The Electrical Contact Potential and the Individual Activity of Single Ions

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The difficulties met with in determinations of the site and the value of the electrical contact potential between different phases are described. They have as yet made it impossible to determine these contact potentials.

The relationship between these contact potentials and the activities and the partition coefficients of single ions is mentioned. As it has been impossible to determine contact potentials, it has also been impossible to determine the activities and the partition coefficients for single ions. This impossibility creates difficulties for an exact definition of Sørensen's pH-values and of Brønsted's concept of acidity, and these difficulties are discussed.

It is shown that by transfers of particles with electric charges from one phase to another not only the total work of transfer, but also the *electrical* part of it must depend on the nature of the particle considered. The electrical contact potential between two different phases therefore is not a single valued function of the nature of the two phases, but it also depends on the nature of the electric particle (ion or electron) to be transferred.

This fact explains the elusive character of the concept of a definite electrical contact potential between two different phases.

Since the discovery of the electrical contact potentials between different substances it has been difficult to ascribe definite values to these potentials. Volta constructed the first galvanic cell, consisting of plates of two different metals, separated by a moist plate. He assumed in the beginning that the electricity was created at the surfaces, where the metals were in contact with the moist plate, but experiments with a condenser made him think that the production of electricity took place mainly at the surface between the two metals ¹.

The condenser experiment of Volta as modified by William Thomson (Lord Kelvin) ² uses a condenser with plates of the two metals whose contact potential is to be measured. One of the plates is connected to a sensitive electrometer, and in the connection between the two plates is introduced a variable electromotive force. The value of that electromotive force which makes

possible the separation of the two condenser plates (after removal of the connection between them) without change in the electrometer is considered as the measure of the contact potential.

Millikan³ later used a thermionic valve for determining the contact potential. In the valve two pieces of different metals could alternately be used as the anode, and Millikan assumed that the contact potential between them is equal to the displacement of the current-voltage curve along the voltage axis, observed when the one anode was replaced by the other.

These two methods have been found to give similar values for the contact potential. The accuracy obtained is not great, but the potential values found are similar in size to the electromotive force of the corresponding galvanic cell. This seems to support the conclusion of Volta that the site of the electromotive force is at the surface between the two metals, but this is erroneous. The quantity determined by the two methods is not the desired contact potential. It is determined by the force field in the air (or vacuum) between the two plates, and thus it is not the potential between two points within the two connected pieces of metal, but the potential between two points just outside the surfaces of the metals. Consequently the potential is in reality equal to the sum of three contact potentials: one between the two metals and two others between the metals and the surrounding air (or vacuum).

The first idea of Volta, that the site of the electromotive force in his galvanic cell was at the surface, where the metals are in contact with the moist plate, later got many adherents. De la Rive, Lodge, W. Ostwald, and most of the physical chemists of Ostwald's and van't Hoff's school, were of this opinion. The source of the electrical energy, given off by the element, must be the chemical processes at these surfaces, and it was also soon found that the electromotive force of a galvanic cell depended on the nature of the solution between the two metal, and that impurities on the surfaces of the two metals and the nature of the gas between the metal plates in the condenser experiments strongly influenced the value obtained for the contact potential.

Much work was done on the determination of the contact potentials at these surfaces, especially by the study of capillary phenomena at the surface of a mercury electrode. This method is based on the hypothesis that the surface tension should have its maximum value, when the contact potential is zero, because then there would not be an electrical double layer at the surface. But after much work had been done, it was found that this hypothesis did not lead to reliable results.

Attempts to determine the contact potential using the Peltier effect (the heat effect at the surface of contact of two metals, when an electric current is passed across it) also failed.

A theoretical calculation of the contact potential between two aqueous solutions of electrolytes was given by Nernst in 1888. The work of Nernst seemed to make it possible, for the first time, to calculate the value of a contact potential between two different phases. Nernst once told me about the enthusiasm of the old v. Helmholtz, when he told him about this result. For nearly a hundred years research on the contact potentials had been going on and now, at last Helmholtz saw the possibility of gaining an understanding of these mysterious and important phenomena.

Later developments, however, have shown that Nernst's solution of the problem is exact only in the limit, when the two aqueous solutions are very dilute, *i. e.* when in reality we have to do with a potential difference between points in the same phase.

In the nineteen-twenties a new interest in the contact potential, especially that between electrolytic solutions, arose. From several sides it was pointed out that the determination of activity or partition coefficients of *individual* ions was connected with the determination of contact potentials between electrolytic solutions (Bjerrum ⁴, Taylor ⁵, Guggenheim ⁶, Brønsted ⁷, Schottky ⁸). An especially clear and exact description of the problem is found in Guggenheim's papers.

