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Electrochemical Constants

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Foreword

A knowledge of standards of electromotive force, resistance, and current are of importance in all fields of electrochemistry. A knowledge of other electrochemical constants, including equivalent conductances, transference numbers, ionization constants, activity coefficients, electrode potentials, and the parameters of electrode kinetics, polarography and electrophoresis, is of importance in studies of electrochemical equilibria and mechanisms.

Research in electrochemistry was one of the first functions of the National Bureau of Standards. Maintenance of standards of electromotive force and determinations of standards of resistance and current were authorized as legal functions of the National Bureau of Standards by an Act of Congress in 1901. At that time, the values of the ampere and faraday were determined with silver coulometers. The standard of electromotive force, the unit of which is the volt, is maintained by a group of standard cells in the Bureau's Electrochemistry Section. This standard is compared periodically with the international standard maintained at the Bureau International des Poids et Mesures, Sèvres, France.

The papers in this volume present some of the latest results, both experimental and theoretical, in the field of fundamental electrochemistry from many leading establishments in the United States and abroad. They were initially presented at the Symposium on Electrochemical Constants, the seventh of a series of twelve symposia held by the National Bureau of Standards during its Semicentennial in 1951. The cooperation of the Office of Naval Research in making possible the symposia series is gratefully acknowledged. The Symposium on Electrochemical Constants was planned and conducted by the Bureau's Electrochemistry Section, Electricity Division—in particular by Dr. Walter J. Hamer, chairman of the symposium, who arranged the program and prepared this volume.

A. V. Astin, *Director,*
National Bureau of Standards.

Contents

1. Problem of Inclusions in the Silver of the Silver Coulometer

By Arthur F. Scott [1]

Introduction

The question of the purity of coulometer silver was a very active field of research during the first 15 years of this century and then, for various reasons, it ceased to attract attention. The suspicion that the silver deposit is not pure arose originally from some early studies of the silver coulometer; it was strengthened considerably by the fact that the value of the faraday determined by the iodine coulometer is about 18 parts per 10^5 greater than the value found with the silver coulometer. This difference is more than can reasonably be attributed to obvious experimental errors. The determination of amount and nature of foreign material in silver crystals deposited in the coulometer was first seriously considered by Lord Rayleigh and Mrs. Sidgwick [1] [2] in 1884, and in the following thirty years it engaged the attention of investigators in many countries.

It is the purpose of this review to describe briefly the efforts which have been made to estimate the amount of inclusions in deposits laid down in the silver coulometer and to attempt to evaluate the experimental results.

Experimental Methods for Estimating Amounts of Included Material in Silver Deposits

Attempts to estimate the amount of inclusions in coulometer silver have been by three different methods: A, determination of the loss in weight of the deposit upon heating; B, direct analysis of volatile material expelled from the deposit; and C, direct analysis of the deposited silver for its silver content.

Estimate of Inclusions by Loss in Weight Upon Heating

This method first employed by Rayleigh and Sidgwick [1] involves drying the silver deposit at around 160° C and measuring its loss in weight when heated to red heat (500° to 600° C). Usually, heating has been performed with the deposit still in the platinum cathode dish. It is assumed that heating to red heat will cause expulsion of all volatile material. Doubtless because of its simplicity, this method has been a favorite one, and seven determinations are on record in the literature.

A postscript to the results of these determinations was presented by Vinal and Bovard [2] in 1916. When the deposit in a platinum

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[1] Chemistry Department, Reed College, Portland, Oreg.

[2] Figures in brackets indicate literature references on page 9.

dish is heated to red heat, there is inevitably some alloying of the Ag and Pt. Removal of the deposit either by HNO_3 or electrolysis leaves a slight stain (brown-to-black) on the Pt wherever the alloying occurred. They showed that this stain has remarkable powers of retaining volatile impurities, which are not removed during drying at less than 200° C but are driven off at red heat. They suggested that these unusual properties of the stain are due, in all probability, to formation of platinum black. Their experiments make it clear that if silver were deposited on platinum dishes bearing stains from previous deposits and the dish with its silver were heated to red heat, the loss in weight would be partly due to loss of inclusions in the deposit and partly to impurities retained by the stain. This finding throws doubt on practically all measurements of inclusions by the loss-on-heating method, which preceded Vinal and Bovard's study; for, although the stain could be removed by heating to redness, only one of the seven previous investigators had mentioned specifically that he had heated his cathode dish to redness prior to each experiment in which that dish served as a cathode.

Direct Determination of Volatile Inclusions

Since attempts to study inclusions by heating the deposits yielded contradictory results, the puzzling situation called for an actual determination of the nature of the inclusions by identifying and measuring the substance expelled from the deposit at 500° to 600° C. Such experiments were carried out in 1905 by Duschak and Hulett [3]. Silver crystals were detached from the cathode dish and were transferred to a tube provided with a manometer and a small side tube, after which the tube was evacuated and sealed. The crystals were then heated and the pressure measured before and after the water vapor present had been condensed in the side tube. As Hulett subsequently pointed out, this method gives uncertain results because of the possibility that heating the tube caused expulsion of gases from the glass. In 1912, Laird and Hulett [4] sought to avoid the difficulties of high-temperature heating by dissolving the silver crystals in molten tin at 400° to 500° C. Working again in an evacuated system and measuring the gaseous materials by fractional condensation, they measured N_2, H_2O, and traces of CO_2 and some oxidizable gas. The N_2 was assumed to result from nitrate ion because molten tin reduces nitrate ion quantitatively. They had difficulty in accounting for the traces of CO_2 and oxidizable gas. It was shown later, however, by Bovard and Hulett [5] that the oxidizable gas was most likely H_2 produced by reduction of water by the molten tin. By the method of fractional condensation, they identified and measured N_2, H_2O, and small amounts of CO_2. To express their results as percent of included material in the deposit, they assumed that the total weight of foreign material equaled the measured weight of H_2O and CO_2 plus the weight of $AgNO_3$ corresponding to the measured amount of N_2.

Direct Analysis of Deposited Silver for Its Silver Content

In this method the silver deposit in a cathode dish is first completely dissolved with HNO_3 and then precipitated as bromide or chloride. The silver halide is filtered, fused, and weighed. From its weight and the known atomic weights of silver and halogen, the weight of silver in the sample can be calculated. Obviously, experience with techniques of atomic weight determinations is a prerequisite for analyses of this kind, and it is not surprising that this method was used only by T. W. Richards and his co-workers. Indeed, Richards' interest in this problem was aroused initially by the difference between the atomic weight of copper as determined electrolytically and chemically.

Two analyses of deposits were made in Richards' laboratory. In the first experiments, Richards, Collins, and Heimrod [6] analyzed the silver deposited in a Rayleigh filter-paper coulometer. Since it has been established [7] that a reducing substance from the filter paper increased the contamination of the deposit, the results are of little significance. In later experiments, Richards and Anderegg [8] analyzed the silver deposited in a porous cup coulometer; the analyses can be accepted without reservation. As a control, they analyzed three samples of pure fused silver by the same technique. In these controls the percentage differences between weights of silver taken and found were +0.002, +0.000, −0.002.

Richards and Anderegg, using the above technique, also analyzed two samples of silver which had been heated to dull red heat in the platinum dish for the purpose of determining inclusions by the heating method.

Results of Experimental Attempts to Determine Inclusions in Coulometer Silver

The results of various experimental attempts to measure inclusions in coulometer silver are presented in figure 1.1. On the left are the results obtained with the standard coulometer; on the right the results of analyses for inclusions in silver obtained in special types of coulometers and under special conditions.

Consider first the estimates of inclusions in silver deposited in a standard coulometer. These estimates, which range from 0.004 to 0.016 percent, are the most reliable values obtained by the three different methods, and appear to be free from any basic fault. Every acceptable experiment on record has resulted in finding some included material. We must conclude, therefore, that the inclusion of foreign material in silver of the standard coulometer is inherent in the deposition process.

Figure 1.1 shows strikingly that the estimates of included material cover a fairly wide range which must reflect either differences in what the three methods measure or variations in the different silver deposits tested.

There is no a priori reason to suppose that the three methods differ seriously in what they measure. Richards' direct method should yield, without ambiguity, the percent of nonsilver material in the deposit. The heating method, provided the dishes are free of platinum black stain, is probably the next most satisfactory. Although it is hard to imagine any included material which would not be volatilized by heating to 600° C, experiments show (right, fig. 1.1) that all material is not expelled and that a correction (0.001 to 0.002 percent) must be applied to compensate for this constant error. The molten-tin method would appear to be subject to two minor reservations: it is incapable of detecting included material present in the form of silver oxide; and the interpretation of the experimental results involves assumptions as to the form of inclusions.

This analysis of the three methods points to the conclusion that if inclusions in deposits are simply constituents of the electrolyte (H_2O-$AgNO_3$), the methods are practically equivalent and that variations in results must be due to differences in samples of silver tested. One experiment in support of this conclusion may be noted here. Bovard and Hulett, employing the molten-tin technique, analyzed silver deposited on platinum dishes, silver dishes, and a silver spiral cathode, using the identical method and technique throughout. The deposits on the platinum and silver cathodes showed, on the average, 0.0075 percent inclusions (left, fig. 1.1), whereas the silver on the spiral cathode averaged 0.022 percent inclusions (right, fig. 1.1). The great difference between the results with the dish and spiral cathodes must reside in the silver and not the method. Concerning the high estimate in the case of the spiral cathode, Bovard and Hulett wrote: "The explanation of this abnormality is not yet forthcoming."

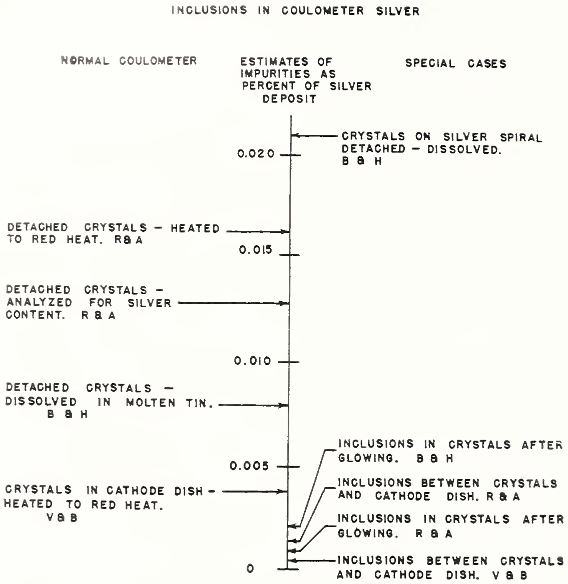

Figure 1.1.

Summary of results of significant measurements of inclusions in coulometer silver.

References B & H [5]; R & A [8]; V & B [2].

If we proceed on the basis that the wide variation in the estimates of inclusions is due to differences in the samples of silver examined, we must accept the corollary thereto: viz, the variability in the purity of silver deposits examined means there is little prospect at this time of finding a universally applicable correction for inclusions in silver deposits.

Since the accepted procedure for measurements with the silver coulometer requires the use of $AgNO_3$ prepared according to the Bureau of Standard's specifications [9], it is of interest to note the magnitude of inclusions in silver deposited from this particular electrolyte. There are two series which can be identified as involving the electrolyte in question. One comprises nine of Vinal and Bovard's measurements by the heating method; the other the entire set of Bovard and Hulett's measurements, by the molten tin method, using silver dishes. The latter gave 0.0077 percent, which represented the total of H_2O, CO_2, and $AgNO_3$ (measured as N_2) as their best value. To convert Vinal and Bovard's results to the same basis the following adjustment seems justified:

Average loss on heating to red heat	0. 0045%
Allowance for Ag from $AgNO_3$ assumed to be same as found by Bovard and Hulett	. 0006%
Allowance for included material not expelled on heating	. 0010%
Total	0. 0061%

This estimated total is about that found by Bovard and Hulett. The mean value from the two different determinations can be stated as 0.007 percent. However, the significance of the agreement between the two different experimental methods and the resulting combined estimate (0.007%) must be limited, in that in the two sets of experiments many other factors besides the preparation of the $AgNO_3$ were very nearly the same. To avoid any misunderstanding, it should be emphasized that the $AgNO_3$ used in the other experiments was probably as pure as that prepared according to the Bureau's specifications. The only conceivable difference between the different samples of $AgNO_3$ would be in the trace of residual acidity, and this would show up in the degree of hydrolysis of the silver ion. The possible importance of this factor will be examined in the following section.

This review of attempts to measure inclusions in deposits of the silver coulometer indicates the following: (1) The inclusion of foreign material in silver deposits is inherent in the deposition process. (2) Measurements of the volatile material expelled from silver deposits indicate that the included material is H_2O, $AgNO_3$, and a trace of CO_2. (3) Estimates of the included material, assuming it to be H_2O and $AgNO_3$, range from 0.006 to 0.016 percent. (4) The three different methods used to estimate inclusions can be accepted as basically equivalent. (5) Variations in the amount of included material must therefore be attributed to variations in the samples of silver tested.

As a final comment, we may note that inclusions in the deposit account for part of the discrepancy (0.018%) between the values of the faraday as found by the silver and iodine coulometers. It is impossible, however, on the basis of the existing experimental data, to conclude what fraction of this discrepancy can reasonably be attributed to inclusions in the deposit of the silver coulometer.

Discussion of Certain Factors Influencing the Inclusion Phenomenon

Most investigators of the inclusion problem have been interested primarily in determining the magnitude of the inclusions rather than the factors influencing them. The only investigators who attempted a systematic study of certain possible factors in the inclusion phenomenon were the Bureau of Standards group [7]. It is beyond the scope of this article to review all evidence pertaining to the various factors which might play a part in the inclusion phenomenon. It is of interest, however, to review some of the evidence and suggestions regarding the factors inherent in the electrolyte alone.

A relation between the form of deposits and condition of electrolyte has been generally accepted. Three distinct forms of silver deposits have been described: (a) well-defined crystals with clean platinum showing between the crystals; (b) a striated deposit; and (c) a fine-grained, compact deposit. The conditions under which these different forms are produced can be summarized as follows: The well-defined crystalline form is deposited from weakly acid solutions of pure $AgNO_3$; the striated form is obtained when either strong reducing agents or hydroxide ion (even in small amounts) are present in the electrolyte; and the fine-grained is obtained by adding acetate ion to the electrolyte or by carrying out the electrolysis in an atmosphere of CO_2. There is evidence also of a correlation between the amount of inclusion and the form of deposit, the amount being least with well-defined crystals and greatest with fine-grained compact crystals. For fine-grained deposit obtained by electrolysis in an atmosphere of CO_2, the included material was of the order of 0.3 percent, about 40 times the amount found in the well-defined crystalline deposit.

It appears, therefore, that both hydrogen-ion concentration and the anion of the electrolyte have some influence on the form of deposit and on the amount of inclusions. The suggested anion effect might arise directly through an adsorption [3] mechanism or indirectly through changes in the hydrolysis of the silver ion. No basis exists for a decision between these two possibilities.

We shall next consider the effects of hydrogen ion concentration on the form and purity of silver deposits. Rosa, Vinal, and McDaniel [7] established that addition of HNO_3 to the electrolyte caused: (1) The number of silver crystals to increase and their size to decrease correspondingly, and (2) the weight of silver to decrease in a uniform manner as the amount of acid added is increased. This decrease can be appreciable, amounting to as much as 0.030 percent for an 0.002 N acid solution, neglecting the effect of hydrolysis of the silver ion. This action of increased hydrogen concentration to reduce the weight of deposit is most curious. There appears to be three possible explanations: (1) Increasing acid concentration reduces the amount of included foreign material, (2) some hydrogen is liberated on the platinum cathode before the deposition of silver gets underway, or (3) hydrogen is liberated concurrently with the deposition of silver. As the evidence now stands, the first two of these explanations face serious objections. The objection [4] to the first is that the percentage decrease in weight which the deposit suffers when the electrolyte is even weakly acid, is greater than the percentage of inclusions in deposits from the normal neutral electrolyte. The second alternative is contradicted by rather direct experimental evidence. Rosa, Vinal, and McDaniel measured, by titration with standard thiocyanate, the first milligram or so of silver deposited from several acid solutions and concluded that the initial deposit corresponded to the current which had passed through the cell.

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[3] In studying the electrolytic growth of a single crystal of silver, Erdey-Gruz [10] found that anions exerted a controlling influence on the rate of growth of different crystal faces irrespective of concentration or current density. The influence of anions was ascribed by Erdey-Gruz to their adsorption on the crystal faces.

[4] Another possible objection may be noted. Bovard and Hulett found, in the only direct measurement of inclusions in a deposit from acid electrolyte, that the amount is greater rather than less than that present in deposits from normal electrolyte. Incidentally, in establishing the relation between increased acidity of electrolyte and reduced weight of deposit, Rosa, Vinal, and McDaniel assumed inclusions to be negligible. No experimental test of the purity of the deposits was made.

With regard to the third possible explanation there is no direct evidence. There is, however, another experiment by Rosa, Vinal, and McDaniel that might relate to this explanation. In their experiment a platinum electrode was first hydrogenated by having the electrode serve as a cathode during the electrolysis of a H_2SO_4 solution. When the hydrogenated electrode was used as the cathode in the electrolysis of a normal $AgNO_3$ solution, it was observed that (1) a larger number of small crystals was deposited; and (2) the amount of silver deposited at the start of the electrolysis was slightly greater than corresponded to the current passed through the cell. The first of these effects is identical to the effect of adding acid to the electrolyte of the standard silver coulometer. On the other hand, the apparent deposition of excess silver, although "not readily explainable," indicates that hydrogen is adsorbed by the platinum cathode and that this hydrogen reduces silver ion. With these experiments of Rosa, Vinal, and McDaniel in mind, it is difficult to avoid the supposition that in electrolysis of an acidified $AgNO_3$ solution the hydrogen ion concentration at the cathode builds up to the point where some hydrogen ion is reduced and adsorbed, with part of it then acting to reduce silver ion and a part escaping as molecular hydrogen. A simple hypothesis [5] of this kind could account for all the known effects of increased acidity of the $AgNO_3$ electrolyte.

Although silver hydroxide is involved in the hydrolysis of silver ion, no attempt has been made to determine the part it might play in the inclusion phenomenon. When it was found that the addition of a minute amount of hydroxide ion to $AgNO_3$ electrolyte resulted in a striated deposit, it was suggested that this effect was due to the presence of colloidal silver hydroxide. Although possibly sound, this suggestion derived in part from the belief that striated deposits were caused only by the movement (as a result of convection current) of colloidal material over the cathodic surface. The role of silver hydroxide in the inclusion phenomenon might be more complex than has generally been supposed. Although silver hydroxide is regarded as a weak, hydrated base, it is conceivable that it is not such a simple compound. To account for their results on the solubility of silver hydroxide in hydroxide solutions, Johnston, Cuta, and Garrett [13] suggested that the hydroxide exists as the polymer $Ag_2(OH)_2$, which could ionize in two stages:

$$Ag_2(OH)_2 \leftrightarrows Ag_2(OH)^+ + OH^- \qquad (1)$$

$$Ag_2(OH)^+ \leftrightarrows 2Ag^+ + OH^- \qquad (2)$$

They concluded that if such a polymer did exist the first ionization would proceed practically to completion and the second ionization, only to a slight extent except at lower pH. The presence of the hypothetical ion $Ag_2(OH)^+$, even in minute amounts in $AgNO_3$ solution, might have interesting consequences. The discharge of this ion might result in the entrapment of silver oxide in the deposit which would be expected to decompose, upon drying, to metallic silver.

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[5] In passing, it may be noted that a current theory [11] to account for the stress (and secondarily the type of crystal structure) in electrodeposits postulates the formation of monatomic hydrogen at the cathode as a prime factor. No attempt has ever been made to study the crystal structure or stress condition of coulometer silver. It is pertinent, however, that Glockler and Kaupp [12] found the structure of silver deposited from 0.1 N $AgNO_3$ solutions to vary markedly with a small change in current density, from 10 to 22 ma/cm². One also is reminded that silver deposits of different investigators have not all behaved in the same way on heating to red heat. Richards and Anderegg reported that "the heating was usually accompanied by a crackling sound," whereas Vinal and Bovard reported no such "crackling sound."

Such behavior would result in the deposition of surplus silver from neutral $AgNO_3$ solutions and hence account for the decrease in weight of the deposit with increasing hydrogen ion concentration.

Although the foregoing discussion is brief, it points to the need for an extensive study of the effects of different factors originating from the electrolyte used in the silver coulometer. A study of the hydrolysis reaction and its equilibrium would appear to be especially desirable. It would be important to study the hydrolysis reaction in the bulk electrolyte, and the shift in the equilibrium that takes place at the cathode surface.

Notes on Two Attempts to Estimate Inclusions by Means of Radioactive Tracers

In concluding this report we shall describe briefly two attempts[6] to test for inclusions in coulometer silver by means of radioactive labeled materials.

In the first [14], S^{35}-labeled $SO_4^=$ was added to the $AgNO_3$ electrolyte of a small coulometer, and the S^{35} in the silver deposit was estimated from its radioactivity. In one series the labeled $SO_4^=$ was added to the electrolyte without carrier, and the concentration of the sulfate was estimated to be 5×10^{-5} mg/ml. In another series, the same amount of labeled sulfate ion was added to the electrolyte, together with 5×10^{-2} mg/ml of inactive sulfate ion as carrier. In the latter experiments the electrolyte was nearly saturated with Ag_2SO_4. In all experiments the deposit, after thorough washing, was dissolved in HNO_3 and the sulfate present was precipitated as benzidine sulfate. To get a suitable sample of precipitate, enough inactive sulfate ion was added to each solution before precipitation to give 7 mg of precipitate. The activities of samples were measured under an end-window G–M tube with the usual precautions. For reference purposes, standard measured portions of the electrolyte were precipitated and treated in exactly the same way as the dissolved silver deposit. The results of these experiments are (1) radioactive sulfate is concentrated by some process in the silver deposit; and (2) the amount of radioactive sulfur so concentrated is apparently not affected by inactive carrier present. Some idea of the extent of the concentration of labeled sulfur is shown by the following calculation. If we assume $AgNO_3$ electrolyte to be trapped in the deposit along with the sulfate and that the ratio of $AgNO_3$ to sulfate in the deposit is the same as in the bulk electrolyte, then the activity of the deposit can be translated to weight of $AgNO_3$ and thence to percentage of $AgNO_3$ in the deposit. On this basis, we find the hypothetical $AgNO_3$ in the deposit to be 5.2 percent of the deposit in the case of the carrier-free experiments and 4.1 percent in the experiments with carrier sulfate present. These absurdly high values rule out the possibility that the radioactive sulfate is retained simply by entrapment of the electrolyte. The fact that the results are substantially the same for electrolytes with and without carrier practically eliminates the possibility that the retention of sulfate ion is a radio-colloid effect. To account for the results one would have to assume that all sulfate in the electrolyte is trapped in the silver or postulate a mechanism whereby the amount of sulfate retained by a given weight of deposit varied directly with the con-

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[6] The writer gratefully acknowledges a grant from Research Corporation which made these experiments possible.

centration of sulfate ion. No speculations regarding possible processes will be offered at this time.

Two further series of experiments with S^{35}-labeled sulfate ion were made. In one, silver was first deposited on a platinum cathode from normal $AgNO_3$, and the cathode so prepared was then used for the deposition of silver from electrolytes containing labeled sulfate ion. Experiments with and without carriers were conducted, and their results agreed with those in which silver was deposited on a platinum-cathode surface. The retention of labeled sulfate ion is therefore, apparently not related to any effect arising from the platinum surface. In other experiments, copper was deposited from $Cu(NO_3)_2$ electrolyte containing labeled sulfate ion, and the deposit had no appreciable activity, showing that no labeled sulfate was included. These experiments suggest that the retention of sulfate by the silver deposit is derived from some property of Ag_2SO_4, most probably its low solubility. Perhaps we have here an example of a phenomenon described by Lowry [15], viz, the precipitation at the cathode, due to the deposition of silver ion, of a substance soluble in concentrated $AgNO_3$ solution but only slightly soluble in water.

In the second experiment [16], carbon-14–labeled methanol was added to the $AgNO_3$ electrolyte. The cathode, a small Pt disk, was removed from the cell from time to time during the electrolysis and its activity measured in a gas-flow counter. The activity increased gradually with time and then leveled off as would be expected if the labeled methanol was uniformly included in growing crystals and no new crystals were formed. Assuming the ratio of methanol to water in the deposit to be the same as in the electrolyte, our calculations showed that the weight of solvent in the silver deposit was of the order of 0.004 percent. This is only an order of magnitude calculation and is based on a single measurement. It is interesting, however, that this is the same order of magnitude as the weight of inclusions in coulometer silver as determined by classical methods. This experiment suggests that labeled methanol might prove to be useful in further studies of inclusions.

References

[1] Lord Rayleigh and Mrs. Sidgwick, Proc. Roy. Soc. **36,** 448; 37, 142 (1884).
[2] G. W. Vinal and W. M. Bovard, Bul. BS **13,** 147 (1916) S271.
[3] L. H. Duschak and G. A. Hulett, Trans. Am. Electrochem. Soc. **12,** 257 (1907).
[4] J. S. Laird and G. A. Hulett, Trans. Am. Electrochem. Soc. **22,** 345 (1912).
[5] W. M. Bovard and G. A. Hulett, J. Am. Chem. Soc. **39,** 1077 (1917).
[6] T. W. Richards, E. Collins, and J. W. Heimrod, Proc. Am. Acad. Sci. **35,** 123 (1899).
[7] E. B. Rosa, G. W. Vinal, and A. S. McDaniel, Four parts, Bul. BS **9,** 151 (1913) S 194; **9,** 209 (1913) S 195; **9,** 493 (1913) S 201; **10,** 475 (1915) S220.
[8] T. W. Richards and F. O. Anderegg, J. Am. Chem. Soc. **37,** 7 (1915).
[9] E. B. Rosa and G. W. Vinal, Bul. BS **13,** 479 (1916) S 285.
[10] T. Erdey-Gruz, Naturwissenschaften **21,** 799 (1933).
[11] M. R. J. Wyllie, J. Chem. Phys. **16,** 52 (1948); R. Glocker and E. Kaupp, Z. Physik. **24,** 121 (1924).
[12] R. Glocker and E. Kaupp, Z. Physik. **24,** 121 (1924).
[13] H. L. Johnston, F. Cuta, and A. B. Garrett, J. Am. Chem. Soc. **55,** 2311 (1933); **56,** 1250 (1934).
[14] T. R. Conway, Senior thesis (1948); K. Lynn Hall, Special project (1948).
[15] T. M. Lowry, Proc. Roy. Soc. **91,** 53 (1914).
[16] William R. Ware, Special student project (1951).

Discussion

Dr. G. W. Vinal, Princeton University, Princeton, N. J.: Dr. Scott mentioned the Pt black observed here. That was really quite important, but it was not recognized at first. With successive experiments, the effect got worse and worse. In fact, I think it caused one of the most discouraging days I ever put in. All at once we recognized the Pt black, and that explained everything. In those days there was a good deal of controversy with Professor Richards at Harvard and Professor Hulett at Princeton. I was sent to Princeton by the Bureau to work jointly with Professor Hulett, and we succeeded in explaining a number of things that had not been understood up to that time. The correspondence with Professor Richards continued. He eventually withdrew practically all of his remarks, but I think that the results that Professor Scott showed here of Richards' conclusions include the error of the Pt black. I am wondering if Professor Scott has seen a note that Richards published in 1915 in the Journal of the American Chemical Society? It is my recollection that in that he withdrew his previous remarks about inclusions in the deposits. We also have a letter from Professor Richards, in which he took back many of the things he said in those early days.

Dr. A. F. Scott: I am familiar with that note that Richards published, I think in 1915, in which he admitted that he had not realized the error contributed by the stain, and that probably all of his results were in error on that account. However, I did find the value I gave in one of his incidental experiments. He carried out five or six experiments by scraping the Ag deposit from the coulometer and then measuring the loss in weight when the crystals were heated in the crucible rather than in the cathode dish. I assumed that this experiment would be somewhat different from the other experiments in which the Ag was heated in the Pt.

Dr. Vinal: The effect of Pt black may be there without one's being able to see the black on Pt. It is only as the amount becomes greater and greater than you finally recognize it.

Dr. W. F. K. Wynne-Jones, University of Durham, Newcastle, England: Dr. Scott, I am not sure I understood correctly your reference to the possibility of the value obtained with the Ag culometer being in error owing to the existence of a complex silver ion.

Dr. Scott: Yes, that is what I was suggesting—that there was a possibility of this hypothetical ion being formed in the solution.

Dr. Wynne-Jones: It seems to me that the existence of a complex ion of the same valency cannot possibly affect the results. The charge is irrelevant. It does not matter what the charge on the ion is, provided the valency on the Ag remains the same, and I understood that was remaining the same; only the charge on the ion was altered. When that ion is discharged at the electrode, something has to happen to the associated hydroxyl. I get two Ag ions, and consequently, it cannot affect the results unless there is an inclusion in the electrode, which is rather a different problem.

Dr. Scott: That is true, but the possibility that I had in mind was that some of this might be deposited in the form of silver oxide.

Dr. W. Blum, National Bureau of Standards: We deal all too frequently, not with a thousandth of 1 percent of inclusions, but with as much as 1 percent of Cr_2O_3 that may be in the bright Cr on your automobile. We explain the presence of oxide by a change in pH in the cathode film, resulting in hydrolysis, which permits the inclusion of this basic material. This can take place with Ag deposition only if there is something less than 100-percent cathode efficiency; in other words, if hydrogen ions are discharged and produce silver oxide, you get a lower efficiency but a higher weight of deposit.

DR. J. O'M. BOCKRIS, Imperial College of Science and Technology, London, England: I would like to ask Dr. Scott to expand his remarks. What was the significance of this 0.004 percent of inclusion? Was this a weight percentage or what?

DR. SCOTT: That experiment was carried out in the hope that by detecting the radioactive methanol present in the deposit we would have some measure of the amount of solvent included in the deposit. The very approximate figure I gave was based on the assumption that the ratio between the methanol and $AgNO_3$ in the deposit was the same as in the electrolyte itself. The 0.004-percent value is a weight percent.

2. Determination of the Faraday Constant by the Electrolytic Oxidation of Oxalate Ions

By D. Norman Craig [1] and James I. Hoffman [1]

Introduction

Part of a program for the electrochemical redetermination of the faraday constant at the National Bureau of Standards is concerned with the possibility of determining this important constant in terms of the Bureau's certified sodium oxalate. Trial experiments showed that this might be done by depositing PbO_2 coulometrically on a Au anode in a PbO-$Pb(ClO_4)_2$ solution and by evaluating the PbO_2 in terms of sodium oxalate. The latter is accomplished by reacting the PbO_2 and sodium oxalate in a $HClO_4$ solution. Although this procedure for determining the faraday in terms of sodium oxalate is indirect, it has, nevertheless, attractive features. Further trial experiments showed that the faraday might be determined directly in terms of sodium oxalate by the electrolytic oxidation of oxalate ions at a Au anode in a supporting solution of H_2SO_4. Therefore, it seemed advisable to investigate the possibility of constructing a coulometer in which the direct oxidation of oxalate ions could be utilized to determine the faraday.

If such a coulometer is to operate accurately, it is necessary for the electrochemical oxidation of oxalate ions to proceed at practical rates and at potentials which preclude the oxidation of other components of the solution. These rates and potentials are discussed in the following section.

Electrolytic Oxidation of Oxalate Ions in Sulfuric Acid Solutions

The oxidation of oxalate ions was studied by making time-potential measurements for various anodes under conditions that were varied in respect to current density and concentration of oxalate ions. The measurements described in this section suffice to show the anode characteristics that are essential for the operation of the oxalate coulometer. The apparatus used in making the measurements is shown in figure 2.1. The Au anode, the anode vessel, and the volume, of supporting solution,[2] approximately 350 ml, were the same as used in the particular coulometer shown in figure 2.4.

Figure 2.2 shows the anode characteristics for the oxidation of oxalate ions at the 1.0-amp rate. It is seen that the potential is relatively constant until the sodium oxalate content of the solution drops to 1.78 g. As this decreases to 1.36 g the potential shows an accelerated

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[1] National Bureau of Standards, Washington, D. C.

[2] In this paper "supporting solution" always refers to an aqueous solution containing 30 percent of H_2SO_4 by weight.

rise, and then it rises abruptly to a value only slightly lower than the steady state value for a supporting solution containing no oxalate.

Figure 2.3 shows the anode characteristics for the 0.1-amp rate and for an initially low concentration of oxalate ions. After the accelerated rise in potential between 19 and 21 min, it is seen that the potential was constant at 1.90 v for a short time. Then there is another accelerated rise in potential and finally the potential rises abruptly and approaches, asymptotically, the steady state potential for a supporting solution containing no oxalate. The "flattening" of the

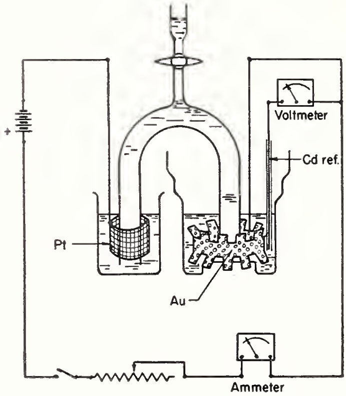

FIGURE 2.1. *Apparatus for time-potential measurements.*

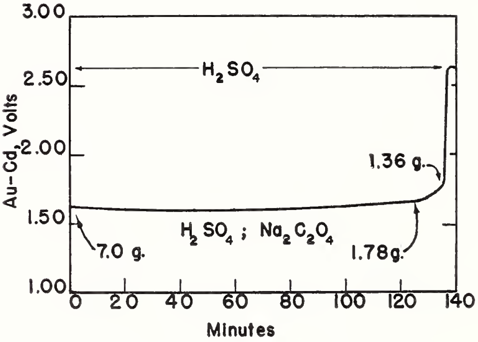

FIGURE 2.2. *Time-voltage curve 1.0 ampere.*

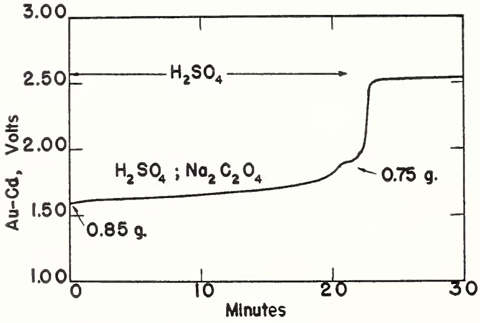

FIGURE 2.3. *Time-voltage curve 0.1 ampere.*

curve at 1.90 v is characteristic and is readily observed for low currents. It is to be noted also that there was only 0.75 g of residual oxalate in the solution when the potential rose abruptly at 0.1-amp rate, whereas there were 1.36 g in the solution when the potential rose abruptly at the 1.0-amp rate. The curves in figures 2.2 and 2.3 show that oxalate ions can be oxidized at practical rates at a Au anode in a supporting solution of H_2SO_4 and at potentials which are much lower than the steady state potential for a similar solution containing no oxalate.[3]

The Oxalate Coulometer

As a result of time-potential measurements two coulometers have been constructed and used. The first was a small coulometer that had a gold-plated–platinum-gauze anode. This coulometer was used to oxidize quantities of sodium oxalate ranging from 5 to 12 g. The second coulometer, shown in figure 2.4, was much larger and had an anode made from perforated sheet Au with an area of 300 cm^2. Larger quantities of sodium oxalate, 67 g, were oxidized in this coulometer. The initial current used in operating the small coulometer varied from 0.1 to 0.7 amp, whereas the initial current used in operating the large coulometer was always 1.0 amp.

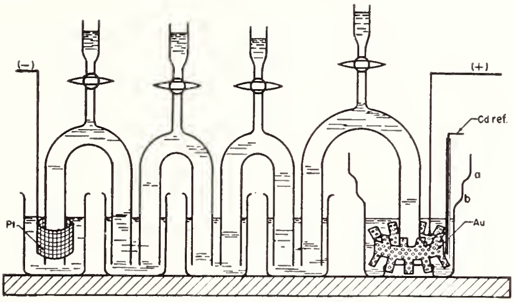

FIGURE 2.4. *Oxalate coulometer.*

Each coulometer consisted essentially of a Pyrex vessel provided with a Au anode as indicated above, a beaker provided with a conventional cylindrical Pt-gauze cathode, and a series of intervening beakers and syphons. The latter served to isolate the anode from the cathode.

After adding supporting solution to the anode vessel and to each of the beakers, the syphons were filled, and a weighed quantity of sodium oxalate was added to the anode vessel. A Cd reference electrode surrounded by a glass tube was then inserted in the solution between the Au electrode and the wall of the anode vessel. The solution in this vessel was then covered with split watch-glasses. These rested on the ledges *a* and *b* and prevented loss of oxalate by spray.

Throughout the electrolysis the potential of the Au anode was measured periodically. These measurements served as guides for stopping

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[3] Time-potential measurements at constant current were made with a Au and a Pt anode, each having the same dimensions. In supporting solutions containing no oxalate it was found that the steady-state potential of the Au anode was higher than that of the Pt anode. This, as expected, shows that the overvoltage of oxygen is greater on Au than on Pt. In supporting solutions containing small quantities of oxalate, it was found that the potential of the Au anode was 1.0 v lower than its steady state potential for a similar solution without oxalate, whereas the steady state potential of the Pt anode was scarcely affected by the addition of small quantities of oxalate to the supporting solution. It is planned to make a further study of the depolarizing effect of oxalate ions on various electrodes.

the electrolysis. In some experiments it was stopped when the potential started to show an accelerated rise corresponding to that shown between 125 and 135 min in figure 2.2. In others the electrolysis was stopped well in advance of any indication of this accelerated rise. Furthermore, in some experiments electrolysis was resumed at a lower current. These variations in the procedure gave rise to variations in the quantity of residual oxalate. However, no attempt was made in any experiment to oxidize all the oxalate by electrolysis. The residual oxalate was determined by titration with $KMnO_4$.

After the electrolysis was stopped the syphons were emptied individually, starting at the cathode. The solution in the beaker adjacent to the cathode beaker was then titrated with permanganate solution. In no experiment did the amount of permanganate required to titrate this solution differ by a measurable amount from that required to titrate an equal volume of supporting solution. This shows that there was no loss of oxalate by diffusion from the anode vessel to the cathode beaker. The solution in the next intervening beaker was titrated likewise, and in a few experiments it was found to contain traces of oxalate. The covers in the anode vessel were then placed in this solution and the titration continued. As the end point was approached the Cd electrode was rinsed by repeatedly plunging it into this solution. The solution in the beaker adjacent to the anode vessel was then titrated, and these two titrated solutions in their respective beakers were used to rinse the syphons. This was done by repeatedly filling and emptying each syphon. During this rinsing procedure the titration of each solution was continued, and the adequacy of the rinsing procedure was judged by the burette readings. A 10-ml burette with 0.05-ml graduations was used in all these titrations, and as the titrations were progressive, the initial and the final readings were of greatest importance. This difference corrected for appropriate blanks gave the volume of permanganate solution equivalent to the residual oxalate that had sprayed onto the cover glasses, adhered to the Cd electrode, and also that which had diffused out of the anode vessel into the intervening syphons and beakers. The remaining and greater quantity of the residual oxalate was confined to the anode vessel. In those experiments in which this quantity was small, all the solution in the anode vessel was titrated, whereas in those with larger quantities weighed aliquots of this solution were titrated, using weight burettes. The sodium oxalate titer of the permanganate solution was then determined, using stock supporting solution as the titrating medium. The residual sodium oxalate, including that in the intervening beakers, was then calculated and subtracted from the weight of sodium oxalate that was placed in the coulometer. This gave the weight of sodium oxalate equivalent to the measured coulombs.

Electric Circuit and Measurement of the Coulombs

Figure 2.5 shows the electric circuit and the arrangement of the apparatus. Throughout the electrolysis the current was so adjusted that the IR drop across the potential terminals of the standard resistor was balanced by the emf of the standard cell in the control circuit. In the experiments with the small coulometer the Bureau's electric equipment for measuring the emf of standard cells was used periodically throughout the electrolysis to measure the emf of the standard cell in the control circuit, whereas in the experiment with the large coulometer, the equipment was used periodically to measure not only the emf of the standard cell but also the IR drop across the standard resistor. The emf values, together with the certified values of the standard resistors, were used to calculate the current. During the first few minutes of each experiment it was necessary to adjust the variable resistors continuously because of a slight rise in the temperature of the solution in the syphons. Thereafter, however, even a current of 1 amp was maintained constant with relative ease.

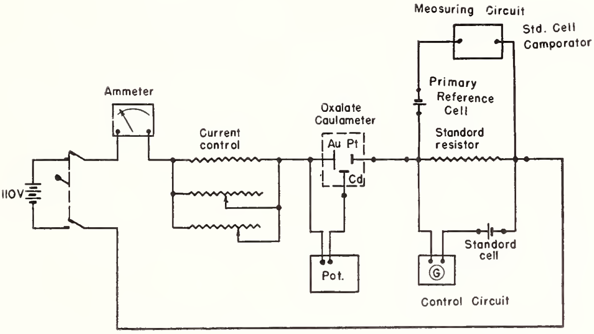

FIGURE 2.5. *Oxalate-coulometer circuit.*

Time measurements were made by means of second pulses supplied by the Bureau's standard crystal clock, which keeps mean-solar time. Since the sixtieth pulse is omitted, the beginning of each minute can be identified.

Accuracy of the Determinations

There are a number of factors that must be considered in estimating the accuracy of any determination of the faraday constant. In the discussion of the accuracy of the oxalate determinations the following factors are considered: Coulometric measurements, mass measurements, determination of residual oxalate, purity of the sodium oxalate, conformity of the anode process with the postulated reaction, effect of isotopes, and atomic weights.

The coulombs (emf/resistance)sec, were measured in terms of very accurate standards of emf, resistance, and time. It is believed that the uncertainty in measuring the coulombs did not exceed 2 parts in 100,000 in any experiment.

There is no difficulty in weighing sodium oxalate. The quantities used in the experiments varied over a wide range. Assuming that the reported density 2.347 is accurate, it is believed that the uncertainty in measuring the mass of the sodium oxalate added to the coulometer did not exceed 2 parts in 100,000 in any experiment.

The residual oxalate in the most unfavorable experiment was about 6 percent of the original amount. An uncertainty of 1 part in 2,000 in the determination of the residual oxalate in that experiment would have caused an uncertainty of only 3 parts in 100,000 in the calculated value of the faraday. In some experiments the residual oxalate was only 1 percent of the original amount.

The purity of at least one element or compound is involved in any electrochemical determination of the faraday. The Bureau's Sodium Oxalate Standard Sample 40E with a certified purity of 99.96_0 percent $Na_2C_2O_4$ was used in all the experiments. The analytical work of H. B. Knowles and W. S. Clabaugh shows that the impurities are anodically inert; therefore, the factor 0.9996_0 was used to calculate the anodically effective mass of each sample. It is seen that the value of this factor as given introduces an uncertainty of 5 parts in 100,000 in the calculated value of the faraday.

The conformity of the anode process in the oxalate coulometer with the reaction $C_2O_4^{--} \rightarrow 2CO_2 + 2\epsilon$ has been tested by varying the rate of electrolysis, and the calculated values of the faraday are independent of the rate if the electrolysis is stopped before the anode potential shows an accelerated rise. Furthermore, the CO_2 liberated by electrolysis has been analyzed for O_2 with a mass spectrometer, and the analyses confirm the above conclusion. Further experimental work bearing on this important question is now in progress.

Because carbon and oxygen are polyisotopic, it was deemed advisable to measure the abundances of the isotopes of carbon and oxygen in the sodium oxalate. In order to do this a sample of the sodium oxalate was dissolved in water and immediately precipitated by the addition of $AgNO_3$. The $Ag_2C_2O_4$ was quickly separated by vacuum filtration and dried in a vacuum oven. By slowly heating a portion of the dried $Ag_2C_2O_4$ in an evacuated reservoir attached to a mass spectrometer, the $Ag_2C_2O_4$ was decomposed into Ag and CO_2. Mass spectrometric measurements of the C^{12}/C^{13} ratio for this CO_2 agreed within 1 percent with the C^{12}/C^{13} ratio for CO_2 from commercial "dry ice"; it was also consistent with the ratio obtained for a wide variety of petroleum source hydrocarbons. The O^{16}/O^{18} ratio, measured with less precision, agreed with that for atmospheric oxygen.[4] It is concluded from these measurements that uncertainties in the abundances of the isotopes of carbon or oxygen in this particular sodium oxalate did not cause an uncertainty of 1 part in 100,000 in the experimental values of the faraday. There is the possibility that electrolytic fractionation of the isotopes of carbon and oxygen occurs during the operation of the coulometer. This, however, would not introduce an experimental error in the value of the faraday because the residual oxalate is determined by titration.

At the present time there are significant discrepancies between the values of the international chemical atomic weights for sodium and carbon and the respective values calculated from mass spectrometer measurements. This is shown by table 1, which includes the atomic weights of hydrogen and iodine for purposes of the discussion that follows the table.

Table 1.

Element	International chemical atomic weights [1]	Chemical atomic weights calculated from mass spectrometer measurements [2]
Hydrogen	1.0080	1.0080
Carbon	12.010	12.011
Oxygen	16.0000	16.000
Sodium	22.997	22.991
Iodine	126.92	126.911

[1] J. Am. Chem. Soc. 72, 1432 (1950).
[2] A. O. C. Nier (private communication).

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[4] The mass spectrometer measurements were made by F. L. Mohler and V. H. Dibeler of the Mass Spectrometer Section.

Using the values in this table, the equivalent weight of sodium oxalate is 67.007 on the basis of the international chemical values and 67.002 on the basis of the mass spectrometer values. Therefore, a value of the faraday in terms of sodium oxalate, based on the international values, would be 7 coulombs greater than a value based on the mass spectrometer values. This is also true for a value of the faraday in terms of iodine. However, if pure oxalic acid were available for use in the oxalate coulometer, an uncertainty of less than 2 coulombs in the value of the faraday would arise from the discrepancy in the atomic weights involved. Furthermore, the mass spectrometer values of the atomic weights involved for oxalic acid would give a higher value of the faraday. For these reasons it is planned to prepare and use oxalic acid in some of the future experiments.

This discussion shows that the errors in measuring the coulombs, mass, and residual oxalate are not only small but purely random, and that no significant uncertainty arises in the value of the faraday because of the existence of the isotopes of carbon and oxygen in the sodium oxalate that has been used. Furthermore, since experimental measurements show that the anode process at low potentials conforms with the postulated reaction, it is concluded that the uncertainties in the equivalent weight and purity of the sodium oxalate are the principal sources of uncertainty in the faraday constant as determined by the sodium oxalate coulometer.

Experimental Results

Seventeen determinations of the faraday constant in terms of the Bureau's certified sodium oxalate have been made; 12 were made with a small coulometer and 5 with a large coulometer. The value obtained in each determination, except the first, expressed as absolute coulombs per gram equivalent of $Na_2C_2O_4$ on the chemical scale, is shown in figure 2.6. The international chemical atomic weights of sodium, carbon, and oxygen, as given in table 1, were used to calculate the equivalent weight of sodium oxalate. It is of interest to compare the oxalate results with the results obtained by Bates and Vinal[5] with the iodine coulometer. Therefore, each of their iodine values and their weighted mean value has been multiplied by 0.999835 in

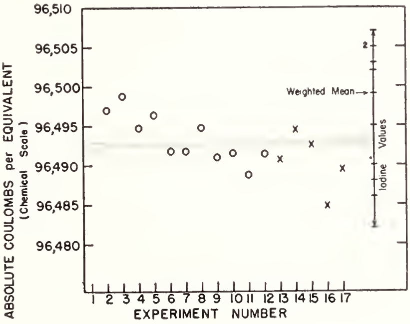

FIGURE 2.6. *Value of the faraday.*

○, 5 to 12 g of $Na_2C_2O_4$;

×, 67 g of $Na_2C_2O_4$.

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[5] S. J. Bates and G. W. Vinal, J. Am. Chem. Soc. **36**, 930 (1914).

order to express their values in absolute coulombs.[6] These converted iodine values are shown in figure 2.6. The mean of the oxalate values is 96,492 ± 3, and the weighted mean of the iodine values is 96,499 coulombs eq^{-1} (chemical scale). Using the factor 1.000273 to convert from the chemical to the physical scale of atomic weights, the respective values of the faraday constant are 9,651.8 and 9,652.5 emu eq^{-1} (physical scale).

Summary

In a study of the electrolytic oxidation of oxalate ions in a supporting solution of sulfuric acid it was found that the reaction $C_2O_4^{--} \rightarrow 2CO_2 + 2\epsilon$ can be carried out at practical rates with a gold anode and at potentials that appear to preclude the oxidation of other components of the solution. An oxalate coulometer was developed in which the above reaction was utilized to determine the faraday constant in terms of the Bureau's certified sodium oxalate. Sixteen experimental values of this important constant have been presented.

The authors are indebted not only to L. J. Clark and H. H. Ellis, who have faithfully assisted with the experimental work, but also to Dr. F. B. Silsbee, Dr. Edward Wichers, and Dr. W. J. Hamer for their helpful advice and unfailing interest.

Discussion

Dr. D. A. MacInnes, Rockefeller Institute for Medical Research, New York, N. Y.: I have a letter here from Dr. S. J. Bates, who, along with Dr. Washburn and Dr. Vinal, did the classical work on the iodine coulometer. The conclusion of the letter is that he is very much delighted that the recent values of the faraday tend to climb up bit by bit to the value as determined by that coulometer. I think it is a very fine instrument, and for that reason I have taken on the overambitious job of repeating some of that early work by Washburn, Bates, and Vinal. I am working hard on the constant-current apparatus and on the redesign of the cell. I think we can have the temerity to enter the field in our laboratory for two reasons. One is that we have had considerable experience from moving boundary methods, with constant-current apparatus. The second is the development of the differential electrometric titration, a method of extreme accuracy. Of course, if we titrate for the iodine that is released or absorbed at the electrode, we have to calibrate our solutions for that element and will have to know whether or not we are dealing with really pure iodine. However, the mass spectrometer is another development that would make it possible to know when you are dealing with mixtures. Thus the high state of purification that has previously been essential might be unnecessary with the new techniques.

It looks as if the physicists may be taking the whole problem away from the chemists and doing it better, but at the same time I think the chemists would like to have the faraday determined by as many methods as possible. For that reason I think the work that is being done by Drs. Craig and Hoffman should go on with all the enthusiasm that they are showing for it.

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[6] The atomic weight of iodine used by Bates and Vinal is the same as the international chemical value given in table 1; therefore, the conversion involves only the change from international to absolute coulombs (1 international coulomb = 0.999835 absolute coulomb).

3. The Faraday and the Omegatron

By H. Sommer [1] and J. A. Hipple [1]

The value of the faraday has been determined by a physical method, using an instrument developed at the National Bureau of Standards called the omegatron. This measurement is particularly significant because this new method is entirely different from the usual electrochemical determination.

In this physical method the value of the faraday is obtained from the defining equation

$$\mathbf{F}=N\epsilon, \tag{1}$$

where N is Avogadro's number, and ϵ is the electronic charge. If we take, for the moment, a hypothetical substance of unit atomic weight M_0, we can write $\mathbf{F}=\epsilon/M_0$, since $M_0=1/N$. It follows that

$$\mathbf{F}=(M/M_0)(\epsilon/M)=A(\epsilon/M), \tag{2}$$

where ϵ/M is the charge to mass ratio of a substance of mass M and isotopic weight A. Thus, in order to obtain $\mathbf{F}$, one must measure the specific charge of a substance whose isotopic weight is known with sufficient accuracy. Actually, the problem becomes one of measuring ϵ/M in absolute units, since the isotopic weights are known quite accurately from mass spectrographic and other data; indeed, the measurement could be made on O^{16}, where $A=16.000$ by definition.

In theory, at least, the absolute (rather than relative) measurement of ϵ/M could be made with any mass spectroscope, including the early instruments of Thomson and Aston. However, in these conventional types of instruments it is not possible to measure with sufficient accuracy the voltages, dimensions, and magnetic-field intensities.

The omegatron makes use of the cyclotron resonance condition to measure ϵ/M, and in practice the measurement is made by observing the ratio of two frequencies. The cyclotron equation relating the angular velocity ω_c of an ion of specific charge ϵ/M in a magnetic field B is

$$\omega_c=\frac{\epsilon B}{M}. \tag{3}$$

Thus, to obtain ϵ/M, it is necessary to measure ω_c and B. Fortunately, we can make use of nuclear resonance techniques to measure B. The frequency of nuclear resonance absorption for protons is related to the magnetic field B by the equation

$$\omega_n=\gamma_p B, \tag{4}$$

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[1] National Bureau of Standards.

where γ_p is a constant which was accurately measured by Thomas, Driscoll, and Hipple.[2] Thus, combining eq (2), (3), and (4), one obtains

$$\mathbf{F}=A\gamma_p(\omega_c/\omega_n).$$

The principle of operation of the omegatron can be explained by referring to figure 3.1. Electrons produced from a tungsten filament are accelerated in the direction of the magnetic field into a box-shaped enclosure, where they create ions by impact. An r-f voltage applied between the top and bottom of the box accelerates these ions in expanding spirals, provided the frequency ω of the applied r-f voltage is the same as the cyclotron resonance frequency ω_c. These resonant ions are collected after they reach a certain radius, and the current to this collector gives the indication of resonance, i. e., that $\omega=\omega_c$. The variation of the radius of the orbit with time is shown in

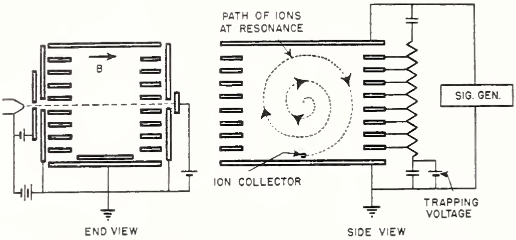

Figure 3.1. *Simplified diagram of the omegatron.*

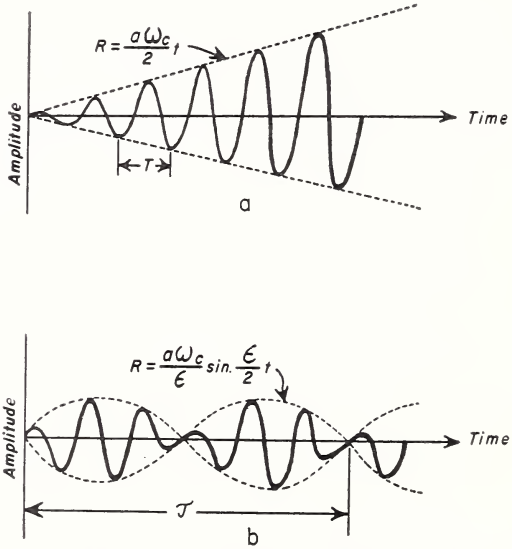

Figure 3.2. *Variation of radius with time in the omegatron.*

a, Resonant condition. $\omega=\omega_c=\frac{eB}{M}$, $T=\frac{2\pi}{\omega_c}$, $a=\frac{eE_0}{M\omega_c^2}$,

b, Nonresonant conditions. $|\omega-\omega_c|=\epsilon\neq0$, $\tau=\frac{4\pi}{\epsilon}$.

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[2] H. A. Thomas, R. L. Driscoll, and J. A. Hipple, J. Research NBS **44**, 509 (1950) RP2104.

figure 3.2 for both the resonant and the nonresonant case. A drawing of the omegatron is shown in figure 3.3, and figure 3.4 shows the omegatron in the magnet gap.

To determine the cyclotron resonance frequency precisely, it is necessary to have a sharp indication of resonance, that is, high resolution, such as the resonance shown in figure 3.5. It can be shown that the resolution is proportional to the number of revolutions the ions make before striking the collector. In order to get the maximum resolution, it is therefore necessary to hold the ions in the box as long as possible. To keep the ions from drifting out axially, i. e., in the direction of the magnetic field, a positive d–c potential is applied to the sides of the box with respect to the top and bottom. This provides a potential well or trapping field that retards the loss of ions. As a result, it is possible to hold the ions for thousands of revolutions and thus obtain a resonance curve, where $\omega/\Delta\omega$ is as high as 17,000, where $\Delta\omega$ is the width of the resonance curve measured at the base.

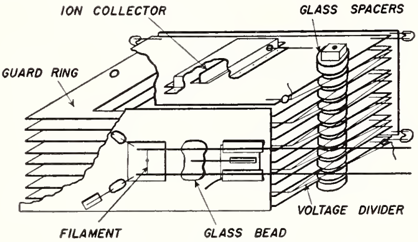

Figure 3.3. *Constructional details of the omegatron.*

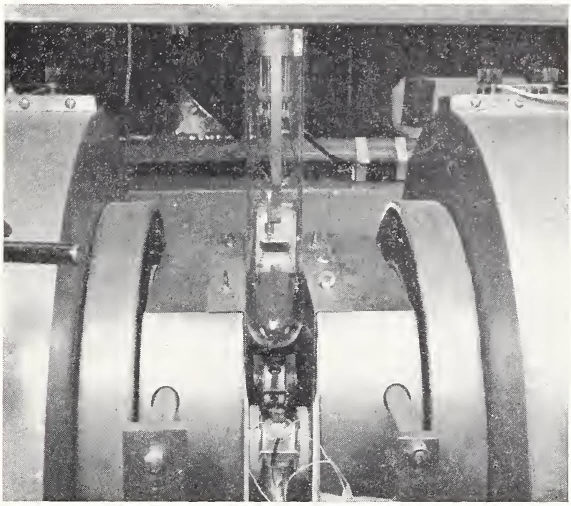

Figure 3.4. *The omegatron, showing nuclear resonance probes.*

Whereas the trapping field is necessary to obtain high resolution, it has the disadvantage of producing a radial electric field, which results in a frequency shift, that is, a displacement in the resonance frequency. This shift can be approximately calculated, and both the experimental shift and the theoretical shift are shown in figure 3.6.

Although this curve could be used for correcting the observed resonance frequency, this is difficult because one is unable to determine exactly when zero trapping voltage exists (e. g., contact potential, surface charges) and because space charge produces an additional

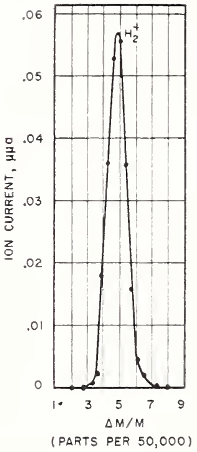

Figure 3.5. *High-resolution peak obtained with the omegatron.*

Magnetic field=4,697 gauss, cyclotron frequency=3.58 Mc, pressure at gage=1.9×10^{-7} mm Hg, electron current=1.0μa, trapping voltage=0.06 v, and r-f voltage=0.5 v rms.

frequency shift, as shown by the difference between the experimental and theoretical curves.

Since both theory and experiment tell us that the frequency shift is proportional to mass, a better method of obtaining the correction

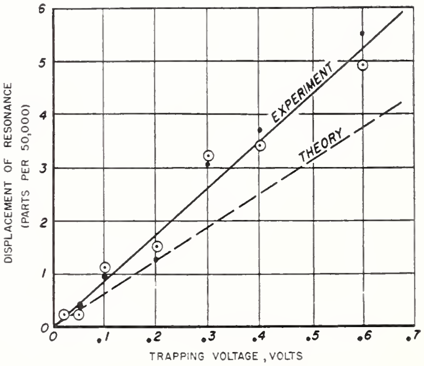

Figure 3.6. *Displacement of the observed resonance frequency due to radial electric field.*

●, increasing trapping voltage; ⊙ decreasing trapping voltage.

is to observe the resonance frequency for two different masses under the same operating conditions in quick succession. This method of correction is given in figure 3.7, which shows the value of $\omega_n/\omega_c=\nu_n/\nu_c$ obtained when making the measurement on two pairs of masses.

Some 45 separate measurements of the value of ω_n/ω_c were made. The arithmetic mean and average deviation of these is

$$\omega_n/\omega_c = 2.792685 \pm 0.000025.$$

The probable error of the arithmetic mean corresponding to the above observational average deviation is 1.13 parts per million.

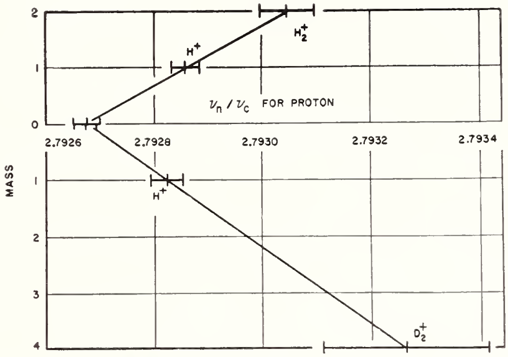

Figure 3.7. *Method of correction for frequency shift.*

By combining the value of ω_n/ω_c with γ_p and the isotopic weight of the proton,[3] and by making generous allowances for other possible errors, we feel that the value of the faraday is

$$\mathbf{F} = 9652.2 \pm 0.3 \text{ emu/g (physical scale)},$$

where the assigned error is estimated to be several times the probable error.

Discussion

Dr. S. E. Wood, Illinois Institute of Technology, Chicago, Ill.: I believe that there have recently been published methods of getting consistent values of the atomic constants. I would like to ask Dr. Sommer how the value that he has obtained by the physical method compares with these published values.

Dr. Sommer: I do not recall the exact values obtained, but we were very pleased with the agreement.

Dr. A. J. Rutgers, University of Ghent, Ghent, Belgium: If I understood correctly, Dr. Sommer, your magnetic field "B" was measured by pulling out the central part of the apparatus and then measuring the nuclear resonance frequency of the proton by inserting a probe. Would removing such a large part of the apparatus change the magnetic field strength at all?

Dr. Sommer: All parts of the omegatron were checked before they went in the apparatus to make sure we had no magnetic materials. Furthermore, at the conclusion of these experiments the omegatron was partially disassembled and a nuclear resonance probe was placed in the region where the ions are accelerated. Then we measured the

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[3] H. Ewald, Z. Naturforschung, **6a**, 293 (1951); C. W. Li, W. Whaling, W. A. Fowler, and C. C. Lauritsen, Phys. Rev. **83**, 513 (1951).

field inside the omegatron with all the usual parts surrounding it and found that the actual magnetic field inside the omegatron was the same as the field measured with the omegatron removed. In addition, before concluding our measurements, we constructed an omegatron entirely out of copper and found no shift in our results.

4. Entended Onsager Equation as Applied to Dilute Aqueous Electrolyte Solutions

By Edward G. Baker and Charles A. Kraus[1]

Introduction

At the time Onsager proposed the conductance equation

$$\Lambda=\Lambda_0-(\alpha\Lambda_0+\beta)\sqrt{C}, \tag{1}$$

it accounted quite satisfactorily for existing conductance data. It was looked upon as a limiting equation which the experimental data approached the more nearly the lower the concentration of the solutions. The theoretical slope of the plots of Λ versus $\sqrt{C}$ appeared to be approached as a limit in practically all cases.

However, as time went on and measurements were carried to lower concentrations and with greater precision, cases were found in which the experimental curves crossed the theoretical line of Onsager and approached Λ_0 from below. This was observed by Shedlovsky for potassium nitrate as early as 1932, and similar observations have subsequently been made by other investigators for other salts.

We have recently measured the conductance of a considerable number of salts to low concentrations, with a relative precision of the order of 0.005 percent. We have found that not only does potassium nitrate deviate from the simple Onsager equation at the lowest accessible concentrations, but all potassium salts for which sufficiently precise data exist do so likewise, The same is true of cesium chloride and cesium and sodium picrates. Sodium iodide exhibits linear deviation, as do all the quaternary ammonium salts that we have measured.

In figure 4.1, curve 1, are plotted values of Λ versus $\sqrt{C}$ for potassium iodide from 10^{-4} N to 10^{-2} N. The straight line represents the simple Onsager equation. As concentration decreases, the experimental points appear to lie closer and closer to the theoretical line, and on this plot they appear to approach the theoretical line tangentially.

However, it should be noted that the deviations with which we are concerned at low concentration are of very small magnitude and cannot be seen clearly when plotted on the scale of curve 1. Curve 2 represents a plot of the same data up to 10^{-3} N on an expanded scale. It will be seen that now the experimental curve intersects the theoretical line at a concentration of 1×10^{-3} N. Below this concentration, the deviations from the Onsager equation are negative. It is clear that here we have to deal with a phenomenon that is quite general but not universal.

In analyzing experimental conductance data, it is best to plot the deviation of their values from the simple Onsager equation as a func-

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[1] Metcalf Research Laboratory, Brown University, Providence, R. I.

tion of concentration. Such a plot for potassium iodide is shown in figure 4.2, where the deviations in Λ-units are plotted against values of C. It will be noted that the deviations below 1×10^{-3} N are negative, with a maximum deviation of 0.07 Λ-unit at approximately 4×10^{-4} N. At 1×10^{-3} N, the deviation curve crosses the zero axis, and thereafter

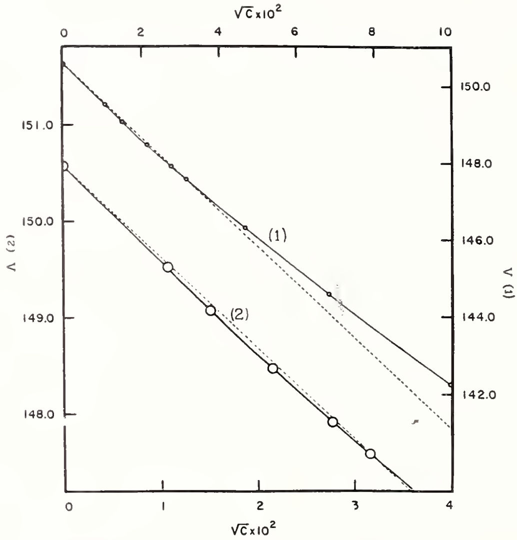

FIGURE 4.1. *Plot of Onsager equation for* KI.

$$\Lambda=\Lambda_0-(\alpha\Lambda_0+\beta)\sqrt{C}.$$

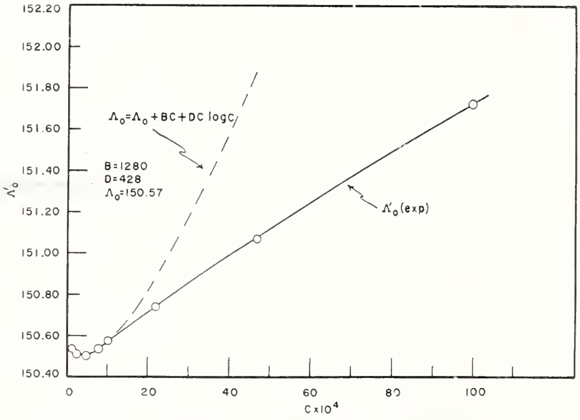

FIGURE 4.2. *Deviation from Onsager's equation for* KI.

the deviations are positive and increase with increasing concentration. The continuous curve represents experimental values.

Onsager [1] [2] and Onsager and Fuoss [2] have examined the theoretical background of the Onsager equation with a view to determining the effect of various approximations that were made in deriving the simple equation. They suggested the addition of terms BC and DC

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[2] Figures in brackets indicate the literature references and notes on p. 33.

log C, where B and D are constants, which they did not evaluate. Fuoss [3] has since attempted the evaluation of these constants.

A number of investigators have made use of the extended Onsager equation in one form or another in an attempt to fit the equation to their data. In this they have not been altogether successful, largely because they lacked the necessary, precise data to sufficiently low concentrations. At the same time, they seem not to have fully understood the properties of the equation.

Properties of the Extended Equation

The extended equation is best written in the form

$$\Lambda_0'-\Lambda_0=BC+DC\log C, \tag{2}$$

where

$$\Lambda_0'=\frac{\Lambda+\beta\sqrt{C}}{1-\alpha\sqrt{C}}. \tag{3}$$

B and D are empirical constants, and α and β have their usual significance. If B and D are zero, values of Λ_0', as calculated by means of eq (3), will yield values of Λ_0 within the limit of experimental error. If B is positive and D is zero, we have the equation of Shedlovsky [4]. Equation (2) expresses the deviation from the simple Onsager equation as a function of concentration.

Since the function (2) has a minimum, we can readily obtain a relation between the concentration at the minimum C_m and the constants B and D [5]. Differentiating eq (2) and equating to zero, we readily obtain the relation

$$0.43+\log C_m=-\frac{B}{D}. \tag{4}$$

At some concentration C^*, greater than C_m, the two terms of the right-hand member of eq (2) are equal and of opposite sign. In this case we have $\Lambda'_{0_{C^*}}=\Lambda_0$ and

$$\log C^*=-\frac{B}{D}, \tag{5}$$

where

$$C^*=2.7\ C_m. \tag{6}$$

If C_m can be determined experimentally, we can obtain the values of B/D, and the value of Λ_0 may be found from the plot of measured values of Λ_0'.

It remains to evaluate D. This is best done by graphical means. If we write $B/D=n$, we may write eq (2) in the form

$$\Lambda_0'=\Lambda_0+D(n+\log C)C, \tag{7}$$

or

$$=\Lambda_0+DC\log C/C^*. \tag{7'}$$

A plot of Λ_0' versus $(n+\log C)C$ or $C\log C/C^*$ should be linear, and the slope should be equal to D.

Examples

Having become acquainted with the characteristics of the extended equation, let us apply it to several examples of actual measurements.

1. *Potassium Nitrate.* The concentration at the minimum, C_m, is found to be 1.4×10^{-3} N, and C^* is 3.78×10^{-3} N; the value of n is 2.42. From the plot of Λ_0' versus C, Λ_0 is found to be 145.12 by interpolation. To find D, we plot values of Λ_0' against values of $C \log C/C^*$. This plot is shown in figure 4.3. The points are numbered in sequence, beginning with the most dilute. The radii of the circles correspond to 0.01 Λ-unit. With the exception of the first, all points lie on a straight line within 0.005 percent. From the plot, D is found to be 89.7; the value of B is then 217.3. For Λ_0 we obtain 145.110. This value is more reliable than that obtained above because in this instance the interpolation was carried out on a linear plot. The numerical equation of the deviation plot may now be written $\Lambda'_0 - \Lambda_0 = 217.3C + 89.7C \log C$.

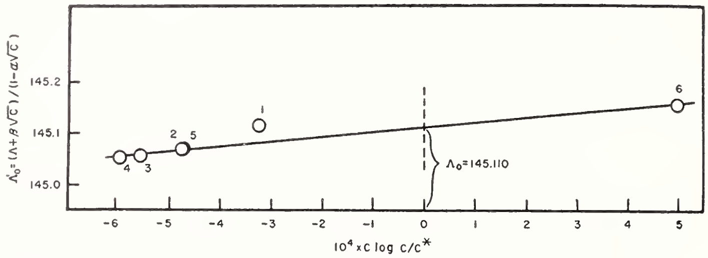

FIGURE 4.3. *Plot of equation (7) for determination of D for* KNO_3.

$n = 2.4225$; $C_m = 14.0 \times 10^{-4}$; $D = 89.7$; $B = 217.3$.

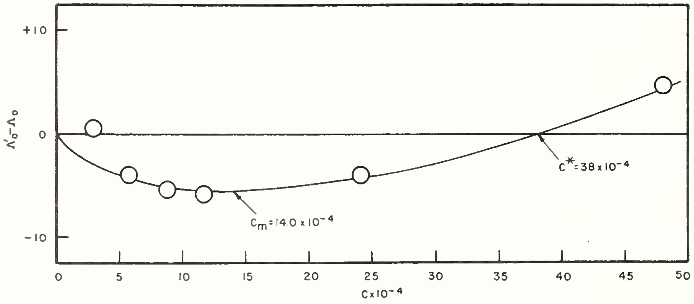

FIGURE 4.4. *Comparison of experimental and computed values (equation 7) for* KNO_3.

$\Lambda_0' = 145.110 + 217.3C + 89.7C \log C$.

In figure 4.4, the continuous curve represents the numerical equation. The experimental values are shown as circles having a radius of 0.01 Λ-unit. In table 1, experimental and calculated values of Λ_0' are compared; the differences Δ are shown in the last column. Neglecting the first point, which is obviously in error, the maximum deviation is 0.005 Λ-unit, with an average deviation of 0.004 Λ-unit. Over the concentration range of these measurements, the conductance of potassium nitrate conforms very closely to the requirements of eq (2).

2. *Potassium Iodate.* The conductance of this salt was measured at lower concentrations by Monk [6] and at higher concentrations by Krieger and Kilpatrick [7]. Their precision was of the order of 0.02 Λ-unit, which is quite adequate with this salt because its deviation is relatively large.

TABLE 1. *Potassium nitrate at 25° C*

Point number	$C\times10^4$	Λ_0' (exp.)	Λ_0' (calc.)	$\Delta\Lambda_0'$
1	2.89432	145.116	145.081	+0.035
2	5.84448	145.071	145.067	+.004
3	8.76103	145.056	145.060	−.004
4	11.6750	145.052	145.057	−.005
5	24.1318	145.071	145.067	+.004
6	48.0272	145.158	145.155	+.003

Values of the constants D, B, n, and Λ_0 were obtained by the method outlined above in the case of potassium nitrate. The numerical equation for this salt is shown in figure 4.5, where the curve represents the equation. The experimental values are shown as circles having radii of 0.02 Λ-unit. For this salt, C_m is 2.20×10^{-3} N, and C^* is 5.94×10^{-3} N. Again, the equation reproduces the experimental value within the limit of experimental error. The depth of the minimum, $\Lambda_0-\Lambda_0{}'_m$ is 0.17 Λ-unit. This is much the largest deviation of any salt for which we have the necessary data. The equation applies to a concentration as high as 6×10^{-3} N.

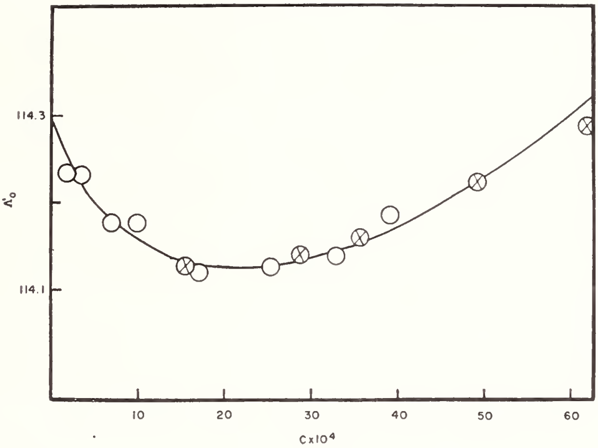

FIGURE 4.5. *Comparison of experimental and computed values for* KIO_3.

○, Monk; ⊗, Krieger and Kilpatrick. $\Lambda_0'=114.295+400.7\,C+180.0\,C\log C$.

Discussion

We have satisfactory data for six potassium salts at 25° C. These data were analyzed by the method described above, and values of characteristic constants were determined. Values of these constants are collected in table 2, the salts being arranged in order of increasing values of C_m or decreasing values of n.

TABLE 2. *Values of characteristic constants for potassium salts at 25° C*

Salt	$C_m \times 10^4$	n	D	B	Λ_0	$\Lambda_0 - \Lambda_0{}'_{\min}$
KBr	1. 69	3. 34	158	528	151. 707	0. 012
KI	3. 69	3. 00	428	1280	150. 572	. 068
KCl	6. 23	2. 77	208	576	150. 027	. 056
$KBrO_3$	8. 84	2. 62	180	472	129. 099	. 069
KNO_3	14. 0	2. 42	89. 7	217	145. 110	. 055
KIO_3	22. 0	2. 226	180	400. 7	114. 295	. 170

The depth of the minimum ranges from 0.012 for potassium bromide to 0.170 for potassium iodate. For the remaining salts the depth varies between 0.05 and 0.07 Λ-unit.

The constants for the different salts vary in an inexplicable fashion. Potassium nitrate has the smallest values of B and D, with a ratio of 2.42, whereas potassium iodide has the largest value of B and D, with a ratio of 3.00. For potassium bromide, $n=3.34$ and $D=158$, which differs little from 180, the value of D for potassium iodate, whose value of n is 2.23. The constants B and D seem to be somewhat related in that they increase together. The extreme variation of n is in the ratio of 1.5/1.0, that of D is 4.7/1, and that of B is 5.9/1.

Addendum [3]

When this paper was presented, the results seemed to establish the minimum in the deviation curves of potassium salts as an intrinsic property of the salts themselves. Check measurements agreed well, and the observed deviations conformed closely with eq (2). However, investigations that have been carried out subsequently [8] indicate that the observed minimum may be due to some unknown source of error.

We have carried out measurements with potassium bromide, potassium iodide and potassium iodate. With these salts, we have found that in some cases the deviation curves exhibit a minimum which at times approximates those of earlier measurements. In other cases, the deviation curves are linear with respect to concentration. These differences in behavior are particularly striking with potassium iodate, which at times has been found to exhibit a pronounced minimum similar to that found by Monk [6] and Krieger and Kilpatrick [7]. On the other hand, we have also obtained linear deviation curves with the same salt. The observed differences appear only at lower concentrations. So, for example, in the case of potassium iodate, the average deviation found at a concentration of 6×10^{-3} N in seven series is only 0.03 percent; at lower concentrations (2 to 5×10^{-4} N), the average deviation for 13 series is 0.2 percent.

There is some evidence which indicates that the observed effects are due to some unknown impurity in the water; there is also evidence that they may at times be due to the salt. One observation that appears to be significant but cannot be accounted for at this time is that when a fresh solution is made up, the conductance drifts toward higher values; it may take as long as 10 or more hours before a steady value is reached. It should be noted in this connection that, with quaternary ammonium salts, under the same conditions, such a drift does not occur. The deviation curves of these salts, moreover, are linear.

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[3] Added October 15, 1952.

The solution of this problem will be forthcoming only with further investigation. At this time, the precise form of the conductance curve for potassium salts remains uncertain. The probability is that it will ultimately be found that the deviation curves of these potassium salts are linear.

References

[1] L. Onsager, Physik. Z. **28,** 277 (1927).
[2] L. Onsager and R. M. Fuoss, J. Phys. Chem. **36,** 2689 (1932).
[3] R. M. Fuoss, Physik. Z. **35,** 59 (1935).
[4] T. Shedlovsky, J. Am. Chem. Soc. **54,** 1405 (1932).
[5] We are indebted to Dr. R. M. Fuoss for suggesting the treatment which follows.
[6] C. B. Monk, J. Am. Chem. Soc. **70,** 3281 (1948).
[7] K. A. Krieger and M. Kilpatrick, J. Am. Chem. Soc. **64, 7** (1942).
[8] Measurements by E. Lowell Swarts and Robert W. Martel.

Discussion

Dr. T. Shedlovsky, Rockefeller Institute for Medical Research, New York, N. Y.: It is a great pleasure to hear about the fine structure of the theory of dilute solutions. That is what Dr. Kraus has been talking about, and I would like to say, for those of us who are not familiar with the magnitudes here, that it is all within a range of 0.1 percent or less. What it means to me is that precision conductance work is not necessarily "old hat." By work of such precision, we may be able to get, as Dr. Kraus suggested at the end of his talk, some very valuable leads, not only about very dilute solutions but about concentrated ones.

Dr. W. F. K. Wynne-Jones, University of Durham, Newcastle, England: I would like to ask Dr. Kraus about the solvent question.

Dr. C. A. Kraus: Our solvent correction, in general, we have under very excellent control. Our solvents ran about 0.35 and 10^{-6}. We corrected the solvent correction.

Dr. Wynne-Jones: It was exactly that second point I was interested in.

Dr. Kraus: It does not amount to very much. It is a matter of 0.03 lamda unit.

Dr. Wynne-Jones: But the total minimum is of the order of 0.05?

Dr. Kraus: The minimum effect runs from 0.012 to 0.17 Λ-unit.

Dr. Wynne-Jones: But the secondary correction you have applied is sufficiently certain to cause uncertainties.

Dr. Kraus: The correction we applied, the water correction, would change our final observed value by the amount of about two or three hundredths of a lamba unit.

5. High Field Conductance of Some Paraffin Chain Electrolytes

By S. Gusman[1] and R. H. Cole[2]

Introduction

A number of salts in aqueous solution or in water-organic solvent mixtures exhibit micelle formation, namely, association of the simple ions into much larger aggregates when the salt concentration exceeds a sharply defined value. In particular, *n*-alkyltrimethylammonium and *n*-alkylpyridonium salts show such behavior if the *n*-alkyl chain is sufficiently long. Ordinary low field conductances of such systems show abrupt and marked deviations from strong electrolyte behavior when a characteristic critical concentration is exceeded.[3]

As Max Wien first showed in 1927,[4] electrolytes generally exhibit an increased conductance if large electric fields are employed for the measurement. For systems of interest here, this effect can be of the order of a doubling in value of conductance for a field of 100 kv/cm if the concentration is greater than the critical value. However, at lower concentrations, the effect is much smaller and of the same order as that for ordinary strong electrolytes. Detailed studies of these effects for various salts, in relation to concentration and solvent nature, can be expected to give useful information about the nature and stability of the micelle. This paper gives an account of our work along these lines.

Measurement of High Field Conductance

The principal difficulty in making conductance measurements at field strengths of the order of tens of kv/cm is that the field can be applied only for very short intervals if excessive heating is to be avoided. An aqueous solution of conductance 10^{-4} mho/cm would boil in about 10^{-3} sec after applying a field of 100kv/cm, and so, of necessity, measurements on such solutions must be made in a matter of microseconds.

In earlier work, voltage pulses in the form of damped sinusoidal waves produced by a spark discharge circuit were used. Average conductances were deduced from the heating produced, or determined by oscillograph records of transient voltages and current. Availability of more convenient and flexible techniques since has made possible methods in which the complications of time-dependent field and indi-

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[1] Rohm & Haas Co., 5000 Richmond Street, Philadelphia, Pa.
[2] Metcalf Research Laboratory, Brown University, Providence, R. I.
[3] G. L. Brown, P. F. Grieger, and C. A. Kraus, J. Am. Chem. Soc. **71**, 95 (1949).
[4] For a discussion of earlier work, see H. E. Eckstrom and C. Schmelzer, Chem. Rev. **24**, 367 (1939).

rect or rather inaccurate measurements can be avoided. A particularly simple approach to the problem has been described by Adcock and Cole [5] in which a constant high voltage is applied for about 1 microsecond to the electrolyte cell in one arm of a Wheatstone bridge and the change in balance of the bridge determined visually or photographically. For the present work, several changes were made to increase the convenience and precision of the method. This is described briefly below.

The schematic diagram in figure 5.1 shows essential features of the apparatus. A 500-foot coaxial cable, left open-circuited, at the remote end, is initially charged to potentials as high as 8,000 v from an ordinary low current supply through a 20-megohm resistor. The 4C35 hydrogen thyratron is then ionized by a triggering voltage pulse and acts as a switch connecting the cable across the conductance bridge network, which is adjusted to have an external impedance equal to the surge impedance of the cable. It is a well-known result of transmission-line theory that a constant voltage of half the charging voltage is developed across the bridge until the cable is discharged by the voltage wave on the cable making a go and return trip (in about 2 microseconds in this case).

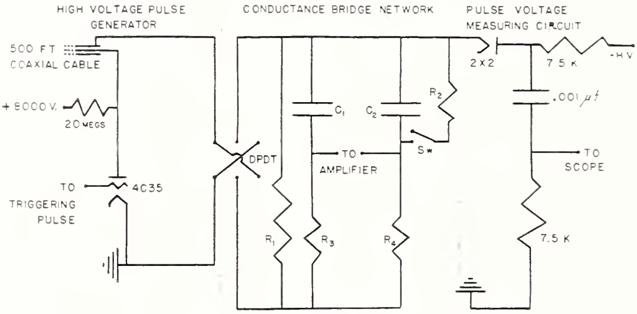

FIGURE 5.1. *High-field-conductance apparatus*

The conductance bridge network serves to compare the conductance of cell C_2 containing the solution of interest with that of cell C_1, which is filled with a KCl solution adjusted to have the same conductance for low fields. The two resistances, R_3 and R_4, serve as ratio arms. The difference of the potentials across them, resulting from change in conductance of C_2 at high field, is amplified and measured as a cathode-ray oscillograph-trace deflection. This is calibrated by introducing a known resistance R_2 and measuring the corresponding change in deflection. The variable resistance, R_1, is adjusted until the bridge impedance matches that of the cable.

The field applied to cell C_2 can be deduced from a knowledge of the transient voltage applied to the bridge, and the electrode spacing. The former is determined by comparing it with a steady negative reference voltage adjusted until no current flows through the 2×2 diode of figure 5.1 when the pulse is applied. The electrode spacing is found from measurements of cell conductance for KCl solutions of known specific conductance.

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[5] W. A. Adcock and R. H. Cole, J. Am. Chem. Soc. **71** 2835 (1939).

High Field Conductances of Paraffin Chain Electrolytes above their Critical Concentrations

For strong electrolytes, conductance has been found to increase with increasing field strength. At very high field strengths, the equivalent conductance approaches a limiting value which is close to the limiting equivalent conductance at infinite dilution, Λ_0. This increase, known as the first Wien effect, may be distinguished from the dissociation field effect, or second Wien effect. The dissociation field effect is generally concerned with increase of conductance resulting from the dissociation of a weak electrolyte under the influence of high field strength. For this type of field effect, it is again anticipated that the maximum high field conductance is equal to or less than Λ_0.

An anomalous type of behavior was noted by Malsch and Hartley [6] for aqueous solutions of hexadecylpyridonium chloride. At low fields, this salt exhibits critical concentration phenomena. It is a strong electrolyte for concentrations less than the critical value, at which point the slope of equivalent conductance Λ versus square root of concentration curve undergoes what appears to be a discontinuous change, such that Λ starts to fall more rapidly with increased concentration. However, at field strengths in the vicinity of 100 to 200 kv/cm, the equivalent conductance increases to a maximum in the immediate vicinity above the critical concentration. The point of particular interest is that high field equivalent conductances become considerably greater then Λ_0.

Malsch and Hartley explain their result in terms of the micelle hypothesis. They assume the presence of micelles containing a large number of positively charged ions, with some smaller number of negative ions bound to the micelles sufficiently to decrease their low field conductance. The high field acts to dissociate some negatives ions from the micelles, thus leaving a more highly charged species. By Stokes' law, the conductance of a micelle should exceed the conductance of the paraffin chain ions from which it is formed, if micelle association with negative ions is not considered. Dissociation of negative ions from the micelle by the high field can, by this hypothesis, explain conductances greater than Λ_0.

There is no theoretical necessity for excluding from consideration miscellar species which, at low field strengths, are more conducting than the unassociated species from which they are formed. Such considerations may account for the experimentally observed maxima in low-field-conductance curves of *n*-hexadecylpyridonium and *n*-octadecylpyridonium iodates in aqueous solution. High-field-conductance results for these salts, reported by Adcock and Cole,[5] show that high fields serve to increase the height of the maxima. The nature of the field effect is in all respects similar to that observed for hexadecylpyridonium chloride by Malsch and Hartley.

Low-field-conductance results for *n*-octadecylpyridonium bromate solutions at 25° C are shown in figure 5.2. For *t*-butanol–water mixtures, the equivalent conductance, Λ, as a function of the square root of concentration is seen to exhibit maxima, but there is no indication of a maximum in the water solution at 25° C. Critical concentration phenomena are not observed for this salt in a 14.71 weight percent *t*-butanol solution. This may result from the critical concentration being below the measurable concentration range.

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[6] J. Malsch and G. S. Hartley, Z. physik. Chem. **A170**, 321 (1934).

High- and low-field-conductance results are shown for *n*-octadecylpyridonium bromate in these various *t*-butanol–water mixtures in figure 5.3. To place the various solvent mixtures on a common basis, the conductance at any particular concentration in a *t*-butanol–water mixture is multiplied by a correction factor. The correction factor is the ratio of the equivalent conductance at the critical concentration in water to the equivalent conductance at the critical concentration in the particular *t*-butanol–water mixture under investigation. This is approximately the correction required to eliminate from consideration viscosity differences among the various solvents if Walden's rule were applicable. Accordingly, the value so obtained is described as a "viscosity corrected" equivalent conductance and denoted by Λ'. The use of the quantity $C^{1/2}-C_b^{1/2}$ as abscissa, where C_b is the critical

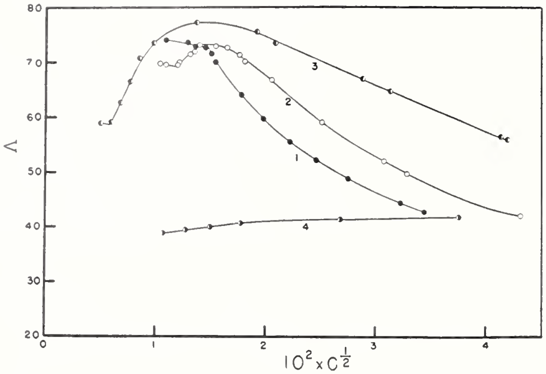

FIGURE 5.2 *Low-field-equivalent conductance for n-octadecyl pyridonium bromate in t-butanol/water mixtures at 25° C.*

(1) Aqueous solution; (2) 1.47 weight percent t-butanol; (3) 5.77 weight percent t-butanol; (4) 14.71 weight percent t-butanol.

