[CONTRIBUTION FROM THE RICE INSTITUTE]

A DETERMINATION OF ABSOLUTE SINGLE ELECTRODE POTENTIALS

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Introduction

It has become important in the study of electrochemical reactions to have more accurate knowledge about the "absolute single electrode potentials." An example of the necessity of this information is furnished in a recent investigation of the so-called "photovoltaic cells" in which light shifts the potential of an electrode. Unless the true potential of the electrode relative to the electrolyte is known, neither the direction nor the relative extent of the effect of light can be found.

Several methods for determining the potential difference which exists at some solid-liquid interfaces have been attempted but due to the conflicting experimental results and to uncertainty in their theoretical basis, Nernst[2] has recommended that the normal hydrogen electrode be used as a standard and that its potential be arbitrarily set equal to zero. This recommendation has been adopted in most cases for a number of years and has proved satisfactory for ordinary electrochemistry since the absolute scale of potential has not the theoretical significance of the absolute scale of temperature. Furthermore, thermodynamical calculations have continually been applied to complete cells, although they have been shown to be applicable to single electrode potentials, and the relative potential of the electrolyte in such treatment is not important since the e.m.f., the heats of reaction and the temperature coefficient of the cell as a whole are employed.

The larger text-books of electrochemistry contain a discussion of the attempts to measure some single electrode potential. The principles involved and the probable sources of error have been too widely discussed for it to be necessary to repeat them at length. It is sufficient here to recall the methods.

The first determination was made with the capillary electrometer by Lippmann and was followed by the experiments of Ostwald and of Paschen[3] with the mercury dropping electrode. The results of the experiments with mercury were found to agree fairly well and as a result the potential of the normal calomel electrode was first assigned a value of +0.56 volts.

Billitzer[4] criticized the theory of the above determination by showing

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[1] National Research Fellow in Chemistry.

[2] Nernst, *Z. Elektrochem.*, **12**, 192, 281 (1906); **7**, 253 (1900); *Z. physik. Chem.*, **35**, 291 (1900); **36**, 91 (1901).

[3] Paschen, *Z. physik. Chem.*, **1**, 583 (1887).

[4] Billitzer, *ibid.*, **48**, 513 (1904); **51**, 166 (1905).

that the solution pressure of mercury is itself a function of surface tension. He reported experiments[5] in which he observed the iso-electric points of colloidal suspensions of metals and also the changes in concentration of solutions of metal salts when fine powders of the corresponding metal were dropped through the solution. The value which he assigned to the normal calomel electrode was —0.18 volt. This method of obtaining a zero electrode appears sound in theory, if we assume than an electrode of the same metal as the fine suspension has the same potential as the smaller particle when immersed in the solution. It remains only to compare the potential of the latter with that of some constant standard electrode.

Freundlich and Mäkelt have repeated[6] some of Billitzer's experiments and confirm them. They found, however, that the potential of the colloidal metals depends on the presence of other ions than the metal ions and they concluded that the potential of the very small particles is not determined by the normal electrode potential of the metal. Furthermore, Freundlich has made a distinction in his "Kapillarchemie" between phase potential-differences and normal electrode equilibrium. Bancroft[7] has expressed the difficulty as follows.

"Billitzer has attempted to determine absolute potential differences by finding solutions in which a given colloidal metal did not move under electrical stress. While the method is good in principle, one cannot reason from the absorption of a finely divided metal to the adsorption of a massive metal."

A method has been devised which eliminates any doubt about the potential of the suspended system when its iso-electric point is being observed.

Experimental Method

It is assumed (1) that the mechanical force on a substance suspended in an electrolyte through which an electric force acts is due to a charge on the suspended system; (2) that the direction of the force is determined by the sign of the charge; and (3) that there is no charge or potential difference relative to the electrolyte when, in an electric field, there is no mechanical force relative to the electrolyte.

Based upon the above assumptions, a determination of the absolute electrode potential of a constant electrode was made as follows. A light metal needle was suspended by a conducting fiber in an electrolyte containing such a concentration of the metal ion that there was no electrical double layer at their interface. This iso-electric condition was indicated by the absence of any mechanical forces when an electric field was applied through the electrolyte. The potential of the needle was at the same time

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[5] Billitzer, *Z. Elektrochem.*, **8**, 638 (1902). Drude's *Ann. Phys.*, **11**, 902 (1903).

[6] Freundlich and Mäkelt, *Z. Elektrochem.*, **15**, 161 (1909).

[7] Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., **1921**, p. 206.

compared with the potential of the standard half-cell. Disregarding the liquid interface or eliminating it by calculation the resultant e.m.f. was taken to be the absolute potential of the constant electrode.

The apparatus employed is represented in Fig 1.