If we cannot determine the electrical potential difference between two electrolytic solutions in connection with each other, we cannot determine the activities of the individual ion species, and conversely, if we do not know the ratio of the activities in the two solutions of at least one individual ion species, we cannot determine the contact potential between them. It is possible, however, to determine the product of the activities of a group of ionic species with a total electric charge of zero (*e.g.* of $K^+ + Cl^-$ or of $K^+ - Na^+$) as the transfer of such a group of ions from one phase to another will result in no net transfer of electricity at all.

As both Guggenheim and Brønsted have pointed out, however, all equilibria and isothermal changes towards equilibria of the individual ions are describable in terms of a new thermodynamic function which they call the electrochemical potential of an ion. This function can be considered as the sum of the chemical potential of the ion, and the electrical potential at the position of the ion. But when an ionic species is present in two different media, this resolution of its electrochemical potential into a chemical term and an electrical term is quite arbitrary and without physical significance, unless the contact potential between the two media is known.

The reason for the failure of the classical definition of the electrical potential difference, when we have to do with points in different media, is that, as we now know, the electricity has an atomistic structure. We cannot determine nor speak of the work necessary for transferring an infinitely small amount of electricity from one medium to another, since we can only transfer the electricity in the form of electrons or ions.

As early as 1899 Gibbs ⁹ wrote in a letter: "Again, the consideration of the electrical potential in the electrolyte, and especially the consideration of the difference of potential in electrolyte and electrode, involves the consideration of quantities of which we have no apparent means of physical measurement, while the difference of potential in pieces of metal of the same kind attached to the electrodes is exactly one of the things which we can and do measure".

And in 1929 Guggenheim wrote: "It has previously been realized that only these" (*i.e.* the electrochemical potentials of individual ions) "and not the u_i " (*i.e.* the chemical potentials of the individual ions) "have any *thermodynamic* importance, but we maintain that only they have any *physical* significance, for only they are definable in terms of physical realities".

This result has consequences for many concepts used by chemists, *e.g.* Sørensen's pH-value and Brønsted's definition of acidity.

The pH-value of Sørensen was defined by him as the negative logarithm of the molar concentration of the hydrogen ion, but on account of later views on electrolytes it was necessary to change from the concentration of the hydrogen ions to the activity of these ions, defined in such a way that in aqueous solutions at the limit of infinite dilution the activity was equal to the molar concentration.

According to our present view on the impossibility of determining the activity of individual ions the pH-values defined in this way cannot be determined by electrometric measurements. The pA_H -values determined by Bjerrum and Unmack in a paper in 1929⁴ by use of a 3.5 molar KCl solution to diminish the contact potential between two electrolytic solutions and calculating the remaining potential by means of Henderson's formula are, as indicated by the authors, not exactly equal to the negative logarithms of the hydrogen ion activities. Their pA_H -values must also depend to a certain degree on the activities of the other ions present, since the transfer of hydrogen ions from one solution to another must be accompanied by the transfer of other ions (in this case, especially K^+ and Cl^-) whose charge can compensate the charge transferred on the hydrogen ions. In spite of this, by using their pA_H values in calculations of thermodynamically definable quantities, one always arrives at the right values, and the pA_H values will generally lead to individual ions activity coefficients which, at increasing dilution, converge to a well defined limit.

Brønsted wished to extend his conception of the acidity of acids to non-aqueous solutions. In order to obtain in non-aqueous solutions a numerical measure of this acidity, as defined by the activity of the hydrogen ions, it was necessary to have a definition of the electrical potential difference between solutions in which the solvents were different. As a conventional definition he made the proposal that the electrical potential in an isolated, homogeneous phase be considered as zero when the phase is electrically neutral, *i.e.* when it contains equal amounts of positive and negative electricity. Guggenheim⁶ admits that Brønsted's definition leads to an electrical potential between different phases which is a potential in the mathematical sense. But he finds that it does not lead to a potential in the strict dynamic sense, *i.e.* it does not measure the work done in any real process.

Brønsted writes⁷ (p. 310—311): "Unsere Betrachtungen haben uns somit dazu geführt, dass auch für Ionen thermodynamische Funktionen definiert werden können, die durch die chemische Beschaffenheit der Lösungen, die die Ionen enthalten, und unabhängig von elektrischen Ladungspotentialen gegeben sind. Es sind derartige Funktionen, die zur Darstellung der chemischen Eigenschaften von Ionenlösungen geeignet sind, und von welchen wir z. B. für unsere Aciditätsdefinition hier Gebrauch machen wollen".