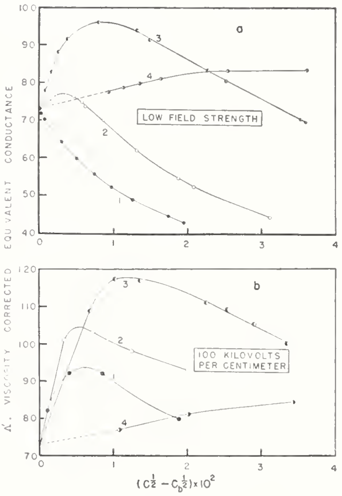

FIGURE 5.3. *High and low field viscosity corrected equivalent conductances for n-octadecyl pyridonium bromate in t-butanol/water mixtures at 25° C.*

(1) Aqueous solution; (2) 1.47 weight percent t-butanol; (3) 5.77 weight percent t-butanol; (4) 14.71 weight percent t-butanol.

concentration, arbitrarily displaces each curve in such a way that all critical concentrations fall at zero on the scale of abscissas.

Figure 5.3 shows that the high-field strength causes each curve to be displaced upward toward higher conductance. The low-field-conductance curves shows that addition of *t*-butanol to the solvent, up to a point, has a similar effect. However, in the immediate vicinity of the critical concentration, the curve for 14.71 percent *t*-butanol lies below that for 5.769 percent *t*-butanol.

In figure 5.4 are shown the curves for percentage increase of conductance due to application of a 100 kv/cm field to the various *t*-butanol–water solutions of this same salt, *n*-octadecylpyridonium bromate. Quite marked reductions of the high field effect are seen to result from addition of *t*-butanol to the solvent and the 14.71 percent *t*-butanol solution behaves as if it were only very slightly associated into aggregates. The nature of the effects here observed very probably results from specific interactions of the various components in the solution rather than from the quite small difference in solvent dielectric constant. It is, nevertheless, possible to account for observed results in terms of the micelle hypothesis by assuming that addition of *t*-butanol to the solvent causes average micelle size to decrease, and that the average degree of association of negative ions with positively charged complexes also decreases. The first assumption can, by a Stokes' law effect, account for a decreased low field conductance as the solvent becomes excessively rich in *t*-butanol. The second assumption is in accord with both increased low field conductance and decreased effect of the high field upon the conductance as a consequence of addition of *t*-butanol to the solvent. These particular assumptions are more illustrative than necessary. Unambiguous interpretation of the results requires further study of the role assigned to specific ion-solvent interactions. Conversely, measurements on other related systems may be expected to give useful information about the consequences of such interactions.

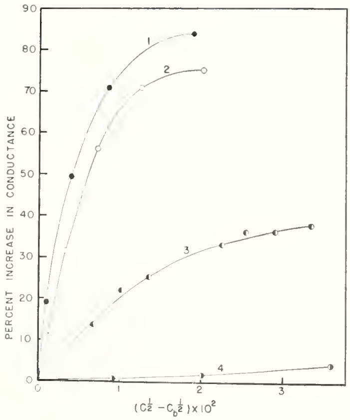

FIGURE 5.4. *Percentage increase in conductance at 100 kilovolts per centimeter as a function of concentration for n-octadecyl pyrdionium bromate in t-butanol/water mixtures at 25° C.*

(1) Aqueous solution; (2) 1.47 weight percent t-butanol; (3) 5.77 weight percent t-butanol; (4) 14.71 weight percent t-butanol.

Discussion

Dr. R. M. Fuoss, Yale University, New Haven, Conn.: I think it is quite legitimate to plot against the difference between the concentrations. What you are doing is simply plotting against the micelle concentration. That is standard practice, as a matter of fact, when you consider light scattering from soap solutions, et cetera, but there is one minor comment about the scale you chose later on. I think it would have been preferable to use the square root of the difference rather than the difference of the square roots.

Dr. S. Gusman: I think you are probably quite correct; however, this scale produced the least distortion of experimental data. The concentration scale that was used might be associated with the micelles. That would be a conventional interpretation.

Dr. W. J. Hamer, National Bureau of Standards: Are your effects distinct from the Wien effect?

Dr. Gusman: No. They are the Wien effect.

6. A Study of Iodide-Iodine Solutions with the Electromotive-Force Centrifuge

By D. A. MacInnes [1] and Margaret Oakley Dayhoff [1]

Introduction

A ready understanding of the effect of a gravitational or centrifugal field on the potential of a simple galvanic cell can be gained with the aid of a mechanical analogy. Consider the system shown in figure 6.1, consisting of masses W_1 and W_2 on a cord passing over a pulley, *P*. If W_1 is greater than W_2 and the system is allowed to operate, then the energy, Z, available is

$$Z=gh(W_1-W_2), \tag{1}$$

where g is the gravitational constant and h the distance through which the weights move. If, however, the masses have the volumes V_1 and V_2 and are immersed in a vessel containing a medium of density, ρ, eq (1) must be modified to give

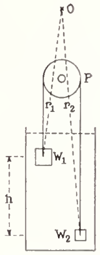

FIGURE 6.1. *Mechanical analogy to the galvanic-cell process.*

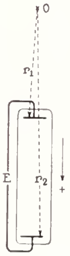

FIGURE 6.2. *Diagram of galvanic cell in centrifugal field.*

$$Z=gh[(W_1-V_1\rho)-(W_2-V_2\rho)] \tag{2}$$

to allow for the buoyancy of the medium. Considerably greater energy may be obtained if the force of gravity is replaced by a centrifugal field. This can be done by mounting the system of weights, pulley, and vessel so that it can be swung n revolutions per second about a center such as O, which is distant r_1 and r_2 from masses W_1 and W_2. Under these conditions the energy obtainable from the mechanism is

$$Z=2\pi^2n^2(r_2^2-r_1^2)[(W_1-V_1\rho)-(W_2-V_2\rho)]. \tag{3}$$

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In the emf centrifuge a simple galvanic cell, shown diagrammatically in figure 6.2, may be represented by

$$(\mathrm{Pt})\underset{r_1}{:}\mathrm{I}_2,\quad \mathrm{BI},\quad \mathrm{I}_2\underset{r_2}{:}(\mathrm{Pt}), \tag{A}$$

in which B is a positive-ion constituent. In this cell two otherwise identical iodide-iodine electrodes, E_1 and E_2, are situated at distances r_1 and r_2 from a center, O, about which rotation takes place. Under these conditions a potential, E, will develop. If the cell operates, with current passing in the direction indicated, the effect will be (a) the removal of a portion of the salt BI from the region of the anode (the inner electrode) and its reappearance at the cathode, and (b) the reaction of uncharged iodine I° to form iodide ion at the cathode, i.e., $I^\circ+\epsilon=I^-$ and the reverse reaction at the anode. For the passage of 1 **F** equivalent, **F**, of current the amounts of material thus transported will be t_B mole of BI from the anode to the cathode region (t_B is the transference number of the positive ion), and 1 mole of I_2 in the reverse direction. Thus, we are dealing with a coupled process in which t_BM_{BI} (M_{BI} is the gram-molecular weight of BI) corresponds to mass W_1, and A_I, the gram-atomic weight of I_2, to W_2. Placing these values in eq (3), we obtain

$$-E\mathbf{F}=Z=2\pi^2n^2(r_2^2-r_1^2)[t_B(M_{BI}-\overline{V}_{BI}\rho)-(A_I-\overline{V}_I\rho)]. \tag{4}$$

Here, volumes V_1 and V_2 have been replaced by the molal and atomic volumes $\overline{V}_{BI}$ and $\overline{V}_I$. The fact that the mechanical energy, Z, may be reversibly transformed into the electrical energy, $-E\mathbf{F}$, in which E is the measured potential of cell A at the speed of rotation n, is also indicated in eq 4. This equation was first obtained by Tolman [1] [2] for cells of type A, though earlier experimental and theoretical work on the effects of gravitational and centrifugal fields on the potentials of galvanic cells was carried out by Des Condres [2]. The discussion given above may be regarded as demonstration or explanation. A rigorous derivation of eq 4 is given in an earlier paper [3], in which it is shown that the terms $\overline{V}_{BI}$ and $\overline{V}_I$ are *partial* molal and *partial* atomic volumes, respectively, and that eq 4 must be modified to include the effect of the complex resulting from the combination of the iodide ion and iodine, which will be further discussed below. This contribution is concerned with modifications of the apparatus used in the earlier work, and with new data on measurements of KI-I_2 and NaI-I_2 solutions.

The Apparatus

The apparatus as used in the earlier research has been described in detail elsewhere [3, 4]. Some modifications have, however, been found desirable in obtaining the results to be described below. The apparatus now in operation is shown schematically in figure 6.3. Rotor R-R is a disk of magnesium 23 cm in diameter and 5 cm thick, turned in a horizontal plane by the pressure of disk D on plate P, which is rotated by synchronous motor M. The rotor speed can be varied by changing the position of disk D with relation to plate P. The potential between electrodes E_1 and E_2 of galvanic cell C can be measured, during the rotation, by electric contacts through mercury commutators

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[2] Figures in brackets indicate the literature references on p. 49.

G_1 and G_2. The temperature of the rotor is found by copper-constantan junction J, commutators G_2 and G_3, and the reference junction in external ice bath I. Thus by shifting the leads of the potentiometer to the appropriate pairs of contacts 1, 2, and 3 the emf of the cell, or the temperature of the rotor may be measured. The cell potentials are considerably affected by radial temperature gradients. Such gradients are minimized by surrounding the rotor with a chamber in which a vacuum of 10μ or better is maintained. This prevents the production of appreciable heat through gas friction. The heat generated at the vacuum bearing is controlled by the circulation of cooling water. The apparatus previously had a set of 22 thermojunctions arranged around the cell so that differences of temperature at radii corresponding to the positions of electrodes E_1 and E_2 could be measured. It has been observed, however, that operating in vacuum this difference of temperature disappears, to 0.001 deg, if the temperature of a fixed point on the rotor remains constant. Commutators G_1, G_2, and G_3 are mounted under the rotor and operate in the vacuum. The temperature of the rotor may be maintained constant by choosing the temperature of the water passing around the rotor bearing, or by keeping the room temperature somewhat lower than that desired for the rotor.

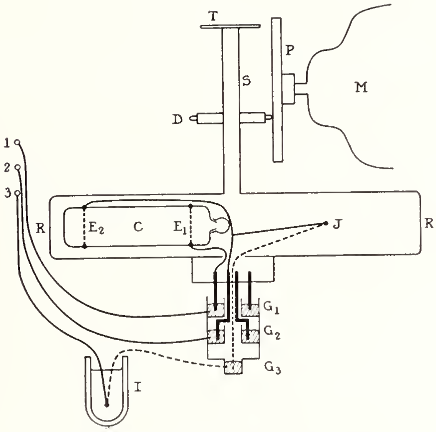

FIGURE 6.3. *Diagram of apparatus.*

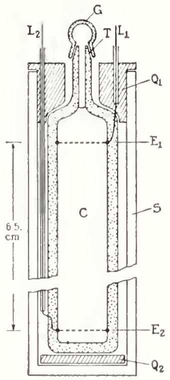

FIGURE 6.4. *The galvanic cell.*

An important change from our previous practice has been in the design of the galvanic cell. For the previous work this consisted of a cylindrical glass vessel with platinum disks sealed into each end and about 8 cm apart. However, it was found that one of the chief difficulties in getting accurate measurements was the presence of minute suspended particles in the solutions, which persisted, as shown by a Tyndall beam, even after extraordinary efforts were made to eliminate them. In a centrifugal field such particles tended to collect on the electrodes and seriously affected the accuracy of the measurements. The difficulty has been largely, if not entirely, removed by the design of cell shown in figure 6.4. Here the electrodes, in glass cell C, are platinum rings E_1 and E_2 sealed into the glass wall several millimeters from the ends of the cell. With this arrangement the particles, under the influence of the centrifugal force, tend to collect harmlessly at these ends, and out of contact with the electrodes. Platinum leads L_1 and L_2 are enclosed in flexible plastic tubing. Filling and removal of the solution are carried out through tube T, which is closed with ground-glass cap G. The cell is held in brass shell S, the space between the shell and the cell being filled with vaseline. This semifluid material helps to equalize the pressure on the cell when in a centrifugal field. Lucite spacers Q_1 and Q_2 keep the glass cell in a fixed position in shell S. Since cell C cannot be made with electrode rings E_1 and E_2 with definite values for radii r_1 and r_2, cell constant K, which is the effective value of the term $(r_2^2-r_1^2)$ in eq (4), has been obtained by calibrating with KI-I_2 solutions, the transference numbers of which are known from the moving boundary measurements of Longsworth [5] and our earlier work with the emf centrifuge. It is important that the counterpoise have the same moment of inertia as the cell, i. e., imitate it closely in distribution of weight, since otherwise the rotor may precess, and thus not rotate about its geometrical center.

Mercury commutators G_1, G_2, and G_3 are described in detail elsewhere [3]. With them it was possible to make measurements, to $1 \mu v$ or better, of potentials developed in the rotor, this precision being necessary because the highest potentials determined are of the order of one millivolt.

The measurements of the speeds of rotation, which ranged between 2,400 and 7,200 rpm, were made with the aid of stroboscopic 2,400 patterns, as described in a paper from this Laboratory [6]. The rotating top surface of shaft S of figure 6.3 carries disk T, which is painted black, with a white radial streak. This surface is illuminated by a stroboscopic lamp, which is operated on alternating current, and yields flashes at the rate of 60/sec. At definite speeds, stationary stroboscopic patterns are observed that are related by the formula $\text{rpm}=(3{,}600\times m)/n$, in which n is the number of bands in the pattern, and m is the "multiplicity." Patterns are observed for integral values of m and n, except when they have a common factor. As the same pattern occurs at a series of related speeds, it is necessary to have a rough preliminary estimate of its value. This is furnished by a scale attached to the adjustment mechanism of disk D. Since stationary patterns could be obtained for indefinite periods, with occasional slight manual adjustments, the accuracy of the speed measurement was nearly that of the a-c source, and was more than necessary for our purpose.

Results and Discussions

The measurements described in this paper were made with KI and NaI, to which varying amounts of iodine were added. In preparing these solutions the best commercial salt was recrystallized several times and dried in an electric oven, followed by heating to 500° in a platinum boat in a current of dried nitrogen. The material was then weighed with the aid of the Richards bottling apparatus [7], after which the salt was dissolved in a weighed amount of conductivity water. Iodine, several times sublimed, was then added by weight to the salt solutions. The stronger iodine solutions were sometimes diluted quantitatively with the appropriate salt solution.

Typical results of measurements in NaI-I_2 solutions are shown in table 1. The two values of E, in microvolts, for each solution and for each speed of revolution, n, are from separate runs of the centrifuge. The agreements in E are of the order of 1 μv. The potentials remained substantially constant, following an initial rise [8],[3] for periods of 30 min. According to eq (4), and the modified expression, eq (5), (given below), values of E/n^2K (in which K is the effective value of $(r_2^2-r_1^2)$) should be independent of the speed of rotation, n, for the measurements on each solution. This is seen to be the case in table 1 to high precision, although the variations are smaller for the two higher speeds, the data for which were used in the computations to be outlined below.

TABLE 1. *Typical data from measurements of potential, E, versus speeds of revolution, n (cell I)*

Revolutions per second	Electromotive force in microvolts		$E/n^2K\times10^3$
	Measurement 1	Measurement 2	
Concentration of NaI=0.19112 Ratio of concentration of I_2 to NaI=0.003146			
40	138.8	139.3	1.0830
80	557.5	557.3	1.0856
110	1,056.1	1,054.3	1.0871
Concentration of NaI=0.19103 Ratio of concentrations of I_2 to NaI=0.021830			
40	139.6	140.5	1.0907
80	562.9	562.2	1.0956
110	1,062.3	1,063.8	1.0951
Concentration of NaI=0.18885 Ratio of concentrations of I_2 to NaI=0.48092			
40	173.8	172.4	1.3187
80	689.0	690.0	1.3130
110	1,304.9	1,304.4	1.3141

TABLE 2. *Results of emf centrifuge measurements on potassium—iodide-iodine solutions at 25° C*

Concentration of KI	$R=C_{\mathrm{I}}^{0}/C_{\mathrm{KI}}$	$E/n^2K\times10^3$		Cell
		Observed	Calculated	
Moles/1,000 g solution				
0.17147	0.005248	0.783_7	0.783_7	II
.18988	.04225	$.797_9$	$.797_9$	I
.18566	$.06206_4$	$.801_4$	$.805_3$	I
.19140	.11675	$.828_6$	$.826_8$	II
.189033	.31970	$.905_5$	$.908_8$	II
.188213	$.5227_2$	$.993_3$	$.995_5$	II
.18697	.6519	1.051_1	1.055_2	I

In table 2, new data, obtained with the present technique, are given for E/n^2K on KI-I_2 solutions, and which are essentially in accord with those given earlier [3]. The results for NaI-I_2 solutions, also obtained with the newer technique, appear in table 3.

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[3] As shown by reference [8], this rise is due to adiabatic compression. A computation indicates that a difference of temperature of 0.04 deg or a potential of about 20 μv, between the electrodes would be developed if the speed were increased rapidly from zero to 7,200 rpm.

Table 3. *Results of emf centrifuge measurements on sodiumiodide-iodine solutions at 25° C*

Concentration of NaI	$R = C_{I0}/C_{NaI}$	$E/n^2K \times 10^3$		Cell
		Observed	Calculated	
Moles/1,000 g of solution				
------------	------------	1.084_3	1.084_3	I
0.19112	0.003146	1.086_3	1.085_9	I
.19103	.021830	1.095_0	1.095_5	I
.19082	.06388	1.115_1	1.117_3	I
.19043	.14829	1.157_0	1.162_2	I
.18944	.35654	1.270_3	1.278_8	I
.18885	.48092	1.344_1	1.352_7	I
.18737	.79898	1.539_3	1.557_3	I

The data in tables 2 and 3 show that the value of E/n^2K increases rapidly as the proportion of iodine in solution ascends. Below it is shown that this is due to the effect of an iodide-iodine complex on the mechanism of the cell.

During the passage of current through cell A the electrochemical reaction $I^- = I^0 + \epsilon$ occurs at the anode and $\epsilon + I^0 = I^-$ at the cathode. Here I^0 represents iodine in an uncharged condition. It may be in the form of I_2 or as I^-_{j+1}, in which j is the number of equivalents of uncharged iodine in an equivalent of the complex. During the passage of 1 **F** through the cell, t_B equivalent of the positive ion, B, will migrate from the region of the anode and appear at the cathode, t_B representing a Hittorf transference number. The remainder of the current is transported in the reverse direction by t_I equivalent of I^- and t_c equivalent of the complex ion. The net loss around the anode is t_B equivalent of the positive ion and $(1 - t_I - t_c) = t_B$ equivalents of negatively charged ions. Thus there is a net loss of t_B equivalent of KI from the region of the anode. Since reverse phenomena occur at the cathode, a transport of t_B equivalent of the salt from one electrode to the other takes place. This is accompanied by the appearance of one equivalent of I^0 at the anode by the electrochemical reaction, and jt_c equivalent of that material by transference.

The transport process per faraday for galvanic cell A is therefore t_B equivalent of BI from the anode to the cathode and $(1 + jt_c)$ equivalents of I^0 in the reverse direction, and eq (4) must be modified to give

$$-E\mathbf{F} = 2\pi^2 n^2 K[t_B(M_B - \overline{V}_{BI}\rho) - (1 + jt_c)(A_I - \overline{V}_I\rho)] \qquad (5)$$

It will be observed that this equation reduces to eq (4), as the proportion of iodine, and thus the transference number, t_c, decreases. Thus, using that equation and the limiting value of E/n^2K obtained by a short linear extrapolation from the data in table 3, the transference number of the sodium ion in 0.19112 normal NaI is found to be $t_{Na} = 0.3827$. An extrapolation of the E/n^2K values for KI in table 2, and Longsworth's [9] moving boundary figure, 0.4887, of the cation transference number at 0.2 *N*. for that salt were used in obtaining the values of the cell constants, $K = (r_2^2 - r_1^2)$, for eq 4 and 5. These constants were found to be 80.22 and 82.20 cm^{-2} for cells I and II, respectively.

To make these computations, and those that follow, it was necessary to use values of the partial molal and atomic volumes, $\overline{V}$, and of the solution densities, ρ. The determination of these constants, by the magnetic float method, is the subject of a recent contribution from this laboratory [10]. In that paper it is shown that $\overline{V}_{\mathrm{KI}}=46.12$ at the concentration used in these experiments. The effect of iodine on this constant was investigated and found to be small. For $\overline{V}_{\mathrm{NaI}}$ the value 35.92 was obtained. The partial atomic volume, $\overline{V}_{\mathrm{I}}$, of iodine was found to be constant at 29.96 for NaI solutions, but for KI solutions varied slightly according to the relation $\overline{V}_{\mathrm{I}}=29.98+1.46m$, in which m is the number of equivalents of I_2 in 1,000 g of solution. These values, based on our most recent data, replace those given in the earlier paper [3].

Table 4. *Equivalent conductances, Λ_m, of potassium- and sodium-iodide-iodine mixtures at 25° C*

Salt	Equivalent per liter		Λ_m	R
	Salt	I^0		
KI	0.18846	0	127.38	--------
Do	.18758	0.15398	115.23	0.82086
Do	.18967	0	127.30	--------
Do	.18921	.080881	120.92	.42746
Do	.19377	0	127.15	--------
Do	.19304	.12585	117.45	.65194
NaI	.19277	0	104.87	--------
Do	.19262	.02752	102.73	.14287
Do	.19246	.05361	100.75	.27854
Do	.19206	.12227	95.56	.63663
Do	.19184	.16062	92.72	.83729
Do	.19484	0	104.77	--------
Do	.19432	.08702	98.17	.44784
Do	.19391	.15662	93.05	.80770

With the aid of conductance measurements on KI and NaI solutions, with varying proportions of added iodine, a test of the validity of eq (5) may be made. The data are given in table 4, which is self-explanatory. The conductances were measured with a bridge of the type described by Shedlovsky [11] with conductance cells of the form employed in other work from this laboratory [12]. The measured equivalent conductances Λ_m (based on the salt concentration) may be expressed by the formula $(\Lambda_{\mathrm{KI}}-\Lambda_m)/R=15.20-3.2R$ for KI and $(\Lambda_{\mathrm{NaI}}-\Lambda_m)/R=15.10-0.51R$ for NaI, in which $R=C_{\mathrm{I}}^0/C_{\mathrm{BI}}$. Assuming Kohlrausch's law of independent ion mobilities, the measured equivalent conductance Λ_m is given by

$$\Lambda_m=\Lambda_{\mathrm{B}}+(1-R/j)\Lambda_{\mathrm{I}}+(R/j)\Lambda_{\mathrm{c}}$$

in which the Λ values are equivalent conductances of ion constituents, and j is, once more, the number of equivalents of uncharged iodine carried by the complex, C. From this equation

$$\Lambda_{\mathrm{c}}=\Lambda_{\mathrm{I}}-(j/R)(\Lambda_{\mathrm{KI}}-\Lambda_m) \tag{6}$$

and also

$$t_{\mathrm{B}}=\Lambda_{\mathrm{B}}/\Lambda_m \text{ and } t_{\mathrm{c}}=R\Lambda_{\mathrm{c}}/j\Lambda_m \tag{7}$$

since transference numbers are in this case the proportion of the total current carried by a given ion constituent. Substituting these values in eq (5), we have

$$-E\mathbf{F}=2\pi^2n^2K\left[\frac{\Lambda_{\mathrm{B}}}{\Lambda_m}(M_{\mathrm{BI}}-\overline{V}_{\mathrm{BI}}\rho)-\left(1+\frac{R\Lambda_{\mathrm{I}}-j(\Lambda_{\mathrm{BI}}-\Lambda_m)}{\Lambda_m}\right)(\Lambda_{\mathrm{I}}-\overline{V}_{\mathrm{I}}\rho)\right] \tag{8}$$

The values of Λ_{K}, Λ_{Na}, and Λ_{I} used with eq (6), (7), and (8) were obtained from the Λ_m figures given in table 4 for the solutions containing no free iodine, together with the transference number 0.4887 for KI from Longworth's work [9] and 0.3827 for NaI, as given above.

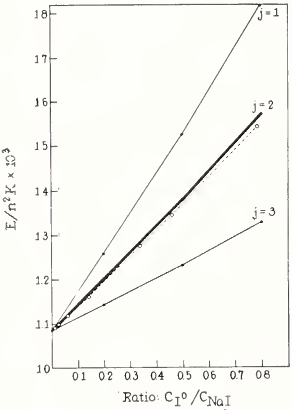

FIGURE 6.5. *Variation of E/n^2K values with the ratio $C_{\mathrm{I}}^0/C_{\mathrm{NaI}}$.*

Assuming that j in eq (8) is an integer, values of E/n^2K have been computed for $j=1$, 2, and 3. The results of this computation for the data for the NaI-I_2 solutions have been plotted against $R=C_{\mathrm{I}^0}C_{\mathrm{NaI}}$ in figure 6.5, on which the observed data for E/n^2K are shown as small circles, connected by a dotted line. The values follow closely the curve based on the assumption of $j=2$, which corresponds to the presence of the complex ion I_3^- in the solutions. There is, however, a small but progressively increasing deviation of the observed from the computed values as the proportion of free iodine is raised. This type of deviation is not found for the KI solutions, as is shown in table 2, the fourth and fifth columns of which contain observed and computed values, with $j=2$, in which there is close agreement, as was also found in our earlier work [3]. In these computations the values of R have been corrected for the small concentration of I_2 from the equilibrium $I^-+I_2=I_3^-$, the mass-law constant used [13] being 1.40×10^{-3}. Table 3 contains corresponding observed and computed figures for the NaI-I_2 solution. The variation of 1.3 percent in the E/n^2K value at the highest iodine concentration is probably connected with the assumption of the validity of Kohlrausch's additivity law for ion mobilities for solutions as concentrated as 0.2 molal, though the matter will be investigated further. This deviation does not affect the method for the purpose of obtaining transference numbers of the pure iodides, since that requires only a short extrapolation from the data for the solutions containing the smaller proportions of iodine.

Summary

The potentials, observed with a galvanic cell with two iodide-iodine electrodes, at two different radii in a centrifugal field, have been studied with solutions of KI and NaI, to which were added varying concentrations of iodine. Using a short extrapolation the transference numbers of NaI have been obtained. The earlier results, using KI, have been confirmed. These, when interpreted with the aid of conductance measurements, indicate the presence of the ionic complex I_3^-. A small deviation from the theory has been found with the results for NaI-I_2 solutions. The emf centrifuge used in our earlier work has been simplified, and a galvanic cell has been utilized, which avoids the collection of suspended particles on the electrodes.

References

[1] R. C. Tolman, Proc. Am. Acad. Arts Sci. **46,** 109 (1910); J. Am. Chem. Soc. **33,** 121 (1911).
[2] Th. Des Condres, Ann. Physik Chem. **49,** 284 (1893); **57,** 232 (1896).
[3] D. A. MacInnes and B. R. Ray, J. Am. Chem. Soc. **71,** 2987 (1949).
[4] B. Roger Ray and D. A. MacInnes, Rev. Sci. Instr. **20,** 52 (1949).
[5] L. G. Longsworth, J. Am. Chem. Soc. **57,** 1185 (1935).
[6] D. A. MacInnes, Rev. Sci. Instr. **14,** 14 (1943).
[7] T. W. Richards and A. G. Parker, Proc. Am. Acad. Arts Sci. **33,** 69 (1906).
[8] J. Beams, J. Applied Phys. **8,** 795 (1937).
[9] L. G. Longsworth, J. Am. Chem. Soc. **57,** 1185 (1935).
[10] D. A. MacInnes and M. O. Dayhoff, J. Am. Chem. Soc. **74,** 1017 (1952).
[11] T. Shedlovsky, J. Am. Chem. Soc. **52,** 1793 (1930).
[12] L. G. Longsworth, T. Shedlovsky, and D. A. MacInnes, J. Exp. Med. **70,** 399 (1939).
[13] G. Jones and B. B. Kaplan, J. Am. Chem. Soc. **50,** 1845 (1928).

Discussion

DR. A. L. FERGUSON, University of Michigan, Ann Arbor, Mich.: I would like to ask Dr. MacInnes if these calculations take into account the hydration of the ions?

DR. MACINNES: What we are measuring here is the Hittorf transference number which includes any effect due to hydration or differential carrying of water. To determine the so-called "true" transference number, and the degree of hydration, involves a great many unsolved questions. What we obtain is the thermodynamic transference number which is the net effect involving any hydration.

DR. FERGUSON: You have the volume there——the volume of what?

DR. MACINNES: That is the partial volume of one of the neutral components, which means the effect that you would get if you added a gram molecule of the substance to an infinite amount of the solution. It is obtained by differentiating an equation relating the density to the concentration.

DR. FERGUSON: But that is the volume of the iodine ion.

DR. MACINNES: No, it is a thermodynamic constant of an electrically neutral component such as KI, just as the transference number is a thermodynamic quantity. The actual galvanic cell mechanism is probably more complex than we assume but partial molal volumes are measurable and the connections are thermodynamic.

Dr. Ferguson: The difference in potential is really a difference produced by the concentration of iodide ion, is it not?

Dr. MacInnes: No, none of this treatment holds unless this solution remains uniform in composition. If we went up from speeds around 7,200 to, say, 60,000, the KI and I_2 move to the outer electrode in the centrifuge and the sedimentation that tends to take place would take place, but the potential would go to zero. What we are measuring is really an electrical measurement of the tendency of that sedimentation to occur. What happens is that in a centrifugal field, when you have moved, for instance, I_2 toward the center of rotation, it has a greater chemical potential than it does further out, because it would take work to move it from the one place to the other.

The solution must be uniform and if sedimentation takes place then our results are off. Now, there is some evidence Dr. Dayhoff has obtained that if you go from aqueous solutions to methanol as solvent there is enough difference between the densities of the solutes and of the solvent so a limited amount of sedimentation takes place at the speeds we used and the potentials tend to drift down. The indication is that we can extrapolate to zero time and get results, although possibly not as accurately as with aqueous solutions.

Dr. J. Th. G. Overbeek, University of Utrecht, Utrecht, The Netherlands: Isn't there a correction for the effect of the centrifugal force on the partial molal volumes?

Dr. MacInnes: Yes, but that correction is outside our limit of error at low speeds.

Dr. Overbeek: Even at 7,000?

Dr. MacInnes: Yes. Tolman made the first computations on that point, and he decided it was outside the limit of error we are dealing with.

Dr. Overbeek: The equation is similar to the one Tolman used. He related the difference in the potential to the difference in the mobilities of the positive and negative ions.

Dr. MacInnes: I have given a thermodynamic derivation and he gave a mixed kinetic and thermodynamic one. His treatment is valid, but it is not of much help. He obtained the same form as the equation I have used, except that a correction term for I_2-iodide complex was not contained in it.

7. Moving Boundary Measurements in Methanol and and Water Solution with Indicator Concentrations Below the Critical Kohlrausch Value

By A. R. Gordon [1] and R. L. Kay [1]

If in a moving-boundary determination of a transference number, the indicator concentration be less than that satisfying the Kohlrausch relation, the apparent transference number, computed from the observed boundary movement, is in general less than its true value. Experiments under these conditions with KCl-potassium diiodobenzoate (KDB) boundaries in methanol solution and with KCl-KIO_3 and KCl-$CdCl_2$ boundaries in aqueous solution, show that the actual indicator concentration a few minutes after the boundary has been formed is greater than its initial value, the concentration behind the boundary being determined by conductance measurements in situ. Such upward adjustment of indicator concentration toward the Kohlrausch value can in favorable conditions be practically complete; for example, in a cell with rising boundary in which the junction was originally formed in the vertical rather than the horizontal plane, correct values of the transference number were obtained from the observed boundary movement with initial indicator concentrations 60 percent below the Kohlrausch value. A theoretical explanation is offered, and the general significance of this effect in moving boundary measurements is discussed.

In the conventional determination of the transference number of a salt MA from the movement of the two-salt boundary MA|MB, it was shown by Kohlrausch [1] [2] that for a steady state

$$t/t_i = C/C_i. \tag{1}$$

Here t and t_i are the transference numbers of the A ion in the leading solution and of the B ion in the indicator solution; C and C_i, the corresponding concentrations. Thus, with a rising boundary, if the indicator ion concentration when the junction is formed is greater (for the given C) than the Kohlrausch concentration C_i^*, defined by eq (1), a diffusion boundary results at the initial position of the junction, and the column of indicator solution formed behind the boundary will have the concentration C_i^*. This question has been discussed in definitive papers by Longsworth [2] and by Dole [3] who have extended the theory to complex polysalt systems.

One case curiously enough, has received little or no attention. If with a rising boundary the indicator concentration is less than the Kohlrausch value, it has been general experience that an apparent transference number, computed from the observed boundary movement, is less than the true value, i. e., if C be expressed in equivalents

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[2] Figures in brackets indicate the literature references on p. 57.

per liter, and V be the volume in liters swept out by the boundary per faraday, CV is less than t. Moreover, under these conditions, the observed CV is found in some cases to change as electrolysis proceeds (a phenomenon sometimes referred to as progression), is frequently dependent on current density, and for given current and indicator concentration is not too reproducible. Transference measurements in this laboratory on nonaqueous solvents, for which the problem of finding suitable indicators and appropriate indicator concentrations is more serious than with water as solvent, led us to study the significance of moving boundary measurements under these conditions.

While case $C_i < C_i^*$ has not been considered hitherto, it can be handled, approximately at any rate, by a modification of Dole's treatment [3]. Define the positive quantities x and y

$$C_i = C_i^* - x \tag{2}$$

$$CV = t - y. \tag{3}$$

The flux of M ion per faraday into a volume enclosed between arbitrary fixed planes above and below the boundary is $(1-t)-(1-t_i)$. This must be compensated by boundary movement; if the assumption, valid for steady-state boundaries [3], be made that the boundary may be treated as a mathematical plane, then

$$(1-t)-(1-t_i) = V(C_i - C). \tag{4}$$

Replacing V by $(t-y)/C$, and noting the relation (1), eq (4) may be rearranged to give

$$y = t_i(x/C_i^*)/(1 - t_i/t + t_i x/tC_i^*). \tag{5}$$

A series of measurements to test eq (5) was therefore undertaken with 0.01 N KCl|KDB boundaries in anhydrous methanol at 25°C. The preparation of chemicals and solutions and the experimental technique for the methanol and the subsequent aqueous measurements have been previously described [4,5]. Cd and Ag—AgCl electrodes on the closed side of the cell served for anion and cation boundaries, respectively; in all cells the graduated tube was 2.5 mm internal diameter corresponding to a cross-sectional area of 0.05 cm^2. The observed CV have been corrected for solvent conductance and volume change at the electrode [6]. The cell (denoted III) is shown in figure 1 of reference [5]; the shearing mechanism in greater detail in figure 7.1 of this paper. The position of the channelled stopcock in the figure is that for filling; by rotating the cock 90° clockwise, indicator solution MB is brought under the leading solution MA at the base of the graduated tube. Results are shown by the open circles of figure 7.2, the abscissas giving the initial indicator concentration C_i^0 in equivalents per liter. The plot suggests a Kohlrausch concentration of approximately 0.008 N, in reasonable agreement with that predicted from conductance measurements on KDB solutions (assuming independent ionic mobilities) and confirmed by conductance measurements in situ, as described below.

Results with initial indicator concentrations below the Kohlrausch value, however, are in definite disagreement with eq (5) if C_i^0 be assumed the same as the effective C_i. To take the measurement at

0.006 N as example: y is 0.0027, t_i and t are 0.4 and 0.5 respectively; thus x/C_i^* should be of the order of 1/750 instead of 1/4, i. e., the actual boundary movement is consistent with an indicator concentration only slightly below the Kohlrausch. To test this, a cell was constructed similar to cell III, but with two fine Pt wires sealed in the walls opposite each other about 5 cm above the stopcock [7, 8]. When the boundary had passed the wires, the current was momentarily interrupted, and resistance between the probe electrodes was determined by an a-c bridge. Naturally, the conditions for such a measurement are far from ideal, and the precision is poor—of the order of 1 or 2 percent. The cell was calibrated in preliminary measurements by determining the apparent resistance for known concentrations of indicator solution. Measurements with $C_i^0 > C_i^*$ gave values of the adjusted indicator concentration of 0.0080 ±0.0001 N (see above).

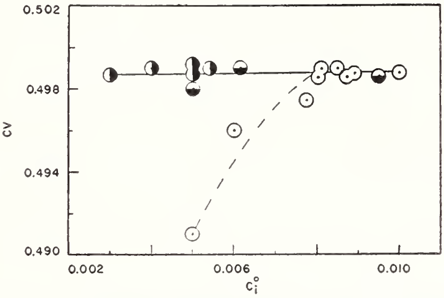

Figure 7.1. *Shearing mechanism of cells III and IV.*

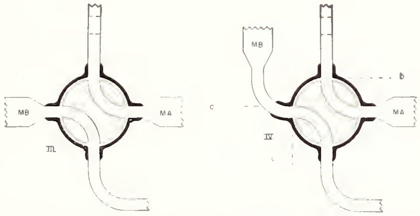

Figure 7.2. *System 0.01 N* KCl|KDB *in methanol at 25° C.*

Current, 0.35 ma. ⊙, cell III; ◒, cell IV, top shearing; ◑, cell IV, side shearing.

With an initial indicator concentration of 0.0060 N, the indicator concentration behind the boundary was found (within experimental precision) to be indistinguishable from this value, as predicted by eq (5).

A glance at figure 7.1 shows that if the column of indicator solution in the graduated tube is at a higher concentration than that in the large filling tube to the left, density differences, even if slight, will tend to decrease the concentration in the graduated tube. Consequently, if a cell were employed which would permit density stabilization in a relatively small volume of indicator solution, one might expect the upward adjustment of concentration to be even more marked. To test this, cell IV of figure 7.1 was constructed, since with it, density stabilization involves the solution only to the level a, i. e., the only reservoir in which (ignoring diffusion) indicator concentration must be increased by density mixing from the graduated tube will be the channel from *a* to *b*.

We also found, to our surprise, that it was possible to form the boundary in the vertical plane at *c*, provided the potential was applied to the cell before rotating the stopcock 90° counterclockwise. This has the advantage that experiments can be carried out with initial indicator concentrations so low that the indicator solution is actually less dense than the leading solution. As will be shown below, an experiment under these conditions is possible because initial upward adjustment of indicator concentration is exceedingly rapid. In cell IV, the volumes *ac* and *ab* (determined by filling with weighed amounts of Hg) are approximately 0.05 and 0.09 cm^3, both values being probably somewhat overestimates.

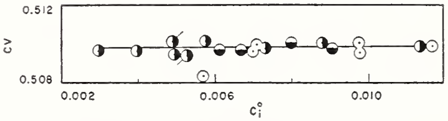

FIGURE 7.3. *System 0.01 N* KCl|KIO$_3$ *in water at 25° C.*

⊙, Cell III; ◒, cell IV, top shearing; ◑, cell IV, side shearing. Current, 0.49 ma, except as noted: ◑, 0.39 ma; ◑, 0.65 ma.

The results with cell IV are also indicated in figure 7.2 when the junction is formed at *b* (top shearing) and at *c* (side shearing). It should be noted that in none of the measurements was there any detectable progression, so that even with cell III at initial indicator concentrations below the Kohlrausch value, a pseudo-steady state must have been attained. The solid line in the figure corresponds to the transference number [4] of chloride ion at this concentration (0.4987), so that with side shearing at any rate, upward adjustment of indicator concentration to the Kohlrausch value must have been practically complete.

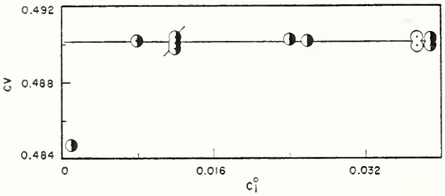

FIGURE 7.4. *System 0.02 N* KCl|CdCl$_2$ *in water at 25° C.*

⊙, Cell III; ◑, cell IV, side shearing. Current, 1.01 ma, except as noted: ◑, 0.71 ma; ◑, 1.17 ma.

Measurements with 0.01 *N* KCl|KIO$_3$ and 0.02 *N* KCl|CdCl$_2$ boundaries in aqueous solution are shown in figures 7.3 and 7.4; here the solid lines correspond to the transference numbers of chloride in 0.01 *N* solution and of potassium in 0.02 *N* solution [5,9], viz., 0.5098 and 0.4901. In neither series was there any progression except in the experiment with 0.001 *N* CdCl$_2$ as indicator, and the observed CV was independent of current. The Kohlrausch concentrations, determined by conductance measurements behind the boundary with $C_i^0 > C_i^*$, are 0.0068 *N* for the iodate and 0.018_0 *N* for the cadmium salt; the ratio of the cadmium and potassium ion concentrations is in reasonable agreement with Cady and Longsworth's value (0.87) for 0.1 *N* KCl solution [7]. The results suggest that here also upward adjustment of indicator concentration to the Kohlrausch value must be practically complete in cell IV except at very low indicator concentrations. This was confirmed by conductance measurements on the indicator solutions with values of C_i^0 well below C_i^*; with both systems, adjustment was complete within the low precision attainable in the measurements.

The question of a possible mechanism for the adjustment process at once arises. It will be remembered that eq (5) was obtained from a consideration of the material balance for the M ion in a volume enclosed between fixed planes above and below the boundary. A similar argument shows that the leading solution lying between the boundary and the upper plane will be deficient in the A ion constituent by y equivalents per faraday, while the indicator solution lying between the lower plane and the boundary will have an equal excess of the B ion constituent. In other words, for electrical neutrality the leading solution will have an excess of y equivalents of M ion and the indicator solution an equal deficit. Neutrality can then be maintained by the passage of y equivalents of M across the boundary in addition to the one equivalent per faraday normally carried by the current. The net effect per faraday is that the solution lying between the boundary and the upper plane contains y equivalents less of MA and the corresponding volume of indicator solution y equivalents more of MB than if their bulk concentrations had been maintained. Density stirring will then tend to decrease the concentration of the leading solution as a whole, and to increase that of the significant part of the indicator solution (in cell IV, between *a* and the boundary). In the actual cells, the relatively large reservoir of leading solution at the top of the graduated tube will make the net decrease in concentration negligible, and in what follows it will be assumed that density stirring maintains the concentration of the leading solution sensibly at its initial value.

The question remains whether a mechanism of the type proposed can account for the actual increases in indicator concentration encountered. Assume, following Dole [3], that diffusion may be neglected, and that the transference numbers are independent of concentration. During a short interval of the electrolysis, let the significant volume (see above) of the indicator solution be V_i, and during this interval let df faradays pass, the corresponding boundary movement being $dV=dV_i$. Since, from eq (3) and (4), $t_i-y=C_iV$,

$$(t_i-y)df=(C_i^*-x)dV_i. \tag{6}$$

During this interval, ydf equivalents of M will cross the boundary to preserve electroneutrality, with a resultant change in concentration of the indicator solution given by

$$ydf=-V_idx. \tag{7}$$

Eliminate df from eq (6) and (7), and introduce the abbreviations $t_i/t=r$, $y/t_i=p$, $x/C_i^*=q$. Equation (7) then becomes

$$-dq=\{p(1-q)/(1-p)\}(dV_i/V_i), \tag{8}$$

in which from eq (5), $p=q/(1-r+rq)$. After making this substitution and simplifying, there results

$$dV_i/V_i=-(1-r)dq/q \tag{9a}$$

$$\ln V_i/V_i^0=(1-r)\ln q^0/q, \tag{9b}$$

where V_i^0 is the initial significant volume of indicator solution (*ac* in cell IV with side shearing) and $q^0=(C_i^*-C_i^0)/C_i^*$.

The significance of eq (9) can perhaps be best illustrated by a numerical example. For the measurement with lowest initial indicator ion concentration of figure 7.2, $q^0=5/8$, $r=4/5$, and $V_i^0=0.05$ cm^3. If it be required that q fall to 0.0001, with a resultant error in the measured CV of the order of 0.0002, V_i will be 0.29 cm^3, i. e., the boundary will have advanced only 4 cm up the graduated tube and still be 1.5 cm below the first line.

The importance of the ratio r of the transference numbers in the adjustment process may be illustrated by the experiment with the most dilute iodate solution of figure 7.3. Here r is approximately 2/3 and q^0 is 38/68; when the boundary has reached the first graduation ($V_i=0.36$ cm^3) q will have fallen only to 0.0015. Since $t_i=0.35$, eq (5) predicts an error in CV measured in the immediate neighborhood of the first line of 0.0016, and this is considerably greater than the experimental precision of the measured t, which is of the order of 0.0002. The actual spacing of the graduations in cell IV must however be born in mind. There is a lower group of four lines, approximately 1.7 cm apart, the lowest 5.5 cm above the stopcock, and a similar upper group of four lines, the lowest 25 cm above b. To obtain precision in the time measurement, the quantities used to compute the transference number are the intervals between the lines of the first group and those of the second. A rough estimate can be made of the error in t, computed in this way, by calculating q (and thus y) for various positions of the boundary. Although q does not fall to 0.0001 until the boundary is 5 cm above the fourth line, the error in the computed t even in the most unfavorable case—line 1 to line 5—is found by graphical integration to be only 0.0002; this is probably the explanation for the fact that no progression was observed in this experiment.

While the final stages of indicator adjustment may be relatively slow, as in the case just considered, initial adjustment is rapid. For example, in the $CdCl_2$ measurements of figure 7.4, r is 0.9. In the experiment with $C_i^0=0.001$ N, the indicator concentration according to eq (9) will have increased to 0.012 N (the concentration for which the density of $CdCl_2$ solutions is the same as that of 0.02 N KCl) when V_i has increased from its initial value of 0.05 cm^3 to 0.06_5 cm^3, a boundary movement of only 3 mm through the channel in the stopcock.

So far no measurements of this kind have been carried out with falling boundaries, but experience suggests [6,10] that adjustment must also take place here, since measurements with such boundaries give the transference number over small ranges of initial indicator concentration. A mechanism of the type discussed above provides a possible explanation for this fact, which is otherwise difficult to explain. If the initial indicator concentration is less than the Kohlrausch value, the case is the same as with rising boundaries, except that density stirring will not help to maintain uniform concentrations throughout the two solutions, and the measured CV, if adjustment is not complete, should be less than t, just as is found in practice. The case $C_i^0 > C_i^*$ with a falling boundary requires perhaps more attention. Here CV tends to be greater than t [6, 10], but if in eq (2) and (3), $-x$ and $-y$ be replaced by $+x$ and $+y$, eq (5) becomes [3]

$$y = t_i(x/C_i^*)/(1 - t_i/t - t_i x/tC_i^*). \tag{10}$$

To maintain electroneutrality, there will be a transfer of y equivalents of the common ion *from* the indicator solution *to* the leading solution, with a resultant gain in the leading solution of y equivalents of salt and a loss in the indicator solution of an equal number of equivalents of indicator; moreover, here, density stirring should ensure uniform composition throughout the significant volumes of both solutions. Naturally, a mechanism such as that proposed must be tested in the laboratory, and measurements with falling boundaries will shortly be under way. If the event show that an adjustment process is operative, it will be of some importance in measurements with nonaqueous solvents, since many indicator ions, suitable as far as mobility is concerned, can only be used in such systems with falling boundaries.

It is also evident that a more precise determination of the indicator concentration behind the boundary is desirable, particularly during the early stages of the adjustment process, and experiments to this end are also under way. Finally, one would expect during adjustment a steep potential gradient across the boundary. An experimental verification of this is a matter of some difficulty, as such a gradient would be more or less masked by the large ohmic drops of the order of 5 to 10 v/cm that are normally encountered in moving boundary measurements. Nevertheless, a study of the potential across the boundary, if possible, should supply useful information as to the nature of the processes that are occurring.

In conclusion, we express our thanks to the National Research Council of Canada for a grant in aid of this research, and for the award to one of us (R. L. K.) of a studentship and a fellowship.

Note added in proof: For recent developments in this research, see A. R. Gordon and R. L. Kay, J. Chem. Phys. **21**, 131 (1953).

References

[1] F. Kohlrausch, Ann. Physik. Chem. **62**, 209 (1897).

[2] L. G. Longsworth, J. Am. Chem. Soc. **67**, 1109 (1945).

[3] V. P. Dole, J. Am. Chem. Soc. **67**, 1119 (1945).

[4] J. A. Davies, R. L. Kay, and A. R. Gordon, J. Chem. Phys. **19**, 749 (1951).

[5] R. W. Allgood, D. J. LeRoy, and A. R. Gordon, J. Chem. Phys. **8**, 418 (1940).

[6] D. J. MacInnes and L. G. Longsworth, Chem. Rev. **11**, 171 (1932).

[7] H. P. Cady and L. G. Longsworth, J. Am. Chem. Soc. **51**, 1656 (1929).

[8] G. S. Hartley, E. Drew, and B. Collie, Trans. Faraday Soc. **30**, 648 (1934).

[9] L. G. Longsworth, J. Am. Chem. Soc. **54**, 2741 (1932).

[10] D. J. MacInnes, et al., J. Am. Chem. Soc. **45**, 2246 (1923); **46**, 1398 (1924); **47**, 1009 (1925); **49**, 1710 (1927).

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[3] There is one significant difference between rising and falling boundaries. With a rising boundary, C_i is less than C; with a falling boundary, e. g., KCl | LiCl, this is not necessarily so. This emphasizes the fact that the conservation eq (4) must be interpreted with caution, since, as written, it would predict an infinite value for V when $C = C_i$, and a negative value when $C_i > C$. The apparent contradiction comes from the fact that boundary movement under these conditions cannot counterbalance the flux of the M ion in the reference volume. It is nevertheless curious that apparently no measurements at such indicator concentrations have been carried out. We propose to investigate the case $C_i > C$, but for the moment, one might hazard the guess that no true two-salt boundary would be formed.

Discussion

Dr. L. G. Longsworth, Rockefeller Institute for Medical Research, New York, N. Y.: May I ask Dr. Gordon if he considers the results of his work as indicative of the effectiveness of density stirring?

Dr. A. R. Gordon: Well, it is hard to say, particularly with the low concentrations we were working with. It seems to me that the very striking difference that you get with those two types of cell indicates that density stirring is probably a good deal more effective than we sometimes think it is. I think I would go that far anyway.

Dr. MacInnes, Rockefeller Institute for Medical Research, New York, N. Y.: I may have missed the explanation of the deviation you get from your indicator concentration.

Dr. Gordon: (Illustrating on blackboard.) Suppose MA is now the trailing solution and MB is the leading. Your boundary is now going down. Suppose MA is too strong, corresponding to your results over here. The boundary will move too fast. You will have a deficit of the indicator ion and an excess of the leading ion because the boundary is moving faster than corresponds to the flux through the reference plane. The trailing solution is long in M ion and the leading is short. It is then just the same type of arithmetic as you had over here.

8. Moving Boundary Separation of Salt Mixtures

By L. G. Longsworth[1]

Introduction

In the moving boundary method for measurement of transference numbers, or for electrophoretic analysis of protein mixtures, gravitational stability requires that each solution that is formed by passage of current be less dense than the one underneath and more dense than the one above. On the other hand if the moving boundary channel is filed with a stationary, dispersed phase, e. g., paper [3, 5] ,[2] glass powder [14], agar [13], silica-gel [2], etc., remixing by gravity appears to be confined to interstices provided by such a packing and separations can thus be effected that are not possible in the Tiselius cell. However, it is only in an unpacked channel that precise optical methods can be used to locate the boundaries and that disturbing effects of electro-osmosis and adsorption can be avoided. It appeared worth while, therefore, to try experiments in the Tiselius cell analogous to those of Kendall, et al., in agar [6], attention being restricted to those boundary systems that would be expected to retain gravitational stability in an unpacked channel.

The principle of the method will be clear from the following outline of a typical experiment. Suppose a short column of an aqueous mixture of Ba, Ca, and Mg chlorides, called the intermediate solution, is interposed, in the vertical channel of the Tiselius cell, between a denser one of CsCl, the leading solution, and a lighter one of LiCl, the trailing solution. This is shown diagrammatically in figure 8.1, a. Since the mobilities, u, of these cations are in the order $u_{\mathrm{Cs}} > u_{\mathrm{Ba}} > u_{\mathrm{Ca}} > u_{\mathrm{Mg}} > u_{\mathrm{Li}}$, each can serve as the trailing ion for the preceding member of the series to give a sharp, two-salt type of moving boundary [9]. Consequently, on passage of current through the solutions in the direction indicated the three species in the mixture will separate as they follow the cesium down the channel until eventually the distribution shown in figure 8.1, b, is attained. The schlieren scanning pattern of figure 8.4, j, shows the refractive index gradients in each of the four boundaries of the two-salt type that are developed in this experiment.

Since each of the solutions of figure 8.1, b, is present in a portion of the channel originally occupied by the CsCl, the Kohlrausch [7, 4] function, $\omega_i = C_i/T_i$, for each has the same value as that, $C_{\mathrm{Cs}}/T_{\mathrm{Cs}}$, for the leading solution. Here C is the equivalent concentration, and T the transference number. Moreover, all of the $BaCl_2$, say, in the intermediate solution of figure 8.1, a, is now present between the two leading boundaries at the so-called Kohlrausch concentration, $C_{\mathrm{Ba}} = C_{\mathrm{Cs}} T_{\mathrm{Ba}}/T_{\mathrm{Cs}}$, and the volume between these boundaries is thus a measure of the barium content of the original mixture. In a channel

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[2] Figures in brackets indicate the literature references on p. 68.

of uniform and known cross section analysis of the mixture is reduced, therefore, to a measurement of boundary position, instead of pattern area as in the conventional electrophoretic analysis of protein mixtures.

Essential for gravitational stability of the system is a parallelism, either direct or inverse, between mobilities and densities of the solutions at the Kohlrausch concentrations. In the present example the density increases with the mobility and the boundaries descend. This appears to be the most common behavior. If, however, the parallelism is an inverse one, i. e., the trailing solution is the densest, the boundaries must rise.

Experimental

The cell used in the present research is shown in figure 8.2 and is identical with that employed for concentration [8] and solvent boundary [11] studies except that a section of 2-cm height is inserted at A. The procedure for filling the cell and forming the boundaries initially is as follows:

With the cell assembled, except for the insertion of the cups, C and C′, the leading solution is introduced to the level of the arrows and the contents of section B isolated by shifting it to the right. The right side of A is then rinsed and filled with the intermediate solution, the filling extending above the junction of A and the top section, while the left side is filled by the addition of more leading solution. Following displacement of section A to the left, B is returned to the center position. The right side of the top section, including the electrode cup, C, is now rinsed and filled with trailing solution while leading solution is added to the left side. If the leading salt is relatively costly, e. g., CsCl, the left side of the top section may equally well be filled with a less dense solution of another chloride, say KCl. Following insertion of the electrodes and introduction of 5-ml portions of a concentrated chloride solution around them, the right electrode

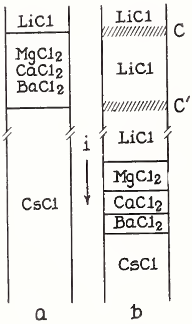

FIGURE 8.1. *Diagrammatic representation of a moving boundary separation of a typical salt mixture.*

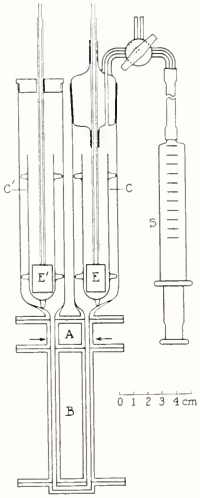

FIGURE 8.2. *The moving-boundary cell.*

vessel is closed, connection with the syringe S of the compensator being retained. Although not shown in the figure the piston of this syringe is driven, with the aid of a threaded rod and gear box, by a small synchronous motor. In the present research the compensator is used to withdraw solution from the cell at a uniform rate, thereby providing a counterflow in the channel against which the boundaries move.

Now, by returning section A to the center position, the 2-cm column of intermediate solution is interposed between the leading and trailing solutions, and, if a potential difference has previously been applied across the electrodes, the boundaries begin their descent. Since the densities of most salt solutions increase with increasing concentration, gravitational stability requires that the value, ω_I, of the Kohlrausch function for the intermediate solution be, in the case of a descending boundary system, equal to or less than that, ω_L, of the leading solution [12, 9]. In practice the intermediate solution is diluted so that $\omega_I < \omega_L$, in which case a concentration gradient remains, in the absence of a counterflow, at the level of the initial boundary between the intermediate and leading solutions, C′ of figure 8.1, b. Similarly, $\omega_T < \omega_I$ and a second concentration boundary remains at C, figure 8.1, b. Since they were not shifted into view from behind the opaque horizontal plates of the cell these boundaries do not appear in the patterns of this paper. In the present research one salt, tetra *n*-propyl ammonium chloride, whose solutions are less dense than water, has been used to follow LiCl at a descending boundary in which case ω_T is made greater than ω_I initially.

Since most of the separations are not complete by the time the boundaries move through the 86-mm clear height of the Tieslius cell, a counterflow is begun, with the aid of the compensator, soon after the boundaries are in the field of the schlieren camera. The counterflow is adjusted so that the boundaries stay in this field until the separation is complete, but it is unnecessary to balance the migration exactly. In most instances the boundaries move slowly with respect to the apparatus. Because of this movement, and the not inappreciable time required for the scanning process, some of the sharp peaks in the patterns appear to be tilted. Although not apparent in most of the patterns, examination of the schlieren bands as the diaphragm approached the undeviated silt image indicated that the counterflow also disturbed slightly the weak gradients at the edges of a boundary. This is probably due to drainage of solution adhering to the wall of the channel and produced the irregularity at k in figure 8.4, j. From the frequent occurrence of inverted peaks in the patterns, it will also be evident that the densest solution at a boundary does not always have the highest refractive index.

Separation Process

It is an interesting feature of the unpacked channel that all stages in the separation of ions of the intermediate solution can be observed and recorded. In the case of the barium-calcium-magnesium mixture an early stage in the process is shown schematically in figure 8.3, a, whereas the corresponding patterns are given in figure 8.4, a-c. At this stage, some of the original mixture, concentrated on passage through the gradient at C′, figure 8.1, b, so that its Kohlrausch function has the value ω_L, is still present between the boundaries at E′ and E″, but this zone soon disappears by their coalescence to give the boundary E of figure 8.3, b, and 8.4, d, e. This boundary then splits and a zone of the pure calcium salt appears as shown schematically between B″ and C″, figure 8.3, c. In the present example the next stage is the disappearance of the calcium-magnesium mixture between B′ and B″ of figure 8.3, c, but this occurs so soon after the splitting of E, figure 8.3, b, that a record of the six boundaries indicated in figure 8.3, c, was not obtained. However, the increase in the pattern area accompanying the coalescence of the B′ and B″ boundaries of figure 8.3, c, is clearly evident in figure 8.4, f. Since calcium is but slightly less mobile than barium, the final stage in the process is the disappearance of the calcium-barium zone by coalescence of the boundaries C′ and C″ of figure 8.3, c, to give the steady-state distribution, figure 8.3, d. The patterns of figure 8.4, f-j, illustrate this. If current is

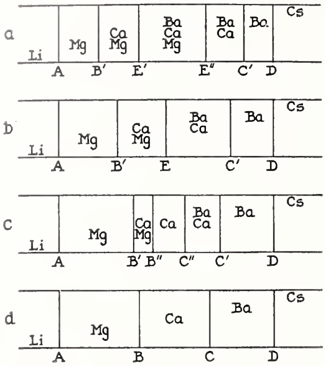

FIGURE 8.3. *Schematic representation of the separation process.*

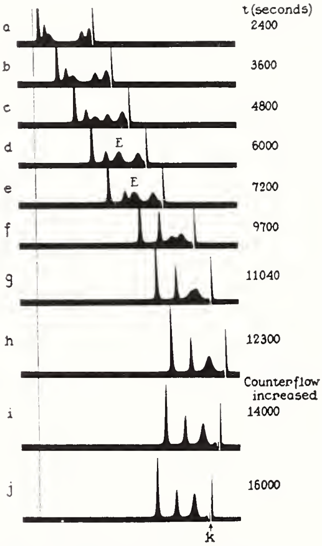

FIGURE 8.4. *Patterns obtained during the separation of a mixture of barium, calcium, and magnesium chlorides.*

constant and electrode processes do not introduce foreign ions into the channel, these boundaries then continue to move indefinitely with no further change in the pattern.

In the unscrambling of mixtures containing more than two or three salts, the patterns become increasingly complex. Moreover, with a column of intermediate solution initially 2 cm. in height the overlapping of the numerous boundaries that develop during the separation tend to obscure them.

Results

Some of the systems that have been studied are listed in table 1 and the corresponding steady-state patterns are shown in figures 8.5 and 8.6. Those of figure 8.5 illustrate the essential features of the method as a technique for quantitative analysis. As the proportions of barium, calcium, and magnesium in the intermediate solution are varied a corresponding change in the length of the zone of separated salt occurs in the pattern, figure 8.5, a, c-f. Comparison of figure 8.5, a, b, shows, on the other hand, that an increase in the concentration of the leading salt causes a contraction of the zones without changing appreciably the relative positions of the boundaries.

Table 1. *Compositions of the solutions for which steady-state patterns are given*

All concentrations are in millimoles per liter of solution.

Leading solution	Intermediate solution			Trailing solution	Figure
100 CsCl	12.5 $BaCl_2$	12.5 $CaCl_2$	12.5 $MgCl_2$	50 LiCl	5, a
100 CsCl	25.0 $BaCl_2$	6.2 $CaCl_2$	6.2 $MgCl_2$	50 LiCl	5, d
100 CsCl	6.2 $BaCl_2$	25.0 $CaCl_2$	6.2 $MgCl_2$	50 LiCl	5, c
100 CsCl	6.2 $BaCl_2$	6.2 $CaCl_2$	25.0 $MgCl_2$	50 LiCl	5, f
100 CsCl	3.1 $BaCl_2$	31.2 $CaCl_2$	3.1 $MgCl_2$	50 LiCl	5, e
150 CsCl	12.5 $BaCl_2$	12.5 $CaCl_2$	12.5 $MgCl_2$	50 LiCl	5, b
100 CsCl	25.0 KCl	25.0 NaCl	25.0 LiCl	100 $N(C_3H_7)_4Cl$	6, a
200 KCl	100 $KClO_3$	100 $KBrO_3$		200 KIO_3	6, b
100 $NaIO_3$	22 Na glycine	22 Na alanine	22 Na valine	50 Na leucine	6, c
200 NaCl	20 Na formate 20 Na butyrate	20 Na acetate 20 Na valerate	20 Na propionate. 20 Na caproate	67 Na caprylate	6, d, e
200 KCl	25 KCl	100 NaCl	25 LiCl	100 LiCl	7, a

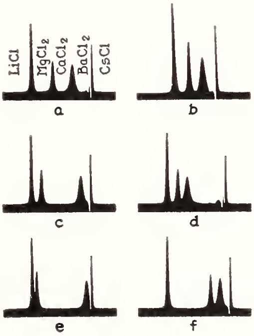

Figure 8.5. *Patterns illustrating the use of the method for quantitative analysis.*

If the necessary transference data are available, as in the case of the chlorate-bromate mixtures, the procedure described below may be used. Of the systems studied this is the only one in which the boundaries ascended and the pattern of one of the mixtures is given in figure 8.6, b. Moreover, the work with this system was done before the 2-cm section, A of figure 8.2, was available, in which case an accurately known volume of intermediate solution was introduced, with the aid of the compensator and a thin-walled glass capillary tube, under the leading solution before forming the boundary with the trailing solution. In the experiment represented by figure 8.6, b, 1.047 ml of the intermediate solution was used, containing 104.7 micromoles each of chlorate and bromate. After separation the heights of the chlorate and bromate zones were 8.01 and 8.49 mm, respectively, in a channel whose cross section was 0.7286 cm^2. Moreover, the Kohlrausch concentrations are $C_{\mathrm{Cl}}T_{\mathrm{ClO_3}}/T_{\mathrm{Cl}}=200\times0.4538/0.5057=179.5$ for the chlorate and $200\times0.423/0.5057=167.3$ for the bromate, so that the values found are 104.8 and 103.6, respectively. These results, together with those for two other mixtures, are given in table 2, where the average difference between the "taken" and "found" values is 0.6 μm, or 0.7 percent.

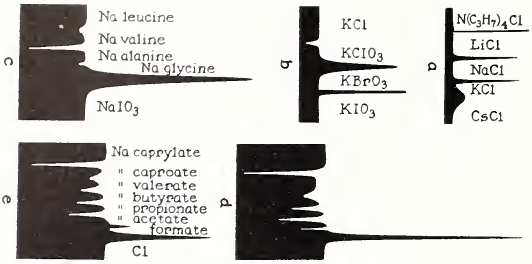

FIGURE 8.6. *Steady-state patterns of typical systems.*

TABLE 2. *Results of moving boundary analyses of chlorate-bromate mixtures*

Average deviation=0.6 μm, or 0.7%

Experiment	Micromoles chlorate		Micromoles bromate	
	Taken	Found	Taken	Found
1	104.7	104.8	104.7	103.6
2	157.1	157.6	55.3	56.2
3	52.4	52.0	153.6	152.8

If the transference data are not available an intermediate solution of known composition can be used to calibrate the system. This is illustrated by the data of table 3 for the barium-calcium-magnesium mixtures. Here the average difference between the observed and computed values is 0.4 μm, or 4.5 percent.

Discussion

In duplicate experiments reproducibility of boundary separations is much better than the differences of tables 2 and 3 would indicate. A possible source of error is that the pattern has been obtained before the steady state is reached. This error may be eliminated, however, by recording patterns at intervals after apparent attainment of the steady state and comparing the boundary separations. These should be constant within the limits of error of measurement of boundary position, i. e., 0.01 mm. Moreover, at a given current the height of each peak in the pattern is constant. Because of the variation of the transference number with both concentration and temperature, it is essential to use the same leading solution, and approximately the same current, in an analytical experiment as in the calibrating one.

TABLE 3. *Results of moving boundary analyses of barium-calcium-magnesium mixtures*

Average deviation=0.4 μm, or 4.5%

Figure 5	Micromoles barium		Micromoles calcium		Micromoles magnesium	
	Taken	Found	Taken	Found	Taken	Found
a	18.8	19.1	18.8	18.8	18.8	18.5
d	37.5	(*)	9.4	8.9	9.4	9.2
c	9.4	9.7	37.5	(*)	9.4	8.7
f	9.4	10.0	9.4	9.0	37.5	(*)
e	4.7	4.9	46.9	47.4	4.7	3.9

*Used in calibration.

Another source of error is in the location of a boundary. In the present research the gradients in most of the boundaries have been symmetrical about the ordinate through the maximum and the position has been taken as that of the midpoint of a chord at some value of the gradient common to all boundaries in the pattern. While this procedure eliminates any error arising from the movement of boundaries during the scanning process, the value obtained is probably not the same as if the boundary was infinitely sharp. A boundary across which only one solute disappears is correctly located by the first moment of the gradient curve [8]. This is not generally true, however, at a boundary, such as those of the present research, across which two salts disappear. This is a result of the unequal refractivities of the two salts and the complex balance between the mixing effect of diffusion and the separating effect of ion migration [9]. From both experiment and theory the correct location of a two-salt boundary is a difficult problem and the lack of a solution limits the precision of the method for quantitative analyses. For example, the percentage errors in table 3 are larger than in table 2 and arise, possibly, from the fact that in the one system only uni-univalent salts are involved whereas in the other the more complex $CsCl$-$BaCl_2$ and $MgCl_2$-$LiCl$ boundaries occur.

A vivid impression of the complexity of a two-salt boundary is obtained from the behavior of the gradients in some of them on interruption of the current. For example, the steady state pattern of a column of NaCl between 0.2 normal KCl and LiCl is shown in figure 8.7, a. On interruption of the current the interdiffusion of KCl and NaCl leads to the appearance of two maxima in the gradient curve, figure 8.7, b, c. This observation confirms qualitatively the computations of Taylor [15]; the phenomena arising from the more rapid diffusion of KCl upward than of NaCl downward. It suggests, moreover, a study, now in progress, of the differential interdiffusion of two similar solutes at a boundary between solutions of the same refractivity.

The pattern of figure 8.7, a, was obtained in a series of experiments in which KCl and LiCl were leading and trailing salts, respectively, and the intermediate solution also contained these, plus NaCl. Under these conditions the steady-state patterns afford a direct analysis of NaCl only, but with the aid of Dole's theory [4] those obtained during the separation may be used to estimate the LiCl and KCl content of the intermediate solutions also.

Still another source of error is the apparent shift of a boundary due to superposition of the gradients of an adjacent boundary. Thus the largest error in table 3, 17 percent, occurs in the magnesium of figure 8.5, e, where the boundary overlap is greatest and produces an effect of the same sign as that observed. Moreover, this error would become more serious as the proportion of a given salt in the intermediate solution, or as the transference number difference, decreased.

Because of the small mobility difference, cesium does not make a satisfactory leading ion for potassium, figure 8.6, a, but it is about the only one available. Iodate was an unfortunate choice as leading ion for glycine, figure 8.6, c, but in this case several others are available. To have the boundaries as sharp as possible the largest current compatible with convection-free electrophoresis should be used. To this end the present work was done in a thermostat at 2° C. It is doubtful, however, if separation of isotopic ions could be effected in the manner outlined here as Brewer, Madorsky and their associates have done in a packed channel [1].

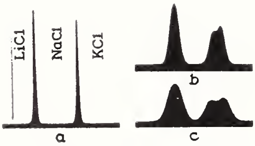

FIGURE 8.7. *Interdiffusion of sodium and potassium chlorides on interruption of the current.*

The vertical enlargement of b and c is twice that of a.

In this research no quantitative analyses of mixtures of organic anions have been attempted. This is due to the inadequacy of the electrode cup, C of figure 8.2, and could be remedied by increasing its volume. In the case of cation mixtures the common anion, chloride, is the one with respect to which the electrodes are reversible and a large number of coulombs can thus be passed through the cell without the electrode processes disturbing the boundaries. With mixtures of slow organic anions, on the other hand, the relatively fast chloride ions at the cathode, E of figure 8.2, migrate quickly through the poorly conducting, overlying solution of the trailing salt in the electrode cup and then fall into the channel. The effective volume of the cup has been increased [16] by interposing a layer of concentrated solution of the trailing salt between the dilute one and the chloride solution bathing the electrode, but this is only partially effective.

The initial appearance of the unwanted chloride ions in the channel is unmistakable. If the steady state has been approached, the boundary separations begin to increase slowly and the maximum gradients in each to decrease. Moreover, the formate-acetate boundary undergoes a reversal, as shown in figure 8.6, d, e, of the sign of the refractive index difference across it. The pattern of figure 8.6, d, was recorded before chloride ions had entered the channel and also before the separation of valerate and caproate was complete. At this stage the formate-acetate boundary is identical with that in a separate experiment involving only these two salts. However, as chloride ions leak through the system and introduce concentration adjustments at each boundary the acetate solution becomes less refractive than the underlying formate and reversal shown in figure 8.6, e, occurs. Otherwise this pattern approximates closely to the steady state, the separation of caproate and valerate being almost complete.

The progressively diminishing effect of the —CH_2— group in reducing the mobility of a fatty acid anion is clearly evident in the sharpness of the inverted boundaries of figure 8.6, e. The large area and maximum gradient in the caprylate-caproate boundary is due, of course, to the two-carbon change. It is of interest that the —CH_2— group has much the same effect in the amino-acid series, figure 8.6, c. Here the two-carbon jump at the alanine-valine boundary is also very much in evidence. In this series the picture is complicated, however, by the fact that valine and leucine are α-amino derivatives of the iso-acids rather than the normal ones. In this connection it may be noted that a preliminary attempt to separate a mixture of butyrate and isobutyrate ions was unsuccessful.

In the separation of the amino acid anions the process is complicated by the high pH, about 11, of the solution. In fact, on passage of current a faint boundary rapidly descends through the underlying iodate solution with the mobility of the hydroxyl ion. Moreover, in the first attempt at their separation sodium caprylate was used as the trailing salt, the pH of the solution being 7. In this case the hydroxyl ions moving into the iodate solution are not replaced from the overlying caprylate and the reaction

$$A^- + H_2O = HA + OH^-$$

leads eventually to the complete disappearance of the intermediate solution as the amino acids lose their charge and fall behind the advancing caprylate boundary. Here A^- represents an amino acid anion. If, however, sodium leucine is used as the following salt a reservoir of hydroxyl ions is thereby provided to replace those lost into the iodate solution and the steady state pattern shown in figure 8.6, c, is obtained.

As mentioned in the introduction the requirement that the less dense solution be above the more dense one represents a serious limitation in the use of an unpacked channel and the more difficult separations, e. g., mixtures of isomeric ions, will probably require a packing. However, suitable leading and trailing electrolytes can usually be found in which case it should always be possible to retain gravitational stability in the separation of the two salts, BR and CR. If B is faster than C and its Kohlrausch solution less dense, the leading and trailing ions must then be selected so that the boundaries rise. If B is faster than C and its solution more dense, the boundaries must descend.

Another research suggested by the present one is to reverse the procedure as follows. If the intermediate solution contains an accurately known quantity of only one salt, the boundary separation in the steady state would then afford an accurate measure of the Kohlrausch concentration, C', and, through the relation $C/C'=T/T'$, of the transference number, T', of this salt. In contrast with the conventional moving boundary determination of transference number, it would be unnecessary to know the quantity of electricity passed and a very small quantity of material would be required.

Although the present research is an obvious adaptation to an unpacked channel of the technique used by Kendall and his associates many years ago, the possibility of duplicating the procedure in the Tiselius cell did not occur to the author until he was visited by A. J. P. Martin in 1947. In the course of the visit Dr. Martin told of some interesting separations, much less ambiguous than those of Kendall but as yet unpublished, that he had made in a silica-gel packed capillary tube. It is a pleasure to acknowledge my indebtedness to Dr. Martin for this stimulating visit and also to D. A. MacInnes of these Laboratories for his many helpful suggestions in the preparation of this manuscript.

References

[1] A. K. Brewer, S. L. Madorsky, et al., J. Research NBS **38**, 137 (1947) RP1764.
[2] R. Consden, A. H. Gordon, and A. J. P. Martin, Biochem. J. **40**, 33 (1946).
[3] Hans-diedrich Cremer and Arne Tiselius, Biochem. Z. **320**, 273 (1950).
[4] V. P. Dole, J. Am. Chem. Soc. **67**, 1119 (1945).
[5] E. L. Durrum, J. Am. Chem. Soc. **72**, 2943 (1950).
[6] J. Kendall, E. R. Jette, and W. West, J. Am. Chem. Soc. **48**, 3114 (1926).
[7] F. Kohlrausch, Ann. Physik **62**, 209 (1897).
[8] L. G. Longsworth, J. Am. Chem. Soc. **65**, 1755 (1943).
[9] L. G. Longsworth, J. Am. Chem. Soc. **66**, 449 (1944).
[10] L. G. Longsworth, J. Am. Chem. Soc. **67**, 1109 (1945).
[11] L. G. Longsworth, J. Am. Chem. Soc. **69**, 1288 (1947).
[12] D. A. MacInnes and L. G. Longsworth, Chem. Reviews **11**, 171 (1932).
[13] Quintin P. Peniston, Hilda D. Agar, and Joseph L. McCarthy, Anal. Chem. **23**, 994 (1951).
[14] Harry Svensson and Inger Brattsten, Arkir för Kemi, Band 1 Nr. 47, 401 (1949).
[15] P. B. Taylor, J. Phys. Chem. **31**, 1478 (1927).
[16] A. Tiselius, Svensk Kemisk Tidskrift **50**, 518 (1938).

9. Diffusion Coefficients of Electrolytes in Dilute Aqueous Solutions

By Herbert S. Harned[1]

Introduction

Until recently, measurements of diffusion coefficients of electrolytes have not been of sufficient accuracy to have real significance in relation to current theories of the subject. Indeed, no objective evidence was available before 1947 which could be cited to show whether Nernst's [1][2] equation for the limiting value of the diffusion coefficient is valid [2].

This discrepancy in our knowledge has been surmounted by the development of two entirely different methods of measurement. The first of these, which utilizes the conductance as a measure of change in concentration with time, is particularly valuable in obtaining differential diffusion coefficients in dilute solutions [3]. The second, known as the Gouy layer interference method, utilizes interference phenomena which accompany the deflection of light by gradients of refractive index in a freely moving boundary. Longworth [4] suggested that a quantitative treatment of this phenomenon would lead to greater precision in the use of optical methods for the study of diffusion. Subsequently, the theory of this interference method was developed by Kegeles and Gosting [5] and the experimental procedure has been described by Gosting, Hanson, Kegeles and Morris [6]. Gosting and Morris [7] measured the diffusion coefficient of sucrose in water and proved that the method was capable of high accuracy. Further improvements in technique were made by Gosting [8] who measured the diffusion coefficient of KCl at 25° C. The Gouy layer method has the advantage of generality and is particularly adaptable to measurements in solutions of higher concentration. The conductance method, specifically for electrolytes, is more valuable for studies in dilute solutions.

In the sequel, we shall discuss the results obtained for the differential diffusion coefficient of KCl in water at 4°, 20°, 25°, and 30° C. The results at 25° C may be used as standard for the calibration of diaphragm cells. The relation of these results and the results for other chlorides and sulfates to current theories of the subject will form the major part of this article.

Diffusion Coefficient of Potassium Chloride in Water

In figure 9.1 the diffusion coefficient of KCl at 25° C obtained by Harned and Nuttall [3] by the conductance method and by Gosting [8] by the Gouy interference method are illustrated. With the exception of the value by the optical method at 0.1 molar, the agreement in the

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[2] Figures in brackets indicate the literature references on p. 78.

region where the results overlap is within 0.1 percent. As these are the most precise results yet obtained and as they have been used as standard for the calibration of diaphragm-cell measurements, table 1 has been prepared. The results in this table were read from a large scale graph of the data and are given at round values of the square root of the concentration. The estimated accuracy is one in the third decimal place. The result at zero concentration was calculated by the Nernst limiting equation. Another series of results obtained by Harned and

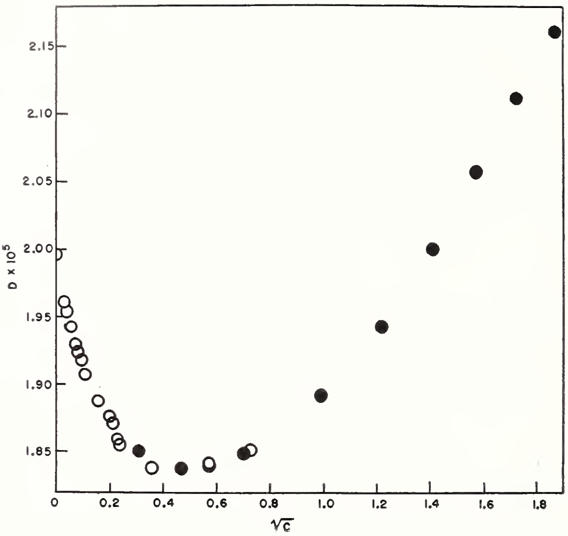

FIGURE 9.1. *Diffusion coefficient of potassium chloride in water at 25°.*

Circle represents conductometric results; dots represent values by the optical interference method.

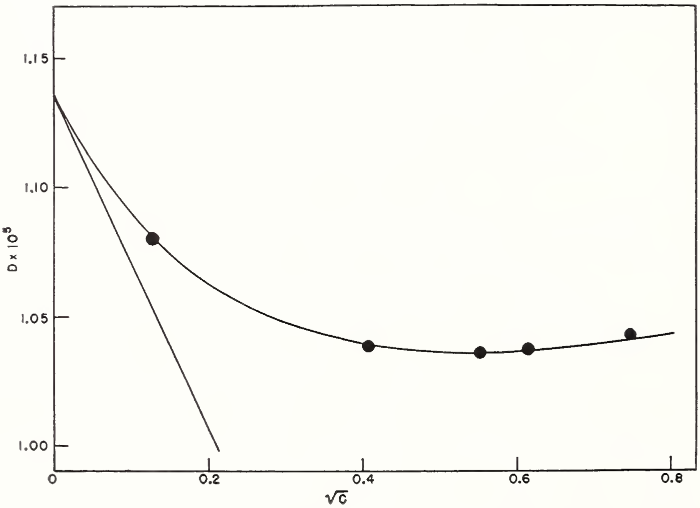

FIGURE 9.2. *Diffusion coefficient of potassium chloride in water at 4°.*

Curves represent theory by eq (1) to (9). Straight line represents the limiting theoretical eq (10).

Blake [9] at 4° C are illustrated by figure 9.2. The straight line represents the limiting law of the Onsager and Fuoss theory. The second column in table 1 contains results read off the curve in figure 9.2 at round values of $c^{1/2}$.

TABLE 1. *Differential diffusion coefficient of potassium chloride at 4° and 25° C at round values of $c^{1/2}$ (c=mole/liter)*

$D\times 10^5$				
$c^{1/2}$	4° C	25° C	$c^{1/2}$	25° C
0.00	(1.135)	(1.996)	0.8	1.861
.02	1.125	1.974	.9	1.875
.04	1.115	1.957	1.0	1.893
.06	1.106	1.942	1.1	1.912
.08	1.098	1.928	1.2	1.936
.1	1.091	1.915	1.3	1.964
.15	1.075	1.889	1.4	1.995
.2	1.063	1.870	1.5	2.029
.25	1.054	1.855	1.6	2.063
.3	1.048	1.844	1.7	2.099
.35	1.043	1.838	1.8	2.135
.4	1.040	1.836	1.9	2.170
.5	1.036	1.836	2.0	2.207
.6	1.036	1.840		
.7	1.039	1.849		

Convenient Forms for Theoretical Calculations

The theory of electrolytic diffusion as developed by Nernst [1] and Onsager and Fuoss [10] leads to equations that may be expressed in the following manner [11, 12, 13].

$$\boldsymbol{D}=K\times 10^{13}(\overline{\boldsymbol{M}}/c)\left(1+c\,\frac{\partial \ln y_{\pm}}{\partial c}\right) \tag{1}$$

$$\left(1+c\,\frac{\partial \ln y_{\pm}}{\partial c}\right)=1-\frac{E\sqrt{c}}{(1+A'\sqrt{c})^2}+Fc-c\psi(d) \tag{2}$$

$$c\psi(d)=\frac{Gc-Hc^{3/2}}{d_0+Gc-Jc^{3/2}} \tag{3}$$

$$(\overline{\boldsymbol{M}}/c)\times 10^{20}=P-Q\frac{\sqrt{c}}{1+A'\sqrt{c}}+R'c\phi(A'\sqrt{c}), \tag{4}$$

where

$$K=1000RT(\nu_1+\nu_2) \tag{5}$$

$$E=1.1514\,\overline{\boldsymbol{S}}_{(f)} \tag{6}$$

$$P=\frac{1.0748}{\nu_1|z_1|}\left(\frac{\lambda_1^0\lambda_2^0}{\Lambda^0}\right) \tag{7}$$

$$Q=\frac{31.322}{(\nu_1 z_1^2+\nu_2 z_2^2)^{1/2}\eta_0(DT)^{1/2}}\left[\frac{|z_2|\lambda_1^0-|z_1|\lambda_2^0}{\Lambda^0}\right]^2 \tag{8}$$

$$R'=\left(\frac{z_2^2\lambda_1^0+z_1^2\lambda_2^0}{\Lambda^0}\right)^2\frac{9.304\times 10^7}{\eta_0(DT)^2}. \tag{9}$$

The slope, $\boldsymbol{S}_{(\boldsymbol{D})}$, of the theoretical limiting law

$$\boldsymbol{D}=\boldsymbol{D}_0-\boldsymbol{S}_{(\boldsymbol{D})}\sqrt{c} \tag{10}$$

is given by the expression

$$\boldsymbol{S}_{(\boldsymbol{D})}=\frac{\alpha}{D^{3/2}T^{1/2}}\left(\frac{\lambda_1^0\lambda_2^0}{\Lambda^0}\right)+\frac{\beta}{\eta_0 D^{1/2}T^{-1/2}}\left[\frac{|z_2|\lambda_1^0-|z_1|\lambda_2^0}{\Lambda^0}\right]^2, \tag{11}$$

where

$$\alpha=\frac{1.3273\times10^{-3}}{\nu_1|z_1|}\mathrm{X}^3 \tag{12}$$

$$\beta=\frac{2.6042\times10^{-8}}{|z_1z_2|}\mathrm{X} \tag{13}$$

$$\mathrm{X}=[\sum\nu_i z_i^2]^{1/2}. \tag{14}$$

In these equations, the concentration is expressed in moles per liter and λ_1^0, and λ_2^0 are the equivalent conductances of the ions of the salts at infinite dilution. The diffusion coefficient, $\boldsymbol{D}$, as a function of concentration is given by eq (1), where $(\overline{\boldsymbol{M}}/c)$ is the mobility term and $[1+c(\partial \ln y_{\pm}/\partial c)]$ the thermodynamic one, derived from the principle that the diffusion coefficient is proportional to the gradient of the chemical potential. The activity coefficient, $y_{\pm}$, is the mean activity of the electrolyte divided by the mean molar concentration. Equation (2) may be used to calculate the thermodynamic term. E is given by eq (6) in which $\boldsymbol{S}_{(f)}$ is the limiting isothermal constant of the Debye and Hückél theory, and $A'\sqrt{c}=\kappa a$, where κ is the reciprocal radius and a the mean distance of approach of the ions in Angstrom units. F is an empirical constant and $c\psi(d)$ the term necessary for conversion of data from the molal to the molar concentration scale. In this equation, d_0 is the density of the pure solvent, and G, H, and J are empirical parameters that depend on the density of the solution.

Equation (4) represents the mobility term, in which P, Q, and R' are expressed by eqs (7), (8), and (9). In these equations, R is the gas constant in ergs; T, the absolute temperature; ν_1, the number of cations; ν_2, the number of anions formed by the dissociation of the electrolyte; z_1 and z_2, the valences of the ions; $\Lambda^0=\lambda_1^0+\lambda_2^0$, η_0 the viscosity of the solvent and D its dielectric constant. The values of R, T, η_0, and D used in computing the numerical constants are given in table 3. Values of $\phi(A'\sqrt{c})$ the exponential integral term of the theory are contained in table 3.

The quantity, $\boldsymbol{S}_{(\boldsymbol{D})}$, appearing in the limiting equation (10) of the Onsager and Fuoss theory has been computed by the use of eq (11), (12), (13), and (14). The parameters α and β for electrolytes of different valence types are compiled in table 2.

TABLE 2. *Parameters of equation (11)*

Valence type	αx10^3	βx10^8
1-1	3.754	3.683
1-2	9.754	3.190
1-3	18.392	3.007
3-2	36.349	2.397
2-2	15.017	1.842

Theoretical Calculations

All data necessary for theoretical calculations of diffusion coefficients of KCl at 4°, 20°, 25°, and 30° C, NaCl and LiCl at 25° C, and lithium, sodium, and cesium sulfates at 25° C are contained in tables 3 and 4. Table 4 contains values of the exponential integral function of the theory $\phi(A'\sqrt{c})$ at appropriate values of $A'\sqrt{c}$. The detailed sources of the data in table 3 are given in previous communications and will not be recorded here. Values of the limiting slopes of the Debye and Hückel theory, viscosities and limiting conductances are recorded

TABLE 3. *Data and parameters for theoretical computations of the diffusion coefficient as a function of the concentration in dilute solutions at constant temperature*

$R=8.13436\times10^7$; $T=273.16+t$; $D(4°)=86.43$; $D(20°)=80.36$; $D(25°)=78.54$; $D(30°)=76.75$; $\eta_0\ (4°)=15.676\times10^{-3}$; $\eta_0\ (20°)=10.087\times10^{-3}$; $\eta_0\ ((25°)=8.949\times10^{-3}$; $\eta_0\ (30°)=8.004\times10^{-3}$.

Symbols or quantities [1]	KCl (4°)	KCl (20°)	KCl (25°)	KCl (30°)	LiCl (25°)	NaCl (25°)	Li_2SO_4 (25°)	Na_2SO_4 (25°)	Cs_2SO_4 (25°)
d	1. 0000	0. 9982	0. 9971	0. 9957	0. 9971	0. 9971	0. 9971	0. 9917	0. 9971
ν_1	1	1	1	1	1	1	2	2	2
ν_2	1	1	1	1	1	1	1	1	1
z_1	1	1	1	1	1	1	1	1	1
z_2	1	1	1	1	1	1	2	2	2
λ_1^0	45. 50	66. 24	73. 52	80. 77	38. 69	50. 11	38. 69	50. 11	77. 27
λ_2^0	46. 17	68. 57	76. 34	84. 18	76. 34	76. 34	79. 8	79. 8	79. 8
Λ^0	91. 67	134. 80	149. 86	164. 95	115. 03	126. 45	118. 49	129. 91	157. 07
A'	1. 170	1. 245	1. 249	1. 253	1. 396	1. 3145	2. 220	1. 982	2. 135
$a(A)$	3. 56	3. 8	3. 8	3. 8	4. 25	4. 0	3. 90	3. 48	3. 75
$S_{(f)}$	0. 4913	0. 5046	0. 5091	0. 5141	0. 5091	0. 5091	1. 7636	1. 7633	1. 7636
$S_{(D)}$	. 6431	----------	1. 170	----------	. 8878	. 9794	2. 1146	2. 5154	3. 3433
D_0	1. 1352	1. 7652	1. 9958	2. 2334	1. 368	1. 612	1. 0413	1. 2302	1. 564
K	4. 6089	4. 875	4. 958	5. 0412	4. 958	4. 958	7. 437	7. 437	7. 437
E	0. 5657	0. 5810	0. 5873	0. 5919	0. 5862	0. 5862	2. 0306	2. 0306	2. 0306
F	. 032	. 0430	. 0490	. 0599	. 2740	. 1287	0. 0	−0. 134	−0. 157
G	. 01248	. 00990	. 00959	. 0094	. 01908	. 01968	. 0414	. 0426	−0. 0026
H	. 00471	. 00336	. 00348	. 0034	. 00223	. 00322	. 01616	. 01818	. 1824
J	. 003137	. 0024	. 00232	. 0023	. 001484	. 002417	. 01077	. 01212	. 01216
P	24. 630	36. 210	40. 253	44. 301	27. 596	32. 515	14. 002	16. 543	21. 097
Q	0. 00049	0. 00423	0. 0057	0. 0077	1. 7326	0. 6959	0. 00389	0. 2307	2. 114
R'	10. 343	16. 62	18. 96	21. 47	18. 959	18. 959	74. 285	88. 241	117. 15

[1] Symbols are the same as those used in reference [12].