A glass vessel A of about 8 cm. diameter and 5 cm. depth had its interior divided into 4 equal spaces or quadrants by 2 intersecting glass partitions B. Their height was 2.5 cm. so that when the vessel was filled with liquid, only the bottom half of the liquid was divided into quadrants. A thin needle C, of the metal whose iso-electric point was to be found, had a shape similar to that of the needle of a quadrant electrometer. It was suspended with its long axis directly over one of the glass partitions, approximately 2 mm. above it and well below the surface of the electrolyte. A light mirror was attached to the needle stem D above the surface of the electrolyte. A spotlight and scale completed the arrangement for observing the motion of the suspended system. The suspension was a long strip of phosphor bronze with its connections soldered so that metallic contact was maintained with the suspended electrode. A round plate of the same metal as the needle, covered the bottom of the vessel and was also divided into 4 insulated parts by the glass partitions. These metal quadrants E were alternately connected and could be raised to any desired potential by a storage battery and suitable resistance. When this was done metal dissolved from one pair of quadrants and deposited on the other pair, the current passing through the electrolyte over the glass partitions. Thus every part of the needle was situated in an electric field such that there would be a resultant horizontal torque on it if it had a charge relative to the solution. Let the straight arrows represent the direction of the applied current; when the suspended system had a positive charge with respect to the solution there was a torque and resultant motion in the direction of the curved arrows. When the sign of the charge was reversed the direction of motion was reversed. 0.1 *M* calomel electrode was used to complete the cell. Electrolytic contact with this constant half-cell was made through the glass tube F dipping into the electrolyte directly over one of the partitions and symmetrically situated with respect to the needle. The e.m.f. between the mercury of the constant half-cell and the suspended electrode was measured with a standard potentiometer and low resistance galvanometer. Arrangements for raising and lowering the suspension, shifting the point F, leveling the apparatus, etc., are not included in the drawing. The apparatus illustrated was mounted on a firm base and inclosed in a bell jar case to prevent local disturbances.

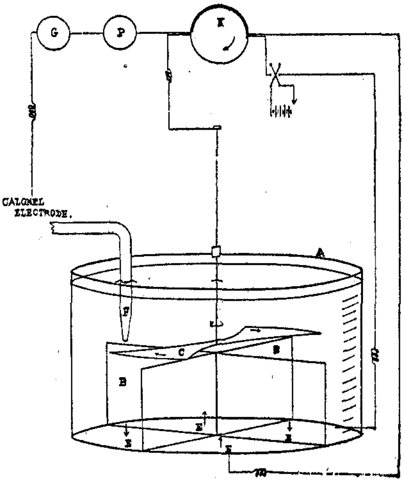

Fig. 1.

"Average Polarization"

The influence of a varying ion concentration on electrode potentials is small compared with the differences in the solution pressures of the metals. It is to be expected, therefore, that very few metals will be found whose solution pressures are such that their ionic concentrations in solution may be adjusted to the iso-electric point. All metals situated above these in the electromotive series must always be negative to electrolytes since there is an upper limit to the concentration which can be attained in solution, and all those below in the electromotive series must be positive to electrolytes containing even a trace of the corresponding metal ion. Thus, zinc was found negative to electrolytes containing the highest zinc ion concentration; also copper was found to be negative in a solution normal with respect to copper ion. Silver, however, which is more electronegative, was found to be positive in electrolytes containing even a small amount of silver ion.

When determining the direction of motion of a metal suspended in an electrolyte several disturbing factors had to be avoided. Obviously disturbances of the liquid must be entirely eliminated. Such are caused by the evolution of gas at the electrodes, diffusion due to large changes in concentration about the electrodes, etc. Another factor must be dealt with in order to find the potential of the needle at the iso-electric point, that is, the change in that potential under the influence of the applied electric force. When a current flows through the needle, its potential relative to the electrolyte changes. The metal$\leftarrow\rightarrow$metal-ion equilibrium is practically non-polarizable, or reversible, for low current densities. Thus some metal must dissolve from one side of the needle and deposit on the opposite side when the potential gradient in solution and the thickness of the needle are appreciable. The needle thus acts as both a cathode and an anode. These two processes are not completely nor equally reversible for appreciable current densities. This has been learned from the fact that the needle shifts its potential to a new value when current is passed, and the new value depends on the strength of the current but is independent of the direction of the current.

In order that the needle may change its potential, the metal must either dissolve at a higher rate than it deposits, thus losing a positive charge, or at a lower rate thus gaining a positive charge. This increase in the rate of one process over the other is due to the difference in polarization of the two processes. It must be remembered that this does not introduce a difference in the number of positive and negative ions in the body of the liquid; it requires only that a trace of metal dissolve in excess of that deposited to make the needle much more negative than before and the trace of metal thus dissolved does not enter the body of the liquid as excess positive ions but must remain as excess positive ions in the double layer at the surface due to the increased electrostatic attraction.

