THE RELATION BETWEEN THE SPECIFIC INDUCTIVE CAPACITY OF AN ELECTROLYTE AND THE ELECTRIC POTENTIAL OF A METAL PLACED IN IT.

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According to the generally accepted Nernst theory of the mechanism of galvanic-current production, the difference of potential between a metal and a solution of one of its salts may be computed from the equation

$$E = \frac{RT}{ne_0} \log \frac{P}{p}, \qquad (1)$$

where R is the gas constant, T the absolute temperature, n the valence of the metal, e_0 the charge carried by one gram-molecular weight of univalent ions, p the osmotic pressure of the ions in solution and P the solution pressure of the metal. On this theory P is an *expansive force* tending to drive ions from the metal into the solution and is opposed by p, the osmotic pressure of the ions already in solution, or, in equilibrium conditions, by the sum of the osmotic pressure of ions in solution and the electrostatic attraction between the metal and the ions in solution.

Of course we have no experimental evidence of the existence either of an osmotic pressure or of the so-called solution pressure in the case of a metal dipping into a solution. It is merely assumed that the ions in the solution exert an osmotic pressure, the magnitude of which can be calculated from the gas laws and that, therefore, in order that the metal may lose ions to the solution, it must exert an expansive force in excess of the osmotic pressure of the ions in solution. The magnitude of this expansive force, *i. e.*, the solution pressure of the metal, can obviously be found only by first determining the values of all the other quantities of the above equation. When this computation is made, using for E the potential difference between the different metals and normal solutions of their respective salts, values for P are obtained which range from 10^{44} atmospheres in the case of magnesium to 10^{-20} atmospheres in the case of copper.

The mere incomprehensibility of such values, attention to which has been called by Lehfeldt,[1] might permit the raising of a question on the theory demanding them. But there are other reasons for doubting the

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[1] Zeit. Phys. Chem., 26, 94, 1898.

validity of the Nernst theory. The solution pressure of a metal, if such exists, depends not only upon the metal but also upon the solvent in which it dips since it has been shown that the potential difference between metal and solution varies for the same metal in different solvents.[1] But it is difficult to imagine why an expansive force within a metal should vary with the surrounding medium when the external (osmotic) pressure is kept constant, or why it should not be effective when the metal is surrounded by air. But we can get what seems to be conclusive evidence against the solution pressure theory by making a simple computation either of the speed with which an ion would have to leave the surface of a magnesium electrode in water, even on the assumption that the solution pressure acts only through a molecular distance, or of the mass of the ions which a magnesium electrode would need to lose in water in order that the solution pressure be balanced by the sum of the osmotic pressure and the electrostatic attraction. Both of these calculations give values which are not only absurd but impossible, the speed of the ion, in the first case, being greater than the velocity of light and the mass of the ions lost, in the second case, being such that the density of the solution would be greater than that of the metal.

In the case of the concentration cell, the solution pressure factor is supposed to cancel out since electrodes of the same metal dip into the same solvent and equation (1) becomes

$$E = \frac{RT}{ne_0} \log \frac{C_1}{C_2}, \tag{2}$$

C_1 and C_2 being the ionic concentrations in the two parts of the cell. Kahlenburg[2] has tested the applicability of this equation to concentration cells in which non-aqueous electrolytes are used and finds that the observed and calculated electromotive forces are far from agreement after due allowance is made for experimental error.

If the Nernst theory is not in accordance with the facts in the few cases cited above, obviously it is not the correct explanation in any case. Furthermore, this theory does not take account of a factor which we know must exist and the recognition of which does away with the necessity of the employment of the two purely hypothetical quantities, the solution pressure of the metal and the osmotic pressure of the ions in the solution. The omitted factor is the specific inductive capacity of the electrolyte.

When a metal is dipped into a solution we know it acquires either a positive or a negative charge with respect to the solution. The former case is supposed to be due to positive ions from the solution having been

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[1] Kahlenburg, Journal Phys. Chem., 3, 379, 1899.

[2] Journal Phys. Chem., 74, 709, 1900.

deposited upon it while in the latter case the metal has lost some of its metallic ions to the solution. In either case there has been a transfer of ions between the metal and the electrolyte, which, presumably, has been brought about by electrical forces, the magnitude of which must depend, other things being equal, upon the specific inductive capacity of the medium. If then a metal, when placed in a liquid of relatively low specific inductive capacity, becomes electronegative by giving off metallic ions, it should become still more electronegative when placed in a liquid of higher specific inductive capacity, for here the cohesion of the surface atoms of the metal would be lessened to a greater extent (assuming cohesion to be an electric attraction) and metallic ions would go into solution more readily.