TABLE 4. *Exponential integral function,* $\phi(A'\sqrt{c})=\phi(\kappa a)$

$A'\sqrt{c}$	$\phi\ (A'\sqrt{c})$	$A'\sqrt{c}$	$\phi\ (A'\sqrt{c})$	$A'\sqrt{c}$	$\phi\ (A'\sqrt{c})$
0	∞	0. 22	0. 6674	0. 7	0. 16304
. 01	3. 5550	. 24	. 6146	. 8	. 13194
. 02	2. 5000	. 26	. 5680	. 9	. 10844
. 03	2. 2778	. 28	. 5268	1. 0	. 09033
. 04	2. 0125	. 30	. 4899	1. 2	. 06477
. 05	1. 8273	. 32	. 4570	1. 4	. 04813
. 06	1. 6667	. 34	. 4269	1. 6	. 03676
. 07	1. 5306	. 36	. 3997	1. 8	. 02876
. 08	1. 4125	. 38	. 3753	2. 0	. 02292
. 09	1. 3148	. 40	. 3527	2. 5	. 01391
. 10	1. 2342	. 42	. 3322	3. 0	. 00908
. 12	1. 0903	. 44	. 3133	4. 0	. 00449
. 14	0. 9709	. 46	. 2858	5. 0	. 00251
. 16	0. 8770	. 48	. 2799	6. 0	. 00158
. 18	0. 7978	. 50	. 2651	7. 0	. 00105
. 20	0. 7277	. 6	. 2054		
. 22	0. 6674	. 7	. 16304		

by Harned and Owen [14]. The details of the calculation of KCl at 4° are described by Harned and Blake, and at 20°, 25°, and 30° by Harned and Nuttall [15]. Similar details for lithium and sodium chlorides are given by Harned and Hildreth [17] and for lithium, sodium [18], and cesium [19] sulfates by Harned and Blake.

Comparison of Theoretical Calculations With Experimental Determinations

The results calculated by eq (1) to (9), using the data in tables 3 and 4, are compared with actual values determined by the conductometric method in table 5. Excellent agreement between theory and observation for KCl is obtained at temperatures from 4° to 30° C. It is to be noted that at 4° the theoretical and observed results are in close agreement from 0 to 0.6 molar, a fact in accord with the behavior of this salt at 25° C. Agreement in dilute solutions is observable for the diffusion coefficients of lithium and sodium chlorides. This fact is clearly indicated by the sensitive plots of the diffusion coefficients of these chlorides against $c^{1/2}$ shown in figure 9.3. Here, the curves illustrate the complete theoretical computation and the straight lines

Table 5. *Comparison of theoretical with experimental diffusion coefficients in dilute solutions*

$D\times 10^5$								
KCl (4°)			KCl (20°)			KCl (25°)		
c	Observed	Calculated	*c*	Observed	Calculated	*c*	Observed	Calculated
0.000	------	(1.135)	0.000	------	(1.765)	0.000	------	(1.996)
.0166	1.080	1.082	.00125	1.736	1.734	.00125	1.961	1.960
.168	1.038	1.039	.00248	1.724	1.723	.00194	1.954	1.953
.307	1.036	1.036	.00367	1.719	1.716	.00325	1.943	1.943
.379	1.037	1.036	.00451	1.709	1.712	.00585	1.931	1.929
.558	1.042	1.040	.01121	1.689	1.690	.00704	1.924	1.924
KCl (30°)			LiCl (25°)			NaCl (25°)		
c	Observed	Calculated	*c*	Observed	Calculated	*c*	Observed	Calculated
0.000	------	(2.233)	0.000	------	(1.368)	0.000	------	(1.612)
.00326	2.172	2.173	.00063	1.348	1.349	.000746	1.586	1.589
.00650	2.154	2.155	.00229	1.335	1.335	.00161	1.576	1.580
.00896	2.146	2.145	.00302	1.331	1.331	.0045	1.562	1.563
.01236	2.139	2.133	.00496	1.326	1.323	.0052	1.559	1.560
			.00792	1.315	1.316	.0077	1.555	1.552
			.00935	1.312	1.313	.0100	1.547	1.546
Li_2SO_4 (25°)			Na_2SO_4 (25°)			Cs_2SO_4 (25°)		
c	Observed	Calculated	*c*	Observed	Calculated	*c*	Observed	Calculated
0.000	------	(1.041)	0.000	------	(1.230)	0.000	------	(1.569)
.00064	1.000	0.999	.00081	1.177	1.173	.00096	1.490	1.490
.00071	0.997	.998	.00147	1.170	1.158	.00120	1.482	1.482
.00210	.973	.975	.00268	1.151	1.142	.00150	1.470	1.475
.00348	.961	.961	.00356	1.137	1.132	.00378	1.435	1.436
.00440	.954	.955	.00448	1.129	1.124	.00468	1.419	1.426
.00573	.946	.948	.00479	1.124	1.122	.00472	1.424	1.426

are plots of eq (10) which represents the limiting law. The maximum deviation from the theory of 0.25 percent occurs with NaCl at $c^{1/2}$ equal to 0.04. It is to be observed that all these results are at concentrations less than 0.005 molar.

The results for Li_2SO_4 appear in very close agreement with theory while those for Na_2SO_4 seem to be slightly higher than the theoretical ones. Both series of values approach the limiting law and limiting value of the diffusion coefficient satisfactorily. With the exception of results at $c^{1/2}$ equal to 0.05, the Cs_2SO_4 values are also in accord with theory. These conclusions are illustrated in a satisfactory manner by graphs in figure 9.4 where the curves represent the

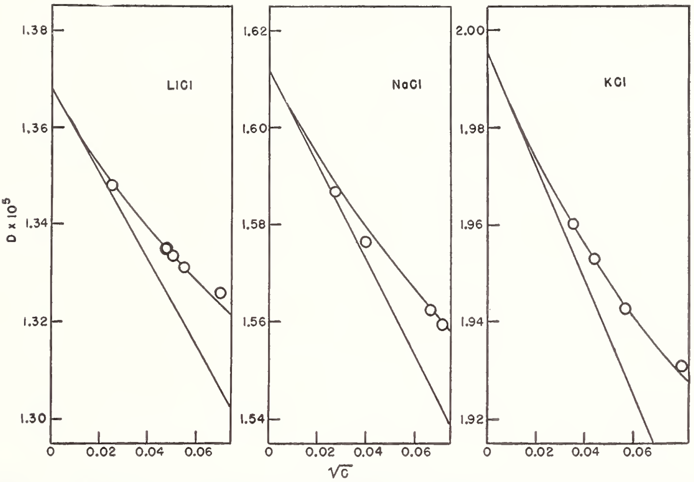

Figure 9.3. *Diffusion coefficients of lithium, sodium, and potassium chlorides in dilute aqueous solutions at 25°.*

Curves represent complete theory by eq (1) to (9). Straight lines represent the limiting theoretical eq (10).

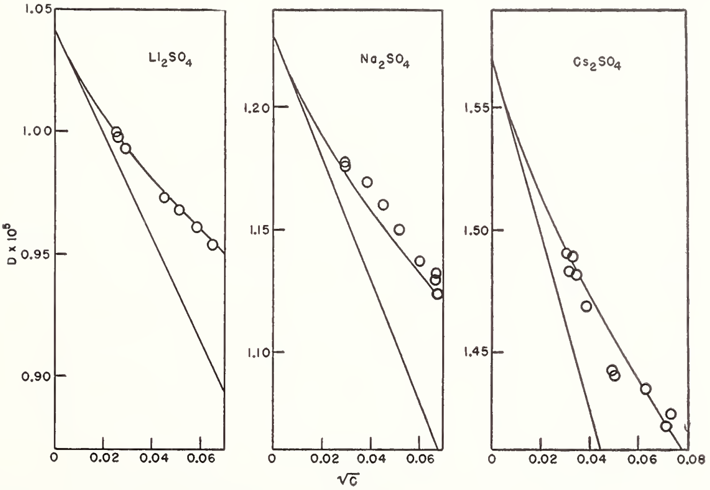

Figure 9.4. *Diffusion coefficients of lithium, sodium, and cesium sulfates in dilute aqueous solutions at 25°.*

Curves represent complete theory. Straight lines represent the limiting eq (10).

complete theoretical calculation and the straight lines are plots of the limiting law.

It should be emphasized that the theory can only be regarded as applicable to dilute solutions. Although the thermodynamic term, $1+c\ (\partial \ln y_{\pm}/\partial c)$, is applicable at all concentrations, the mobility term $(\overline{\boldsymbol{M}}/c)$, includes Coulombic interaction only and disregards other interactions. Further, no viscosity correction has been applied. A good illustration of this contention is provided by figure 9.5, in which the diffusion coefficient of LiCl is plotted against $c^{1/2}$. The conductometric results in the very dilute solutions are represented by circles. The values at the higher concentrations were obtained by Stokes [20], who employed an improved diaphragm-cell method. The curve in this figure represents the complete theoretical calculation. It is apparent from this figure that the theory only holds from 0 to about 0.01 molar.

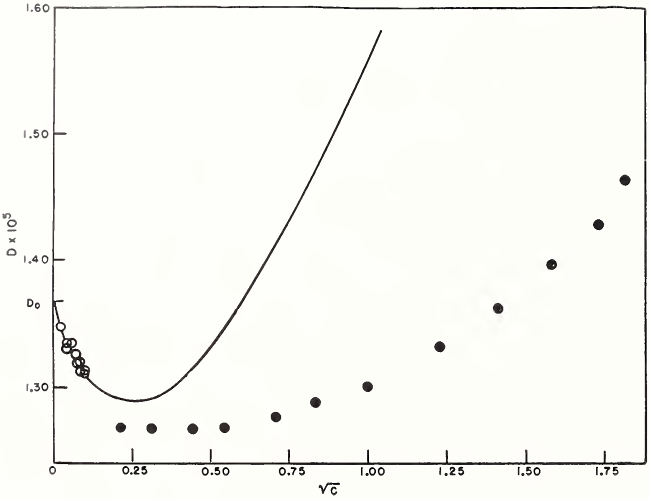

FIGURE 9.5. *Deviation from theory for concentrated lithium-chloride solutions at 25°.*

Curve represents the theory by eq (1) to (9). Conductometric results are given by the circles. Dots illustrate values determined by the diaphragm cell method.

Diffusion Coefficients of Magnesium and Zinc Sulfates in Dilute Aqueous Solutions

The alkali chlorides are completely ionized in dilute solutions, and therefore favorable agreement with theory should be expected. The ionization constants of $LiSO_4^-$ and $NaSO_4^-$ as estimated from conductance data by Righellato and Davies [21] are of the order of 0.2, which is high enough to cause only minor effects in solutions less than 0.005 molar. Very much greater ion pair formation occurs with electrolytes of the 2–2 valence type. Money and Davies [21] obtained 0.0063 for the ionization constant of $MgSO_4$, and Owen and Gurry [22] obtained 0.0049 for the ionization constant of $ZnSO_4$ by careful examination of conductance data.

Harned and Hudson have determined diffusion coefficients of magnesium [23] and zinc [24] sulfates in water at concentrations between

0.0005 and 0.005 molar. Their results are shown in figure 6. The top curve represents values for $MgSO_4$ and the graph just below it those for $ZnSO_4$. The lowest curve was obtained from the theoretical eq (1) to (9), which presuppose complete ionization. The fact that the experimental observations indicate a more rapid diffusion than those predicted by theory indicates that ion-pairs migrate more rapidly than the ions. Harned and Hudson obtained a correction factor for the effect of ion-pair formation, which may be expressed by the equation,

$$\boldsymbol{D}_{\mathrm{obs}}/\boldsymbol{D}_{\mathrm{calc}}=1+(1-\alpha)\left[\lambda_m^0\Big/\frac{\lambda_1^0\lambda_2^0}{\lambda_1^0+\lambda_2^0}-1\right], \qquad (15)$$

where α is the degree of dissociation of MSO_4^- and λ_m^0 the mobility of the undissociated ion-pair in conductance units. Using this equation, they obtained 46 and 44 for λ_m^0 for magnesium and zinc sulfates,

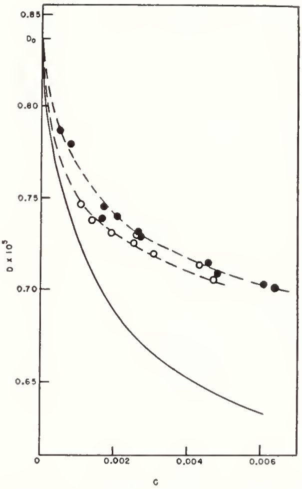

FIGURE 9.6. *Diffusion coefficients of zinc sulfate and magnesium sulfate in dilute aqueous solutions at 25°.*

Cirlces are for zinc sulfate, dots for magnesium sulfate, and soild curve represents the theory by eq (1) to (9).

respectively, whereas the mean ionic mobility, $\lambda_1^0\lambda_2^0/(\lambda_1^0+\lambda_2^0)$ is 31.9. They also found that λ_m^0 did not vary with concentration. They concluded that the assumption of ion-pair formation is consistent with conductance data, diffusion coefficient data, the theory of Onsager and Fuoss and known behavior of activity coefficients of these electrolytes. It is interesting to note that the correction factor represented by eq (15) remains unity if the mobility of the ion-pair equals the mean mobility of the ions. Consequently, considerable ion association can occur without observable effect on the diffusion coefficient.

Further Considerations Regarding Electrolytes of Different Valence Types

Two other 1–1 electrolytes, KNO_3 and $AgNO_3$ have been shown by Harned and Hudson [25] and Harned and Hildreth [26] to conform with theory in dilute solutions. Further, as far as can be estimated by the available data, the diffusion coefficient of $K_4Fe(CN)_6$ [27] also shows no marked deviation from theory.

On the other hand, the diffusion coefficients of $CaCl_2$ determined by Harned and Levy [28] and $LaCl_3$ measured by Harned and Blake [29] are somewhat lower than those estimated by theory. However, data for both of these salts approach satisfactorily the values estimated by the limiting eq (10). The cause of these unexpected departures from theory is under careful scrutiny.

Retrospect and Prospect

In retrospect, certain positive conclusions can be drawn from these conductometric measurements: (1) The Nernst limiting equation for the diffusion coefficient at infinite dilution is valid, (2) the principle that the flow of a component is determined by the gradient of the Gibbs' chemical potential is correct, and (3) the theory of electrophoresis applied to the diffusion of electrolytes by Onsager and Fuoss may provide an approximation for the mobility term. This conclusion is confirmed by the accuracy of the calculations illustrated by table 5. In all cases, the limiting expression of theory is approached satisfactorily as concentration of the electrolyte approaches zero. The precise extension of theory to higher concentrations is a matter of extreme difficulty.

In prospect, the recent development of precise measurements of diffusion coefficients by the conductance method, the Gouy layer interference method and the improved diaphragm cell has converted an old subject into a new field of numerous possibilities. With the additional help of radioactive tracers for the study of self-diffusion, real advances should be made in the elucidation of phenomena accompanying the simplest of all physical chemical irreversible processes, the movement of a component in one direction and the opposite movement of the component which takes its place.

A major part of the work presented here was contributed by Drs. Douglas M. French, Ralph L. Nuttall, Arthur L. Levy, Clarence L. Hildreth, Jr., Charles A. Blake, Jr., and Robert M. Hudson. For the long hours spent upon this task and for the spirit of cooperation, the senior member of this group takes this as an occasion to express his sincere appreciation.

References

[1] W. Nernst, Z. Physik. Chem. **2,** 613 (1888).
[2] Summaries of the methods of measurement of diffusion coefficients are contained in articles by L. J. Longsworth, Ann. N. Y. Acad. Sci. **46,** 211 (1945) and by H. S. Harned, Chem. Rev. **40,** 461 (1947).
[3] H. S. Harned and D. M. French, Ann. N. Y. Acad. Sci. **46,** 267 (1945). H. S. Harned and R. L. Nuttall, J. Am. Chem. Soc. **69,** 736 (1947). These articles contain detailed descriptions of the apparatus and techniques of the conductance method.
[4] L. G. Longsworth, Ann. N. Y. Acad. Sci. **46,** 211 (1945); J. Am. Chem. Soc. **69,** 2510 (1947).
[5] G. Kegeles and L. J. Gosting, J. Am. Chem. Soc. **69,** 2516 (1947).
[6] L. J. Gosting, E. Hanson, G. Kegeles, and M. S. Morris, Rev. Sci. Instr. **20,** 209 (1949).
[7] L. J. Gosting and M. S. Morris, J. Am. Chem. Soc. **71,** 1998 (1949).
[8] L. J. Gosting, J. Am. Chem. **72,** 4418 (1950).

[9] H. S. Harned and C. A. Blake, Jr., J. Am. Chem. Soc. **72,** 2265 (1950).
[10 L. Onsager and R. M. Fuoss, J. Phys. Chem. **36,** 2689 (1932).
[11] C. A. Blake, Jr., Dissertation (Yale University, June 1951).
[12] H. S. Harned and B. B. Owen, The physical chemistry of electrolytic solutions (Reinhold Publishing Corp., New York, N. Y., 1950).
[13] H. S. Harned, Chem. Rev. **40,** 461 (1947).
[14] Reference [12], p. 119, 128, and 172.
[15] Reference [9].
[16] H. S. Harned and R. L. Nuttall, J. Am. Chem. Soc. **71,** 1460 (1949).
[17] H. S. Harned and C. L. Hildreth, Jr., J. Am. Chem. Soc. **73,** 650 (1951).
[18] H. S. Harned and C. A. Blake, Jr., J. Am. Chem. Soc. **73,** 2448 (1951).
[19] H. S. Harned and C. A. Blake, Jr., J. Am. Chem. Soc. **73,** 5882 (1951).
[20] R. H. Stokes, J. Am. Chem. Soc. **72,** 763 (1950); **72,** 2243 (1950); **73,** 3527 (1951).
[21] E. C. Righellato and C. W. Davies, Trans. Faraday Soc. **26,** 592 (1930).
[22] B. B. Owen and R. W. Gurry, J. Am. Chem. Soc. **60,** 3074 (1938).
[23] H. S. Harned and R. M. Hudson, J. Am. Chem. Soc. **73,** 7880 (1951).
[24] H. S. Harned and R. M. Hudson, J. Am. Chem. Soc. **73,** 3781 (1951).
[25] H. S. Harned and R. M. Hudson, J. Am. Chem. Soc. **73,** 652 (1951).
[26] H. S. Harned and C. L. Hildreth, Jr., J. Am. Chem. Soc. **73,** 3292 (1951).
[27] H. S. Harned and R. M. Hudson, J. Am. Chem. Soc. **73,** 5083 (1951).
[28] H. S. Harned and A. L. Levy, J. Am. Chem. Soc. **71,** 2781 (1949).
[29] H. S. Harned and C. A. Blake, Jr., J. Am. Chem. Soc. **73,** 4255 (1951).

Discussion

DR. W. BLUM, National Bureau of Standards: Progress in what we might call applied electrochemistry will depend on more knowledge in these fundamental fields. In electrodeposition processes we are concerned with so-called cathode films, i. e., with the very thin boundary layer of solution next to the cathode, which is quite different in its composition from that of the body of the solution. We know that material enters into that film by migration, *diffusion*, and convection. So far as I know, it is not now possible for anyone, especially in dealing with concentrated solutions, to make even the first approximation as to what to expect in those cathode films. I hope that complete work like Dr. Harned's will help ultimately in these problems.

10. Septa in Standard Cells

By Marion Eppley [1] and George D. Vincent [1]

Introduction

It is safe to say that all cadmium standard cells in use, other than primary standards, replicas of primary standards, and cells for special purposes, have some device that holds the materials of the anode and cathode in place in case the cell is carelessly handled. To accomplish this, a septum, or barrier, of a porous material is usually inserted in each limb of the cell. These are termed "portable" cells, and in this country are almost invariably of the unsaturated type.

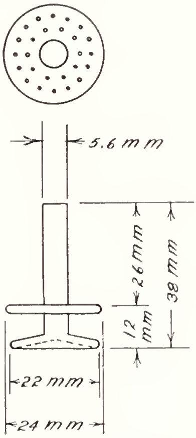

FIGURE 10.1 *Porcelain septum.*

Septa have been made of a number of materials. Perhaps the first was unglazed porcelain of the form shown in figure 10.1 [1].[2] Among other septa that have been used are 1. Perforated porcelain disks locked in place above Hg_2SO_4 by projections in the cell container.[3] 2. In this laboratory, a short length of glass tubing covered at one end with linen cloth. This septum is satisfactorily inert but requires too much fitting to be practical. 3. Fibrous asbestos or Pyrex glass-wool held in place by a glass disk fused at right angles to a glass rod, which projects upward, and held in place by a cork disk above the solution. This septum is complicated. 4. Glass fibre-cloth over plug-type septa. This septum is mechanically good. 5. Cellulose sponge. Appears to not have enough spring to hold it in place in the cell. 6. Stainless-steel split washer, coated with Saran or Teflon, and closed at the bottom with linen or glass-cloth. Now under consideration.

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[1] The Eppley Laboratory, Inc., Newport, R. I.
[2] Figures in brackets indicate literature references on p. 97.
[3] Private communication from Dr. G. W. Vinal.

7. Spirals closely wound from glass-cloth tape and from tapes and strips of certain plastics. Not too successful mechanically. 8. A springy, hard plastic in the form of a split washer covered at bottom with linen. Gives promise of great usefulness. 9. Short sections of tubing made of soft plastics covered at the lower end with linen. 10. A synthetic rubber containing combined silicon and covered with linen. Very inert. 11. Plastic materials. 12. Treated cork with a central hole and partly covered with linen [2]. This type is very generally used today.

Effect of Septa, and an Indicator of Stability of Equilibrium

By its presence a chemically inert septum affects only slightly the equilibrium of a cell, which is not surprising, as the major effect of a septum should lie in the degree to which it introduces deleterious substances. As the cell system is complicated and very sensitive to small concentrations of foreign substances, chemical analysis does not serve as a method of determining small contaminations, so some other method must be sought.

The best assay of the quality would be to maintain a cell at a temperature constant to the degree necessary to hold the emf within the range giving the desired precision and to observe the emf for a suitable period of time. This is an essential test, but alone not an adequate one. The reason for a supplemental test is that cells sometimes have been found, especially among those with a very low-acid electrolyte, or among very old cells, which exhibit emf close to the accepted limits of constancy after they have been maintained for a month or more at a temperature controlled to within say 0.02° C, but which, if the temperature is suddenly changed a few degrees, become erratic. They usually settle down again after a period at a regulated temperature, but cells with these characteristics are always unreliable.

Although these conditions are never observed in properly made cells, unless they are older than their useful life or have been abused, there is a need to detect them, or rather to show with the highest degree of certainty practicable that they are absent.

These conditions suggest a test on which to base a prediction of the future behavior of cells. Hence for many years we have made determinations of the effect of abrupt temperature changes on the emf of our cells and for a long time past have used these results as a routine manufacturing control. The technique of the tests varies from one type of cell to another. As we believe that a detailed description of our methods would be of no great scientific interest, we have omitted procedures, except in broad terms.

The general pattern followed in the routine determination of the "hysteresis" of unsaturated cells with septa is to place them in an enclosure, maintained at a temperature above that of the room, for a predetermined period of time, after which the cells are shifted to a region of lower temperature as quickly as practicable and their emf read after the lapse of appropriate intervals of time.

The steady emf value at the lower temperature is then subtracted from the highest emf value observed at the lower temperature after the cells were shifted to it. The resulting difference is expressed as the percentage of the steady emf value at the lower temperature, or often, as a matter of convenience, as the percentage of 1 v.

The temperature coefficients of the cathode and anode of a cadmium cell are different: 0.00031 v/deg at 20° C for the cathode [3] and −0.00035 v/deg at 20° C for the anode [3], or −0.00004 v/deg for the cell as a whole.

As the heat capacities of the cathode and anode are not the same, every cadmium cell should show some temperature hysteresis. This hysteresis should vary in magnitude with the heat capacity of the liquid or air bath, and with the magnitude and rate of the temperature change, but in a stable cell, should be reproducible under uniform conditions.

It is with the changing hysteresis caused by reactive impurities or by physical or chemical interruption of a required distribution of concentrations within the cell, that we are interested. It perhaps could be called "augmented hysteresis."

Effect of Septa That Introduce No Foreign Substances

In spite of the usefulness of temperature hysteresis as a criterion of the equilibrium status of a cadmium cell, this phenomenon varies somewhat for groups of unsaturated standard cells. Hence, an attempt to demonstrate an effect that may be only of a few microvolts in the case of septa that introduce no deleterious substances can be carried out best on cells of the saturated type.

Accordingly, the authors in August 1951 performed the following experiment with five test and five control saturated cells, 0.05 *N* in H_2SO_4, differing only as to grain size of $CdSO_4.\frac{8}{3}H_2O$. Neither group had septa of a foreign material. Materials used were as follows: Cadmium sulfate was purified by a chemical process developed in this laboratory and further purified by three crystallizations from distilled water. It was free from manganese, a most objectionable impurity [4]. The Hg_2SO_4 was a gray electrolytic compound [5]. The solid $CdSO_4.\frac{8}{3}H_2O$ in rather finely ground state, was mixed with the Hg_2SO_4.

A 12½-percent cadmium amalgam was used. Both the cadmium and the mercury were redistilled, the mercury after washing in a column of dilute nitric acid and undergoing an electrolytic treatment [6].

In the controls, crystals of $CdSO_4.\frac{8}{3}H_2O$ of suitable size were placed over the Hg_2SO_4 and the amalgam.

In the test cells, finely divided $CdSO_4.\frac{8}{3}H_2O$ was placed to a depth of about 1.5 cm on the cathode, and to a somewhat less depth on the anode. Both groups were heated at 39.3° for 16 hr, and then cooled to room temperature and left for 3 days. Heating and cooling the test cells had the purpose of cementing the finely divided $CdSO_4.\frac{8}{3}H_2O$ into a homogeneous plug

All the cells were then immersed for 2 days in an oil bath at 32.95°±0.05°, after which they were suddenly returned to an oil bath at 28.23°±0.02°.

The cells were measured at 32.95°, 2 hr after they were immersed in the bath and were continued for 26 hr. Readings at 28.23° were taken over 216 hr. The cells were then returned to the bath at 32.95°, and readings taken over 48 hr.

The average emf of the five control and the five test cells at 32.95°, 23.23°, and again at 32.95° are given in table 1 at the elapsed times.

TABLE 1. *Hysteresis effects in saturated standard cells with and without* $CdSO_4 \cdot \frac{8}{3}H_2O$ *septa*

Time of readings		Average emf, 32.95° C; controls (5 cells)	Average emf, 32.95° C; test cells (5 cells)
Hours	*Minutes*	*Volts*	*Volts*
0	------	(a)	(a)
2	------	1.017971	1.017966
3	------	1.017970	1.017968
4	------	1.017968	1.017966
21	------	1.017967	1.017966
22	------	1.017967	1.017965
26	------	1.017968	1.017966
		Average emf, 28.23° C	Average emf, 28.23° C
0	0	(b)	(b)
0	4	1.01798	1.01825
0	11	1.018019	1.018248
0	19	1.018031	1.018243
0	26	1.018046	1.018244
0	39	1.018071	1.018246
1	2	1.018102	1.018246
1	42	1.018142	1.018243
2	34	1.018173	1.018241
9	40	1.018229	1.018238
18	45	1.018235	1.018235
29	15	1.018233	1.018233
75	0	1.018234	1.018232
104	0	1.018232	1.018230
216	0	1.018232	1.018231
		Average emf, 32.95° C	Average emf, 32.95° C
0	0	(c)	(c)
0	2	1.01825	1.01810
0	5	1.01822	1.01805
0	8	1.018156	1.018007
0	13	1.018095	1.017978
0	20	1.018039	1.017965
0	37	1.018001	1.017963
1	03	1.017973	1.017960
2	01	1.017968	1.017962
7	00	1.017966	1.017962
23	15	1.017965	1.017963
48	56	1.017965	1.017963

[a] Cells transferred to 32.95° bath.
[b] Cells transferred to 28.23° bath.
[c] Cells transferred to 32.95° bath.

The curve of figure 10.2 shows emf plotted against time. The differences in the two sets of emf are slight, as expected, and might be caused by lag in arrival at saturation because of difference in grain-size of $CdSO_4 \cdot \frac{8}{3}H_2O$ between the control and test cells. Hysteresis because of difference in grain size was noted by Wold [7].

We have found as the result of long experience that cells with or without septa exhibit what we call, respectively "positive hysteresis" or "negative hysteresis". In the first type, when a cell is suddenly transferred from a higher to a lower temperature, the emf rapidly rises to a higher value than that finally attained, and then decreases more slowly to this final steady value. In "negative hysteresis" the emf rises quickly toward the final steady value for the lower temperature until slightly below it, and then mounts more slowly until the steady value is reached. Figure 10.2 shows that the curve for the test cells is characteristic of "positive hysteresis"; that for the controls, of "negative hysteresis".

To show the characteristic form of a curve that exemplifies "positive hysteresis", a period in our production records was chosen where there were many determinations of hysteresis of cells with cork septa, and data for cells were chosen at random.

The 10 cells for which the data were assembled had been held at room temperature (23.4°) and were then immersed in an oil bath at 32.9° ±0.02°. After readings were taken at various times, these cells were taken from the oil bath at 32.9° and immediately immersed in an oil bath at 28.02° ±0.02°, after which further readings were made. Pertinent data are given in tables 2 and 3.

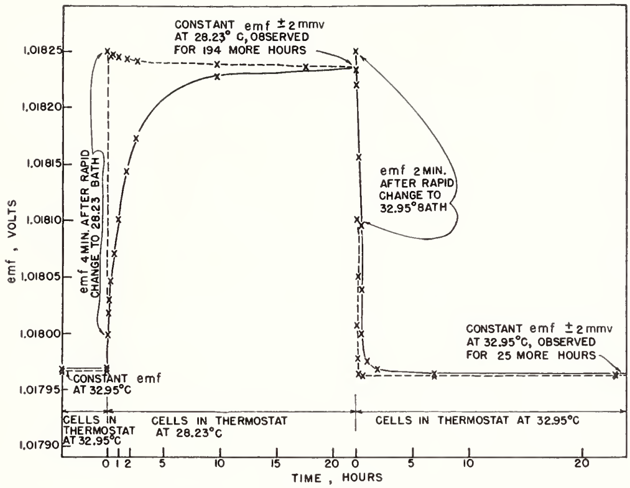

FIGURE 10.2. *Hysteresis curves for saturated cells with and without* $CdSO_4.8/3H_2O$ *septa.*

——————, cells with solid plug of $CdSO_4$;

– – – – – – – – –, cells with large crystals of $CdSO_4$.

TABLE 2. *Hysteresis effects in unsaturated cells for rise in temperature*

Ten precision cells, 0.04 *N* H_2SO_4, unsaturated, cork and linen septa. Serial numbers 96215, 96829 to 96832 97503 to 97507. Data for rise in temperature: 23.4° to 32.9° C

Time in bath at 32.9° C		Electromotive force (avg of 10 cells)
Hours	Minutes	
		Volts
0	[a] 0	[b]1.019180
0	6	8783
0	14	8891
0	24	8989
0	42	9080
0	60	9098
1	30	9101
2	30	9105
4	--------	9110
6	--------	9110
7	15	9109
23	--------	9107
52	30	9108
72	--------	9107
96	--------	9110
175	--------	9110
192	--------	9111

[a] August 10, 1936, starting date.
[b] Average of 10 cells at 23.4° C.

Figure 10.3 shows emf against time for the transfer to the higher temperature and the same for the transfer to the lower temperature, both plotted to the same scale.

On the transfer to a higher temperature the average emf for the cells dropped in 6 min from 1.019180 v (the value for 23.4°) to 1.018783 v. In 4 hr, the emf returned to a steady value of 1.019110 v, which was closely the value observed throughout the remaining 188 hr of test. The maximum lack of agreement with the final constant value was 328 μv, at the end of the first 6 min after a 9.5-deg rise in temperature.

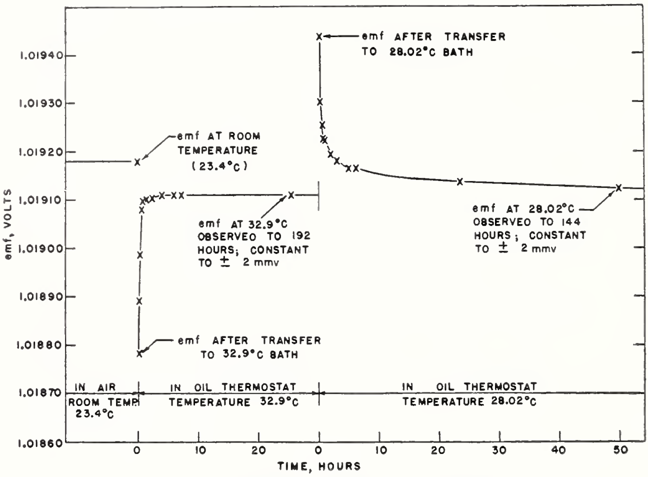

Figure 10.3. *Hysteresis curves for unsaturated cells.*

Table 3. *Hysteresis effects in unsaturated cells for drop in temperature*

Ten precision cells, 0.04 *N* H_2SO_4, unsaturated cork and linen septa. Serial numbers 96215, 96829–96,832, 97503 to 97507. Data for drop in temperature: 32.9° to 28.02° C

Time in bath at 28.02° C		Electromotive force (avg of 10 cells)
Hours	Minutes	
		Volts
0	[a] 0	[b] 1.019111
0	12	9437
0	24	9302
0	36	9256
0	54	9227
1	12	9223
2	06	9193
3	--------	9180
5	--------	9165
6	--------	9164
23	--------	9136
50	--------	9121
71	--------	9119
144	--------	9121

[a] August 18, 1936, starting date.

[b] Average of 10 cells at 32.9° C.

When the cells were transferred from 32.9° C ±0.02° to 28.02° C, the average emf rose in 12 min from 1.019111 to 1.019437 v, or 326 μv, a rise of almost the identical value as that during the drop, but in twice the time. In 72 min, the emf had returned to within 0.01 percent of the final steady value at 28.02°, and in 3 hr to within 0.006 percent of the final steady value, taken as 1.019121 v. Inspection of the second part of the curve of figure 10.3 shows that the final return to a steady value is less abrupt than in the case of the rise in temperature. The initial change is a rapid rise from the lower emf corresponding to the higher temperature to a temporary value higher than the final steady value.

Effect of Septa Made of Materials Usually Considered Inert

On March 26, 1927, the senior author of this paper received in Berlin, Germany, five portable normal cadmium cells, which were secured for him by the Physikalisch-Technische Reichsanstalt, through the kindness of Dr. Jaeger and Dr. von Steinwehr of that Institution.

These cells had barriers similar to that shown in figure 10.1 and, by appearance, were unglazed porcelain of fine texture, with the horizontal disk-like portions covered with cloth, probably linen, which came up above the lower surface of the upper disks. On the Hg_2SO_4 side, no solid $CdSO_4 \cdot \frac{8}{3}H_2O$ was visible below the septum, whereas above the septum was a compacted mass of crystals. On the amalgam side, solid $CdSO_4 \cdot \frac{8}{3}H_2O$ was below the septum and in contact with the amalgam, with none above the septum.

After they were compared with the Reichsanstalt standards, they were transported most carefully to the Eppley Research Laboratory, now the Eppley Foundation for Research, where emf comparisons were made in June 1927. The intercomparisons were satisfactory for portable cells.

In September 1927 a lemon-yellow line was visible on some of them around the outer edge of the upper horizontal porcelain disk, just above the linen. In September 1951 three of these cells showed this lemon-yellow coloration. One had a dark, greenish discoloration throughout the cloth. The fifth cell showed no discoloration. These yellow discolorations suggested the presence of basic mercuric sulfate and the possibility that atmospheric oxygen, absorbed by the porous porcelain or linen while these were in air, had been released to the mercurous ion, with resultant oxidation to the basic mercuric compound. The dark discoloration suggested presence of basic mercurous sulfate caused by reduction of the acidity of the electrolyte by action with the glass as described by Vinal and Howard [8].

Similar yellow coloration has been observed by other investigators. F. E. Smith related a "yellow tint" in the Hg_2SO_4, in one instance, to its proximity to a small bubble of air imprisoned between the glass and paste. Hulett made a similar remark [9]. There is one difference, however, in the cells we are discussing. In all four the discoloration was not on the Hg_2SO_4 side of the cell, but on the amalgam side.

Eppley [9] described a technique to remove or lessen the atmospheric oxygen that may be adsorbed or trapped in cadmium cells. We have used this technique since 1928 and find it to be routine to make normal cells that agree to within better than 4 μv among themselves and agree with accepted values to better than 4 μv. We have observed one group of such cells with frequent intercomparisons with the values of the National Bureau of Standards, and they have been constant to within ±4 μv for approximately 13 years. Therefore, it can be stated confidently that unglazed porcelain can introduce reactive matter, presumably O_2, into a cadmium cell. Linen can also be suspected.

Fibrous asbestos, in connection with septa, when properly treated, does not seem to cause undesired effects, when it is intimately mixed in small amount with the Hg_2SO_4. Mixed with the Hg_2SO_4 in larger quantities it does appear to increase hysteresis. This effect is produced by other substances, among which are cut-up linen thread.

Apparently, the increase in hysteresis by fibrous substances in the Hg_2SO_4 is caused by some interference with the concentration of the solution in the interstices and vicinity of the paste after a change of temperature.

Effect of Cork Septa in Various Combinations

Vosburgh, working in this laboratory in 1923, comprehensively investigated the hysteresis of cells with cork septa in many and various combinations. Without going into details of his experiments, as a result of comparisons of the hysteresis of his cells he came to certain conclusions, the two most interesting of which are that "the cork over the Hg_2SO_4 makes much more difference than the cork over the amalgam," and, speaking again of the cork over the Hg_2SO_4, "that the action of the cork consists in altering the solution in some way rather than in merely pressing on the Hg_2SO_4 and Hg." Vosburgh also published a paper on portable unsaturated cells with cork septa, in which he showed that hysteresis decreased with increased acidity in the electrolyte [2].

Effect of Untreated Cork and of the Solid Extracted from Cork by Boiling

George B. Jennings and Lewis S. Wolfer, of this laboratory, also conducted experiments to determine the location of augmented hysteresis effects and their cause. They first set out to produce cells of high hysteresis by mixing with the Hg_2SO_4 ground-up, untreated cork in certain cells, and in others, the gummy to brittle solid recovered by evaporation to dryness from the aqueous infusion of cork made by boiling. These cells had septa of treated cork of the usual form. The electrolyte was $CdSO_4$ solution 0.03 N in H_2SO_4.

They found that by taking the electrolyte from their cells and using it in cells with the usual Hg_2SO_4 washed in the customary manner, no increase in hysteresis resulted, such cells showing the customary behavior for their type. But, when they recovered the Hg_2SO_4 from their cells, removed the cork and solid from infusion to greatest extent practicable, washed it with $CdSO_4$ solution 0.03 N in H_2SO_4, and made cells with this Hg_2SO_4, high hysteresis still was exhibited.

It could be considered then, that material from cork affected the Hg_2SO_4 adversely, but not the electrolyte. It well could have been that the used and recovered electrolyte also was affected adversely, but that the cells being constructed with septa, the electrolyte was unable to diffuse into the Hg_2SO_4 to upset the equilibrium there during the time the cells were observed.

In 1931, Vosburgh and Elmore reported on the effect of cork and cork extract on hysteresis [10].

Aqueous Cork Extract

When "raw" corks in quantity are boiled in distilled water, the infusion is the color of strong tea, even after so short a time as 6 hr.

In 1945 approximately 3 liters of an infusion was boiled down to about 500 ml, evaporated from a crystallizing dish in a ventilated oven at 40° to about 30 ml, and finally evaporated to dryness in a platinum dish.

The dry preparations were lustrous, hard, very dark brown or black, and somewhat brittle, although when ground in a mortar tended to mat together under pressure.

An arc spectrogram in the ultraviolet of the material, using graphite electrodes and a 90-v d-c arc, when compared with an adjacently photographed spectrogram of Hilger's "R. U. Powder", showed it to consist principally of Ca, with relatively large quantities of Fe, Si, Al, K, and Mg, and lesser amounts of Mn, Ba, and Na. Traces of Bi, B, Cu, Te, and Li were identified.[4] Although it consisted almost entirely of organic matter, no analysis for it was made. When ignited with a blast-flame, the matter consumed itself like punk, leaving a very light, black ash.

Cork Extract in Cadmium Sulfate Solution (at Room Temperature)

In July 1946 several hundred untreated corks of the form used in unsaturated cells were placed in a Pyrex flask and covered with a solution of $CdSO_4$ 0.03 *N* in H_2SO_4 and of a concentration approximately that corresponding to a temperature of 4° C. The flask was rubber-stoppered and placed in the dark for 2½ months at room temperature, after which the solution was clear with a light yellowish tint. In August 1951 the color was unchanged to the eye, and the solution was still clear.

At the end of the 2½-month period 10 cells without septa were made with the clear solution and with materials customarily used in this laboratory. They were closed with rubber stoppers.

Twenty cells were made as controls at the same time, and, except for the solution, which had had no corks soaked in it, were the same as the test group.

Shortly after assembling, a grayish, gelatinous-looking cloud, suggestive of the "mother" in vinegar, was observable over the Hg_2SO_4, in the test group. As the cells stood undisturbed, the cloud settled in 6 weeks to a layer of 2 mm over the Hg_2SO_4. Some smudges of material appeared in the cross arm and in some cases in the negative limb. In August 1951 no difference was observed, except that a thin, uneven brownish film had appeared on top of the grayish layer.

Six weeks after assembling the cells, and after the intervals stated in table 10.4, the comparative data listed therein were gathered.

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[4] A spectrogram of another sample prepared at another time showed the same metallic constituents.

TABLE 4. *Hysteresis of unsaturated cells, without septa, showing the effect of soaking cork in the* $CdSO_4$ *solution*

	Controls (untreated solution)	Test cells (corks soaked in solution)
Electromotive force at 6 weeks (volts)	1.0193	1.0194
Internal resistance at 6 weeks (ohms)	165	165
Hysteresis (39° to room temperature):		
6 weeks (%)	0.000	0.02+
8½ months (%)	>.01	<.12
10 months (%)	.0045	.14
29 months (%)	.0035	.311

Separation of Solids from Cork Infusion Prepared by Boiling

About 600 ml of an infusion of cork (by boiling) was saturated with $CdSO_4$ at room temperature[5] by rapid stirring overnight in air. The next morning, a dirty-white scum, somewhat foamy, was at the top of the solution, and a brown flocculent suspension that showed little or no tendency to separate out was distributed throughout it. In a separatory funnel 5 cm in diameter the layer of scum was about 5 mm thick. The $CdSO_4$ used for saturation gave in water a slightly acid solution; pH about 3.1.

In order to ascertain if the scum and suspension were a result of the rate of stirring and/or the oxidation of some component of the cork, the above experiment was repeated in the absence of air. Before the addition of the solid $CdSO_4 \cdot \frac{8}{3}H_2O$ the solution was divided in half and each stirred about 10 hr in flasks provided with rubber stoppers with inlet and outlet tubes and a hole for the stirrer, so that any O_2 of the air above the solution could be displaced by a flow of N_2 during stirring. Stirring in one flask was at a high rate of speed; in the other, at a low rate, about 180 rpm. No whitish scum was evident in any of the flasks.

Another identical solution stirred violently in air for 10 hr also gave no whitish scum. All three flasks, however, had the brown flocculent suspension mentioned, and the last solution on cooling in an ice chest for 2 days (to see if raising the density of the $CdSO_4$ solution would cause a separation) gave no evidence of any separation into two components.

No further attempt to bring about the separation of the white scum was made.

Next, six portions of 200 ml each of a filtered freshly made cork infusion were placed in 250-ml Pyrex flasks. To five of these flasks dilute H_2SO_4 was added in volumes calculated to give normalities of 0.02, 0.04, 0.06, 0.08, and 0.12, after saturation with $CdSO_4 \cdot \frac{8}{3}H_2O$ by stirring overnight at room temperature (about 23° C).

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[5] Saturation, and other determinations, at room temperature were considered satisfactory because of the variation in the cork extracts. Trends only could be hoped for, and time had to be considered.

All the solutions had brownish flocculent suspensions, the color of the suspension in the "neutral" solution being by far the darkest.

Finally, the six solutions were suction filtered through filter paper in a Buchner funnel.

The densities of the six filtered (which were light yellow) solutions, determined on a Westphal balance, and their average pH, as determined on a Beckman and a Leeds & Northrup pH meter, were as shown in table 5.

TABLE 5. *Filtered cork infusion saturated with* $CdSO_4 \cdot \frac{8}{3}H_2O$ *without or with added acid*

The temperature was 21.5° for the first three values and 23.0° for the last three.

Normality (H_2SO_4)	Density g/ml	pH (26.5° C)
Neutral	1.612	3.31±0.03
0.02	1.614	1.90±0.02
.04	1.615	1.42±0.02
.06	1.617	1.20±0.01
.08	1.617	1.06±0.02
.12	1.614	0.89±0.05

Six new solutions of $CdSO_4$ were then made. The first was "neutral", being made with distilled water; the other five by saturating dilute solutions of H_2SO_4 of appropriate acid concentration with $CdSO_4$. The normalities by titration against 0.0709 *N* NaOH, using methyl red as indicator, were as given in table 6. The calculated values obtained from dilution data are also given. Their pH, measured as above, are also given in table 6.

TABLE 6. *Saturated solution of* $CdSO_4 \cdot \frac{8}{3}H_2O$, *containing no cork infusion*

Normality, calculated (H_2SO_4)	Normality, titrated	pH (26.5° C)
Neutral	0.0006	3.46±0.04
0.02	$.0191_0$	1.63±0.04
.04	$.0393_7$	1.26±0.03
.06	$.0590_4$	1.12
.08	$.0788_2$	1.02±0.02
.12	$.115_4$	0.90±0.05

Cells Made with Cork Infusion as Electrolyte; Also with the Solid from Cork Infusion Added to the Depolarizer

For these experiments four series of cells, each series consisting of six groups of three cells each, were made as designated in table 7.

All cells were made with no septa. Performance of these cells is given in table 7.

Table 7. *Performance of unsaturated cells modified by materials from cork infusions*

Series I. Filtered cork infusions saturated with $CdSO_4 \cdot \frac{8}{3}H_2O$ of acidities as given above, table 5. Series II. Cadmium sulfate solutions of various acidities containing no cork extracts, table 6; separated flocculent suspensions of respective acid infusions, table 5, added to mercurous sulfate. Series III. Same as series II, except that all suspensions added to mercurous sulfate were from a neutral infusion of cork, saturated with $CdSO_4 \cdot \frac{8}{3}H_2O$. The suspension was from an infusion that had been saturated with N_2; however, it was filtered and washed in air. Series IV. Control cells: cadmium sulfate solutions of various acidities, table 6; no foreign material added to electrolyte or to mercurous sulfate.

Age	Acidity					
	Neutral	0.02*N*	0.04*N*	0.06*N*	0.08*N*	0.12*N*
	Series I, 3 cells					
Days	*Volts*	*Volts*	*Volts*	*Volts*	*Volts*	*Volts*
5	1.01576	1.01715	1.01775	1.01799	1.01817	1.01826
6	1.01521	1.01711	1.01771	1.01796	1.01811	1.01817
10	1.01479	1.01702	1.01763	1.01788	1.01802	1.01819
11	1.01471	1.01703	1.01770	1.01795	1.01806	1.01821
12	1.01463	1.01703	1.01767	1.01792	1.01807	1.01822
18	1.01402	1.01692	1.01762	1.01789	1.01809	1.01824
30	1.01363	1.01685	1.01758	1.01789	1.01804	1.01823
129	1.01042	1.01571	1.01683	1.01724	1.01750	1.01807
	Series II, 3 cells					
3	1.01809	1.01814	1.01814	1.01826	1.01826	1.01832
4	1.01814	1.01818	1.01817	1.01827	1.01824	1.01829
8	1.01819	1.01821	1.01820	1.01826	1.01822	1.01825
9	1.01820	1.01822	1.01822	1.01831	1.01827	1.01830
10	1.01820	1.01821	1.01821	1.01828	1.01824	1.01828
16	1.01815	1.01814	1.01817	1.01823	1.01820	1.01823
28	1.01820	1.01818	1.01822	1.01826	1.01819	1.01824
127	1.01820	1.01822	1.01830	1.01828	1.01821	1.01824
	Series III, 3 cells					
4	1.01781	1.01797	1.01816	1.01802	1.01818	1.01807
5	1.01774	1.01796	1.01813	1.01798	1.01811	1.01799
6	1.01774	1.01790	1.01806	1.01793	1.01805	1.01798
10	1.01769	1.01784	1.01801	1.01790	1.01796	1.01801
12	1.01778	1.01788	1.01809	1.01793	1.01802	1.01805
24	1.01778	1.01793	1.01806	1.01795	1.01805	1.01806
123	1.01755	1.01789	1.01806	1.01791	1.01793	1.01817
	Series IV, 3 cells					
2	1.01828	1.01824	1.01818	1.01821	1.01821	1.01811
6	1.01829	1.01826	1.01821	1.01824	1.01823	1.01818
7	1.01829	1.01825	1.01820	1.01823	1.01821	1.01817
8	1.01827	1.01823	1.01820	1.01823	1.01822	1.01820
14	1.01823	1.01823	1.01817	1.01823	1.01822	1.01821
26	1.01825	1.01825	1.01820	1.01826	1.01819	1.01818
125	1.01822	1.01826	1.01817	1.01817	1.01809	1.01813
	Hysteresis [1] of Cells. 12 to 18 days					
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
Series I	+0.238	+0.195	+0.191	+0.174	+0.151	+0.057
Series II	+.032	+.025	+.000	−.007	−.012	−.017
Series III	−.012	+.006	+.039	+.010	+.065	+.051
Series IV	−.003	−.012	−.010	−.010	−.011	−.016
	Hysteresis [1] of Cells—4 months					
Series I	+0.526	+0.412	+0.396	+0.363	+0.318	+0.155
Series II	+.118	+.070	+.024	+.006	+.006	+.001
Series III	+.266	+.201	+.132	+.156	+.137	+.057
Series IV	+.007	−.014	−.008	−.004	+.006	−.011

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[1] The hysteresis number was calculated by subtracting the equilibrium emf at room temperature from the emf observed about 2 hr. after removing the cells from an oven at 38.8° C. The cells were in the oven 2 to 4 hrs., and after removal cooled to room temperature in quiet air. The hysteresis is expressed in percentage of the emf of the cell.

Indications of Reactions

All cells made with infusions, or with solid from infusions, first showed precipitates over the Hg_2SO_4, which extended later from the cathode into the amalgam limb.

In all cells with electrolytes of the infusion made by boiling and later acidifying and saturating with $CdSO_4$ (table 5) there were precipitates over the Hg_2SO_4, which were larger with increasing acidity. Moreover, the Hg_2SO_4 was discolored, being darkest in the neutral cells and becoming lighter as the acidity of the electrolyte was greater. So were the precipitates.

Over the Hg_2SO_4 in the cells with electrolyte $0.02\ N$ in H_2SO_4, there was a flocculent very dirty white precipitate. The Hg_2SO_4 was darkened, but less so than that in the neutral cells. The flocculent precipitate was noticeably greater in quantity than that over the Hg_2SO_4 of the neutral cells, and lighter in color.

Cells with solid from infusions mixed with the Hg_2SO_4 were somewhat less definite in exhibiting precipitates, but this is to be expected, as the solid would have to go into solution in the spaces between the Hg_2SO_4 grains and then diffuse into the electrolyte above. This should be a slow process. The Hg_2SO_4 in these cells showed a discoloration, but it was not evenly distributed.

The Hg_2SO_4 in cells that had "neutral" electrolyte were coated with a dark-brown homogeneous layer 0.5 to 1 mm im thickness. In the cells with acid electrolytes, there was a progressive lessening of the thickness of the deposit and a lightening of its color as the acidity increased. Moreover, the particles of the added brown substance became more and more evident as the acidity of the electrolyte increased, indicating again that the brown substance, which separates out when cork infusion is saturated with $CdSO_4$, is more soluble in neutral to low-acid solutions than in those of higher acidity. (Approximately the same quantity of the brown material was added to each cell.)

Effect of Infusions Upon White Mercurous Sulfate

To observe the effect upon white Hg_2SO_4 of filtered infusions of various acidities which were saturated with $CdSO_4\cdot\frac{8}{3}H_2O$ 12 glass tubes of the form shown in figure 10.4 were made, each marked as closely as possible 10 mm above the sealed-off lower end, measured outside, and filled to the reference mark with white electrolytic Hg_2SO_4 tamped lightly into place. Ten milliliters of each solution listed in table 5 was then added. There were two tubes with infusion of each acidity, one with a solution that had been saturated with

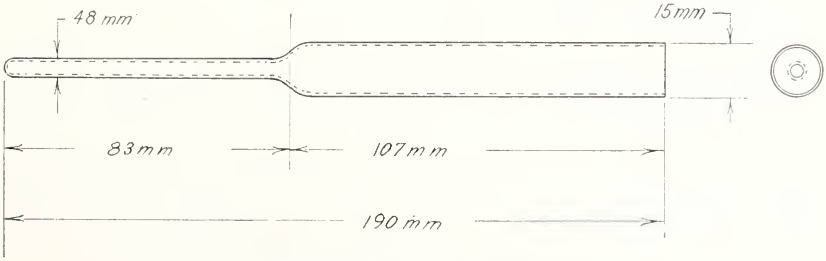

FIGURE 10.4. *Reaction tube.*

$CdSO_4 \cdot \frac{8}{3}H_2O$ under nitrogen and the other with a solution saturated in air.

The tubes were closed with rubber stoppers, kept either in the dark or in a dimly lighted room during observation, shaken from time to time, and the solids allowed to settle for 2 days.

In addition, another tube, X, was filled as described, but with the solution of 0.03 *N* $CdSO_4$ in which corks had been steeped at room temperature.

After the settling period all the solids, except that in the last tube, X, gained in volume, the solids of the 0.02 *N* solutions gaining the most. There was a change in texture between the solids of the neutral and 0.02 *N* solutions. The solid of the neutral solution was compact and fine-grained throughout, whereas that of the 0.02 *N* solution was compact and less fine-grained in its lower section, with a layer of flocculent material on top. The 0.04 *N* through 0.12 *N* solutions also had solids of fine, compact lower portions, over which were flocculent layers of about the same thickness, except that in the 0.02 *N* solution that had been saturated in air there was more flocculent deposit. From 0.04 *N* the color of the lower mass showed a consistent change. In the neutral solution, the color was a dark mouse gray for about 7 mm from the top surface. There was a sharp boundary line at this distance below the top, from which plane downward the color shaded from dark gray to light gray at the bottom of the tube. Ignoring for the moment the top layer in solutions 0.02 to 0.12 *N*, inclusive, the color in these shaded off in the same manner, the tints becoming lighter as the acidity increased, until the 0.12 *N* tubes became almost white throughout. The color of the flocculent upper layer graded from dark gray in the 0.02 *N* tube to almost white in the 0.12 *N* tube.

The solution in the last tube, X, had a solid that showed no change in volume. It was white throughout. There was a fine, persistent suspension in the solution, white like the solid.

A few other tubes had suspensions, but not in regular occurrence. When first observed the color of the solutions seemed slightly greenish in some tubes, but this most certainly changed to colorless later on as a very light dirty-white precipitate separated out on the shoulders of the tubes.

Two small samples of Hg_2SO_4, one from the top and one from bottom, were removed from the "neutral" tube with a capillary pipette. Each was spread upon a microscope slide, and covered with a cover glass, and in a thin layer was light brownish yellow.

No metallic Hg could be seen, even at a magnification of about 1,200 diameters. Globules of Hg are plainly visible, at about half the magnification, in gray Hg_2SO_4.

It is felt most strongly, therefore, that the change of color observed in the neutral reaction tube was not caused by a reduction in which metallic Hg is formed.

Gallic and Tannic (Digallic) Acids, and Solid from Water and from Alcoholic Extracts of Cork

As a result of reasoning of a very elementary nature, it was concluded early in these experiments that cork extract must contain tannic acid (digallic acid). It was found that both solid cork and aqueous extract of cork gave positive reactions to the $FeCl_3$ and KCN tests. Since these are group tests and not specific, it was thought well to include gallic acid in any investigation of the effect of tannic acid.

Neutral and 0.03 N $CdSO_4$ solutions were saturated with gallic acid and with tannic acid. With no Hg_2SO_4 present there was no reaction visible. However, when either white Hg_2SO_4 was added to the solution, or the same salt with finely divided Hg incorporated in it, a reaction occurred in each case. The reaction products were more copious with gallic aid than with tannic. For gallic acid, the precipitate was reddish brown to dark brown; for tannic acid, dark brown to almost black and in some cases greenish black. Gassing was noted with gallic acid, but not with tannic acid.

It is stated [11] that cork contains approximately 20 percent of tannic acid, but it is not felt that the above tests prove anything definitely, except that gallic and tannic acids bring about precipitates with Hg_2SO_4.

Cells with Cork Extract and Gallic and Digallic Acids

On June 29, 1951, five groups of four cells each without septa were set up, using as the electrolyte unsaturated $CdSO_4$ solution (concentration approximately equal to saturation at 4° C), which was 0.03 N in H_2SO_4. They were plugged at the top with rubber stoppers.

To the depolarizer of each cell of the five groups was added one of the following:

(1) Group Ia: A substance prepared as follows. Corks were boiled in water for 4 hr. The colored solution resulting was evaporated on a water bath to a brittle solid residue, which was very dark brown.

(2) Group IIa: 0.025 g of a substance Soxhlet extracted from corks with ethyl alcohol. The corks had previously been boiled in water for 40 hr, with rinsing and changes in water every 4 hr, to remove the water-soluble materials. After evaporation of the alcohol, a waxy light-chocolate-brown residue remained.

(3) Group IIIa: 0.025 g of tannic (digallic) acid.

(4) Group IVa: 0.025 g of reagent grade gallic acid.

(5) Group Va: No additions. The control group.

The physical appearance of the cells containing the materials extracted from corks with water and with alcohol was the same as the controls, except that particles of added materials could be seen in and on the Hg_2SO_4. In group IIIa, the Hg_2SO_4 was darkened somewhat. In group IVa, the Hg_2SO_4 was darkened to a greenish black, and the electrolyte was yellowish. Some slight gassing was observed in the Hg_2SO_4 gallic acid mixture during the first 2 weeks, after which no further gassing was observed. The performance of these cells is given in table 8.

TABLE 8. *Electromotive force and hysteresis* [1]

Age	Group Ia. Water extract from corks		Group IIa. Alcohol extract from corks		Group IIIa. Tannic acid		Group IVa. Gallic acid		Group Va. Controls	
	emf	Hysteresis	emf	Hysteresis	emf	Hysteresis	emf	Hysteresis	emf	Hysteresis
Days	*Volts*	*Percent*	*Volts*	*Percent*	*Volts*	*Percent*	*Volts*	*Percent*	*Volts*	*Percent*
19	1.01891	+0.141	1.01927	+0.043	1.01912	+0.047	1.01866	+0.006	1.01937	−0.008
47	1.01906	+.133	1.01921	+.021	1.01919	+.035	1.01882	+.082	1.01936	−.012
69	1.01906	+.157	1.01921	+.039	1.01911	+.053	1.01882	+.084	1.01929	−.001

[1] See footnote to table 7 for method of calculating hysteresis number.

Septa of Plastic Materials

From time to time, various materials have been used as septa in standard cells in this laboratory. It was desired to retain the desirable mechanical properties found in cork washers, but to use a material that would not require any special treatment to remove harmful substances.

Gum rubber was tried early in the experimentation, but no natural rubber with satisfactory physical properties was found to be satisfactory chemically, for even "pure-gum" rubbers of "low-sulfur content" produced a blackening in the plug and adjacent mercury.

"Silicon rubber" does not cause any visible blackening. The hysteresis in new cells made with septa of a certain variety of synthetic rubber containing silicon was very slight, of the order of ±0.001 percent for a 17-deg C drop. At the age of 15 months it was found to be 0.007 percent. This substance would be somewhat more difficult to use as a septum than cork, tending to "chatter" when being seated in the tubes, thereby inducing breakage. The same comment applies to natural rubbers. An irridescence on the surface of the electrolyte has been observed in cells made with septa of "silicon rubber."

A plastic believed to be a polyvinyl was found to have more desirable mechanical qualities. However, the hysteresis of cells with septa of this material was found to increase with time, being +0.010 percent at 7 months of age, +0.050 percent at 15 months, and +0.078 percent at 26 months. When chips of the material were mixed with the Hg_2SO_4, these values of hysteresis were increased by 0.02 to 0.03 percent, at all ages.

Methacrylate plastic the form of Lucite, was fabricated into a sort of "spring washer" to maintain the tight fit necessary in construction of a rugged cell. Cells with septa of Lucite washers and linen showed a zero hysteresis at 5 months of age, for a sudden 17-deg C drop. At 1 year the same test disturbed the emf by 0.003 percent; at 2 years, by 0.021 percent; and at 3 years, by 0.039 percent.

Conclusions

Septa that introduce no appreciable concentration of a foreign substance into a standard cell change the shape of its hysteresis curve, as compared with that of a cell of the same type and materials without a septum.

Cork contains substances, soluble in water, in aqueous $CdSO_4$ solution, and, in the same with a small concentration of H_2SO_4, which affect the behavior of a cadmium standard cell adversely. One of these substances, the brown flocculent suspension that separates out when an aqueous-cork infusion is saturated with $CdSO_4\frac{8}{3}H_2O$ is less soluble in aqueous $CdSO_4$ solutions with more acid, i. e., up to 0.12 *N* than in aqueous $CdSO_4$ solutions with less acid.

The material extracted by boiling alcohol from corks that have been boiled in distilled water for 40 hr has less adverse effect on the behavior of a cadmium standard cell than the material extracted from raw corks by boiling in distilled water.

Augmented hysteresis in a cadmium standard cell containing cork septa is the result of a reaction or reactions between the Hg_2SO_4 and one, some, or all of the materials introduced into the cell by the cork, and the reaction (or reactions) is a function of H_2SO_4 concentration, within the limits studied.

The hysteresis produced by the addition of the materials extracted from cork can be made negligible, to all practical purposes, by the presence of a small concentration of sulfuric acid in the electrolyte. This confirms the findings of Vosburgh [2].

It may be stated here that high hysteresis is in almost every case associated with a lower value of emf than that which has been accepted as characteristic for the particular type of cell.

It is finally concluded that "plastics", as a class, have desirable properties as materials for septa in standard cells.

References

[1] U. S. Patent 631,044, August 15, 1899, R. O. Heinrich, Berlin, Germany.
[2] W. C. Vosburgh and M. Eppley, J. Opt. Soc. Am. **9,** 65 (1924).
[3] F. E. Smith, Proc. Phys. Soc. (London) **22,** 36 (1910).
[4] M. Eppley, J. Franklin Inst. **201,** 24 (1926).
[5] G. A. Hulett, Phys, Rev. **32,** 262 (1911).
[6] F. A. Wolff and C. E. Waters, Bul. BS **4,** 10 (1907) S71.
[7] P. I. Wold, Phys. Rev. **27,** 329 (1908).
[8] G. W. Vinal and M. L. Howard, BS J. Research **11,** 255–275 (1933) RP588.
[9] M. Eppley, Trans. Am. Electrochem. Soc. **53,** 150 (1928).
[10] W. C. Vosburgh and K. L. Elmore, J. Am. Chem. Soc. **53,** 2819 (1931).
[11] Int. Crit. Tables **2,** 248, 1st ed. (1927).

Discussion

Dr. A. White, General Electric Co., West Lynn, Mass.: I would like to address a question to Dr. Eppley. We have centrifuged some cells to improve their portability. In some the hysteresis has been reduced, and in others it has remained the same. Is there some explanation for that?

Dr. M. Eppley: I would like to know their make. That would be a good thing to have done in any laboratory. You have probably compacted in some cases the Hg_2SO_4. That has made them more portable, I would say. In compacting, you have lessened the volume between the grains of your depolarizer, and you would expect them to come to equilibrium more quickly. That would be in the right direction.

On the other hand, if you had any impurity in there, whatever it might be, something that got in from the cork or otherwise, I would expect that that impurity would have more effect when there was less solution than with more. That is, you have made the volume in between the grains less, and if you did not get rid of that impurity (if, for example, it was an adsorption or something of the sort), you probably would slow down the return to equilibrium. Does that seem sensible, Dr. Silsbee?

Dr. F. B. Silsbee, National Bureau of Standards: Yes.

11. Aging of Standard Cells

By F. X. Lamb[1]

In coming to Washington to speak before this group on the occasion of the fiftieth anniversary of the National Bureau of Standards, it seemed only fitting and proper to reflect on some of the technical events that have occurred during those 50 years. In this paper I shall refer particularly to the subject of standard cells.

As is well known and recorded in history, as well as in the Patent Departments of Germany and the United States, Dr. Edward Weston invented the cadmium-type cell prior to 1891 and obtained his patents in 1892. Dr. Weston actually began production of his cells in 1891 in a branch laboratory of the Weston Company in Berlin, Germany, primarily because of the availability of chemicals superior in purity and because of the advantages gained by being close to the Reichsanstalt. The Weston form of cell, both saturated and unsaturated, has been made without interruption over the intervening 60 years from 1891 by the Weston Corporation.

Although no person living can recite from personal experience the problems attendant to the early production of cells, we know from recorded data that one of the most difficult problems was to produce cells without having available cell ingredients of required purity or knowing how to produce them commercially of the required purity. As we all know, great strides have been made in chemistry and methods of refining chemicals over the past half century. This is particularly so since World War I. Today in the United States not only are chemicals available of very high purity, but the refining procedure has been developed to the point where chemical purity is a matter of willingness, patience, and cost rather than lack of knowledge.

Without any reflection except that of pride for the cells made in the early days by Dr. Weston, it can be said that present-day cells do differ somewhat from those made 50 years ago. The changes, however, are in the refinements associated with the advance of the technical frontier rather than in premise or in fundamentals.

Among the changes that have taken place during the past 50 years, resulting from the efforts of many workers in the field, might be listed the following: Improved methods for the refining of the ingredients; improvement in the sealing off of cells to make them truly hermetically sealed; improvement in the thermal shielding; change from soda-lime to borosilicate glass for the containers; improved methods of filling and retaining the ingredients within the glass containers; and improvements in the housing.

Although the passage of time has obscured the details of the difficulties encountered by Dr. Weston during the early days of cell manufacture, it is recorded that "considerable difficulties were overcome only after years of sustained efforts." This is borne out by the story that in the early days of cell manufacture, keen interest was always shown in the number of good cells produced as a per-

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[1] Assistant Chief Engineer, Weston Electrical Instrument Corporation, Newark, N. J.

centage of the total. Today, cells are made with such exactness that rejects are usually restricted to mechanical failures, such as glass breakage.

Notwithstanding the advances that have been made in the art of standard-cell manufacture, one may ask "Just how good are standard cells?" and "How do you as a manufacturer know, since you send your product out to industry and seldom see it again?" The answer is that there are data available. Some has been accumulated and published by Vinal, Craig, and Brickwedde [2] and more recently by Vinal.[3] Further, many cells are periodically returned to the Weston plant for recertification. These data are accumulated and subjected to analysis.

However, as cells that have been sent out and later returned can only add to data on cells after an unknown service, it seemed warranted that we at Weston obtain additional data relative to cells where the service conditions were known. To this end we have over the past many years made it a practice to select at random one or more cells for life tests from the successive groups manufactured. These cells are set aside and periodically checked. Periodically we also obtain cells from other makers for comparison purposes and test them side by side with our own. The data thus collected have heretofore been classified as confidential. In this paper these data are being disclosed for the first time and are presented herewith. The available records cover a period of 20 years and date back to 1930.

At this point it is important to state that while the data are complete and unabridged, the figures are not fully applicable to cells that would be shipped to a user. Cells having a change as great as some few of those being reported upon would normally be rejected by inspection and test run during the normal aging period of 6 months to 1 year before a cell is standardized and considered as ready for shipment. Attention is also directed to the phenomena where it is quite common for new cells to increase in emf for a short period of time, after which they reverse the trend, decrease in emf at a moderate rate, then stabilize, and thereafter begin a slow drift downward, which invariably continues throughout their life.

The data presented covers the life of the cells after initial standardization at about 1 year from the date of assembly. It is a summary of 305 standardizations made on 45 cells.

The average change of 80 microvolts per year on this group of cells compares favorably with the average change of 85 microvolts per year reported by Vinal, Craig, and Brickwedde [4] and with a weighted average drift of 71 microvolts per year reported by Vinal.[5]

Considering that the cells being reported on were all "as made," with no preselection, the groups from which the cells were taken represent rather excellent control and manufacture.

To assist further in evaluating the data collected from these cells, a graph is presented (fig. 11.1) to show both the individual values of the drift of the cells and a curve for the average value of the drift. The unbroken curve is for the average value of the drift with all values of standardization included and is in accordance with the values shown in table 1. The broken portion of the curve is obtained by omitting

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[2] G. W. Vinal, D. N. Craig, and L. H. Brickwedde, Trans. Electrochem. Soc. **68**, 139 (1933).

[3] G. W. Vinal, Primary batteries (John Wiley & Sons, New York, N. Y., 1950).

[4] See footnote 2.

[5] See footnote 3.

those observations shown at the top of the graph representing a few cells where the drift was in excess of 200 microvolts per year for the first several years. This is justifiable, as previously mentioned. Further, it is worthy of mention that those cells which exhibited a drift in excess of 200 microvolts were manufactured prior to 1940.

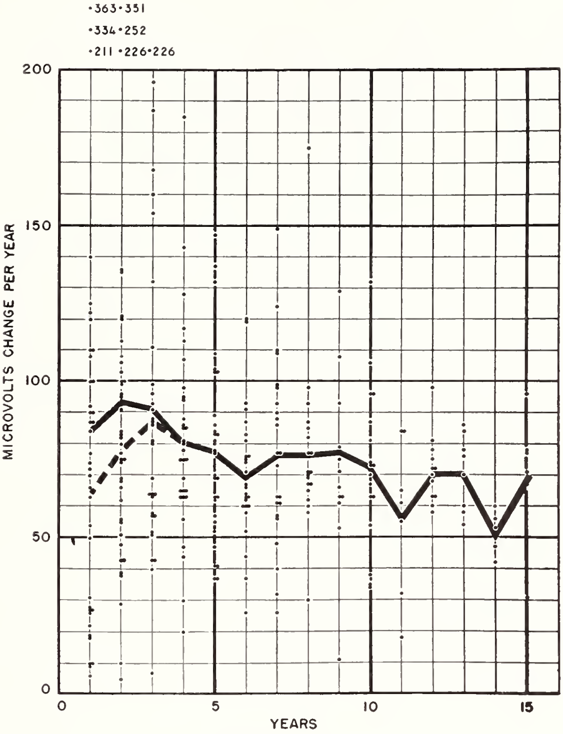

FIGURE 11.1

TABLE 1.

Elapsed time after initial standardization	Average change, all cells
Years	*μv/yr*
1	85
2	94
3	92
4	81
5	78
6	70
7	77
8	77
9	78
10	73
11	57
12	71
13	71
14	52
15	70
Weighted avg ------	80

It is hoped that the data presented will be of some use to those concerned with standard cells. If it served no other purpose, it is convincing evidence that cell quality is being maintained, and that those concerned with their manufacture recognize their responsibility and are keeping faith with those who purchase their product.

The data presented is useful, however, in that it indicates that if standard cells are not mishandled, or subjected to abnormal conditions, their constancy is remarkable and the voltage drift is within relatively narrow limits. The data presented also confirms the statement that for measurements requiring great precision, for example 0.02 percent or better, which corresponds to a 200-microvolt change, it is recommended that cells be recertified at intervals of 1 or 2 years.

In conclusion, it is only fitting to comment on the assistance rendered by the National Bureau of Standards to those of us concerned with the maintenance of precision standards. The Bureau has been of inestimable help, without which it would have been impossible to carry on the work to the high degree of accuracy required for standard-cell manufacture and certification.

We in these United States are indeed fortunate to have available the services of so fine an organization as that of the National Bureau of Standards. Its history over these past years has been one of service with integrity, a combination which we all value and of which those who comprise its staff may be justly proud.

12. Standard Cells and the Unit of Electromotive Force

By Walter J. Hamer, Langhorne H. Brickwedde, and Phyllis R. Robb [1]

Introduction

One of the legal responsibilities of the National Bureau of Standards is the maintenance of standards of electromotive force (emf) for the United States including certification of standards of emf for industrial concerns, Government agencies, universities, and standardizing laboratories. The national standard of emf, the unit of which is the volt, is maintained at the National Bureau of Standards by a group of saturated cadmium cells [2] [1] [3] consisting of a cadmium-amalgam negative, a mercury-mercurous sulfate positive in a saturated aqueous solution of cadmium sulfate. Part of the present NBS primary group of standard cells was constructed in the years 1906 to 1913 and another part in 1932. Other cells made annually or biennially, with the war years excepted, supplement the primary group.

The volt, although an important unit, is a secondary one. Its value is established experimentally through Ohm's law and the absolute ohm and ampere. Early in this century the practical standard of resistance was a Hg column of specified dimensions, and the practical standard of current was defined by the amount of Ag deposited in a specified time under specified conditions. At the present time (since January 1, 1948) the ohm is evaluated in absolute units in terms of inductance and frequency [2, 3, 4, 5] and the ampere in absolute units by the measurement of a force produced by the current in a current balance [6, 7, 8]. These absolute measurements are involved, require painstaking work and, therefore, are unsuitable for determinations of the volt as frequently as such determinations are demanded. To circumvent the necessity of frequent absolute measurements, standard cells are constructed, their emf are determined in relation to absolute current and resistance, and these cells are then used to maintain the volt in the interim.

The validity of this procedure rests on the assumption that the emf of standard cells are independent of time. Obviously, all of a group of identical cells may increase or decrease in emf without evident departures from an assigned mean. Today we have arrived at a state where we believe that the precision of cell measurements and the agreement of cells within the group indicate that the standard is not drifting by more than 0.6 μv, or 6 parts in 10 million, per year. This does not imply, however, that absolute determinations, which are the only proof of the constancy of the cells, are so precise.

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[1] National Bureau of Standards, Washington, D. C

[2] Historically, these cells are referred to as Weston cells after Edward Weston, who first proposed them in 1892. The term "Weston Normal Cell" refers to the so-called "neutral" type of cell, in which a saturated aqueous solution of cadmium sulfate is used.

[3] Figures in brackets indicate the literature references on p. 113.

History of the United States Unit of Electromotive Force

In 1893 the Chicago International Electrical Congress[4] chose the Clark cell[5] as the standard of emf, and assigned to it a value of 1.434 v at 15° C, based on units of current and resistance then accepted and in conformity with the report of November 1892 of the Committee of the Board of Trade of Great Britain. By an act of the United States Congress, July 12, 1894, definitions were adopted for electrical units substantially equivalent to those adopted at Chicago. The National Academy of Sciences, acting on authority of the United States Congress, prepared and published on February 9, 1895, detailed specifications for realizing the international ampere and the international volt by the silver coulometer and the Clark standard cell. Thus, in 1895 the Clark cell was the legal standard of emf in the United States. It was assigned a value of 1.434 v at 15° C.

In the years immediately following 1893, most countries adopted 1.434 v for the Clark cell at 15° C. Later work showed that cells made with specially purified Hg_2SO_4 had an emf of 1.4337 v at 15° C, or an emf 0.0003 v lower than the cells made prior to the meeting of the Chicago International Electrical Congress. Germany, however, recommended and adopted 1.4328 v at 15° C for the Clark cell in 1898. Their lower value was based on different values of the ohm and ampere. Although the German value was not universally accepted, it was a more nearly correct value as later experiments showed. Also, during the years 1893 to 1905, the Weston cell (see footnote 2) was found to have many advantages over the Clark cell and at an informal international conference[6] at Charlottenburg in October 1905, the Weston normal cell was first proposed for adoption in maintaining the volt. This informal recommendation, however, was not officially adopted until 1908 (see below).

In 1906 the United States standard of emf was defined in terms of the Clark cell made with specially purified Hg_2SO_4 and of the Weston normal cell, whose emf was expressed in terms of its measured emf difference from the Clark cell. The Clark cells were assigned a value of 1.42110 v at 25° C. This was based on the value 1.434 v at 15° C adopted by the Chicago International Electrical Congress and legalized by the U. S. Congress, less the correction of 0.0003 v for the use of specially purified Hg_2SO_4, and less the temperature correction calculated from the emf-temperature coefficient determined by Callendar and Barnes [10], i. e., $1.434-0.0003-0.0126=1.4211$ v. The mean of the Weston normal cells made at NBS, and then on hand, was 1.01890 v at 25° C in terms of the Clark cells at 25° C. Thus in 1906 the standard of emf in the United States was a group of Weston normal standard cells, whose mean emf was taken to be 1.01890 v at 25° C.

In 1908 the International Conference on Electrical Units and Standards [11] met in London and officially accepted the Weston

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[4] This Congress was composed of delegates from Austria, Canada, France, Germany, Great Britain, Italy, Mexico, Sweden, Switzerland, and the United States.

[5] The Clark cell was devised by Latimer Clark in 1872 [9]. It consists of a Zn-amalgam negative, a Hg-Hg_2SO_4 positive in a saturated solution of $ZnSO_4$.

[6] The International Electrical Congress in St. Louis in 1904 recommended that the various governments concerned appoint members to an International Commission to consider inequalities known to exist in the electrical units as maintained in the various countries. In accordance with this recommendation, the Physikalisch-Technische Reichsanstalt invited representatives of the various standardizing laboratories to a conference at Charlottenburg.

Normal Cell on the recommendation of the Charlottenburg Conference of 1905. The London Conference further adopted provisionally 1.0184 v as the emf of the Weston Normal Cell at 20° C, and recommended for the emf-temperature coefficient of the Weston Normal Cell the formula based on the measurements of Wolff [12] at NBS. By this formula, the Weston Normal Cell at 25° C had an emf of 1.018174 v, which is 0.000726 v lower than the value then accepted in the United States. This discrepancy was caused largely by the fact that the United States had accepted 1.4337 v for the Clark cell at 15° C, whereas the German value of 1.4328 v at 15° C had proved to be a more nearly correct value. The London Conference still felt, however, that further work was needed and recommended that additional experiments be made.

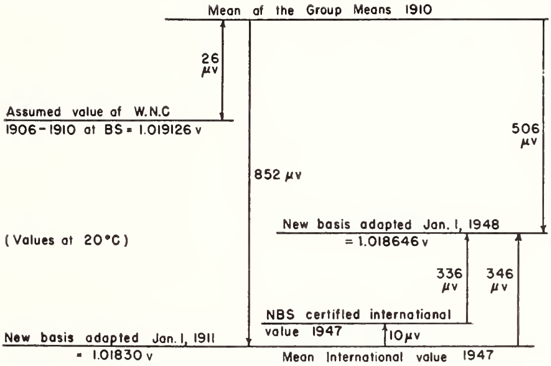

FIGURE 12.1. *Effect of changes in the volt for the United States from 1906 to 1951, inclusive.*

(Not drawn to scale.)

Accordingly, scientists from England, France, and Germany met with American scientists at the National Bureau of Standards in 1910, and as a result of their experiments with a large number of Weston Normal Cells and silver-coulometer determinations adopted 1.01830 v as the emf of the Weston Normal Cell at 20° C. The fact that this was necessarily only an approximation to the "true" or "absolute" value was indicated by prefixing the adjective "international," and 1.01830 was taken by mutual agreement as the emf of the Weston Normal Cell in "international volts." This is the value familiar to most scientists and found in nearly all textbooks. This value stood until 1948 when the United States and other countries went over to absolute units. On the new absolute basis the value of the Weston Normal Cell at 20° C becomes 1.018646 v. This value is now of historical interest only.

In figure 12.1, the effect of changes in the value of the United States unit of emf in international and absolute units is given from 1906 to 1951. The values are all given for a typical Weston Normal Cell at 20° C, the temperature chosen as reference by the London International Electrical Conference. In 1906 the NBS primary group of 12 cells had an emf of 1.019126 v at 20° C, based on the calculations and experiments described above. Early in 1907, however, one cell was broken, and in 1908 several of the remaining cells were accidentally damaged in the temperature-coefficient work. Seven other cells made in 1906, which had shown exceptionally good characteristics, were made the Bureau's reference cells in February 1908. The mean of this group of seven cells was 14 μv below the group of 1906. The group of seven cells served officially as the standard of emf from 1908 to 1911 and had a mean value of 1.019112 v. In 1910 the mean of the group means of the cells submitted by England, France, Germany, and the United States was 40 μv higher than the mean of the NBS older cells, or 26 μv higher than the value assumed by NBS in 1906 for the primary group. This difference of 40 μv (0.04 μv) was later found to be largely caused by an aging effect of these cells, the duration of which was about 2 years. In other words, the difference between the Bureau's older group of cells, and the new cells made by the four countries in 1910 decreased by 37 μv, and hence became insignificant within about 2 years. As the Bureau's older group was then 6 years old (4 years at start of comparison), the new cells made by the four countries were judged to decrease in emf with time; an increase in emf of the older cells was deemed extremely unlikely.

Those who met in Washington in 1910 still realized, however, that the Hg ohm and the Ag coulometer were not fundamental standards for resistance and current, and believed that absolute units based on the cgs system were more desirable. Accordingly, the standardizing laboratories of several nations continued their absolute measurements and determinations of the relation between absolute units and the international units then in use.[7] It was not until 1948, however, that the absolute scale based on mechanical units become a reality. Two World Wars had caused delays in the necessary experimental work. As a result of determinations of the relation between absolute units and the international units in various countries, it was found that the mean ratio was 1.000490 for the ohm and 0.99985 for the ampere [13]. Therefore, through Ohm's law the ratio for the volt is 1.00034. As international comparisons of the ampere are not feasible, the conversion factors in transportable units were chosen, and the International Committee on Weights and Measures in October 1946 announced [14]:

1 mean international ohm=1.00049 absolute ohms.

1 mean international volt=1.00034 absolute volts.

The mean international units were the averages of units maintained in national laboratories of France, Germany, Great Britain, Japan, USSR, and the USA that took part in the international comparisons before the outbreak of World War II.

Specifically, the units maintained in the United States differed from the above averages by a few parts in a million, and the conversion factors were

1 international ohm (USA)=1.000495 absolute ohms.

1 international volt (USA)=1.00033 absolute volts.

The International Committee set the date January 1, 1948, for the

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[7] This does not imply that methods for absolute measurements were not known in 1910, but that sufficient accuracy of the measurements had not been attained. Actually the work of Gauss in 1833 and of Weber in 1851 showed the possibility of measuring electric and magnetic quantities in terms of mechanical units. [13].

change to absolute units.[8] Likewise, other countries had their own conversion factors. In essence, therefore, on January 1, 1948, the absolute volt and absolute ohm were identical in all countries.

Between 1906 and 1951, the progress in the science of electrical measurements, as formally recognized by international agreements, had led to a number of changes in the unit of emf in the United States. The magnitude and significance of these changes are summarized in table 1. The emf of a typical saturated cadmium cell and the standard electrode potential of the Ag-AgCl electrode at 25° C in terms of the national standard at various periods in the history of the United States are listed. The effect of the conversion from international to absolute units is shown in terms of a quantity well known to chemists. Although the changes are not large, care should be exercised in making comparisons of literature data prior to 1948 with data reported since January 1, 1948.

Table 1.—*Effect of changes in the unit of the United States standard of electromotive force on the electromotive force of saturated cadmium standard cells at 20° C and on the standard electrode potential of the silver-silver chloride electrode at 25° C as certified by NBS.*

Year	Standard cell	Silver-silver chloride electrode
	Volts	*Volts*
1906	1.019152	0.22258
1910	1.019152	.22258
1911	1.018300	.22239
1912	[a] 1.018337	.22240
1913	1.018300	.22239
1947	1.018310	[b] .22239
1948	1.018646	.22246
1951	1.018646	.22246

[a] Effect of aging of reference group. Correction for this was made and incorporated by 1913.
[b] Value of 0.22239 v is that given by H. S. Harned and R. W. Ehlers [15].

The change from international to absolute volts causes no change, however, in many electrochemical and physical chemical constants, for example, activity coefficients obtained from emf measurements. Activity coefficients of HCl determined from measurements of the cell:

$$H_2(g)|HCl(aq)|AgCl(s), Ag(s)$$

are given by the equation

$$\frac{(E-E^0)\text{ volts}}{(RT/\mathbf{F})\text{ volts}}+\ln m_H m_{Cl}=\ln \gamma_H \gamma_{Cl},$$

and the volt cancels on the left side of this equation. Therefore, the value of the activity coefficient of HCl is the same whether the emf of the cell is measured in international or in absolute volts. Of course, E, E^0, and $RT/\mathbf{F}$ must be measured or expressed in the same units. The same holds for pH values, ionization constants, and like quantities. Conversion from international to absolute units does

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[8] It had been suggested that absolute volts be used to designate the new unit to distinguish it from the older unit. The National Bureau of Standards, however, took the view that it was preferable to drop the adjective "absolute" and use only "volt." It was deemed advisable to speak of only one kind of volt and to do so from the time of the change. When the National Bureau of Standards uses the term "volt," "absolute volt" is therefore implied.

affect the values of the faraday, standard electrode potentials, redox potentials, electron charge, electron volt, free-energy changes, and ionic mobilities. Conversion factors for these and other quantities are given elsewhere [16].

Modifications in Standard Cells

In maintaining the standard of emf, it is assumed that between absolute determinations the emf of the cells in the reference group remains constant. As pointed out above, it is obvious that a group of identical cells may increase or decrease so uniformly that departures from the assigned mean may not be evident. Modifications in the type of cells used for a primary standard are desirable. An alternative type of standard cell using an entirely different electrochemical system would be most valuable, for if changes of emf with time in two different cell systems occurred, they would not be likely to follow the same pattern. However, the prime requirement of constancy has not been as well realized in other systems as in the cadmium-mercury one. Further, the measurement of emf differences of a half volt or thereabouts with the precision required imposes a problem, though not an insurmountable one.

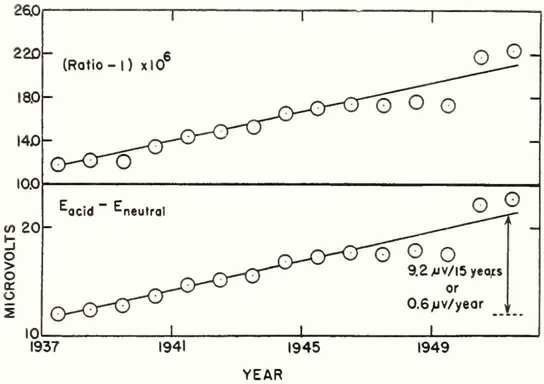

Figure 12.2. *Ratios and differences in acid and neutral saturated cadmium cells.*

In order to have different kinds of cells in its primary standard, the NBS has effected in recent years several modifications in Weston normal cells. These modifications include (1) acid cells, (2) acid cells with deuterium oxide, and (3) substitution of quartz for glass as container material for both acid and neutral cells. Thus, including neutral cells in glass, 10 ratios may be obtained, and these ratios may be followed over a period of years.

The first modification that was effected was the construction of acid cells. In the so-called "neutral" Weston normal cell, Hg_2SO_4 hydrolyzes to form basic mercurous sulfate and H_2SO_4 of an equilibrium concentration. Although these cells are stable in emf and basic mercurous sulfate, once formed, appears to have no effect on the stability of the cell, many experimenters have felt that better cells would be obtained if H_2SO_4 were added in sufficient amount to prevent the formation of the basic salt. Accordingly, in 1932 a group of cells were constructed that were 0.04 N in H_2SO_4. Higher concentrations of acid cause the formation of appreciable quantities of gas at the cadmium amalgam. These cells were studied for a number of years and then incorporated into the primary group in 1937.

In figure 12.2, the ratio of the emf of acid and neutral cells in the NBS primary group is shown as a function of time for the past 15 years (in the figure $(\text{Ratio}-1)\times 10^6$ is plotted for convenience). This ratio has varied with the neutral cells decreasing and the acid cells increasing in emf in terms of the group mean. In the lower part of the figure, the differences in emf between acid and neutral cells are shown as a function of time. Over a 15-year period this difference has shifted by 9.2 μv, or 9.2 ppm, or 6 parts in 10 million (0.0006 mv) per year. This shift is very much beyond the precision and accuracy of most scientific investigations, but is a real effect.

Of course, we cannot decide from these measurements which type of cell is changing in emf with time, or which type is more stable. Recourse, therefore, has been made to measurements of the temperature coefficient and effect of age on the stability of the two types. In table 2, the differences of the emf at 20° C. from those at 25°, 28°, and 30° C. are given for a group of 46 cells of different ages and acidities but of similar construction to the cells in the NBS primary group.

