutions does not seem possible, however, owing to our incomplete knowledge concerning distribution and ionization in nonaqueous solutions.

IV. Concentration Double Cell of a New Type.

(9) Observations concerning the e. m. f. of the following concentration cell may finally be mentioned:

— 0.2 *M* sod. salic. (aq. sol.) | *M* dimethyl tol. + salic. acid *nitrobenzene* | 0.2 *M* dimethyl tol.
HCl (aq. sol.) | 0.1 *M* dimethyl tol. + salic. acid *nitrobenzene* | 0.2 *M* sod. salic aq. sol. +

e. m. f. observed at room temperature: 0.066 volt (constant).

(Concerning the experimental arrangement compare Fig. 4.)

This cell cannot contain any diffusion potentials at all according to the measurements of distribution and conductivity described above; the total e. m. f. observed must be located at the four-phase junctions.

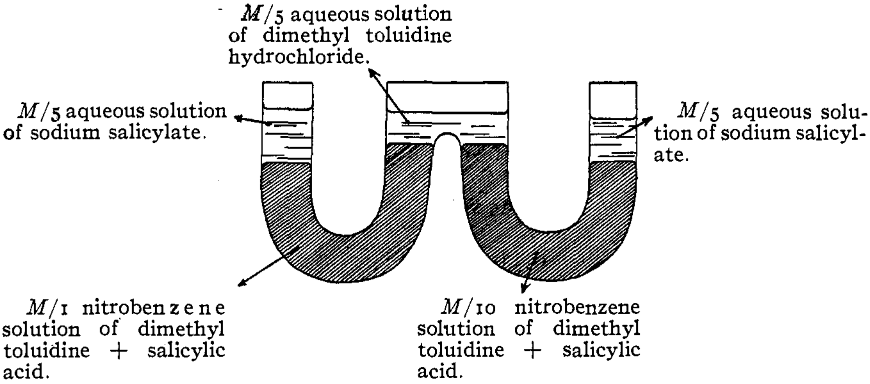

Fig. 4.

Comparing this cell with those described on page 2053, it is easily understood that the e. m. f. observed here must equal the sum of those previously described, which is actually the case: 0.031 + 0.035 volt = 0.066 volt.

A concentration double cell of this type is especially fit for arranging a *large number* of alternating nitrobenzene and aqueous layers in such a way as to produce a considerable e. m. f. because the same aqueous solution is at both ends of the cell, and also because it contains no diffusion potentials at all. Experiments concerning such cell arrangements will be communicated later.

Summary.

(1) The e. m. f. of cell arrangements consisting of aqueous and nitrobenzene solutions is measured; the solutions which are in contact with each other always contain one common ion. This makes it most easily possible to calculate from the thermodynamic formula those potential differences which exist at the nitrobenzene-water interphase.

(2) Preliminary experiments are described, in order to test the nature of ionic conduction in nitrobenzene and in order to prove the applicability of the thermodynamic formula at the phase junctions in question.

(3) The e. m. f. of cells which consist of two nitrobenzene solutions of different concentrations in contact with each other between two identical aqueous solutions is then measured. It can be proved that the total e. m. f. of these systems is practically entirely located at the phase junctions and not at the junctions of the two nitrobenzene solutions. *This result can be understood without an elaborate theoretical explanation by contemplating the diagrams of the cells. If the e. m. f. observed was located at the junction of the two nitrobenzene solutions it would certainly not be possible to reverse the direction of the e. m. f. by changing the aqueous solutions such as is actually the case.*

(4) Ostwald had assumed that membranes or layers of water-immiscible electrolytes between two aqueous solutions produce e. m. f. owing to a selective ionic permeability; this would mean that in the membrane the mobility of the anion, *i. e.*, far exceeds that of the kation, thus producing a diffusion potential. According to this hypothesis then, the e. m. f. produced by a water-immiscible layer is not located at the phase junction but inside the layer or membrane. This theory does not agree, therefore, with the experimental results obtained here.

(5) Cremer's experiments on biphasic water-nitrobenzene cell arrangements do not support the theory of different mobilities of anions and kations, because the e. m. f. observed by him is also located at nitrobenzene-water interphases. This is due to the fact that the distribution of electrolytes between water and nitrobenzene is much more complicated than was assumed by Cremer; the salt contained in the aqueous solution invades the nitrobenzene on one side to a much larger extent than on the other side, as can be shown by means of conductivity measurements. In the experiments described here the aqueous and nitrobenzene solutions are selected in such a way that their ionic concentration is not changed appreciably by electrolytes passing from either phase into the other, if the equilibrium of distribution is established. For this reason it can be claimed that these experiments furnish a better argument for the problem in question.

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