If this be true, in a two-solution cell having electrodes of the same metal, not only should the electrode in the solution of higher specific inductive capacity be electronegative with respect to the other electrode, but the electromotive force of such a cell should be proportional to the difference in the specific inductive capacities of the two solutions.

This latter relation can be directly subjected to experiment and suggests a method of experimentally checking up the simple theory above stated.

Of course we do not know and have no means of measuring the specific inductive capacity of any ordinary electrolytes, but electromotive force measurements can be made when liquids of very slight conductivity are used as electrolytes. To eliminate as many variables as possible, it seemed best to measure the electromotive forces between identical electrodes using as electrolytes various mixtures of two liquids rather than a number of pure liquids.

The specific inductive capacities of mixtures of ethyl alcohol and water,[1] benzene and acetone,[2] acetone and water,[3] methyl alcohol and water,[4] chloroform and ethyl alcohol,[5] ether and chloroform,[6] and others have been determined for different percentages of one in the other.

The plan of this investigation was to use these mixtures as electrolytes and measure the electromotive force between electrodes of the same metal, one placed in a certain mixture of two liquids, the other placed in a different mixture of the same liquids. Since, in general, the specific inductive capacity of a mixture of two liquids does not vary linearly

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[1] W. Nernst, Wied. Ann., 60, 1897.

[2] P. Drude, Zeit. Phys. Chem., 23, 267, 1897.

[3] P. Drude, Zeit. Phys. Chem., 23, 267, 1897.

[4] P. Drude, Zeit. Phys. Chem., 23, 267, 1897, and E. A. Harrington, Phys. Rev., VII., 581, 1916.

[5] J. C. Philip, Zeit. Phys. Chem., 24, 18, 1897.

[6] W. D. Coolidge, Wied. Ann., 69, 125, 1899.

with the concentration of one in the other, we have here a means of determining whether the electromotive force is dependent upon the difference in concentration of the two mixtures, or upon their difference in specific inductive capacity, if upon either. The method first employed was as follows: The bottom of a glass U-tube was closed with a gelatine plug. One arm was then filled with water, and the other with a mixture of water and ethyl alcohol, the specific inductive capacity of which was known. Into these liquids were put electrodes of the same metal, and the electromotive force measured by the condenser and ballistic galvanometer method.

Various metals were tried as electrodes but freshly electroplated copper yielded the most consistent results. The electromotive force rapidly fell off, however, after the electrodes were immersed, and because of the high resistance of the cell (several megohms) a reading could not be made at once, the time of condenser charge being about fifty seconds. In order to cut down the resistance of the electrolytes, and also to mask the effect of any impurities which might be present in either the water or the alcohol, equimolecular solutions of copper chloride ($CuCl_2$) in water and in alcohol were substituted for the pure liquids, the idea being that the specific inductive capacity of each solvent would be changed by the same amount thus keeping their difference constant.

With one-hundredth normal solutions of $CuCl_2$, which proved the most satisfactory, and electrodes of about two hundred square centimeters surface, bent in the form of open hollow-cylinders twenty-five millimeters in diameter, a condenser of ten micro-farads capacity was fully charged in less than one second. With these conditions the electrodes could be removed from the plating bath, rinsed in distilled water, immersed in the U-tube, and the electromotive force measured, all in about two seconds. In Fig. 1 the variations of the electromotive force with time are shown.

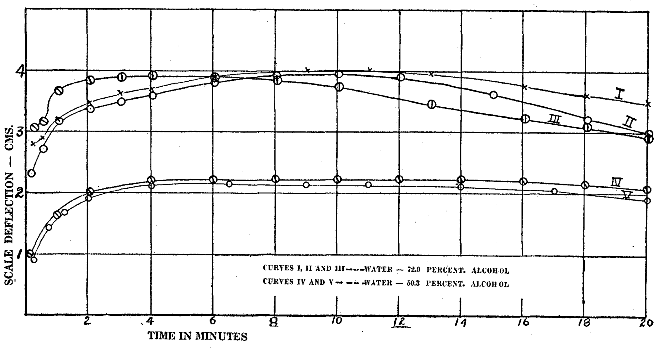

Fig. 1.