This change in potential of the needle may be termed the "average polarization" since it is the mean between tha of the cathodic and anodic processes. It has not been found possible to apply sufficient electric force through the electrolyte to move the needle without causing some average polarization. Average polarization increases with decreasing metal-ion concentration while on the other hand, with high ion concentration, conductivity is high and a greater current density is necessary to produce the proper potential gradient.

Average polarization decreases with decreasing size or thickness of the needle. During some of the experiments the needle was constructed of a fine wire of diameter approximately 0.5 mm. With this arrangement the needle could be moved without the polarization exceeding 0.05 volt. We may thus conclude that the average polarization was not appreciable in the experiments of Billitzer where the particles and wires were much smaller.

In order to observe the iso-electric point of the needle it was necessary to know accurately the amount of the average polarization. This was, therefore, measured by the method usually employed in determining polarization.

A motor-driven commutator was placed in the quadrant and potentiometer circuits. This is represented by K in Fig. 1. During one half-turn of the commutator the current passed the quadrants while on the other half-turn the potentiometer P was allowed to balance the e.m.f. of the chain, needle–electrolyte–calomel-electrode, so that no current was indicated by the galvanometer G. This arrangement, together with the fact that the point of contact of the two electrolytes F was symmetrically situated with respect to the equilibrium position of the needle, eliminated the effect of concentration polarization in solution on the observed e.m.f. of the chain. Concentration polarization in solution is the difference in potential between parts of the solution due to the difference in concentration of the solvent, which in turn is caused by the unequal mobilities of the ions. However, even when current was passing the quadrants, the point F was at the potential of the solution at the center of the needle.

With the above arrangement the potential of the needle relative to the calomel electrode, and its direction of motion and, therefore, its charge relative to the electrolyte could be observed simultaneously. At the point where the needle reverses its direction of motion the e.m.f. of the chain must give the absolute potential of the standard electrode.

Experimental Results

The combined results of a large number of observations will be found in Table I. The first values were obtained with a needle and 4 quadrants constructed of silver and the last 3 values, as indicated, were obtained with copper. The electrolyte in the case of silver was a silver nitrate solution of various strengths and in the case of copper, copper sulfate was used. It was not found practicable to use lower concentrations of silver nitrate or higher concentrations of copper sulfate.

In the first and third columns are the potentials of the needle relative to the 0.1 *N* calomel electrode. The silver nitrate solution was joined to the electrolyte of the standard electrode through a saturated solution of ammonium nitrate, thus reducing the e.m.f. from this source to a value which may be neglected. The copper solution was joined directly to the potassium chloride solution. The second and fourth columns give the sign of the charge of the needle relative to the electrolyte as indicated by its

TABLE I

NEEDLE POTENTIALS RELATIVE TO THE CALOMEL ELECTRODE AND THE ELECTROLYTE

SILVER NEEDLE

$E_n \longleftrightarrow$ 0.1 *N* calomel Volts	Charge relative to electrolyte		$E_n \longleftrightarrow$ 0.1 *N* calomel Volts	Charge relative to electrolyte
+0.44	+		+0.20	+
+0.42	+	Below	+0.20	?
+0.40	+	Above	+0.10	?
+0.38	+		+0.07	−
+0.30	+		+0.05	−
+0.27	+		±0.00	−
+0.24	+		COPPER NEEDLE	
+0.22	+		−0.03	−
....	..		−0.05	−
....	..		−0.10	−

direction of motion in the electric field. This motion reversed when the current was reversed and the deflections were approximately proportional to the potential gradient.

Discussion

Between the values of E_n = +0.20 volt and +0.10 volt the needle did not move at all or its motions were so irregular that they appeared to be due to disturbances in the solution. Above these values of E_n the needle was distinctly positive and below them distinctly negative to the electrolyte. This indicates that the absolute potential of the 0.1 *N* calomel electrode lies between —0.020 volt and —0.10 volt. The value found by Billitzer was —0.13 volt. Since he observed the iso-electric point of very light particles his determination of that point is undoubtedly more accurate. This new method of determination removes the doubt about the true potential of the suspended system at its iso-electric point.