TABLE 2. *Differences in the electromotive forces of standard cells of different acidities and ages at 20° C from the electromotive forces at 25°, 28°, and 30° C*

Age	Number of cells	(20−25)° C	Δ[a]	(20−28)° C	Δ[a]	(20−30)° C	Δ[a]
Neutral (21 cells)							
Years		*μv*	*μv*	*μv*	*μv*	*μv*	*μv*
10	7	227. 5	3. 2	382. 4	4. 4	494. 6	5. 2
20	7	228. 6	4. 2	384. 2	4. 9	495. 9	8. 3
40	7	231. 0	4. 5	386. 2	5. 5	501. 7	5. 0
Mean		229. 0	4. 0	384. 3	4. 9	497. 4	6. 2
Acid (25 cells)							
3	7	222. 5	0. 4	372. 9	0. 8	484. 5	0. 9
9	7	221. 2	. 3	372. 9	. 5	483. 6	. 7
15	9	219. 7	2. 5	371. 9	3. 7	480. 1	2. 7
18	2	222. 1	0. 1	373. 6	0. 0	483. 5	0. 2
Mean		221. 1	0. 8	372. 6	1. 3	482. 6	1. 1

[a] Mean deviation.

It will be noted that the average deviation from the mean is much larger for neutral cells than for acid cells, being approximately 5 μv for the former and 1 μv for the latter. Therefore, acid cells exhibit less variation in behavior than neutral cells and are probably more reliable. It will also be noted that the emf-temperature coefficients of acid and of neutral cells differ and that the emf-temperature coefficient for acid cells is more constant with age. This observation also suggests that acid cells are more reliable. Our observations on acid cells are not very different from those given by Vigoureux and Watts [17].

The second modification that was effected was the substitution of deuterium oxide for ordinary water as the electrolyte solvent. An account of these cells is given in papers by Brickwedde and Vinal [18, 19]. In figure 12.3, the relation between the emf of saturated standard cells and the mole percent of deuterium oxide is shown. The total change in going from pure-water solution to pure deuterium-oxide solution is only 395μv, which is well within the range of 2,100μv of the specialized potentiometer [20] used in the intercomparison of primary-group cells. The cause of the change in emf resulting from substitution of deuterium oxide for water has been given in the papers of Brickwedde and Vinal [18, 19].

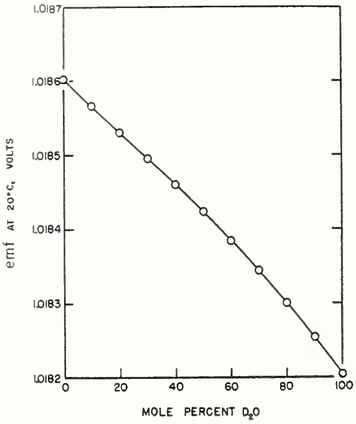

FIGURE 12.3. *Effect of deuterium oxide on the electromotive force of saturated cadmium standard cells at 20° C.*

In 1949 four groups of standard cells containing either deuterium oxide or water were prepared. Each cell was made 0.02 *N* in H_2SO_4. In figure 12.4 the average 2-year change in emf for each group of cells is given in terms of the standard deviation. The average change is greater for the H_2O groups than for the D_2O groups, but the standard deviations are the same. Unfortunately, these observations cover only a 2-year period, a period during which standard cells are known to age, and, therefore, no definite conclusions may be drawn at this time as to the relative stability of water and deuterium-oxide cells. At this time, these observations could be considered to reflect effects

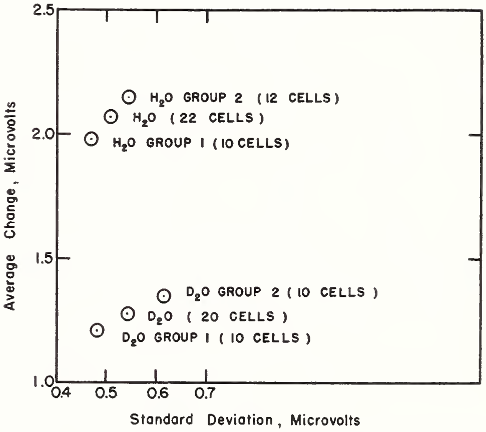

FIGURE 12.4. *Statistics on the changes in the electromotive forces at 28° C from 1949 to 1951 of standard cells made with water or deuterium oxide.*

of experimental technique rather than differences inherent in the chemistry of the cells. Definite conclusions will be possible only after more extensive observations.

The third modification that was effected was the substitution of a fused-quartz cell container [21] for the Kimble standard flint glass container that has been used at the National Bureau of Standards for many years. It has been realized for a long time that the alkali of glass may neutralize the acid in acid standard cells (neutral cells should not be affected as Hg_2SO_4 should hydrolyze to maintain the equilibrium concentration of H_2SO_4), thereby affecting the stability of the cell [22, 23, 24]. It was felt that fused quartz may, therefore, be a better container. Details of their construction have been given elsewhere [21] and will not be repeated here.

Seven satisfactory saturated standard cells were made in these containers. Eight control cells in Kimble glass were made at the same time. Five acid cells (0.02 *N* in H_2SO_4) were made in both types of containers and two neutral cells in quartz and three neutral cells in glass. Readings of the emf were taken at intervals during 1949, 1950, and 1951. If we take the cell average for 1951 and subtract the average for the same cell in 1949, we obtain an emf difference that is a measure of the change in emf of that cell over a 2-year period. These emf differences at 28°C are given in table 3.

TABLE 3. *Differences in the electromotive force of standard cells in quartz and glass containers between 1951 and 1949 (1951 value minus 1949 value)*

Quartz		Glass	
Acid	Neutral	Acid	Neutral
μv	*μv*	*μv*	*μv*
1.9	1.7	3.8	3.9
3.4	3.5	3.6	9.4
1.6	--------	2.2	11.9
1.6	--------	3.8	--------
1.1	--------	1.9	--------

Average change for quartz=2.1_1. Average change for glass=5.0_6.

The average change in emf for glass containers is higher than for quartz containers. In addition, the changes in emf vary less in the quartz group than in the glass. Greater average change and greater variability in emf seem to be the case for glass in both neutral and acid cells. The sample size, however, was too small to draw definite conclusions between the behaviors of acid and neutral cells in the two types of containers. Additional cells will be obtained and further studies made.

International Comparisons

Annually or biennially, the National Bureau of Standards transports by messenger saturated standard cells that have been compared with the NBS primary standard cells to the Bureau International des Poids et Mesures[9] for comparisons against the international group maintained there. The National Bureau of Standards measures the emf of its cells immediately prior to transport to the International

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[9] For a brief history of the International Bureau, see the discussion of F. B. Silsbee under standard cells at the end of this paper.

Bureau and immediately after their return. Except on very rare occasions, the two measurements have agreed within a microvolt, showing that transportation by messenger had not affected the cells.

Comparisons with the International Bureau (BIPM) since World War II are shown in figure 12.5. Differences between the NBS and BIPM values reported for the NBS cells are given. Reported differences are represented by the shaded circles. In 1946, 1948, and 1950 the values for the NBS cells differed by +10.0, +9.0, and $-0.7_9 \mu$v from the BIPM values for the same cells. However, BIPM reported their results in international volts in 1946 and 1948 and in absolute volts in 1950. If their international values of 1946 and 1948 are converted to absolute volts, using their conversion factor of 1.00034, the differences between the BIPM and NBS values for the same cells are −0.2, −1.2, and -0.7_9 for 1946, 1948, and 1950, respectively. The difference between the two groups of cells, those at NBS and those at BIPM, each maintained differently and by different staffs, has not varied on the average by as much as 1 μv since World War II. Of course, in arriving at the respective conversion factors, cognizance had been taken of the 10-ppm difference between the BIPM and NBS units that existed prior to January 1, 1948.

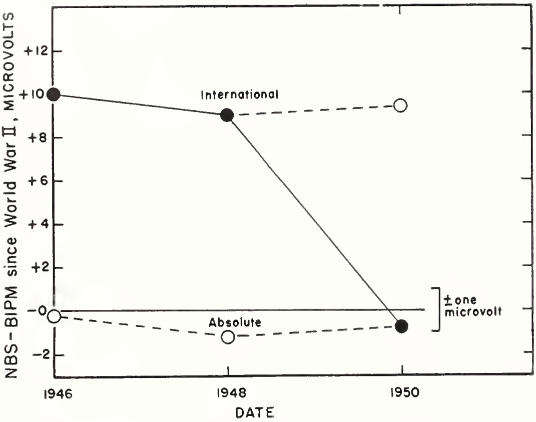

FIGURE 12.5. *Comparisons of electromotive forces certified by the National Bureau of Standards with the Bureau International des Poids et Mesures since World War II.*

●, Reported; ○, calculated. Conversion factors, 1.00033 (United States), 1.00034 (international).

In table 4, comparisons made in 1950 with BIPM and other countries are listed. In column 2 are shown the difference in the volt from BIPM, of the National Physical Laboratory (England), Laboratoire Central des Industries Electriques (France), the Electrotechnical Laboratory (Japan), the Institut de Metrologie d'U. R. S. S. (Russia), and the Deutsches Amt fur Mass and Gewicht (Germany), who submitted cells to BIPM in 1950. The mean of the differences from the BIPM unit for the countries contributing to international comparisons is−2.02 ppm. If we omit the Russian and the German values, the mean difference is only +0.16 ppm. The numbers represent the relative changes in the unit since the comparison of 1947, on which were based the various conversion factors that equalized the absolute units adopted in the several countries on January 1, 1948.

In column 3 of table 4, the differences of the units of other countries from the U. S. unit are listed. The mean difference for the participating countries is only −1.25 ppm. Comparisons have been carried out at the National Bureau of Standards for the national laboratories of Sweden, Israel, and the Union of South Africa.

Table 4. *Results of international comparisons of various units of electromotive force in 1950*

Country	BIPM unit minus national unit	NBS unit minus national unit
	ppm	*ppm*
United States	-0.7_7	----------
England	-2.2_0	-1.4_3
France	$+0.0_9$	$+0.8_6$
Japan	$+3.5_4$	$+4.3_1$
Russia	−23.0	−22.2
Germany	+10.2	+11.0
Mean	−2.02	

It may be concluded, therefore, that the United States volt is in excellent agreement with the average unit maintained in the other standardizing laboratories of the world. It may also be concluded that the methods employed at the National Bureau of Standards, especially for the past 10 years, in maintaining the volt are sound. In the future, studies of standard cells made acid with H_2SO_4, standard cells with solvents of deuterium oxide, and standard cells made in quartz containers should make possible the maintenance of the volt with even more confidence than was possible in the past.

The authors express their appreciation to George W. Vinal, who for 25 years was charged with responsibility of maintaining the United States unit of emf, for his suggestions and encouragement during the initial phases of these studies.

References

[1] Edward Weston, German Patent 75,194 (Jan. 5, 1892); The Electrician **30,** 741 (1893).
[2] J. L. Thomas, C. Peterson, I. L. Cooter, and F. R. Kotter, J. Research NBS **43,** 291 (1949) RP2029.
[3] H. L. Curtis, C. Moon and C. M. Sparks, J. Research NBS **21,** 375 (1938) RP1137.
[4] P. Vigoureux, Nat. Phys. Lab. Collected Researches **24,** 277 (1938); F. E. Smith, **11,** 209 (1914).
[5] L. Hartshorn and N. F. Astbury, Phil. Trans. Roy. Soc. (London) [A] **236,** 423 (1937).
[6] H. L. Curtis, R. W. Curtis, and C. L. Critchfield, J. Research NBS **22,** 485 (1939) RP1200.
[7] R. W. Curtis, R. L. Driscoll, and C. L. Critchfield, J. Research NBS **28,** 133 (1942) RP1449.
[8] P. Vigoureux, Phil. Trans. Roy. Soc. (London) [A] **236,** 133 (1937).
[9] Latimer Clark, Proc. Roy. Soc. (London) **20,** 444 (1872).
[10] H. L. Callendar and H. T. Barnes, Proc. Roy. Soc. (London) **62,** 117 (1897).
[11] Report of International Conference on Electrical Units and Standards, 1908 (refer to appendix 2 of reference [13] for reprint of this report).
[12] F. A. Wolff, Trans. Am. Electrochem. Soc. **13,** 187 (1908).
[13] F. B. Silsbee, NBS Circular 475 (June 30, 1949).
[14] NBS Circular C459 (1947); see also appendix 6 of reference [13].

[15] H. S. Harned and R. W. Ehlers, J. Am. Chem. Soc. **55,** 2179 (1933).
[16] G. W. Vinal, J. Wash. Acad. Sci. **38,** 265 (1948).
[17] P. Vigoureux and S. Watts, Proc. Phys. Soc. **45,** Part 2, 172 (1933).
[18] L. H. Brickwedde and G. W. Vinal, J. Research NBS **20,** 599 (1938) RP1094.
[19] L. H. Brickwedde and G. W. Vinal, J. Research NBS **27,** 479 (1941) RP1435.
[20] H. B. Brooks, J. Research NBS **11,** 223 (1933) RP586.
[21] G. W. Vinal, L. H. Brickwedde, and W. J. Hamer, Compt. Rend. de la Quinzieme Conference de l'Union Internationale de Chemie Pure et Appliquee, Amsterdam, 92 (1949).
[22] H. von Steinwehr, Proc. Congres Int. d'Electricite, Paris, 2d section, Report No. 7, 9 (1932).
[23] A. N. Shaw, H. E. Reilley, and R. J. Clark, Phil. Trans. Royal Soc. London **229,** 134 (1930).
[24] G. W. Vinal and M. L. Howard, BS J. Research **11,** 255 (1933) RP588.

Discussion

Dr. D. A. MacInnes (Rockefeller Institute for Medical Research): Could you tell us something about the International Bureau?

Dr. F. B. Silsbee, National Bureau of Standards: Perhaps some of the audience may not know that back in 1875 there was an international agreement called the Convention of the Meter, to which some 17 nations subscribed and under that treaty there were set up three organizations: first, an official International Conference on Weights and Measures; second, an International Committee on Weights and Measures (a body of 15 or 17 individual experts, no two of which can be from the same country but otherwise selected for their individual competence in the field of measurement); and, third, under the direction of the latter, there was created an International Bureau of Weights and Measures located on ground donated by the French Government.

For many years the Bureau and Committee had jurisdiction only over length and mass, but in 1921 this jurisdiction was extended by an amendment to the treaty to cover electricity, photometry, and the thermometric scale. In 1921 the International Bureau set up satisfactory apparatus for the comparison of standard cells and one-ohm resistors and several of the more highly industrialized countries donated to the International Bureau standard cells and standard resistors, which have been kept there ever since.

Beginning about 1935 a series of biennial comparisons was initiated; standards were sent to Paris by the various national laboratories and then returned to the originating laboratory at the end of each comparison. The mean value that Dr. Hamer showed on the slide was the average for each comparison of the units of all four nations active in the comparisons. It was assumed to be constant. On two occasions the French and the Germans have voluntarily changed their unit because they were convinced they had drifted materially.

During the war period there were no comparisons, and since then there have not been complete comparisons with Russia. There are two German laboratories now, but comparisons with them have been rather sporadic. The International Bureau has a group of some 47 cells, and the average of this group seems to have remained very closely the same as that of our group here at the National Bureau of Standards and as that of the National Physical Laboratory in England. I think that none of those three units have changed materially, and the final slide of Dr. Hamer showed that agreement as it stands now.

Dr. A. J. Rutgers, University of Ghent, Belgium: When you want to keep this fundamental group of cells very constant some things may change—H_2SO_4 may come in. Would it not be advisable to add the acid in the form of a buffer solution?

DR. W. J. HAMER: I think that is a very good suggestion. I believe some work with buffer solutions has been done by Vosburgh. When you add a buffer solution you are, of course, adding more materials that could cause harm. Nevertheless, I think your suggestion is a good one.

DR. H. H. UHLIG, Massachusetts Institute of Technology, Cambridge, Mass.: I should like to ask why heavy water changes the potential of a standard cell.

DR. HAMER: In a standard cell, water takes part in the cell reaction. The cell reaction is

$$\mathrm{Cd(s)+Hg_2SO_4(s)}+\frac{8/3}{m-8/3}\,(\mathrm{CdSO_4}\cdot m\mathrm{H_2O})\,(\mathrm{l}) = \frac{m}{m-8/3}\left(\mathrm{CdSO_4}\cdot\frac{8}{3}\,\mathrm{H_2O}\right)(\mathrm{s})+2\mathrm{Hg(l)},$$

where m is the number of moles of water associated with 1 mole of $CdSO_4$ in the saturated solution. Mrs. Brickwedde, in making up the cells, did not only change the solvent but used cadmium sulfate with heavy water of hydration. The difference in emf between a cell with ordinary water and one with heavy water is related merely to the differences in the free-energy changes of the cell reactions and involves both the solvent and the solid phases.

DR. UHLIG: I asked the question because I wondered whether, in the standard cell, one might not be measuring the polarized Hg potential. This means that if Cd is added to Hg, we measure essentially the potential of an alloy, with Hg polarized by small corrosion currents to the same potential as the alloyed Cd. The potential, therefore, is of Hg on which hydrogen atoms are adsorbed, and would change the potential to an active value almost but not exactly equal to the reversible potential of Cd in Hg. In heavy water, deuterium is adsorbed instead of hydrogen, which polarizes Hg to a slightly different potential, because the overvoltage value differs from that of hydrogen. I wonder if this might he a possible explanation.

DR. HAMER: I would not think so. I think it is mostly just the difference in the cell reactions. In other words, we could change the solvent to ethyl alcohol and get a difference in emf corresponding to a difference in free-energy changes, or a change in the solid phases.

DR. W. F. K. WYNNE-JONES, University of Durham, Newcastle, England: I agree with Dr. Hamer. Surely in any cell of this sort the thermodynamics should show quite clearly that one is dealing simply with the different phases present. The only possible effect is the one Dr. Hamer mentioned, and that is the change in the solid phase. Dr. Uhlig's idea is interesting, but it just can't be right. We certainly haven't the wrong chemical process in the cell.

DR. UHLIG: Wouldn't it be worthwhile to check this by arranging a cell where water of hydration does not enter? It seems to me there would be a smaller effect of heavy water if no water of hydration were involved.

DR. HAMER: It could be checked in an unsaturated cell, but $CdSO_4$ is less soluble in heavy water than in ordinary water, and a comparison based on equal concentrations (or solubility) would show that the emf difference would be larger rather than smaller, as the emf increases on dilution of electrolyte.

Dr. V. K. LaMer, Columbia University, New York, N. Y.: This is one of the most reversible cells we ever had, isn't it?

Dr. M. Eppley, The Eppley Laboratory, Inc., Newport, R. I.: Yes, but a reversible cell owes its reversibility to the maintenance of the original conditions. If you come to other conditions, the cell is no longer reversible. This cell comes as nearly to being reversible as a cell can be.

Dr. Uhlig: This is what I am driving at. The separate open-circuit potentials of Hg, and Cd in mercury, are represented as shown in figure A. Upon alloying Hg with Cd and immersing in an electrolyte a small corrosion current is set up between Hg and Cd atoms, which cathodically polarizes Hg to the potential E_{obs} (corrosion potential). Similarly, Cd is anodically polarized from its reversible value also to E_{obs} (neglecting small IR drops in the electrolyte and amalgam). Cd is polarized much less than is Hg, but some polarization must occur, since current flows. Evidence for this current comes from the accumulation of hydrogen in standard cells on long-time aging. Since the overvoltage of deuterium on Hg differs from that of hydrogen on Hg, it follows that the corrosion currents differ in the two solvents, and therefore the polarized potential of Cd in Hg differs. Therefore, heavy water, in addition to the usually considered thermodynamic effect, can influence the potential by changing the local-action currents.

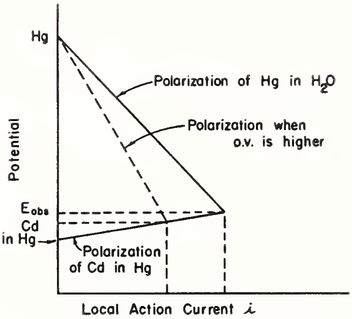

Figure A. *Effect of local-action currents on observed potential (E_{obs}) of Weston Standard Cell.*

(Dr. Uhlig communicated the following comments for insertion in the discussion:)

The effect of local-action currents presented above leads to an *increase* in the potential of the Weston cell when D_2O is substituted for H_2O, because the *O. V.* of D_2 is larger than for H_2. The effect, of course, is much smaller than the thermodynamic effect mentioned by Dr. Hamer, which produces change of potential in the opposite direction. The local-action currents, however, on the Cd-amalgam surface very likely explain the slight change of potential on aging of standard cells. A measurable shift in potential can conceivably occur through effects of impurities on overvoltage or polarization of Hg, in this way altering the local-action currents. Impurities that increase the overvoltage lead to a larger measured potential for the cell, whereas those that decrease overvoltage have the opposite effect.

The magnitude of the local-action current can be calculated from values for the activities of Cd amalgam and dissolved ions, and the hydrogen overvoltage on Hg. This approach makes use of the observations of Wagner and Traud (Z. Elektrochem. **44**, 391 (1938)) that corrosion of Zn amalgam in hydrochloric acid can be expressed quantitiatively as an equivalent current that polarizes Hg to the potential of the amalgam in the same acid environment. Their investigation constituted proof that amalgams, like most metals, corrode by reason of short-circuited local-action cells, even though Hg cathodes and Cd anodes of the amalgam are on an atomic scale.

The activity of the amalgam electrode can be calculated from the potential of the Weston Cell (1.0181 v at 25° C), the E^0 values for $Cd \rightarrow Cd^{++} + 2\epsilon$(0.402 v) and $2Hg \rightarrow Hg_2^{++} + 2\epsilon$(−0.799 v), and the activity of Hg_2^{++} in saturated $CdSO_4$. The expression for the emf of the cell at 25° C is the following:

$$1.0181 = 0.402 + 0.799 - \frac{0.0591}{2} \log \frac{(Cd^{++})}{(Cd)} - \frac{0.0591}{2} \log \frac{1}{(Hg_2^{++})},$$

where $(Hg_2^{++}) = 4.8 \times 10^{-6}$.

The activity of Hg_2^{++} above is calculated from the activity of SO_4^{--} in saturated $CdSO_4$ and the solubility product of Hg_2SO_4 (6.2×10^{-7}, Corrosion Handbook, p. 1138, edited by H. H. Uhlig (John Wiley & Sons, Inc., 1948)). The activity of SO_4^{--} is obtained from the solubility of $CdSO_4 \cdot \frac{8}{3}H_2O$, namely, 0.06627 mole $CdSO_4$/mole H_2O (L. H. Brickwedde, J. Research NBS **36**, 377 (1946)), or 3.68 molal, and the activity coefficient for 3.5 molal $CdSO_4$ equal to 0.035 (The Physical Chemistry of Electrolytic Solutions, H. Harned and B. Owen, 2d ed, p. 427, Reinhold Pub. Co., 1950). Therefore, the log ratio of the activity of Cd^{++} to activity of Cd in Hg is given by $\log (Cd^{++}/Cd) = 0.88$. With this log ratio, it is possible to calculate the potential difference E_H of the hydrogen electrode and Cd-amalgam electrode in saturated $CdSO_4$. The latter contains about 0.03 mole H_2SO_4/litre (L. H. Brickwedde and G. W. Vinal, J. Research NBS **27**, 479 (1941) RP1435), the pH of which is assumed for present purposes to be 1.5, and the partial pressure of hydrogen is equal to 1 atmosphere. Then

$$E_H = 0.402 - \frac{0.0591}{2} \log \frac{(Cd^{++})}{(Cd)} - 0.059 \text{ pH} = 0.29 \text{ v}.$$

If the pressure of H_2 is less than 1 atmosphere, as is expected, the value for E_H would be somewhat larger.

The above potential is available to polarize Hg beyond the equilibrium potential for evolution of hydrogen. The accompanying current, equal to the local-action current, can be calculated from the hydrogen overvoltage values (*O.V.*) for Hg. Kortüm and Bockris (Electrochemistry, **II**, 759, Elsevier Pub., 1951) give the following value for Hg in 0.2 *N* H_2SO_4

$$\text{O.V.} = \frac{2.303\, RT}{0.52\, F} \log \frac{i}{6 \times 10^{-12}},$$

where i is in amp/cm². Setting the overvoltage above equal to 0.29 and solving for i, one obtains 2.1×10^{-9} amp/cm². This is equivalent to the liberation of (0.008 ml H_2/cm²)/yr.

Hence for the Weston Cell, the reversible potential E (therm.) can be expressed in terms of the polarized or observed potential E (obs.) as follows: E (therm.) $= E$ (obs.) $+ f(i)$, where $f(i)$ is the additive term to the potential resulting from polarization of the Cd electrode in accord with the local-action current, i. Hence, the thermodynamic potential E (therm.) is always greater than the observed value, the difference in general being small, although presumably measurable. From Wagner and Traud's data on anodic polarization of Zn amalgam, $f(i)$ is in the order of (13 mv/ma)/cm^2; hence, the corresponding potential shift for 2.1×10^{-9} amp/cm^2 is 3×10^{-8} v.

In this regard, the value 2.1×10^{-9} amp/cm^2 should be looked upon as a minimum value, with the actual value probably being higher. An increase, in some instances, by a factor of 100 is not inconceivable. For one thing, metallic impurities in the amalgam would tend in general to decrease hydrogen overvoltage, thereby increasing corrosion and local-action currents and producing hydrogen far in excess of the calculated (0.008ml/cm^2)/yr, as is sometimes observed. Even if the amalgam were pure, the overvoltage on either solid or liquid Cd amalgam may be lower than that for pure Hg. Dissolved oxygen and depolarizers from cork, possibly contaminating the electrolyte, would tend to increase the local-action currents above the calculated value *without* accompanying accumulation of hydrogen gas, but with the expected effect on the polarized potential of Cd and of the cell.

All these effects point to local-action currents on the surface of Cd amalgam as an important if not primary source of potential drift in Weston standard cells.

Dr. Hamer: I think your discussion refers to the stability of the cell rather than to the question of the difference in the emf (open-circuit voltage) of standard cells made with water or deuterium oxide.

Dr. J. O. M. Bockris, Imperial College of Science and Technology, London, England: I don't fully understand Prof. Uhlig's idea. The cell must be working reversibly if no actual change in the concentration of reactants is detectable over a period of years. It would not suffice to test the explanations for the effect of heavy water on the emf of the cell merely by removing the water of hydration from the reaction. Change of medium changes the solvation energy of the ions and hence the emf of the cell. It would be relatively easy to calculate the change in emf of the cell to be expected upon change from water to deuterium oxide throughout, assuming the usual cell reaction stated and complete reversibility. Then we could see if this new figure was in agreement with the experimental one.

Dr. Eppley: I tried to measure the potential of Hg in a $CdSO_4$ solution. There is no definite potential that I have ever been able to find. Of course, you would expect there would be practically no Hg ion there because the Cd would be forcing it the other way. That is the explanation I have given. Is that a correct explanation? Now the depolarizer, so-called, is not a depolarizer but is a device whereby you maintain a concentration of Hg ions over the Hg. Of course, if we use it up, everything goes wrong.

Dr. G. W. Vinal, Princeton, N. J.: I agree.

Dr. Hamer: Your explanation for the potential of Hg in solutions of $CdSO_4$ appears plausible. We have made no studies of this type at the Bureau. The Hg-Hg_2SO_4 electrode is one of the second kind, but ceases to be of this type when Hg_2SO_4 becomes depleted.

13. Thermal-Diffusion Phenomena in Electrolytes and the Constants Involved

By H. J. V. Tyrrell[1]

The phenomena that occur in nonisothermal electrolytic systems are not as widely known as those associated with isothermal systems in which a concentration gradient exists, although the two cases are superficially similar in many respects. If a temperature gradient exists in a solution, there is a tendency for a concentration gradient (Soret effect) to ensue, i.e., for one component to become concentrated in either the hot or the cold portion of the cell [1, 2].[2] This change in concentration is distinct from changes associated with convection processes, and, indeed, can only be measured if precautions are taken to minimize, or control, convection. In suitable cells [3] a condition of dynamic equilibrium is established after a sufficient time, and a reproducible concentration difference δc obtained for a temperature difference δT. The quantity $(1/c)dc/dT$ so measured is known as the Soret coefficient σ. If the solute is an electrolyte, the temperature gradient is coexistent with a potential gradient which arises from different speeds with which ions tend to diffuse in a temperature gradient. This thermal-diffusion potential should be a function of time, changing as the Soret equilibrium is established, and reaching a constant limiting value when the condition of dynamic equilibrium is established. Experimental proof of existence of such a potential may be obtained by measuring the emf $(\delta\phi)$ of a cell of the type [4, 5, 6]:

$$\text{Reversible electrode} \underset{T}{\Big|} \text{Electrolyte} \underset{T+\delta T}{\Big|} \text{Reversible electrode.}$$

The average value of $d\phi/dT$ obtained depends on the activity of the ion to which the electrodes are reversible, and on the nature and relative numbers of all the ions present in the solution. For example, the initial emf per unit temperature interval developed by Ag-AgCl electrodes in a dilute KCl solution is about 0.36 mv/° C more positive than that obtained from the same electrodes in an HCl solution of the same mean activity (the hot electrode is taken as positive). The variation of emf of such a cell with time has recently been qualitatively demonstrated [7]. This behavior is essentially similar to that of an isothermal electrolytic system in which a concentration gradient exists, and the thermal diffusion potential to a concentration diffusion, or "liquid-junction" potential. Similar phenomena have been observed in solid electrolytic systems especially by Reinhold and coworkers. This work has been reviewed by Wirtz [8] and is not discussed here.

Attempts to treat these phenomena by classical thermodynamic ("thermostatic", c. f., Eckart [9]) methods meet the difficulty that

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[1] Sheffield University, Sheffield, England.

[2] Figures in brackets indicate the literature references on p. 129.

nonisothermal systems never attain to true equilibrium; there is always an irreversible flow of heat from the high to the low temperature region. Usually entropy changes arising from this and other such irreversible processes have been ignored, as in Thomson's theory of thermocouples [10], and the resulting equations justified empirically.

A "quasithermostatic" treatment of this kind was used by Eastman [11] and later, by Wagner [12] to derive equations for the Soret coefficient σ and the thermal diffusion potential; latterly, identical equations were developed using improved thermodynamic methods [13, 14]. Formally similar equations may also be obtained kinetically [8, 5] and the theoretical position therefore seems to be satisfactory. All the equations involve an energy term (or its equivalent), the "heat of transfer Q^*", which is characteristic of each constituent of the system. This concept was introduced by Eastman [11] to explain the specificity of the observed effects; the failure of earlier attempts to explain the Soret effect without the use of such a quantity has been described by Hartley [15].

Eastman considered the system as of two parts, one (I) at temperature T and the other (II) at $T+\delta T$, both portions being in contact with reservoirs of infinite heat capacity at the appropriate temperatures. If 1 mole of component A is withdrawn from (I), heat Q^*_A must be withdrawn from the reservoir at temperature T. If this amount of A is then introduced into (II), heat Q^*_A is given to the reservoir at $T+\delta T$. The entropy difference between these two processes is

$$\delta\partial = Q^*_A/T - Q^*_A(T+\delta T) = \frac{Q^*_A \cdot \delta T}{T^2}\cdot$$

In an isothermal system this entropy change is zero, but in general, not so for a nonisothermal one. Q^*_A was termed the heat of transfer of component A, and the entropy of transfer S^*_A defined as the quotient Q^*_A/T. A more formal definition has been developed by de Groot [13] in terms of Onsager's phenomenological equations and the "principle of microscopic reversibility" [16]. These equations are formal relationships between a flow vector, J (e. g., of matter, energy) and the force vector causing the flow, e. g., in an i-component system in which a flow of matter and energy are simultaneously occurring, we may write

$$J_i = \sum_k a_{ik} X_k + b_i X_u \quad (i=1, 2, \ldots, j) \tag{1}$$

$$J_u = \sum_k b'_k X_k + c X_u, \tag{2}$$

in which J_i is the flow vector of the ith component; X_k, the force vector causing the flow of the kth component; J_u, the flow vector of energy; X_u, the force vector causing the flow of energy; and a_{ik}, b_i, b'_k, c are constants. Quantities Q_k are defined in terms of b_i and a_{ik} as follows:

$$b_i = \sum_k a_{ik} Q_k \quad (i=1, 2, \ldots, j). \tag{3}$$

Multiply (1) throughout by Q_k, sum over all values of i, and subtract from (2) to obtain

$$J_u - \sum J_i Q_i = \sum_k b' X_k - \sum_i \sum_k Q_i a_{ik} X_k - \sum_i Q_i b_i X_u + c X_u. \tag{4}$$

The following relationships hold between the constants of the Onsager equations (principle of microscopic reversibility): $a_{ik}=a_{ki}$, $b_i=b'_i$. Using these and (3), eq (4) becomes,

$$J_u=\sum_i J_i Q_i+X_u(c-\sum b_i Q_i). \tag{5}$$

If there is no force causing energy flow, i. e., no temperature gradient, $X_u=0$ and

$$J_u=\sum_i J_i Q_i.$$

Thus, by the principle of microscopic reversibility, the quantities Q_i gain a physical meaning, viz., the energy transported by 1 mole of component i. This is related to Eastman's heat of transfer by $Q_i^*=Q_i-\overline{H}_i$. $\overline{H}_i$ is the partial molar heat content of the ith component. In an electrolytic solution any transfer of a positive ion must be accompanied by that of a negative ion, i. e., heats of transfer of single ions cannot be obtained directly from any experiment involving transfer of matter.

The most general forms of the resulting equations for an ideal solution are (de Groot, [13]):

Soret coefficient [3] of ith component

$$\sigma_i=\frac{1}{n_i}\frac{dn_i}{dT}=-\left[Q_i^*/RT^2-\frac{z_i\sum_k z_k n_k Q_k^*}{RT^2\sum_k z_k^2 n_k}\right],$$

where n_i is the number of molecules (ions) of the ith constituent.

Initial value of thermal diffusion potential

$$J_1=+\sum_i (t_i Q_i^*/z_i \mathbf{F}T)$$

k_i, z_i are the transference number and valency, respectively, of the ith ion.

Final value of thermal diffusion potential

$$J_2=+\frac{\sum_i n_i z_i Q_i^*}{\mathbf{F}T\sum_i n_i z_i^2}.$$

For a uni-univalent electrolyte in a neutral solvent these reduce to

$$\sigma_+=\sigma_-=-\frac{Q_+^*+Q_-^*}{2RT^2}. \tag{6}$$

$$J_1=+\frac{t_+Q_+^*-t_-Q_-^*}{\mathbf{F}T}. \tag{7}$$

$$J_2=+\frac{Q_+^*-Q_-^*}{2\mathbf{F}T}. \tag{8}$$

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[3] The above Soret coefficients are not quite the same as the majority of existing experimental values which are expressed in terms of gram equivalents per liter.

Equation (6) implies that, if the heat of transfer of an ion is regarded as constant and characteristic of that ion, Soret coefficients measured for a series of uni-univalent salts should be additive and independent of concentration. Available experimental values for electrolytes, the best of which are shown in table 1, have mostly been obtained from experiments on concentrated solutions, for which the assumption that $\mu_i = \mu_i^0 + RT \ln n_i$ made in the theoretical treatments, strictly does not apply. They are no more than approximately additive, vary considerably with concentration, and with the experimental technique used. They agree in not assigning positive values to the Soret coefficient of any electrolyte in water, and in the high negative values found for acids and bases as compared with neutral salts. Inspection suggests that Soret coefficients decrease with increasing temperature interval, i. e., with increasing mean temperature, in the few cases where comparison is possible, and change with changing solute concentration. There are a number of experimental difficulties involved in the direct measurement of the effect [19], and it has been suggested, in particular, that a positive value of the Soret coefficient might not be detected with the existing experimental techniques [20]. Direct studies of the Soret effect in electrolytes have not yet, therefore, provided satisfactory verification of the theoretical equations.

TABLE 1. *Comparative values of Soret coefficients*

Salt	$-\sigma \times 10^3$ (A)[a]	$-\sigma \times 10^3$ (B)[a]		$-\sigma \times 10^3$ (C)[a]
		(i)[a]	(ii)[a]	
KCl	------------	1.68	1.29 (2 *N*)	------------
	------------	1.53	0.94 (1 *N*)	6.3 (1 *N*)
	0.14 (0.5 *N*)	----	------------	------------
KBr	------------	2.33	2.13 (3 *N*)	------------
	------------	2.06	1.33 (1 *N*)	------------
	1.15 (0.1 *N*)	----	------------	7.2 (0.1 *N*)
KI	------------	0.62	0.45 (1 *N*)	3.1 (1 *N*)
	0.08 (0.1 *N*)	----	------------	------------
KOH	------------	----	5.5 (4 *N*)	------------
	6.2 (1 *N*)	----	11.83 (1 *N*)	------------
	5.3 (0.1 *N*)	----	------------	------------
NaCl	------------	2.48	1.46 (1 *N*)	5.5 (1 *N*)
NaBr	------------	----	2.06 (1 *N*)	------------
NaI	------------	----	0.79 (1 *N*)	------------
NaOH	------------	----	8.8 (4 *N*)	------------
	------------	----	12.5 (1 *N*)	------------
HCl	1.3 (4 *N*)	----	2.3 (4 *N*)	------------
	2.9 (1 *N*)	----	5.6 (1 *N*)	------------

[a] Sources: (A) Chipman [17], Temperature interval 20° to 30° C; (B) Tanner [3], Temperature interval (i) 25° to 49° C, (ii) 25° to 39° C; (C) Hiby and Wirtz [18], Temperature interval 30° to 80° C (Clusius-Dickel type of cell).

Thermal diffusion potentials cannot be measured in isolation. Two types of cell have been used in which they have been measured in conjunction with other potentials, one of the form indicated above, and the other, studied by Podzus [21] of the form:

$$\begin{array}{c|c|c|c|c} \text{Reversible electrode} & \text{Solution I} & \text{Solution II} & \text{Solution I} & \text{Reversible electrode.} \\ & T & T & T+\delta T & T \end{array}$$

The emf of the first includes the difference in potential of the two electrode solution interfaces due to the true temperature coefficient of the electrode potential, the thermal diffusion potential in the electrolyte, and the thermoelectric effects in the metallic conductors. That of the second does not include the true temperature coefficient of the electrodes, but involves two liquid-junction potentials which must be calculated. Modern work has been confined to measurements on cells of the first type [5,6,7,22]. Similar cells were also used by Lange [23], who measured the Peltier heats evolved or absorbed at an electrode-solution interface when a given quantity of electricity passed across it. His results included a term characteristic of the solution alone, and compared quite well with the emf results of Richards [4], but this method has not been developed further.

It is clear from eq (7) that, if heat of transfer of an ion is independent of concentration, the initial thermal diffusion potential should also be independent of the dilution of the electrolyte, provided the ionic transference numbers remain constant. Hence, the effect of dilution in, for example, the cell.

$$\text{Ag}\ \underset{T_1}{\Big|}\ \text{AgNO(aq.)}\ \underset{T_2}{\Big|}\ \text{Ag}$$

should be predictable from ordinary thermodynamic principles as only the isothermal electrode-solution potentials should be affected. The following equation would, on this view, hold at the start of the experiment,

$$\frac{d\phi}{dT}=\frac{d\phi^0}{dT}+\frac{R}{z_r\mathbf{F}}\ln m_r+\frac{R}{z_r\mathbf{F}}\ln f_r+\frac{RT}{z_r\mathbf{F}}\frac{d}{dT}(\ln f_r)-J_1 \qquad (9)$$

If $\ln f_r$ and $d/dT(\ln f_r)$ are calculated from the simple Debye-Hückel equation, it can be shown that $(d\phi^0/dT-J_1)$ varies slightly with concentration for cells of the above type [7]. This variation cannot at present be verified by an independent method as no Soret coefficient data exist for the same concentration range.

The general form of eq (7) has been tested by experiments on the cell,

$$\text{Ag}\ \underset{T_1}{\left|\begin{array}{c}\text{AgNO}_3\ (m_{\text{A}})\\ \text{KNO}_3\ (m_{\text{K}})\\ \text{HNO}_3\ (m_{\text{H}})\end{array}\right|_{T_2}}\ \text{Ag},$$

where m_{A}, m_{K}, m_{H} are concentrations in gram moles per liter. If m_{A} and the total ionic strength of the solution are kept constant, and the ratio $m_{\text{A}}:m_{\text{K}}:m_{\text{H}}$ varied from 1:1:0 to 1:0:1, it is possible to write [7]

$$t_{\text{H}}=a+bt_{\text{A}}$$

$$t_{\text{K}}=c+dt_{\text{K}},$$

in which a, b, c, d are constants, and the ionic mobilities are assumed to possess their limiting values. Equation (9), therefore, becomes

$$\frac{d\phi}{dT}=C+\frac{2RT}{\mathbf{F}}(a\sigma_{\text{H}}+c\sigma_{\text{K}})+\frac{2RT}{\mathbf{F}}t_{\text{A}}(\sigma_{\text{A}}+b\sigma_{\text{H}}+c\sigma_{\text{K}}). \qquad (10)$$

Thus $d\phi/dT$ should be a linear function of t_{A}. Figure 1 shows that this is so in one example studied. The slope of this lines are consistent with (10) and the available experimental values of Soret coefficients, though individual coefficients cannot be calculated from this type of thermal-cell data alone.

Such calculations have been carried out by Goodrich et al., who studied the cells,

$$\mathrm{Hg, HgO}\ \underset{T_1}{\Big|}\ \mathrm{MOH}\ \underset{T_2}{\Big|}\ \mathrm{HgO, Hg}$$

$$\mathrm{Ag, AgBr}\ \underset{T_1}{\Big|}\ \mathrm{MBr}\ \underset{T_2}{\Big|}\ \mathrm{AgBr, Ag,}$$

where M represents one of a homologous series of symmetrical tetra-alkyl ammonium cations $(NR_4)^+$. As the molecular weight increased, the cation transference number decreased and $d\phi/dT$ became a linear function of the anion transference number. This would be expected from the form of eq (7) if the heat of transfer of the cation tended to a constant value, since on rewriting,

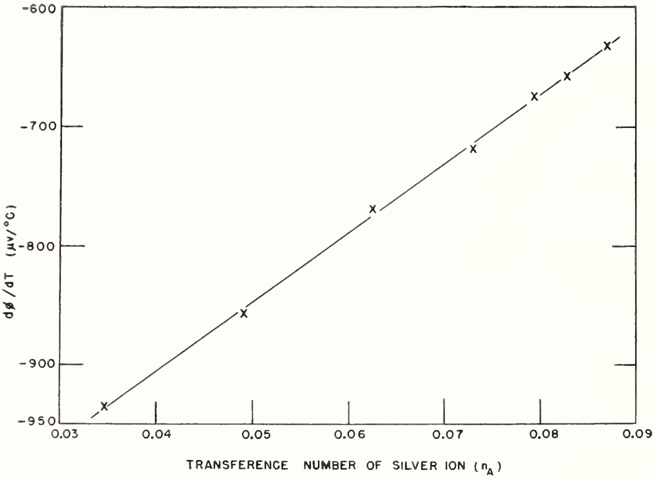

FIGURE 13.1. *Variation of electromotive force of thermal cells, prepared with a mixture of silver nitrate, potassium nitrate, and nitric acid, with transference number of the silver ion.*

C=0.005 g equivalent/liter; μ=0.05.

$$Fd\phi/dT=K-S_+^*+t_-(S_+^*+S_-^*),$$

where K is a constant. The calculated Soret coefficients were positive for certain salts [24], and similar values could in fact fit the data of figure 13.1 quite well. There is thus the possibility of a discrepancy between directly measured and calculated values.

This evidence supports the general form of the equation for the initial value of the thermal diffusion potential, and suggests that the heat of transfer of an ion is not entirely independent of concentration even in dilute solutions. Further verification of the equations might be obtained from a study of time variation of the thermal diffusion potential as the Soret equilibrium is established. Such a variation has been shown to occur [7], but there is as yet no satisfactory quantitative data available.

Nature of the Heat of Transfer

No experimentally accessible quantities involve the heat of transfer of a single ion alone. The sum of two ionic heats of transfer of an ion pair may, in principle, be obtained from a measurement of the Soret coefficient of the salt. Also, a single ionic heat of transfer may be measured in conjunction with an unknown constant characteristic of a single electrode system and its associated metallic leads, according to the Goodrich method. All conclusions concerning the magnitudes of heats of transfer must be based on measurements of the above kinds.

There is at present no generally accepted set of values for heats of transfer of salts in water. In spite of this, three different tabulations of heats of transfer of single ions exist (table 2), each based on a different set of values for heats of transfer of salts, and derived therefrom by means of different assumptions concerning the single heat of transfer of one ionic species. The first was due to Eastman [11] who used thermo-electric data obtained by Podzus [21], and assumed that all ionic heats of transfer were positive, and, that, in a closely related series, they varied in the same order as the mobilities. Wirtz [25] concluded from kinetic arguments that $Q^*_{\mathrm{Li}^+}$ was zero, and fitted his values to the Soret coefficient results of Hiby and Wirtz [18]. Goodrich and coauthors assumed [6] the heat of transfer of large symmetrical tetra-alkyl ammonium ions to tend to zero with increasing molecular weight.

Table 2. *Heats of transfer of single ions at 25° C (kcal/g ion)*

Ion	Eastman	Wirtz	Goodrich et al.
H^+	+2.77	----------	----------
Li^+	+0.030	+0.00	−3.02
Na^+	+.268	+2.3	−1.80
K^+	+.298	+2.6	−1.55
Rb^+	+.328	+2.1	----------
NH_4^+	+.00	----------	−2.06
Cl^-	+.00	+0.00	----------
Br^-	[1]+1.07	+ .40	+0.155

[1] Calculated by Eastman's method from data on Ag-AgBr electrodes in nonisothermal cells. Tyrrell and Hollis [5].

Values of J_1 for a series of bromides have been calculated from these figures, and these, together with the difference functions, $\Delta J = J_{\mathrm{LiBr}} - J_{\mathrm{MBr}}$, where M is another member of the bromide series, are shown in table 3.

Eastman's and Goodrich's figures were calculated from thermoelectric data, and although very different, give comparable values of J_1, and almost identical values of function ΔJ. Differences in ΔJ values are no larger than would be expected from the different experimental figures from which they were derived. In other words, both tabulations give an adequate summary of thermoelectric data on which they were based. Goodrich's set, however, formulated without reference to the experimental Soret coefficients, yields positive values in certain cases, while Eastman's starting from the postulate that all heats of transfer are positive, inevitably leads to negative Soret coefficients in all cases. Wirtz's figures, based mainly on his Soret coefficient values, do not give comparable values of J_1 and ΔJ, thus emphasizing the discrepancy noted earlier between the results obtained from thermal cells and those obtained from direct measurements of the Soret effect. Attempts to assign energy quantities measurable only in the form of a sum of terms characteristic of the constituent ions of a salt, to the individual ions, are rarely completely satisfactory, and in this case there is, at present, some disagreement concerning the exact value of the sum. Hence the figures in table 3 are of doubtful value; on the whole, Goodrich's assignment seems based on the most reasonable assumptions.

TABLE 3. *Thermal diffusion potentials and values of ΔJ calculated from the data in table 2.*

Investigator	J_1 (mv/°C)			
	LiBr	NaBr	KBr	NH$_4$Br
Eastman	−0.105	−0.082	−0.060	−0.077
Wirtz	−.038	+.091	+.148	--------
Goodrich	−.158	−.117	−.120	−.155
	ΔJ (mv/°C)			
Eastman	--------	−0.023	−0.045	−0.028
Wirtz	--------	−.129	−.186	--------
Goodrich	--------	−.041	−.038	−.003

If the heat of transfer of a single ion were known, calculations of the true temperature coefficient of a single electrode potential, the absolute potential of a single electrode, and the absolute partial molal entropy of a single ion in solution would be possible. Such calculations have been carried out in several different ways, and the results of the most reliable ones do not differ markedly. Considering one parameter only, the absolute partial molal entropy of the hydrogen ion in a solution of unit activity at 25° C as calculated by several authors (table 4), lies between −1.5 and −6.3 eu. The choice of any particular value from which to construct an absolute scale of partial molar ionic entropies from Latimer's relative scale [26] is however scarcely less arbitrary than his original choice of $S^0_{H+}=0$, in view of this variation.

The definition of heat of transfer of an ion pair makes clear its relationship to other, more familar, energy quantities. It is the heat absorbed per mole from the surroundings at the point from which

TABLE 4. *Representative calculations of the absolute partial molal entropy of the hydrogen ion*

Sources [a]	$\overline{S}^0_{H+}$	Method
	eu	
A	−5.4	Indirectly measured temperature coefficient of the cell: Lippmann electrode | Soln. $a_{H+}=1$ | H$_2$:Pt.
B	−5.4	Thermoelectric, using Eastman's entropies of transfer of ions.
C	−2.1	Thermoelectric.
D	−1.5	Lattice energies, etc. Corresponds to absolute potential of −0.495 v for calomel electrode.
E	−6.3	Data of D recalculated to value of −0.56 v for potential of calomel electrode.

[a] A, Lee and Tai [27]; B, Bernhardt and Crockford [22]; C, Goodrich, Goyan, et al. [6]; D, Latimer, Pitzer, and Slansky [28]; and E, Recalculated for this table, assuming whole change resided in ion-entropy term.

the ion pair is transferred, and that evolved when it is introduced into its new surroundings. In other words, it is the energy of interaction between the entity transferred and the surrounding solvent molecules. The magnitude of the heat of transfer of an ion pair is known to be of the order of a few kilocal. mol. $^{-1}$ and the entity transferred must therefore be the ion pair together with a solvent sheath. The heat of transfer is, accordingly, the energy of interaction between solvent molecules in the solvate sheath and solvent molecules beyond the region of local order induced by the ions. It might therefore be termed the heat of solution of the hydrated ion pair (c. f., Wirtz [25], p. 498). This quantity is not itself experimentally accessible, though it represents a part of the heat of solution of the salt as normally understood. This may be formally expressed as follows (uni-univalent salt): Heat absorbed per mole on solution,

$$\Delta H_S = \Delta H_I + \Delta H_{II} = \Delta H_I + \Delta H'_{II} - (Q^*_+ + Q^*_-) \quad (11)$$

in which ΔH_I is the energy absorbed in the breakdown of the solid lattice; ΔH_{II}, the energy absorbed during solvation of the ions and dispersion in the solvent (usually called the heat of solvation [29]), and $\Delta H'_{II}$ is this quantity omitting the energy associated with the second-order forces here identified with the heat of transfer. Both ΔH_I and ΔH_{II} are very much larger than the heat of transfer, which is of the order of the uncertainty in ΔH_{II}. Thus the above equation cannot at present be used to calculate heats of transfer. However, changes in heat of solution with concentration should be due almost entirely to changes in the heat of transfer term with concentration as ΔH_I and ΔH_{II} should be independent of concentration. Such changes would probably be small in the dilute solutions used in the thermal-cell experiments. For example, a heat change of 30 cal/mole of dissolved salt would be quite large for a dilution from 0.01 to 0.001 *m*, yet a change of this magnitude would only have produced a change of about 1 percent in the slope of the lines used by Goodrich to calculate heats of transfer (fig. 4, ref. [6]). Soret coefficient measurements have, however, been carried out over concentration ranges in which the heat of solution may change an appreciable extent. Although coefficients drawn from different sources may differ considerably (table 1) in absolute magnitude, there is qualitative agreement concerning the direction in which the coefficient changes with changing concentration, insofar as material for comparison is available. In table 5 Tanner's data [3] for the change of the Soret coefficient on dilution are compared in a qualitative manner with the published heats of dilution [30]. It is clear that a positive heat of dilution (i. e., evolution of heat) corresponds in general to an algebraic decrease in the Soret coefficient with dilution and vice-versa. This corresponds with the requirements of eq (11). The exceptions are the lithium salts which showed no detectable Soret coefficient in Tanner's experiments yet have a large positive heat of dilution, and $(NH_4)_2SO_4$ which has a negative heat of dilution and a more negative Soret coefficient in dilute than in strong solution. No quantitative comparison has been attempted; in many cases, the change in σ is of the correct order of magnitude. Also, certain minor variations in σ, observed by Tanner, have not been accounted for. However this correlation, while not conclusive, supports the above view of the heat of transfer as a measure of weak interactions between the solvate sheaths of the ions of the ion pair and the surroundings solvent molecules. It is not therefore characteristic of the salt alone but of the solvent also.

Rather similar conclusions may be reached using a kinetic model of the liquid state. Wirtz [25] has discussed thermal diffusion phenomena in terms of the "place exchange (Platzwechsel) theory". The motions of ions in solution are regarded as taking place in a series of discontinuous jumps between one rest position and the next. Such transfers can only occur if the ion has energy q, which is made up of three parts. The ion must acquire sufficient energy by collision processes to overcome the attraction of the surrounding molecules, this energy being designated as q_H (Hemmungsenergie). It moves into a hole formed in the solvent by expenditure of energy q_L (Lochbildunsgenergie). To do this, it passes through the cage of solvent molecules which surrounds it when a pair of these swing apart sufficiently far to allow it to pass. This last process requires energy q_R (Rückschwingungsenergie). Hence, $q=q_H+q_L+q_R$.

Table 5. *Relation between heat of dilution and the change in Soret coefficient with decreasing concentration*

Salt	Sign of change in Soret coefficient	Sign of heat of dilution in concentration range considered	Salt	Sign of change in Soret coefficient	Sign of heat of dilution in concentration range considered
KCl	+	−	$(NH_4)_2SO_4$	−	−
KBr	+	−	NH_4NO_3	+	−
KI	+	−			
KOH	−	+	$MgSO_4$	−	+
K_2SO_4	+	−	$CdSO_4$	−	+
KNO_3	+	−	$CuSO_4$	−	+
			$NiSO_4$	−	+
NaCl	+	−	$ZnSO_4$	−	+
NaBr	+	−			
NaOH	−	+	$AgNO_3$	+	−
Na_2SO_4	+	−	$PbNO_3$	+	−
$NaNO_3$	+	−			
			H_2SO_4	−	+
$BaCl_2$	−	+	HCl	−	+
$SrCl_2$	−	+			

Development of these views leads to the conclusion that the energy of activation of the mobility of an ion in an electric field can be identified with q, and that the heat of transfer is q_H-q_L. The equations for the value of the Soret coefficient and the thermal diffusion potential obtained by Wirtz are identical with those obtained thermodynamically. They may also be obtained by Eyring's method [31], providing the rate determining step is taken as the simultaneous transfer in opposite directions of solute and solvent. This view, based on some unpublished calculations of the author's differs from that outlined earlier [5] and makes the treatment very similar to that of Wirtz. Since separate values of q_H, q_L, and q_R cannot be obtained from q, heats of transfer cannot be calculated from or related to the temperature coefficient of mobility of an ion.

If the above ideas are correct, the heat of transfer of a salt assumes some importance as a direct measure of the weak forces binding the hydrated ion pair in the solvent. Unfortunately, no generally accepted table of these quantities can be constructed at present, since the different methods of measuring them give results which are, superficially at least, incompatible. Apart from the experimental difficulties inherent in Soret coefficient measurements, the concentrations at which they have been carried out are much higher than those used in the recent thermal-cell measurements from which new values of heats of transfer have been derived [6, 24]. Changes in the heat of transfer of a salt with changing concentration are to be anticipated and the available data suggests that they bear the expected relation to the heat of dilution. Improved methods of measuring Soret coefficients in dilute solution might provide confirmation of these views, and, in conjunction with an extension of thermoelectric measurements, lead to an acceptable table of heats of transfer.

References

[1] C. Ludwig, Sitz. Ber. Akad. Wiss. Wien **20,** 539 (1856).
[2] M. C. Soret, Ann. Chim. Phys. (5^{e} série) **22,** 293 (1881); Arch. Sci. phys. et nat. (3^{e} série) **3,** 48 (1879).
[3] C. C. Tanner, Trans. Faraday Soc. **23,** 75 (1927).
[4] T. W. Richards, Z. phys. Chem. **24,** 39 (1897).
[5] H. J. V. Tyrrell and G. L. Hollis, Trans. Faraday Soc. **45,** 411 (1949].
[6] J. C. Goodrich, F. J. Goyan, E. E. Morse, R. G. Preston, and M. B. Young, J. Am. Chem. Soc. **72,** 4411 (1950).
[7] H. J. V. Tyrrell and G. L. Hollis (in publication).
[8] K. Wirtz, Phys Z. **44,** 221 (1943).
[9] C. Eckart, Phys. Rev. **58,** 267 (1940).
[10] J. J. Thomson, Proc. Roy. Soc., Edinburgh (1854), p. 123; Collected papers I, 237–41.
[11] E. D. Eastman, J. Am. Chem. Soc. **48,** 1482 (1926); **50,** 292 (1928).
[12] C. Wagner, Ann. Physik. (5) **3,** 629 (1929); **6,** 370 (1930).
[13] S. R. de Groot, J. Phys. Rad. **8,** 193 (1947).
[14] L. D. Tuck, J. Chem. Phys. **18,** 1128 (1950).
[15] G. S. Hartley, Trans. Faraday Soc. **27,** 1 (1931).
[16] L. Onsager, Phys Rev. **37,** 405 (1931).
[17] J. Chipman, J. Am. Chem. Soc. **48,** 2577 (1926).
[18] J. W. Hiby and K. Wirtz, Phys. Z. **41,** 77 (1940).
[19] See, for example, I. Prigogine, L. de Brouckère, and R. Amand, Physica **16,** 577 (1950).
[20] G. S. Hartley, Disc. Faraday Soc. **3,** 128 (1948).
[21] E. Podzus, Ann. Physik (4), **27,** 859 (1908).
[22] H. A. Bernhardt and H. D. Crockford, J. Phys. Chem. **46,** 473 (1942).
[23] E. Lange and Th. Hesse, Z. Elektrochem. **38,** 428 (1932). **39,** 374 (1933).
[24] H. J. V. Tyrrell and G. L. Hollis, J. Am. Chem. Soc. **73,** 2401 (1951).
[25] K. Wirtz, Z. Physik. **124,** 482 (1948).
[26] Cf. W. M. Latimer, K. S. Pitzer, and W. V. Smith, J. Am. Chem. Soc. **60,** 1829 (1938).
[27] F. H. Lee and Y. K. Tai, J. Chinese Chem. Soc. **8,** 60 (1941).
[28] W. M. Latimer, K. S. Pitzer, and C. M. Slansky, J. Chem. Phys. **7,** 108 (1939).
[29] c. f. O. K. Rice, Electronic structure and chemical binding (McGraw-Hill, p. 400, 1940).
[30] H. H. Landolt, Landolt-Bornstein Physikalischchemisch tabellen, (Berlin, J. Springer).
[31] S. Glasstone, K. Laidler, and H. Eyring, The theory of rate processes, chap. X (McGraw-Hill, 1941).

Discussion

Dr. J. O'M. Bockris, Imperial College of Science and Technology, London, England: I would like to ask about the thermocouple effects. Do you keep the metallic junctions at the same temperature?

Mr. H. J. V. Tyrrell: No; the measured emf does include thermoelectric effects in the conductors, but these are kept constant and do not affect the conclusions drawn from the emf measurements.

Dr. Bockris: In regard to your theoretical treatment you say that the system is losing heat continuously, i. e., the processes are irreversible and yet your equations are based on classical thermodynamics.

Mr. Tyrrell: The system is an irreversible one like a thermocouple. Thomson applied classical thermodynamics to this system and obtained an answer subsequently confirmed by methods which do not involve the contradiction of applying classical methods to an irreversible process.

Dr. Bockris: But you do use classical methods.

Mr. Tyrrell: Not for the nonisothermal part of the system. The cell treated as consisting of two isothermal electrode solution interfaces separated by a zone of solution in which the temperature gradient exists. Classical methods are applied to each isothermal zone, and the potential gradient in the nonisothermal zone is calculated from de Groot's equations, which are based on Onsager's method.

Dr. V. K. LaMer, Columbia University New York, N. Y.: Dr. Holtan of Norway, has been working with this problem and has just published his paper in J. Chem. Physics. He has studied a number of these. He does not use any single ion potential.

On the history: Thomson, of course, superimposed the irreversible process on the reversible. Boltzman disagreed. Eastman and Wagner come back to the old view, but it is very important to note that in the famous paper of Onsager in 1931 he pointed out that is not correct. Onsager's principle is going to solve this problem. The new treatment that Holtan presents is that he equates the entropy which is produced in the irreversible process to the entropy that is transported in the reversible process. The important thing is that he can get the square root relationship for the thermal diffusion cell which can only be determined by kinetics, by a simple hypothesis. There appears to be real power in his method.

I am sorry Guggenheim is not here. We have had this matter of single electropotentials for many years. It was in a bad state until Guggenheim told us it was impossible to measure a single potential. I hope we won't complicate the field again.

Dr. W. M. Latimer, University of California, Los Angeles, Calif.: I had expected that from Dr. Guggenheim, but I didn't expect it from you. I want to congratulate Dr. Tyrrell on his very excellent presentation on an extremely difficult problem. I don't know any concept in thermodynamics that is as difficult as the concept of the entropy of transfer. I hope your prediction about this other approach is correct, but I remain a little skeptical.

Eastman's early work was followed by a longer series of experiments by his students that were interrupted first by the war and later by Eastman's death, but these results referred to as Goodrich's results were really done by a group of Eastman's students. After the data were pretty cold they put them together and did the best they could. They were at considerable disagreement as to the interpretation of their own data, so I think one should not put too much reliance upon their conclusions because the experiments were not completed. One other remark: We have evidence from other sources that the entropy of hydrogen ion must be very close to zero in water solution.

Dr. Bockris: Do you relate the heat of transfer to the heat of dilution?

Mr. Tyrrell: The heat of dilution would represent the change in the heat of transfer with concentration but not the absolute value of this quantity.

Dr. Bockris: Cannot the heat of dilution be calculated theoretically?

Mr. Tyrrell: The calculation is valid only in dilute solutions. The correlation pointed out in the paper was one between heats of dilution and changes in Soret coefficients in concentrated solutions.

14. Thermoelectric and Thermomagnetic Effects[1]

By Herbert B. Callen[2]

Introduction

Of all physical scientists the physical chemist is probably the one most vitally interested in thermodynamics and therefore most acutely aware of its limitations. Despite the fact that the generality of thermodynamics is so frequently stressed, its limitations are in fact severe. In particular, it is a science of state functions rather than of processes, whereas in practice we are much more interested in the processes themselves than in their terminal states. In recent years a science of "irreversible thermodynamics," with applicability to real physical processes, has been in development, and the theory of thermoelectric and thermomagnetic effects has played a central role in this development. As a set of simple and basic irreversible processes these effects have provided both a motivating challenge and a proving ground for irreversible thermodynamics. This role in turn invests the thermoelectric and thermomagnetic effects with a very particular interest to the thermodynamicist, in addition to that which they deserve by virtue of their relation to the electron theory of solids.

Irreversible Thermodynamics

The theory of irreversible processes may be considered to date back to 1854 when Lord Kelvin [1][3] presented a suggestive line of reasoning leading to the well-known Kelvin relations among the thermoelectric effects. Although Kelvin well realized, and carefully stressed, the lack of rigour of his "proof," this caution was unfortunately abandoned by his scientific heirs. Despite the fact that the "quasi-thermodynamic" method has the dubious honor of giving not only the correct answer but, in fact, any answer whatsoever, it still appears as the "proof" of the Kelvin relations in almost all current texts on thermodynamics. The theory of irreversibility lay dormant under the weight of a sort of Aristotilian authoritarianism until 1931, when Onsager [2] formulated a general relation of reciprocity in the mutual interference of simultaneous irreversible processes. This theorem, based on the principle of microscopic reversibility, forms the basis of a major line of development of the theory of irreversible thermodynamics [3]. Applications of the Onsager reciprocal relations to the thermoelectric and thermomagnetic effects permits a complete and rigorous treatment of the thermodynamic relations among the effects. Recently another approach to the theory of irreversibility has been taken [4, 5] by the investigation of the relationship between thermo-

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[3] Figures in brackets indicate the literature references on p. 141.

dynamic fluctuations and irreversibility. A theorem that is the analog of the Nyquist electrical noise formula relates the generalized resistance in any dissipative system to the spectral density of the fluctuating forces of the system in equilibrium. One feature of the theorem is that the admittance matrix, which relates the response of a system to a number of simultaneous forces, is symmetric. In the zero frequency limit this result reduces to the Onsager reciprocity theorem, and it constitutes a generalization of that theorem. Again the thermomagnetic effects provide an application for this development of the theory, for the measurement of the "a. c. Hall effect" has become important in the investigation of solids. We have not yet made any quantitative applications of the reciprocity theorem in the nonzero frequency range, so that we are here able only to indicate the direction of these newer developments.

The reciprocity theorem of Onsager was first explicitly applied to the thermoelectric and thermomagnetic effects by the author in 1948 [6]. Not only was the well-known Bridgeman relation obtained, but it was shown that certain other relations, also of completely general validity, exist as well. These relations were given only in a rather complicated parametric form which was solved explicitly only for small values of the magnetic field. Recently, however, Mazur and Prigogine [7] have shown that a particular inversion of the fundamental equations so simplifies the analysis as to yield all relations in an explicit form. The thermodynamic analysis of the thermoelectric and thermomagnetic effects might thus be considered to be complete, except for the unique roles played by the adiabatic Nernst and Hall effects. These two effects pose particular problems and were therefore omitted from the analysis in my 1948 paper. Mazur and Prigogine [7] have given an approximate treatment of these two effects, valid for metals in special conditions. A general thermodynamic treatment may, however, be given, thus completing the thermodynamic theory of all the thermomagnetic effects and of all the thermodynamic relations among them.

The Onsager Reciprocal Relations

Stated simply, the Onsager theorem requires a particular symmetry of the matrix connecting the responses of a system to a set of applied forces, providing that the forces and responses are appropriately defined. This symmetry is simply that inversion of the magnetic field transforms the matrix into its adjoint. The response and forces must be so defined that the sum of products of corresponding forces and responses shall be equal to the rate of production of entropy accompanying the process. The simultaneous processes of interest in the thermoelectric and thermomagnetic effects are the flow of heat and of electricity and the associated entropy production may be easily expressed. Ignoring thermal expansion effects (i. e., neglecting terms such as $P\delta V$), the first law of thermodynamics gives

$$T\vec{S}=\vec{W}-\mu\vec{J}, \tag{1}$$

where $\vec{S}$ is the entropy current density, $\vec{W}$ is the total internal energy current density, $\vec{J}$ is the particle current density, and μ is the electrochemical potential. Since both $\vec{W}$ and $\vec{J}$ are divergenceless, we find

$$\dot{S}=\nabla\vec{S}=\nabla\left(\frac{1}{T}\right)\vec{W}-\nabla\left(\frac{\mu}{T}\right)\vec{J}. \tag{2}$$

A reasonable definition of the heat flow is

$$\vec{Q}=\vec{W}-\mu\vec{J}, \tag{3}$$

whence

$$\dot{S}=\left(\nabla\frac{1}{T}\right)\vec{Q}-\frac{1}{T}(\nabla\mu)\vec{J}. \tag{4}$$

Thus if $\vec{Q}$ and $-\vec{J}$ are selected as measures of the response of the system, it is satisfactory to take $\nabla(1/T)$ and $(1/T)\nabla\mu$ as the associated forces. The Onsager theorem can now be applied. If we assume the magnetic field to be in the z-direction and all flows to occur in the x–y plane, and if we further assume isotropy in the x–y plane, we find

$$\left.\begin{aligned}
-J_x&=L_{11}\frac{1}{T}\nabla_x\mu+L_{12}\frac{1}{T}\nabla_y\mu+L_{13}\nabla_x\frac{1}{T}+L_{14}\nabla_y\frac{1}{T}\\
-J_y&=-L_{12}\frac{1}{T}\nabla_x\mu+L_{11}\frac{1}{T}\nabla_y\mu-L_{14}\nabla_x\frac{1}{T}+L_{13}\nabla_y\frac{1}{T}\\
Q_x&=L_{13}\frac{1}{T}\nabla_x\mu+L_{14}\frac{1}{T}\nabla_y\mu+L_{33}\nabla_x\frac{1}{T}+L_{34}\nabla_y\frac{1}{T}\\
Q_y&=-L_{14}\frac{1}{T}\nabla_x\mu+L_{13}\frac{1}{T}\nabla_y\mu-L_{34}\nabla_x\frac{1}{T}+L_{33}\nabla_y\frac{1}{T}
\end{aligned}\right\}. \tag{5}$$

The coefficients L_{11}, L_{13}, and L_{33} are even functions, whereas L_{12}, L_{14}, and L_{34} are odd functions of the magnetic field. These are, essentially, the equations upon which I based the analysis of the thermoelectric and thermomagnetic effects in 1948. As mentioned above, however, Mazur and Prigogine showed that the analysis is greatly simplified by inversion of these equations in such a way that the particle currents and the temperature gradients, which are the experimentally controlled variables, are taken as independent. Whereas it might seem at first to be just as convenient to make the inversion at the end of the analysis as at this point, the actual simplification becomes apparent with the realization that there is no need to actually make the inversion explicitly at this point, but only in such a symbolic way as to preserve the symmetry content of the equations. We can thus write

$$\left.\begin{aligned}
-\vec{J}&=S_{11}\frac{1}{T}\nabla\mu+S_{12}\nabla\frac{1}{T}\\
\vec{Q}&=S_{12}\frac{1}{T}\nabla\mu+S_{22}\nabla\frac{1}{T}
\end{aligned}\right\} \tag{6}$$

where the S's are now 2×2 matrices. The internal symmetry of the S-matrices is a consequence of the isotropy condition, but the equality of S_{12} and S_{21} is a consequence of the Onsager theorem. From eq (6) we find

$$\left.\begin{aligned} \frac{1}{T}\nabla\mu &= S_{11}^{-1}(-\vec{J}) - S_{11}^{-1}S_{12}\nabla\frac{1}{T} \\ \vec{Q} &= S_{12}S_{11}^{-1}(-\vec{J}) + (S_{22} - S_{12}S_{11}^{-1}S_{12})\nabla\frac{1}{T} \end{aligned}\right\}. \tag{7}$$

But each of the S-matrices is a sum of a spherical and antisymmetric tensor, and hence all S-matrices commute. This gives us a new set of equations with a symmetry indicated by

$$\left.\begin{aligned} \frac{1}{T}\nabla\mu &= \mathbf{S}_{11}(-\vec{J}) - \mathbf{S}_{12}\nabla\frac{1}{T} \\ \vec{Q} &= \mathbf{S}_{12}(-\vec{J}) + \mathbf{S}_{22}\nabla\frac{1}{T} \end{aligned}\right\}. \tag{8}$$

It is convenient to introduce the electric-current density $e\vec{J}$, the electrochemical potential *per unit charge* $(1/e)\mu$, and to write the equations in terms of ∇T instead of $\nabla(1/T)$. Then

$$\left.\begin{aligned} -\frac{1}{e}\nabla\mu &= [T\mathbf{S}_{11}/e^2]\,(e\vec{J}) - [\mathbf{S}_{12}/Te]\nabla T \\ \vec{Q} &= -T[\mathbf{S}_{12}/Te]\,(e\vec{J}) - [\mathbf{S}_{22}/T^2]\nabla T \end{aligned}\right\} \tag{9}$$

or

$$\left.\begin{aligned} -\frac{1}{e}\nabla\mu &= \mathbf{S}'_{11}(e\vec{J}) - \mathbf{S}'_{12}\nabla T \\ \vec{Q} &= -T\mathbf{S}'_{12}(e\vec{J}) - \mathbf{S}'_{22}\nabla T \end{aligned}\right\} \tag{10}$$

The internal symmetry of the $\mathbf{S}'$-matrices is identical to that of the original S-matrices because of the isotropy, and we thus finally write our basic equations in the desired form

$$\left.\begin{aligned} -\frac{1}{e}\nabla_x\mu &= \mathbf{L}_{11}eJ_x + \mathbf{L}_{12}eJ_y - \mathbf{L}_{13}\nabla_x T - \mathbf{L}_{14}\nabla_y T \\ -\frac{1}{e}\nabla_y\mu &= -\mathbf{L}_{12}eJ_x + \mathbf{L}_{11}eJ_y + \mathbf{L}_{14}\nabla_x T - \mathbf{L}_{13}\nabla_y T \\ Q_x &= -T\mathbf{L}_{13}eJ_x - T\mathbf{L}_{14}eJ_y - \mathbf{L}_{33}\nabla_x T - \mathbf{L}_{34}\nabla_y T \\ Q_y &= T\mathbf{L}_{14}eJ_x - T\mathbf{L}_{13}eJ_y + \mathbf{L}_{34}\nabla_x T - \mathbf{L}_{33}\nabla_y T \end{aligned}\right\}. \tag{11}$$

The $\mathbf{L}$'s are now our basic kinetic coefficients, and two properties of these coefficients should be noted First, the coefficients $\mathbf{L}_{11}$, $\mathbf{L}_{13}$, and

L_{33} are even functions, whereas L_{12}, L_{14} and L_{34} are odd functions of the magnetic field. Second, we should note that each of the coefficients is uniquely defined except L_{13}. There is a residual arbitrariness in the value of L_{13}, which arises from the fact that μ is thermodynamically indeterminate within the additive constant Ts_0, where s_0 is the electronic specific entropy at absolute zero. From (3) we see that this makes $\vec{Q}$ indeterminant within the additive quantity $Ts_0\vec{J}$, and from (11) this, in turn, makes L_{13} indeterminant within the additive quantity Ts_0/e. The standard convention that the entropy is zero at the absolute zero of temperature makes all quantities definite and is in harmony with calculations of the kinetic coefficients based on physical models. We shall therefore adopt this convention throughout, and all quantities appearing in our analysis thereby become uniquely defined.

The Electrochemical Potential

Although our eventual aim is to erect a thermodynamical theory, in which models play no part, it is nevertheless both admissible and necessary to employ a model of a solid so as to suggest appropriate definitions of the basic elements of the thermodynamic theory. We accordingly wish, in this section, to discuss the electrochemical potential from the point of view of the band theory of solids. Schematically, a solid may be represented as in figure 14.1, in which vertical distances represent energies, and in which the region on the right represents the interior of the solid and that on the left the space outside the solid. The solid lines represent some particular energy levels in the material—as, for instance, the limits of conduction bands, or specific impurity levels, etc. The dotted line, or "Fermi level", represents an energy such that an allowed state of this energy would have equal statistical probabilities of being occupied by an electron or of being empty. The height of this dotted line, relative to some arbitrary datum energy, represents the *electrochemical potential.* Under certain conditions (as, for example, when there are inhomogeneities in the solid) the allowed energy levels may vary with position, as indicated in figure 14.2, but if the system is in equilibrium, the electrochemical potential remains everywhere constant. A significant theorem [8] of Slater and Wannier now identifies the height of a *solid* line in figure 14.2, relative to some arbitrary datum energy, as the purely *electrical potential.* Choosing the energy at infinity as the datum energy, and choosing a particular

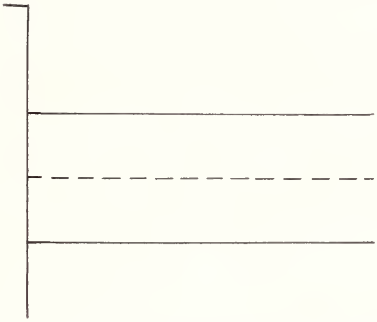

FIGURE 14.1. *Energy-level diagram of solid.*

allowed energy level within the solid as an indicial level, the local resolution of the electrochemical potential μ into electrical and chemical components μ_e and μ_c may be made as indicated in figure 14.3. The electrical potential is thus the energy of some indicial energy state relative to a datum energy, and the *chemical potential* is the energy of the Fermi level relative to the indicial energy state. The sum of these two, or the energy of the Fermi level relative to the datum energy, is the electrochemical potential.

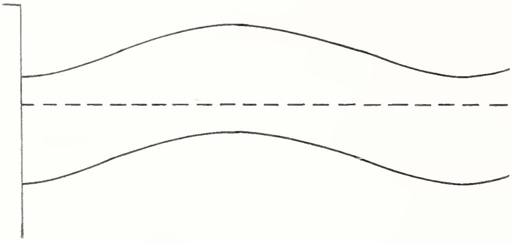

Figure 14.2. *Energy-level diagram of perturbed solid.*

With these definitions in mind, it is of interest to compare the behavior of metals and of nonmetals. For our purposes, a metal will simply be a solid in which there is a very high density of allowed energy levels in the neighborhood of the Fermi level, whereas a nonmetal will be a solid with a very low density of levels near the Fermi level. We now consider a simple experiment in which n electrons are removed from the solid, where n is taken small compared to the number of unit cells in the crystal. For both the metal and nonmetal the electrical potential well in the interior of the solid is depressed by the coulomb potential of the n electrons, and the potential outside the solid rises according to Coulombs law, as shown in figure 14.4. Near the surface of the nonmetal the behavior of the electrical potential will be complicated, and will not be of direct interest to us (this region constitutes the "Shockley exhaust layer"). Although the behavior of the electrical potential in the interior is thus similar for the metal and nonmetal, the behavior of the chemical potential is very different in the two. For the chemical potential changes in each case by just such an amount as to depopulate n energy levels. This will necessitate a very small change of μ_c in the metal, with its high density of levels, but will require a large shift in the nonmetal. We thus see that a

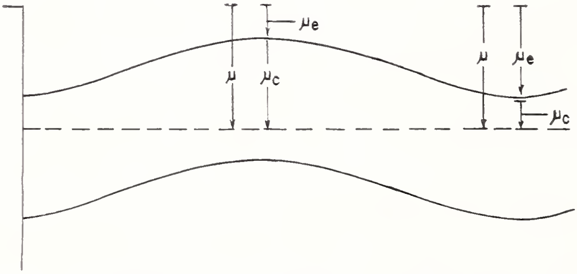

Figure 14.3. *Resolution of μ into $\mu_e + \mu_c$.*

metal is characterized by the fact that $(\partial\mu_c/\partial n)_T \simeq 0$, and consequently that at constant temperature changes in electrochemical potential arise almost entirely from the purely electrical potential. This fact will be of paramount importance in our later discussions.

Before leaving this general discussion of the different types of potentials we recall two basic properties of the electrochemical and electrical potentials. First, that the condition of thermodynamic equilibrium with respect to matter transfer is the equality of the electrochemical potential and not of the electrical potential. Thus a metal and semiconductor placed in contact to produce a rectifying boundary will come to different electrical potentials, with a strong electrical field across the interface, but the electrochemical potential will remain constant across the boundary. Second, that the actual force experienced by a particle between two collisions is determined only by the electrical potential gradient and not by the electrochemical potential gradient. *The motion of a particle between two collisions is affected solely by the electrical potential gradient, whereas the net motion averaged over many collisions is affected solely by the electrochemical potential gradient.* These facts may be readily visualized in terms of a particular air molecule in a room. Here the gravitational potential replaces the electrical potential and the "gravito-chemical" potential replaces the electrochemical potential. The air molecules distribute themselves through the room so that the gravito-chemical potential will be everywhere a constant, independent of height, and there is consequently no net flow of molecules in any direction. Nevertheless, a single molecule suddenly introduced into the room will immediately start to fall downward under the action of the gravitational potential gradient. Only if the molecule is observed over many collisions, will it be seen to have no *net* tendency to fall. It is thus important to realize that observations short with respect to the mean free time of the particles yield information only on electrical (or gravitational) potentials, whereas observations that are long compared to the mean free time of the particles yield information only on the electrochemical (or gravito-chemical) potentials.

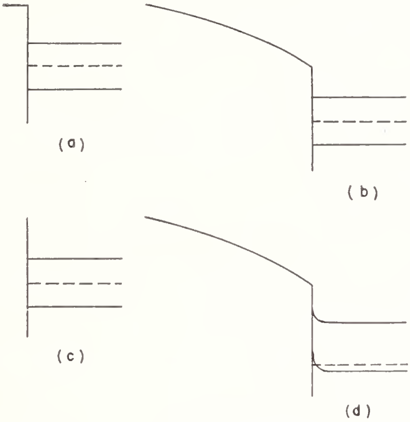

FIGURE 14.4. *In (a) and (b), a metal is shown before and after the removal of n electrons; (c) and (d) show a nonmetal before and after the removal of n electrons.*

Measurement of the Transverse Adiabatic Effects

As already mentioned, the adiabatic Hall and Nernst effects require particular attention. Whereas the definitions of the various other effects will be self-evident, the definitions of these two transverse adiabatic effects deserves some comment here. In particular, we shall give the definitions and show in this section that these definitions are reasonable and practical from the experimental point of view. We will also see that they are the only reasonable definitions that can be taken while preserving the thermodynamic generality. The adiabatic Hall effect is concerned with the appearance of a transverse potential gradient when a current flows in a magnetic field. Thus

$$R_a \equiv \frac{(\text{potential gradient})_y}{HeJ_x} \tag{12}$$

with the conditions

$$\nabla_x T = Q_y = J_y = 0. \tag{13}$$

To complete this definition we must now be specific as to the meaning of the term "potential gradient"—in particular, indicating whether the gradient of the complete electrochemical potential or perhaps only of the electrical potential is implied. This choice is, in turn, dictated by consideration of just what is actually measured in a real laboratory experiment. In such an experiment the lateral edges of the sample would be connected to metallic probes leading to some instrument such as a quadrant electromenter. The quadrant electrometer then yields a number that should be related in some manner to the Hall coefficient. It is clear that the electrometer measures the difference in electrical potential of the two probes (note that the electron density is low in the space between the electrometer plates, so that the electrometer vane makes a measurement in a time small with respect to the collision time). This does not mean, however, that one measures the difference in electrical potential across the sample, for the equilibrium between the probe and the sample edge implies a continuity of the *total* electrochemical potential. That is, the difference in μ, between the probes is equal to the difference in μ across the sample, whereas the electrometer reading gives the difference in μ_e between the probes. However, we have the thermodynamic relation

$$\Delta\mu = \Delta\mu_e + v\Delta P - s\Delta T + \frac{\partial\mu_c}{\partial n}\,\Delta n, \tag{14}$$

where v is the partial specific volume of the electrons, s is the partial specific entropy of the electrons, and n is the electron concentration. As the experiment is all at constant atmospheric pressure, we have $\Delta P = 0$, and as the probes are metallic, we have also, in accordance with the discussion of the previous section, that $\partial\mu_c/\partial n \simeq 0$. Thus

$$\Delta\mu = \Delta\mu_e - s\Delta T, \tag{15}$$

and $\Delta\mu_e$ and ΔT are measured by electrometer and thermometer, whereas s is a thermodynamic property of the metallic probes, which may be presumed to be known (and is rendered definite by the convention that $s = 0$ at $T = 0$). The measurement therefore, suffices to yield the difference in the total electrochemical potential across the sample, and we therefore interpret the definition of the adiabatic Hall effect in terms of a gradient of the total electrochemical potential.

It is interesting to note that this is the only satisfactory definition that could be given, for the resolution of $\nabla\mu$ into $\nabla\mu_e$ and $\nabla\mu_c$ within the sample is generally impossible. This may be seen by writing (14) in the form (putting $\nabla P=0$)

$$\nabla\mu=\nabla\mu_e-s\nabla T+\frac{\partial\mu_c}{\partial n}\nabla n \tag{16}$$

and noting that both $\nabla\mu_e$ and ∇n are unknown. Only in a metal, where the last term of (16) vanishes, can the resolution be unambiguously made. Thus we are forced to define the adiabatic effects in terms of $\nabla\mu$, avoiding thereby the necessity of the above resolution, if we desire to maintain general thermodynamic validity for both metals and nonmetals.

The Thermomagnetic Effects

For purposes of completeness, we now retabulate the definitions of the effects of interest and give the expressions for the thermomagnetic coefficients in terms of the kinetic coefficients.

a. *The Absolute Thermoelectric Power.*

The basic thermoelectric coefficient is the absolute thermoelectric power, the thermoelectric power of a thermocouple being the difference of the absolute thermoelectric powers of the two materials composing the thermocouple. In the presence of a magnetic field the definition of the absolute thermoelectric power may conveniently be taken as

$$\epsilon\equiv\frac{1}{e}\nabla_x\mu/\nabla_x T \quad \text{with} \quad J_x=J_y=\nabla_y T=0, \tag{17}$$

whence

$$\epsilon=\boldsymbol{L}_{13}. \tag{18}$$

b. *The Isothermal Electric Conductivity.*

$$\sigma_i\equiv-eJ_x\Big/\frac{1}{e}\nabla_x\mu \quad \text{with} \quad \nabla_x T=\nabla_y T=J_y=0, \tag{19}$$

whence

$$\sigma_i=\boldsymbol{L}_{11}^{-1}. \tag{20}$$

c. *The Adiabatic Electric Conductivity.*

$$\sigma_a\equiv-eJ_x\Big/\frac{1}{e}\nabla_x\mu \quad \text{with} \quad \nabla_x T=Q_y=J_y=0, \tag{21}$$

whence

$$\sigma_a=(\boldsymbol{L}_{11}-T\boldsymbol{L}_{14}^{3}\boldsymbol{L}_{33}^{-1})^{-1}. \tag{22}$$

d. *The Isothermal Heat Conductivity.*

$$\mathrm{K}_i\equiv-Q_x/\nabla_x T \quad \text{with} \quad J_x=J_y=\nabla_y T=0, \tag{23}$$

whence

$$\mathrm{K}_i=\boldsymbol{L}_{33}. \tag{24}$$

e. *The Adiabatic Heat Conductivity.*

$$\mathrm{K}_a \equiv -Q_x/\nabla_x T \quad \text{with} \quad J_x = J_y = Q_y = 0, \tag{25}$$

whence

$$\mathrm{K}_a = (\boldsymbol{L}_{33}^2 + \boldsymbol{L}_{34}^2)/\boldsymbol{L}_{33}. \tag{26}$$

f. *The Isothermal Hall Effect.*

$$R_i \equiv \frac{1}{e} \nabla_y \mu / H e J_x \quad \text{with} \quad \nabla_x T = \nabla_y T = J_y = 0, \tag{27}$$

whence

$$R_i = \boldsymbol{L}_{12}/H. \tag{28}$$

g. *The Adiabatic Hall Effect.*

$$R_a \equiv \frac{1}{e} \nabla_y \mu / H e J_x \quad \text{with} \quad \nabla_x T = Q_y = J_y = 0, \tag{29}$$

whence

$$R_a = (\boldsymbol{L}_{12} + \boldsymbol{L}_{13} \boldsymbol{L}_{33}^{-1} \boldsymbol{L}_{14} T)/H. \tag{30}$$

h. *The Isothermal Nernst Effect.*

$$\eta_i \equiv -\frac{1}{e} \nabla_y \mu / H \nabla_x T \quad \text{with} \quad J_x = J_y = \nabla_y T = 0, \tag{31}$$

whence

$$\eta_i = \boldsymbol{L}_{14}/H. \tag{32}$$

i. *The Adiabatic Nernst Effect.*

$$\eta_a \equiv -\frac{1}{e} \nabla_y \mu / H \nabla_x T \quad \text{with} \quad J_x = J_y = Q_y = 0, \tag{33}$$

whence

$$\eta_a = (\boldsymbol{L}_{14} - \boldsymbol{L}_{13} \boldsymbol{L}_{33}^{-1} \boldsymbol{L}_{34})/H. \tag{34}$$

j. *The Ettingshausen Effect.*

$$(\mathrm{Ett}) \equiv \nabla_y T / H e J_x \quad \text{with} \quad J_y = Q_y = \nabla_x T = 0, \tag{35}$$

whence

$$(\mathrm{Ett}) = T \boldsymbol{L}_{14} / H \boldsymbol{L}_{33}. \tag{36}$$

k. *The Leduc-Righi Effect.*

$$(\mathrm{Leduc}) \equiv \nabla_y T / H \nabla_x T \quad \text{with} \quad J_x = J_y = Q_y = 0, \tag{37}$$

whence

$$(\mathrm{Leduc}) = \boldsymbol{L}_{34} / H \boldsymbol{L}_{33}. \tag{38}$$

The fundamental set of kinetic equations can now be written in the matrix form

$$\begin{bmatrix} -\frac{1}{e}\nabla_x\mu \\ -\frac{1}{e}\nabla_y\mu \\ Q_x \\ Q_y \end{bmatrix} = \begin{bmatrix} \partial_i^{-1} & HR_i & -\epsilon & -H\eta_i \\ -HR_i & \sigma_i^{-1} & H\eta_i & -\epsilon \\ -T\epsilon & -TH\eta_i & -\mathrm{K}_i & -H\mathrm{K}_i(\text{Leduc}) \\ TH\eta_i & -T\epsilon & H\mathrm{K}_i(\text{Leduc}) & -\mathrm{K}_i \end{bmatrix} \cdot \begin{bmatrix} eJ_x \\ eJ_y \\ \nabla_x T \\ \nabla_y T \end{bmatrix} \tag{39}$$

and we further find the relations

$$\mathrm{K}_i\,(\text{Ett}) = T\eta_i \tag{40}$$

$$\mathrm{K}_a - \mathrm{K}_i = H\mathrm{K}^2{}_i\,(\text{Leduc})^2 \tag{41}$$

$$\sigma_i^{-1} - \sigma_a^{-1} = H^2\eta_i\,(\text{Ett}) \tag{42}$$

$$R_a - R_i = \epsilon\,(\text{Ett}) \tag{43}$$

$$\eta_i - \eta_a = \epsilon\,(\text{Leduc}) \tag{44}$$

Any experimental situation can be directly analyzed in terms of eq. (39), yielding an expression in terms of standard thermomagnetic coefficients. The author here makes a strong recommendation that this set of equations be adopted as standard and basic in discussions of thermomagnetic effects.