Curves *I*, *II* and *III*, representing the widest variations of six different determinations for a one-hundredth normal water solution of $CuCl_2$ in one arm of the U-tube and an equimolecular solution of a 72.9 per cent. alcohol mixture in the other, indicate a relatively rapid rise in the electromotive force followed at once by a gradual decrease, and are characteristic of the curves obtained when the higher percentage mixtures of alcohol were used. Curves *IV* and *V*, for conditions differing only from those above in that a 50.33 per cent. alcohol mixture was substituted for the 72.9 per cent. mixture, show a slower rate of decrease in the electromotive force and are characteristic of the curves obtained when the lower percentage mixtures of alcohol in water were used. It will be noticed that in both these sets of curves, but particularly for the set obtained with the 72.9 per cent. mixture, that although different determinations show different initial electromotive forces and different rates of both rise and fall of electromotive force, yet all rise to practically the same maximum. Other concentrations of $CuCl_2$ were tried and although the shape of the curves was much changed, yet the maximum remained practically constant. This maximum being the only point on the curves which could be consistently reproduced it was taken as a characteristic electromotive force. Of course it does not represent the electromotive force of a cell of identical electrodes, for the surfaces of both electrodes change after immersion in the liquids, and in about fifteen minutes show a change of color, probably due to the formation of cuprous chloride. It is probable that the maximum shown in each of these curves merely represents an electromotive force at a time when the surfaces of both electrodes are changing at the same rate. But whatever chemical change has taken place, if chemical affinity is an electrical attraction, this change should also be dependent upon the specific inductive capacity of the solution, and it would therefore seem possible that a comparison of these maxima for the different percentage mixtures might still show a relation between the difference in the specific inductive capacities of the two solutions and the electromotive force of the cell, differing only in magnitude from that to be expected if neither electrode underwent any change after immersion in its electrolyte.

In Fig. 3, Curve I, these maximal electromotive forces, obtained when a one-hundredth normal solution of $CuCl_2$ in different concentrations of alcohol in water were in one arm of the U-tube, and a one-hundredth normal solution of $CuCl_2$ in water in the other, are plotted against the difference in specific inductive capacities of the two solutions. The data from which this curve is plotted are given in Table I.

For comparison, in Fig. 2, curves are given showing the relation between specific inductive capacity and concentration. These are plotted from the data given in the literature cited above.

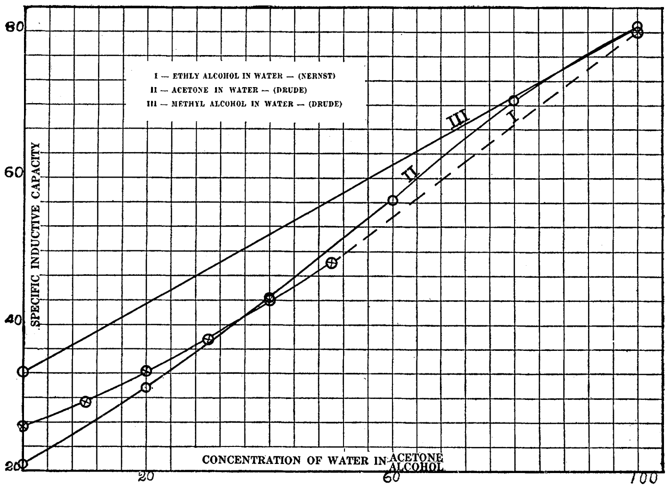

Fig. 2.

On account of the uncertainty as to the correct interpretation of the relation represented in Curve I, Fig. 3, due to the continual change on the surface of both electrodes and to the method used in determining a *characteristic* electromotive force, it was decided to begin the work on a new plan, eliminating, as far as possible, all causes for a changing electrode.

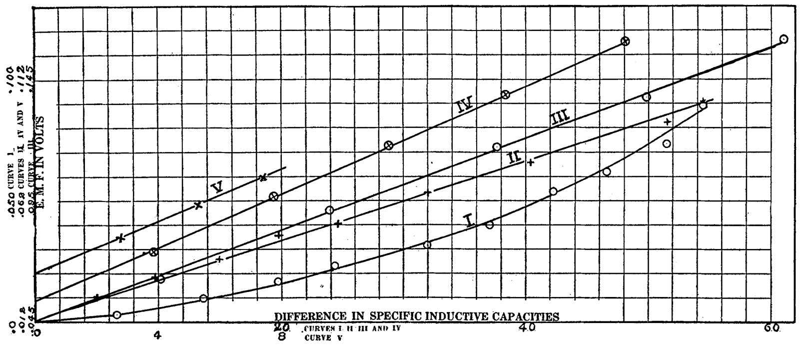

Fig. 3.