Contrary to the view taken by Freundlich and Mäkelt, the colloidal particles appear to be in electrochemical equilibrium in the solutions used by Billitzer. Other ions whose effect on the potential of the colloid was attributed to absorption evidently do not disturb electrochemical equilibrium. On the other hand, adsorption in such a case may be explained by stating the conditions of the electrochemical equilibrium. This requires that every kind of ion in the solution must be in equilibrium with any electrode immersed in the solution, as otherwise some chemical reaction would proceed and one ion would displace another until equilibrium is established. For example, a silver electrode in silver nitrate solution is not only in equilibrium with silver ions but may be regarded as both an oxygen electrode and a hydrogen electrode in equilibrium with both oxygen ions and hydrogen ions. Likewise, any ion which is capable of an equilibrium must set up that equilibrium. Sodium ion must deposit sodium on silver until equilibrium is established, even though it requires only a minute amount of sodium to balance the solution pressure of massive silver. The sodium of course will not exert the solution pressure of massive sodium but will have a concentration determined by the well-known logarithmic relation. If the silver electrode is very finely divided, with high specific surface, and the oxygen, hydrogen or other substances do not penetrate the silver uniformly, then the amount of substance present per gram of silver will also be increased. However, there is no reason to suppose that the potential of the substance depends on specific surface so long as the concentrations remain the same. The colloidal suspensions and massive electrodes of the same metal used by Billitzer appear to have had the same potential within the limits of the above determination.

These experiments have no direct bearing on the discussion of phase potential-difference by Freundlich except as they indicate that the colloidal solutions used by Billitzer were in electrochemical equilibrium with their solutions. As the needle used in these experiments is unquestionably a reversible electrode, the determination of absolute potential in this manner cannot be complicated by a distinction between phase potential-difference and e.m.f. of the interface unless the former can be imagined as a different kind of potential difference which can influence the motions of the electrode without influencing the equilibrium of the reversible ion.

Summary

An example of the need of a knowledge of the absolute electrode potentials has been found in a recent investigation of the exchange of radiant, chemical and electrical energy at the electrodes of "photovoltaic cells."

The principal methods for determining the absolute electrode potential-difference of some constant half-cell have been recalled.

An apparatus has been described for a determination based on the method which appears most sound in theory. It was designed to eliminate the doubt about the potential of the suspended system while observing its iso-electric point.

It was found that the potential of a needle suspended in an electrolyte and subjected to an electric force depends on the strength of the force. The dependence was attributed to the difference in the polarization of the cathodic and anodic processes at the needle. The polarization decreased with decreasing size of the needle.

Employing a silver needle at its iso-electric point as a zero electrode the absolute electrode potential of the 0.1 N calomel electrode was found to be between —0.20 volt and —0.10 volt at 25°. This is a confirmation of the results of Billitzer who gave the value, —0.13 volt. This determi-

nation, however, eliminates the objections which have been advanced to the use of Billitzer's value of the absolute potential.

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THE SOLUBILITY OF TRINITROTOLUENE IN ORGANIC SOLVENTS[1]

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Introduction

Believing that there exists a serious lack in the fundamental data which should be available for all substances, and that such information will find practical application in the industries, serve for the development of methods of separating mixtures of such substances, or find other more purely scientific uses, the writers have undertaken the determination of some of the solubility constants now unknown. Accordingly, a study has been made of the solubility of α or 2:4:6 trinitrotoluene (TNT) in a number of the more common organic solvents.

Materials

Trinitrotoluene.—The trinitrotoluene used in the following determinations was a fine, crystalline product which had but a slight yellow color. Its setting point was 80.6°, as compared with 80.65° by Guia and Molinari,[4] and 80.35°±0.3° by Bell and Herty.[5] It was obtained by recrystallizing Grade I commercial trinitrotoluene from hot benzene after filtering off any insoluble matter present, evaporating with air the mechanically held benzene, crystallizing from boiling 95% alcohol, again dissolving in boiling 95% alcohol, and precipitating it from solution by pouring it into about 2 volumes of cold distilled water. The mixture was allowed to stand in a dark place for several hours in order to cool it thoroughly and effect complete crystallization. The crystals were then separated by filtration, washed several times with cold distilled water, and finally washed once with cold 95% alcohol to facilitate drying. They were allowed to dry in the air on filter paper away from strong light, and the faintly yellow, fluffy product was then transferred to desiccators over sulfuric acid, and allowed to stand in a dark place for several weeks before using. It was found that under these conditions, even when kept for 9 months or more, no further yellowing of the substance took place.

Solvents. **Purification.**—Commercial C.P. solvents were further purified, the method employed depending upon the solvent.

Water was redistilled and boiled immediately before use.

Ether was purified by being allowed to stand in contact with an excess of metallic sodium for longer than a week with frequent agitation. When there was no further evolution of gas, the pure ether was distilled.

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[4] Guia and Molinari, *Ber.*, **47**, 1718 (1914).

[5] Bell and Herty, *J. Ind. Eng. Chem.*, **11**, 1124 (1919).