References

[1] Lord Kelvin (Sir W. Thomson), Collected Papers I, p. 232–291 (University Press, Cambridge, 1882).
[2] L. Onsager, Phys. Rev. **37,** 405 (1931). See also, H. B. G. Casimir, Rev. Mod. Phys. **17,** 343 (1945).
[3] S. R. DeGroot, Thermodynamics of irreversible processes. (North-Holland Publishing Co., 1951).
[4] H. B. Callen and T. A. Welton, Phys. Rev. **83,** 34 (1951).
[5] R. F. Greene, Irreversibility and thermodynamic fluctuations, thesis, University of Pennsylvania (1951).
[6] H. B. Callen, Phys. Rev. **73,** 1349 (1948).
[7] P. Mazur and I. Prigogine, J. Phys. radium **12,** 616 (1951).
[8] J. C. Slater, Phys. Rev. **76,** 1592 (1949).

15. Absolute Half-Cell Potentials

By Reuben E. Wood [1]

To present a paper on the subject of abolute half-cell potentials is a difficult assignment indeed. There is perhaps no more controversial subject in electrochemistry nor one on which competent investigators hold such considerably divergent views. This paper reviews [1][2] a few experiments and calculations on which speculation about absolute electrode potentials has been based. The short review will necessarily be somewhat superficial.

The half-cell reaction for the calomel cell may be written as in eq (f) of table 1. The absolute electrode potential of this half-cell may be defined as $E_{abs} = -\Delta F/\mathrm{F}$, where ΔF is the free-energy increment corresponding to the change in state written, and F is the faraday. One way of evaluating this potential would be to tabulate a set of changes in state, the free energy of each of which could be evaluated, and the sum of which changes in state would be represented by eq (f).

TABLE 1. *Reaction of calomel half-cell* [1]

(a)	$Na^+_{(g)} = Na^+_{(aq)}$	$\Delta F_{hyd} = -89.7$ kcal.
(b)	$Na_{(g)} = Na^+_{(g)} + e^-_{(g)}$	$\Delta F_b = 118.1$ kcal.
(c)	$Na_{(s)} = Na_{(g)}$	$\Delta F_c = 18.7$ kcal.
(d)	$Hg + Na^+_{(aq)} + Cl^-_{(aq)} = HgCl + Na_{(s)}$	$\Delta F_d = 68.76$ kcal.
(e)	$e^-_{(g)} = e^-_{(in\ Hg)}$	$\Delta F_e = 104.5$ kcal.
(f)	$Hg + Cl^-_{(aq)} = HgCl + e^-_{(in\ Hg)}$	$\Delta F = 11.4$ kcal.
		$E_{abs} = -0.495$ v.

[1] W. M. Latimer, K. S. Pitzer, and C. M. Slansky, J. Chem. Phys. 7, 108 (1939).

Latimer, Pitzer, and Slansky [2] used the set of changes in state shown in table 1. ΔF_e is from photoelectric experiments. ΔF_b is from the ionization potential of gaseous sodium. ΔF_c is a free energy of sublimation. ΔF_d involves just standard free energies of formation and solution. ΔF_a the free energy of hydration of sodium ions, is perhaps the least direct and least certain of the set. It was calculated by Latimer, Pitzer, and Slansky from electrostatic relations involving three parameters: the radius of the sodium ion, the dielectric constant of the solvent in the immediate vicinity of the ion, and the temperature coefficient of this dielectric constant. The ionic radius that the authors used was not the ordinary crystal radius but a larger one. This larger radius was used because the electrostatic theory calls not for that of the ion but for that of the cavity in which the charge is situated in the solvent. Their choice of a value for the radius was based on the fact that the free energies of hydration of various ions should be inversely proportional to the ionic radii. But

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[1] The George Washington University, Washington, D. C.

[2] Figures in brackets indicate the literature references on p. 150.

if the free energy of one ion can be evaluated, the free energies of the others can be calculated from thermodynamic data. Latimer and associates found that by adding 0.1 A to the crystal radii of the halogen ions and 0.85 A to the crystal radii of the alkali metal ions, values for ΔF_{hyd} for all of these ions could be calculated which were nearly proportional to the assumed radii. Those investigators plausibly argue that the radius corrections for positive and negative ions should differ because of the effect on cavity size of the water dipole orientation, which will be different around positive and negative ions.

It is conceded by Latimer et al. [2] that in addition to uncertainty about the exact values to be assigned to the radii, there is some uncertainty about what value to use for the dielectric constant of the solvent in the immediate vicinity of the ions. And there is doubtless the related problem of applying equations valid for cavities in continuous media to problems about systems of atomic and molecular dimensions. Moreover, although the assumption of a constant additive correction for the ionic radii of all the alkali metal ions and another constant correction for the radii of the halogen ions is the simplest and perhaps the only practical one, the question can be raised as to whether this correction should not perhaps vary somewhat with the size of the ion.

It is not entirely clear from the paper what the authors estimate is the probable uncertainty in kilocalaries for ΔF_{hyd}, but they do compare their value of 15 kcal for the chloride ion with 18.1 kcal proposed by Eastman and Young and they say that "this agreement is probably as good as can be expected."

As shown in table 1, the Latimer, Pitzer, and Slansky calculations give -0.50 v for the absolute electrode potential of the normal calomel half-cell. It should be stressed that this calculated potential is very sensitive to the free-energy values. An uncertainty of 1 kcal in ΔF_{hyd}, for example, would represent an uncertainty of 43 mv in E.

The literature indicates that almost any conceivable statement about absolute electrode potentials will be stoutly attacked from some quarter. In view of the strong criticism by Frumkin [3] of the Latimer, Pitzer, and Slansky paper, one is perhaps laying his neck neatly across the chopping block in asserting the validity of their method. However, there seems to be little ground for objection to viewing as absolute potentials the half-cell potentials calculated by this method. Reservations concerning the accuracy of the values so found are probably justified in view of the uncertainties that have been mentioned. In fact, these uncertainties suggest that a thermodynamic calculation of this kind will always leave something to be desired in the accuracy of the calculated absolute half-cell potential.

Other methods for measuring absolute electrode potentials have been proposed, some of which will be described. If any of these can be established as valid, even only under special conditions, the absolute potentials thus found could be used in the above-discussed calculation to obtain values for the energies of hydration of ions.

Perhaps the pheonomenon most discussed as a possible experimental basis for determining absolute electrode potentials is the effect of applied potential on the surface tension of a metal in contact with an electrolyte. Lippmann's [4] capillary electrometer is the classical apparatus embodying this effect, and the phenomenon is accordingly called electrocapillarity. Figure 15.1 is a sketch of a simple apparatus with which electrocapillarity can be observed and measured. When the externally applied potential difference between the Hg in the calomel cell and the Hg in the capillary tube is increased (the Hg in the capillary tube being connected to the negative side of the external potential source), it is found that the height of the Hg in the capillary tube goes through a minimum corresponding to a maximum in the Hg surface tension.

A number of measurements of the potential of this maximum have been made with Hg in contact with various electrolytes. The proposed use of this phenomenon to calculate the absolute electrode potentials is based on the theoretical conclusion that an uncharged Hg surface will have a greater surface tension than a charged one conversely that the maximum surface tension of Hg in contact with an electrolyte will occur when the Hg is neither charged positively nor negatively with respect to the solution with which it is in contact. It is then argued that if there is no charge at this boundary, there is no potential difference. If this reasoning is accepted, one can further argue, with reference to an apparatus such as that shown in figure 15.1, that, under the condition of maximum surface tension, the only two potential differences in the circuit are the externally applied potential and the calomel cell potential, which must be equal and opposite in sign. This, of course, assumes that the usual kind of corrections can be made for any liquid-junction potentials in the salt bridge.

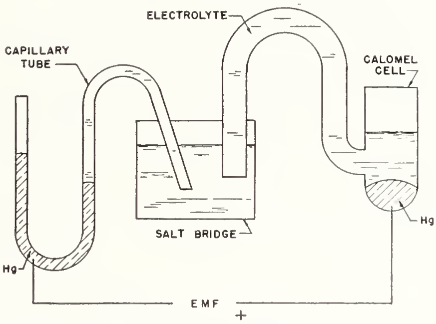

Figure 15.1. *Electrocapillary experiment.*

Table 2 reproduces some of the values obtained by several investigators for the external potential difference required to give a maximum surface tension to the Hg in the capillary tube. The values are selected from a list tabulated by Grahame [1]. The variable is the composition of the electrolyte in contact with the Hg in the capillary tube.

If the preceding argument were strictly correct, all the values in column 3 of table 2 would have to be identical within the experimental accuracy, as they would all be evaluations of the absolute electrode potential of the calomel cell. And it might be noted here that there are some substances which, dissolved in the electrolyte in the capillary tube, will give even more markedly divergent values for E. Among the factors that have been viewed as involved in these discrepancies in values of E for different electrolytes, factors that it is necessary to deal with in interpreting electrocapillary effects, are adsorbed ions and oriented dipoles at the phase boundary. It is pertinent to state that

Grahame adduces from independent evidence that adsorption in the case of the alkali carbonates, hydroxides, and sulfates would be expected to be small or negligible, and he states that there is also good reason to believe that alkali fluorides are not adsorbed, although the necessary data for proving this conclusively are not yet available.

Table 2. *External potential difference required to give a maximum surface tension to the mercury in a capillary tube*

Electrolyte	Concentration	E for maximum surface tension
	M	*Volts*
NaF	1.0	−0.472
	0.1	−.472
	.01	−.480
	.001	−.482
NaCl	1.0	−.556
	0.3	−.524
	.1	−.505
KI	1.0	−.82
	0.1	−.72
	.01	−.66
	.001	−.59
K_2CO_3	.5	−.48
NaOH	1.0	−.48
Na_2SO_4	0.5	−.48

This paper will not attempt to examine the effects of adsorbed ions and oriented dipoles at interfaces. Perhaps the paper to be presented by Dr. Overbeek will provide a basis on which to judge whether or not such factors seriously impair the possibility of using electrocapillary data to evaluate absolute electrode potentials.

One objection that has been raised to the calculation of the absolute potential of the calomel cell from experiments with an apparatus like that shown in figure 15.1 is that under the condition of maximum surface tension the system is not in true equilibrium. The Hg in the capillary tube is polarized, and there will always be flowing a small but measurable polarization current. This objection can be dealt with experimentally. Palmaer [5] used instead of the calomel reference cell a mercury-mercury–cyanide half-cell in conjunction with the capillary electrometer, in which the electrolyte was the same mercury-cyanide solution. He found that with the right concentrations the maximum surface tension occurred with zero applied external potential. This would represent a true equilibrium condition. Incidentally, a solution which in experiments of this kind and related kinds corresponds to a zero metal-electrolyte potential difference with no externally applied potential has frequently been referred to as a null solution or the metal-electrolyte system as a null electrode.

Palmaer then measured the potential across a whole cell made up of his null electrode and a calomel half-cell to evaluate the absolute potential of the calomel cell. The result was a value of about −0.5 v for the calomel cell, assuming the absolute potential of the mercury-mercury–cyanide half-cell to be zero.

Electrocapillarity has been studied with other liquid-metal systems. For example, Frumkin and Gorodatzkaja [6] determined the external applied potential necessary to give Tl amalgams a maximum surface tension. To calculate the absolute electrode potential of a calomel half-cell, three data are needed: The absolute electrode potential of the Tl amalgam half-cell, the potential of a whole cell composed of a Tl amalgam half-cell and a calomel half-cell, and the contact potential difference between Tl amalgam and Hg. it is necessary to consider the contact potential because the free-energy change in the whole cell will include a term representing the free energy required to transfer electrons from one metallic conductor to the other. For many of the pure metals these contact potential differences have been satisfactorily evaluated on the basis of the photoelectric effect, but the author does not know of a value to use for the Tl amalgam–Hg contact potential.

The scraped-electrode experiment is closely related to the electro capillary experiments. It does not, however, involve surface-tension measurements. When a metal is dipped into an electrolytic solution the metal will assume a charge with respect to the solution, the magnitude of which charge is a function of the metal-electrolyte potential difference and of the electrical capacity of the interface. Of course, the possibility of complicating effects from adsorption and dipole orientation mentioned in connection with electrocapillarity must be borne in mind here also. In the experiments to be described the only case of interest is the one for which the assumed charge is zero, and so the magnitude of capacity at the interface need not be considered.

Chalmers [7] adapted the scraped-electrode experiment of previous investigators to the case of Cd electrodes in a $CdSO_4$ solution. He cut a stick of Cd in two and put the two pieces in a $CdSO_4$ solution. The two Cd electrodes were connected externally to a galvanometer. With a piece of glass rod he then scraped shavings off of one of the electrodes. He found that for all concentrations of $CdSO_4$ less than 1 *N* the electrode being scraped acquired a positive charge as indicated by the current that flowed in the galvanometer. For concentrations greater than 2 *N* the current flowed in the opposite direction. The apparatus was not sufficiently sensitive to determine much more closely the concentration at which the current became zero and reversed its direction.

The interpretation of this experiment would be that in solutions less concentrated than 1 *N*, Cd is negatively charged with respect to the solution. When an electrode is scraped, its surface area is increased. This increases the capacity of the interface and in order to maintain the equilibrium potential, negative charges must flow through the galvanometer to the scraped surface. Conversely, for more concentrated solutions the metal is positively charged and scraping causes current to flow in the opposite direction. At a concentration between 1 and 2 *N* the Cd is presumably uncharged with respect to the solution. A Cd electrode in an approximately 1 *N* $CdSO_4$ solution would then be a null electrode.

If, now, one argues, as with the capillary electrometer, that the apparent lack of charge on the electrode means that the absolute potential of the half-cell is zero, one can calculate the value for the absolute potential of the calomel cell. The potential difference of a whole cell comprising a calomel half-cell and this null Cd half-cell should be about 0.7 v. The Cd-Hg contact potential is reported by Schultze [8] to be 0.84 v. This calculation would give a value for the calomel half-cell of about +0.15 v.

Billitzer [9] observed the direction of motion of particles of Ag powder suspended in Ag-salt solutions and subject to electrical fields. With a certain concentration of Ag ions, the Ag particles did not move either way under the influence of the electrical field. He interpreted this to mean that under these conditions the Ag was not charged. Treating these results in the way just described for the Cd null electrode leads to a similar value, namely, about +0.18 v for the normal calomel half-cell.

The discrepancy between the results of Chalmers and Billitzer and the results with the capillary electrometer is typical of discrepancies to be found among other results that will not be mentioned here. One must necessarily conclude that the interpretation of some of these experiments is invalid or at least requires elaboration. Chalmers attempts to reconcile these results by proposing that there exists an "amalgam" of hydrogen, sodium, or other atoms at the surface of the Hg in a capillary electrometer, and that there is a contact potential difference between this superficial "amalgam" and the body of the Hg of about 0.7 v. It is true, of course, that at thermodynamic equilibrium there should be a certain concentration of these atoms in the Hg. In fact, it is only because of the high overvoltage of hydrogen on Hg that many of the electrocapillary experiments can be done at all. However, it seems reasonable to think that any such contact potential would vary with the concentration of the amalgam. If hydrogen atoms are important in Chalmers' amalgam, for example, then one would expect much different values for the electrocapillary maximum when the electrolyte in the capillary tube is half-normal Na_2SO_4 or molal NaOH. The data previously presented indicate that the values are the same for these two cases.

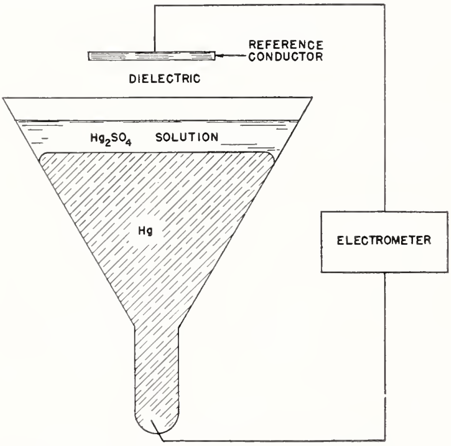

Figure 15.2. *Contact potential experiment.*

The last method to be discussed, which has been proposed as a method for determining absolute electrode potentials, is a contact potential measurement. Figure 15.2 can be used to describe the Kelvin method of contact potential measurement and to show how it has been proposed to apply this method to absolute-electrode-potential measurements. In an apparatus used by Klein and Lange [10] the reference conductor was a copper plate coated with polonium. The polonium served to ionize the dielectric between the copper plate and the conductor below it. Suppose for the moment that the $HgSO_4$ solution shown in the sketch is absent, and that the Hg surface and the Cu plate are separated by an ionized gas. If there is a potential difference between the two metal surfaces, the gas ions will move preferentially to one conductor or to the other, causing a current to flow in the electrometer circuit. When the electrometer has been charged to such a potential as to bring the Cu and Hg surfaces to the same potential, the current will cease to flow. The reading of the electrometer will be the sum of the contact potential differences in the circuit. This method has been used to evaluate metal-metal contact potential differences and it has been found difficult to obtain reproducible results and ones that agree with photoelectric results, presumably because of the presence of foreign substances—adsorbed gases, for example,—on the metal surfaces.

Klein and Lange set up an apparatus in principle like that sketched in figure 15.2. In one experiment the conductor under the reference electrode was Hg. In another experiment the conductor below the reference electrode was a saturated Hg_2SO_4 solution over Hg. The difference in the potential indicated by the electrometer for these two experiments should represent a contact potential difference between Hg and Hg_2SO_4 solution. From these experiments Klein and Lange give a figure of −0.555 v, which they call "the absolute Volta potential" for the Hg-Hg_2SO_4 couple. For purposes of comparison, from the value just quoted, the absolute Volta potential of the normal calomel half-cell can be calculated to be −0.22 v.

Klein and Lange treat their absolute Volta potentials as though they were absolute potentials in the sense of the definition adopted at the beginning of this paper, in that they calculate from their values, values for the heats of hydration of the ions. For example, from such a calculation they give for the heat of hydration of sodium ions a value of −101 kcal. Latimer's corresponding value is −89.7 kcal.

There are serious objections to the interpretation of this kind of experiment as a measurement of absolute potentials. There are three phase boundaries: Metal-electrolyte boundary, electrolyte-dielectric boundary, and metal-dielectric boundary. That these latter two boundaries do introduce extraneous potentials into the circuit appeared evident even from the results of the Klein and Lange experiments. They found a 0.13-v difference in the absolute Volta potential if the experiments were carried out under hydrogen instead of under argon. The value they found when dry air was present was about 50 mv more negative than with argon, and the value when moist air was present was about 50 mv more positive than with argon. And experiments under nitrogen gave values about 10 mv different than experiments under argon.

Such extraneous potentials can be attributed to a number of possible causes, among which, as suggested, would be the existence of an adsorbed layer on the metal or on the solution, or the presence of oriented dipoles at phase boundaries. Conceivably some of the objections could be lessened if such experiments could be devised to be done in an evacuated apparatus, using electrolytes of very low vapor pressure. The Faraday method of measuring contact potentials involves varying the capacity between the reference conductor and the other conductor; it does not require an ionized atmosphere to be present. Both on theoretical grounds, however, and in view of the experimental difficulty that has been experienced in getting good metal-metal contact potentials by these methods, there would seem to be some doubt that such methods would be fruitful in measuring contact potential differences between metals and electrolytes from which values absolute potentials could be correctly calculated.

References

[1] For rather full revews and bibliographies in the field, see: J. A. Chalmers, Phil. Mag. **33,** 599 (1942); D. C. Grahame, Chem. Rev. **41,** 441 (1947).
[2] W. M. Latimer, K. S. Pitzer, and C. M. Slansky, J. Chem. Phys. **7,** 108 (1939).
[3] A. Frumkin, J. Chem. Phys. **7,** 552 (1939).
[4] G. Lippmann, Ann. Phys. **5,** 494 (1875).
[5] W. Palmaer, Z. Elektrochem. **9,** 754 (1903); Phys. Chem. **59,** 129 (1907).
[6] A. Frumkin and A. Gorodatzkaja, Z. Phys. Chem. **136,** 451 (1928).
[7] J. A. Chalmers, Phil. Mag. **34,** 349 (1943).
[8] R. Schultze, Z. Physik. **92,** 212 (1934).
[9] J. Billitzer, Z. Elektrochem. **8,** 638 (1902); Ann. Physik. **11,** 902, 937 (1903); Z. Phys. Chem. **51,** 166 (1905).
[10] O. Klein and E. Lange, Z. Elektrochem. **43,** 570 (1937).

Discussion

Dr. J. O'M. Bockris, Imperial College of Science and Technology, London, England: There is often an impression among physical chemists that the potential of the electrocapillary maximum is a rough measure of the absolute potential difference between a metal and its solution. Dr. Wood mentioned this but did not develop the influence that the orientation of dipoles at the surface of the electrode exert upon this potential difference. This has been commented upon largely by Lange. These dipoles exist, even though there is no charge on the surface. You get an attraction between the metal and the dipoles for various reasons. Often people have said "at the e. c. m. there is no charge on the electrode, hence there is no orientation and therefore, there is no potential difference due to dipoles," but that does not follow. Further, the potential difference brought about by the dipole may be quite appreciable so that the potential of the electrocapillary maximum may not be a very good approximation at all for the absolute potential.

This does not invalidate the fact that measurements of electrocapillary phenomena on solid metals seem to have been entirely neglected, but they would be very helpful. I think possibly it might be worth mentioning that in the e. c. m. experiments carried out in the past, the solutions were insufficiently purified so that disagreement between the results may have been due to the different effect of various impurities on the χ potential.

Dr. Th. G. Overbeek, University of Utrecht, Utrecht, The Netherlands: I found that Dr. Wood, although he presented an interesting paper, did an injustice to Lange in giving the impression that the Volta potential should not be anything quite definite. In my opinion, as Lange defines it, between two metals or between a metal and a solution, it is something that is completely sound; whereas the Galvani potential, as Lange calls it, the difference between the interiors of two different phases, is something very debatable and which we know nothing about at this moment. It would be a pity if someone would confound the two ideas. The Volta potential difference is very different; it is completely sound; it is the difference of the potentials in the vacuum just outside the phases, not the interior. One can easily understand that these Volta potentials are susceptible to the influence of absorption. It is different when oxygen or hydrogen or other gases are present, but that does not invalidate the measurement.

Dr. R. E. Wood: Maybe I misinterpreted Lange's treatment but I did understand that they calculated hydration energies from his values, which I suppose would imply a treatment of the Volta potentials as if they were potentials having something to do with the thermodynamic relationships. If I am wrong, I would be glad to be set right.

Dr. Overbeek: As I remember it was hydration energy. You may talk about hydration energy by bringing an ion from the vacuum through the phase boundary into the liquid and hydrate it there, and you may call hydration energy just the last step and omit the transgressing through the phase, and that is just the difference in the two potentials.

Dr. Bockris: It should possibly be clear that in Lange's method no attempt is made to measure the "absolute potential-difference" between metal and solution. Thus, discussion of Andaner's method, termed "Lange's method" by Dr. Overbeek, within the terms of reference of Dr. Wood's paper, seem not wholly relevant. The main criticism of Lange's method, as a method of measuring Volta potential differences, is that an ambiguity in the metal-air and air-solution interface exists.

Dr. Overbeek: As far as I remember, he has used the same setup. For instance, with Ag he measures the Volta potential difference between Ag and Hg and that between $AgNO_3$ in contact with Ag and Hg, and the difference in these two potentials would give the potential difference between Ag and $AgNO_3$ solutions. I can't see the objection. One can, of course, see that it is composed of three steps.

Dr. Bockris: Do you remember the results of the experiments in measuring the concentration of the salt on the potential difference?

Dr. Overbeek: Yes, $AgNO._3$ [O. Klein and E. Lange, Z. Elektrochemie **43**, 570–584 (1937).]

Dr. Bockris: The effect of the salt concentration on the potential of the solution-air interface was satisfactorily evaluated only at small concentrations.

Dr. Overbeek: Lange reminded me about 2 months ago of the fact that the Volta potential difference between Ag and $AgNO_3$ followed quite correctly Nernst's law with a difference of 58 mv up to concentrations of about 1 molar $AgNO_3$. He found that the Volta potential above the solution was quite insensitive to the composition of the gas atmosphere. The Volta potential above the metal, however, is sensitive to the gas atmosphere, but Lange could produce evidence that the Volta potential of Hg in an atmosphere of an inert gas was not very different from that of Hg in a vacuum, which consequently gave a suitable reference state for this type of measurement.

Dr. A. J. Rutgers, University of Ghent, Ghent, Belgium: One historical remark. I remember quite well that in a paper by Lorentz in 1905 the Volta potential was defined in the same way as in the present conference.

16. Standard Potentials in Aqueous Hydrochloric-Acid Solutions Containing Organic Compounds

By H. D. Crockford[1]

Introduction

Harned and Owen [1, chap. 11][2] in the first edition of their monograph give a summary of data available at the time of publication for the calculation of standard potentials in cells of the type:

$$H_2|HCl(m),\quad S(X),\quad H_2O(Y)|AgCl\text{-}Ag,$$

in which S is an added organic compound of weight percent X. They discuss possible correlations between the standard-cell potentials and the dielectric constant of the solvent media and present curves to illustrate relations in data existing at that time. In chapters 11 and 12 they discuss the determination of activity coefficients of the acid in various solvents by equations containing the ion-size parameter and the "salting-out" constant. In their second edition they list additional references to studies concerned with standard potentials of the above cell, but do not test the data with the relations discussed in the first edition. Additional data have become available for studies with the above cell since publication of the second edition.

This paper applies the considerations of Harned and Owen [1] to the data[3] that have become available since the publication of their first edition. Also included is a discussion of the determination of standard-cell potentials with special consideration to the ion-size parameter.

Except when otherwise noted, the symbols used will be those of Harned and Owen. Potentials are given in international volts in accordance with the usage employed in the original papers and by Harned and Owen. Page references to Harned and Owen are the same for both the first and second editions.

Values of the Standard-Cell Potentials

At the time of publication of the first edition of Harned and Owen [1], data were available for the above cell for HCl in pure water [2], in two concentrations of methanol in water [3], in three concentrations of ethanol in water [4, 6], in two concentrations of glycerol in water [5], in one 2-propanol solution [6], and in four solutions of dioxane in water [7]. Additional data have been published for one more glycerol solution [11], five concentrations of ethylene glycol [15, 16], four concentrations of *d*-glucose [14], three concentrations of 2-propanol [13],

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[1] University of North Carolina, Chapel Hill, N. C.

[2] Figures in brackets refer to literature references on p. 163.

[3] Complete data for the various calculations and the exact values used in the plots can be obtained from the author.

and two concentrations of ethanol [12]. Also available are two additional concentrations of glycerol [18] and two solutions of *d*-fructose [17]. The various solutions that have been studied, with the temperatures and concentrations employed, are given in table 1.

TABLE 1. *Researches on standard potentials with the cell:* $H_2|HCl(m)$, $S(X)$, $H_2O(Y)|AgCl\text{-}Ag$

Component S	Composition (weight percent of S)	Temperature	Investigators
Methanol*	10, 20	0° to 40° C in 5-deg intervals.	[3]
Do*	100	25°	[8]
Ethanol*	10, 20	25°	[6]
Do	10, 20	0° to 40°, in 5-deg intervals	[12]
Do*	100	25°	[9]
Do*	100	25°	[10]
Do*	71.8, 100	25°	[4]
Glycerol*	3.06, 21.2	25°	[5]
Do	10, 30	0° to 40°. in 5-deg intervals	[18]
Do	50	0° to 40°, in 5-deg intervals	[11]
Dioxane*	20, 45, 70, 82	0° to 50°, in 5-deg intervals	[7]
2-Propanol*	10	25°	[6]
Do	10, 20, 30	0° to 40°, in 5-deg intervals	[13]
Ethylene glycol	5, 10, 15, 20, 30, 40, 60.	25°	[16] [15]
d-Glucose	5, 10, 20, 30	25°	[14]
d-Fructose	5, 10	25°	[17]

*Data considered by Harned and Owen [1].

Table 2 gives the standard potentials of the various cells together with the weight and mole percents of the organic components and the dielectric constants of the solvent media. The standard potentials

TABLE 2. *Standard potentials of the cells:* $H_2|HCl(fm)$, solvent (N_2), $H_2O(N_1)|AgCl\text{-}Ag$ at 25°

N_1, N_2=mole fraction; X=weight percent of nonaqueous component.

	X	N_2	D_0	E_m^{0*}	E_N^{0*}
Water*	0	0	78.54	0.22239	0.01602
Methanol-water*	10	.0588	74.0	.21545	.01124
Do*	20	.1233	69.2	.20881	.00710
Methanol*	100	1.0	31.5	−.0101	------
Ethanol-water*	10	0.0417	72.8	.21442	.01123
Do*	20	.0891	67.0	.20736	.00763
Ethanol*	100	1.0	24.3	−.0740	------
Glycerol-water*	3.06	0.01	77.1	.2196	.0146
Do	10	.0211	75.5	.21650	.01448
Do*	21.2	.05	72.5	.2084	.0117
Do	30	.077	70.1	.20221	.01005
Do	50	.165	64.0	.18398	.00407
Dioxane-water*	20	.0487	60.8	.20303	.00554
Do*	45	.1433	38.5	.16352	−.02002
Do*	70	.3231	17.7	.06395	−.10049
Do*	82	.4823	9.5	−.0413	−.19339
2-propanol-water	5	.0168	74.9	.21807	.01350
Do	10	.0332	71.4	.21383	.01118
Do	20	.0704	64.1	.20637	.00775
Ethylene glycol-water	5	.0152	76.9	.21905	.01455
Do	10	.0311	75.7	.21635	.01380
Do	15	.0486	74.2	.21330	.01275
Do	20	.0678	72.8	.21020	.01177
Do	30	.1110	69.8	.20360	.00955
Do	40	.1623	66.6	.19720	.00800
Do	60	.2991	59.4	.18070	.00285
d-Glucose-water	5	.0057	77.3	.21863	.01468
Do	10	.0106	76.1	.21419	.01271
Do	20	.0246	73.4	.20451	.00835
Do	30	.0413	70.5	.19355	.00336
d-fructose-water	5	.0057	77.3	.21900	.01499
Do	10	.0106	76.1	.21502	.01354

*Data considered by Harned and Owen [1].

are given for both molality and mole fraction. All data are for 25° C All values given are those of the original papers, except for the 21.2-mole percent glycerol solution. Here a new value has been calculated based on a revised value for the dielectric constant and a reconsideration of the original data. The values for 10 and 20 weight percent of ethanol are those of Harned and Calmon [6] rather than those of Patterson and Felsing [12]. The differences between the values obtained in the two investigations are 0.00025 and 0.00021 v for the 10 and 20 weight percent solutions respectively. These differences are not significant in the considerations that follow. The value for the 10 weight percent propanol solution is that of Felsing and Moore [13]. Their value is higher by 0.00020 v than that of Harned and Calmon [6]. Not included in the table are a number of intermediate values for ethanol, which may be estimated from the data of Harned and Fleysher [4]. These data have been omitted because they do not fall in the range of the other values considered in this paper.

As only five solutions in table 2 have dielectric constant values less than 59, the study of the data of this table is essentially one of solutions of high dielectric constant. These five solutions (pure ethanol and methanol and the three higher concentrations of dioxane) have dielectric values well below those of the remainder of the table, and so do not fit in with the table as a whole.

Correlation of the Standard Potentials with the Dielectric Values

Harned and Owen [1, p. 337] plot the values of E_m^{0*} *versus* $1/D$ for those starred solutions of table 2 that have $1/D$ values of 0.01645 and lower. The resulting figure is therefore a high dielectric study. They also include in their figure dashed lines for plots of E_m^{0*} calculated from the Born equation. This equation, derived from applications of the electrostatic theory to solutions of varying dielectric constant, may be given, for 25° C, in the following form [1, p. 338]:

$$\frac{E_N^0 - E_N^{0*}}{0.05915} = 1.210\times10^2 \frac{D_1 - D_2}{D_1 D_2} \sum 1/b_j. \qquad (1)$$

In this expression E_N^0 and E_N^{0*} are the standard potentials for solutions of dielectric constants D_1 and D_2, and $\sum 1/b_j$ is the sum of the reciprocals for the radii of the individual ions. From crystallographic data Harned and Owen calculate $\sum 1/b_j$ to be 1.2; If a mean ionic diameter of 5.0 A is assumed, the value would be 0.8; if a mean diameter of 4.3 is assumed, the value would be 0.93. Harned and Owen state that the curves obtained have slopes roughly equivalent to the slopes of the Born lines plotted for $1/b_j$ equal to 1.2 and 0.8. They point out that while the curves are not straight lines, they show pronounced individual behavior.

In figure 16.1 values of E_m^{0*} *versus* $1/D$ are plotted for data available to Harned and Owen, plus data that have been published since the original figure was drawn. Also included are the Born equation plots for $\sum 1/b_j$ equal to 1.2 and 0.8. A number of features are brought out by the additional data. The monohydric alcohols, ethanol, methanol, and 2-propanol, fit roughly on a curve falling between the two Born lines. The additional glycerol data fit on a straight line located below the lower ($\sum 1/b_j=1.2$) Born line. The ethylene glycol curve follows fairly closely the glycerol curve for the lower concentrations but departs from it at the higher concentrations. The two carbohydrates, *d*-glucose and *d*-fructose, give points that fall on a fairly straight line well below the glycerol curve. The additional values for 2-propanol fit in well with the data for the other monohydric alcohols. The one dioxane value that can be plotted with these data falls on a curve with the monohydric alcohols. Thus, three distinct sets of curves are indicated, one consisting of the two carbohydrates, another consisting of glycerol and ethylene glycol, and the third including the monohydric alcohols. So there appears to be considerable correlation between the positions of the various curves and the chemical nature of the added organic substances.

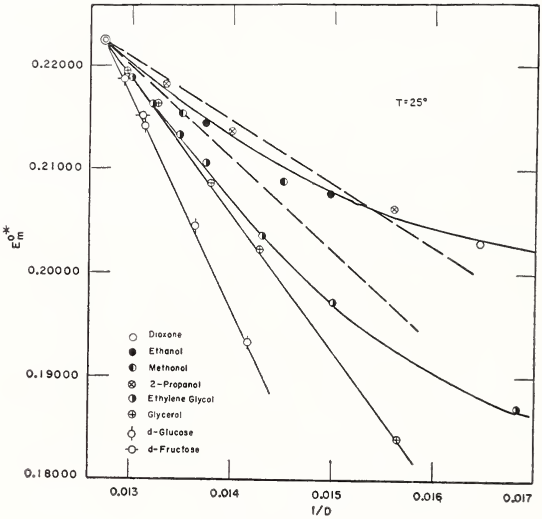

FIGURE 16.1.

If the values for E_c^{0*}, the standard electrode potentials expressed in molarity, are plotted, essentially the same distribution is secured, since the function relating values of E_c^{0*} and E_m^{0*} contains as the only variable the density of the solutions. The densities of all the solutions considered in figure 16.1 vary only slightly from unity.

Now, if the values of E_N^{0*} are plotted against the values of $1/D$, a considerable change in relative positions of the points results, since the relation between this potential and E_m^{0*} is given by the expression

$$E_N^{0*}=E_m^{0*}-0.1183\log(1000/M_{xy}), \qquad (2)$$

where M_{xy} is the mean molecular weight of the solvent. M_{xy} is greatest in the higher concentrations of glycerol and ethylene glycol. Although the molecular weights of the added carbohydrates are large, the concentrations are not sufficiently great to produce much increase in the mean molecular weight. As eq (2) shows, the calculation of E_N^{0*} always results in a smaller numerical value than the E_m^{0*} value. The decrease is most pronounced in the solutions of lower molecular weight. There are corresponding smaller decreases in the ethylene glycol and glycerol solutions. The result is a figure in which the *d*-glucose and *d*-fructose points fall again on a single curve and the remaining points roughly along another curve. In other words, the ethylene glycol and glycerol values now fall among the approximate curve for the monohydric alcohols. This plot was not given by Harned and Owen [1]. Because it does not bring out any new correlations other than those of figure 16.1, it is not included here.

Harned and Owen [1, p. 339] give a plot of E^{0*}_m *versus* $1/D$ over a wide variation of dielectric constant. This plot includes, in addition to the lower dielectric values of table 1, a number of values for ethanol computed from the data of Harned and Fleysher [4]. No additional data have become available since the preparation of this figure. Consequently, it will not be reproduced. No correlations not apparent in figure 16.1 are brought out by this plot.

Harned and Owen employ a plotting procedure in which the function $(E^{0*}_N - 0.05915 \log N_1)$ is plotted against $1/D$. Harned and Calmon [6] employ the function $(E^{0*}_m - 0.05915 \log N_1)$. The basis for these procedures are the equations

$$E^0_N - (E^{0*}_N - 0.05915 \log a_w) = 0.05915 \log \frac{f_{H_3O^+} f_{Cl^-}}{f^*_{H_3O^+} f^*_{Cl^-}} \qquad (3)$$

$$E^0_m - (E^{0*}_m - 0.05915 \log a_w) = 0.05915 \log \frac{\gamma_{H_3O^+} \gamma_{Cl^-}}{\gamma^*_{H_3O^+} \gamma^*_{Cl^-}} \qquad (4)$$

These equations were derived by Harned and Owen [1, p. 337], for solutions of high water content from considerations of the thermodynamic relationships for the reaction

$$H^+ + Cl^- + H_2O = H_3O^+ + Cl^-.$$

For solutions of high water content, a_w may be replaced by N_1, producing the relations plotted by Harned and Owen [1] and Harned and Calmon [6]. A plot of $(E^{0*}_m - 0.05915 \log N_1)$ *versus* $1/D$ by Harned and Calmon resulted in a curve upon which all the points available to these investigators fell, except for the 21.2 weight percent glycerol solution. A plot of $(E^{0*}_N - 0.05915 \log N_1)$ *versus* $1/D$ by Harned and Owen [1, p. 338] resulted in all the starred points (except for the pure ethanol and methanol and the three highest dioxane solutions) falling on the same curve. This last curve has a position much higher than the two Born curves plotted in figure 16.1. Harned and Owen stated that this striking result might prove of importance in organizing data of this kind if it were verified by future experimental investigations.

The plots of these functions for the data available to Harned and coworkers, and data which have become available since the publications of the original curves, are given in figures 16.2 and 16.3. The single curve relations indicated in the plots of Harned and Owen [1] and Harned and Calmon [6] no longer hold. In the $(E^{0*}_m - 0.05915 \log N_1)$ plot, three distinct sets of curves similar in relative position to the three sets of curves in figure 16.1 are found. In fact, the correlation for the monohydric alcohols is better in this figure than in figure 16.1. In the $(E^{0*}_N - 0.05915 \log N_1)$ plot, the combined effect of M_{xy} values and the N_1 values is to raise the more concentrated ethylene glycol values above the values for the monohydric alcohols. A similar effect, although not nearly so pronounced, is found in the more concentrated glycerine solutions. The relative position of the curve for the *d*-glucose and *d*-fructose is little changed due to the very high water content and the comparatively low mean molecular weight

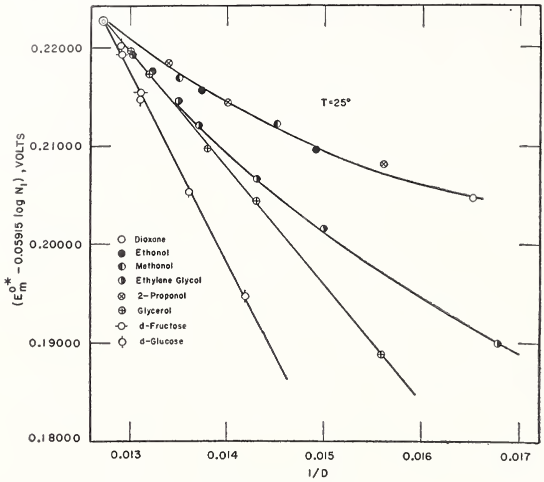

FIGURE 16.2.

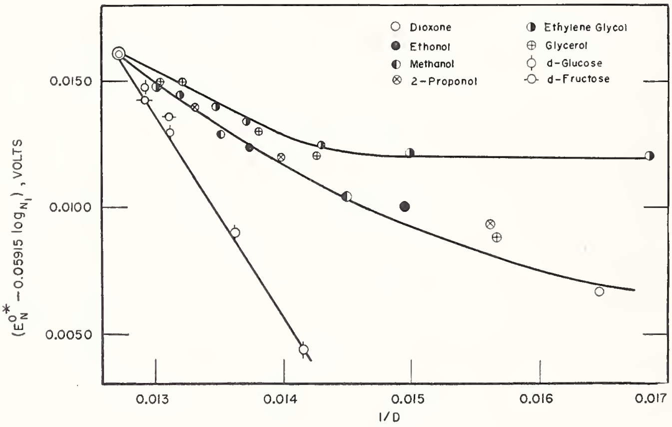

FIGURE 16.3.

of the solvents. Therefore, the order of the sets—carbohydrates, ethylene glycol and glycerol, and monohydric alcohols—found in figure 16.2 is changed to carbohydrates, monohydric alcohols, and ethylene glycol and glycerol.

Thus, the indications of single curves, based on eq (3) and (4) and the earlier data, are not upheld by the more recent data. However, distinct groups of curves based on the structures of the added compounds are clearly indicated and are quite pronounced in the E_m^{0*} *versus* $1/D$ plot.

Determination of Standard Potentials

The usual procedure for determination of standard-cell potentials is to plot the function $E^{0\prime}$, as defined by eq (5), against the molality and then extrapolate to zero concentration.

$$E^{0\prime}\equiv E+2k \log m-\frac{2kA\sqrt{c}}{1+\overset{0}{a}B\sqrt{c}}-2k \log (1+0.002mM_{xy})=E^{0}+f(m). \tag{5}$$

The constants A and B include the temperature and the dielectric constant of the solvent medium. In using this expression, various values of the ion-size parameter $\overset{0}{a}$ can be employed, or the denominator of the fractional term can be considered as having a value of one in accordance with the Debye-Hückel limiting law. If the data are reasonably accurate, extrapolation can be carried out with a high order of accuracy. In some cases, it is necessary to include the so-called E_{Ext} term, which is introduced by the theoretical treatment of Gronwell, LaMer, and Sandved [1, p. 332]. However, as Harned and Owen point out, in the case of HCl solutions in which the dielectric constant has a value of approximately 60 or higher, the effect of this term is not significant. Therefore, it has not been included in considerations discussed in this paper. In using eq (5), it is noted that if $f(m)$ is zero, the value, of $E^{0\prime}$ is independent of the molality and is equal to E_{m}^{0*}.

In accordance with the treatment used by Harned and Thomas [3], the term $f(m)$ may be identified with the salting-out constant often introduced into the expression used for calculating the activity coefficient of an electrolyte from theoretical considerations. For HCl this expression is

$$\log \gamma_{\pm}=-\frac{A\sqrt{c}}{1+\overset{0}{a}B\sqrt{c}}-\log (1+0.002mM_{xy})+Bc+D'c^{2}. \tag{6}$$

Bc is a term introduced to account for the change produced in the dielectric constant by the addition of the electrolyte. While such an effect certainly exists, the introduction of a simple linear term to account for it can be considered as little better than empirical. In cases where the calculated activity coefficient does not agree with the experimental, the introduction of the second correction term $D'c^{2}$ is sometimes used. This again is an empirical operation. Now, if the value of the activity coefficient from eq(6) is introduced into the expression

$$E_{m}^{0}-E=0.1183 \log m+0.1183 \log \gamma_{\pm},$$

the following equation results if the $D'c^{2}$ term is omitted.

$$E_{m}^{0}=E-\frac{0.1183A\sqrt{c}}{1+\overset{0}{a}B\sqrt{c}}+0.1183 \log m-0.1183 \log(1+0.002\,mM_{xy})+B'c. \tag{7}$$

In this expression, $B'=0.1183B$. The equation is specialized for a uni-univalent electrolyte and a temperature of 25°. Now a plot of the right side of eq(7) against concentration should give a straight line of zero slope, provided the proper value of the ion-size parameter is used. Again the plot of the first four terms on the right side of the expression, which in eq(5), were defined as $E^{0\prime}$, should give a line of zero slope, provided the proper ion-size value is used and the salting-out constant has a value of zero. If the salting-out constant does not have a value of zero, and if higher powers of c do not apply, a straight line of finite slope should be obtained, and the salting-out constant could be determined from its slope.

In calculations concerned with the ion-size parameter, certain doubts arise concerning its significance. Often straight lines, within the limits of error of the data, can be obtained for more than one value of the ion-size parameter. Parameter values that give a reasonably straight line with zero slope over certain concentration ranges can usually be found. However, such values in some cases are undoubtedly too high. Equation (7), without the $B'c$ term but with the proper value of $\overset{0}{a}$, could not be expected to hold for a molality of more than about 0.02. Above this concentration, complicating factors would undoubtedly come into play.

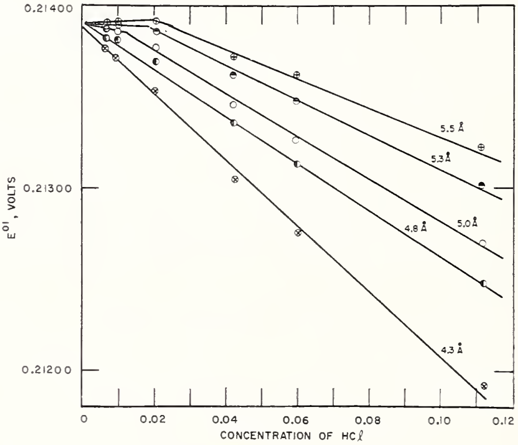

FIGURE 16.4.

In order to study available data to see if any conclusions could be drawn concerning the ion-size values, eq(7) has been applied to certain of the solvent mixtures in table 1.

2-Propanol. Using the original data of Moore and Felsing [13], eq(7) was applied to the 5, 10, and 20 weight percent solutions of 2-propanol. All three solutions showed the same characteristics, so only the 10 percent data will be discussed. Figure 16.4 shows the plots obtained when various values of the ion-size parameter are used. A reasonably straight line is secured with an ion-size value of 4.8 A. A value of 5.0 produces a break in the curve, and this break becomes more pronounced as the value of $\overset{0}{a}$ is increased. A straight line of zero slope is obtained when a value of 5.2 A is used. The straight line extends to a value of about 0.02 molality. Above this value for $\overset{0}{a}$ the curves show a positive slope for the lower concentrations. The question may then be raised as to whether 4.8 or 5.2

represents a better value for the ion-size parameter. Certainly, the former value will enable one to calculate a salting-out constant that would reproduce the activity coefficients over the entire concentration range. A conservative conclusion would be that the ion-size parameter has a value of 5.0±0.2. However, another question arises. Would additional data at higher concentrations show a break in the curve calculated for an ion size of 4.8 A?

d-Glucose and d-Fructose. A consideration of the data of Crockford and Sakhnovsky [17] for *d*-fructose and Crockford, Knight, and Williams [14] for *d*-glucose shows that a straight line of zero slope is secured in all solutions studied up to a concentration of approximately 0.10 *m*, when an $\overset{0}{a}$ value of 6.6 is used. This is a surprisingly high value, and it is further surprising that it can be used up to this high a concentration. The plots for the 5 weight percent solution for *d*-glucose are given in figure 16.5. These plots show the same characteristics as the plots of the other concentrations. Unfortunately, the data for *d*-fructose do not extend above a molality of 0.10. However, the 5 weight percent *d*-glucose data extend to approximately 0.7 *m*, so that further consideration of the data is possible. It is noted that a straight line is secured over the entire concentration range when a maximum value of 5.0 A is used. Whatever other conclusions may be drawn concerning these two carbohydrates, certainly a much higher value of the ion-size parameter applies to their solutions than to the solutions of the other substances studied.

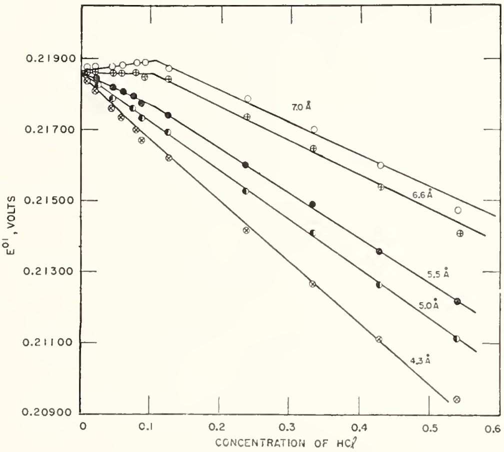

FIGURE 16.5.

Glycerol. The study of glycerol data was made on the 25° values obtained by Crockford, Knight, and James [18], using 10- and 30-percent solutions and on the 50-percent solution of Harned and Nestler [11]. Unfortunately, no data for concentrations over 0.1 *m* are available. Comparable results were found with these three solutions, so only the 50-percent data of Harned and Nestler [11] will be discussed. The results are shown in figure 16.6. A maximum value for the ion parameter of 5.0 A continues to give a straight line. A line of zero slope for an $\overset{0}{a}$ value of 6.3 A is obtained for concentrations up to approximately 0.05 *m*. Thus, a fairly high value for the ion-size parameter is indicated.

Ethylene Glycol. A detailed study for three solutions was made by Crockford, Knight, and Staton [15] with this substance in very low acid concentrations. A value of 4.3 A for the ion-size parameter was obtained. The data of Knight, Masi, and Roesel [16] for higher concentrations indicate that a possible value of 4.5 A gives a straight line over the entire concentration range. This range is approximately 1 *m* in certain of the solutions. A value of 4.3 A seems to be characteristic of ethylene-glycol solutions.

A value of 4.3 A for the ion-size parameter is indicated in *methanol* solutions, using the data of Harned and Thomas [3], and in *ethanol* solutions, using the data of Harned and Calmon [6]. In both solvents straight lines of zero slope are obtained, extending to a molality of approximately 0.015, with a value of 5.0 A. It is interesting to note that the best value for HCl in *pure water* is 4.3 A, although a value of 5.6 A gives a straight line of zero slope up to a molality of approximately 0.04. For *dioxane* solutions Harned and Owen [1] give 5.0, 5.4, and 5.6 A as the best $\overset{0}{a}$ values for the 20-, 45-, and 70-percent solutions. These values give a horizontal line up to approximately 0.02 *m*.

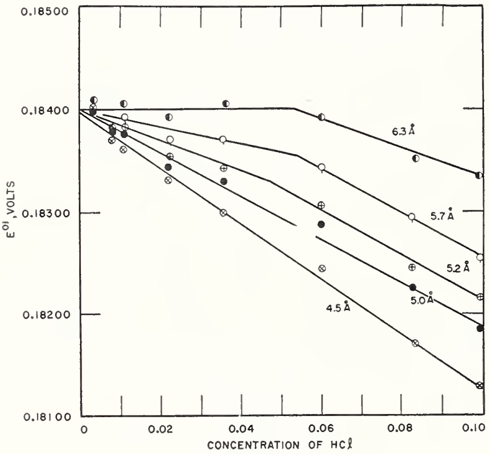

FIGURE 16.6.

A consideration of figure 16.1 leads to the following conclusions. The substances with the highest $\overset{0}{a}$ values for the curve of zero slope are *d*-glucose, *d*-fructose, and glycerol, those giving the lowest curves in the figure. The region of zero slope also extends over the greatest concentration range in these solutions. These substances also show the highest value for the $\overset{0}{a}$ parameter when the entire concentration range is considered. The methanol, ethanol, and 2-propanol solutions, which give the upper set, are those with the lowest values of $\overset{0}{a}$ when the entire range of concentrations is considered. These solutions all give a value of approximately 5.0 for $\overset{0}{a}$ when the horizontal portions of the curves are considered, but the extent of the region of zero slope is quite small. Ethylene glycol, which falls into a separate group with glycerol, shows a value of 4.3 A for both the over-all value and for the flat part of the curve. Little significance is attached to these conclusions. They are not clear-cut conclusions, and studies over wider concentration ranges might change certain of the $\overset{0}{a}$ values.

Studies of the salting-out constants are even more inconclusive. Larger values are indicated for this magnitude for the *d*-glucose and glycerol solutions than for the monohydric alcohols. No conclusions can be drawn about the *d*-fructose because of the limited concentration range. Ethylene glycol also appears to give a somewhat higher value than the monohydric alcohols. A very general but vague conclusion may be drawn that the lower curves are characteristic of the substances with the higher values of the salting-out constant. It is felt that until more data over wider ranges of concentration are secured, the determination of salting-out constants for the solutions studied is little more than the securing of magnitudes to make experimental data fit certain equations.

Summary

1. All available electromotive-force data for cells of the type

$$H_2|HCl(m),\quad S(X),\quad H_2O(Y)|AgCl\text{-}Ag$$

have been studied to determine possible correlation between the standard-cell potentials and the dielectric constants of the various solutions. Data are available in which S is *d*-glucose, *d*-fructose, dioxane, methanol, ethanol, 2-propanol, glycerine, or ethylene glycol. Plots of E^{0*}_m, $(E^{0*}_m - 0.05915 \log N_1)$, and $(E^{0*}_N - 0.05915 \log N_1)$ *versus* $1/D$ show definite similarities for similar types of compounds.

2. The various plotting procedures that can be used in determining standard-cell potentials have been applied to the available data for the purpose of studying the ion-size parameters. Certain conclusions can be drawn concerning the ion-size parameters and the relative positions of the curves in the plots referred to above. However, it is felt that these conclusions are far from significant. Likewise, a study of the salting-out constants for the various solutions leads to little correlation between these magnitudes and the relative positions of the $1/D$ *versus* potential curves.

References

[1] Herbert S. Harned and Benton B. Owen, The physical chemistry of electrolytic solutions (Reinhold Publishing Co., 1st. ed., 1943. 2d. ed., 1950).

[2] H. S. Harned and R. W. Ehlers, J. Am. Chem. Soc. **54**, 1350 (1932); **55**, 2179 (1933).

[3] H. S. Harned and H. C. Thomas, J. Am. Chem. Soc. **57**, 1666 (1935); **58**, 761 (1936).

[4] H. S. Harned and M. H. Fleysher, J. Am. Chem. Soc. **47**, 82 (1925).

[5] W. W. Lucasse, J. Am. Chem. Soc. **48**, 627 (1926); Z. Physik Chem. **121**, 254 (1926).

[6] H. S. Harned and C. Calmon, J. Am. Chem. Soc. **61**, 1491 (1939).

[7] H. S. Harned, et al., Am. J. Sci. **33**, 161 (1937); J. Am. Chem. Soc. **58**, 1908 (1936); **60**, 334 (1938); **60**, 336 (1938); **60**, 339 (1938); **60**, 2128 (1938); **60**, 2130 (1938); **60**, 2133 (1938); **61**, 44 (1939); **61**, 48 (1939); **61**, 49 (1939).

[8] G. Nonhebel and H. Hartley, Phil. Mag. [6] **50**, 298, 729 (1923).

[9] J. W. Woolcock and H. Hartley, Phil. Mag. [7] **5**, 1133 (1928).

[10] P. S. Danner, J. Am. Chem. Soc. **44**, 2832 (1922).

[11] H. S. Harned and F. H. M. Nestler, J. Am. Chem. Soc. **68**, 665 (1946).

[12] A. Patterson and W. A. Felsing, J. Am. Chem. Soc. **64**, 1478 (1942).

13] R. L. Moore and W. A. Felsing, J. Am. Chem. Soc. **69,** 1076 (1947).
[14] J. P. Williams, S. B. Knight, and H. D. Crockford, J. Am. Chem. Soc. **72** 1277 (1950).
[15] H. D. Crockford, S. B. Knight, and Helen Staton, J. Am. Chem. Soc. **72** 2164 (1950).
16] S. B. Knight, J. F. Masi, and Dorothy Roesel, J. Am. Chem. Soc. **68,** 661 (1946).
[17] H. D. Crockford and A. A. Sakhnovsky (unpublished research).
[18] H. D. Crockford, S. B. Knight, and F. W. James (unpublished research).

Discussion

DR. G. SCATCHARD, Massachusetts Institute of Technology, Cambridge, Mass.: May I raise a little question of history? I made some measurements in 1923, that might have been in Harned's book on HCl, ethanol, and sucrose, because it was the inversion of sucrose that first interested me in this problem. I explained them to my satisfaction by assuming that the solution was what I called quasi-ideal and that the sucrose was hydrated. I assumed I could calculate the number of molecules from the activity of the water. My results for sucrose, which I think would have fallen well below those for glucose, could be accounted for that way. I think you might have a good chance for accounting for your third and last slide for glucose, fructose, glycerol, and ethylene glycol by taking hydration into account, though I am quite sure the quasi-ideal picture is too simple. I don't remember those measurements very well myself, but I think they should have been in the book.

DR. H. D. CROCKFORD: They were in the book by Harned and Owen.

DR. V. K. LAMER, Columbia University, New York, N. Y.: I would like to remark that this problem shows up in another field. If you have worked in reaction velocity, you have seen the same thing coming up. And if you work in solubility, you will see them.

J. O'M. BOCKRIS, Imperial College of Science and Technology, London, England: Have you calculated numerical values from the formula you put on the board?

DR. CROCKFORD: No, I haven't.

17. Use of Potential Diagrams in the Interpretation of Inorganic Chemistry

By Wendell M. Latimer[1]

Within the past fifty years, thermodynamics has become a highly effective tool for the interpretation of inorganic chemistry. It is now possible to state the potential, or driving force, for most reactions, and, if the reaction is reversible, to give the conditions for equilibrium.

Table 1. *Oxidation-reduction couples*

	E^0
Reducing agent: ↓	*Volts*
$Li = Li^+ + e^-$	3.04
$Ba = Ba^{++} + 2e^-$	2.90
$Na = Na^+ + e^-$	2.71
$Al = Al^{+++} + 3e^-$	2.30
$Zn = Zn^{++} + 2e^-$	0.762
$Fe = Fe^{++} + 2e^-$	.440
$H_2 = 2H^+ + 2e^-$	.000
$Cu^+ = Cu^{++} + e^-$	−.167
$2I^- = I_2 + 2e^-$	−.53
$Cu = Cu^+ + e^-$	−.55
$Fe^{++} = Fe^{+++} + e^-$	−.771
$2Br^- = Br_2 + 2e^-$	−1.07
$2Cl^- = Cl_2 + 2e^-$	−1.36
$2SO_4^{=} = S_2O_8 + 2e^-$	−2.01
$2F^- = F_2 + 2e^-$	−2.85
↑ Oxidizing agent:	
$Cu \underline{\;-0.55\;} Cu^+ \underline{\;-0.167\;} Cu^{++}$ $Fe \underline{\;0.44\;} Fe^{++} \underline{\;-0.77\;} Fe^{+++}$	

Table 1 is a familiar example of the arrangement of oxidation-reduction couples in a series of increasing power of the oxidizing agent and decreasing power of the reducing agent, starting at the top and going down the column. This table can be expanded to include hundreds of couples and is useful in predicting the direction and potential of reactions. Thus chlorine will oxidize all reducing agents that stand above it, and the potential of the reaction is the algebraic difference in the values for the two couples.

If an element occurs in the table in several oxidation states, the potential values give definite information with regard to the relative stabilities of the several states. Thus from table 1 we see that Fe^{++} is stable and

$$Fe + 2Fe^{+++} \rightarrow 3Fe^{++},$$

while Cu^+ is unstable and

$$2Cu^+ \rightarrow Cu^{++} + Cu.$$

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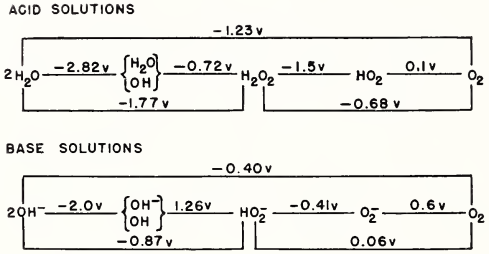
In general, if a given state is a better oxidizing agent than the next higher state, disproportionation will occur as in the example of Cu^+ and Cu^{++} just cited. This is one of the reasons why a diagram that shows the potential values relating all the oxidation states of an element is extremely useful in giving a rapid summary of the essential chemical behavior of that element.

The first diagram that I propose to discuss is that for the H_2O-O_2 system. It is of singular interest not only from the importance of water and oxygen, but because these potentials determine the stability of oxidizing agents in aqueous solutions. Here we have the four one-electron steps in the reduction of O_2 to $2H_2O$. It will be observed that all the intermediate states are thermodynamically unstable. Hydroxyl, OH, and perhydroxyl, HO_2, are known only at very low concentration but the H_2O_2 disproportionation,



$$2H_2O_2 = 2H_2O + O_2 \qquad E^0 = 1.0 \text{ v}.$$

is slow because of the activation energy required to break the O—O bond. In fact, H_2O_2 is so stable that the potential of H_2O_2-O_2 couple may be measured directly. This couple is reversible, and the value −0.68 v in acid solutions is significant with respect to the rapid oxidation of reducing agents in acid aqueous solution by atmospheric O_2. Thus iodide (I^--I_2; $E^0 = -0.53$ v) is rapidly oxidized, whereas bromide ($Br^- = Br_2$, $E^0 = -1.06$ v) is not oxidized.

It may also be noted that H_2O_2 is unstable with respect to the products of its disproportionation, H_2O and HO_2,

$$3H_2O_2 = 2HO_2 + 2H_2O.$$

An interesting example of this reaction appears to be the formation of $Ca(O_2)_2$ by the action of H_2O_2 upon CaO_2.

The over-all potential of the H_2O-O_2 couple, −1.23 v, is not highly significant and in most cases the oxidation of H_2O to O_2 probably does not even involve the mechanism of the intermediate states given in this diagram. With a single electron oxidizing agent, such as Ag^{++}, hydroxyl may be formed as the first step, but in most cases, the evolution of O_2 occurs from a surface and intermediate surface compounds are involved. As a rule, these oxidations require about 0.5-v overvoltage (about 1.23 v). This is the approximate overvoltage generally required for the evolution of H_2 from most surfaces. As a result, the stability of oxidizing and reducing agents in water solution is extended, as illustrated in figure 17.1. The full line at the

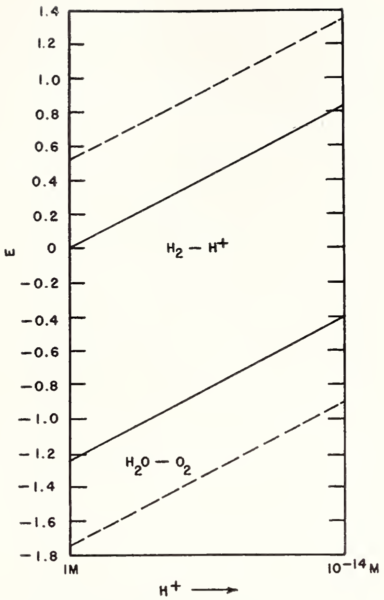
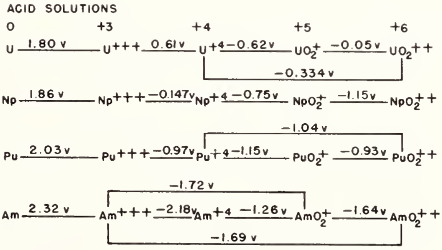


FIGURE 17.1. *Regions of stability oxidizing and reducing agents in water solutions.*

top gives the thermodynamic potential for H_2 evolution as a function of pH and the lower line the potential for O_2 evolution. In practice, the range of stability is extended about a half-volt, as indicated by the dotted lines.



With these general stability relationships in mind, we shall examine the potential diagrams of uranium, neptunium, plutonium, and americium, as typical examples of elements with several oxidation states, and see what conclusions may be drawn with regard to their chemistry in aqueous solutions.

First, it may be noted that the metals are all highly electropositive, even more electropositive than aluminum (Al-Al^{+++}; $E^0 = 1.66$ v). Hence they should dissolve in 1 M H^+ solution, but since they are all high-melting, the activation energies will be large and the reactions probably slow. In the case of uranium, 1 M H^+ can oxidize the metal to the +IV ion, but with the other elements the reaction will stop at the +III ion, since the III-IV potentials are negative.

Atmospheric oxygen will, of course, rapidly oxidize U^{+++} and will also take U^{+4} to UO_2^{++}. The +V state of uranium is highly unstable with respect to disproportionation. The UO_2^+-UO_2^{++} couple involves only a single-electron transfer; hence the reduction of UO_2^{++} will probably be fast with strong reducing agents. The reduction of UO_2^+ to U^{+++} involves breaking U—O bonds, and this reduction may be somewhat slow, in spite of the high instability of UO_2^+.

It will be noted that all of the states of neptunium are stable with respect to disproportionation. Oxygen should rapidly oxidize Np^{+++} to Np^{+4}, but the reaction should stop there. A fairly powerful agent, such as chlorine, is required to oxidize Np^{+4} to NpO_2^{++}.

The most remarkable feature of the plutonium chemistry is the similarity of the potentials of the Pu^{+++}-Pu^{+4}, Pu^{+4}-PuO_2^+, and PuO_2^+-PuO_2^{++} couples. Thus solutions of Pu^{+4} will disproportionate to an equilibrium state with appreciable concentrations of Pu^{+++}, Pu^{+4}, PuO_2^+, and PuO_2^{++}. The same will be true of solutions PuO_2^+ to an even greater extent. There is no other example in all inorganic chemistry of an equilibrium with appreciable concentrations of four different oxidation states.

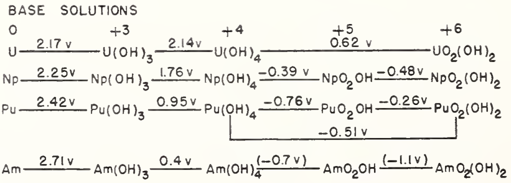
The chemistry of americium shows marked differences. Am^{+4} is unstable in 1 M H^+ by 0.92 v; hence the state is essentially nonexistent in acid solution. AmO_2^+ is also slightly unstable, but moderate concentrations of the ion will exist in equilibrium with Am^{+++} and AmO_2^{++}. The potential required to oxidize Pu^{+++} to PuO_2^{++} is only about a volt, while the Am^{+++}-AmO_2^{++} potential is -1.69 v. An extremely powerful oxidizing agent is thus required to form AmO_2^{++}. Conversely, AmO_2^{++} is an extremely powerful oxidizing agent. In high acid, it will evolve oxygen by the oxidation of the water. In other words, the chemistry of americium may be summarized by stating that Am^{+++} is highly stable.

It might also be noted that neptunium, plutonium, and americium are so highly radioactive that appreciable concentration of H_2O_2 are formed by the action of the radiation upon water. Hence it is difficult to keep NpO_2^{++}, PuO_2^{++}, and AmO_2^{++} in solution because they are readily reduced by the peroxide (H_2O_2-O_2 $E^0 = -0.68$v).

The potential diagrams, of course, give no information on the solubilities of the salts of the various ions. However, for many salts the free energies are known and the solubilities may be calculated. Thus from the following free energies $NpF_3, -342$ kcal, Np^{+++}, -128.4 kcal, F^-, -66.08 kcal.

$$NpF_3 = Np^{+++} + 3F^- \qquad \Delta F^0 = 15.5 \qquad K = 1 \times 10^{-11}.$$

In order to complete the picture, we should consider the potential relations in basic solution. These follow.



The chemistry on the alkaline side is not nearly as interesting because the compounds are insoluble. For the +6 state the potentials relate the insoluble acids. In a NaOH solution the values should have been given for the sodium salts because they are less soluble, but our knowledge of these solubilities is still limited.

A number of changes in stability relations may be noted. Thus Am IV and Am V are stable with respect to disproportionation. Pu V is even less stable than in acid solution. All of the neptunium states are stable, which is the same situation as is found in the acid range. U III is just barely stable. The data on U V in alkaline solution are not very definite, but U V is probably less stable than in acid.

In all of this discussion the potential diagrams have been merely a convenient method of summarizing the thermodynamic data. The data are, of course, the essential item, and the point that I wish to stress is the fact that it is now possible to give a very complete thermodynamical interpretation of the oxidation-reduction reactions of every element.

Discussion

Dr. J. A. Christiansen, University of Copenhagen, Copenhagen, Denmark: May I ask about the reaction where molecular oxygen acting as an oxidant, is reduced to hydrogen peroxide? The reaction between metallic silver and oxygen in the presence of a cyanide solution, for example, has been known for many years to be of this type, and we have recently been able to reconfirm this fact.

Dr. W. M. Latimer: That is correct; molecular oxygen acting as an oxidant may be reduced to hydrogen peroxide.

Dr. Christiansen: I was interested in knowing the potential of the reaction $H+O_2+2\epsilon=HO_2^-$.

Dr. Latimer: You see, I have written HO_2^- (shown on slide).

Dr. Andre Juliard, Narberth, Pa.: It would be interesting to make a diagram of that last reaction (reference made to slide.)

Dr. Latimer: Yes, I think that would be interesting to do. If you wanted to study an element thoroughly, it would be important to make the diagram as a function of pH.

18. Determination of Activity Coefficients

By Robert A. Robinson[1]

Introduction

When I was honored by an invitation to address this symposium on the subject of activity coefficients, and I considered the historical development of this topic, the part played by workers on the American continent appeared as an impressive contribution. The classical treatise of J. Willard Gibbs and the pioneer work of A. A. Noyes and G. N. Lewis must ever remain as monuments of the early days of our subject. The National Bureau of Standards has housed the laboratories in which S. F. Acree, W. J. Hamer, and R. G. Bates have made their precise electromotive-force measurements on cells containing buffered solutions; A. R. Gordon, in Toronto, has made outstanding contributions to the use of cells with transference and to the art of direct vapor-pressure measurements. To H. S. Harned and B. B. Owen we are indebted for a school of physical chemistry that has mastered the somewhat intractable amalgam cell and has studied hydrochloric acid under a wide variety of conditions as regards concentration, temperature, solvent, and the presence of neutral salts. V. K. LaMer and his colleagues have developed both solubility determinations and the measurement of cells containing polyvalent salts, while nearby, at the Rockefeller Institute, D. A. MacInnes, T. Shedlovsky, and L. G. Longsworth have done so much to validate theoretical predictions by their measurements of very dilute solutions. To G. Scatchard at the Massachussetts Institute of Technology are due extensive and accurate measurements of the freezing-point depression; R. P. Smith has perfected the technique of measuring the boiling-point elevation of a solution to a pitch where it competes in accuracy with other activity-coefficient measurements and T. F. Young at the University of Chicago has done much to clarify our knowledge of the heat-content function and to demonstrate the importance of the incomplete dissociation of an electrolyte. Finally, P. Debye and L. Onsager, who are now faculty members in your universities, have provided that fundamental theory that supports our experimental work.

Activity Coefficients

The activity coefficient, f (more accurately, the mean ionic activity coefficient on the mole-fraction scale), of an electrolyte dissociating into ν ions, of which ν_+ are cations and ν_- anions, is defined in terms of its partial molal free energy by

$$\overline{F}=\overline{F}^0+\nu RT \ln fN, \tag{1}$$

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where $\overline{F}^0$ is the free energy in a standard state, usually so selected that $f \rightarrow 1$ as $N \rightarrow O$, and N is the mean ionic mole fraction defined by $N = (N_+^{\nu_+} N_-^{\nu_-})^{1/\nu}$, where N_+ is the mole fraction of cations and N_- the mole fraction of anions. The quantity f is a function of temperature, pressure, and concentration, while $\overline{F}^0$ is a function of temperature and pressure only. The variation of f with temperature is given by

$$-\nu RT^2\left(\frac{\partial \ln f}{\partial T}\right)_{P,N} = \overline{L} = \overline{H} - \overline{H}^0, \tag{2}$$

where $\overline{L}$ is the relative partial molal heat content, while the variation with pressure is given by

$$\nu RT\left(\frac{\partial \ln f}{\partial P}\right)_{T,N} = \overline{V} - \overline{V}^0, \tag{3}$$

where $\overline{V}$ is a partial molal volume. While $\overline{F}^0$ does *not* denote a free energy at infinite dilution, the condition that $f \rightarrow 1$ as $N \rightarrow 0$ at all *temperatures and pressures* suffices to make $\overline{H}^0$ and $\overline{V}^0$ a heat content and a volume respectively at *infinite dilution*. $\overline{L}$ and $(\overline{V} - \overline{V}^0)$ are functions of temperature and pressure, and integration of eq (2) and (3) may therefore require some ingenuity. The variation of f with concentration requires extrathermodynamic considerations of a statistic-kinetic nature, of which the Debye-Hückel theory is an example.

It may be more convenient to measure concentrations on another scale; if concentrations are measured in molalities, we have

$$\overline{F} = \overline{F}^0 + \nu RT \ln \gamma m \tag{4}$$

and for the molality scale

$$\overline{F} = \overline{F}^0 + \nu RT \ln yc, \tag{5}$$

where m and c are mean values defined in the same way as N. The value of $\overline{F}^0$ depends on the concentration scale adopted.

To the electrochemist a knowledge of activity coefficients is important in many ways, of which three may be mentioned. (a) The determination of the standard potential of a cell usually involves an equation of the type $E^0 = [E - k \ln m] - k \ln \gamma$. A first approximation to E^0 is obtained by extrapolating the term in brackets against some function of m. A better value of E^0 results if an estimate of the activity coefficient can be made and the right side of the equation extrapolated to infinite dilution. (b) A knowledge of activity coefficients is essential to the use of the law of mass action. (c) As the driving force causing the diffusion of an electrolyte is the concentration gradient of the chemical potential, the activity coefficient must be known as a function of concentration in order to compute a diffusion coefficient.

The following methods are available for measuring an activity coefficient: (a) Measurement of emf of a cell without transference, (b) measurement of emf of a cell with transference, combined with a knowledge of the transference number, (c) measurement of freezing-point depression, (d) measurement of boiling-point elevation, (e) vapor-pressure measurements, and (f) solubility measurements.

This is not the place to discuss in detail the results of activity-coefficient measurements, but perhaps a survey of what has been achieved may be useful and point the way to further work. Stokes and I [1] [2] have reviewed recently activity coefficients of 119 electrolytes in aqueous solution at 25° C. Data for $CoBr_2$ and CoI_2 [2] and for $UO_2(NO_3)_2$, UO_2Cl_2, and $UO_2(ClO_4)_2$ [3] have been added since. At this temperature our knowledge is extensive as regards variety of electrolytes and range of concentration. At other temperatures there is much work to be done. Smith has demonstrated that the technique of very accurate boiling-point measurements can be mastered, and it is regretted that no one has extended his work on NaCl and KBr [4] to other salts. At the other end of the temperature scale Scatchard [5] has brought freezing-point measurements to a similar degree of high accuracy, and extensive data are available on a large number of salts. Recently, there has been a revival of this technique as applied to alkaline earth perchlorates [6].

Much information could be correlated if adequate data on partial molal heat contents and heat capacities were available. A. L. Robinson [7] and Gucker [8] have made valuable additions to this field, but the importance of such measurements makes one regret that there have been so few to extend this work.

It is easy to quote examples of excellent agreement between activity coefficients derived from a variety of experimental measurements and, indeed, in nearly all cases where comparison is possible, the agreement is within the limits of experimental error. Two anomalous cases of interest to electrochemists—H_2SO_4 and $CdSO_4$—are outstanding examples of the need for further work.

The water activity of H_2SO_4 has been measured by four independent methods within the last 16 years.

Harned and Hamer [9] combined the cells:

$$H_2 \mid H_2SO_4(m) \mid PbSO_4, PbO_2, Pt. \qquad \text{Cell I.}$$

$$H_2 \mid H_2SO_4(m) \mid HgSO_4, Hg. \qquad \text{Cell II.}$$

the emf of the first being

$$E = E_0 + (RT/2\mathrm{F}) \ln \gamma_{\mathrm{H}}^2 \gamma_{\mathrm{SO_4}} m_{\mathrm{H}}^2 m_{\mathrm{SO_4}} - (RT/\mathrm{F}) \ln a_{\mathrm{w}}$$

and that of the second

$$E' = E'_0 - (RT/2\mathrm{F}) \ln \gamma_{\mathrm{H}}^2 \gamma_{\mathrm{SO_4}} m_{\mathrm{H}}^2 m_{\mathrm{SO_4}},$$

where $E + E' - E_0 - E'_0 = -(RT/F) \ln a_{\mathrm{w}}$.

The a_{w} values derived by this method are given in the second column of table 1 and their validity is dependent on the assumption that each cell is behaving reversibly. Strong support for this assumption came from the calculations of Stokes [10], who showed that each cell would yield an independent value of a_{w}; his calculated values are in the next two columns of table 1. (The data for cell 1 between 9 and 17 m in his paper should appear as data for cell 2).

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[2] Figures in brackets indicate the literature references on p. 182.

TABLE 1. *Water activities of sulfuric-acid solutions at 25°*

m	Harned and Hamer	Cell I	Cell II	Vapor pressure	Stokes
3	0.8506	0.8505	0.8508	0.8514	0.8515
4	------	.7771	.7776	.7795	.7800
5	.6980	.6981	.6985	.7030	.7033
6	------	.6197	.6201	.6252	.6260
7	.5453	.5453	.5458	.5497	.5509
9	------	------	.4175	.4165	.4180
11	------	------	.3171	.3110	.3112
13	------	------	.2378	.2304	------
15	------	------	.1763	.1698	------
17	------	------	.1289	.1252	------

The agreement between these two measurements is so good that one's confidence in the correctness of these a_w values should be very high. It is disconcerting, therefore, to find that direct vapor-pressure measurements of Shankman and Gordon [11] give a_w values (recorded under vapor pressure in table 1) that are substantially different. Our difficulty is increased by a new set of measurements by Stokes [12] based on a method in which a stationary state is set up between solution at 25° C. and pure water at a lower temperature. His a_w values are given in the last column of table 1. The methods used by Shankman and Gordon and by Stokes, although both vapor-pressure measurements, have so little in common that they must rank as independent methods, and it is, therefore, difficult to discard their mean as a close approximation to the truth. If we agree with this, we are forced to recognize that the two cells of Harned and Hamer are erroneous over a concentration range that includes 5 m. It is not beyond the imagination to believe that one of the electrodes, Hg, Hg_2SO_4 or Pt, PbO_2, $PbSO_4$ should be irreversible, but that both should be irreversible to such an extent that equal errors are introduced seems to be straining coincidence too far. If we have faith in the concordant results of Shankman and Gordon and Stokes, we must seek an explanation of the discrepancy in the results of Harned and Hamer in the one feature common to both their cells, the hydrogen electrode. It has always been thought most unlikely that there is any irreversibility of this well-tested electrode, but the results of so much careful work suggest that this possibility merits further study.

I have attempted to deduce a_w values from freezing-point measurements combined with thermal data. Such values would extend only to 6.25 m, the composition of the eutectic, but would cover a useful part of the concentration range in dispute. Unfortunately, the only thermal data I have been able to find are those derived from the cell measurements of Harned and Hamer, and it is hardly proper to use their data to decide between the validity of cell determinations as against direct vapor-pressure measurements of a_w. Further determinations of the freezing-point depression of H_2SO_4 solutions, along with partial molal heat content and heat-capacity measurements, would be a most useful contribution.

The second electrolyte to which I would like to refer is $CdSO_4$. La Mer and Parks [13] have made a careful study of the cell

$$\text{Cd-Hg}|\text{CdSO}_4(m)|\text{PbSO}_4,\ \text{Pb-Hg},$$

while Robinson and Jones [14] made isopiestic vapor-pressure measurements on this salt. The activity coefficients obtained by these two methods are given in table 2. For the activity coefficient at saturation, 3.68 m, there is a discrepancy of about 20 percent. It is true that up to 1 m the vapor-pressure results are supported by data from freezing-point measurements, but too much emphasis should not be put on this agreement as thermal data required for correction of the activity coefficients from the freezing point to 25° C may not have been of the requisite accuracy. The discrepancy remains to be resolved. I can see little use in repeating either set of measurements, both of which were made with great care; once again we see how useful would be some freezing-point measurements along with the necessary thermal data.

TABLE 2. *Activity coefficients of cadmium sulfate at 25°*

m	0.1	0.5	1.0	2.0	3.0	3.5
From electromotive force	0.150	0.066	0.046	0.033	0.029	0.028
From vapor pressure	.150	.061	.041	.032	.033	0.035

Activity Coefficients in Mixed Salt Solutions

We shall now consider the matter of activity coefficients in mixed salt solutions and, in particular, the variation of the activity coefficient of one salt when the total ionic strength is kept constant but the molalities of the two salts vary. What has been termed "Harned's rule" applies to many pairs of electrolytes and, for a pair of 1:1 electrolytes, may be stated in the form

$$\left.\begin{aligned} \log \gamma_1 &= \log \gamma_{1(0)} - \alpha_{12} m_2 \\ \log \gamma_2 &= \log \gamma_{2(0)} - \alpha_{21} m_1. \end{aligned}\right\}. \qquad (6)$$

where γ_1 is the activity coefficient of the first electrolyte in a mixed solution, $\gamma_{1(0)}$ its value in a solution containing the first electrolyte only, and α_{12} is a function of $m=(m_1+m_2)$ but not of $x=m_1/m$, where m_1 amd m_2 are the molalities of the electrolytes. The second of these equations has a similar meaning for the second electrolyte. The validity of this rule has been verified in may cases; the proof usually depends on emf measurements on cells of the type

$$H_2|HX, MX|AgX, Ag,$$

HX being a halide acid, MX a halide salt, and AgX a silver halide. Cells of this type give γ_{HX} directly and γ_{MX} only by indirect calculation, because it can be shown that

$$\alpha_{21} = \alpha_{12} + (55.51/m^2) \log a_{w(1)}/a_{w(0)} \qquad (7)$$

$a_{w(1)}$ being the water activity of a solution containing the first electrolyte only and $a_{w(0)}$ the value when only the second electrolyte is present. Very careful measurements have been made by Güntelberg [15] where X=Cl, and M=Li, Na, K, and Cs. The rule has been shown to apply [16] when HX=HCl, and the added electrolyte is

$NaClO_4$, $KClO_4$, $HClO_4$, $BaCl_2$, $AlCl_3$, $CeCl_3$, $LaCl_3$, or $Na_2S_2O_6$. For a polyvalent electrolyte it is the total ionic strength and not the total molality that is kept constant. Hawkins [17] has shown that in some cases the rule is valid at a total molality as high as $6m$. A few cases are known where the rule does not apply. One example is the NaOH-NaCl pair, for which Harned and Cook [18] contrived the cells

$$H_2|NaOH, NaCl|Na_xHg|NaOH|H_2$$

$$Ag, AgCl|NaOH, NaCl|Na_xHg|NaCl|AgCl, Ag$$

to measure γ_{NaOH} and γ_{NaCl} separately. The rule does not apply in cases where chemical interaction is to be expected, for example, mixtures of $CaCl_2$ and $ZnCl_2$ [19].

Another approach has been devised by Owen and Cooke [20]. As a thermodynamical consequence of Harned's rule

$$(\alpha_{21}+\alpha_{12})x-2\alpha_{21}=(55.51/xm^2)\log a_{w(0)}/a_{w(x)} \tag{8}$$

where $a_{w(x)}$ is the water activity of a solution containing xm of the first electrolyte and $(1-x)m$ of the second electrolyte. For the special case of a solution containing the first electrolyte only

$$\alpha_{12}-\alpha_{21}=(55.51/m^2)\log a_{w(0)}/a_{w(1)}. \tag{9}$$

Thus from a series of vapor-pressure measurements of mixed electrolytes of constant total molality, the right side of eq (8) can be plotted against x. The plot should be linear if Harned's rule holds, and from the slope and intercept, α_{12} and α_{21} can be evaluated.

The converse of this proposition is not necessaruly true: the linearity of the plot of the right side of eq (9) against x is not conclusive proof that Harned's rule applies. This may be shown by replacing eq (6) by

$$\begin{aligned}\log \gamma_1&=\log \gamma_{1(0)}-\alpha_{12}m_2-\beta_{12}m_2^2\\ \log \gamma_2&=\log \gamma_{2(0)}-\alpha_{21}m_1-\beta_{21}m_1^2,\end{aligned} \tag{10}$$

from which it may be shown that

$$\begin{gathered}2x^2m(\beta_{21}-\beta_{12})/3+x[(\alpha_{21}+\alpha_{12})-2m(\beta_{21}-\beta_{12})]-2\alpha_{21}=\\ 55.51/2xm^2 \log a_{w(0)}/a_{w(x)},\end{gathered} \tag{11}$$

which, when $x=1$, becomes

$$(\alpha_{12}-\alpha_{21}-2m(\beta_{21}-\beta_{12})/3=(55.51/m^2)\log a_{w(0)}/a_{w(1)}. \tag{12}$$

Thus, as long as β_{12} and β_{21} are equal in magnitude and sign, the right side of eq (11) will be linear in x; moreover, β_{12} and β_{21} could be large in magnitude but, if they were not appreciably different, departure from linearity of the plot of eq (11) might be difficult to detect.

Returning to the case where Harned's rule applies, we should consider a remarkable claim by Glueckauf, McKay, and Mathieson [21] which, if valid, will have far-reaching consequences. They considered the system $UO_2(NO_3)_2$-$NaNO_3$ but, taking the simpler case of a pair of 1:1 salts, they claim to have established that, while α_{12} and α_{21} may be functions of $m(=m_1+m_2)$, the sum $(\alpha_{12}+\alpha_{21})$, is a constant independent of m. They based their argument on the thermodynamical necessity that

$$\left(\frac{\partial \log \gamma_1}{\partial m_2}\right)_{m_1}=\left(\frac{\partial \log \gamma_2}{\partial m_1}\right)_{m_2}, \tag{12}$$

whence, for a pair of salts to which Harned's rule is applicable,

$$\left(\frac{\partial \log \gamma_{1(0)}}{\partial m_2}\right)_{m_1}-\alpha_{12}-m_2\left(\frac{\partial \alpha_{12}}{\partial m_2}\right)_{m_1}=\left(\frac{\partial \log \gamma_{2(0)}}{\partial m_1}\right)_{m_2}-\alpha_{21}-m_1\left(\frac{\partial \alpha_{21}}{\partial m_1}\right)_{m_2}$$

equivalent to

$$\frac{d \log \gamma_{1(0)}}{dm}-\alpha_{12}-(1-x)m\frac{d\alpha_{12}}{dm}=\frac{d \log \gamma_{2(0)}}{dm}-\alpha_{21}-mx\frac{d\alpha_{21}}{dm}$$

and as this must be true for all values of x:

$$xm\frac{d\alpha_{12}}{dm}=-xm\frac{d\alpha_{21}}{dm}$$

or

$$(\alpha_{12}+\alpha_{21})=\text{constant}. \tag{13}$$

It is not easy to test this experimentally. The one case in which cells can be constructed to measure α_{12} and α_{21} separately, i. e., the NaOH-NaCl pair, has already been referred to as, unfortunately, a system to which Harned's rule does not apply and cannot be used to test the constancy of $(\alpha_{12}+\alpha_{21})$. The isopiestic vapor-pressure method, as applied by Owen and Cooke for the KCl-LiCl pair, does give α_{12} and α_{21} separately, but the experimental accuracy needed limits the method to concentrated solutions.

In my laboratory C. K. Lim [22] has made isopiestic measurements on KCl-NaCl mixtures at 25° C, using NaCl as reference salt. This system has the advantages that the salts can be obtained in a high degree of purity, the solutions are free from hydrolysis, and the activity coefficients, $\gamma_{1(0)}$ and $\gamma_{2(0)}$ of the single salts in aqueous solution are known accurately. We shall use α_{12}, m_1, etc., for KCl, α_{21}, m_2, etc., for NaCl. We found that the isopiestic ratio $(R=m_R/m$, where m is the total molality of the mixed salt solution, and m_R is the molality of the NaCl solution of the same vapor pressure) could, for a given value of x, be represented by

$$R=a+bm+cm^2 \tag{14}$$

over the range $2\leq m\leq 5$. Thus, with a stock solution containing KCl and NaCl in a particular ratio, 8 to 10 measurements of the isopiestic ratio between $m=2$ and $m=5$ sufficed to determine the parameters, a, b, and c, of eq (14), which are, of course, functions of x. From measurements on five stock solutions we derived the values given in table 3.

The last two columns give average and maximum differences, for each value of x, between values of R calculated by eq (14) and those measured experimentally. Translated into terms of water activity, an interpolation formula of this type represents the experimental data with a maximum error of 0.00010 and an average error of 0.00002 in log a_w. It is now possible to calculate R at round values of m and thence a_w, using the a_W values of the reference salt [23]. The latter can be calculated conveniently by the empirical formula $1+\log a_w=0.99785-0.01172\ m_R-0.0013\ m_R^2$, valid over the range $1.8 \leq m_R \leq 6$. The values of a_W derived in this way are the $a_{W(x)}$ values required in eq (8). Thus for each m we get values of $a_{W(x)}$ at five values of x; a sixth is obtained from the a_W data of solutions containing KCl only ($x=1$). For this case there is a convenient empirical formula, $1+\log a_W=0.99934-0.01295\ m_{KCl}-0.0005\ m_{KC}^2$ valid over the range $1 \leq m_{KCl} \leq 4.8$.