Curve I, Ethyl Alcohol-Water (solutions of $CuCl_2$)—Cu electrodes—Electrode in water solution electronegative.) Curve II, Ethyl Alcohol-Water, Hg_2Cl_2 electrodes; Electrode in water electropositive. Curve III, Acetone-Water, Hg_2Cl_2 electrodes, Electrode in water electropositive. Curve IV, Methyl Alcohol-Water, Hg_2Cl_2 electrodes, Electrode in water electropositive. Curve V, Urea Solution-Water, Platinum electrodes, Electrode in water electropositive.

After considerable experimentation the following method was adopted: The so-called calomel electrode was substituted for the copper and a quadrant electrometer replaced the condenser and ballistic galvanometer. The cells were made by sealing a platinum wire in the bottom of a glass U-tube of about 15 mm. diameter, and eight centimeters length. Enough mercury was then poured into two such tubes to cover the platinum wires. Distilled water, which had been standing over mercurous chloride in a glass flask for more than a week, was then shaken up with the mercurous chloride in the same flask, and one tube filled with it while the other tube was similarly filled with a known mixture of alcohol and water, also containing mercurous chloride. Sufficient mercurous chloride was used so that after settling on the mercury in the bottom of the tube a layer from three to five millimeters deep was formed. The liquids in the two tubes were then connected by means of a piece of purified asbestos rope, the asbestos being inside a small glass U-tube for convenience in handling, and the platinum wires leading to the electrodes were connected to the quadrants of the electrometer.

The deflection of the electrometer needle, charged to about 250 volts from two hundred dry cells, was measured on a scale two and one half meters distant. A scale deflection of one centimeter corresponded to a difference of potential on the quadrants of the electrometer of .0194 volt. As the telescope was such that the tenths of a millimeter could be estimated with a fair degree of accuracy, the error in reading the scale deflection should not, therefore, have caused an error in the electromotive force determination of as much as .0005 volt. The leads from the electrometer and the cells were enclosed within earthed screens, so that working conditions were quite satisfactory.

The calomel electrodes behaved somewhat similarly to the copper. The electromotive force began to rise immediately after the cell was made, but much more slowly than in the case of the copper electrodes in the $CuCl_2$ solutions, requiring from three fourths of an hour to six or eight hours to reach a maximum. This maximum, however, was not followed by a decline, but usually remained approximately constant as long as the cell was kept, several days in some cases.

The results of the work with calomel electrodes in the alcohol and water solutions are shown in Table II. and in Curve *II* of Fig. 3. No two of the trials represented in the table were taken on the same cell but fresh electrodes were prepared for each determination.

The same experiment was then repeated with other mixtures substituted for the ethyl alcohol-water mixtures, but in every other respect identically the same process was followed. The results obtained with acetone-water mixtures are shown in Table III. and in Curve *III*, Fig. 3. In Table IV. and in Curve *IV*, Fig. 3, are given the results obtained when methyl alcohol-water mixtures were used.

TABLE I.

No. of Determinations.	Percentage (by weight) of Alcohol in H_2O.	Sp. Ind. Cap. of Mixture (Nernst).	Diff. in Sp. Ind. Cap of Two Solutions.	E.M.F. in Volts (Copper Electrodes).	Average Deviation from Mean.
7	11.04	73.10	6.90	.005	.001
10	21.84	66.15	13.85	.009	.004
3	31.48	60.25	19.75	.017	.001
4	38.78	55.75	24.25	.023	.001
11	42.52	53.60	26.30	.025	.006
6	50.33	48.25	31.75	.031	.002
4	59.68	43.25	36.75	.039	.001
10	63.27	41.25	38.75	.045	.005
6	69.42	38.20	41.80	.053	.002
7	72.90	36.50	43.50	.055	.002
7	79.42	33.70	46.30	.063	.002
5	90.90	28.90	51.10	.074	.001
4	100.00	26.00	54.00	.088	.002

TABLE II.