Brønsted further writes that his ion functions defined above cannot be determined by the common electrometric methods, but finally concludes: "Dass die Ionenfunktionen für ungleiche Medien durch die direkten thermodynamischen Methoden nicht messbar sind, besagt, dass sie auch thermodynamisch nur von untergeordneter Bedeutung sein können. Man darf daraus

jedoch nicht schliessen, dass sie überhaupt bedeutungslos sind. Speziell für den Begriff der Acidität, wie er oben definiert worden ist, müssen wir z. B. annehmen, dass er eine grosse kinetische Bedeutung besitzt, wenn es auch mit Schwierigkeiten verbunden wäre, den Aciditätseinfluss von der allgemeinen Wirkung des Mediums zu trennen". This idea of Brönsted that the acidity, determined according to his instructions, has a great kinetic significance does not seem to have been shown by him to be probable much less to have been proved, and it does not agree with the statement of Guggenheim according to which the chemical potentials of individual ions do not have any physical significance.

Brönsted has not given a laboratory method by the use of which we can determine the acidity by means of his definitions. So far I can see, Brönsted's proposal leads to an electrical potential difference between two phases which is determined by the electric field outside the two phases and thus to an electrical potential difference between them, equal to the work done by transferring an unit of electricity from a point just outside the surface of one phase to a point just outside the surface of the other phase. This is the electrical potential difference between two points outside the two phases, and not between two points inside the two phases.

Brönsted's definition can perhaps be used in the following way for the experimental determination of the difference in acidity of two phases. In each of the two phases is placed a hydrogen electrode and in the connection between the two hydrogen electrodes is introduced a variable electromotive force. The two phases are also used as plates in a condenser and these parts of the phases are each in direct connection with the part of the same phase, containing a hydrogen electrode. Finally one of the phases is connected with a sensitive electrometer. The value of the variable electromotive force, by which the condenser plates can be separated without change in the electrometer, will then be a measure of the sought for acidity difference. A practical difficulty arises when the two phases are both liquids. If the two plates in the condenser are placed horizontally the bottom plate can of course be a liquid, but the top plate can not. In that case it will therefore be necessary to use two condensers with the two liquid phases as bottom plates and as top plates two plates of same metal. The sought for acidity difference will then be measured by the value of the variable electromotive force by which it is possible to separate the plates in both condensers without change in the sensitive electrometer connected with the condensers.

Such a determination will certainly be very difficult to perform and will scarcely lead to an experimentally well defined value of the acidity difference, and as the result will be only the determination of a conventionally defined acidity difference of no great interest, I think that it will not pay to try it.

The concept of an electrical contact potential between two different phases is as elusive in character as the concept of absolute velocity in space. Not only is this potential difficult to determine experimentally, and apparently without physical interest, but also, from an atomistic point of view, it is not a single-valued potential which can be used in calculations of the electric work of transfer of all the different species of electrically charged particles from one phase to another. This can be seen in the following way. If we knew

exactly the positions of all the electrons and nuclei in two insulated and homogeneous pieces of two different phases in contact with each other, we could calculate in principle by means of Coulomb's law, the electric force in all points in and around the two pieces (except in the interior of the electrons and the nuclei), and we could therefore also calculate the classical electrical potential at all these points. But in order to obtain a phenomenological value for the electrical potential difference between the two different phases we would further have to determine the mean value in time and space of the electrical potential in the interior of the two phases. The space, however, over which we have to take the mean value is not given in a definite way. *E.g.*, how near should we go to the electrons and to the nuclei? It depends on the particle considered. And what weight should we assign to the potentials at the different points inside the two phases in the determination of the mean value? It is not sufficient to assume that an amount of electricity transferred to a phase is infinitely divisible and spread over the available space according to Boltzmann's distribution law. If we wish to use the mean value in calculations of the work of transfer of an electron or of a particular ion the mean value must be determined corresponding to the properties of this particular electrically charged particle. We thus arrive at the conclusion that a general and single-valued mean for the electrical contact potential which can be used in calculations of the electrical work of transfer of all species of particles with electric charge, does not exist.

There is also the other difficulty that according to the rules of quantum mechanics (Heisenberg's uncertainty relations) we cannot know exactly the positions and the velocities of the particles at a definite time. This uncertainty, however, does not seem to preclude the existence of a well defined and single-valued electric contact potential.

If we wish to use the concept of a definite electrical contact potential, we have to introduce a conventional definition for it, and when using such a conventionally defined potential we must always remember that it is not a physical reality, but only a mathematical device. It can be used in intermediate calculations, but must not appear in final expressions.

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