TABLE 3. *Parameters of equation (14)*

x	a	$-b$	c	Average deviation	Maximum deviation
				Percent	*Percent*
0.1955	1.0002	0.0099	0.00059	0.01	0.02
.3306	.9905	.0104	.00023	.02	.05
.5038	.9907	.0170	.00058	.03	.07
.6575	.9829	.0172	.00018	.03	.10
.7958	.9808	.0203	.00032	.01	.03

The function given by the right side of eq (8) can now be plotted against x (fig. 18.1 is a plot of $(1/x)\log a_{w(x)}/a_{w(0)}$ against x) and from the intercept and slope, calculated by the method of least squares, values of α_{12} and α_{21} (table 4) can be obtained. Figure 18.1 shows that the experimental data lie very close to straight lines. Inspection of this figure shows that the point at $m=2$, $x=0.1955$ is slightly low and the point at $m=4$, $x=0.1955$ slightly high, but these discrepancies are within the experimental error, and no significant conclusion can be drawn from such random departures from linearity. On the contrary the results suggest that Harned's rule can be applied in this case. Using eq (8) to calculate log $a_{w(x)}$ from the α_{12} and α_{21} values of table 4 and comparing them with the observed (or, more correctly, with those derived from the experimental data by the interpolation eq (14)), I find the following deviations in log $a_{w(x)}$ between the calculated and "experimental" data.

m	2	2.5	3	3.5	4	4.5	5
Avg dev.×10^5	1	1	1	4	4	4	1
Max. dev.×10^5	3	2	3	10	10	10	2

These deviations are accounted for by the use of the interpolation eq (14). The results show that $(\alpha_{12}+\alpha_{21})$ is almost constant, except at $2m$, where a considerable change in α_{12} and α_{21} is reflected in only a small change in log $a_{w(x)}$. These results, therefore, support the claim that $(\alpha_{12}+\alpha_{21})$ is independent of m. I have now taken the weighted mean of $(\alpha_{12}+\alpha_{21})$ over the range of $m=2$ to $m=5$, i.e., $(1/\sum m^2)\sum_{m=2}^{m=5} m^2(\alpha_{12}+\alpha_{21})$ and found it to be 0.0168. As $(\alpha_{21}-\alpha_{12})$ can be obtained from eq (9), using the vapor-pressure data of single salt solutions

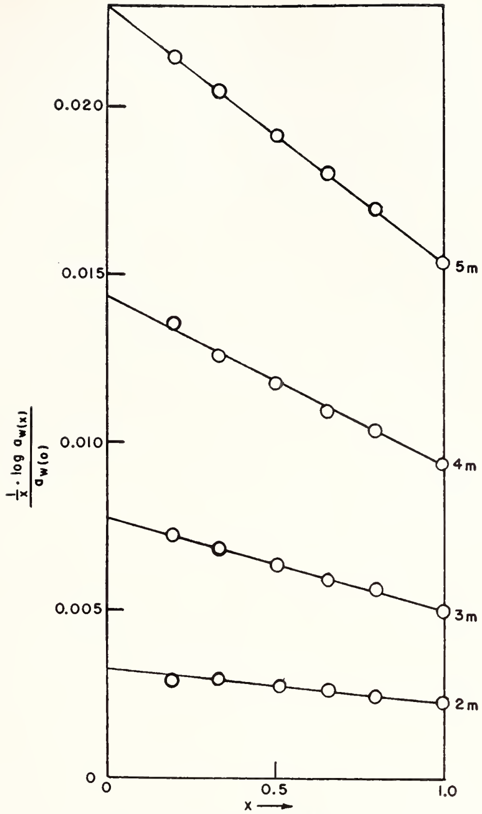

FIGURE 18.1. *Plot of (1/x) log $a_{w(x)}/a_{w(0)}$ against x for potassium-chloride–sodium-chloride system.*

only, a set of α_{12} and α_{21} values can be calculated such that $(\alpha_{12}+\alpha_{21})$ is constant. The following values so calculated, represent the "experimental" values of log $a_{w(x)}$ with the deviations shown:

m	2	2.5	3	3.5	4	4.5	5
$-\alpha_{12}$	0.0069	0.0069	0.0071	0.0075	0.0080	0.0084	0.0087
α_{21}	.0238	.0237	.0240	.0244	.0248	.0252	.0256
Avg dev. × 10^5	3	2	3	4	5	5	3
Max. dev. × 10^5	4	4	6	8	11	8	5

TABLE 4. *α_{12} and α_{21} for* KCl-NaCl *system*

α_{12} refers to KCl, α_{21} to NaCl

m	$-\alpha_{12}$	α_{21}	$(\alpha_{12}+\alpha_{21})$
2	0.0091	0.0224	0.0133
2.5	.0074	.0234	.0159
3	.0074	.0236	.0162
3.5	.0069	.0245	.0176
4	.0076	.0248	.0172
4.5	.0081	.0253	.0172
5	.0087	.0256	.0169

These deviations are slightly greater than those found when no restriction is placed on the constancy of ($\alpha_{12}+\alpha_{21}$) and are still accountable for by use of interpolation eq (14). These results are, therefore, fully consistent with the contention that ($\alpha_{12}+\alpha_{21}$) is constant over the range $2 \leq m \leq 5$. If $(\alpha_{12}+\alpha_{21})=0.0168$ at lower concentrations, then, knowing ($\alpha_{21}-\alpha_{12}$) from vapor-pressure data on single solutions, we can calculate α_{12} and α_{21} in very dilute solution. The predicted values are shown by the broken lines of figure 18.2.

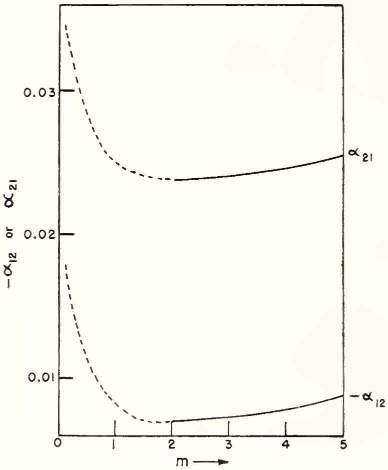

FIGURE 18.2. *Plot of* $-\alpha_{12}$ *and* α_{21} *against m for potassium-chloride-sodium-chloride system.*

For the KCl-LiCl system investigated by Owen and Cooke ($\alpha_{12}+\alpha_{21}$) does not seem to be constant between $m=1$ and $m=3$, since they obtained the following values:

m	* α_{12}	* $-\alpha_{21}$	($\alpha_{12}+\alpha_{21}$)
1	0. 0637	0. 0361	0. 0276
2	. 0681	. 0306	. 0375
3	. 0727	. 0275	. 0452

* α_{12} refers to LiCl, α_{21} to KCl.

Although their plots corresponding to eq (8) were very close to linearity, indicating that Harned's rule would be a close approximation at all three concentrations, nevertheless, the ($\alpha_{12}+\alpha_{21}$) values are inconsistent with the requirement of eq (12) and (13). Let us now apply eq (10) to this system, i. e., assume that there is a slight deviation from Harned's rule, beyond the limit of the experimental accuracy, and subject the system to the restriction imposed by eq (12). We get

$$\frac{d \log \gamma_{1(0)}}{dm}-\alpha_{12}-(1-x)\,m\,\frac{d\alpha_{12}}{dm}-2(1-x)\,m\,\beta_{12}-(1-x)^2m^2\,\frac{d\beta_{12}}{dm}$$

$$=\frac{d \log \gamma_{2(0)}}{dm}-\alpha_{21}-xm\,\frac{d\alpha_{21}}{dm}-2xm\,\beta_{21}-x^2m^2\,\frac{d\beta_{21}}{dm},$$

whence

$$xm\,\frac{d\alpha_{12}}{dm}+2xm\beta_{12}+2xm^2\,\frac{d\beta_{12}}{dm}-x^2m^2\,\frac{d\beta_{12}}{dm}$$
$$=-xm\,\frac{d\alpha_{21}}{dm}-2xm\beta_{21}-x^2m^2\,\frac{d\beta_{21}}{dm}, \quad (15)$$

and therefore,

$$\frac{d\beta_{12}}{dm}=\frac{d\beta_{21}}{dm}, \quad \text{or} \quad (\beta_{12}-\beta_{21})=\text{constant.}$$

To simply the calculation we made the further *arbitrary* assumption that β_{12} and β_{21} are independent of m, and found the best values of α_{12}, α_{21}, β_{12} and β_{21}, which fit the experimental data of Owen and Cooke and are consistent with eq (15). Using the following values to substitute in eq (11),

$$\beta_{21}=-0.00304,\ \beta_{12}=-0.00147,$$

$$-\alpha_{21}=0.0365 \text{ at } 1\ m,\ 0.0317 \text{ at } 2\ m,\ 0.0291 \text{ at } 3\ m,$$

$$\alpha_{12}=0.0645 \text{ at } 1\ m,\ 0.0687 \text{ at } 2\ m,\ 0.0751 \text{ at } 3\ m,$$

$$(\alpha_{12}+\alpha_{21})=0.0190+0.0090\ m,$$

We calculated, for $m=2$, the quantity $q=1/xm^2 \cdot \log a_{w(0)}/a_{w(x)}$ and in table 5 have compared these calculated values with those observed by Owen and Cooke and also with the values calculated by eq (8), using their α_{12} and α_{21} values. A similar comparison is made in figure 18.3, in which the scale is enhanced by plotting $(q-0.000675\,x)$ rather than q against x. Without claiming that eq (11) is better than eq (8), the comparisons in table 5 and in figure 18.3 make it clear that eq (11) is, at least, equally effective.

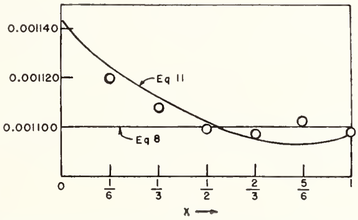

FIGURE 18.3. *Plot of* $(1/xm^2)\log a_{w(0)}/a_{w(x)}-0.000675=Y$ *against* x *for the potassium-chloride–lithium-chloride system.*

○, Experimental points.

TABLE 5. *Values of* $q=(1/xm^2)\log a_{w(0)}/a_{w(x)}$ *for the potassium-chloride–lithium-chloride system at* $m=2$

x	q (observed)	q (eq 11)	q (eq 8)
1/6	0.001233	0.001236	0.001213
1/3	1333	1335	1325
1/2	1437	1438	1438
2/3	1547	1545	1550
5/6	1664	1657	1662
1	1773	1771	1775

The differences in table 5 are very small; a change of the order of 2×10^5 in log a_w would give perfect agreement in nearly all cases, and it would require a considerable advance in accuracy to distinguish between the two equations. We have, as a result of these calculations, concluded that eq (8) based on Harned's rule as contained in eq (6) and eq (11) based on the more complicated eq (10) are equally effective in representing experimental results for KCl—LiCl, yet the former is thermodynamically inconsistent with eq (12), while the latter, although more complicated, is thermodynamically more satisfactory. Practically, it makes no difference which we use to represent a_w but it does make a difference if we are calculating γ. In table 6 values of log $\gamma_2/\gamma_{2(0)}$ are given for KCl, assuming either a linear or a quadratic variation of log γ. It will be seen that the two methods lead to a difference of as much as 2 percent in γ; this may not be large for some purposes, but is not inappreciable.

In conclusion, it may be noted that nearly all our information about mixtures comes from pairs of electrolytes of which HCl is one component. Further work will be needed to explore the complexities of mixed electrolyte solutions and to outline a picture of interactions that occur between components of such a solution; even when the data are available, considerable care is required in their interpretation in view of the different equations that we have found can be used, with equal effectiveness, to represent experimental results of the highest accuracy.

TABLE 6. *Values of* log $\gamma_2/\gamma_{2(0)}$ *for potassium chloride at* $m=2$

x	⅓	½	⅔	1
log $\gamma_2/\gamma_{2(0)}$ eq (8)	0.0204	0.0306	0.0408	0.0612
log $\gamma_2/\gamma_{2(0)}$ eq (11)	.0218	.0332	.0449	.0693

References

[1] R. H. Stokes, Trans. Faraday Soc. **44,** 295 (1948); R. A. Robinson and R. H. Stokes **45,** 612 (1949).

[2] R. A. Robinson, H. J. McCoach, and C. K. Lim, J. Am. Chem. Soc. **72,** 5783 (1950).

[3] R. A. Robinson and C. K. Lim, J. Chem. Soc., 1840 (1951).

[4] R. P. Smith et al., J. Am. Chem. Soc. **61,** 497, 500, 1123 (1939); **63,** 1351 (1941).

[5] G. Scatchard, et al., J. Am. Chem. Soc. **54,** 2676, 2690, 2696 (1932); **55,** 4355 (1933); **56,** 805, 807, 1486, 2314, 2320 (1934).

[6] D. E. Nicholson with W. A. Felsing, J. Am. Chem. Soc. **72,** 4469 (1950). A small correction to their data appeared in **73,** 3520 (1951).

[7] A. L. Robinson, et al., J. Am. Chem. Soc. **54,** 1311, 3120 (1932); **55,** 4733 (1933); **56,** 2637 (1934); **60,** 1265 (1938); **63,** 958, 1582 (1941); Chem. Rev. **30,** 195 (1942).

[8] F. T. Gucker, et al., J. Am. Chem. Soc. **54,** 1358 (1932); **55,** 1013 (1933); **57,** 78 (1935); **58,** 2118 (1936); **59,** 447, 2152 (1937); **61,** 459 (1939).

[9] H. S. Harned and W. J. Hamer, J. Am. Chem. Soc. **57,** 27 (1935).

[10] R. H. Stokes, J. Am. Chem. Soc. **67,** 1686 (1945).

[11] S. Shankman and A. R. Gordon, J. Am. Chem. Soc. **61,** 2370 (1938).

[12] R. H. Stokes, J. Am. Chem. Soc. **69,** 1291 (1947).

[13] V. K. La Mer and W. G. Parks, J. Am. Chem. Soc. **53,** 2040 (1931).

[14] R. A. Robinson and R. S. Jones, J. Am. Chem. Soc. **58,** 959 (1936).

[15] E. Güntelberg, Z. Physik. Chem. **123,** 199 (1926); Studier over Elektrolyt Activiteter, G. E. C. Gads. Forlag, Copenhagen, 1938.

[16] H. S. Harned, et al., J. Am. Chem. Soc. **48,** 326 (1926); **53,** 3377 (1931); **57,** 1865 (1935); M. Randall and G. F. Breckenridge, J. Am. Chem. Soc. **49,** 1435 (1927); S. R. Bates and J. W. Urmston, J. Am. Chem. Soc. **55,** 4068 (1933); P. G. Murdock and R. C. Barton, J. Am. Chem. Soc. **55,** 4074 (1933); C. M. Mason and D. B. Kellam, J. Phys. Chem. **38,** 689 (1934).
[17] J. E. Hawkins, J. Am. Chem. Soc. **54,** 4480 (1932).
[18] H. S. Harned and M. A. Cook, J. Am. Chem. Soc. **59,** 1890 (1937).
[19] R. A. Robinson and R. O. Farrelly, J. Phys. Chem. **51,** 704 (1947).
[20] B. B. Owen and T. F. Cooke, J. Am. Chem. Soc. **59,** 2273 (1937).
[21] E. Glueckauf, H. A. C. McKay, and A. R. Mathieson, J. Chem. Soc. S299 (1949).
[22] C. K. Lim, Thesis, University of Malaya, 1950.
[23] R. A. Robinson, Proc. Roy. Soc. New Zealand **75,** 203 (1945); R. H. Stokes and B. J. Levien, J. Am. Chem. Soc. **68,** 333 (1946).

Discussion

Dr. A. R. Gordon, University of Toronto, Toronto, Canada: I think, in view of what Dr. Robinson says, there is one thing that must be remembered in any static vapor-pressure measurement: the whole result depends on whether you have your solution properly outgassed. When you get up to high concentrations, the problem of outgassing is more serious. You freeze, pump-off, melt, et cetera, but there is always the question as to whether you have really measured what you thought you had. I would say that the matter is still somewhat up in the air. What do you say?

Dr. H. S. Harned, Yale University, New Haven, Conn.: I would like to make one statement. The maximum deviation between the emf and vapor-pressure results amounts to maybe a couple of percent in the activity of the water but only to 1.4 mv in emf. Most of the agreement is very much closer than that. So you see we are dealing with a rather fine point. When you put hydrogen and lead oxide electrodes in a sulfuric-acid solution of 5 or 9 molecules, one does not want to make any further prognostication. You just say, "This is what we get by the electromotive-force method," and hope for the best. Up to about 5 molal the agreement is excellent. That is pretty good. Then it goes off a little bit, but 1.4 mv is what we are talking about. The cells, themselves, appeared to be reproducible to within about a tenth of a millivolt. However, I will not start any argument or claim anything, and I notice that Gordon here is very quiet about it. There is one thing that can be done in matters of this sort. Of course, that is up to anybody who cares to spend 2, 3, or 4 years straightening this out. The whole situation should be gone into again.

Dr. R. A. Robinson: One point I would like to raise. What is the condition of our knowledge of the freezing point of these very strong sulfuric-acid solutions? We know it fairly accurately in dilute solutions, but have we any good data around about 5 or 6 molal?

Dr. T. F. Young, University of Chicago, Chicago, Ill.: Of course, even if we had, the heats of dilution would be missing, so it would not do us much good. The enthalpy data are very complicated.

Dr. Robinson: I felt that instead of repeating vapor-pressure and emf measurements we should try to arrive at a solution by a third and truly independent method.

Dr. W. J. Hamer, National Bureau of Standards: It has been some time since I have thought about this problem, but there are two points I would like to point out. Our results from 0 to 17.5 molal were not obtained with both PbO_2 and Hg_2SO_4 electrodes, but only with Hg_2SO_4 electrodes. Results with the PbO_2 electrodes were obtained only up to 7 molal. The reason we didn't run PbO_2 over the total concentration range was that we got a reaction of PbO_2 with sulfuric acid at molalities above 7.0 molal. It is possible that some reaction may occur at somewhat lower concentrations. The agreement between the emf and vapor-pressure data is very good from 0 to 3 or 5 molal, from 5 to 12 molal, and above 14 molal.

In line with what Dr. Robinson said about a third independent method, I suggest an investigation of transference numbers over the particular concentration range in question. We obtained transference numbers for sulfuric acid by means of cells with and without liquid junction. Such measurements, if they can be obtained with sufficient accuracy, would throw light on the accuracy of the emf and vapor pressure data.

Dr. Robinson: I want to ask Dr. Hamer if he has some idea what that reaction might be.

Dr. Hamer: I probably should not have brought that point up; my memory has failed me on that point. I believe that oxygen is formed. In any case, we had evidence of the formation of gas at very high concentrations of sulfuric acid, that is, above 7 or 8 molal.

Dr. A. L. Pitman, Naval Research Laboratory, Washington, D. C.: There has been some research done on concentrated solutions on sodium hydroxide and potassium hydroxide. Dr. Kegeles might give us some comments on the checks obtained between emf and vapor-pressure measurements on the very concentrated solutions of sodium hydroxide. As I recall it, the activity of water is computed from vapor-pressures and emf data, and their work checked very well at high concentrations. That is, in this case the matter of outgassing seemed to be no problem.

Dr. Young: Dr. Hamer, could the solubility of the electrode material have anything to do with the results? Of course, if you have the sulfate ion reacting with the hydrogen ion forming bisulfate ion in concentrated solutions, the compositions of the solutions would not be what was intended. Is there any possibility of that?

Dr. Hamer: We are only comparing the two cells up to 7 molal. We made solubility corrections only for the dilute range. However, the agreement between emf and vapor-pressure data is perfect between 0 and 3 molal, between 5 and 12 molal, and above 14 molal; solubility doesn't seem to be the answer. I think the divergence is accentuated in the water activity; for activity coefficients the agreement is good.

Dr. Robinson: One point I would like to make about the sodium-hydroxide results. I would not agree that the vapor-pressure results and the emf are concordant. The disagreement is larger than that for sulfuric acid.

19. Equilibria and Reaction Rates in Dilute Electrolyte Solutions

By George Scatchard [1]

At the September 1950 meeting of the American Chemical Society I presented a study of equilibria and reaction rates in dilute electrolyte solutions based upon Kirkwood's treatment [1, 2] [2] of the "higher terms" of the Debye theory. Soon afterward Mayer [3] published a new treatment, which demands a revision of my study and serves as an excellent basis for a comparison of various methods.

Mayer's treatment avoids the difficulties of nonintegrability. If he has introduced other difficulties, they are not yet apparent. He uses the grand canonical ensemble for solutes, and therefore works at constant potential of solvent rather than at constant pressure. Like the Debye treatment, Mayer's applies strictly only to spherical, nonpolarizable ions. He claims that his result is valid through terms in $c^{3/2}$, and hopes that it is approximately accurate to much higher concentrations.

Mayer's result is most conveniently expressed as a function of the ratio to kT of the free energy of attraction of two ions at their distance of nearest approach, $b_{ts}=-\epsilon^2 z_t z_s/DkTa_{ts}$, and of the ratio of this distance to the thickness of the ionic atmosphere, $x_{ts}=\kappa a_{ts}$, in which ϵ is the protonic charge, D the dielectric constant, k Boltzmann's constant, T the absolute temperature, and κ the Debye function defined as

$$\kappa^2=(4\pi\epsilon^2 N/1000\ DkT)\textstyle\sum_i c_i z_i^2,$$

in which N is Avogadro's number, c_i the concentration of species i in moles per liter, z_t, z_s, and z_i the valences of the t, s, and i ions, respectively, and a_{ts} the closest distance of approach of a t ion to an s ion.

The expression for the activity coefficient of species t is

$$\ln \gamma_t = z_t \sum_{s=1}^{\sigma} \frac{c_s z_s}{\sum\limits_{i=1}^{\sigma} c_i z_i^2} \sum_{\nu=0}^{\infty} b_{ts}^{\nu-1} f_\nu(x_{ts}) - z_t^2 \sum_{s=1}^{\sigma} \sum_{r=1}^{\sigma} \frac{c_s z_s c_r z_r}{\left(\sum\limits_{i=1}^{\sigma} c_i z_i^2\right)^2} \sum_{\nu=0}^{\infty} b_{sr}^{\nu-1} g_\nu(x_{ts}). \tag{1}$$

The first sum gives the effect of pair interactions of a molecule of species t with each of the other ions in solution. The second sum gives the effect of change of ionic strength when a t ion is added upon the interactions of all the possible ion pairs in the solution. Note that the explicit expressions of the concentration occur as ratios of the equivalent concentration of ion s or r to the ional concentration, so that the only functions of concentrations are $f(x)$ and $g(x)$. It is

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[2] Figures in brackets indicate the literature references on p. 192.

convenient to list each of the lower members of the series and to give the general expression for the higher ones:

$$f_0 = -x^2/3 \qquad g_0 = 0 \tag{2}$$

$$f_1 = e^{-x}(1+x) - 1 \qquad g_1 = e^{-x}(1+x+x^2/2)/2 - 1/2 \tag{3}$$

$$f_2 = e^{-2x}x/4 + x/4 \qquad g_2 = e^{-2x}x(1+2x)/16 - x/16 \tag{4}$$

$$f_3 = -E_i(-3x)x^2/6 \qquad g_3 = e^{-3x}x^2/24 \tag{5}$$

$\nu \geq 4$

$$f_\nu = \frac{x^2}{\nu!}\int_1^\infty e^{-\nu xy}y^{2-\nu}dy \qquad g_\nu = \frac{x_{\varepsilon}}{4(\nu-1)!}\int_i^\infty e^{-\nu xy}y^{3-\nu}dy \tag{6}$$

The limiting value of f_ν for $\nu \geq 4$ is proportional to x^2, and the limiting value of g_ν is proportional to $x^3 \ln x$ when $\nu = 4$, and to x^3 when $\nu > 4$ so the limiting value of the contribution of terms in $\nu \geq 4$ to $\ln \gamma_t$ is proportional to x^2.

The zeroth term reduces to van der Waals' f times the total concentration. It is compensated at least in part by a similar term, with the molal volume replacing b, when $\ln \gamma$ is reduced to constant pressure.

The first term vanishes if all the ions have the same size. I had calculated the effect of ions of two different sizes on the first two terms of this series by the Debye method [4]. Extension to three different sizes would have been very complicated. In Mayer's treatment the complications are only additive for any number of ions, and the effect on the higher terms is no more complicated than on the lower ones.

The second term corresponds to the Debye-Hückel expression. If all values of a_{rs} are the same, it agrees with the Debye-Hückel expression to terms in x^2 but continues to increase for large values of x instead of approaching an asymptote. It is a little difficult to analyze the difference because it is hard to translate Mayer's mathematical treatment into physical terms. Debye followed the van der Waals method of giving the central molecule a radius equal to its diameter and treating all the other molecules as points. Mayer does not consider specifically the repulsion of more than two molecules at a time. Since it appears that the other ions do not swamp out the pair interaction as rapidly as in the Debye treatment, it is probable that Mayer takes into account at least part of the exclusion sphere of both molecules.

The third term vanishes for symmetrical solutions ($z_- = -z_+$). It is here that the integrability difficulties first appear, and there is a peculiar difficulty in this term. In the term proportional to x^2 Kirkwood differs from LaMer, Gronwall, and Greiff [5] by a constant times ($\ln 2/3 - 1/6$). Kaneko [6] agrees with Kirkwood in the first term and with LaMer, Gronwall, and Greiff in the second, Mayer agrees with the latter in the first term and with Kirkwood in the second. I believe that Mayer's answer is preferable, but the differences are not important.

Gronwall, LaMer, and Sandved [7] computed the fourth and sixth terms of $\ln \gamma_\pm$ for symmetrical solutions of ions with equal radii, for which all odd terms vanish, and LaMer, Gronwall, and Greiff [5] computed the third and fourth term of $\ln \gamma_\pm$ for unsymmetrical solutions with equal radii. Each term depends upon the preceding ones, and a continuation to higher terms would be very complicated. Mayer and Poirier [8] have computed the first ten terms of functions proportional to $f_\nu(x)$ and $g_\nu(x)$. Each term is independent of the preceding ones, and the complications do not increase rapidly as ν gets larger. The absolute values of these terms are independent of the sign of b_{ts}; for positive values of b_{ts} all terms beyond the second are negative, and for negative values of b_{ts} the odd terms, beginning with the third, are positive.

Figure 19.1 shows $\nu!(\nu-3)f_\nu(x)$ and $\nu!(\nu-3)g_\nu(x)$ as functions of x for $\nu=4$ to $\nu=10$. The factor $\nu!(\nu-3)$ is chosen because the limit of $f_\nu(x)$ as x approaches zero is $x^2/\nu!(\nu-3)$. So the asymptote of each $f_\nu(x)$ curve at zero concentration is x^2. The curves for odd values of ν are given as broken lines as the sign of their coefficients is the opposite to that of b_{ts}.

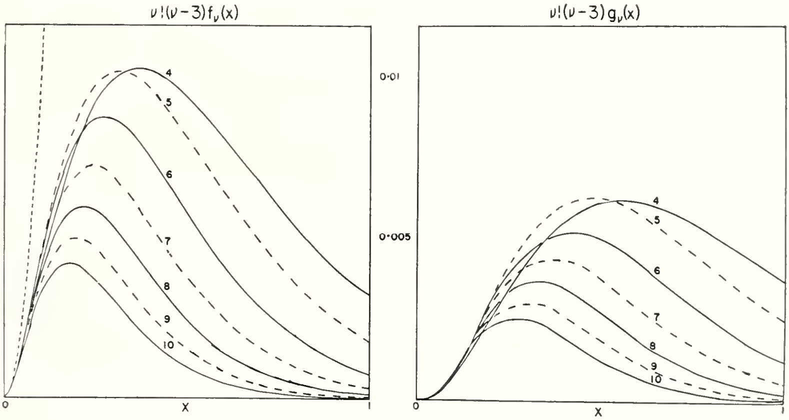

FIGURE 19.1. *Mayer expansion.*

Gronwall, LaMer, and Sandved [7] obtained an infinite series in b_{ts} for the term proportional to x^2, which is identical with that of Mayer. Kirkwood [1, 2] obtained a closed sum for this series.

The great difficulty in a power series in b_{ts} is that, although the series is always convergent, it converges very slowly for large values of b_{ts}. The maximum initial slope $b_{ts}^{\nu-1}/\nu!(\nu-3)$ occurs for ν approximately equal to $|b_{ts}|$. In water at room temperature b_{ts} is approximately $-7z_tz_s/a_{ts}$. So for two trivalent ions with a radius of 5 angstroms, the maximum is not reached by the tenth term. It is apparent that the direct power series computation will be too tedious. We may, however, reach an approximate solution by combining the results of Kirkwood with those of Mayer.

Kirkwood works in terms of the function

$$B_{ts}=\int_0^{b_{ts}} \frac{1}{x_4}(e^x-1-x-x^2/2-x^3/6)dx$$

$$=\{b_{ts}^3[E_i(b_{ts})-\ln b_{ts}-C_0]-e^{b_{ts}}[2+b_{ts}+b_{ts}^2]+[2+3b_{ts}+3b_{ts}^2+11b_{ts}^3/6]\}/6b_{ts}^3 \quad (7)$$

and obtains a result equivalent to

$$\sum_{\nu=4}^{\infty} b_{ts}^{\nu-1}/\nu!(\nu-3) = b_{ts}^2 B_{ts}. \tag{8}$$

We will define q_{ts} by the relation

$$q_{ts} = \sum_{\nu=4}^{\infty} b_{ts}^{\nu-1} f_\nu(x_{ts}). \tag{9}$$

From Kirkwood we know the asymptote of q_{ts} at low values of x_{ts}, which is proportional to x_{ts}^2. From Mayer we can calculate a more exact function of x_{ts} to as large values of ν as we have the patience. We may combine the two by taking the difference between the Kirkwood asymptote for ν from 4 to ∞ and the Mayer asymptote for ν from 4 to $(n-1)$, multiply it by $n!(n-3)\, f_\nu(x_{ts})/x_{ts}^2$, and add it to the Mayer sum. Similarly we will define $k_{s\tau}$ by the relations

$$k_{s\tau} = \sum_{\nu=4}^{\infty} b_{s\tau}^{\nu-1} g_\nu(x_{s\tau}). \tag{10}$$

We take the above difference between the two asymptotes for $k_{s\tau}$, multiply it by $n!(n3-)g_\nu(x_{ts})/x_{ts}^2$, and add it to the Mayer sum for k. We will designate by q'_{ts} and $k'_{s\tau}$, the various approximations of q_{ts} and of $k_{s\tau}$.

Figure 19.2 shows the relations of some of the approximations for the first term. The abscissas are b_{ts} from -15 to $+15$, and the ordinates are log $q'_{ts}/b_{ts}^2|B_{ts}|x_{ts}^2$ for various values of x_{ts}. The fine horizontal lines are log $24f_4(x_{ts})/x_{ts}^2$. They correspond to calculating the whole expression as though it came from the fourth term. The subtraction of log $b_{ts}^2 B_{ts}$ makes this approximation independent of b_{ts}, and the subtraction of log x_{ts}^2 gives a convenient separation of the lines. These curves are exact for all values of x_{ts} when b_{ts} is zero, and for all values of b_{ts} when x_{ts} is zero. The broken lines correspond to stopping the Mayer series at $\nu=10$, but making no correction for the difference between the Kirkwood and Mayer asymptotes. They are also exact for all values of x_{ts} when b_{ts} is zero, and give better approximations for small finite values of b_{ts} than the fine lines, but the deviations are greater for x_{ts} equal to zero than for finite values of x_{ts}. The dotted lines, for negative values of b_{ts}, correspond to adding only half the tenth term and should give better approximations of the alternating series than the broken lines. The full lines correspond to taking the Mayer series through the tenth term and making the correction for the difference between the Kirkwood and the Mayer asymptotes, as described in the last paragraph.

For positive values of b_{ts}, the true value lies between the full and broken lines, since for large values of ν, $f_\nu(x_{ts})/f_{(\nu-1)}(x_{ts}) \cong (b_{ts}/\nu)e^{-x_{ts}}$, which is always positive and, for finite values of x_{ts}, is less than b_{ts}/ν. When x_{ts} is small, or when the difference between the two curves is small, the true value is much nearer the full than the broken line. For a negative value of b_{ts}, the full line should give a better approximation than for the equivalent positive b_{ts}, but it is not possible to tell the sign of the error. The full lines appear to give excellent approximations for $|b_{ts}|$ less than 10, but the uncertainty increases for larger values. B_{ts} passes through zero at $b_{ts}=0$. For negative b_{ts}, $|B_{ts}|$ increases rapidly enough to compensate for any decrease shown in figure 19.2, so that q'_{ts} increases at least as rapidly as b^2_{ts}. For small, positive b_{ts}, (B_{ts}) increases a little more rapidly than for equivalent negative values, and for large positive b_{ts}, there is an exponential increase, so that q'_{ts} increases much more rapidly than b^2_{ts}.

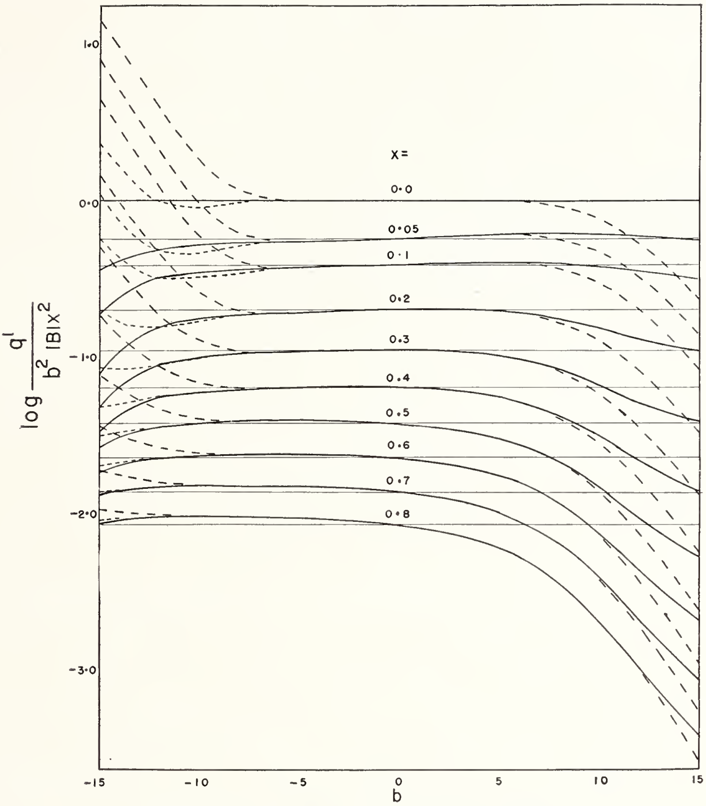

Figure 19.2. *Mayer-Kirkwood treatment.*

— — —, $\nu=4$ to 10; - - - - -, $\nu=4$ to 10½ (10); ———, $\nu=4$ to $10+11$ to ∞ as 10.

The method of Bjerrum [9] may now be discussed in the light of these results. Bjerrum obtained an approximate solution for the deviations from the Debye-Hückel approximation proportional to x^2, and extended it to higher concentrations by treating the deviations formally as due to association of ions of opposite sign. Scatchard and Epstein [2] refined the treatment to make it consistent with Kirkwood's value for the asymptote. The method is very satisfactory for symmetrical electrolytes. It lays too much stress upon ions of opposite sign, however, for unsymmetrical solutions.[2]

Because of the asymmetry of B_{ts} as a function of b_{ts}, q_{ts} is smaller when z_s has the same sign as z_t than when the signs are opposite, but

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[2] Bjerrum made an error in his treatment of the unsymmetrical case. Scatchard and Epstein made a lesser error, which, however, concealed the importance of the above argument. The last factor in their eq 20 should read

$$[B_{AB}-(z^2_A B_{AA}/z^2_B+z^2_B B_{BB}/z^2_A)/2] \text{ and not } [B_{AB}-(B_{AA}+B_{BB})/2].$$

because of the factor b_{ts}^2, it is larger for a bivalent ion of the same sign than for two univalent ions of opposite sign, and larger for a trivalent ion of the same sign than for three univalent ions of opposite sign. It is not pleasant to attribute the interaction of polyvalent ions of the same sign to association with lower valence ions of the opposite sign, particularly as it leads to association constants which depend greatly upon the other ions present.

Olson and Simonson [10] have called attention to the fact that the Debye-Hückel approximation, and particularly the Debye-Hückel limiting law, is quite insufficient to represent the effect of dilute electrolytes on equilibria or reaction rates between ions. They note that for a reaction in which the ions all have charges of the same sign the rate is a function of the concentration of the ion of the opposite sign rather than of the ionic strength. The statement of these authors that this behavior is inconsistent with the Debye theory or any of its extensions is quite erroneous. The only case of real discrepancy with the theory which they show is the rate of the reaction $Co(NH_3)_5Br^{++}+OH^-=Co(NH_3)_5Br\ OH^+\rightarrow CO(NH_3)_5OH^{++}+Br^-$ in very dilute solutions. This discrepancy would be explained if the concentration of OH^- were about 5×10^{-5} less than they believed it to be.

They have discussed particularly the rate of the reaction

$$S_2O_3^{=}+Br\ O\ Ac^-=(S_2O_3\cdot Br\ O\ Ac)^{\equiv}\rightarrow S_2O_3\cdot OAc^{=}+Br^-$$

and equilibrium in the reaction

$$Fe^{+++}+H_2O=FeOH^{++}+H^+$$

in solutions of univalent ions of the opposite sign. The reactions are of the same type electrostatically, except for the absolute sign of the charges and the direction of the reaction. Figure 19.3 shows how log K for such a reaction varies with the salt concentration as calculated, with a for every ion pair equal to 4.5 angstroms, by Mayer's method extended through Kirkwood's asymptote, in solutions with the univalent ions of sign opposite to those of the reacting ions, and univalent bivalent and trivalent ions of the same sign as the reacting ions. On the left the abscissas are ionic strengths, on the right they are concentrations of the ion of opposite charge. The asymptote at zero concentration is the same for all three curves on the left and varies as 1, $\sqrt{3/2}$ and $\sqrt{2}$ on the right, but the curves on the left spread quickly, and those on the right come together even more rapidly. The theory

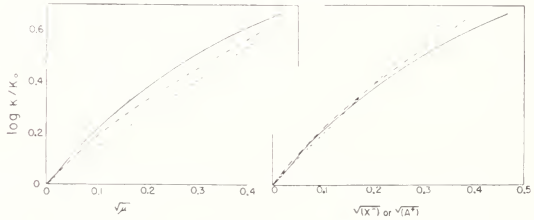

FIGURE 19.3. *Changes in "constants" with ionic strength* $B^{++}+A^{+}=C^{+++}$ *(or* $Y^{=}+X^{-}=Z^{\equiv}$*).*

Mayer theory, 4.5 A in water. ...., Debye limiting law; ———, in AX; — — —, in $BX_2(A_2Y)$; - - - - -, in $CX_3(A_3Z)$.

agrees very nicely with the finding of Olson and Simonson that the concentration of ions of the opposite sign gives better correlation than the ionic strength down to very low concentrations. The change with ionic strength is about 20 percent greater than for the bromoacetate thiosulfate reaction, which indicates that a larger size will fit the measurements better.

The large deviations from simple theory come in solutions of high valence ions of opposite sign to the reacting ions. Figure 19.4 shows the results of similar calculations for univalent ions of the same sign as the reactants and for univalent, bivalent and trivalent ions of the opposite sign, and with ionic strengths as abscissas. The change in the Debye limiting slope or in the effect of univalent ions shows how much smaller the scale must be. This effect is very sensitive to the size of the ions. If the size be taken as 7 angstroms rather than 4.5, the curve for a 3–1 salt falls to about that of the 2–1 salt in figure 19.4. The measurements of LaMer and Fessenden [11] correspond to a value somewhat greater than this, but to a size nearer 7 angstroms than 6. Their measurements with salts of the alkaline earths also correspond to sizes between 6 and 7 angstroms and to sizes that increase slightly in the order barium, calcium, and magnesium.

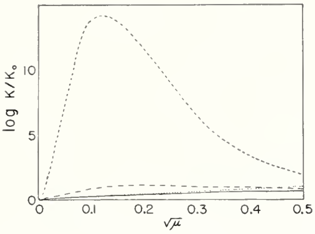

FIGURE 19.4. *Changes in "constants" with ionic strength* $B^{++}+A^{+}=C^{+++}$ (*or* $Y^{=}=X^{-}=Z^{=}$).

Mayer theory, 4.5 A in water. ...., Debye limiting law; ———, in AX; — — —, in $A_2Y(BX_2)$; -----, in $A_3Z(CX_3)$.

Four and a half angstroms was chosen as the smallest reasonable and practicable size. A larger size would be more typical. There is no reason, of course, that all the ions should have the same size. Giving them reasonable variations would give some changes in the shape of the curves. However, we do not expect too good agreement when we recall that the theory assumes spherical ions. This assumption might not be too bad for hydrated Fe^{+++}, $FeOH^{++}$, and H^{+}, or even for $S_2O_3^{=}$. It must be very wrong for $BrCH_2CO_2^{-}$, however, and even worse for the critical complex. It is stretching the theory to apply it to such cases, but such are the cases which are interesting and important.

Mayer's treatment of dilute electrolyte solutions is compared with older studies. The troublesome infinite series is approximated by using Kirkwood's asymptotic relation. The results for the effect of electrolyte concentrations on equilibrium constants and rate constants for reactions between ions all of the same sign agree with the experimental findings of Olson and Simonson that the concentration of ions of opposite sign is more important than the ionic strength, and with those of LaMer and Fessenden that the valence of the ions of opposite sign is extremely important.

References

[1] J. G. Kirkwood, Chem. Rev. **19,** 275 (1936).
[2] G. Scatchard and L. F. Epstein, Chem. Rev. **30,** 211 (1942).
[3] J. E. Mayer, J. Chem. Phys. **18,** 1426 (1950).
[4] G. Scatchard, Physik. Z. **33,** 21 (1932).
[5] V. K. LaMer, F. H. Gronwall, and L. J. Greiff, J. Phys. Chem. **35,** 2245 (1931).
[6] S. Kaneko, Research Electrochem. Lab. Tokyo, No. 403 (1937).
[7] T. H. Gronwall, V. K. LaMer, and K. Sandved, Physik. Z. **29,** 308 (1928).
[8] J. Poirier, J. Chem. Phys. (in press).
[9] N. Bjerrum, Kgl. Danske Videnskab. Selskab. **7,** 9 (1926).
[10] A. R. Olson and T. R. Simonson, J. Chem. Phys. **17,** 1167 (1949).
[11] V. K. LaMer and R. W. Fessenden, J. Am. Chem. Soc. **54,** 2351 (1932).

Discussion

Dr. T. F. Young, University of Chicago, Chicago, Ill.: When Dr. Mayer gave us at Chicago a preliminary preview of his paper on electrolytes I wished I might have the comments of other members of this group, especially of Dr. Scatchard, so I was delighted when I saw on the program the abstract of Dr. Scatchard's paper on "Equilibria and Reaction Rates in Dilute Electrolyte Solutions."

Dr. V. K. LaMer, Columbia University, New York, N. Y.: We are all indebted to Dr. Scatchard for making this deep analysis of what looks like a promising theory. Those of us who have been working in this field for the last 25 years have seen many of these abnormalities experimentally. Dr. Scatchard brought out clearly that there is little difference, as shown in the two pictures. I am also pleased that they are learning at Berkeley after 25 years that these abnormalities really exist and that there is an effect over and above the ionic-strength principle, which appears in solutions containing high valence ions of high and opposite sign. Had Bronsted not seen so many of these important abnormalities in his solubility work of 1916–1920, he could have announced the principle of ionic strength in 1920. Instead, he presented the principle of specific interaction between ions of opposite sign.

Dr. J. Th. G. Overbeek, University of Utrecht, Utrecht, The Netherlands: I understand that Mayer's theory gives a better mathematics in handling interaction between ions. Have you got any idea whether it would be more worth while to try to get the series worked out better or to introduce something like specific interactions when the ions come near? At some stage the last-mentioned correction will become unavoidable. The question is, at which stage?

Dr. G. Scatchard: I have come to think of that as the Pitzer objection. I have been present twice with Dr. Pitzer of California when this theory has been presented, and each time he has raised the question of repulsive forces. He makes the objection that it is not worth while to develop in detail a theory that treats the ions as hard spheres. I disagree with him for small ions. What I want to do next is to work with proteins, for which there is room for doubt. You are probably particularly interested in polyelectrolytes, and there I think it is very necessary to get something better than hard spheres.

20. Electrolytic Solutions Under Pressure[1]

By Benton B. Owen [2]

Introduction

Calculation of effects of pressure on activities of electrolytes in real solutions almost always involves partial molal volumes. Formal relationships employed depend on particular standard and reference states chosen to complete the definitions of activities and activity coefficients. In the following discussion, mainly concerned with condensed phases, the activity, $a_2(=a_{\pm}^{\nu})$, and activity coefficient, $\gamma_2(=\gamma_{\pm}^{\nu})$, of a solute (2) are defined by

$$RT \ln a_2 = \overline{F}_2 - \overline{F}^0 \tag{1.1}$$

$$\gamma_2 = a_2/m \tag{1.2}$$

$$\lim_{m \to 0} \gamma_2 = 1 \tag{1.3}$$

at all temperatures and pressures. $\overline{F}_2 - \overline{F}_2^0$ is the relative partial molal free energy of the solute and m its molality. This conventional identification of a_2 with m at all pressures, P, in the limit at infinite dilution requires that $\overline{F}_2^0$, the partial molal free energy of the solute at unit activity, be a function of P (as well as T). Consequently, it follows from the equation

$$RT \ln K = -\Delta F^0 \tag{1.4}$$

that any equilibrium constant, K, expressed in terms of activities defined as above, must also be a function of P.

Differentiation of eq (1.1) and (1.2) with respect to pressure at constant temperature and composition yields

$$\left(\frac{\partial \ln a_2}{\partial P}\right)_{T,m} = \frac{\overline{V}_2 - \overline{V}_2^0}{RT} \tag{1.5}$$

$$\left(\frac{\partial \ln \gamma_2}{\partial P}\right)_{T,m} = \frac{\overline{V}_2 - \overline{V}_2^0}{RT} \tag{1.6}$$

where $\overline{V}_2$ and $\overline{V}_2^0$ are the partial molal volumes of the solute at any concentration, m, and in the standard state (unit activity). To fulfill the condition that m be constant during differentiation of $\overline{F}_2^0$, the standard state must be one in which m is independent of P. Such a state is the "hypothetical 1-molal solution," in which each of the quantities m, a_2, and γ_2 is unity. As a consequence of the

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[1] Contribution No. 1099 from the Department of Chemistry of Yale University.

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choice of this standard state and of infinite dilution as reference state (eq (1.3)), γ_2 is independent of P in both the hypothetical 1-molal solution and at infinite dilution. It therefore follows from eq (1.6) that $\overline{V}_2^0$ represents the partial molal volume of the solute both at unit activity and at infinite dilution. Similarly, the convention that γ_2 be independent of T in the standard and reference states requires that $\overline{H}_2^0$ represents the partial molal heat content of the solute both at unit activity and at infinite dilution.

Differentiation of eq (1.4) at constant temperature and composition leads to

$$\left(\frac{\partial \ln K}{\partial P}\right)_{T,m}=-\frac{\Delta V^0}{RT}, \tag{1.7}$$

where ΔV^0 represents the increase in volume accompanying the reaction when each of the reactants and products is at unit activity. ΔV^0 is determined from the molal volumes of any pure phases and the partial molal volume, $\overline{V}_2^0$, of each constituent in any mixed phases taking part in the reaction.

These equations form the basis for calculation of effects of pressure on electrolytic solutions, and indicate the role of partial molal volumes in such calculations. Since the standard state for such solutions is a hypothetical one, unrealizable experimentally, practical evaluation of $\overline{V}_2^0$ depends upon extrapolation to infinite dilution. For this purpose it is customary to use the apparent molal volume defined by

$$n_2\phi_v=V-n_1V_1 \tag{1.8}$$

in terms of n_1 and n_2, the numbers of moles of solvent and solute, V, the total volume of the solution, and V_1, the molal volume of the pure solvent. For the solvent in electrolytic solutions, the pure liquid solvent is chosen as standard state, so $\overline{V}_1^0$, is equal to the molal volume, v_1. At any concentration $\overline{V}_2$ is related to ϕ_v by

$$\overline{V}_2=\phi_v+\frac{m^{1/2}}{2}\left(\frac{\partial\phi_v}{\partial m^{1/2}}\right)_{T,P} \tag{1.9}$$

and at infinite dilution

$$\overline{V}_2^0=\phi_v^0 \tag{1.10}$$

It now remains formally to represent partial molal volumes as functions of P before eq (1.5), (1.6), and (1.7) can be integrated. For this purpose the partial molal compressibility

$$\overline{K}_2=-\left(\frac{\partial\overline{V}_2}{\partial P}\right)_{T,m} \tag{1.11}$$

is introduced. It has been shown [1][3] that for strong electrolytes in aqueous solutions, the equations

$$\overline{K}_2^{(P)}=\overline{K}_2\left[\frac{B+P_e+1}{B+P_e+P}\right]^2 \tag{1.12}$$

and

$$\overline{K}_2^{0\,(P)}=\overline{K}_2^0\left[\frac{B+1}{B+P}\right]^2 \tag{1.13}$$

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[3] Figures in brackets refer to literature references on p. 204.

should closely represent the partial molal compressibility, $\overline{K}_2^{(P)}$ or $\overline{K}_2^{0(P)}$, at pressure P in terms of two parameters B and P_e, which are independent of P. B is characteristic of the pure solvent, and may be determined from its compressibility [2, 3]. The evaluation [3, 4] of P_e is based upon Tammann's [5] hypothesis that, in electrolytic solutions, the solvent behaves as if it were subjected to a constant "effective pressure", P_e, in addition to the external pressure, P. P_e is a property of the solution and a function of concentration.

In the following paragraphs, existing sources of values of partial molal volumes and compressibilities will be given, and extent and limitations of present knowledge of these quantities discussed. Examples will be given of their evaluation from experimental data and, in the absence of data, their estimation by "practical rules." ΔV^0 for some important types of ionic reactions will be considered, and some calculations of pressure effects illustrated.

Apparent Molal Volumes, and the Problem of Extrapolation

Densities, or specific volumes, are the primary data from which apparent molal volumes are calculated. On the m-scale, the equation used is

$$\phi_v=\frac{M_2}{d}-\frac{1000}{d_0 d}\left(\frac{d-d_0}{m}\right), \tag{2.1}$$

where M_2 is the molecular weight of the solute, and d_0 and d the densities of solvent and solution, respectively. This equation, derivable from eq (1.8), shows the sensitivity of ϕ_v to uncertainties in the density measurements at small values of m. Since the basic eq (1.5), (1.6), and (1.7) for pressure derivatives all involve $\overline{V}_2^0$, the extrapolation of ϕ_v to infinite dilution is of fundamental importance. A reliable extrapolation requires very precise density data at high dilutions and use of a proper functional relationship between ϕ_v and concentration. Neither of these conditions has been met in the literature in most of the evaluations of $\overline{V}_2^0$. The usual procedure has been to plot ϕ_v against $c^{1/2}$ and extrapolate linearly from about tenth normal to infinite dilution. It was first shown by Masson [6] that for most strong electrolytes experimental results may be expressed by

$$\phi_v=\phi_v^0+S_v c^{1/2} \tag{2.2}$$

over a wide concentration range, and that the necessary condition that ϕ_v^0 be an additive property of the constituent ions is very nearly fulfilled by values of ϕ_v^0 derived by extrapolations based upon this equation. Extensive tables of values of ϕ_v^0 and S_v so obtained are available in the literature [1, 7, 8].

The empirical values of S_v are also nearly additive for a series of simple salts. This requires that ϕ_v be nearly additive at all concentrations. To test this conclusion objectively, Zeldes [10] evaluated by the method of least squares, the parameters of the equation

$$\phi_v=\phi_v^0+S_v c^{1/2}+bc^{3/2} \tag{2.3}$$

for each of 15 alkali halides. His sources of data for these salts were essentially the same as those of references [1, 8]. Then, on the assumption that ϕ_v is an additive property of the individual apparent molal ionic volumes, ϕ_i, at all concentrations, he evaluated the parameters of the equation

$$\phi_i = \phi_i^0 + S_i c^{1/2} + b_i c^{3/2} \tag{2.4}$$

for each of the eight ionic species concerned, by a least squares [11] procedure, which involved the data for all the salts simultaneously. The results of Zeldes' calculations are given in tables 1 and 2. The last three columns in table 2 contain values of ϕ_v^0, S_v, and b computed by adding the appropriate ionic parameters in table 1. These are compared in table 2, with the corresponding "observed" values of ϕ_v^0, S_v, and b obtained by fitting eq (2.3) to the data for the salts individually. The concordance of these two sets of parameters indicates that for each of the 15 alkali halides ϕ_v may be estimated to within about ±0.1 cm^3 up to saturation. This conclusion is of practical importance and raises interesting questions about the structure of concentrated solutions.

Table 1. *Parameters of equation 2.4*

Ion	ϕ_i^0	S_i	b_i
Li^+	−1.09	1.254	−0.0530
Na^+	−1.55	1.784	.0015
K^+	8.54	1.926	.0050
Rb^+	13.74	1.936	.0044
Cs^+	21.09	1.877	0
Cl^-	[1] 18.10	0.281	.0096
Br^-	25.05	.060	−.0035
I^-	36.68	−.341	−.0061

[1] ϕ_i^0 for Cl^- given arbitrary value 18.10 to conform with table 3, of Owen and Brinkley [1].

Table 2. *Parameters of equation (2.3)*

Electrolyte		Observed from eq (2.3)			Computed from eq (2.4)		
Range[1]		ϕ_v^0	S_v	b	ϕ_v^0	S_v	b
13.8	LiCl	17.06	1.456	−0.0271	17.01	1.535	−0.0434
13.2	LiBr	23.97	1.375	−.0595	23.96	1.314	−.0565
8.4	LiI	35.53	0.931	−.0725	35.59	0.913	−.0591
5.3	NaCl	16.50	2.034	.0120	16.55	2.065	.0111
5.5	NaBr	23.50	1.765	0	23.50	1.844	−.0020
6.7	NaI	35.14	1.330	0	35.13	1.443	−.0046
3.8	KCl	26.66	2.190	.0150	26.64	2.207	.0146
4.6	KBr	33.62	2.006	0	33.59	1.986	.0015
5.6	KI	45.23	1.620	0	45.22	1.585	−.0011
6.0	RbCl	31.94	2.127	.0133	31.84	2.217	.140
5.17	RbBr	38.70	2.030	0	38.79	1.996	.0009
2.78	RbI	50.40	1.650	0	50.42	1.595	−.0017
7.5	CsCl	39.08	2.192	0	39.19	2.158	.0096
4.18	CsBr	46.20	1.900	0	46.14	1.937	−.0035
2.9	CsI	57.82	1.540	0	57.77	1.536	−.0061

[1] Greatest concentration at which data were considered.

A serious criticism of the foregiong treatment is that it does not make full use of theory. Where very accurate data are available at low concentrations, it is possible to use the Debye-Hückel theory to perform extrapolation to infinite dilution. The theoretical equation for ϕ_v in dilute solutions may be written [12]

$$\phi_v = \phi_v^0 + \tfrac{2}{3} S_v \Omega_v c^{1/2} + \tfrac{1}{2} K_v c + 2.303 \nu RT \, S_f A' \left[\frac{\partial \ln a}{\partial P} \right] \theta c, \qquad (2.5)$$

where S_v and S_f are the theoretical limiting expressions for the variations of $\overline{V}_2$ and log $\gamma_\pm$ with $c^{1/2}$, K_v an empirical constant, A' the ratio $\kappa a/c^{1/2}$ and Ω_v and θ explicit functions of κa. For this discussion it is sufficient to know that tables are available [8, 9] for the evaluation of Ω_v and θ, and that these functions become unity at infinite dilution.

If the a-parameter is independent of P, eq (2.5) may be written

$$\phi_v - \tfrac{2}{3} S_v \Omega_v c^{1/2} = \phi_v^0 + \tfrac{1}{2} K_v c \qquad (2.6)$$

and a plot of $\phi_v - \tfrac{2}{3} S_v \Omega_v c^{1/2}$ against c should be linear in dilute solutions, and permit a short, theoretically sound extrapolation. Such a plot for KCl at 25° C is shown in figure 20.1. Similar linear plots have been obtained for NaCl [12], $NaClO_4$ [13], and HCl [12]. Wirth [13] found that his data for $HClO_4$ fit eq (2.5), rather than (2.6), indicating that for this acid at least a is not independent of P.

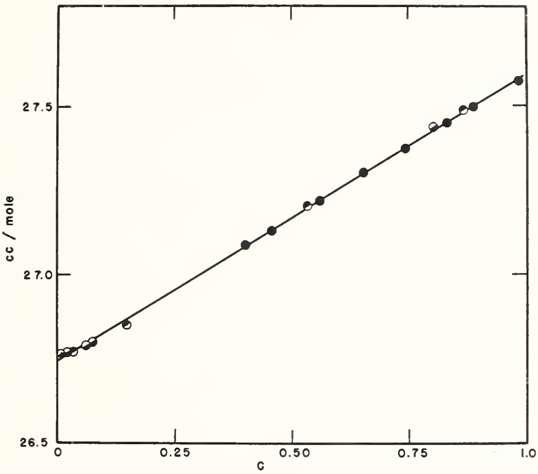

FIGURE 20.1. *Plot of* $\phi_v - 2.517\Omega_v c^{\frac{1}{2}}$ *against c for potassium chloride at 25°;* $a = 3.8 \times 10^{-8}$.

●, Data of A. Kruiz, Z. phys. Chem. **B34,** 1(1936); ◓, Kruis, Z. phys. Chem. **B34,** 13(1936); ◒, W. Geffcken and D. Price, Z. phys. Chem. **B26,** 81(1934).

Table 3 contains the few values of ϕ_{v0} derived by extrapolations based on eq (2.5) and (2.6). These results are probably the most accurate values available for $\overline{V}_2^0$. They are lower, by a few tenths (cm^3), than the values obtained by use of eq (2.2) and data for more concentrated solutions, because the experimental slopes, S_v (table 2), are all somewhat lower than 2.517, the estimated [8, 12] value of the theoretical limiting slope, $\tfrac{2}{3}S_v$.

In addition to need for more accurate data at high dilutions, improvement in our knowledge of $\overline{V}_2^0$ requires further research on the extrapolation. For electrolytes of higher valence types, it may prove necessary to consider the effect of pressure upon the "extended terms" [14, 15] of the Debye-Hückel theory [16]. Also, the pressure derivative of the dielectric constant of water should be redetermined before any numerical value for the theoretical limiting slope, $\frac{2}{3}\boldsymbol{S}_v$, be accepted with confidence.

TABLE 3. *ϕ_v^0, or $\overline{V}_2^0$, obtained by equations (2.5) and (2.6) at 25° C*

Electrolyte	ϕ_v^0	$a\times10^5$	Reference
HCl	17.755	4.4	[12]
$NaCl$	16.538	4.0	[12]
KCl	26.742	3.8	[12]
$NaClO_4$	42.847	4.4	[13]
$HClO_4$	44.039	4.8	[13]

Some ionic equilibria involve a dissolved gas as one of the reactants, but little is known about partial molal volumes of gases in solution. The only extensive direct measurements of $\overline{V}_2$ for gases in water were made by Krichevsky and Iliinskaya [20] by the method of Horiuti [21]. Their results are given in table 4. In the few cases where comparison is possible, the values in this table agree with results in the literature to within 1 or 2 cm³. Attempts to estimate $\overline{V}_2$ from gas solubility data have been made [22], but the results differ from those in table 4 by as much as 5 to 10 cm³, and are of doubtful accuracy because of approximations involved in their calculation. Further work on this subject would be rewarding. Knowledge of the partial molal volumes of CO_2 and O_2 in pure water and in 0.725 molal NaCl (the same ionic strength as sea water) would permit calculations of considerable importance to biology and oceanography.

TABLE 4. *Partial molal volumes of dissolved gases in water* [20].

Gas	$\overline{V}_2^0$ (cm³/mole)		
	0°	25°	50°
H_2	24	26	24
N_2	41	40	38
CO_2	32	33	33
CO	37	36	32
O_2	31	31	32
CH_4	36	37	38

Mixtures of Electrolytes

In recent years, Wirth [17] and Wirth and Collier [13] evaluated partial molal volumes of electrolytes in ternary aqueous mixtures at 25° C and 1 atmosphere. They studied the electrolyte pairs KCl-NaCl, KBr-NaCl, K_2SO_4-NaCl, HCl-NaCl, and $HClO_4$-$NaClO_4$, and their results comprise all the available experimental information concerning the partial molal volumes of components in solutions of mixed strong electrolytes. Wirth [23] has also studied acetic acid in mixtures with sodium acetate and with NaCl. In face of this scarcity of data, it has been necessary in some physicochemical calculations to use hypothesis or assumptions regarding behavior of electrolytes in mixtures.

It was found [17] that in KCl-NaCl and KBr-NaCl solutions the partial molal volumes of KCl and KBr depend only on the total volume ionic strength. It is convenient to assume that this simple behavior is characteristic of the electrolytic components in all mixtures. The assumption of this behavior does not accurately describe the systems [13, 18] HCl-NaCl and $HClO_4$-$NaClO_4$, but it was used for estimating the partial molal volumes of constituents in sea-water [1], and made it easy to demonstrate the difference between effects of pressure upon ionic equilibria in fresh water and in salt water.

Another procedure for estimating volume effects in mixtures is based on the assumption of the independence of apparent ionic volumes. This assumption is equivalent to the statement that apparent ionic volumes are additive at all concentrations, and appears justified by the results for alkali halides shown in tables 1 and 2. It is not nearly so successful in representing the results for higher valence type electrolytes, but offers a convenient basis for estimating volume corrections for chemical reactions, such as dissociation, or hydrolysis, when these reactions do not proceed too far toward completion. A calculation of this kind will be outlined later.

Recently some progress has been made in proposing rules by which volume behavior of mixtures can be expressed with high precision. In a ternary solution containing n_2 and n_3 moles respectively of electrolytic solutes (2) and (3) dissolved in n_1 moles of solvent (1), the mean apparent molal volume is defined by

$$(n_2+n_3)\phi_v(\text{mean})=V-n_1V_1, \tag{3.1}$$

where V is the total volume of solution. Young [19] proposed to express ϕ_v (mean) in terms of the apparent molal volumes, ϕ_2' and ϕ_3', of the individual solutes (2) and (3) each in its binary solution with solvent (1), and each at the same molality as the total molality of the ternary solution. For the simplest case, two uni-univalent salts in water, Young postulates that

$$(n_2+n_3)\phi_v(\text{mean})=n_2\phi_2'+n_3\phi_3', \tag{3.2}$$

and this is in close agreement with Wirth's data [17] on KCl-NaCl and KBr-NaCl mixtures. It follows from definitions and eq (3.2) that if a ternary system is formed from two binary solutions at constant total molality, the volume change of mixing is zero. In any case where volume change of mixing is not zero, the behavior of the resulting ternary solution can be conveniently expressed by amending eq (3.2) to read

$$(n_2+n_3)\phi_v(\text{mean})=n_2\phi_2'+n_3\phi_3'+\Delta V(\text{mixing}). \tag{3.3}$$

Young's [19] calculations show that the equation

$$\Delta V(\text{mixing})=kn_2n_3/n_1 \tag{3.4}$$

permits representation of Wirth's [18] results on the system HCl-NaCl-H_2O with high precision with the aid of a single empirical constant, k. It is not known whether the results [13] on the system $HClO_4$-$NaClO_4$-H_2O can be so simply represented, but it is not unlikely that eq (3.3) will prove useful in any event.

Partial Molal Compressibilities

The apparent molal compressibility is defined by

$$\phi_K = \frac{M_2}{d}\beta - \frac{1000}{d_0 d}\left(\frac{\beta_0 d - \beta d_0}{m}\right) \tag{4.1}$$

when β and β_0 are the isothermal coefficients of compressibility of solution and pure solvent, respectively. Coefficients β and β_0, hereafter referred to as compressibilities, are derived from two kinds of experiments, (1) measurements of compression, the relative volume change produced by pressure increments of several hundred atmospheres or more, and (2) measurements of the velocity of sound through liquids at atmospheric pressure.

For the pure solvent the Tait [24] equation

$$k_0 = \frac{v_0 - v_0^{(P)}}{v_0} = \frac{C}{v_0}\log\left(\frac{B+P}{B+1}\right) \tag{4.2}$$

has been shown [3, 4] to express the compression, k_0, for the pressure increase 1 to P. Constants B and C are independent of pressure, and C/v_0 is practically independent of temperature. This equation yields the compresibility by differentiation. Thus

$$\beta_0 = \frac{0.4343 C/v_0}{B+1} \tag{4.3}$$

at $P=1$. The extrapolative nature of the evaluation of β_0 by eq (4.3) should not be overlooked. Measurements of k_0 are not sufficiently accurate to test the validity of eq (4.2) below about 200 bars, but an indirect test is afforded by eq (4.3).

Measurements of u, the velocity of sound through a liquid, permit calculation of the isothermal coefficient of compressiblility if γ, the ratio of specific heats, C_p/C_v, is known. Thus, for pure solvent

$$\beta_0 = \frac{\gamma_0 \times 10^6}{u_0^2 d_0}, \tag{4.4}$$

where β_0 is given in bars^{-1} if u_0 is expressed in centimeters per second. The agreement between values of β_0 obtained by eq (4.3) and (4.4) is satisfactory for water.

The compressibilities of solutions at atmospheric pressure are not as well known as β_0. Measurements of sound velocities by different investigators usually agree within 1 part in 1,500, but the specific heats ratio, γ, is not generally known with comparable accuracy in electrolytic solutions. Unlike eq (4.4), which as adapted to solutions simply by dropping the subscripts, eq (4.2) is not adapted to solutions without radical changes. Constant C remains unchanged, but B is augmented by the effective pressure, P_e, and an entirely new term is introduced. The final equations

$$k = \frac{v - v^{(P)}}{v} = x_1 \frac{C}{v}\log\left(\frac{B+P_e+P}{B+P_e+1}\right) - \frac{x_2}{v}(\psi_2^{(P)} - \psi_2), \tag{4.5}$$

and

$$\beta = \frac{0.4343 x_1 C/v}{B+P_e+1} - \frac{x_2}{v}\frac{\partial \psi_2}{\partial P} \tag{4.6}$$

are due to Gibson [2, 4], and result from combination of the Tait equation with a modification of Tammann's [5] hypothesis. Quantity ψ_2 is the specific volume of the pure liquid solute, v the specific volume of the solution, and x_1 and x_2 the weight fractions of solvent and solute, respectively. Although ψ_2 appears in these equations only in its change with pressure, which ordinarily is small compared to β_0, the value of β may depend significantly on assumptions regarding the terms in ψ_2.

For dilute solutions ψ_2 may be neglected because x_2 is small, but P_e can not be evaluated very accurately from data on dilute solutions. For moderate concentrations the compression of the pure liquid solute may be set equal to that of the pure solid solute, if this is known, or $\partial\psi_2/\partial P$ may be assumed constant and, by substituting $(P-1)\,\partial\psi_2/\partial P$ for $\psi_2^{(P)}-\psi_2$ in eq (4.5), evaluated simultaneously with P_e from measurements of k for two or more values of P. In very concentrated solutions, or at very high pressures, eq (4.5) must begin to break down along with Tammann's hypothesis upon which it is based. It is evident, therefore, that evaluation of β from compressions is more laborious and more uncertain than evaluation of β_0, and that both involve extrapolation to atmospheric pressure. Evaluation from sound velocity data avoids these difficulties, but requires acurate measurements of the specific heats ratio. Lack of such measurements practically limits the available values of ϕ_K, with few exceptions, to results obtained from compressions [2, 4, 5].

These results have been extrapolated according to the equation

$$\phi_K=\phi_K^0+S_K c^{1/2} \tag{4.7}$$

to evaluate ϕ_K^0, or $\overline{K}_2^0$. Tables of $\overline{K}_2^0$, obtained in this manner are readily available [1, 8] and need not be reproduced here. The need for very precise data at high dilutions and for a more complete theoretical treatment of the extrapolation of ϕ_K is obvious.

In the complete absence of data from which ϕ_K and $\overline{K}_2^0$ may be calculated in solutions of mixed electrolytes, the assumption has been made that $\overline{K}_2^0$ for each solute depends only on the total volume ionic strength. On the basis of this assumption, partial molal compressibilities in 0.725 NaCl solutions have been estimated and tabulated [1]. Some of these values were used in illustrating the effect of pressure on ionic equilibria in sea water.

$\Delta\overline{V}^0$ For Ionic Reactions

Dissolution of a solid salt in water involves an ionic reaction for which $\Delta\overline{V}^0$ can be simply calculated. Thus for the reaction

$$C_{\nu_+}A_{\nu_-}\ (\text{solid})\rightleftarrows\nu_+C^{z_+}+\nu_-A^{z_-} \tag{5.1}$$

$\Delta\overline{V}^0$ is given by

$$\Delta\overline{V}^0=\nu_+\overline{V}_C^0+\nu_-\overline{V}_A^0-V_2^s, \tag{5.2}$$

where $\overline{V}_2^s$ is the molal volume of the solid salt, M_2/d_2^s; and $\overline{V}_C^0$ and $\overline{V}_A^0$ the partial molal ionic volumes. If $\overline{V}_2^0$ is known for the salt, eq (5.2) may be used in the equivalent form

$$\Delta\overline{V}^0=\overline{V}_2^0-V_2^s, \tag{5.3}$$

but in most cases, particularly for salts of low solubility, it is necessary to employ eq (5.2), and evaluate the sum of the ionic volumes by the additivity principle which is rigorously valid at infinite dilution. Table 1 contains values of $\overline{V}_i^0$ for 8 simple ions, and more extensive tables are available in the literature [1, 26]. As in the assignment of numerical values to other individual ionic properties in solution, these tables of $\overline{V}_i^0$ require some basis for the partition of $\overline{V}_2^0$ among its constituent ions. An interesting attempt to perform this partition in an absolute sense is described by Fajans and Johnson [26], who also give references to earlier work. Owen and Brinkley [1] preferred to use the simple convention that $\overline{V}_i^0$ is zero for the H^+ ion as the basis for partition. This convention makes $\overline{V}_i^0$ for the Cl^- ion equal to $\overline{V}_2^0$ for HCl, and has the practical advantage of being consistent with the established convention that the standard electrode of the H^+ ion is zero.

Table 5 contains values of $\Delta\overline{V}^0$ and $\Delta\overline{K}^0$ for dissolution of some slightly soluble salts, and the calculated effect of pressure on the equilibrium constants.

The effect of pressure on the ionization of weak electrolytes is a subject of such importance that it is particularly desirable to know $\Delta\overline{V}^0$ for ionization reactions with high precision. For the fundamental reaction

$$H_2O \leftrightarrows H^+ + OH^-$$

$\Delta\overline{V}^0$ is the difference between $\overline{V}_i^0$ for the two ions and V_1. The value of V_1 is M_1/d_1, and is known accurately at all temperatures. The ionic volume of the OH^- ion is probably not known to better than ±0.3 cm^3, and should be carefully redetermined by new data on some trio of electrolytes such as HCl, NaOH, and NaCl. Table 6 contains estimates of $\Delta\overline{V}^0$ and $\Delta\overline{K}^0$ for the ionization of water based upon data now available. Calculations at other temperatures are not as dependable as those at 25° C, but the trend with temperature is believed to be real.

TABLE 5. *Effect of pressure upon the dissolution of salts in water at 25°* [1]

Reaction	$\Delta\overline{V}^0$	$10^4\Delta\overline{K}^0$	$K^{(P)}/K$				
			$P=200$	$P=400$	$P=600$	$P=800$	$P=1000$
Anhydrite $\rightleftarrows Ca^{++} + SO_4^{--}$	−49.3	−142	1.47	2.12	3.00	4.20	5.80
Calcite $\rightleftarrows Ca^{++} + CO_3^{--}$	−58.3	−157	1.58	2.44	3.69	5.52	8.10
Aragonite $\rightleftarrows Ca^{++} + CO_3^{--}$	−55.3	−157	1.54	2.32	3.44	5.01	7.18
Magnesite $\rightleftarrows Mg^{++} + CO_3^{--}$	−52.3	−169	1.50	2.21	3.18	4.49	6.24
Witherite $\rightleftarrows Ba^{++} + CO_3^{--}$	−61	−185	1.61	2.53	3.88	5.84	8.60

[1] B. B. Owen and S. R. Brinkley, Jr., Chem. Rev. **29**, 461 (1941).

In estimating $\Delta\overline{V}^0$ for the ionization or weak electrolytes other than water, a complication is often introduced by the ionization reaction itself. Thus, if the reaction $HA \leftrightarrows H^+ + A^-$ proceeds very far at experimental concentrations, the ions must contribute to the apparent molal volume calculated from the density and the stoichiometric molality of the acid. The apparent molal volume, ϕ_u, of the undissociated acid may be written in terms of the measured apparent

TABLE 6. *Effect of pressure upon the equilibrium constant of the reaction* $H_2O \rightleftarrows H^+ + OH^-$ *in pure water* [1] [2]

P	$K^{(P)}/K$				
	5° C	15° C	25° C	35° C	45° C
Bars					
1	1	1	1	1	1
200	1.24_6	1.225	1.202	1.180	1.16_3
400	1.54_3	1.490	1.435	1.384	1.34_5
600	1.8_{96}	1.80_0	1.703	1.61_2	1.54_5
800	2.3_{17}	2.16_3	2.009	1.86_8	1.7_{66}
1000	2.8_{16}	2.58_5	2.358	2.15_4	2.0_{09}
$\Delta \overline{V}^0$	−26.1	−24.9	−23.4	−21.8	−20.6

[1] B. B. Owen and S. R. Brinkley, Jr., Chem. Rev. **29**, 461 (1941).
[2] $\Delta \overline{K}^0 = -52 \times 10^{-4}$ (at 25° C) used at all temperatures.

molal volume ϕ_v and a correction term. If the degree of dissociation, α, is known and is not large at the experimental concentrations, it is satisfactory to assume the additivity of ϕ_i at all concentrations and express the correction term by

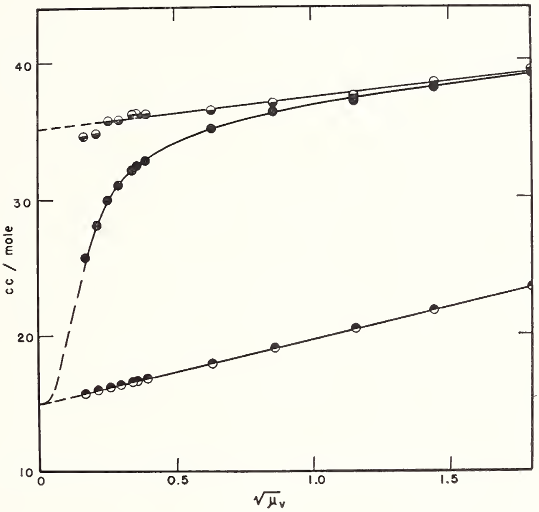

FIGURE 20.2. *Plots of the apparent molal volumes of sulfuric acid and its constituents against volume ionic strength at 25°.*

Data of I. M. Klotz and C. F. Eckert, J. Am. Chem. Soc. **64**, 1878(1942). ●, Observed values; ◓, calculated for $2H^+ + SO_4^=$; ◒, calculated for $H^+ + HSO_4^-$.

$$\Delta\phi = \sum \phi_i - \phi_u. \tag{5.5}$$

For the reaction considered, $\sum \phi_i$ is obtained by combination of measured values of ϕ_v in simple binary solutions. For example,

$$\sum \phi_i = \phi_v(\mathrm{NaA}) + \phi_v(\mathrm{HCl}) - \phi_v(\mathrm{NaCl}); \tag{5.6}$$

The value of ϕ_u is determined by successive approximations, for ϕ_u is approximately equal to ϕ_v in the more concentrated solutions where

α is small. Using an approximate value of ϕ_u to estimate a rough value of $\Delta\phi$, approximate values of ϕ_u are calculated and plotted. For an undissociated neutral molecule, a plot of ϕ_u against $c_u = c(1-\alpha)$ should be linear, as has been demonstrated [27] with undissociated H_3PO_4. For an undissociated charged acid radical, however, ϕ_u should be plotted against the square root of the volume ionic strength for an approach to linearity [28]. A plot of this kind for the ions of H_2SO_4 is shown in figure 20.2.

Table 7. *Dissociation of weak electrolytes*

Reaction	$\Delta\overline{V}^0$	$10^4\Delta\overline{K}^0$	Reference
$H_2O \rightleftharpoons H^+ + OH^-$	−23.4	−52	[1]
$H_2CO^3 \rightleftharpoons H^+ + HCO_3^-$	−29	--------	[1]
$HCO_3^- \rightleftharpoons H^+ + CO_3^{--}$	−27.8	−87	[1]
$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	[1] −9.2	−17	]1[
$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	−20.2	--------	[28]
$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	−16.2	--------	[27]
$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{--}$	−28.1	--------	[27]

[1] O. Redlick and J. Bigeleisen, Chem. Rev. **30**, 171 (1942), report the value −11.47.

There is only a small number of undissociated weak electrolytes for which ϕ_u^0 is known. Table 7 contains values of $\Delta\overline{V}^0$ and $\Delta\overline{K}^0$ calculated for their dissociation.

References

[1] B. B. Owen and S. R. Brinkley, Jr., Chem. Rev. **29**, 461 (1941).
[2] R. E. Gibson, Am. J. Sci. **35A**, 49 (1938).
[3] R. E. Gibson, J. Am. Chem. Soc. **56**, 4 (1934).
[4] R. E. Gibson, J. Am. Chem. Soc. **57**, 284 (1935).
[5] G. Tammann, Uber die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen, p. 36. Voss, Leipzig (1907).
[6] D. O. Masson, Phil. Mag. [7] **8**, 218 (1929).
[7] A. F. Scott, J. Phys. Chem. **35**, 2315 (1931).
[8] H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolytic Solutions, 2d ed. (Reinhold Publishing Corp., New York, N. Y., 1950).
[9] G. Scatchard and L. F. Epstein, Chem. Revs. **30**, 211 (1942).
[10] Private Communication from Dr. Henry Zeldes, Oak Ridge National Laboratory, Oak Ridge, Tenn.
[11] S. Kaneko, J. Chem, Soc. Japan **57**, 665 (1936).
[12] B. B. Owen and S. R. Brinkley, Jr., Ann. N. Y. Acad. Sci. **51**, 753 (1949).
[13] H. E. Wirth and F. N. Collier, Jr., J. Am. Chem. Soc. **72**, 5292 (1950).
[14] T. H. Gronwall, V. K. La Mer, and K. Sandved, Physik. Z. **29**, 358 (1929).
[15] V. K. La Mer, T. H. Gronwall, and L. J. Greiff, J. Phys. Chem. **35**, 2245 (1931).
[16] P. Debye and E. Hückel, Physik. Z. **24**, 185 (1923).
[17] H. E. Wirth, J. Am. Chem. Soc. **59**, 2549 (1937).
[18] H. E. Wirth, J. Am. Chem. Soc. **62**, 1128 (1940).
[19] T. F. Young, Record of Chem. Progress **12**, 81 (1951).
[20] I. Kritchevsky and A. Iliinskaya, Acta Physicochimica U. R. S. S. **20**, 327 (1945).
[21] J. Horiuti, Sci. Pap. Inst. Phys. Chem. Research **17**, 125 (1931).
[22] I. Kritchevsky and J. Kasarnovsky, J. Am. Chem. Soc. **57**, 2168 (1935).
[23] H. Wirth, J. Am. Chem. Soc. **70**, 462 (1948).
[24] P. G. Tait, The Physics and Chemistry of the Voyage of H. M. S. Challenger, Vol. II, Part IV, S. P. LXI.
[25] E. H. Lanman and B. J. Mair, J. Am. Chem. Soc. **56**, 390 (1934).
[26] K. Fajans and O. Short, J. Am. Chem. Soc. **64**, 668 (1942).
[27] J. S. Smith, Dissertation, Yale University (1943).
[28] I. M. Klotz and C. F. Eckert, J. Am. Chem. Soc. **64**, 1878 (1942).

21. Standardization of the pH Scale

By David I. Hitchcock[1]

Introduction

The use of pH numbers as a quantitative means of expressing the acidity or alkalinity of aqueous solutions is now widely accepted in many branches of science, and the advantages of this notation need no comment here. The need for a restandardization of the scale arose because the accepted method of measuring pH gives a number which is not the same as the negative of the logarithm of the concentration of hydrogen ions.[2] Since the extent of this discrepancy is of the order of 0.1 pH, standardization is of no great moment to those concerned only with approximate control. The actual measurement of a difference in pH, however, is reproducible within 0.005 pH or better. For use in the calculation of chemical equilibria, accurately defined values are needed, for a variation of 0.01 in pH implies a variation of 2.3 percent in a concentration. Since the pH scale is arbitrary at best, it would be desirable to have general agreement on the values to be assigned to reproducible standard solutions. During the past quarter of a century, workers in several laboratories have attempted to provide as rational a basis as possible for a revised pH scale, and their results agree, in many instances, within a few thousandths of a pH unit.

Measurement of pH

The symbol pH was originally intended to denote $-\log C_H$, which is the same as $\log (1/C_H)$. Except for approximate calculations, this definition has been discarded in favor of an operational definition, based essentially on the method that Sørensen [1][3] proposed for the measurement of pH. The difference in pH between two solutions, S and X, is obtained from the electromotive force (emf) of the cell

$$H_2;\ \text{solution X: salt bridge: solution S};\ H_2 \qquad \text{(I)}$$

by the equation

$$pH_x - pH_s = E/k, \qquad (1)$$

in which E is the emf of cell I in volts, and k is 2.3026 RT/F, or $1.984 \times 10^{-4}T$. For reasons of practical convenience, the emf of cell I is obtained as the difference between two readings of the cell

$$H_2;\ \text{solution X or S: salt bridge: reference electrode} \qquad \text{(II)}$$

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[2] In this discussion, the term "hydrogen ion" and the symbol H^+ will refer to the hydrated ion as it exists in aqueous solutions. The charge of the ion will be omitted in symbols with subscripts, as C_H for hydrogen-ion concentration.

[3] Figures in brackets refer to literature references on p. 212.

and the pH is calculated by the equation

$$pH_x = pH_s + (E_x - E_s)/k, \qquad (2)$$

in which E now refers to the emf of cell II. If the reference electrode is reproducible and constant, the pH may be calculated from a single measurement by the equation

$$pH_x = (E_x - E_0)/k, \qquad (3)$$

in which E_0 is the emf that cell II would have if the H_2 electrode were bathed by a solution of pH zero. Actually, such a strongly acid standard is not used, but the value of E_0 is obtained from measurements with solutions of moderate acidity.

The salt bridge in cells I and II is usually a saturated solution of KCl (4.16 *N* at 25° C.). The reference electrode in cell II is a calomel half-cell containing either 0.1 *N* or saturated KCl solution. For most pH measurements at the present time, the H_2 electrode of cell II is replaced by a glass electrode. The use of the glass electrode was fully discussed by Dole [2], and an electronic bridge suitable for precise measurements was described by Hitchcock and Mauro [3].

It is evident from a comparison of eq (2) and (3) that the standardization of the pH scale may be expressed in terms of the pH of a standard solution or of the E_0 value of a reference electrode.

Standardization by Solutions of a Strong Acid

The pH values assigned in 1909 by Sørensen [1] to a series of buffer solutions were based on an E_0 value for the 0.1 *N* calomel electrode at 18° C. This value was obtained from measurements with mixtures of 0.1 *N* solutions of HCl and NaCl, together with several assumptions which are no longer tenable. Although Sørensen's pH values were widely adopted during the two decades following his pioneer work, they cannot be regarded as equal to $-\log C_H$, and only an arbitrary significance can now be ascribed to them.

On the basis of the same measurements, with some additional data, Sørensen and Linderstrøm-Lang [4] proposed a new scale of paH values, regarding paH as the negative of the logarithm of the activity of hydrogen ions. This scale was based on empirical equations which had been found to represent the activity coefficients of HCl. This scale, 0.04 higher than the original pH scale, is essentially the same as the current revised pH scale.

A similarly increased pH value for 0.1 *M* HCl may be calculated from an activity coefficient published by Scatchard [5]. He used a flowing junction between the acid solution and the salt bridge, and concluded that the potential difference at such a junction was constant when the salt bridge was saturated KCl and the HCl solution was 0.1 *M* or more dilute.

Later work has served to emphasize the arbitrary nature of the pH value assigned to any solution of a strong acid, either with or without added salt. This arises because of the impossibility of measuring, without the use of an arbitrary assumption, either the activity coefficient of a single ionic species or the magnitude of a single liquid junction potential. Although the latter cannot be measured, it is believed to be especially large at a junction with a strongly acid solution because of the very high mobility of the hydrogen ion.

This early work on standardization was discussed by Clark [6].

Standardization by Buffer Solutions

It was suggested by Cohn, Heyroth, and Menkin [7] that the value of E_0 and the standardization of the pH scale might be based on H_2 electrode measurements of cells containing buffer solutions, together with an accurate value for the dissociation constant of the buffer acid. This method was utilized by MacInnes [8] with his collaborators [9], who had previously obtained accurate values for the thermodynamic dissociation constant of acetic acid by the application of the Debye-Hückel theory to conductance measurements. Their solutions contained acetic acid with sodium acetate at ionic strengths of about 0.001 to 0.01. They obtained for each solution a pH value from a measurement of cell II, assuming an E_0 value for use in eq (3). From the pH they subtracted the logarithm of the buffer ratio, C_A/C_{HA}, after correcting the stoichiometric concentrations for the slight ionization of the acid. This difference, when plotted against the square root of the ionic strength, was found to yield a straight line. The position of this line along the ordinate axis was adjusted by changing the value of E_0 until the intercept at zero ionic strength was equal to the negative of the logarithm of the true ionization constant. The final value of E_0 was used as the basis for a pH scale.

This procedure was based on an attempt to make pH equal, as nearly as possible, to $-\log C_H f$, where f is the mean activity coefficient of the buffer acid. Writing the law of mass action for the ionization in the form

$$\mathrm{pH} - \log (C_A/C_{HA}) = \mathrm{p}K + \log f \tag{4}$$

and making use of the limiting law of Debye and Hückel

$$-\log f = A\sqrt{\mu} \tag{5}$$

where μ is the ionic strength, we obtain the equation

$$\mathrm{pH} - \log (C_A/C_{AH}) = \mathrm{p}K - A\sqrt{\mu}. \tag{6}$$

Their results fitted this equation, except that the observed slope was definitely greater than the theoretical value of A in the limiting law. This deviation may be due to the effect of a varying liquid junction potential, included in the measured value of E. They stated that the method yields pH values which are not equal to $-\log C_H f$, but are probably as close as they can be adjusted to such equality without modifying eq (3).

Similar measurements with buffers of higher ionic strength, 0.01 to 0.1, were made by Hitchcock and Taylor [10], who extrapolated their data in a different way. In eq (4) they regarded pH as $-\log C_H f_H$ and the last term as $\log (f_A/f_{HA})$. The distinction between f_H and the mean activity coefficient vanishes in the extrapolation if the buffer acid is uncharged, but it must be considered if the buffer acid is itself an anion, such as $H_2PO_4^-$. In place of the limiting law, these authors made use of the equation

$$-\log f = A\sqrt{\mu} - B\mu, \tag{7}$$

in which A is the theoretical constant of Debye and Hückel and B is an empirical factor which may or may not be constant. By combining eqs (3), (4), and (7) they obtained the relation

$$E'' = E - k\mathrm{p}K - k \log \frac{C_A}{C_{HA}} + kA\sqrt{\mu} = E_0 + kB\mu. \tag{8}$$

The left member of eq (8), which contains only known quantities, was plotted against the ionic strength, with the results shown in figures 21.1 and 21.2. The points for each series of dilutions of an acetate buffer fell on a straight line, but the slope depended on the buffer ratio and on the cation of the buffer salt. The intercepts, however, differed by only 0.2 millivolt. In the case of 1:1 borate of phosphate buffers, the lines had to be curved to fit the points, but the average intercept (±0.1 mv) was identical with that given by the acetate data. Such agreement would be expected if the liquid junc-

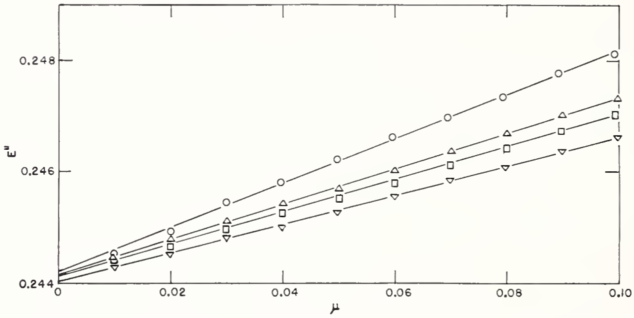

Figure 21.1. *Extrapolation of hydrogen-electrode data for acetate buffers.*

○, acetic acid: potassium acetate=1:1; △, acetic acid: sodium acetate=1:4; □. acetic acid: sodium acetate=1:1; ▽, acetic acid: sodium acetate=4:1. From Hitchcock and Taylor [10].