No. of Trials.	Per Cent. (by Weight) of Alcohol in H_2O.	Sp. Ind. Cap. of Mixture (Nernst).	Diff. of Sp. Ind. Cap. of Water and Mixture.	E.M.F. in Volts (Calomel Electrodes).	Average Deviation from Mean.
4	8.00	75.00	5.00	.021	.002
10	15.44	70.30	9.70	.030	.003
5	24.00	65.00	15.00	.037	.002
16	31.61	60.25	19.75	.048	.006
9	40.00	55.00	25.00	.051	.003
9	50.16	48.37	31.63	.064	.003
7	65.67	40.00	40.00	.076	.002
11	90.9	28.88	51.10	.093	.004
14	100.00	26.00	54.00	.102	.004

TABLE III.

No. of Trials.	Per Cent. (by Weight) of Acetone in H_2O.	Sp. Ind. Cap. of Mixture (Drude).	Diff. in Sp. Ind. Cap. of H_2O and Mixture.	E.M.F. in Volts (Calomel Electrodes).	Average Deviation from Mean.
13	20	70.6	10.3	.064	.004
15	40	57.0	23.9	.091	.005
10	60	43.5	37.4	.117	.002
15	80	31.5	49.4	.136	.006
14	100	20.5	60.4	.159	.006

Mixtures of ethyl alcohol in ether, ethyl alcohol in chloroform, and acetone in ethyl alcohol were also tested as to the direction only of the electromotive force between calomel electrodes. In each case the electrode in the liquid of higher specific inductive capacity was electropositive with respect to the one in the liquid of lower specific inductive capacity.

Table IV.

No. of Trials.	Per Cent. (by Weight) of Methyl Alcohol in Water.	Sp. Ind. Cap. of Mixture (Drude).	Diff. in Sp. Ind. Cap. of Water and Mixture.	E.M.F. in Volts (Calomel Electrodes).	Average Deviation from Mean.
8	20.45	71.2	9.7	.040	.002
8	40.61	61.5	19.4	.063	.001
8	60.32	52.3	28.6	.084	.002
8	80.65	42.7	38.2	.104	.002
8	100.00	33.2	47.7	.125	.003

Table V.

No. of Trials.	Concentration of Urea in Water.	Sp. Ind. Cap. of Solution (Harrington).	Diff. in Sp. Ind. Cap of Solution and Water.	E.M.F. in Volts (Pt. Electrodes).	Average Deviation from Mean.
9	Normal	81.51	2.78	.046	.002
9	2 N	83.98	5.25	.060	.004
9	3 N	86.17	7.44	.071	.003

One other case was investigated because of its apparent anomalous behavior in regard to specific inductive capacity. As one might expect when a liquid or salt is dissolved in a liquid of higher specific inductive capacity, the specific inductive capacity of the resulting solution is generally somewhere between that of the two components. But several cases have been discovered where the specific inductive capacity of the solution is higher than that of either component. One such case, viz., that of urea in water, has recently been investigated by E. A. Harrington,[1] at different concentrations and the specific inductive capacity of the solution is shown to *increase* almost linearly with the concentration. The calomel electrode could not be used here because of chemical action with the solution. Both copper and platinum electrodes were tried, both giving deflections in the same direction, but although larger in the case of copper, the results obtained with platinum electrodes were the more consistent and these only are given in Table V. below. The relation between the difference in specific inductive capacities of the liquids in the two tubes and the E.M.F. of the cell is shown in Curve *V*, Fig. 3.

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[1] Phys. Rev., 7, 581, 1916.

Discussion of Results.

Because of the uncertainty as to the full meaning of Curve *I* no importance is attached to more than the *direction* of the E.M.F. On the Nernst theory the osmotic pressure of copper ions must be greater in the water solution than in the alcohol solution because of the greater dissociation in water. Since the solution pressure of copper is of such exceedingly small magnitude, 10^{-20} atmos., copper ions must be forced upon the electrodes against a pressure which is practically zero. It follows then that more ions will be deposited upon the electrode in the water solution than upon the one in the alcohol solution and consequently give an electromotive force reversed in sign from that actually found. On the simple theory mentioned in the first part of this paper, both copper electrodes lose ions when immersed in their respective electrolytes because of the weakening of the cohesion of the surface atoms due to the relatively high specific inductive capacity of the liquids. But more ions are lost in the water solution than in the alcohol solution because of the higher specific inductive capacity of the former and therefore the electrode in the water solution becomes electronegative with respect to the one in the alcohol solution.

Curves *II*, *III* and *IV* show the relation between the difference in specific inductive capacities of the liquids in the two parts of the cell and the E.M.F. of the cells with calomel electrodes for ethyl alcohol-water, acetone water and methyl alcohol-water mixtures, respectively. Attention may be called to two points indicated in each of these three curves. In the first place, the employment of the calomel electrode removed the disturbance due to a continually changing surface of the electrode and yielded results which seem to admit of but one interpretation, viz., that the electromotive force of the cells here used is strictly proportional to the difference in the specific inductive capacities of the two electrolytes in each case.

In the case of the methyl alcohol-water mixture, the specific inductive capacity varies linearly with the concentration but in each of the other two cases, as will be observed from Fig. 2, the deviation from a straight line relation is sufficient to allow us to conclude that difference in specific inductive capacities rather than difference in concentrations is the factor upon which the E.M.F. depends. That the curves should all lie on the same straight line is hardly to be expected because the ions leaving the electrode are attracted to some degree by the solution and the magnitude of this attraction depends not only upon the specific inductive capacity of the solution but also upon the nature of the attracting molecule. This latter factor would of course be different in each of the three different cases and may be the cause of the different slopes in the three curves.

No particular importance is to be attached to the intercepts of these curves on the potential axis. This merely means that some change has taken place in one or both electrodes but that this is the same for all concentrations and has the effect only of shifting the origin along the potential axis.

The second point of importance in connection with curves *II*, *III* and *IV* is the direction of the E.M.F. In the case of reversible electrodes of the second class, such as is the calomel electrode, the negative ion acts as the carrier; that is, the calomel electrode gives results of the same character as would be expected of a metallically conducting modification of chlorine. This being the case, the electromotive force should be opposite in sign, from any theory, to that obtained with electrodes of the first class. In the case at hand, if there is an appreciable difference in the chlorine ion concentration about the two electrodes it must be the greater about the one in water because of its higher dissociating power than that of the ethyl alcohol, acetone or methyl alcohol mixtures. If now the solution pressure were the same at both electrodes, the greater osmotic pressure of the ions in the water solution would make the electrode on that side electronegative instead of electropositive as it is found to be. The only way we should have then of explaining the experimental results would be to assume that not only is the solution pressure less in the ethyl alcohol, acetone and methyl alcohol mixtures but that it is *directly proportional to the specific inductive capacity of the liquid, in which the electrode is placed*, a very unnatural property to ascribe to an expansive force within the electrode. The experimental results are exactly as postulated, however, by the theory that the loss of ions from an electrode is proportional to the specific inductive capacity of the electrolyte.

In Curve *V*, the data for which were obtained with platinum electrodes in urea solutions, we have again a linear relation between the difference in the specific inductive capacities of the electrolytes and the electromotive force of the cell. In this case the solution pressure factor cancels out, since, according to the Nernst theory, the solution pressure of a metal is the same in an aqueous solution as in water. This would mean either that the ion concentration about the electrode in water would have to increase as higher concentrations of urea were used in the other tube or that the ion concentration about the electrode in the urea solution would have to *decrease with* the concentration of urea. On the other hand, if ions are lost more readily from the electrode which is immersed in the liquid of higher specific inductive capacity, then the relation represented in Curve *V*, as well as the direction of the E.M.F., is only what we should expect.

It should be added that the results of this investigation are in complete agreement with the work of Miss Finney[1] in which the theory here set forth was assumed along with the hypothesis that the more electropositive metals have the higher specific inductive capacity. In an investigation which is still in progress, Professor Sanford has recently established the validity of this latter hypothesis. This substantiates the interpretation which Miss Finney gave to her results, viz., that the higher the specific inductive capacity of a solution, the more electronegative is an electrode of any given metal placed in it.

SUMMARY.

1. The potential difference between electrodes of the same kind in a two-solution cell has been measured for a number of different percentage mixtures of two liquids for four different cases, and in each, after disturbing influences were removed, is shown to be strictly proportional to the difference in the specific inductive capacities of the two solutions.

2. In the two cases investigated with copper electrodes, one with platinum and six with calomel electrodes, the direction of the electromotive force of the cell is in accordance with the theory that the loss of ions from an electrode is dependent upon the specific inductive capacity of the electrolyte rather than upon the concentration of those ions in the electrolyte and a solution tension of the electrode.

It is a pleasure to acknowledge a debt to Professor Sanford, of the Department of Physics, for valuable suggestions and continued interest throughout the work, and to Professor Young, of the Department of Chemistry, for helpful suggestions and criticisms in the earlier part of this work.

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[1] PHYS. REV., *6*, 5, 1915.