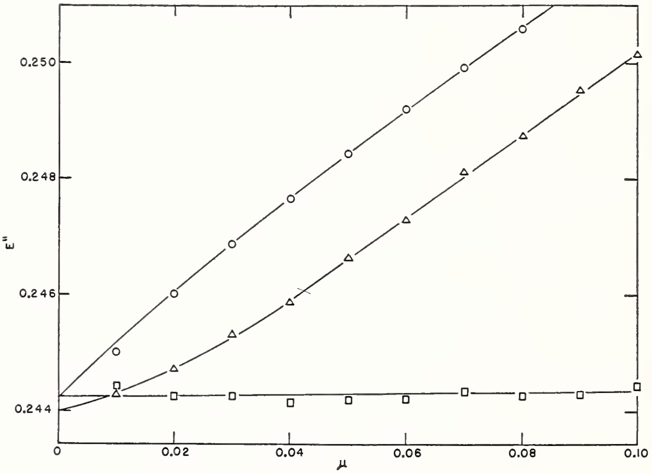

Figure 21.2. *Extrapolation of hydrogen-electrode data for 1:1 buffers.*

○, phosphate; △, borate; □, glycolate. From Hitchcock and Taylor [10].

tion potential in cell II were constant or if it were proportional to the ionic strength. In the former case, provided that eq (7) were valid, the pH calculated by eq (3) would be equal to $-\log C_H f_H$.

Standardization by Cells Without Liquid Junction

Very extensive measurements, aimed at the standardization of the pH scale, have been carried out in recent years at the National Bureau of Standards. The method was described by Hamer and Acree [11], and some of the numerous results were reviewed by Bates [12]. The emf of the cell without liquid junction

$$\mathrm{H_2;\ buffer\ solution,\ NaCl,\ AgCl;\ Ag} \qquad \text{(III)}$$

is related to the product of ionic activities in the solution by the exact equation

$$E = E^0 - k \log C_{\mathrm{H}} f_{\mathrm{H}} C_{\mathrm{Cl}} f_{\mathrm{Cl}}. \qquad (9)$$

Values of E^0 for this cell had been obtained by Harned and Ehlers [13], who applied the method of extrapolation suggested by Hitchcock [14] to measurements of cell III with dilute HCl solutions as electrolyte. If eq (9) is rewritten in the form

$$-\log C_{\mathrm{H}} f_{\mathrm{H}} f_{\mathrm{Cl}} = \log C_{\mathrm{Cl}} + (E - E^0)/k \qquad (10)$$

each measurement of cell III, with buffer plus chloride as electrolyte, yields a definite value for the acidity function defined by the left member. When such data were obtained for the same buffer with varying small amounts of chloride, it was found that this acidity function was a linear function of the chloride concentration, so that a short extrapolation gave $-\log (C_{\mathrm{H}} f_{\mathrm{H}} f_{\mathrm{Cl}})^0$, the value of the function for the buffer without chloride. The pH could then be obtained from the relation

$$\mathrm{pH} = -\log C_{\mathrm{H}} f_{\mathrm{H}} = -\log (C_{\mathrm{H}} f_{\mathrm{H}} f_{\mathrm{Cl}})^0 + \log f^0_{\mathrm{Cl}} \qquad (11)$$

if the value of the last term were known. The choice of a value for f^0_{Cl} is an arbitrary assumption, since the activity coefficient of a single ionic species cannot be measured. A number of plausible assumptions yielded pH values for a given buffer which were in close agreement at ionic strengths below 0.01 to 0.02. Perhaps the simplest assumption is that used by Bates [12] in estimating the pH of a solution containing 0.01 M acetic acid and 0.01 M sodium acetate. He assumed that f^0_{Cl} for this solution was the mean of the activity coefficient of HCl, at infinite dilution, in 0.01 M NaCl, and the activity coefficient of this salt itself. Since the logarithms of these coefficients differed by less than 0.001, Bates' estimate of the pH of this buffer, 4.714 at 25°, seems highly reliable.

Standard Solutions for Checking Electrodes

Table 1 gives a comparison of pH values obtained in the writer's laboratory, from cells with salt bridges, with those obtained at the National Bureau of Standards, from cells without liquid junction. The three solutions included are those recommended by Smith and

Bates [18], who gave pH values to two decimal places for temperatures from 0° to 60° C. Similar values were also recommended by the British Standards Institution [19]. Additional standards of higher acidity and alkalinity were described by Bates, Pinching, and Smith [20].

The pH values assigned to these standard solutions provide a means for putting all pH determinations on a uniform basis, consistent with the postulate that pH shall be equal, as nearly as possible, to $-\log C_H f_H$ for sufficiently dilute solutions.

Other Measures of Acidity

It was pointed out by Guggenheim [21] that in an acid-base equilibrium, as defined by Brønsted, the properties of the solution depend upon the ratio of the concentrations of acid and base. The determining factor for this ratio is never the activity of hydrogen ions $C_H f_H$, but in some cases it may be either C_H itself or $C_H f^2$, where f, the mean activity coefficient of the acid, is a physically definite quantity. In simple cases $C_H f^2$ may be identical with $C_H f_H f_{Cl}$, which can be obtained from the emf of cell III by eq (10) if the concentration of chloride ions is known. The suggestion that $C_H f_H f_{Cl}$ might be a useful measure of acidity was also made by Hitchcock [22]. The fact that this function for an acetate buffer is nearly independent of dilution is illustrated in figure 21.3, which appeared in the review by Bates [12]. Here the lowest curve is $-\log C_H$, the second is pH on Sørensen's scale, the third is the revised pH, and the line at the top is $-\log (C_H f_H f_{Cl})$. Bates expressed the opinion that the approximate constancy of the latter function, as the buffer is diluted, detracts from its usefulness as a practical unit of acidity, but this conclusion may be questioned. However, the function $C_H f_H f_{Cl}$ has not been generally

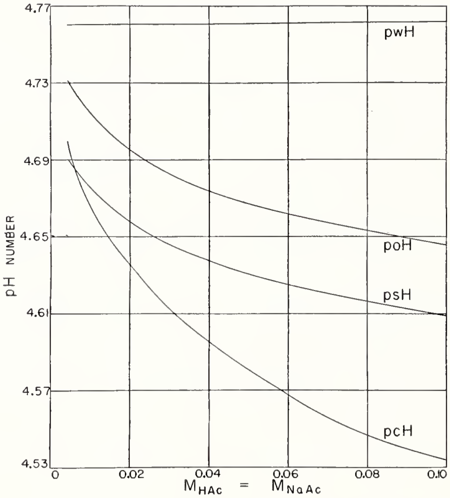

FIGURE 21.3. pH *values for acetate buffers on four different scales as a function of concentration*

From Bates [12].

adopted as a unit of acidity, and its measurement is more cumbersome than the usual pH measurement.

Table 1. *Standard solutions for checking electrodes*

Solution	pH			Cell	References
	15°	25°	38°		
0.05 *M* KH phthalate	--------	4.008	4.025	II	[10]
	4.000	4.005	4.027	III	[15]
0.025 *M* KH_2PO_4 0.025 *M* Na_2HPO_4	--------	6.857	6.835	II	[10]
	6.896	6.860	6.840	III	[16]
0.01 *M* $Na_2B_4O_7 \cdot 10H_2O$	--------	9.177	9.078	II	[10]
	9.273	9.177	9.081	III	[17]

The measurement of C_H may be still more difficult. Guggenheim [21] suggested that in some cases C_H could be obtained from a cell without liquid junction by the use of a H_2 electrode and a sodium amalgam electrode. Redlich and Klinger [23] suggested that $C_H f_H$ could be obtained, for solutions following the ionic strength principle, from the emf of the cell

$$H_2;\ \text{solution, TlBr (satd.), AgBr (satd.); Ag.}$$

It appears that this cell would also yield a measure of C_H, for sufficiently dilute solutions, if the solubility of the TlBr were determined. So far, however, these suggestions have not led to the publication of any results.

In the special case of solutions containing a constant excess of an inert salt, Brønsted [24] showed that the classical equations for mass action and emf are valid in terms of concentrations. This principle was applied by Güntelberg and Schiödt [25] and by Kilpatrick and Chase [26] to the calculation of C_H from the emf of cells with salt bridges. Hitchcock and Peters [27] verified the Brønsted principle by the use of 0.025 *M* acetate or phosphate buffers in solutions containing NaCl to give a constant ionic strength of 0.16. They obtained values of C_H from the emf of a cell without liquid junction, using a glass electrode and a Ag-AgCl electrode. For each buffer, with acid-base ratios varied from 1/9 to 9/1, the C_H values yielded a constant value of K_c, the classical dissociation constant in terms of concentration. Later work has shown that the calculation of C_H is less certain if the cell includes a salt bridge, except in a few special cases.

Conclusion

Although the activity of hydrogen ions cannot be defined without the use of an arbitrary assumption, the most rational basis for a uniform pH scale is one which makes pH equal to $-\log C_H f_H$, as nearly as possible, for dilute solutions. Such a uniform scale will result from the general adoption of the standards now recommended by the National Bureau of Standards and the British Standards Institution. Further work should be done to determine whether $-\log C_H$ or $-\log C_H f^2$ is more useful than pH as a measure of acidity or alkalinity and whether simpler methods can be found for the measurement of these quantities.

References

[1] S. P. L. Sørensen, Compt. rend. trav. lab. Carlsberg **8**, 1 (1909); Biochem. Z. **21**, 131 (1909).

[2] M. Dole, The Glass Electrode (John Wiley & Sons, New York, N. Y., 1941).

[3] D. I. Hitchcock and A. Mauro, Yale J. Biol. Med. **22**, 309 (1950).

[4] S. P. L. Sørensen and K. Linderstrøm-Lang, Compt. rend. trav. lab. Carlsberg **15**, No. 6 (1924).

[5] G. Scarchard, J. Am. Chem. Soc. **47**, 696, 3107 (1925).

[6] W. M. Clark, The Determination of Hydrogen Ions, 3d ed. (Williams & Wilkins Co., Baltimore, 1928).

[7] E. J. Cohn, F. F. Heyroth, and M. F. Menkin, J. Am. Chem. Soc. **50**, 696 (1928).

[8] D. A. MacInnes, Cold Spring Harbor Symposia on Quantitative Biology **1**, 190 (1933).

[9] D. A. MacInnes, D. Belcher, and T. Shedlovsky, J. Am. Chem. Soc. **60**, 1094 (1938).

[10] D. I. Hitchcock and A. C. Taylor, J. Am. Chem. Soc. **59**, 1812 (1937); **60**, 2710 (1938).

[11] W. J. Hamer and S. F. Acree, J. Research NBS **23**, 647 (1939). RP1261.

[12] R. G. Bates, Chem. Rev. **42**, 1 (1948).

[13] H. S. Harned and R. W. Ehlers, J. Am. Chem. Soc. **55**, 2179 (1933).

[14] D. I. Hitchcock, J. Am. Chem. Soc. **50**, 2076 (1928).

[15] W. J. Hamer, G. D. Pinching, and S. F. Acree, J. Research NBS **36**, 47 (1946). RP1690.

[16] R. G. Bates and S. F. Acree, J. Research NBS **34**, 373 (1945) RP1648.

[17] G. G. Manov, N. J. De Lollis, P. W. Lindvall, and S. F. Acree, J. Research NBS **36**, 543 (1946) RP1721.

[18] E. R. Smith and R. G. Bates, Compt. rend. duinzième Conférence, International Union of Pure and Applied Chemistry, Amsterdam, p. 118 (1949).

[19] British Standard 1647:1950, pH Scale (British Standards Institution, London, 1950).

[20] R. G. Bates, G. D. Pinching, and E. R. Smith, J. Research NBS **45**, 418 (1950) RP2153.

[21] E. A. Guggenheim, J. Phys. Chem. **34**, 1758 (1930).

[22] D. I. Hitchcock, J. Am. Chem. Soc. **58**, 855 (1936); **59**, 2753 (1937).

[23] O. Redlich and H. Klinger, J. Am. Chem. Soc. **61**, 2983 (1939).

[24] J. N. Brønsted, Trans. Faraday Soc. **23**, 430 (1927).

[25] E. Güntelberg and E. Schiödt, Z. physik. Chem. **135**, 393 (1928).

[26] M. Kilpatrick, Jr., and E. F. Chase, J. Am. Chem. Soc. **53**, 1732 (1931).

[27] D. I. Hitchcock and R. Peters, J. Am. Chem. Soc. **68**, 1753 (1946).

22. Significance of Constants Involved in Electrochemical Double Layers

By J. Th. G. Overbeek [1]

Introduction

The electrical properties of the phase boundary, which may be summarized under the heading "electrochemical double layer," have been investigated in many ways. First there is the purely *electrochemical* approach. Strictly, one should consider the double layer in any electrochemical experiment in which phase boundaries are involved, that is, in all measurements on galvanic cells either in equilibrium or at finite current. Practically, however, more detailed considerations of the double layer are restricted to the fields of thermionic work functions, overpotentials, polarization currents, membrane potentials, oil-water and air-water potentials, and especially electrocapillarity. Many problems in ion exchange also require consideration of the double layer.

Second, those working in *colloid science* are interested in the electrochemical double layer, because it is now regarded as the direct cause of the stability of hydrophobic colloids [1].[2] Moreover, the double layer exerts an influence on titration curves of proteins and other hydrophilic colloids; it is at the basis of the electroviscous effect; it explains the formation and dissolution of coacervates and the solubility of globulins. In the physiological field it is related to the permeability of cell membranes.

Finally, *electrokinetic* phenomena which lie between electrochemistry and colloid chemistry and form a striking proof of the extension in space of the double layer should be mentioned. The most important of these, although not the most suitable for interpretation, is *electrophoresis* which has been so significant in the development of protein science.

It is no wonder, therefore, that investigators in such different fields do not always speak the same language. Between naive optimists who take the charge and potential of the double layer for granted and pessimists like Guggenhein [2], who deny the possibility of acquiring any knowledge on the potential difference between two phases or the course of the potential in one phase, almost any point of view can be found.

It is the object of this paper to show that a very sensible middle course can be steered which, recognizing in principle the point of view of the pessimists, escapes its sterility in many practical cases. Our ultimate aim is to obtain a complete description of the structure of the double layer, or what may be called a map of the phase boundary, giving the distribution of nuclei and electrons from which all desirable information could be calculated. Unfortunately, we are still far from this ideal, and must content ourselves with much less detail. Our

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[2] Figures in brackets indicate the literature references on p. 225.

data are usually restricted to charge and potential difference in the double layer and to its free energy. The interpretation of the relation between charge and potential (or of the capacity of the double layer) adds some information on the structure, especially on the extension of the double layer in space.

It should be realized, however, that the investigator of the double layer is in a rather uneasy position. It has been emphasized many times that potential differences between different phases are as inassessable as are single ionic activities or diffusion potentials. In passing a suitable test body from one phase to another electrical work $e\Delta\phi$ is always accompanied by chemical work $\Delta\mu$ and the two cannot be separated without arbitrariness. How then is it possible to attribute importance to the potential difference in a double layer? Anticipating our arguments we mention that a double layer potential is only part of a total potential difference between two phases, and although it seems to have the character of a single-phase boundary potential, it is in fact determined as the potential difference of a galvanic cell related to a suitable zero. This can be most easily shown by thermodynamic consideration of a double layer when part of a galvanic cell.

Thermodynamics of the Double Layer [3, 4]

The double layer will be considered as situated at one of the phase boundaries of a galvanic cell. Our considerations will be restricted to situations in which no current flows.

Extension to current carrying cells is possible as a first approximation by assuming that the structure of the double layer is analogous to that at rest, although charge and potential may be modified.

Current-free situations occur with two very different systems, i. e., (a) with a reversible electrode in true thermodynamic equilibrium and (b) with a perfectly polarizable electrode. Experimentally, there is a great difference between (a) and (b) in that with the reversible electrode the emf of the cell is completely determined by the composition of the phases, whereas with the polarizable electrode the potential difference at the cell is a parameter which can be freely changed.

To simplify the discussion we shall choose two examples which, incidentally, are the best investigated cases in this field.

For the reversible double layer, that on AgI will be chosen and for the polarizable one, that on Hg. To incorporate these two double layers in galvanic cells, a second electrode is necessary. It is fundamentally irrelevant whether this second electrode is a reversible type or one connected to the cell by a liquid junction which is supposed to suppress the diffusion potential. For thermodynamic calculations the reversible electrode is more suitable, but in most experiments the liquid junction is used.

The two cells considered are:

a. Reversible case,

Pt | Ag | AgI | solution, H_2O, Ag^+, I^- and other ions | saturated KCl (or NH_4NO_3) | Hg_2Cl_2 | Hg | Pt.

b. Polarizable case,

Pt | Hg | solution, H_2O, ions | saturated KCl | Hg_2Cl_2 | Hg | Pt.

For simplicity all ions will be assumed to be univalent.

Charge and Potential of the Polarizable Double Layer

The notion of *charge* is rather simple in that it is considered to be typical for the phase boundary between Hg and solution that no current can pass through it. By imposing a potential difference between the two Pt electrodes of cell (b) a small amount of electricity passes through the Pt to the Hg and on the other side from the calomel electrode through the liquid junction to the solution. These two amounts of electricity must be equal and of opposite sign and may be considered as the charges of the Hg and solution sides of the double layer, provided we start with an uncharged double layer. The absence of charge on the Hg can be experimentally ascertained, for according to the Lippmann relation it is characterized by a maximum in the interfacial tension of Hg.

The *potential difference* between Hg and solution is, however, not directly assessible. We know the potential difference, E, imposed on the cell, but it is composed of three contributions, i. e., the potential: Hg|solution, saturated KCl|Hg, and the diffusion potential, which cannot be separated from each other without arbitrariness. But when *changes in the potential difference*, dE, are considered, they can be located only at the polarizable interface, Hg|solution, because the potential at the other two interfaces are completely determined by the composition of the phases and these do not change measurably by the passing of the small quantity of electricity necessary to charge the double layer. So, calling the potential difference between Hg and solution, $\Delta\phi$, we have

$$d\Delta\phi = dE. \tag{1}$$

In the zero point of charge there is no double layer, but there may be and probably is a difference in potential between the two phases as a consequence of orientation of dipoles and polarization of surface atoms. Calling this potential difference χ, $\Delta\phi$ may be divided into the unknown χ and a potential difference D, directly connected with the presence of the double layer, thus

$$\Delta\phi = \chi + D \tag{2}$$

This double layer potential D is experimentally assessible according to

$$D = E - E_0. \tag{3}$$

where E_0 is the cell potential at the zero point of charge. From D and the charge density σ, the integral or differential capacity ($C_{\text{int.}}$ and $C_{\text{diff.}}$) of the double layer can be derived according to

$$C_{\text{int.}} = \sigma / D \tag{4}$$

$$C_{\text{diff.}} = \partial\sigma / \partial D = \partial\sigma / \partial E. \tag{5}$$

All this relates to the double layer between Hg and a solution of a given composition. Changing the composition of the solution one finds different relations between σ and D and usually a shift of the zero point of charge. For example, if thio-urea [5] is added to the aqueous solution the Hg must be made more negative to reach the zero point of charge. This shift amounts to 100 mv for 0.01 N thio-urea, increases to a maximum of about 450 mv, and is directly proportional amount of thio-urea adsorbed on the Hg.

With the small amounts of thio-urea involved it is inconceivable that the diffusion potential changes by more than a few millivolts. Consequently the change in E_0 may be considered here as a change in

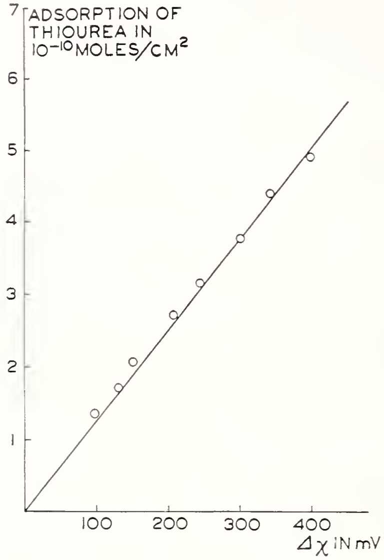

FIGURE 22.1. *Adsorption of thiourea in the zero point of charge plotted against the shift in* χ.

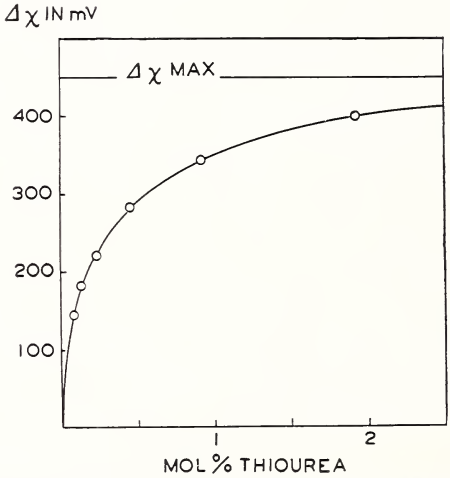

FIGURE 22.2. *Shift in* χ *as a function of the concentration of thioureo.*

the χ potential caused by the oriented adsorption of thio-urea (or by the replacement of oriented water by thio-urea). This is illustrated in figures 22.1 and 22.2.

Although for changing composition our arguments are not as conclusive as for constant composition, involving as they do an assumption about the diffusion potential, there are many cases like that just cited, where the shift in E_0 is so large and the concentrations involved so small, that one may confidently identify the change in E_0 with a change in χ potential.

Charge and Potential of the Reversible Double Layer

Next, we shall consider the reversible double layer. The galvanic cell which was indispensible in the polarizable case could be omitted here, because the double layer is not supposed to be influenced by a certain amount of electricity passing through it. We might, therefore, study the double layer of AgI in an aqueous suspension without any electrical attachment whatever. The advantage of using the cell described above lies in underlining the analogy between the two systems considered.

The emf of the AgI cell can as in the case of Hg be divided into several potential jumps; i. e., Ag|AgI, AgI| solution, the diffusion potential, saturated KCl|Hg and Hg|Ag. Of these only the one at the AgI| solution interface and the diffusion potential are variable, and as with the Hg case there are many variations of the total potential which can be ascribed nearly exclusively to variations at the boundary between AgI and solution. When the solution contains a certain amount of electrolytes, say in a concentration of 0.1 N or higher, the concentration of Ag^+ or I^- ions can be changed by several decades without practically influencing the total amount of electrolyte.[3] These changes in Ag^+ or I^- ions will therefore not affect the diffusion potential, but the potential difference between AgI and solution will vary according to the Nernst equation. In these circumstances

$$dE = d\Delta\phi = \frac{RT}{\mathbf{F}}\, d \ln a_{\mathrm{Ag}^+} = -\frac{RT}{\mathbf{F}}\, d \ln a_{\mathrm{I}^-}. \tag{6}$$

The notion of *charge* of the double layer on AgI is less obvious than that on Hg. Experimentally we can only determine adsorption of *salts* on the phase boundary, and it seems artificial to assign one of the ions to the solid phase and the other to the solution. Nevertheless of all the ions present in the solution Ag^+ and I^- take a very special position. Only salts containing Ag^+ or I^- ions can modify the potential difference according to eq (6). They appear to be more strongly adsorbed than other salts. They are the only ions which can be incorporated into or withdrawn from the lattice, and the good reversibility of the AgI electrode proves that this process runs easily. It seems reasonable, therefore, to assume that adsorbed Ag^+ or I^- ions are incorporated in the lattice and that all the other ions remain in the solution phase.

For double layers of the reversible type on other substances, analogous suppositions about the charge should be made. Reversibility means that the transition of the potential determining ions from the lattice to the solution and *vice versa* is unhampered. The charge of the solid phase arises therefore from the adsorption of these ions (e. g., Ag^+ and halide ions on silver halides; OH^- ions, H^+ ions and metal ions on oxides and hydroxides; metal ions and electrons on metals; etc.).

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[3] The solubility product of AgI is only 10^{-16}.

The charge density of the double layer on AgI is then

$$\sigma = e(\Gamma_{Ag^+} - \Gamma_{I^-}), \tag{7}$$

where Γ_{Ag^+} and Γ_{I^-} represent the number of ions adsorbed per square centimeter.

First, this hypothesis defines a *zero point of charge* which can be used as a point of reference for the double layer potential. According to different methods [6, 7] this zero point of charge is found in aqueous solutions at a silver ion concentration of $10^{-5.6}$ *N*, thus rather asymmetrically, as the point of equivalence is at $c_{Ag^+} = c_{I^-} = 10^{-8}$ *N*.

Second, adsorption isotherms for Ag^+ or I^- can now be converted with the help of (6) and (7) into relationships between charge density σ and double layer potential *D*.

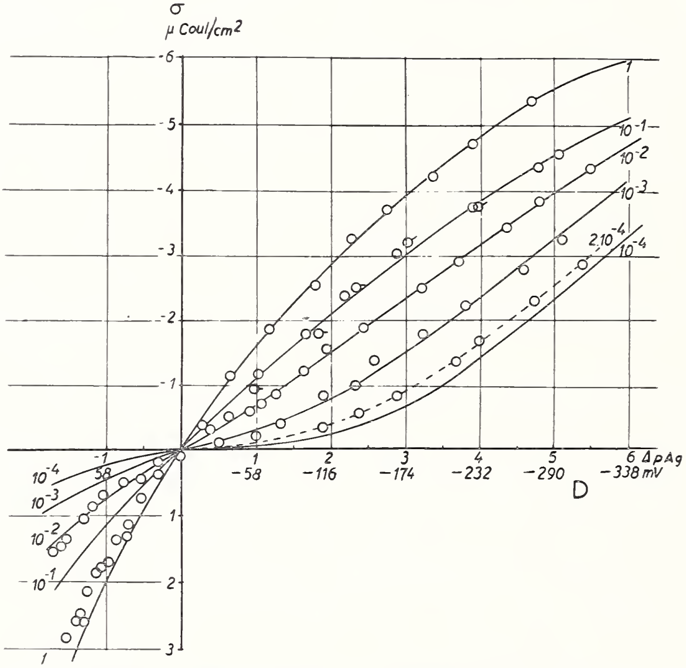

FIGURE 22.3. *Adsorption of* NaI *and* $AgClO_4$ *or* $AgNO_3$ *on* AgI *expressed as charge per square centimeter against the double-layer potential D in aqueous solutions.*

According to eq (3,6) there is a direct relation between *D* and the pAg (= −log C_{Ag}) of the solution. E. L. Mackor, Rec. trav. chim. (1952.; J. A. W. Van Laar, thesis, Utrecht).

○, Points in $NaClO_4$ solution, ○-, points in 0.1 *N* in $NaNO_3$ solution. The drawn curves refer to measurements by J. A. W. Van Laar in KNO_3-$NaNO_3$, 1:7 (Thesis, Utrecht).

For illustration a number of such $\sigma - D$ relationships are given in figure 22.3.

It should be realized, however, that the choice of eq (7) for the charge density cannot be a universal one. As soon as Ag^+ or I^- play a part in formation of the solution side of the double layer, they will form a part of the analytically determined adsorption Γ, without giving rise to a charge of the AgI. Suppose, for instance, that in the zero point of charge (obtained by a suitable solution of $AgNO_3$) more $AgNO_3$ is added to the solution. The surface potential will become more positive according to (6), silver ions will be adsorbed and charge the surface, but at the same time some silver ions in the solution will be pushed away from the surface by electrostatic forces. Consequently,

$$\sigma > e(\Gamma_{Ag^+} - \Gamma_{I^-}). \tag{8}$$

An even more extreme case is formed by a mixture of pure AgI and pure water. We do not have available any means to determine an adsorption in this case, so $\Gamma = 0$ but as the solution contains equivalent amounts of Ag^+ and I^- and the equivalence point and the zero point of charge are not coincident the surface will be charged by I^- ions, which are compensated in the solution by Ag^+.

Equation (7) as a means of defining the charge density of the surface can therefore be applied only when a sufficient excess of ions is present in the solution so that the part of the Ag^+ or I^- in the solution side of the double layer is negligible. If this is not the case, more detailed knowledge about the structure of the double layer is necessary to determine σ from the analytical adsorption of Ag^+ and I^- ions.

Free Energy of the Double Layer

A phase boundary can be considered to be the seat of a certain amount of free energy and this surface free energy is in part due to the presence of a double layer. When specific adsorption is absent, the free energy G_s of the double layer can be described by the Lippmann relation:

$$\frac{\partial G_s}{\partial D} = -\sigma \tag{9a}$$

or

$$G_s = G_s(\sigma = 0) - \int \sigma dD. \tag{9b}$$

Now it is evident that the free energy of the phase boundary is a completely determined quantity and its value cannot be influenced by uncertainties that may be present in the quantities σ or D. An analysis of the thermodynamics leading to the Lippmann relation is therefore necessary. It leads to the conclusion that for the polarizable interface

$$\frac{\partial G_s}{\partial E_{cell}} = -\sigma \tag{10}$$

and for the reversible interface

$$\frac{\partial G_s}{\partial \mu_{AgNO_3}} = -(\Gamma_{Ag^+} - \Gamma_{I^-}), \tag{11}$$

where μ_{AgNO_3} is the thermodynamic potential of $AgNO_3$. The relations (10) and (11) contain only measurable quantities and are therefore free from the ambiguities mentioned above.

The change in free energy G of the polarizable cell (b) can at constant temperature, pressure and composition be represented by

$$dG = E_{cell}\, dQ + G_s d\omega$$

where Q is the charge flowing through the cell, G_s the free energy of the interface per cm^2 and ω the interface between Hg and solution.

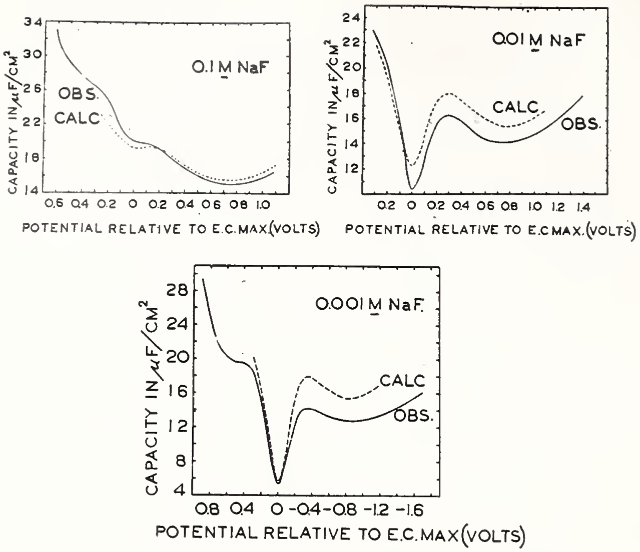

FIGURE 22.4. *Differential capacity of the double layer calculated by Grahame.*

The capacity of the nondiffuse part of the double layer is taken from figure 22.6.

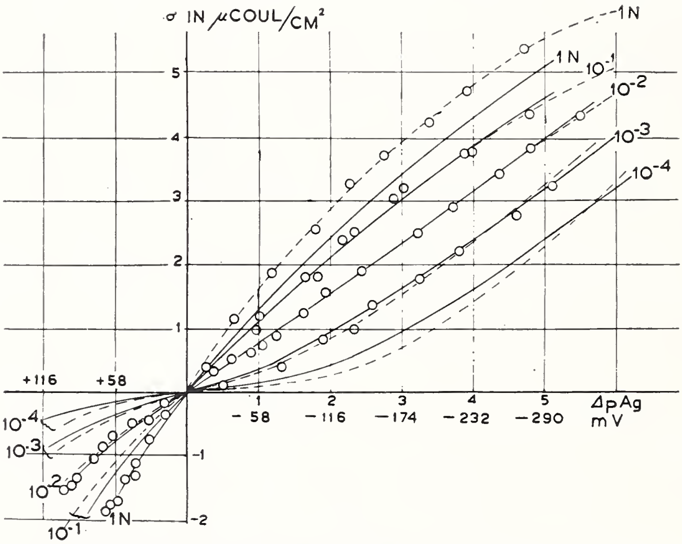

FIGURE 22.5. *Comparison of experimental and calculated relations between charge and potential.*

Capacity of the molecular condenser taken from figure 22.7. Superficial charge σ against double layer potential: ----------------, experimental: ________________, calculated.

Subtracting $d(E_{\text{cell}} \cdot Q)$ from both sides and applying a well-known property of a total differential, we find

$$d(G - E_{\text{cell}} Q) = -Q\,dE_{\text{cell}} + G_s\,d\omega$$

$$\left(\frac{\partial G_s}{\partial E_{\text{cell}}}\right)_{\omega} = -\left(\frac{\partial Q}{\partial \omega}\right)_{E} = -\sigma. \qquad (10)$$

The change in free energy of a suspension of AgI in water containing $AgNO_3$ and of course a slight amount of dissolved AgI can be expressed, neglecting the dissociation of the water which is immaterial to our problem, at constant temperature and pressure by $dG = \mu_{H_2O} dn_{H_2O} + \mu_{Ag^+} dn_{Ag^+} + \mu_{I^-} dn_{I^-} + \mu_{NO_3^-} dn_{NO_3^-} + G_s d\omega$. Subtracting $d(\mu_{Ag^+} n_{Ag^+} + \mu_{I^- n} n_{I^-} + \mu_{NO_3^-} n_{NO_3^-})$ from both sides, applying the condition of electroneutrality, $n_{Ag^+} = n_{I^-} + n_{NO_3^-}$, the condition of saturation with AgI, $\mu_{Ag^+} + \mu_{I^-} = \text{const.}$ and the equation $\mu_{Ag^+} + \mu_{NO_3^-} = \mu_{AgNO_3}$ we obtain $d(G - \mu_{Ag^+} n_{Ag^+} - \mu_{I^-} n_{I^-} - \mu_{NO_3^-} n_{NO_3^-} = \mu_{H_2O} dn_{H_2O} - (n_{Ag^+} - n_{I^-}) d\mu_{AgNO_3} + G_s d\omega$ and consequently

$$\left(\frac{\partial G_s}{\partial \mu_{AgNO_3}}\right)_{\omega, n_{H_2O}} = -\left[\frac{\partial (n_{Ag^+} - n_{I^-})}{\partial \omega}\right]_{n_{H_2O}, \mu_{AgNO_3}, \mu_{H_2O}} = -(\Gamma_{Ag^+} - = \Gamma_{I^-}). \tag{11}$$

Interpretation of Charge and Potential of the Double Layer

After having shown how charge and potential of the double layer are obtained it is necessary to indicate how they may be interpreted. With a double layer on a metal, the charge on the metal side is a surface charge. The charge in the solution, which is carried by ions is a space charge the extension of which is governed by the opposing tendencies of diffusion and electrical attraction. With double layers on other solid substances the charge of the solid phase is usually assumed to be a surface charge although recently Grimley and Mott [18] suggested that this charge may also have the character of a space charge. Whatever the situation near the interface may be, it will be clear that the structure of the double layer far from the interface can be described by using macroscopic properties of the phases as is done in Gouy's [9] and Chapman's [10] theory of the diffuse double layer. The uncertainties about the detailed structure near the phase boundary may be avoided by the conception of the "molecular condenser", introduced by Stern [11]. This molecular condenser also serves to correct for some all too obvious deviations from ideal behavior of the solutes near the interface.

To show the extent the Gouy-Stern theory may explain experimental data, we give a few results obtained by Grahame [12] for the double layer between Hg and solutions of NaF and results obtained by Mackor [13] and the writer for the double layer on AgI. For the first, a comparison is made between measured and calculated capacities of the double layer, in the second experimental and calculated surface charges are shown as a function of the double layer potentials. For both the double layer was represented by a diffuse Gouy-Chapman layer, followed immediately by a molecular condenser. The potential in the diffuse layer was assumed to obey the Poisson-Boltzmann equation

$$\nabla^2 \psi = -\frac{4\pi}{\epsilon} \sum_i i n_i z_i e \ \exp.\ (-z_i e \psi / kT)$$

where ∇^2 is the Laplace operator, ϵ the dielectric constant of the solution, n_i the ionic concentration and z_i the ionic valency. The capacity of the molecular condenser was assumed to be a certain function of the charge of the double layer as shown in the figures 22.6 and 22.7.

Summarizing, one finds that the charge of the double layer and the extra potential difference it superimposes upon the inassessable potential difference χ existing already between the uncharged phases are known.

Theory explains this extra potential difference by localizing part of it as a diffuse double layer in the solution phase, possibly another part as a diffuse layer in the second phase and a third part somewhere near the phase boundary. For this third part it is assumed only that the potential difference is completely determined by the charge. So both in the empirical and theoretical approach, detailed statements on the potential difference between different phases are avoided as they should be.

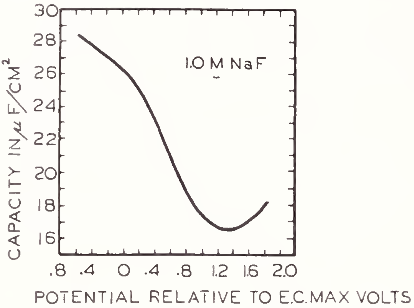

FIGURE 22.6. *Differential capacity of molecular condenser on mercury derived from the experimental curve at* 1.0 *M* NaF *and used to calculate the capacities at lower concentrations of* NaF (*see fig.* 22.4).

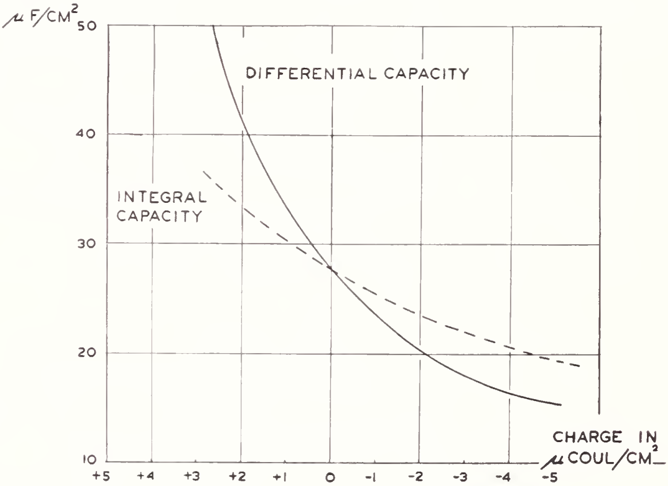

FIGURE 22.7. *Capacity of molecular condenser on silver iodide used to calculate the curves of figure* 22.5.

Can the χ Potential in Principle be Known?

As there seems to be no direct experiment which can lead to a knowledge of the χ potential, it may be asked whether this notion should not be completely eliminated from our considerations.

The present writer answers this question in the negative. In the first place, to avoid speaking of a potential difference between phases would force us to clumsy and unnecessary circumlocutions. Moreover, although we do not yet possess the means of determining the χ potential it is a well defined quantity. If we were better able to handle the wave equation it would be possible to solve the problem of the distribution of particles and charges in the region of the phase boundary and hence the average potential at every point of space should be determined.

Although in each phase this average potential is a very variable function of phase, it could be averaged over large enough regions of the phase and thereby give a value for the potential of the phase.

Electrokinetics and the ζ Potential

A different method of attack on the problem of double layer is found in electrokinetic experiments, wherein shearing motions of the double layer along the phase boundary are studied. This subject, which of necessity is concerned with irreversible processes, is more difficult than the equilibrium situation. Even if we disregard the possible influence of the roughness of the phase boundary [14], the uncertainty about values of viscosity and dielectric constant in the double layer introduces uncertainties in interpretations of electrokinetic effects.

The basic equation for electro-osmotic velocity along a plane wall formulates the equality of the force on the electric charge and the viscous drag of the liquid:

$$\frac{d^2v}{dz^2}=-\rho E=\frac{\epsilon}{4\pi}\frac{d^2\psi}{dz^2}E, \tag{12}$$

where z is the coordinate perpendicular to the phase boundary, v the velocity of the liquid, ψ the potential in the double layer and E the field strength along the phase boundary.

Usually the viscosity and the dielectric constant are considered to be constant up to a plane, where shearing just begins to be possible. Integration of eq (12) leads then to the Helmholtz-Smoluchowski equation:

$$\frac{v}{E}=\frac{\epsilon\zeta}{4\pi\eta}, \tag{13}$$

where v is the velocity of the liquid far from the phase boundary and ζ the potential at the plane of shear, the potential of the liquid far from the phase boundary being taken as zero.

When one drops the hypothesis of the constancy of ϵ and η the integration leads to

$$\frac{v}{E}=\frac{1}{4\pi}\int\frac{\epsilon}{\eta}d\psi. \tag{14}$$

Guggenheim [15] has remarked that it would be more natural to calculate $\int\epsilon d\psi$ or $\frac{1}{4}\pi\int\epsilon d\psi$ from electrokinetic experiments than to calculate ζ. However, when one doubts the constancy of ϵ, it seems consistent to doubt that of η as well and therefore turn to eq (14).

This equation, although correct, is rather unfruitful. It gives only some information on the zero point of charge, for, whatever the values of ϵ and η, the integral in (14) is zero when $d\psi$=zero, which implies zero charge of the double layer.

For double layers which are not extremely compact, that is for double layers in dilute solutions, the assumption of constant ϵ and η over the major part of the double layer seems justified. In these cases the ζ-potential may not only be calculated from (13), but it may be interpreted as the potential drop over a large part of the double layer in the solution. It is therefore reasonable to compare ζ with the total potential of the double layer and to expect ζ to be somewhat (or much) smaller than D. Such a comparison would become almost meaningless when electrokinetics are expressed through

$$\int \epsilon d\psi \text{ or } \int (\epsilon/\eta)\, d\psi.$$

Unfortunately the cases where D and ζ have both been determined on one and the same object are very rare and as far as modern accurate work is concerned nearly restricted to some experiments on glass by *Rutgers* [16] and on AgI by *Troelstra* [17].

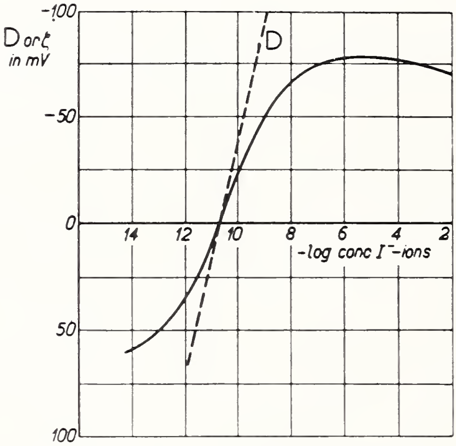

FIGURE 22.8. *D and ζ of silver iodide against the logarithm of the* I^- *ion concentration in the solution.*

From experiments by Troelstra we derive figure 22.8, in which it is seen that the zero point of charge and that of electrokinetic motion coincide and that, at least near this zero, ζ seems to be a nearly constant fraction of D. For higher potentials it is difficult to derive reliable values of ζ from the electrophoretic velocity [18] although one would expect that with D continuously rising ζ would rise less and less because at high potentials the double layer gets more compressed and for the greater part in regions with high viscosity.

Turning to the theoretical interpretation of the structure of the double layer, one would expect ζ to resemble especially that part of D that, according to theory, is located in the liquid phase. Until now such comparisons have met with little success probably because adequate experimental material is lacking. It would be very much worth while to try to fill this gap in our knowledge.

References

[1] E. J. W. Verwey and J. Th. G. Overbeek, Theory of the stability of lyophobic colloids (Amsterdam, 1948).

[2] E. A. Guggenheim, J. Phys. Chem. **33,** 842 (1929); Trans. Faraday Soc. **36** 139, (1940); Thermodynamics, especially chap. 10, (North-Holland Publishing Co., N. Y.; Amsterdam, 1949).

[3] For a more extensive treatment see J. Th. G. Overbeek in H. R. Kruyt, Colloid Science 1, Chap IV, Elsevier, Amsterdam (in press).

[4] E. L. Mackor, Rec. trav. chim. **70,** 841 (1951).

[5] A. Frumkin, Ergebn. exakt. Naturw. **7,** 235 (1928). See also E. L. Mackor, Rec. trav. chim. **70,** 841 (1951).

[6] J. A. W. van Larr, Thesis, Utrecht (to be published).

[7] I, M. Kolthoff and J. J. Lingane, J. Am. Chem. Soc. **58,** 2457 (1936).

[8] T. B. Grimley and N. F. Mott, Discussions Faraday Soc. **1,** 73 (1947).

[9] T. B. Grimley, Proc. Roy. Soc. London A 201, 40 (1950). G. Gouy, J. physicuq (4) 9, 457 (1910). Ann. d. phys. (9) 7, 129 (1917).

[10] D. L. Chapman, Phil. Mag. 6 **25,** 475 (1913).

[11] O. Stern, Z. Elektrochemie **30,** 508 (1924).

[12] D. C. Grahame, Chem. Revs. **41,** 441 (1947).

[13] L. E. Mackor, Rec. trav. chim. **70,** 841 (1951). J. Th. G. Overbeek and L. E. Mackor, Comptes rendus de la troisiéme rèūnion du Comité International de Thermodynamique et de cinétique electrochimique.

[14] See J. J. Bikerman, Surface chemistry for industrial research, New York 386, 403 (1947). J. Phys. Chem. **46,** 724 (1942).

[15] E. A. Guggenheim, Trans. Faraday Soc. **36,** 139 (1940).

[16] A. J. Rutgers, Physica **5,** 46 (1938); Nature **157,** 74 (1946).

[17] S. A. Troelstra and H. R. Kruyt, Kolloid. Z. **101,** 182 (1942).

[18] J. Th. G. Overbeek in H. Mark and E. J. W. Verwey, Advances in Colloid Science III, New York **97ff,** 1950.

Discussion

Dr. J. O'M. Bockris, Imperial College of Science and Technology, London, England: I should like to congratulate Prof. Overbeek on his attitude towards this subject, because he is less pessimistic than some workers. Lange has also tried to make a more rational approach to the definition of potentials at a metal-solution interface. It is now possible to calculate the dielectric constant of the solution as as function of potential, and taking these revised values into account makes quite appreciable differences to the calculated charge in the diffuse layer.

Dr. J. Th. G. Overbeek: I think you refer to the new calculation by Grahame.

Dr. Bockris: I am referring primarily to some calculations we have been doing recently (Bockris et al, Trans. Faraday Soc. 47, 756 (1951).

Dr. Overbeek: Well, of course it might affect the innermost parts of the double layer.

Dr. Bockris: The dielectric constant in the Helmholtz layer turns out to be a good way off the minimum saturation value, expect at very high electrode potentials. In the diffuse layer, the mean dielectric constant may be as low as 45.

Dr. G. Scatchard, Mass. Institute of Technology, Cambridge, Mass.: Were you saying χ is independent of the $AgNO_3$ concentration?

Dr. Overbeek: That was the χ between the $AgNO_3$ solution and the gas phase above the $AgNO_3$, and it was onl ydependent upon the $AgNO_3$ when its concentration came in the neighborhood of 1 eq/liter.

Dr. Scatchard: What is the order of magnitude of conductance of AgI?

Dr. Overbeek: These measurements are done on suspensions of fairly small particles. It may be they are less regularly formed than larger pieces and that their conductance is larger. We find, for instance, that the order of magnitude is 10^{-6} ohm^{-1} cm^{-1}, perhaps somewhat lower. We know this is the order of magnitude because we have special difficulties in doing electrokinetic measurements on AgI, which indicate a conductance of the same order as that of distilled water. We cannot make a direct measurement of the conductance without treating the AgI so that it is not a representative sample.

Dr. T. Shedlovsky, Rockefeller Institute for Medical Research, New York, N. Y.: The AgI is not on the electrode as a continuous film?

Dr. Overbeek: No, you can only determine the absorption of the AgI when the surface is very large. We use AgI as a fine suspension or as a collodial solution. It is for simplicity that I have drawn the AgI to be present on the electrode but for the whole thermodynamics of the cell it is not essential for the AgI to be attached to the Ag electrode.

Dr. Shedlovsky: What is affecting the potential of the Ag electrode, absorption of the Ag or of the iodide?

Dr. Overbeek: We can argue that the potential difference of the cell when it is reversible depends upon the cell reaction which apart from the process at the liquid junction is given by,

$$\begin{gathered}\mathrm{Ag(metal)} + \mathrm{I}^{-}(\mathrm{conc.}=c) + \mathrm{HgCl(solid)} \rightarrow \\ \mathrm{AgI(solid)} + \mathrm{Cl}^{-}(\mathrm{saturated}) + \mathrm{Hg(metal)}.\end{gathered}$$

The emf of this cell changes only with changes of the concentration of I^- ions. The potential difference between Ag and AgI, both being solid substances with a given chemical composition, is constant. If I measure potential differences between Ag and Hg, I know that, apart from a constant, it is equal to the potential difference between Ag electrode and the solution, and consequently apart from another constant, to the potential difference between AgI and the solution. One can picture that most easily. That is what I have done on the blackboard by just interposing AgI between the Ag and the solution, but it is not necessary for the kind of measurement we have done. I think the simplification is not essential.

Dr. Shedlovsky: Isn't the function of AgI simply to fix the Ag ion activity and so make it an iodide electrode?

Dr. Overbeek: I quite agree with you there; yes.

Dr. J. V. Petrocelli, The Patent Button Co., Waterbury, Conn.: As I see it, at present, we have a fairly good picture of the double layer at the Hg metal electrode. How are we going to picture, kinetically, the Ag electrode? In other words, Hg has these ions absorbed very close to it. Now, if you have a piece of Ag in the solution, what do you have on the surface, solid particles of AgI or Ag ions?

Dr. Overbeek: You mean the silver electrode I have used in my experiment?

Dr. Petrocelli: Yes. Can the mechanisms you have described be applied to the metal? When we are talking about the double layer, we would like to see a picture of the orientation of the ions and their position on the metal also.

Dr. Overbeek: I have tried to make not a picture of the double layer on the silver but on the silver iodide. The silver electrode only comes in as a means to bring electric charges in the form of Ag^+ ions to or from the solution.

23. Some Stepping Stones on the Path to the True Explanation of the Mechanism of Overvoltage

By Alfred L. Ferguson [1]

There are two good reasons why this topic is appropriate at a symposium on electrochemical constants. First, during the last twenty years progress has been made in the discovery and elimination of factors responsible for much of the uncertainty in measurements of overvoltage. Second, it has been a field of investigation that illustrates to a remarkable degree the point that every conceivable means must be used to test the proposed equipment to assure that it is telling the truth.

A few illustrations of this are worth while. Max Le Blanc [1] [2] carried out extensive and carefully controlled experiments on polarization and overvoltage with a moving-coil oscillograph.

Figure 23.1 shows a set of his curves. These curves, of which *abc* is a section, represents changes in potential across the total cell, including the IR through the solution and the sum of the electrode potentials. At *a* the circuit was closed and part *ab* shows the manner in which the potential increased during about 0.02 sec. At *b* the circuit was opened, and part *bc* shows the manner in which the potential decreased during about 0.02 sec. The resistance through the cell was measured and the way the IR potential changed with time is indicated by lines $a'x—xb'—b'x'$. If the distance $a'x$ be subtracted from the beginning of *ab*, and $b'x'$ from the beginning of *bc*, the remainders should show the manner in which the potentials due to polarization of the electrodes change with time on charge and discharge. Since the potential drop through the solution is of a purely IR nature it should rise and fall vertically as it does. The significant point is that there is no break in the *ab* curve as it passes through the line xb' or in *bc* as it passes through *d*. This would indicate that the portions of the electrode polarization above xb' on charge and below *d* on discharge are also due to a resistance. Thus his work appeared to provide convincing support of the then popular "transfer resistance" theory of polarization.

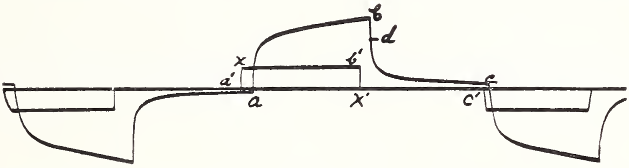

Figure 23.1. *Charge and discharge oscillogram typical of many obtained by LeBlanc with a moving-coil oscillograph.*

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[1] Department of Chemistry, University of Michigan, Ann Arbor, Mich.
[2] Figures in brackets indicate literature references on p. 240.

The most important difficulty, however, in this work is that Le Blanc failed to appreciate that the operation of his moving coil galvanometer required such a high current that the polarization phenomenon he was attempting to measure was itself polarized. Thus, the method was discarded, and was not revived until the vacuum tube became available for amplification purposes.

The first scientist to revive the moving coil method through the use of a vacuum tube amplifier was Dr. Homer Denison Holler [2]. Like Le Blanc, Holler obtained photographs of complete charge and discharge cycles. The outstanding importance of this work, like that of Le Blanc, was its apparent support for the "transfer-resistance" theory of overvoltage. However, like the equipment of Le Blanc, it did not tell the truth.

Figure 23.2 is a sample curve taken from the publication by Holler. The cell in this case consisted of two bright Pt electrodes in H_2SO_4; the current was 0.5 amp; the time interval of charge and discharge was 0.13 sec. He considered that the curves at the start of charge and discharge were vertical and concluded that "this instantaneous change was doubtless due to resistance."

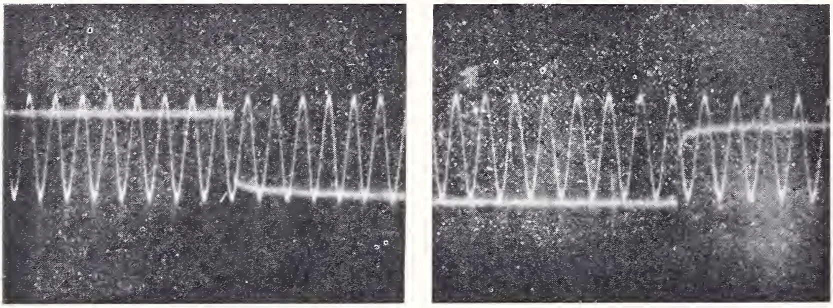

Figure 23.2. *Curve showing variation in potential of a bright platinum electrode in sulfuric acid during the closing and opening of the circuit, obtained with a moving-coil oscillograph.*

Holler placed the reference electrode near the electrode to be measured but between the anode and cathode. Thus, an IR drop through the solution was included in the measured values. Holler mentioned that this was true and pointed out that there might be a resistance at the electrode-electrolyte interface of the nature of "transfer resistance" as proposed by Newbery. Later the present author showed that, if the reference electrode is placed *behind* the electrode being measured, and, if the film speed is greatly increased, there is no vertical section to the curves, and therefore no potential of an IR nature at the electrode-electrolyte interface.

Most of the basic work done on polarization may be classed under two headings: (1) direct, and (2) commutator. The primary distinction between them is that by the former, measurements are made with current flowing, while by the latter, measurements are made with the current interrupted. It was universally found that the direct method invariably gave the higher values.

The direct method generally involves a reference electrode placed in front of the electrode, the potential of which is measured, whereby the potential might contain an IR drop through the solution between the electrodes. If true, then that IR would completely disappear instantly when the circuit is opened, while the true polarization would decrease more or less gradually. Those supporting the commutator method contend that the rapid drop is due to this IR plus a possible IR through some part of a film at the electrode-electrolyte interface, and explains why the direct method gives the higher values.

By the commutator method there could be no IR included in the measured value since no current is flowing. However, it had been demonstrated that directly after the circuit is opened even the true polarization drops exceedingly rapidly, and those who support the direct method maintain that the commutator method gives lower values because a portion of the true polarization has disappeared before the measuring equipment can detect it. The major activities during the latter part of the last century and to some extent to the present, therefore, resolved themselves into the development and perfection of equipment and methods which would decide which of the two methods gives the true values for polarization.

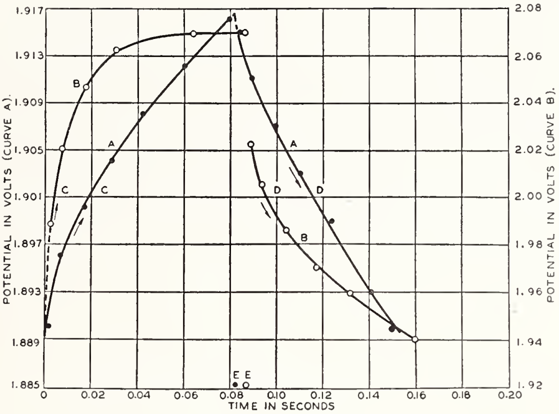

FIGURE 23.3. *Curves showing the change in potential with time both on charge and discharge obtained with a commutator-potentiometer combination.*

● *A*=expt. 5, table 1; ○ B=expt. 9, table 1; *C*=charge; *D*=discharge; *E*=end of charge and beginning of discharge.

One trend was to devise a commutator that would permit extrapolation of the increasing value on charge to the end of the charge period, and permit extrapolation of the rapidly decreasing potential on discharge back to the beginning of the discharge interval. If both extrapolations gave the same value, it was assumed to be the correct value. It has been demonstrated that such an end cannot be attained by a commutator involving brushes, and it is questionable whether the true value can be obtained by any similar method.

The curves of figure 23.3 are typical of those obtained with a rather complex commutator arrangement by which it was possible to simultaneously secure sufficient points on both charge and discharge cycles. The left parts are for the charge intervals and the right for the discharge. The first value on charge was obtained 0.002 sec after the circuit was closed; the first value on discharge was obtained about 0.002 sec after the circuit was opened, yet the potential had dropped about 38 mv during this interval of open circuit or nearly one-third of the total polarization. It was not possible, however, from these curves to say whether this difference is due to an IR drop or the very rapid fall of a true polarization potential.

Another point in connection with any interrupter method is well demonstrated here by a comparison of the charge curves in these two sets of curves. The only difference between the two is the charging current density (c.d.). For the *a* set the c.d. was 90 ma/cm^2 and for the *b* set 9 ma/cm^2. At the former the charge potential had reached its equilibrium value, while in the same time interval, about 0.085 sec, the value reached at the latter was distinctly less than its maximum. Therefore, whatever the type of interrupter method, the charge interval must be sufficiently long to allow the electrode to reach its equilibrium value.

The other approach has been to devise equipment that would determine whether the final charge values given by the commutator and direct methods are the same; also to determine whether the direct method must inevitably contain an IR drop.

The most ardent supporter since 1914 [3] of the theory that a potential of an IR nature existed at the electrode-electrolyte interface is Dr. Edgar Newbery; in fact, it is frequently referred to as the Newbery "transfer-resistance" theory, though the existence of such a resistance was proposed by Fechnor [4] in 1831 and named by him "transfer resistance."

All of Newberry's early efforts were concentrated on perfecting a commutator that would prove his ideas. When the commutator was demonstrated to contain inherent errors, he adopted the cathode-ray oscilloscope [5]. Based upon his curves, he makes the following statements: "The most striking feature of each of these curves is the clear gap which appears between the upper and lower sections. The existence of this gap provides conclusively that there is an instantaneous fall of potential at the electrode the moment the exciting current is interrupted. It is obvious that this rapid fall must be due to the presence of a passive resistance, transfer resistance, between the electrode and the electrolyte." It has been shown since, however, that errors were inherent in his cathode-ray oscillograph.

Up to about 1930 three major questions remained, namely, (1) Which method, if either, gives a true measure of polarization potential? (2) Is it possible for both methods to give the same value and the true value? (3) Is there such a thing as "transfer resistance"? The equipment required to answer these questions is one that would photograph potential changes during complete charge and discharge cycles, and one that would distinguish between a potential of an IR nature and a true polarization.

Eliminating all details as to equipment involved, figure 23.4 shows curves typical of dozens obtained through its use.

The curves marked K represent changes in cathode potentials during complete charge and discharge intervals. The line marked K^1 shows the stable equilibrium potential obtained for the same system under the same conditions but by the direct method. These curves demonstrate that both methods give the same value under proper conditions.

The I and I^1 curves are given by the corresponding two methods when the circuit is closed and opened through a pure resistance. If the equipment was telling the truth, these charging and discharging curves should be vertical lines, since they represent purely IR potentials; but since they are not, it means that this equipment was not telling the truth in this respect. It did, however, show that if the conditions are proper, the two methods give the same values. It was still necessary to develop equipment that would give a vertical line for an IR type of potential and a curved line for a true polarization.

As the result of cooperation from the Westinghouse Research Laboratories and new improvements in direct-current amplifiers, the necessary equipment was finally assembled.

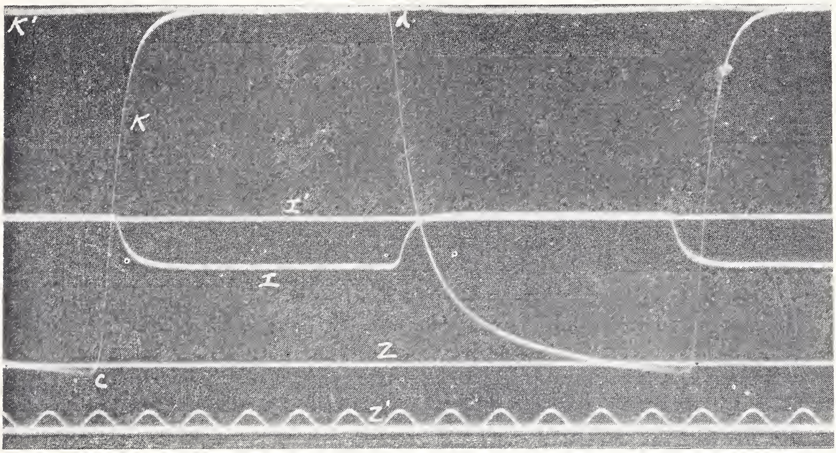

Figure 23.4. *Charge and discharge curves by both the direct and commutator methods through the use of the Westinghouse Oriso galvanometer oscillograph.*

Figure 23.5 is typical of hundreds of photographs taken by this equipment. These happen to be curves for a Ni cathode. Curves for anodes are similar and are not given here.

To obtain the curves in figure 23.5, a constant current was passed through the cell until the potential had reached a stable value, which took a different length of time for each c. d. In some cases more than an hour was required. A record of the stable value is given by the upper-left horizontal line *I*. The charging circuit was then opened and the decay of this potential photographed (curve *K*). Immediately following this, the potential representing only the IR drop through the solution between the anode and cathode was recorded and is represented by the line *I*. Arrangements were such that the start of this line could be superimposed upon the horizontal portion of the *K* curve, and the circuit opened at the same spot as for the *K* curve. The line drops vertically, as it should, since it is a pure IR potential, to the zero current position indicated by the lower horizontal portion marked *I*. As soon as possible a third potential curve was recorded; this was a combination of the same IR through the solution and the cathode potential already photographed. It is represented by K_i. The start

Figure 23.5. *Overvoltage decay curves for a nickel cathode.*

of this curve was also superimposed upon the K and I curves, and the circuit was again opened at the same spot. The line dropped vertically a distance equal to the IR portion, which, of course, was the same as the I curve, then continued to drop, giving a curve identical with the K curve.

The I curve demonstrates that the equipment does give a vertical line for the disappearance of a potential of an IR nature. The K_i curve demonstrates that the electrode potential plus an IR potential shows a vertical drop identical to an IR which it contains, then falls off in exactly the same manner as the curve having only a polarization potential, K.

Since the potential curve K contains no vertical section, it proves that the cathode potential for this cathode and these c. d.'s, as measured by the direct method, contained no IR drop. For every metal used, either as anode or cathode, and for c. d.'s up to 30 ma/cm^2, which is as high as worked with at that time, there was no vertical section. In other words, there is no such thing as "transfer resistance", in any of this work, at least. At the same time, we believe it demonstrated that the direct method gives correct, accurate, and reproducible values for overvoltage if properly carried out.

The results of such measurements for several metals at different c. d.'s are recorded in table 1. In figure 23.5, and for all similar systems worked with, it was observed the overvoltage appeared to consist of two parts; when the circuit was first opened there was a part that dropped very rapidly, the remainder continued to drop very slowly. The values in column (2) give the total overvoltages; those in column (3) the part contained in the first, or rapid, stage. Column (4) gives a sort of average percentage that these early values are of the total. These percentages vary from 14 for Zn to 86 for smooth Pt. The most significant fact, however, is that the remaining part of the overvoltage, i. e., that which drops slowly, is independent of the c. d. for any metal. This fact becomes especially significant when one realizes that so many workers in this field attempt to relate overvoltages to the log of c. d.'s by an equation similar in form to that suggested originally by Tafel [6]: Overvoltage$=a+b \log I$.

On the basis of work done up to about 1935 the following points had been established: (1) The commutator method, using brushes, contains inherent errors. (2) The commutator method gives identical values with the direct method only if sufficient time is allowed for the potential on charge to reach a maximum stable value. (3) Overvoltage measurements may be duplicated to a few millivolts if properly carried out. (4) There is no type of IR drop in oxygen or hydrogen overvoltages on any of the ordinary metals up to 30 ma/cm^2. (5) The overvoltage decay curves are different for different metals. (6) For no metal studied are the decay curves of the anode and cathode equal or similar. (7) All hydrogen overvoltage decay curves are divided into two sections; the first part decays exceedingly rapidly, and its magnitude is a function of both c. d. and electrode material; the second part decays relatively slowly, and its magnitude is not a function of c. d. (8) The fraction that the rapidly decaying part is of the total overvoltage varies between 14 percent and 86 percent for different metals.

Attention was next directed to securing additional accurate and reproducible data that would assist in explaining mechanisms of overvoltage phenomena.

Table 1. *Summary of hydrogen overvoltage values*

Cathode	(1) Current density	(2) Total over voltage	(3) Initial over-voltage drop	(4) Percentage of total	(5) Residual over-voltage
	ma/cm^2	*mv*	*mv*		*mv*
Platinized Pt	0.485	8	0	20	8
Do	3.32	29	4		25
Do	5.58	38	7		31
Do	9.05	43	13		30
Palladium	1.00	46	20	65	26
Do	2.08	62	33		29
Do	3.85	81	52		29
Do	5.43	93	61		32
Do	8.94	111	79		32
Do	13.54	127	95		32
Smooth Pt	2.20	140	120	86	20
Do	5.02	162	138		24
Do	7.26	162	142		20
Gold	6.75	484	128	26	356
Do	8.87	485	126		359
Do	12.26	491	131		360
Antimony	0.460	525	27	17	498
Do	1.55	579	75		504
Do	2.95	615	105		510
Do	4.55	617	117		500
Do	5.80	632	135		497
Do	7.88	652	154		498
Zinc	1.05	897	92	14	805
Do	1.24	901	97		804
Do	2.84	939	127		812
Do	3.33	939	129		810
Do	4.62	942	140		802
Do	7.15	985	175		810
Silver [a]	2.40	480	260	57	220
Do [a]	4.40	506	295		210
Do [a]	6.50	520	310		210
Nickel	3.10	494	315	65	179
Do	4.09	509	332		177
Do	5.72	520	346		174
Cadmium [a]	1.79	1,078	590	55	488
Do [a]	2.42	1,116	620		496
Do [a]	3.00	1,117	625		492

[a] Curves still have a distinct slope; values correspond to a time ⅙ second after the interruption of the charging circuit.

During the early experiments on overvoltage, for currents below the decomposition potential, it was observed that the stability of the electrode potential was sensitive to agitation of either the electrode or solution. Accordingly, several series of experiments were designed to produce conditions that would influence the rate of diffusion of active material away from or toward the electrode-solution interface.

For the first series, the cathode was charged at some definite c. d. until a stable potential was obtained; the circuit was then opened and the cathode potential allowed to decay. The solution had been saturated previously with H_2. The experiment was then repeated under the same conditions, except that the solution was agitated by H_2 bubbles. The curves in figure 23.6 are typical for several c. d.'s. For the top curve, the solution was still; for the bottom, it was agitated. Three important things are noticed: (1) with the still solution (top curve) the stable value is −0.024 v, and with the stirred (bottom curve) it is only −0.006 v; (2) the rate of discharge for the stirred solution is much greater than for the still; (3) in both, the decay curves pass through the regular values, indicated by points *b* and *d*, for the H_2 electrode in this solution, without any change whatever. In other words, whatever is producing the overvoltage potential appears to be exactly the same as that causing the regular potential and the values above and below the regular potential.

These experiments provided considerable support for our ideas that (1) hydrogen ions may be discharged at potentials more positive than the potential of the H_2 electrode in the same solution, (2) the back potential in the "residual current" range is due to the reionization of atomic hydrogen liberated at the applied potential by the "residual current", (3) the potential of the H_2 electrode is due to ionization of hydrogen atoms in the platinized Pt electrode, which atoms are maintained in equilibrium with hydrogen gas through the medium of the Pt, (4) the more negative values, in the "overvoltage region" are also produced by ionization of atomic hydrogen resulting from discharge of hydrogen ions at these more negative values, (5) the high negative values are due to inability of hydrogen atoms to escape from the electrode-electrolyte interface by (a) diffusion into the electrode, (b) diffusion into the solution, (c) combination to form molecular hydrogen, or (d) combination with the electrode material, at a rate sufficient to maintain equilibrium.

FIGURE 23.6. *Cathode overvoltage decay curves for both still and agitated hydrogen saturated solutions.*

Top line is for a still solution: stable potential −0.024 v, current density 0.454 ma. Bottom line is for the same solution but stirred; stable potential is −0.006 v, current density 0.454 ma.

In the next experiments, the solution was previously saturated with N_2, and some were stirred and others not. It is sufficient to say that these experiments lead to the same conclusions as those saturated with H_2.

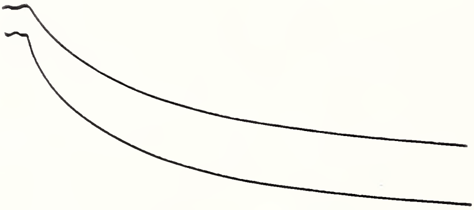

FIGURE 23.7. *Decay cathode potentials starting from stable positive values in a nitrogen-saturated stirred solution.*

For the top curve the stable cathode potential is +0.013 v at a current density of 0.459 ma. For the bottom curve the stable cathode potential is +0.003 v at a current density of 0.911 ma.

To determine whether the decay curves are any different if they start from stable potential values in the "residual current" range, curves were produced in this region and a typical set is shown in figure 23.7. These were obtained also in a N_2 saturated solution. For the top curve the stable cathode potential is +0.013 v and for the bottom +0.003 v. There is no apparent difference in the nature of these decay curves than those starting in the overvoltage range. Another point of interest is that for the top curve at c. d. 0.459 ma/cm^2 the potential is +0.013 v, or is in the "residual current" range, while, for an identical solution and all conditions the same except the solution is still, the same c. d. produces a potential in the true overvoltage region of −0.013 v. These curves are typical of many, and show there is apparently no difference between the behavior of the discharge process in the overvoltage or residual current range.

According to several theories, residual current does not discharge hydrogen ions but builds up a double electric layer producing a sort of condenser effect. Considerable work has been done to test this idea by maintaining the current constant at various values in some cases below and others above the "residual current" range, thus giving positive and negative cathode potentials. The time was varied up to 60 minutes after a stable value had been obtained. There was no further change in potential, and the discharge curves were all of the same type, for any c. d. These stable values could be duplicated to within a few millivolts. Such results show that stable values in both undervoltage or overvoltage ranges depend only upon c. d. and not on the quantity of electricity passed. In other words, active material is not stored after the potential has become stable.

In the next experiments attention was focused on the charge part of the cycle. Equilibrium values were obtained at many c. d.'s above and below the decomposition potential in still and stirred solutions, saturated in some cases by H_2 and in others by N_2. In these the current was held constant until the potential became constant. For very low currents, in some cases this required several hours. The time required decreased rapidly with increasing c. d.'s. Table 2 contains a summary of results.

TABLE 2. *Current-potential data for platinized platinum electrodes in 2 N sulfuric acid*

Current	$\log_{10}$ current	Stable polarized cathode potential			
		Hydrogen solutions		Nitrogen solutions	
		Still	Stirred	Still	Stirred
ma	*amp*$\times 10^6$	*v*	*v*	*v*	*v*
0.0020	0.30	0.000	0.000	+0.088	+0.092
.0054	.73	.000	.000	+.038	+.072
.0096	.98	−.001	.000	+.022	+.061
.0196	1.29	−.002	.000	+.015	+.051
.0468	1.67	−.005	.000	+.006	+.040
.103	2.01	−.007	−.001	.000	+.030
.132	2.12	−.008	------	−.001	------
.224	2.35	−.010	−.003	−.005	+.021
.452	2.66	−.014	−.005	−.010	+.012
.895	2.95	−.017	−.009	−.014	+.004
.911	2.96	------	------	−.016	+.003
1.30	3.11	−.019	−.012	−.017	−.001
3.85	3.59	−.028	−.022	−.027	−.016
7.73	3.89	−.035	−.030	−.034	−.026
9.25	3.97	------	------	−.037	−.030
13.5	4.13	−.043	−.039	−.042	−.037
17.5	4.24	------	------	−.047	−.042

All values reproducible to ±1 mv are referred to the H_2 electrode in the given solution. There are several things to be noted: (1) Nearly 0.01 ma may be passed through a still solution saturated with H_2 without developing more than a few tenths of a milivolt overvoltage; (2) when H_2 is bubbled through a solution previously saturated with H_2, nearly 0.1 ma may be passed before reaching 1-mv overvoltage; (3) for a solution saturated and stirred with N_2, about 1.3 ma may be passed before the overvoltage reaches 1 mv.

Some of the data in table 2, together with others, all in N_2 saturated solutions, and below the decomposition potential, are represented as curves in figure 23.8. The vertical line on the right represents the potential of the H_2 electrode in this solution. These are regular decomposition potential curves. The points marked *x* were obtained by passing a constant current until the potential became constant. Those represented by solid dots were obtained by applying a known constant potential until the current dropped to a stable value. Bubbles of H_2 actually formed at a potential below the potential of the H_2 electrode in this solution. Each point, in most instances, required several hours to obtain a stable value.

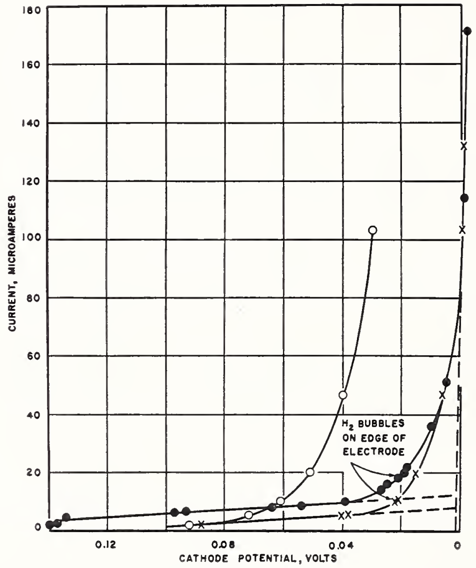

FIGURE 23.8. *Regular decomposition potential curves in a nitrogen-saturated solution.*

x, polarizing constant in still solution; ○, polarizing current constant in stirred solution; ●, polarizing current from a constant potential in still solution.

For the curve with open circles N_2 was bubbled through the solution. The last point is for 0.1 ma. These curves, which are in the residual current region, if extended, pass through the decomposition potential and far into the overvoltage region not shown (see figs. 23.9 and 23.10), with no change in their general nature, indicating that the mechanism of the reaction taking place at the electrode is the same throughout the total range of the curves.

Since it is customary to plot overvoltage against log of c. d., results for N_2 saturated solutions in table 2, together with others in the overvoltage region, were so plotted (fig. 23.9). It will be noted the curves take no account of particular values at which bubbles are formed or such things as undervoltage, normal hydrogen voltage, or overvoltage.

In the curve for still solutions there is a tendency for the data to fall into two straight lines that intersect at a potential of about -0.020 v and at a c. d. of about 0.005 amp. The slope of the lower section is 0.016, of the upper portion, 0.037. There is a similar tendency to form two straight-line sections for the stirred solutions; the slope of the lower section is 0.029, of the upper, 0.046. The point of intersection is at about the same c. d. as in the still solution but at a slightly less negative potential.

The results for H_2 saturated solutions are represented by curves in figure 23.10, for both still and stirred solutions. There is no tendency for a straight line in either case. Some other investigators have reported straight lines and have formulated theories based upon such findings.

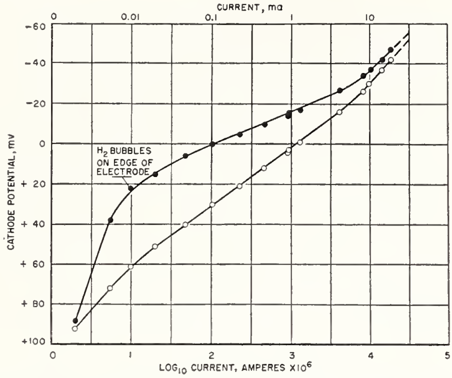

FIGURE 23.9. *Stable cathode potentials in both the residual current and overvoltage ranges against the log of current densities in nitrogen-saturated solutions, both still and stirred.*

Cathode potential—log₁₀ current curves for platinized platinum in 2 *N* sulfuric acid saturated with nitrogen ●, still solution; ○, stirred solution.

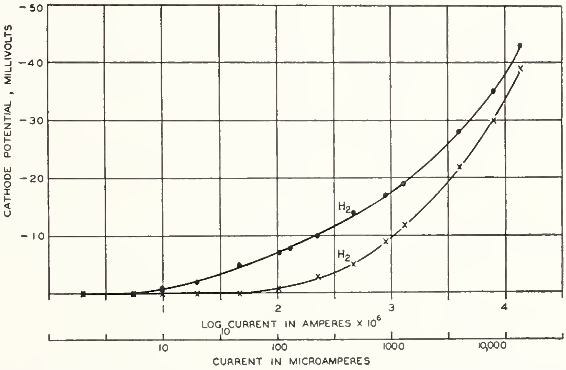

FIGURE 23.10. *Curves for stable cathode potentials in both the residual current and overvoltage ranges against the log of the corresponding currents in hydrogen-saturated solutions, both still and stirred.*

●, still; X, stirred.

The next experiments were designed to study changes of cathode potential with time from the instant the polarizing circuit was closed for still and stirred solutions saturated by either H_2 or N_2 at various c. d.'s. Resultant curves are called charge curves.

For solutions saturated with H_2 the initial value was that of a H_2 electrode in the solution. Three typical curves are shown in figure 23.11. Number 1 is for a c.d. of 1.30 ma in a still solution. The final stable value after 1 minute was −0.035 v. Number 2 is for a still solution at a c.d. of 0.896 ma. Number 3 is also at a c.d. of

0.896 ma, but the solution is stirred by H_2. The final stable values are reproducible to ±0.001 v. In all cases, the curves are of the same general shape and are nonlinear until the final stable value is reached. Curves 2 and 3 illustrate the effect always obtained by agitation. In both cases, the c.d. was 0.896 amp, but the stable value in a still solution was −0.018 v, in the stirred solution only −0.008 v.

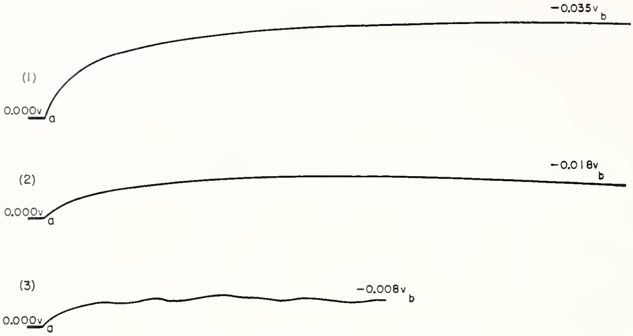

FIGURE 23.11. *Curves representing the change of cathode potential with time for hydrogen-saturated solutions.*

Curve (1) is for a still solution at a constant current of 1.30 ma. Curve (2) is for a still solution at a constant current of 0.896 ma. Curve (3) is for a stirred solution at a current of 0.896 ma.

Figures 23.12 and 23.13 show curves typical of those at low c.d.'s in N_2 saturated solutions, both still and stirred. The first portion of each was recorded oscillographically; the remaining was taken with the potentiometer and stopwatch. Combination of results by both methods gave smooth, continuous curves, demonstrating that the oscillograph was giving correct values. In all N_2 saturated solutions, in this series of experiments, the stable initial value was approximately

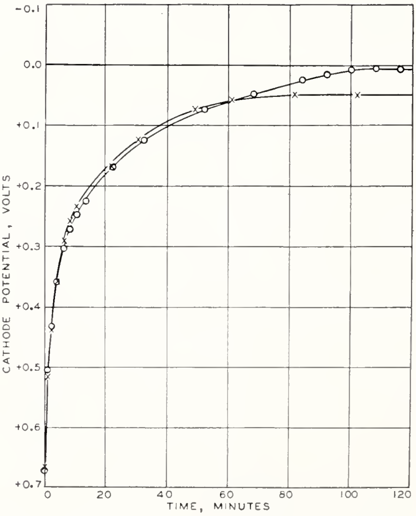

FIGURE 23.12. *Cathode potential-time curves in still and agitated nitrogen-saturated solutions in the residual current range.*

○, still; X, stirred.

+0.668 v. To produce this value, the proposed cathode was short-circuited for 6 to 8 hours with a Hg_2SO_4 electrode placed in the same solution but separated so no diffusion could take place between the electrodes. N_2 was bubbled through the cathode solution continuously. The electrode to be used as cathode was then disconnected from the Hg_2SO_4 electrode and made cathode with approximately the same known c.d.'s as used previously for the solutions saturated with H_2.

For c.d.'s at or below 0.0472 ma the curves had the same general appearance as those in figure 23.12, the major difference being the time required to reach the final stable value. In all such cases, the stable value was positive to the H_2 electrode in the same solution. For H_2 saturated solutions, the stable value for the stirred solution was more positive than in the still. At c.d. 0.0472, used for the curves in figure 23.12, the stable value in the stirred solution was 50 mv more positive than in the still.

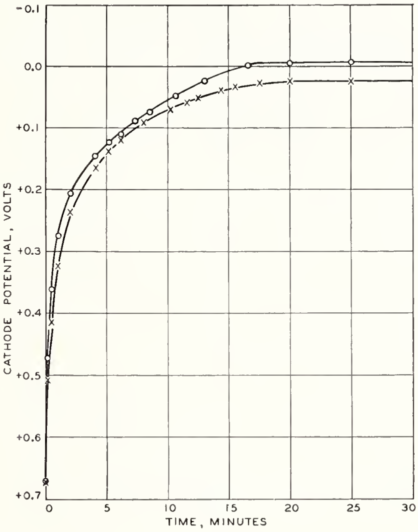

Figure 23.13. *Cathode potential-time curves in still and agitated nitrogen-saturated solutions, mostly in the residual current range.*

○, still; X, stirred.

The curves in figure 23.13 are included because it happened that at c.d. 0.227 ma, which was used for the curves in that figure, the stable value in the still solution was in the overvoltage region, −10 mv, while in the stirred solution it was in the "undervoltage" region, +40 mv.

At c.d. 1.33 ma the stable values in the still and stirred solutions are in the overvoltage region; for still solutions the value is −0.019 mv, for stirred, −0.001 mv. (Graphs not shown but are of typical type.)

All these charge curves, in H_2 saturated and N_2 saturated solutions, support the view expressed previously that there is nothing unique about mechanisms of the reactions below, at, or above the decomposition potential or reversible H_2 electrode in any given solution.

Most of the modern theories maintain that current that passes below the decomposition potential builds a double layer at the interface.

The proposed mechanism for the double layer differs according to the particular investigator proposing it, but in all cases, is of the nature of a condenser. Ions are supposed not to be discharged in the residual-current range. These theories are based largely upon the assumption or supposed experimental findings that cathode potential-time curves are linear. The curves shown here are by no means linear, and they are typical of dozens obtained in this laboratory under a variety of conditions.

The curves just described are more satisfactorily explained by the theory proposed earlier by the author that hydrogen ions may be discharged during the residual-current range as well as above. The hydrogen atoms formed tend to reionize immediately, building up a back potential that eventually becomes approximately equal to the applied potential. The current that passes after this stable situation is reached is required to maintain the necessary concentration of atomic hydrogen at the interface through combination to form molecular hydrogen, or through diffusion into the solution or the metal, or through reionization, to maintain the stable potential.

References

[1]. Max Le Blanc, Die elekbromotorischem Krafte der Polarisation, Abhandl. Deut. Bunsen-Ges. **3,** (1910).
[2]. H. D. Holler, Sci. Pap. NBS **20,** 153 (1925) S504.
[3]. E. Newbery, J. Chem. Soc. **105,** 2422 (1914).
[4]. Fechnor, Massbestemmunger uber die galvanische Kette, Leipzig (1931).
[5]. E. Newbery, Trans. Electrochem. Soc. **58,** 187 (1930).
[6]. J. Tofel, Z. Phys. Chem. **50,** 641–712 (1905).

Discussion

Dr. H. D. Holler, Naval Research Laboratory, Washington, D. C.: After 27 years I ought perhaps to make a few comments on the paper published in 1924, to which Professor Ferguson referred (illustrating on blackboard). If you pass a current through a cell and measure the potential of one of the electrodes, for example, the cathode, with a half-cell, the potential that you observe depends on the electric field surrounding the electrode, and the position of the half-cell. The purpose of the amplifier and oscillograph was simply to illustrate a method by which the IR drop might be differentiated from the emf component, and I think it served its purpose. As with other techniques, its satisfactoriness depends upon its sensitivity and the order of magnitude of the quantities measured. I also passed an alternating current through the cell, and with the amplifier-oscillograph technique measured the a-c voltage across the electrode and half-cell also, bringing the voltage into phase with the current, so that the voltage divided by the current gave a resistance value.

Of course, the resistance thus observed depends not only on the conductivity of the electrolyte but on the shape and size of the electrode and the film resistance on the electrode surface. Taking all of these factors into account, whether an IR drop is going to be observed or not depends on the magnitudes of their different effects. For example, if the film resistance is high, the IR drop may not be eliminated from the observation by simply bringing the tip of the half-cell into contact wity the electrode surface. Such a resistance can be measured by the amplifier-oscillograph technique or by the adaptation of a Wheatstone bridge, using a-c or d-c, if the resistance is sufficiently large to be measurable.

Dr. D. N. Craig; National Bureau of Standards: I am curious as to whether or not there was any way of establishing the point at which gold was dissolved from the electrode. We have found that when we study overvoltage of oxygen on gold in sulfuric acid we can always find some gold in the solution.

Dr. A. L. Ferguson: Well, that would have been included in the remainder of this paper if I had had time to go into it. The work has been extended in an entirely new direction, and one of these extensions is to make use of this as a method for determining the nature of the material that is on those electrodes, and I think that has opened up an entirely new field. Considerable work is in progress at the present time. Gold electrodes have not been used, but silver, copper, and nickel have been used so far.

Dr. J. H. Bartllet, University of Illinois, Urbana, Ill: Hickling and Salt have observed decay curves of hydrogen overvoltage. Do you have objections to the interrupter method which they used?

Dr. Ferguson: I think some excellent work has been done by certain interrupter methods, but I feel that the interrupter method may not be giving the true value for two reasons: it does involve extrapolation; but the main question I raise is whether or not the potential, in the very brief interval on charge, has an opportunity to reach its maximum. I am afraid they are getting a reproducible value, but one that is not the maximum. All of our work has been done by leaving the charge potential on in every case for a time sufficient for the electrode to reach an equilibrium value that remained constant for long periods of time and may be duplicated to about 1 mv. However, to reach this condition always required several minutes and in certain cases several hours. One of the most outstanding objections that has been raised to overvoltage work is the lack of reproducibility of values. By the method adapted by us it is possible to reproduce the values by using different electrodes in different samples of solution and by different men to within a very few millivolts.

24. Parameters of Electrode Kinetics*

By J. O'M. Bockris [1]

Introduction

The change in emphasis from studies of equilibrium processes to those of a kinetic nature, manifest in many electrochemical studies of postwar years, and particularly in electrode kinetics, makes a collection of the parameters of electrode reactions of particular relevance. The principal difficulty of making such a collection rests upon the comparatively recently acquired knowledge of the large effect that small trace impurities have upon electrode processes. This is true particularly for hydrogen evolution, for which the experimental knowledge is of largest extent. A considerable part of the earlier experimental work is thus open to doubt.

In the following, experimental difficulties are briefly reviewed, some general equations, which define the parameters of greatest importance, are deduced, and a review of the more reliably known parameters is then given.

Experimental Difficulties

Preparation of Electrolyte

Results of measurements of overpotential under apparently the same conditions, recorded in the older literature, show a marked irreproducibility. That much of this irreproducibility, particularly for experiments with Hg electrodes, is due to traces of impurities in the electrolyte is implicit in the work of Levina and Sarinsky [60].[2] This aspect was examined in detail by Bockris and Conway [12], who found that traces of impurities of about 10^{-10} g mol/liter caused appreciable changes in the H_2 overpotential at a given current density on Ni electrodes, and that the time variation of this quantity was also much less in highly purified solutions. Detailed experiments on the effect of trace impurities on electrode processes other than the evolution of H_2 have not yet been made. According to Randles and Somerton [77], however, the velocity of redox reactions at inert-metal electrodes is irreproducible in ordinarily purified solutions, and, in general, measurements of any electrode process in which the effect of trace impurities has not been examined must remain in doubt.

Detailed technique for preparation of appropriately pure solutions is recorded elsewhere. In summarizing, the following points may be briefly noted. Water must be distilled several times in all-glass apparatus,[3] a criterion of its purity being that the conductance be less

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*Manuscript received Sept. 1951; literature taken into account up to July 1951.

[1] Department of Inorganic and Physical Chemistry, Imperial College of Science and Technology, London S. W. 7, England.

[2] Figures in brackets indicate the literature references on p. 260.

[3] Glass used in the construction of apparatus should be exclusively borosilicate glass free from arsenic.

than about 1.10×10^{-7} mho cm^{-1}. Distillation of organic solvents involves the additional difficulty of removing traces of organic depolarizers, e. g., formaldehyde in methyl alcohol. Reagents used in preparing solutions should if possible be baked, preferably in a stream of H_2, to remove organic impurities. The most important method for ultrapurification of solutions is preelectrolysis at an auxiliary electrode.[4] The necessary number of coulombs required sufficiently to purify a solution must be established by experiment, the criterion being that preelectrolysis is sufficient when its further use no longer affects the observed results. The necessary amount of preelectrolysis may vary for the same system owing to the difficulty of obtaining an absolutely reproducible initial state of the solution before preelectrolysis. In general, the potential of the auxiliary electrode used must be more negative (for cathodic processes) than any used during the experiment. Functions of cathodic preelectrolysis are (1) reduction of oxidizing agents, (2) removal of foreign cations by deposition, and (3) adsorption of capillary active material. The last might be best achieved by the inclusion of an electrode of very large surface area, e. g., platinized Pt, in the solution. However, this would involve concomitant changes resulting from possible contamination of the solution with Pt.[5] [6]

Cell

It has only recently become general practice in kinetics to construct cells entirely of glass, so that contamination with rubber cannot occur. It has been established that tap grease affects reaction rates [60], presumably by adsorption of traces upon the electrode surface, and its use on taps, joints, etc., should be avoided. In processes affected by oxygen depolarizers, joints must be sealed with the solution. Rubber tubing in gas trains is to be avoided as is any kind of cement for affixing electrodes (even inorganic cements have proved deleterious). Gas-purifying trains deserve careful design. Certain liquids should be avoided because they may decompose leading to harmful impurities in the solution. Purification of gases by passage through charcoal at liquid-air temperatures is an important method, if it is done after the main impurities have been removed by chemical methods.

State of Electrode Surface

Assuming the existence of a "sufficiently" highly purified solution, it is still not possible to obtain reproducible results until a standard way of preparing an electrode surface is known. In earlier work, the difficulty of attachment of a solid metal to a glass surface was often met by use of organic cement, which undoubtedly increased the concentration of poisons in the solution. Attempts were made to treat the electrode surface by immersing it in various acids (etching), etc. Such methods probably introduce further surface impurities and undesirable films on the electrode surface, rather than removing them. Also, they could be reproduced only with great difficulty, the surface obtained usually being covered with an oxide film. Bockris and Conway [11] introduced a method in which the solid electrode in wire

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[4] The first use of this method seems to have been by Lewis and Jackson [62]. It remained unused until the work of Aten and Zieren [3], who studied the hydrogen electrode obtained with smooth Pt in preelectrolitically purified solutions.

[5] Watson [89], found that even the presence of Pt conductivity electrodes in a cell affect results of hydrogen overpotential measurements on Hg, although the solution was in contact with them only during its preparation.

[6] For detailed discussion of preelectrolysis and conditions, see references [27, 5, 76, 71].

form is heated in a stream of oxygen-free H_2 until oxide films are removed, and thereupon sealed in H_2 into a thin glass bulb, which can then be broken with a glass probe after introduction into oxygen-free solutions. This method allows sealing of most metals satisfactorily to glass sheaths. For metals, e. g., Ag, for which attachment to glass is difficult, special seals involving other metals can be used [27]. Bockris and Conway's method has the advantage that it prepares a uniform surface under easily reproducible conditions; this surface consists with most metals of the pure metal with a hydrogen layer on the surface. It is always possible to remove the oxide films occurring on metals in air by passage of a H_2 stream, though the time and temperature needed depends upon the metal. In some instances, e. g., if graphite has been used in the rolling or drawing of the wire, as is sometimes done with tungsten, it may be necessary first to heat the surface in oxygen, to eliminate carbon and then reduce as described above.

The technique of manipulating solid electrodes within cells has been considerably improved by the introduction of parallel ground-glass joints by Potter [76]; these enable a vacuum to be achieved in the apparatus, while at the same time the position of electrodes within it can be controlled.

Even when an electrode has been produced in a reproducible state, in a pure solution, it may be difficult to maintain the surface in a constant state during the electrode process. Thus, in the O_2 evolution reaction $2OH \rightarrow H_2O + 1/2O_2 + 2\epsilon$, oxide films of changing character make the observed kinetics complex. Irreversible oxidation or reduction processes produce products that tend to cover the electrode. Satisfactory techniques have not yet been developed here; it may be suggested that they consist in the use of rapidly renewed surfaces, e. g., dropping, or vibrating electrodes, or of very short current pulses, so that the process only occurs for a time sufficient to build up a few molecular layers from the discharged ion on the surface. The latter method was first successfully applied to measurements of metal overpotentials by Roiter, Juza, and Poluynan [81].

Electric Circuit [7]

The fundamental difficulty of measuring the potential of an electrode at which a current is passing concerns the inclusion of an ohmic component of potential in the apparent measured overpotential. Commutator devices for avoiding this difficulty have recently been improved and are now satisfactory for use up to c. d.'s of at least 1 amp/cm^2 in solution of unit normality [41]. At higher c. d.'s, use of an extrapolation method to zero distance of the Luggin capillary from the electrode surface has been recently used [10]. At c. d.'s below about 10^{-6} amp/cm^2, it becomes important to insulate all components of the circuit by wax blocks, and to use screened leads throughout the circuit. It is undesirable to use a water thermostat because of the danger of electrical leaks. An appropriate air thermostat for temperatures from −10 to 80° C is described by Potter [76].

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[7] A theoretical difficulty, which may be mentioned under this heading, concerns the equivalent electric circuit that has to be devised before significant results can be evaluated from measurements of the impedance and phase angle during electrode reactions. In many cases, lack of knowledge of the appropriate circuit is a major difficulty.

Technique of Examination of Dependence of Current on Overpotential [8]

In some electrode processes different results are obtained according to whether the values of overpotential at a given c. d. are measured after long or short polarizations. Such discrepancies are considerably reduced upon preelectrolytic purification of the solution for the H_2 evolution reaction. Usually, short polarizations at a given c. d. appear more desirable because they reduce the probability of deposition of impurities upon the electrode surface. (For effects of various types of experiments upon results, see [5]). In some processes, long polarizations are necessary because of the setting up of equilibria unconnected with solution impurities, e. g., for the evolution of H_2 on Hg from alkaline solutions, where Na deposition also occurs [19].

Some Equations of Electrode Kinetics [8]

Introduction

The development of systematic equations to describe the processes of electrode kinetics is comparatively new. The first systematic collection of such equations is due to Potter [76], who showed that the slope of the Tafel line (η—log c.d. relation) is essentially dependent upon the number of electrons taking part in the rate-determining reaction. Bockris and Potter [18], have developed the detailed equations for the kinetics of the H_2 evolution reaction. Parsons [69] has given a treatment of the overpotential c. d. and overpotential-concentration relations for any electrode reaction under certain limiting conditions.

In the following a brief summary is given of some essential equations relating to a hypothetical general electrode process with the object of making manifest the essential parameters involved in electrode reactions.

Current-Potential Relation in an Electrode Process

In any general electrode process $A+B+\ldots\rightarrow C+D+\ldots$, it may be assumed that the over-all reaction passes through several intermediate stages, of which one can usually be assumed to be the rate-determining step.[9] Let it be assumed that one act of this rate-determining step, namely, the step that it is desired to determine in examining the mechanism of the over-all reaction, involves the passage of λ electrons from the electrode to the ions in the initial state of the reaction for the over-all reaction to go once to completion. Let a_I be the product of the activities of the ions in the initial state, $\overrightarrow{k}$ the velocity constant for the forward direction of the rate-determining reaction, and κ the transmission coefficient for the reaction. The forward velocity of the reaction $\overrightarrow{v}$, is

$$\overrightarrow{v}=a_I\overrightarrow{k}, \tag{1}$$

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[8] The electrode reactions, the kinetics of which are considered in this paper, concern processes dependent upon activation overpotential. In experimental values reported, concentration and ohmic overpotential are supposed to have been eliminated. (For detailed examination of ohmic errors, see the extensive work of Ferguson [32]).

[9] For a treatment of the relations between the free-energy change in the intermediate reactions, and the free energy of activation of the over-all reaction, see Watson [86].

and the cathodic current is hence

$$\overrightarrow{i}=\overrightarrow{v}\lambda\mathbf{F} \tag{2}$$

where **F** is the charge on an ion in the initial state (i. e., 1 faraday per gram ion for univalent ions).

Let a potential difference exist between the metal electrode and the solution such that the difference between the inner potentials of electrode and solution is $\Delta\phi$. If cations are being deposited and the electrode is positive with respect to the solution, this potential difference retards the flow of reactants over the energy barrier of the rate-determining step. If ΔG_1^* is the standard free energy of activation of the rate-determining reaction with respect to the initial state in the absence of a potential difference between the electrode and the solution, and then, if the inner potential of the electrode is more positive than that of the ions in their initial state by $\Delta\phi_c$, this will make ΔG_1^* more positive by $\beta\lambda\mathbf{F}\Delta\phi_c$, where β is the fraction of the potential difference $\Delta\phi_c$, through which the ions pass between their passage from the solution to the transition state (hence, $0<\beta<1$; β is a function of the symmetry of the potential-distance relation for the rate-determining reaction). Utilizing the fundamental equation,

$$\overrightarrow{k}=\kappa\frac{kT}{h}\exp\left[-\frac{\Delta G_1^*}{RT}\right], \tag{3}$$

from the transition state theory, where R, k, T, and h have their usual meanings, eq (1) (2) and (3) give

$$\overrightarrow{i}=\kappa\lambda\mathbf{F}\frac{kT}{h}a_{\mathrm{I}}\exp\left[-\frac{\Delta G_1^*+\beta\lambda\Delta\phi_c\mathbf{F}}{RT}\right]. \tag{4}$$

By a similar argument, for the reverse direction of the rate-determining reaction

$$\overleftarrow{i}=\kappa\lambda\mathbf{F}\frac{kT}{h}a_{\mathrm{F}}\exp\left[-\frac{\Delta G_2^*-(1-\beta)\lambda\Delta\phi_c\mathbf{F}}{RT}\right], \tag{5}$$

where a_{F} is the product of the activities of the entities in the initial state of the reverse step, and ΔG_2^* is the standard free energy of activation of this step.

When

$$\overrightarrow{i}=\overleftarrow{i}=i_0, \quad \Delta\phi_c=\Delta\phi_r, \tag{6}$$

which is the value of $\Delta\phi_c$ corresponding to the reversible electrode potential. From eq (4), (5), and (6),

$$\overrightarrow{i}=i_0\exp\left[-\frac{\beta\lambda\eta\mathbf{F}}{RT}\right], \tag{7}$$

and

$$\overleftarrow{i}=i_0\exp\left[\frac{(1-\beta)\lambda\eta\mathbf{F}}{RT}\right], \tag{8}$$

as $\Delta\phi_c - \Delta\phi_r$ can be placed equal to η, the activation overpotential at the net c.d. i_c, where,

$$i_c = \overrightarrow{i} - \overleftarrow{i}. \tag{9}$$

From eq (7), (8), and (9)

$$i_c = i_0 \left\{ \exp\left[-\frac{\beta\lambda\eta\mathbf{F}}{RT}\right] - \exp\left[\frac{(1-\beta)\lambda\eta\mathbf{F}}{RT}\right] \right\}. \tag{10}$$

This relation is valid at all c. d.'s and potentials if the rate-determining reaction is the same throughout. At c. d.'s sufficiently small so that $\exp[-(\beta\lambda\eta\mathbf{F})/\mathrm{RT}]$ can be taken with sufficient accuracy as $1-(\beta\lambda\eta\mathbf{F}/RT)$ then eq (10) becomes

$$i_c = -\lambda \frac{i_0 \eta \mathbf{F}}{RT}, \tag{11}$$

so that i_c and η are linearly related at sufficiently low numerical overpotentials.

Hence,

$$\lambda = -\frac{RT}{\mathbf{F} i_0} \left(\frac{\partial i_c}{\partial \eta}\right)_{\eta \to 0}; \tag{12}$$

λ is termed the electron number of a reaction. To measure λ it follows from eq (12) that measurements of i_c as a function of η are necessary at limitingly low c. d.'s. To avoid the difficulties (e. g., depolarization) which sometimes occur in doing this, another method is available. Equation (10) can be written as

$$i_c = i_0 \exp\left[-\frac{\beta\lambda\eta\mathbf{F}}{RT}\right][1-f], \tag{13}$$

where f is

$$\exp\left[\frac{\lambda\eta\mathbf{F}}{RT}\right]. \tag{14}$$

When the departure of the Tafel line from linearity due to the reverse current in eq (10) is just detectable experimentally, then f is just distinguishable from zero. Let the smallest detectable value of f be f_s. Experiment shows that $f_s = 0.05$. Hence, from eq (14),

$$f_s \bumpeq 0.05 = \exp\left[\frac{\lambda\eta_s\mathbf{F}}{RT}\right] \tag{15}$$

Hence, at 20° C, when η_s is numerically expressed in volts,

$$\lambda = \frac{0.075}{\eta_s}. \tag{16}$$

This method of determination is often more convenient than that using eq (12).[10]

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[10] A third method for obtaining λ is given by Parsons [69]; this is applicable when measurement of η as a function of i_c *through* the reversible potential is possible.

In the special case of (10) for which η is sufficiently negative for $\exp\left[\frac{(1-\beta)\lambda\eta\mathbf{F}}{RT}\right]$ to be negligible, eq (10) becomes

$$i_c = i_0 \exp\left[-\frac{\beta\lambda\eta\mathbf{F}}{RT}\right], \tag{17}$$

or

$$\eta = \frac{RT}{\beta\lambda\mathbf{F}} \ln i_0 - \frac{RT}{\beta\lambda\mathbf{F}} \ln i_c. \tag{18}$$

(18) is Tafel's equation, in which

$$a = \frac{RT}{\beta\lambda\mathbf{F}} \ln i_0 \tag{19}$$

$$b = 2.303\, \frac{RT}{\beta\lambda\mathbf{F}}, \tag{20}$$

$$\alpha = \beta\lambda. \tag{21}$$

α is hence a complex quantity.

Current as a Function of Temperature

From (4), under the condition $i_c = \overrightarrow{i}$, there results

$$i_c = \kappa\lambda\mathbf{F}\, \frac{kT}{h}\, a_{\mathrm{I}} \exp\left[-\frac{\Delta S_0^*}{R} - \frac{\beta\lambda\mathbf{F}\Delta\phi_r}{RT}\right] \exp\left[-\frac{\Delta H_0^* + \beta\lambda\mathbf{F}\eta}{RT}\right] \tag{22}$$

If the effect of temperature on ΔS_0^*, $\Delta\phi_r$ and a_{I} is taken to be negligible, and neglecting the effect of the linear term in T, (22) becomes at $i=0$

$$i_c = i_0 = \text{const} \exp\left[-\frac{\Delta H_0^*}{RT}\right], \tag{23}$$

so that the evaluation of ΔH_0^*, the standard heat of activation of the forward direction of the rate-determining step at the reversible potential, follows from a plot of log i_0 against $1/T$. This method is the most convenient for the evaluation of ΔH_0^*; it is probably sufficiently accurate if statistical analysis can be applied to the evaluation of log i_0. The more exact theory of the dependence of overpotential on temperature follows. From eq (18) and (21)

$$\eta = \frac{RT}{\alpha\mathbf{F}} (\ln i_0 - \ln i_c), \tag{24}$$

$$\left(\frac{\partial\eta}{\partial T}\right)_{i_c} = \left[\frac{R\alpha\mathbf{F} - \frac{\partial\alpha}{\partial T} RT\mathbf{F}}{(\alpha\mathbf{F})^2}\right] (\ln i_0 - \ln i_c) + \frac{RT}{\alpha\mathbf{F}} \frac{\partial}{\partial T} \ln i_0. \tag{25}$$

From (22), log i_0 can be written as

$$\ln i_0 = \ln K + \ln T + \frac{\Delta S_0^*}{R} - \frac{\Delta H_0^*}{RT}, \tag{26}$$

where K is a constant. Hence,

$$\frac{\partial}{\partial T} \ln i_0 = \frac{1}{T} + \frac{\Delta H_0^*}{RT^2} = \frac{\Delta H_0^* + RT}{RT^2}. \tag{27}$$

From eq (24), (25), and (27),

$$\left(\frac{\partial \eta}{\partial T}\right)_{i_c} = \frac{\eta \mathbf{F}\left(\alpha - \frac{\partial \alpha}{\partial T} T\right) + \Delta H_0^* + RT}{\alpha \mathbf{F} T}. \tag{28}$$

Experimentally, for some reactions α is constant with temperature while for others, b is constant with temperature. If α is constant with temperature,

$$\left(\frac{\partial \eta}{\partial T}\right)_{i_c} = \frac{\alpha \eta \mathbf{F} + \Delta H_0^* + RT}{\alpha \mathbf{F} T}, \tag{29}$$

and if b is constant with temperature, $\partial \alpha / \partial T = \alpha / T$, so that

$$\left(\frac{\partial \eta}{\partial T}\right)_{i_c} = \frac{\Delta H_0^* + RT}{\alpha \mathbf{F} T}, \tag{30}$$

ΔH_0^* can therefore be calculated from either eq (29) or (30) or, in general for eq (28), if the value of $\partial \alpha / \partial T$ is known.

Free Energies and Entropies of Activation

From (4)

$$i_0 = \kappa \lambda \frac{\mathbf{F} k T}{h} a_I \exp\left[-\frac{\Delta G_0^* + \beta \lambda \Delta \phi_r \mathbf{F}}{RT}\right]. \tag{31}$$

From eq (31), it is possible in principle to evaluate ΔG_0^* and hence ΔS_0^*, knowing ΔH_0^* from eq (23), (28), (29) or (30). The evaluation of ΔG_0^* from eq (31) depends on some chosen standard state for a_i and values of ΔG_0^* and ΔS_0^* are consequently dependent upon the arbitrary choice of this state, e. g., a_i may be expressed in gram ions/liter.

However, evaluation of ΔG_0^* from eq (31) requires a knowledge of the numerical value of $\Delta \phi_r$ and this is a matter of considerable difficulty. Approximately, this could be regarded as the metal-solution potential difference at the reversible potential. This was formerly taken as the difference between the reversible electrode potential of the metal in the solution on the hydrogen scale and the electrocapillary maximum [11] in this solution, on the assumption that, at the electrocapillary maximum, the potential of the metal is that of the solution. This assumption, however, neglects the potential difference at the metal-solution interface due to dipoles of the solvent, oriented in a definite direction to the electrode.[12] It is, therefore, more correct to write.

$$\Delta \phi_r = \Delta \phi_r' + \mathrm{X}, \tag{32}$$

---

[11] The experimental values of electrocapillary maxima are somewhat uncertain. See Frumkin [33, 34], Butler [24], Frumkin [36], and Pentland [71].

[12] These may be oriented in a definite direction at the electrode, even at a "charge-free" interface, because of the image forces induced in the surface by the dipoles in contact with it.

where $\Delta\phi_r'$ is the reversible potential of the electrode in the system considered with respect to the potential of the electrocapillary maximum of the electrode in the solution, and X is the additional surface potential described.[13] Values of X are not readily determinable. At present, calculations of ΔG_0^* and ΔS_0^* can only be made in a relative way, namely, by assuming that X is zero. Values of ΔG_0^* and ΔS_0^* for various processes on different electrodes thus calculated will have a relative meaning if X is the same at the electrocapillary maximum for the various systems. In dilute solutions, this seems a reasonable assumption.

Note on True and Apparent Surface Areas

In most electrode kinetics, it is tacitly assumed that the apparent surface area of the electrode is equal to the true one when calculating c.d. For most electrodes, true area is larger than apparent area by a factor of about two or three, and reference to the Tafel equation shows that the difference between values of overpotential calculated with the true or apparent area is about 30 mv (when $b \simeq 0.1$), which is negligible for many reactions exhibiting high potential. For platinized Pt and similar surfaces, the correction has importance.

Summary

From the equations deduced above, the most important parameters characterizing an electrode reaction are seen to be i_0, α, λ, and ΔH_0^*, ΔG_0^*, ΔS_0^*, and the potential of the electrocapillary maximum. In the literature, only i_0 and to a lesser extent ΔH_0^* are extensively recorded.

Markedly few applications of statistical methods have been made in studies in electrode kinetics. With work on solid metals such applications are usually essential. A summary of the pertinent methods is given by Bockris and Potter [18].

Experimental Values of Parameters

Introduction

A critical selection has been made of the available determinations of the parameters of a number of electrode reactions. In selecting values, attention has been given to the purity of the solution. Relevant work containing, for example, alternative values, is referred to, but the numerical values are not quoted when, in the author's opinion, more relevant determinations have been recorded. In some cases numerical values have been calculated from results recorded graphically by authors, and this procedure necessarily entails some loss of accuracy. In such calculations it is often convenient to employ the Tafel equation in the form

$$\eta = \frac{RT}{\alpha \mathbf{F}} \ln \frac{i_0}{i_c},$$

where i_0 is the exchange current and i_c is the c. d. at the overpotential, η.

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[13] Note that the surface potential, X, referred to here, is similar to the g (dipole) of Lange [58].

An estimate of reliability of the work involved has been made in most cases and is represented by the letters: *A*, apparently satisfactory; *B*, although careful technique used, deficiencies apparent in light of present knowledge; and *C*, values require confirmation. Unless otherwise stated, the temperature at which values are recorded is 20° C. In all cases, i_0 is in amperes per apparent square centimeter, and ΔH_0^* is in kilocals per gram mole of reactants in the initial state. In the "remarks" column of the tables, "N" followed by a number refers to notes in the table. Accuracy data has been quoted where possible. In the literature it is often either not stated, or only stated as limits, the statistical significance of which is not given. "Probable errors" and 95 percent probability limits quoted refer to the usual statistical significance of these terms.

Hydrogen Evolution

TABLE 1. *Hydrogen evolution on mercury cathodes in aqueous acid solutions*

Solution	i_0	α	ΔH_0^*	References	Remarks
0.1 N HCl	9×10^{-13}	0.48	----------	[48]	A, N. 1, 2.
0.1 N HCl	5×10^{-13}	.51	21.1±0.6	[15]	A, N. 3, 4, 5.
0.1 N HCl	6×10^{-13}	.50	21.6±0.2	[75]	A, N. 6, 7, 8.
1 N HCl	2×10^{-12}	.49	24	[52]	A, N. 9.
3 N HCl	8×10^{-11}	.41	9		
5 N HCl	4×10^{-11}	.48	10		
7 N HCl	3×10^{-11}	.54	19 lower T's, 6 higher T's.		
10 N HCl	2×10^{-11}	.61	16	[10]	A, N. 10.
5 N HCl	1×10^{-11}	.51	----------		
0.1 N H_2SO_4	2×10^{-13}	.51	----------	[48]	A, N. 11.
0.25 N H_2SO_4	8×10^{-13}	.50	21.1±0.5	[51]	A, N. 11.
5 N H_2SO_4	9×10^{-13}	.50	----------	[48]	A, N. 12.

NOTES

1. The constants of the Tafel equation reported by Jofa agree to within about 9 mv with those of Levina and Sarinsky [60]. Russian determinations up to 1943 are discussed by Frumkin [35].
2. Values of i_0 and α at lower concentrations than 0.1 N can be obtained from Levina and Sarinsky [60]. They differ little from the results at 0.1 N HCl.
3. Probably error on the "a" constant of Tafel equation is ±0.012 v; on b ±0.003 v. The errors on i_0 for this and all other data in the table is probably at least ± 50 percent because of the long extrapolation needed for the evaluation of i_0.
4. ΔH_0^* values quoted are mean results over the temperature range 0° to 40° C.
5. The α term was found to vary over the whole temperature range. The mean temperature coefficient is $(2.34 \pm 0.19)\times10^{-3}$° C^{-1}.
6. Values of overpotential in different experiments were reproducible to ±0.005 v. Depolarization occurred above 35° C and below current densities of 10^{-6} amp/cm^2.
7. ΔH_0^* values quoted are mean results over the temperature range 0° to 91.3° C.
8. According to Post and Hiskey, α varies from 0.505 to 0.55 while the temperature increases from 0° to 91.3° C; according to Bockris and Parsons it increases from 0.47 to 0.54 over the temperature range 0° to 40°.
9. Values quoted computed from published, small-scale figures. Values of ΔH_0^* obtained from plot of log i_0 against $1/T$. Large variation in parameters with concentration are far outside errors of computation.
10. Values extrapolated from measurement at current densities $>10^{-3}$ amp/cm^2.
11. Apparent discrepancies between the results of Jofa [48] and Jofa and Mikulin [51] are discussed by Frumkin [35].
12. Values for dilute solutions reported in table 1 are probably the most certain presently available in electrode kinetics. Note that to calculate α to three significant figures it is necessary to know b to ±0.0002 v., at present an unattainable accuracy. Limits in the accuracy of α values are complexly related to those for b. As an extreme example [76] if $b=0.104$ and the 95-percent limits of b are ±0.016, then α has the probable value of 0.56 and the 95-percent limits of 0.48 to 0.71. Note that errors in i_0 are also distributed skewly if those on log i_0 are normally distributed. The latter distribution follows from the assumption that errors in overpotential at a given current density are normally distributed.

The agreement obtained for values of i_0 in dilute solutions is completely satisfactory. Values of ΔH_0^* must still be regarded as uncertain because calculation of ΔH_0^* depends on knowledge of $d\alpha/dT$, and experimental agreement has not yet been reached in regard to this quantity (see [68] and [17]). For an analysis of the difficulty involved in the computation of ΔH_0^* see [68]. In the absence of detailed data concerning the variation of α with T, it is better to calculate ΔH_0 from a plot of log i_0 against $1/T$, for which knowledge of $d\alpha/dT$ is unnecessary. The inaccuracy inherent in values of i_0 does not seriously affect ΔH_0 values obtained in this way if statistical methods are correctly applied (see [76]). Evaluation of Post and Hiskey's results in this way gives about 19.2 kcal for ΔH_0.

For other work (see [53] (very high current densities, see discussion in Frumkin, [35]); [60] (salt effect); [50] (perchloric acid); [78] (streaming electrode); [2] (salt effect); [25] (very low current densities); [15] (effect of pressure); [7] (kinetics in buffer solutions).

Table 2. *Hydrogen evolution on mercury cathode in aqueous alkaline solutions*

Solution	i_0	α	ΔH_0^*	Reference	Remarks
0.1 N LiOH	2×10^{-16}	0.57	--------	[19]	A, N. 1, 2.
0.2 N LiOH	3×10^{-16}	.58	--------		
0.1 N NaOH	3×10^{-15}	.58	--------		
0.2 N NaOH	3×10^{-15}	.60	--------		
0.002 N KOH	8×10^{-18}	.59	--------		
0.02 N KOH	5×10^{-18}	.64	16 ±2		
0.1 N KOH	4×10^{-16}	.62	17 ±2		
0.01 N $Ba(OH)_2$	10^{-26}	1.3	--------		
0.02 N $Ba(OH)_2$	10^{-18}	1.1	--------		

Notes

1. ΔH_0^* values calculated from (29) as α approximately independent of temperature. ΔH_0^* values calculated from plot of log $i_0/1/T$ yield 12 kcal approximately, but accuracy in this case is difficult to assess owing to insufficient data to apply statistical methods.
2. For other work, probably vitiated by impurities, see [22, 55, 2].

Table 3. *Hydrogen evolution on mercury cathodes in aqueous-alcoholic and alcoholic solutions*

Solution	i_0	α	ΔH_0^*	References	Remarks
0.01 to 0.5 N HCl, EtOH, $N=1$	2×10^{-11}	0.5	------------	[61]	A, N=molar fraction.
0.1 N HCl.MeOH, $N=0.06$	4×10^{-13}	.53	------------	[15]	A, N. 1, 2, 3.
0.1 N HCl.MeOH $N=0.20$	5×10^{-13}	.55	------------		
0.1 N HCl.MeOH, $N=0.36$	1×10^{-13}	.59	23.2 ±1.0		
0.1 N HCl.MeOH, $N=0.56$	9×10^{-14}	.60	------------		
0.1 N HCl.MeOH, $N=0.83$	4×10^{-13}	.57	------------		
0.1 N HCl.MeOH, $N=0.95$	4×10^{-13}	.59	------------		
0.1 N HCl.MeOH, $N=1.00$	1×10^{-12}	.58	19.7 ±0.4		
0.1 N HCl.MeOH, N=1.00	2×10^{-12}	.56	20.6 ±0.6 for liquid Hg; 19.2 ±0.6 for solid Hg.	[17]	A, N, 4, 5, 6. N. 7.

Notes

1. Probable eror on "*a*" and "*b*" values of Tafel equation, about± 0.015 and ±0.003 v, respectively. It is somewhat less in pure methanol solutions.
2. Comments on ΔH_0^* values made in N. 1, 4, and 12 of table 1 apply here.
3. A break in the Tafel lines occurs in pure methanol solutions between current densities of 10^{-6} to 10^{-5} amp/cm^2. This is due to the slow specific adsorption of Cl ions in methanol on the Hg cathodes (see [28]).
4. Probable error on "*a*" value is ±0.016 and on "*b*" value ±0.004.
5. ΔH_0^* values evaluated by log i_0 /(1/T) method. Coefficient α is constant with temperature up to about 10° C whereafter it increases proportionally with temperature.
6. Measurements were made over the temperature range −70° to +20° C. There is a sharp decrease of α from about 0.62 on solid Hg to about 0.54 on liquid Hg at the melting point.
7. For other work, see [67] and [25].

Table 4. *Hydrogen evolution on nickel cathodes in aqueous acid solutions*

Normality of HCl	i_0	α	ΔH_0^*	References	Remarks
0.0003	2×10^{-7}	0.58	-------	[64]	A.
0.0012	2×10^{-7}	.58			
0.013	3×10^{-7}	.58			
0.15	1×10^{-6}	.58			
0.00004	3×10^{-7}	.63	-------	[59]	A.
0.90	6×10^{-6}	.56			
0.01	4×10^{-7}	.63	-------	[57]	A, N. 1.
0.10	7×10^{-7}	.63			
0.94	1×10^{-6}	.61			
0.001	2×10^{-7}	.63	6.7 ±1.2	[18]	A, limits quoted represent 95% confidence limits. N. 2, 3, 4.
0.01	2×10^{-7}	.64	9.9 ±0.09		
0.1	9×10^{-7}	.56	6.9 ±1.3		
1.0	4×10^{-6}	.53	16.3 ±2.1		

Notes

1. Values of α evaluated from the published figures; authors state $\alpha=0.54$.
2. 95 percent confidence limits of log i_0 are ±0.2, ±0.1, ±0.2, ±0.1 for increasing concentrations, respectively; similar limits of b are ±0.012, ±0.003, ±0.006, ±0.09.
3. Values of ΔH_0^* calculated from log i_0/(1/T) method; increases with increase of temperature.
4. These data, together with the corresponding data in table 5, are the most accurate hitherto recorded for solid cathodes.

TABLE 5. *Hydrogen evolution on nickel cathodes in aqueous alkaline solutions*

Normality of NaOH	i_0	α	ΔH_0^*	References	Remarks
0.001	3×10^{-7}	0.54 to 0.51.	-------	[64]	A.
0.0075	4×10^{-7}				
0.047	1×10^{-6}				
0.42	2×10^{-6}				
0.0083	2×10^{-7}	.54	-------	[59]	A.
0.041	5×10^{-7}	.58			
0.28	1×10^{-6}	.88			
0.001	1×10^{-7}	.56	7.6 ±2.1	[18]	A, limits quoted represent 95% confidence limits. N. 1, 2.
0.007	2×10^{-7}	.58	4.9 ±1.1		
0.12	4×10^{-7}	.58	5.7 ±1.1		

NOTES

1. 95 percent confidence limits of log i_0 are ±0.04, ±0.2 and ±0.2 with increasing concentrations, respectively similar limits for b are ±0.004, ±0.009, ±0.004.
2. Values of ΔH_0^* calculated from log $i_0/(1/T)$ method; α is constant with increase of temperature.

TABLE 6. *Hydrogen evolution on nickel cathodes in nonaqueous solutions.*

Solution	i_0	α	ΔH_0^*	References	Remarks
0.1 N NH_4Cl in liq. NH_3	6×10^{-9}	0.491	7.1	[73]	A, N. 1. Temp=50° C
1 N HCl in HCOOH, N=1	10^{-7}	.42		[9]	C, N. 2.
1 N HCl in MeOH, N=1	10^{-6}	.53		[9]	C, N. 2.
1 N HCl in Glycol, N=1	10^{-5}	.53		[9]	C, N. 2. N. 3.

NOTES

1. ΔH_0^* calculated by Parsons [68].
2. Pyrogallol solutions used to purify hydrogen; inadequate purification of solutions; electrodes prepared by sealing into glass in air.
3. For other work, see [59] (ethyl alcohol over small current-density range); and [9] (water-organic solvent mixtures).

TABLE 7. *Stoichiometric number of the hydrogen evolution reaction on nickel cathodes in aqueous alkaline solutions*

The stoichiometric number of an electrode reaction represents the number of times the rate-determining reaction proceeds for one complete over-all reaction of the electrode reaction considered to take place. It is, therefore, a valuable diagnostic criterion of the mechanism of an electrode reaction [46, 69, 76]. It is closely connected to the electron number [18]. The stoichiometric number is given by the equation

$$\mu=-2\,\frac{i_0\mathbf{F}}{RT}\left(\frac{\partial\eta}{\partial i_c}\right)_{\eta\to0}$$

(cf. eq (12)). Its determination is difficult because it involves an accurate determination of $\left(\frac{\partial\eta}{\partial i_c}\right)_{\eta\to0}$, and results not evaluated by appropriate statistical methods are of little value.

Solution	References	Remarks
0.001 to 0.2 N NaOH 2.0±0.1	[18]	A, 0.1 is 95% confidence limit. μ is invariant with temperature, concentration and time. N. 1, 2.

NOTES

1. In derivation of the error on μ it has been assumed that the errors in log μ are normally distributed. Hence, the errors in μ are skew; however, to the first place the quoted values in this case are symmetrical.
2. For other work, see [63].

Table 8. *Hydrogen evolution on copper cathodes in aqueous acid solutions.*

Normality of HCl	i_0	α	ΔH_0^*	References	Remarks
0.001	2×10^{-7}	0.48	10.1 ±1.0	[14]	A, N. 1, 2, 3.
0.01	2×10^{-7}	.49	11.1 ±1.3		
0.1	2×10^{-7}	.50	9.9 ±1.5		

NOTES

1. The 95% confidence limits on the b constant of the Tafel equation are ±0.010, ±0.007, and ±0.014 for three solutions, commencing with the most dilute, respectively. Corresponding limits for log i_0 are ±0.3, ±0.3, ±0.8.
2. ΔH_0^* was evaluated from a plot of log i_0 against 1/T. Taking into account the confidence limits, it is concluded that b is invariant with concentration at a given temperature and with temperature at a given concentration.
3. For other work, see [6, 9, 4].

Table 9. *Hydrogen evolution on copper cathodes in aqueous alkaline solutions*

Normality of NaOH	i_0	α	ΔH_0^*	References	Remarks
0.005 N NaOH	4×10^{-7}	0.42	0.42	[14]	A, temperature 15° to 17° C. N. 1.
.02 N NaOH	5×10^{-7}	.51	.51		
.15 N NaOH	1×10^{-6}	.50	.50		

NOTES

1. 95 percent confidence limits on b are ±0.066, ±0.009, ±0.014 for the three solutions, starting with the most dilute, respectively. Corresponding limits for log i_0 are ±1.04, ±0.17, and ±0.41.

Table 10. *Stoichiometric number of the hydrogen evolution reaction on copper cathodes in alkaline solutions*

Solution	μ	References	Remarks
0.01 N NaOH to 0.23 N NaOH	2.0 ±0.1	[14]	A, ±0.1 is 95% confidence limit. N. 1.

Table 11. *Hydrogen evolution on copper cathodes in nonaqueous solutions*

Solution	i_0	α	ΔH_0^*	References	Remarks
1 N HCl in glycol, N=1	10^{-7}	0.53	------	[9]	C, N. 1, 2.
1 N HCl in HCOOH, N=1	10^{-10}	.65	------	[9]	C.

NOTES

1. See N. 2, table 6.
2. For other work see [42, 9].

TABLE 12. *Hydrogen evolution on various metals in aqueous acid solutions*

Metal solution	i_0	α	References	Remarks
Al, 2 N H_2SO_4	10^{-10}	0.6	[70]	C, N. 1, 2.
Au, 1 N HCl	10^{-5}	.7	[41]	C, N. 3, 4. 16° C
Au, 1 N HCl	10^{-6}	1.3	[16]	B, N. 3.
Be, 1 N HCl	10^{-9}	0.5	[8]	C, N. 4. Dissolved at c.d. 10^{-3}.
Bi, 1 N HCl	10^{-8}	.4	[41]	C, N. 4. 16° C
Bi, 1 N HCl	10^{-7}	.6	[16]	B.
Cd, 1 N HCl	10^{-7}	.3	[41]	C, N. 4. 16° C
Cd, 2 N H_2SO_4	10^{-5}	.3	[70]	C, N. 1.
Fe, 1 N HCl	10^{-6}	.4	[41]	C, N. 4. 16° C
Fe, 2 N H_2SO_4	10^{-6}	.5	[70]	C, N. 1.
Ga, 0.2 N H_2SO_4	2×10^{-7}	.50	[23]	B, 87° C
Mo, 2 N H_2SO_4	10^{-6}	.5	[70]	C, N. 1.
Mo, 1 N HCl	10^{-6}	.5	[8]	C, N. 4.
Mo, 1 N HCl	10^{-6}	1.5	[16]	B, N. 5.
Nb, 1 N HCl	10^{-7}	0.6	[8]	C, N. 4, 6.
Pb, 0.01 to 8 N HCl	2×10^{-13}	.48	[54]	A, N. 6, 7, 8.
Pb, 0.1 N H_2SO_4	1×10^{-13} for $i<4\times10^{-6}$.	.48	[56]	A, N. 8.
	2×10^{-12} for $i>4\times10^{-6}$.	.48		
Pt, 2 N H_2SO_4	10^{-4}	.5	[70]	C, N. 1.
Pt (smooth), 1 N HCl	10^{-3}	1.5 to 2.0	[10]	A, N. 14.
Pd, 0.6 N HCl	2×10^{-4}	2.0	[37]	A, N. 13.
Pd, 1.0 N KOH	1×10^{-4}	0.45		
Sb, 2 N H_2SO_4	10^{-9}	.58	[70]	C, N. 1.
Sn, 1 N HCl	10^{-10}	.45	[41]	C, N. 4.
Sn, 1 N HCl	10^{-8}	.45	[70]	C, N. 1.
Sn, 2 N H_2SO_4	10^{-7}	.45	[70]	C, N. 1.
Sn, 1 N HCl	10^{-8}	.4	[13]	C, N. 1.
Ta, 2 N H_2SO_4	10^{-9}	.8	[70]	C, N. 1.
Ta, 1 N HCl	10^{-5}	.7	[16]	B, N. 10, 11.
W, 1 N HCl	10^{-6}	.6	[41]	C, N. 4.
W, 1 N HCl	10^{-7}	.6	[70]	C, N. 1.
W, 2 N H_2SO_4	10^{-6}	.6	[70]	C, N. 1.
W, 1 N HCl	10^{-6}	1.5	[16]	B, N. 5.
W, 5 N HCl	1×10^{-5}	0.53	[10]	A, N. 12, 15.

NOTES

1. Pecherskaya and Stender [70] used open beakers; the electrodes and solution were in contact with picein; the purification of solutions was inadequate. The discrepancies that can arise between experiments carried out under not fully satisfactory conditions are manifest in the present table by comparing the results of various workers on W. Much larger discrepancies would be apparent if some of the older, and even less well controlled experimental work had been included.
2. See also [41].
3. Electrode plated.
4. See N. 2, table 7.
5. Electrode sealed into glass in hydrogen. Pecherskaya and Stender sealed electrodes with picein; Hickling and Salt [41], and Bockris [8] sealed with Faraday's cement, or sealed in air to glass; Bockris and Ignatowicz [13] melted Sn electrodes into glass holders and scraped the surface with sharp knife.
6. Surface was scraped with a sharp knife before use.
7. Hydrogen evolved on electrode for several hours before measurements were made.
8. See also [49].
9. See also [41 and 16].
10. Electrode sealed to glass in 99% argon, 1% nitrogen atmosphere.
11. Results for Ta particularly irreproducible under experimental conditions of work hitherto reported. Time variation is considerable. See also [9].
12. Results extrapolated from about 10^{-3} amp/cm^2.
13. See also [44].
14. See also [20].
15. Except for results from work under class A, all parameters given in this table must be regarded as very approximate (e. g., i_0 correct to within a power of 10, etc.).

TABLE 13. *Stoichiometric number of the hydrogen evolution reaction on silver cathodes*

Solution	μ	References	Remarks
0.075 N HCl	2.2	[76]	A, 95% limits, $-0.3-+0.5$.

Table 14. *Stoichiometric number of the hydrogen evolution reaction on platinum cathodes*

Solution	μ	References	Remarks
1 N KOH	1.3	[47]	B, limits doubtful, greater than those for silver given in table 13.

Table 15. *Hydrogen evolution on various metals (except Hg) in nonaqueous acid solutions*

Metals	Solution	i_0	α	References	Remarks
Au	1 N HCl in MeOH	10^{-6}	1	[16]	B, N. 1.
Bi	1 N HCl in MeOH	10^{-8}	1	[16]	B.
Mo	1 N HCl in MeOH	10^{-10}	1.5	[16]	B, N. 2.
Ta	1 N HCl in MeOH	10^{-10}	1	[16]	B, N. 4.
W	1 N HCl in MeOH	10^{-11}	1.5	[16]	B, N. 3, 5, 6.

1. Electrode plated.
2. Electrode sealed to glass in hydrogen.
3. See N. 5, table 12.
4. See N. 10, table 12.
5. For other work, see [42, 9, 13, 16].
6. Results given in this table must all be regarded as very approximate (cf. N. 13, table 11). It is obviously more difficult to obtain sufficiently pure nonaqueous solutions.

Deuterium Evolution

Table 16. *Deuterium evolution on mercury cathodes in aqueous acid solutions*

Solution	i_0	α	ΔH_0^*	References	Remarks
0.2 N D_2SO_4	8×10^{-13}	0.52	20.9	[22]	B. 25°C.
0.1 N DCl	3×10^{-12}	.48	22.4 ± 0.5	[74]	A, N. 1, 2

Notes

1. Values of ΔH_0^* quoted is mean from calculation of ΔH_0^* by three methods: (a) Use of eq (29), on assumption that α is independent of temperature (in fact, it varies from 0.48 to 0.50 over the range 4° to 70° C), (b) plot of log i_e against $1/T$ at various potentials with extrapolation to ΔH_0^*; (c) plot of log i_0 against $1/T$. Authors quote 22.5 ±0.3 as result, this being obtained from use of eq (29) with mean values of α.
2. For work on dropping electrodes, see [63, 66, and 40].

Evolution of Oxygen

Table 17. *Oxygen evolution on platinum anodes in aqueous acid solutions*

Solution	i_0	α	ΔH_0^*	References	Remarks
0.2 N H_2SO_4	6×10^{-10}	0.50	18.7	[21]	B, N. 1.
0.1 N H_2SO_4	9×10^{-12}	.60	----------	[45]	B, N. 2.
0.1 N H_2SO_4	1×10^{-8}	.45	----------	[80]	B, N. 3.
HNO_3, pH 0.5 to 4.5	7×10^{-11} to 2×10^{-10}	.51	----------	[79]	B, N. 4, 5.

1. i_0 at 14° C and ΔH_0^* at 35° C. Coefficient α quoted is mean over whole temperature range (values 273° K, 0.54; 287 ±0.49; 308 ±0.49; 330 ±0.50; 354 ±0.49).
2. "Resistant wax" in contact with solution.
3. Electrode occasionally cathodically activated, pretreatment by washing with various acids and alkalies. Values also given at 10 and 30° C; values too irreproducible to allow reasonable evaluation of ΔH_0^*.
4. Standard error on a approximately ±0.05; on b approximately ±0.026.
5. In concentrated acid solution, b tends to increase with increase of concentration.
6. For other work, see [9].

Table 18. *Oxygen evolution on platinum and gold anodes in aqueous alkaline solutions*

Metal	Solution	i_0	α	ΔH_0^*	References	Remarks
Pt	0.1 N NaOH	4×10^{-13}	0.81	------	[45]	B.
Pt. (platinized).	0.1 N NaOH	5×10^{-11}	.74	------	[45]	B.
Au	0.1 N NaOH	5×10^{-13}	.74	------	[45]	B.
Pt	0.1 N NaOH	4×10^{-13}	1.0	25.3	[84]	N. 1, 2, 3.
Pt	NaOH and KOH, pH 9 to 14.	1×10^{-10}	0.51	------	[79]	B, N. 4, 5.

Notes

1. Measurements made against saturated calomel electrodes [1].
2. No information given on variation of α with temperature. This is considered to be constant in extrapolation to the reversible potential; the ΔH_0^* value is therefore doubtful.
3. Insufficient experimental description given to assess class of work (but compare agreement of i_0 value with that of Hoar [45]).
4. In concentrated alkaline solution, b tends to decrease with increase of concentration.
5. For other work, see [43].

Evolution of Nitrogen

Table 19. *Evolution of nitrogen on various cathodes from aqueous azide solutions*

Metal	Solution	i_0	α	References	Remarks
Pt	NaN_3	10^{-76}	0.98	[83]	A, N. 1, 2, 3.
Ir	NaN_3	10^{-75}	1.0	[83]	A, N. 1, 2, 3.
Pd	NaN_3	10^{-81}	1.1	[83]	A, N. 1, 2, 3.

Notes

1. Observed overpotentials reproducible to about ±0.015 v.
2. The coefficient α is found to be proportional to T.
3. The rate of nitrogen evolution is independent of pH up to 9.4 above which oxygen is evolved.

Evolution of Halogens

Table 20. *Chlorine and bromine evolution from aqueous solution on platinum and iridium cathodes*

Metal	Solution	i_0	α	References	Remarks
Pt	1 N HCl	5×10^{-3}	0.48	[26]	B, Cl_2 evolv. N. 1.
Ir	1 N HCl	4×10^{-5}	.73	[26]	B, Cl_2 evolv. N. 2.
Ir	1 N KBr	3×10^{-3}	.6	[26]	B, Br_2 evolv. N. 3, 4.

Notes

1. Chlorine electrode attacked, oxygen evolution at higher c. d.'s; rotating electrodes in all measurements.
2. Measurements made 10° to 80° C. Approximate values of log i_0 at 10° C, −4.8; 20° C, −4.4; 40°C, −4.3; 80° C, −4.2. Plot of log i_0 against $1/T$ departs markedly from linearity. Coefficient α at temperatures given above 0.69, 0.73, 1.05, 1.07, respectively.
3. In cathodic dissolution reaction large deviation from Tafel equation observed.
4. For other work, see [39].

TABLE 21. *Deposition of metals from simple aqueous solution onto cathodes of the same metal*

Metal	Solution	i_0	α	ΔH_0^*	References	Remarks
Fe	1.25 *M* $FeSO_4$	10^{-8}	0.5	----	[81]	B, N. 1.
Zn	0.5 *N* $ZnSO_4$, 0.005 *N* H_2SO_4	10^{-5}	.5	----	[81]	B, N. 2.
Cu	1 *M* $Cu(NO_3)_2$	10^{-10}	.76	36	[72]	B, N. 3, 4.
	0.1 *M* $Cu(NO_3)_2$	10^{-11}	.62	30		
	0.01 *M* $Cu(NO_3)_2$	10^{-11}	.55	20		
	0.001 *M* $Cu(NO_3)_2$	10^{-9}	.22	----		
Ni	0.5 *M* $NiSO_4$, pH 2.3	10^{-6}	.52			
	0.5 *M* $NiSO_4$, pH 4.4	10^{-6}	.72	--------	[82]	B, N. 5.
	0.5 *M* $NiSO_4$, pH 5.5	10^{-7}	.89			
	0.5 *M* $NiSO_4$, pH 6.7	10^{-5}	.56	--------		N. 6.
	0.5 *M* $NiSO_4$, pH 7.9	10^{-5}	.62			

NOTES

1. Electrodes were vacuum melted and degassed; they were, however, in contact with picein. The effect of picein, or similar organic materials, on the rate of deposition of metals, is not known from direct experiment. From studies of the hydrogen evolution reaction its presence in solution is known to affect the kinetics; hence kinetics of metal deposition measured in its presence must be suspect.
2. Same general remarks as 1. Monocrystals used.
3. No information on time variation given; paper also records some measurements in alcohol-water mixtures.
4. Coefficient α increases with temperature, e.g., for 1 *M* $Cu(NO_3)_2$ value of α are 16° C, 0.69; 27° C, 0.76; 37° C, 0.84; 47° C, 0.94. ΔH_0^* values calculated from plot of log i_0 against $1/T$. For 0.001 *M* $Cu(NO_3)_2$, log i_0 constant from 23° to 58° C.
5. Acetate buffer used; electrodes varnished.
6. Roiter, Juza, and Poluynan used a cathode-ray oscillographic method of determination, and thus avoided difficulties due to crystal growth, change of surface area, etc. Their work seems the most significant hitherto carried out in the field.

In Philbert's and Salt's work, the exchange currents can be obtained more exactly from the published data than the values tabulated.

Much other data exists in literature, particularly by Essin [30] and his coworkers. However, most of this suffers from one or more of following defects: (1) Other types of polarisation (e.g., concentration) are included in the measured overpotential, (2) crystal growth, change of surface area with time, etc., gives very complex results of little significance to fundamental aspects of subject, (3) solutions used are complex and mainly of technological interest (but see [31 and 30]).

TABLE 22. *Electron exchange reactions at a mercury dropping electrode in aqueous solutions*

Reaction	Base solution	k	ΔH_0^*	References	Remarks
$FeO_{x_3}^{4-}/FeO_{x_3}^{3-}$	0.5 *M* K_2O_x	>1		[77]	B, N. 1.
Eu^{2+}/Eu^{3+}	1 *M* KCl	2.1×10^{-4}	9		
	1 *M* KI	1.6×10^{-3}	9.5		
	1 *M* KCNS	8×10^{-3}	7.5		
V^{2+}/V^{3+}	1 *M* $HClO_4$	4×10^{-3}	6.5		
$VO_{x_3}^{4-}/VO_{x_3}^{3-}$	0.5 *M* K_2O_x	1.4×10^{-3}	5.5		
Cr^2/Cr^3	1 *M* KCl	1×10^{-5}	------		
$Cr(CN)_6^{4-}/Cr(CN)_6^{3-}$	1 *M* KCN	2.5×10^{-1}	Small		
Ti^3/Ti^4	1 *M* tartaric acid	9×10^{-3}	7		

NOTES

1. Definition of k: "If an electrode is at equilibrium with equal concentrations c moles cm^{-3} of oxidized and reduced forms of reacting substnace, then the rates of the opposing reactions at the electrode surface are equal to k moles cm^{-2} sec^{-1}, where k is the rate constant of the reaction (dimensions cm sec^{-1})."

Redox Processes

TABLE 23. *Electron exchange reactions at a platinum electrode in aqueous solutions*

Process*	Concentration	i_0	α	References	Remarks
$Fe^3+e \rightarrow Fe^2$	$C_{Fe}=5\times10^{-3}$	2×10^{-3}	$0.58\pm.02$	[38]	A.
	$C_{Fe}=1.5\times10^{-2}$	5×10^{-3}	$0.58\pm.02$	--------	N. 1.

*Platinum electrode.
1. For other work, see [85, 86, 87, 88].

TABLE 24. *Electron exchange reactions at solid metal electrodes in aqueous solutions*

Metal	Reaction	Base solution	k	ΔH_0^*	References	Remarks
Pt	$FeOx_3^{-4}/FeOx_3^{-3}$	0.5 M K_2Ox	9×10^{-3}	3	[77]	B.
Au			5×10^{-3}	----		
Ag	----------	----------	1×10^{-3}	----		
Pt	$Fe^{-4}(CN)_6^{4-}/Fe(CN)_6^{-3}$	M KCl	9×10^{-2}	4		
Pt	----------	0.5 M K_2SO_4	13×10^{-2}	0		
Pt	$Fe^2(aq)/Fe^5(aq)$	M $HClO_4$	5×10^{-3}	9		

TABLE 25. *Metal ion exchange reactions at dilute amalgam dropping electrode in aqueous solutions*

Reacting ion	Indifferent electrolyte	k	ΔH_0^*	References	Remarks
Tl^+	1 M KNO_3	>1	------	[77]	B.
Cd^{2+}	1 M KNO_3	~0.6	~5		
Pb^{2+}	1 M KNO_3	>1	------		
Zn^{2+}	1 M KNO_3	3.5×10^{-3}	8.8		
Do	1 M KCl	4×10^{-3}	8.6		
Do	1 M KBr	8×10^{-3}	9.3		
Do	1 M KCNS	1.7×10^{-2}	7.0		
Do	1 M KI	7×10^{-2}	5.6		
Cu^{2+}	1 M KNO_3	4.5×10^{-2}	9		
$CuEn_2^2$	EnHCl-En	3.7×10^{-2}	0	[77]	N. 1.
$Cu(NH_3)_2$	NH_4Cl-NH_3	1.1×10^{-2}	5	[77]	N. 2.
Bi^{34}	1 M $HClO_4$	3×10^{-4}	10	[77]	
Do	1 M HCl	>1	------		
Na^+	1 M NMe_4OH	~4×10^{-1}	------		
K^+	1 M NMe_4OH	~1×10^{-1}	------		
Cs^+	1 M NMe_4OH	~2×10^{-1}	------		

NOTES

1. 1 M of ethylene diamine hydrochloride containing 1 M of ethylene diamine.
2. 1 M of ammonium chloride containing 1 M of ammonia.

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References

[1] J. N. Agar, Discussion Faraday Soc. **1,** 81 (1947).
[2] J. N. Agar and J. Llopis, An. Soc. esp. Fis. Quim. **43,** 1087 (1947).
[3] A. H. W. Aten and Frl. M. Zieren, Rec. trav. chim. Pays-Bas (1929).
[4] A. M. Azzam, Thesis (London, 1949).
[5] A. M. Azzam, J. O'M. Bockris, B. E. Conway, and H. Rosenberg, Trans Far. Soc. **46,** 918 (1950).
[6] E. Baars, Sitzber. Ges. Beford. Naturw. Marburg **63,** 213 (1928).
[7] V. S. Bagotski and I. E. Yablokova, J. Phys. Chem., U. R. S. S. **23,** 413 (1949).
[8] J. O'M. Bockris, Trans. Far. Soc. **43,** 417 (1947).
[9] J. O'M. Bockris, Trans. Far. Soc., Discuss. **1,** 95, 225 (1947).
[10] J. O'M. Bockris and A. M. Azzam, Nature **165,** 403 (1950), Trans. Faraday Soc. **48,** 145 (1952).
[11] J. O'M. Bockris and B. E. Conway, J. Sci. Instr. **25,** No. 8 (1948).

[12] J. O'M. Bockris and B. E. Conway, Trans. Far. Soc. **45,** 989 (1949).
[13] J. O'M. Bockris and S. Ignatowicz, Trans. Far. Soc. **44,** 519 (1948).
[14] J. O'M. Bockris and N. Pentland, Trans. Faraday Soc. **48,** 833 (1952).
[15] J. O'M. Bockris and R. Parsons, Trans. Far. Soc. **45,** 916 (1949).
[16] J. O'M. Bockris and R. Parsons, Trans. Far. Soc. **44,** 860 (1948).
[17] J. O'M. Bockris, R. Parsons, and H. Rosenberg, Trans. Far. Soc. **47,** 766 (1951).
[18] J. O'M. Bockris and E. C. Potter, J. Electrochem. Soc. **99,** 169 (1952); J. Chem. Phys. **20,**, 614 (1952).
[19] J. O'M. Bockris and R. G. H. Watson, J. Chim. Phys. **49,** 1 (1952).
[20] M. Bonnemay and R. Busso, J. chim. phys. **46,** 455 (1949).
[21] F. P. Bowden, Proc. Roy. Soc. **26,** 107 (1929).
[22] F. P. Bowden and H. F. Kenyon, Nature **135,** 105 (1935).
[23] F. P. Bowden and E. A. O'Connor, Proc. Roy. Soc. **128A,** 317 (1930).
F. P. Bowden and E. R. Rideal, Proc. Roy. Soc. **120A,** 59, 80 (1928).
[24] I. M. Barclay and J. A. V. Butler, Trans. Far. Soc. **36,** 128 (1940).
[25] F. P. Bowden and E. P. Grew, quoted in Ann. Rep. C. S. 112 (1938).
[26] F. T. Chang and H. Wick, Z. physik. Chem. (1935).
[27] B. E. Conway, Thesis (London, 1949).
[28] M. Devenathen, Thesis (London, 1951).
[29] P. Dolin, B. V. Erschler, and A. N. Frumkin, Acta Physicochim. **13,** 793 (1940).
[30] O. A. Essin, Acta Physicochim. **16,** 102 (1942).
[31] O. A. Essin and M. Loschkarev, Acta Physicochim. **10,** 513 (1939).
[32] A. L. Ferguson, Discuss. Far. Soc. **1,** 50 (1947).
[33] A. N. Frumkin, Actualités sci. 373 (1933).
[34] A. N. Frumkin, Physik. Z. Sowjetunion **4,** 239 (1933).
[35] A. N. Frumkin, Acta Physicochim. **18,** 23 (1943).
[36] A. N. Frumkin, J. Colloid Sci. **1,** 277 (1946).
[37] A. N. Frumkin and N. Aladjalowa, Acta physicochim. **19,** 1 (1944).
[38] H. Gerischer, Z. Elektrochem. **54,** 366 (1950).
[39] S. Glasstone and A. Hickling, J. Chem. Soc. **10** (1934).
[40] J. Heyrovsky, Chem. Rev. **24,** 125 (1939).
[41] A. Hickling and F. W. Salt, Trans. Far. Soc. **36,** 1226 (1940).
[42] A. Hickling and F. W. Salt, Trans. Far. Soc. **37,** 224 (1941).
[43] A. Hickling and S. Hill, Discuss. Far. Soc. **1,** 236 (1947).
[44] M. Hitzler and C. A. Knorr, Z. Elektrochem. **53,** 233 (1949).
[45] T. P. Hoar, Proc. Roy. Soc. **142A,** 628 (1933).
[46] J. Horiuti, J. Res. Inst. Catalysis, Hokkaido, Univ. **1,** 8 (1948).
[47] J. Horiuti and M. Ikusima, Proc. Imp. Acad. Tokyo **15,** 39 (1939).
[48] Z. A. Jofa, quoted by A. N. Frumkin (1943).
[49] Z. A. Jofa, J. Phys. Chem. Russ. **19,** 117 (1945).
[50] Z. A. Jofa and A. N. Frumkin, J. Phys. Chem. Russ. **20,** 110 (1946).
[51] Z. A. Jofa and K. P. Mikulin, J. Phys. Chem. Russ. **18,** 137 (1944).
[52] Z. A. Jofa and V. Stepanova, J. Phys. Chem. Russ. **19,** 125 (1945).
[53] B. Kabanov, Acta Physicochim. **4,** 846 (1936).
[54] B. Kabanov and Z. A. Jofa, Acta Physicochim. **10,** 616 (1939).
[55] H. F. Kenyon, Thesis (Cambridge, 1938).
[56] Y. Kolotyrkin and N. Bune, J. Phys. Chem. Russ. **21,** 581 (1947).
[57] Y. Kolotyrkin and A. N. Frumkin, Compt. rend. Acad. Sci. U. S. R. S. **33,** 445 (1941).
[58] E. Lange, Z. Elektrochem. **55,** 76 (1951).
[59] A. Legran and S. Levina, Acta Physicochim. **12,** 243 (1940).
[60] S. Levina and V. Sarinsky, Acta Physicochim. **7,** 475, 491 (1937).
[61] S. Levina and M. Silberfarb, Acta Physicochim. **4,** 275 (1936).
[62] G. N. Lewis and R. F. Jackson, Z. Physik. Chem. **56A,** 193 (1906).
[63] P. D. Lukovstev and S. Levina, J. Phys. Chem. Russ. **21,** 599 (1947).
[64] P. D. Lukovstev, S. Levina, and A. N. Frumkin, Acta Physicochim. **11,** 21 (1939).
[65] O. H. Mueller and J. Heyrovsky, Coll. Czech. Chem. Comm. **7,** 281 (1935).
[66] J. Novak, Coll. Czech. Chem. Comm. **9,** 207 (1937).
[67] I. C. Novoselski, J. Phys. Chem. Russ. **11,** 369 (1938).
[68] R. Parsons, Thesis (London, 1948).
[69] R. Parsons, Trans. Far. Soc., in press (1951).
[70] K. A. Pecherskaya and V. V. Stender, J. Applied Chem. Russ. **19,** (12), 1303 (1946).
[71] N. Pentland, Thesis (London, 1951).
[72] G. Philbert, J. Chim. Phys. **40,** 157 (1943).
[73] V. A. Pleskov, Acta Physicochim. **11,** 305 (1939).
[74] B. Post and C. F. Hiskey, J. Am. Chem. Soc. **73,** 161 (1951).

[75] B. Post and C. F. Hiskey, J. Am. Chem. Soc. **72,** 4203 (1950).
[76] E. C. Potter, Thesis (London, 1950).
[77] J. E. B. Randles and K. W. Somerton, Private communication (1951).
[78] A. Rius and J. Llopis, Anal. Fis. Quim. **42,** 897 (1946).
[79] A. Rius, J. Llopis, and P. Gandia, An. real. Soc., esp. Fis. Quim. **46B,** 225 (1950).
[80] V. A. Roitar and R. Jampolskaya, Acta Physicochim. **7,** 247 (1937).
[81] V. A. Roitar, V. A. Juza, and E. S. Poluynan, Acta Physicochim. **10,** 389, 843 (1939).
[82] F. W. Salt, Discuss. Far. Soc. **1,** 169 (1947).
[83] H. P. Stout, Trans. Far. Soc. **41,** 64 (1945).
[84] H. P. Stout, Discuss. Far. Soc. **1,** 107 (1947).
[85] K. Vetter, *Z.* Physik. Chem. **194,** 284 (1950).
[86] K. Vetter, *Z.* Physik. Chem. **196,** 360 (1951).
[87] K. Vetter, *Z.* Elektrochem. **55,** 121 (1951).
[88] K. Vetter and G. Maneke, *Z.* Physik. Chem. **195,** 270, 338 (1950).
[89] R. G. H. Watson, thesis (London, 1951).
[90] A. Wetterholm, Trans. Far. Soc. **46,** 861 (1950).
[91] K. Wirtz, *Z.* Physik. Chem. **36*B*,** 435 (1937).

Discussion

Dr. J. A. Christiansen, University of Copenhagen, Copenhagen, Denmark: Dr. Bockris, you spoke of one rate-determining step. Don't you believe that there may be more than one rate-determining step?

Dr. J. O'M. Bockris: Yes, I could illustrate that for you.

Dr. Christiansen: In reaction kinetics we very often meet with a sequence of consecutive reactions, i. e., reactions that are in series not in parallel. In that case the reciprocal steady speed of reaction becomes a sum of different members, which separately may be called reciprocal speeds, e. g., one of the unimolecular type, the next of the bimolecular type a. s. o. By integrating the expression, we get in that case an expression of the form

$$t=A_1 \ln \frac{a}{a-x}+A_2\left(\frac{1}{a-x}-\frac{1}{a}\right)+\cdots,$$

i. e., a reaction of a mixed type. I should be very much surprised if similar sequences did not occur also in electrodekinetics. The case where the reactions are in parallel is more complicated.

Dr. Bockris: I thought you were speaking of simultaneous reactions.

Dr. Christiansen: The above integrated equation is that for consecutive reactions.

Dr. Bockris: The equation on the board is quite correct. The equations for some special cases of consecutive reactions of hydrogen evolution reaction have been worked out by Potter and myself (J. Electrochem. Soc. **99,** 169, 1952) and for one case of simultaneous reactions by Azzam and me (Trans. Faraday Soc. **48,** 145, 1952).

Dr. H. H. Uhlig, Mass. Institute of Technology, Cambridge, Mass.: What do you do about the long-time measurement when hydrogen slowly enters the metal? Even though your solution is pure, you may still have a time factor.

Dr. Bockris: Yes, of course, it certainly occurs mostly in the case of palladium. You do find a time element there. I don't think it occurs markedly in many other cases so long as spurious changes due to solution impurities are removed. In nickel it is very slow, although diffusion of hydrogen certainly takes place there (Bockris and Conway, Trans. Faraday Soc. **45,** 989, 1949).

25. Electrokinetic Researches in Capillary Systems and in Colloidal Solutions

By A. J. Rutgers and M. De Smet [1]

Introduction

There is, in general, an electric double layer in the interface between two phases. This double layer manifests itself in the so-called electrokinetic phenomena, which become conspicuous in systems of strongly developed surface. They can be divided into two groups, accordingly as they occur:

A. In capillary systems, where we have electro-osmosis (*EO*), streaming currents (*SC*), and streaming potentials (*SP*).

B. In colloidal solutions, where we have electrophoresis (*EPh*), centrifugation potentials (*CP*), and ultrasonic vibration potentials (*UVP*).

The electrokinetic phenomena can, on the other hand, be classified according to their cause:

A′. Cause electrical, effect mechanical: electro-osmosis (in capillaries) and electrophoresis (in colloidal solutions).

B′. Cause mechanical, effect electrical: streaming currents and streaming potentials (in capillaries), and centrifugation potentials and ultrasonic vibration potentials (in colloidal solutions).

In table 1 these effects are tabulated, together with their formulas.

TABLE 1. *Classification of electrokinetic phenomena* [a]

Cause System	Electrical	Mechanical
Capillary	$Q_{EO}=\frac{D\zeta}{4\pi\eta}\epsilon\Omega$ (A)	$E_{SC}=\frac{D\zeta}{4\pi\eta}\frac{dp}{dl}\Omega$ (B) $V_{SP}=\frac{D\zeta}{4\pi\eta}\frac{dp}{dl}\Omega R$ (C)
Colloidal solution	$V_{EPh}=\frac{D\zeta}{4\pi\eta}\epsilon$ (D)	$i=nD\zeta aV$ (E) $V_{CP}=\frac{nm'}{\sigma}\frac{D\zeta a}{\rho}\frac{\omega^2}{2}(r_2^2-r_1^2)$ (F) $\phi_{UVP}=2\frac{nm'}{\sigma}\frac{D\zeta a}{\rho}wv_0$ (G)

[a] In these formulas, Q_{EO} is the volume of liquid transported per second, D the dielectric constant, ζ the electrokinetic potential, η the viscosity, ϵ the electric field strength, Ω the area of the cross section through the capillary (or capillary system) which is filled with liquid; ω the circumference of the capillary; R the electric resistance of the capillary filled with liquid; in the colloidal solutions, n is the number of colloid particles per cubic centimeter, a their radius, v their speed, m' their apparent mass, ρ their frictional coefficient ($=6\pi\eta a$ according to Stokes' law); i the density of the electric current accompanying the motion of the particles of speed v; σ the electric conductivity coefficient of the solution; w the velocity of propagation of the ultrasound wave; v_0 the velocity amplitude of the liquid particles owing to the ultrasound wave.

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Electro-osmosis, Streaming Potentials, and Surface Conductance

The formula (A) for *EO* demands no further explanation. The formula (C) for *SP* can be used, if R, the resistance of the capillary, is known. For a capillary of length $l=5$ cm, radius $=5\times 10^{-3}$ cm, filled with a solution of $\sigma=2\times 10^{-7}$ ohm^{-1} cm^{-1}, we calculate $R=3\times 10^{11}$ ohms; surface conductance may depress this value to about 10^{11} ohms. To measure R we constructed a resistor with units of 10^6, 10^7, 10^8, and 10^9 ohms; this resistor was then connected in series with the capillary; a direct voltage of 20 v applied, and the drop in voltage over the capillary measured with an electrometer valve potentiometer.

One can also try to avoid the measurement of R in the following way: A capillary or capillary system of cross section Ω, circumference ω, conducts the electric current by volume conductance σ and surface conductance σ_S in parallel. We therefore have

$$1/R=\frac{\sigma\Omega}{l}+\frac{\sigma_S\omega}{l}. \tag{1}$$

In the case of a single capillary,

$$1/R=\frac{\sigma\pi r^2}{l}+\frac{\sigma_S 2\pi r}{l}=\frac{\sigma\pi r^2}{l}\left(1+\frac{2\sigma_S}{r\sigma}\right). \tag{2}$$

If this value of R is substituted in eq (C) of table 1, we obtain

$$V_{SP}=\frac{D\zeta}{4\pi\eta\sigma\left(1+\dfrac{2\sigma_S}{r\sigma}\right)}\,p. \tag{3}$$

This formula cannot be used directly, as σ_S is not known a priori. If we assume that σ_S can be neglected, we obtain the Helmholtz-Smoluchowski formula

$$V_{SP}=\frac{D\zeta}{4\pi\eta\sigma}\,p. \tag{4}$$

All the earlier measurements of *SP* have been interpreted by this formula.

We decided to compare ζ-values obtained in the following ways: (1) From *EO* measurements and intrepretation by formula (A), (2) from *SP* measurements and interpretation by eq (C) of table 1, and (3) from *SP* measurements and interpretation by formula (4). The corresponding ζ-values given in the figures are labeled ζ_{E0}, ζ_R, and ζ_σ.

The apparatus is shown in figure 25.1, A. Contact with air is avoided; change in concentration of the solution is effected by pressing (by means of purified N_2) one drop of a concentrated solution of electrolyte into our liquid; one drop gives a change in concentration of 1 μeq/liter (or even 0.1 or 0.01 μeq/liter) at low concentrations and of 100 μeq/liter at high concentrations. *SP* can be measured between the electrodes E_1 and E_2 clearly shown in figure 25.1 B, by means of an electrometer valve potentiometer when the capillaries are in the vertical position; the solution is then pressed from the big cylindrical vessel to the small reservoir on the top of the capillary (fig 25.1, B). When *EO* is to be measured, the capillaries are filled halfway and then brought into the horizontal position (shown by figure 25.1, C). The big vessel empties itself in the pearshaped vessel and the thread of liquid is moved into position, i. e., one end of the thread of liquid is brouhgt under the window, where its speed of displacement (if an electric potential is applied to E_1, E_2) can be measured by the microscope with the eye-piece micrometer (*M* in fig. 25.1, C). The applied potential was varied, e. g., 600, 500, 400, 300, and 600 v; at each voltage the speed was measured 10 times. Concordant values of ζ_{EO} may be obtained in this way.

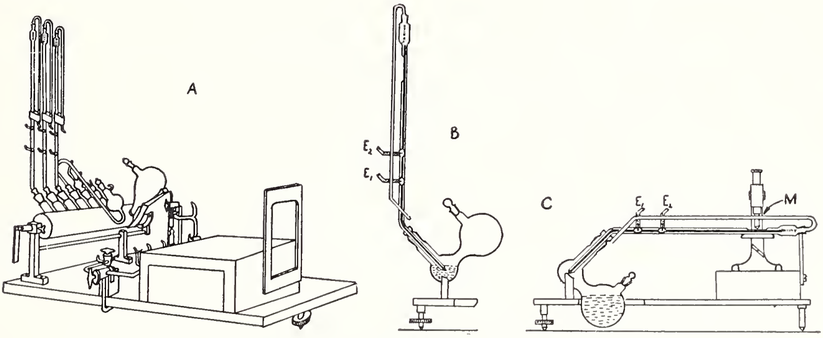

FIGURE 25.1 *Apparatus for measurements of streaming potentials.*

In figure 25.2, for example, we give curves for ζ_{EO}, ζ_R, and ζ_σ obtained as described above for solutions of KCl; the radius of the capillary in this case was $5x10^{-3}$ cm[2]. The agreement between ζ_{EO} and ζ_R proves the accuracy of the experimental technique and the adequacy of eq (A) and (C), whereas the systematic deviation of the curve σ_σ proves the inadequacy of eq (4) and proves that surface conductance is of importance at low concentrations. In fact, at $c=0$, $\sigma_S=7x10^{-10}$ohm^{-1}; $\sigma=2x10^{-7}$ohm^{-1}cm^{-1}; $2\sigma_S/r\sigma=1.4$; at $c=200\mu$eq/liter, $\sigma_S=37x10^{-10}$ohm^{-1}; $\sigma=300x10^{-7}$ohm^{-1}cm^{-1}; $2\sigma_S/r\sigma=0.05$.

Thus, we see that formula (4) gives good results at high concentrations but is not reliable at low concentrations. Especially the maximum in the ζ_σ curves, found by all previous workers, who interpreted their results with the aid of eq (4) and which, incidentally, was explained by Stern, must be attributed to the failure of eq (4).

Results in Aqueous Solutions of Electrolytes

With the experimental *EO* technique, described in the previous section, we have determined (ζ—log *c*) curves at concentrations between 0.01 and 10.000 μeq/liter for solutions of (a) NH_4NO_3, $LiNO_3$, KNO_3, HNO_3, $CsNO_3$, $AgNO_3$, (b) KCl, KNO_3, KI, KOH, K_2SO_4, $K_4Fe(CN)_6$, (c) $Ca(NO_3)_2$, $Ba(NO_3)_2$, $Mg(NO_3)_2$, $Zn(NO_3)_2$, (d) $Al(NO_3)_3$, $La(NO_3)_3$, $Ce(NO_3)_3$, (e) $Th(NO_3)_4$, (f) crystalviolet, and (g) sodium *i*-butylnaphtalene sulfonate. Some of the results are given in figures 25.3 and 25.4. The curve for KCl also holds approximately for the other uniunivalent salts; the curve for $Ca(NO_3)_2$ holds also for $Ba(NO_3)_2$, $Mg(NO_3)_2$, and $Zn(NO_3)_2$.

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[2] We also obtained results for solutions of KOH, HCl, and $CaCl_2$. They showed results similar to KCl.

We will not go into a detailed discussion of these results but make the following points: From fig. 25.3 we see that the electrokinetic potential ζ behaves very much the same as the total electrochemical potential ϵ of a glass electrode, i. e., decrease of $(-\zeta)$ with increase of H^+ ions and an increase of $(-\zeta)$ with increase of OH^- ions, followed, however, at still higher concentrations of KOH by a decrease of $(-\zeta)$, which is different from the behavior of ϵ. The curves for ζ as a function of pH obtained for various silicates by other workers agree in general shape with those obtained by us for glass.

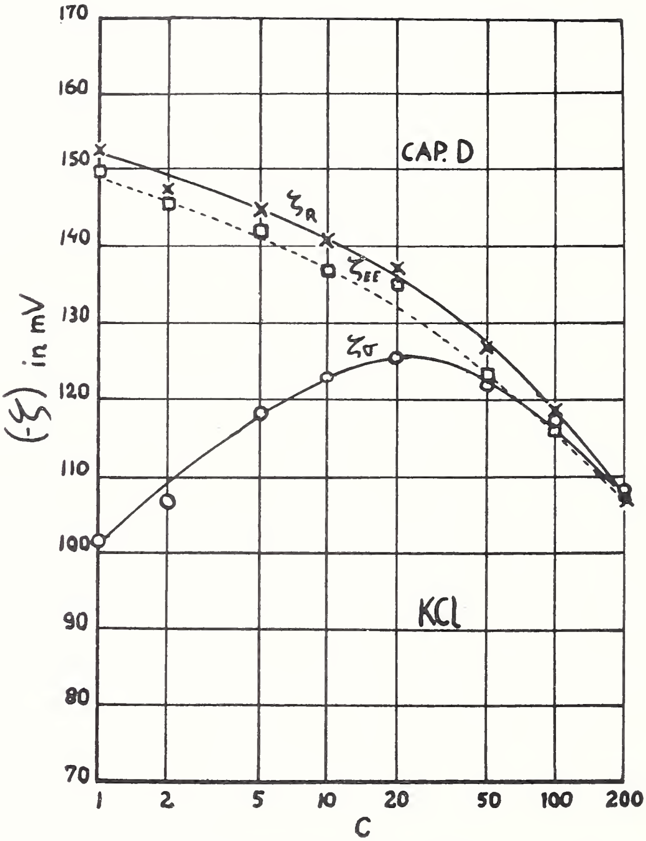

FIGURE 25.2. *Values of the electrokinetic potentials (electrosmosis, streaming potentials, and surface conductance) for* KCl.

The degree of parallelism between ζ and ϵ was studied by us more carefully with a special apparatus that allowed the simultaneous measurement of ζ and ϵ at one interface (fig. 25.5); the wall of the capillary inside the mantle is extremely thin. To mention only one result, for solutions of KOH we found a steady linear increase of ϵ with low c (for Jena 16^{III}-glass), and, as already stated, an increase followed by a decrease, for $(-\zeta)$. Hence no simple explanation of $(\zeta-c)$ behavior in terms of $(\epsilon-c)$ behavior is possible.

Let us now return to figure 25.4; here we see that for monovalent cations, the bend in the $(\zeta-\log c)$ curves lies at $c=50-100$ μeq/liter;

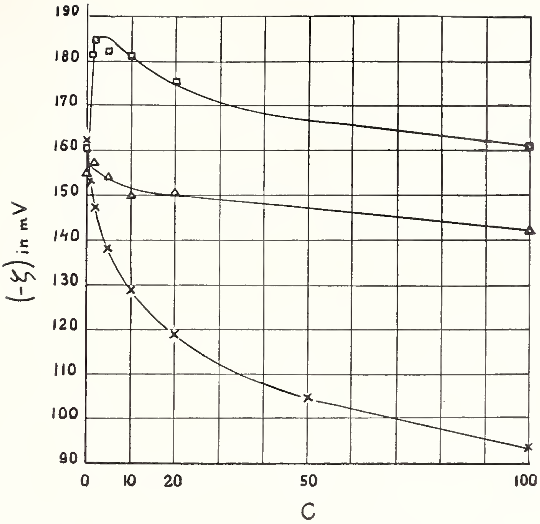

FIGURE 25.3. *Relation between electrokinetic potential and concentration for* HNO_3, KOH, *and* KNO_2.
×, HNO_3; □, KOH; △ KNO_3.

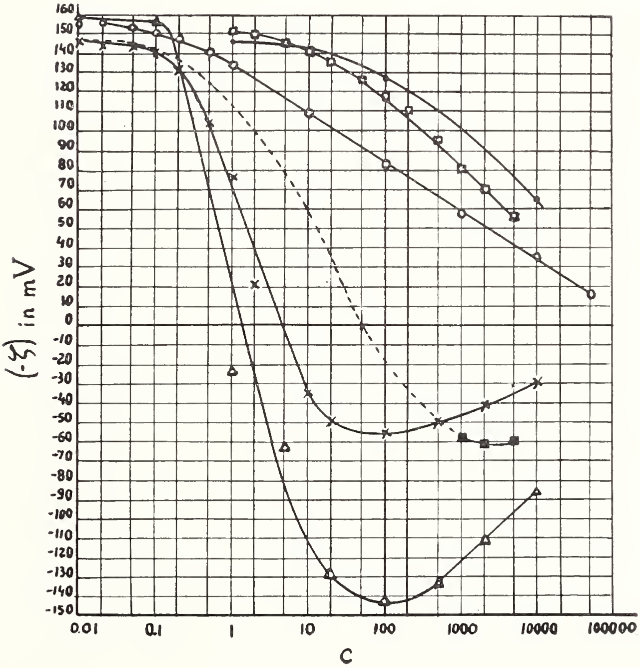

FIGURE 25.4. *Relation between electrokinetic potential and concentration for various substances.*
□, KCl; ○, $Ca(NO_3)_2$; ×, $Al(NO_3)_3$; △, $Th(NO_3)_4$; ■, cristalviolet; ●, Na isobutyl naphthalene sulfonate.

for divalent cations at $c = 0.1-1$ μeq/liter. As a consequence, bivalent cations cause a decrease of $(-\zeta)$ at much lower concentrations than univalent cations. In colloidal solutions, the corresponding phenomenon known as Schulze and Hardy's rule is of the greatest importance. This effect can be accounted for quantitatively. The theory is based on the following idea: The cations are attracted toward the interface, because here the electrostatic potential is negative; bivalent cations are attracted more strongly than univalent cations. We therefore compared the $(\zeta - \log c)$ curve for K^+ ions at a normal glass wall for which $\zeta = -130$ mv, with the curve for Ba^{++} ions at the same glass wall for which the ζ potential had been lowered to -65 mv by the addition of 50 μeq/liter of HCl. Although ζ for the glass wall differed, the K^+ ions and the Ba^{++} ions had the same potential energy at these tqo walls, and, in fact, the general shape of their $(\zeta - \log c)$ curves proved to be the same (fig. 25.6).

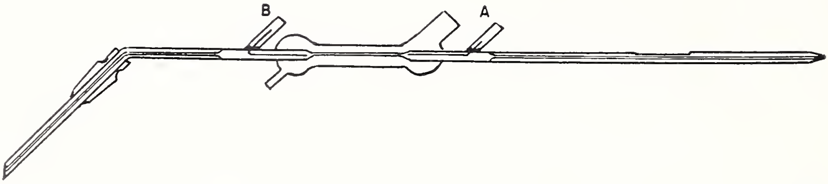

Figure 25.5. *Apparatus for simultaneous measurement of electrokinetic potential and total electrochemical potential.*

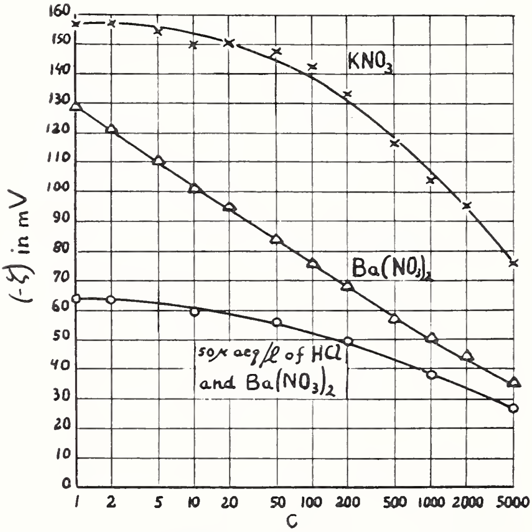

Figure 25.6. *Electrokinetic potential of* K^+ *and* Ba^{++} *as functions of concentration.*

Surface Conductance

Values of σ_S can be obtained from values of R by eq (1). Direct-current measurements of R, as described above, may be readily made between 1 and 10 μeq/liter. At higher concentrations they are disturbed by polarization and R must then be determined by an a-c method. However, a-c measurements are only possible if R is reduced by a factor of about 5,000. We therefore constructed a "ring system", a system of closely fitting concentric rings, ground off to equal heights, and kept in position by thin sealed-over Pt wires (fig. 25.9). For this system $\Omega=0.08$ cm^2, $\omega=40$ cm, $l=1$ cm.

Figure 25.7 shows the values of σ_S for solutions of a normal electrolyte and for solutions of Th $(NO_3)_4$, in which the sign of ζ is reversed. It is interesting to note that σ_S passes through a very low minimum,

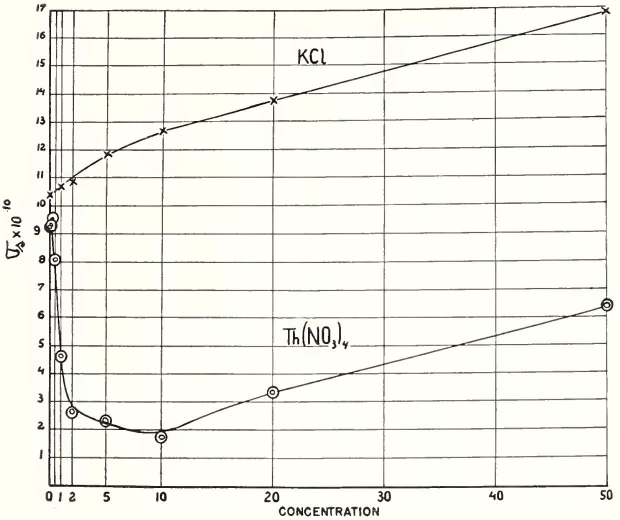

FIGURE 25.7. *Values of surface conductance of* KCl *and* $Th(NO_3)_4$.

when ζ passes through zero. This observation agrees with Smoluchowski's equation for σ_S,

$$\sigma_S=\left(\frac{D\zeta}{4\pi}\right)^2\frac{1}{\eta\delta}. \tag{5}$$

Here δ is the thickness of the diffuse layer. The experimental value of σ_S in pure water, however, leads to a value of δ that is much smaller than expected in a solution of 1 μeq/liter, namely, [$\delta_{\text{exp}}=5\times10^{-7}$cm; $\delta_{\text{theor.}}=1.6\times10^{-5}$cm]. The formula for σ_S is easily understood if we write it as:

$$\sigma_S=\frac{D\zeta}{4\pi\eta}\times\frac{D\zeta}{4\pi\delta}=\frac{v}{\epsilon}\times q, \tag{6}$$

i. e., as a speed per unit field times a charge per square centimeter.

Research in Nonaqueous Solutions

A first group of solvents, CH_3OH, C_2H_5OH, n- and i-C_3H_7OH, and CH_3COCH_3 were examined in an *EO* apparatus, very similar to that described above. Results are shown in figure 25.8; the solute was KI. The solvents are similar to water, in so far, that their dielec-

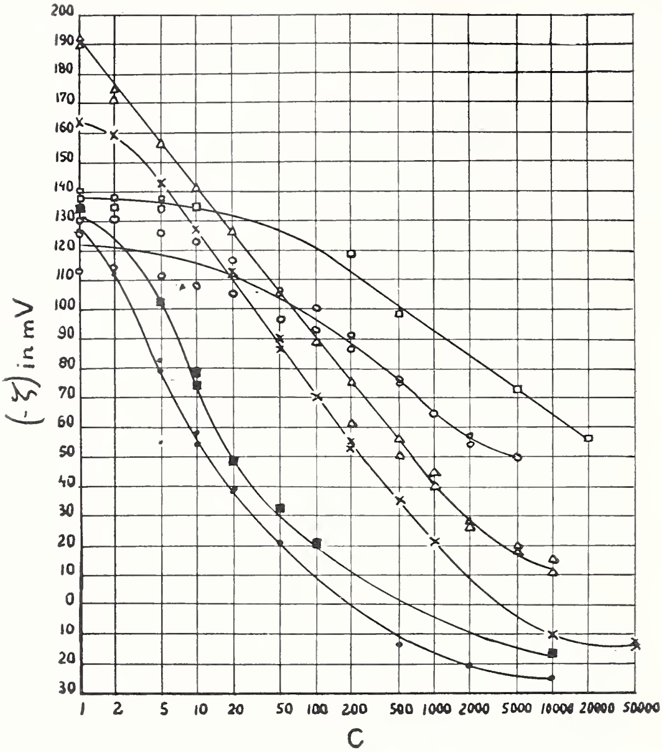

FIGURE 25.8. *Zeta potential for* KI *in various solvents.*
□, Water; △, acetone; ○, methylalcohol; ×, ethylalcohol; ■, propylalcohol; ●, isopropylalcohol.

tric constant is not very small, and that they show a measurable electrolytic dissociation as determined by the base-acid chain. Some results for the pure solvents, values of log $K_{\text{diss.}}$, and results obtained by others are given in table 11.

TABLE 2. *Values* [1] *of* $(-\zeta)$ *and log* $K_{\text{diss.}}$ *for some pure organic liquids*

Solvent	Quincke and Tereschin	Coehn and Raydt [2] (acetone)	Coehn and Raydt [2] (water)	Fair-brother and Balkin	DeSmet and Delfosse	D	Log $K_{\text{diss.}}$
Water	60	264	140	55	148	80	—14.20
Methyl alcohol	40	238	133	------	123	35	—16.86
Ethyl alcohol	80	233	130	------	170	24	—17.63
Acetone	------	230	129	62	230	21	--
n-Propyl alcohol	------	184	104	55	139	19.5	—19.85
i-Propyl alcohol	------	------	------	------	150	18.3	—20.65

[1] Measurements by Dr. Delfosse and Dr. de Ley

[2] Coehn and Raydt's ζ-values are only relative. In their first column, the value $\zeta=-230$ mv for acetone has been arbitrarily chosen; in the second, the value ζ-=140 mv for water.

No evidence in support of Coehn and Raydt's rule (parallelism between ζ and D) was found. There seems to be, however, a parallelism between the concentration of the bend in the (ζ—log c) curves, and the value of $K_{\text{diss.}}$.

Researches in Solvents of Low Dielectric Constant

Things become very different, if we try to extend electrokinetic measurements to solvents of low dielectric constant, such as dioxane ($D=2.22$) and benzene ($D=2.28$). If a direct voltage V is applied to the ends of a capillary thread of benzene or dioxane, no EO is observed. We, therefore, decided to increase the sensibility of our apparatus by replacing the capillary by a capillary system (fig. 25.9), consisting of a number of closely fitting concentric rings. For such a system we can easily prove that

$$Q_{EO}=\frac{\rho}{\rho+\rho_1+\rho_2}\frac{D\zeta}{4\pi\eta}\frac{V}{l}\Omega \qquad (7)$$

if V/l is the electric field strength, and ρ, ρ_1, and ρ_2 are the factors of resistance against flow for the first side capillary, the ring system, and the second side capillary, respectively.

If the ring system is sufficiently narrow, the first factor is of the order unity, and the value of Ω/l may be 5,000 times larger for the ring system than for a single capillary. Thus the sensibility of the apparatus is multiplied by a factor of 5,000. The measurements were carried out in solutions of $(i\text{–}C_5H_{11})_4$ N-picrate (tiap) in pure dioxane and in dioxane-water mixtures, varying in dielectric constant from 2.22 to 3.94. Values of c were 0, 10^{-7}, 5×10^{-7}, 10^{-6}, 5×10^{-6}, 10^{-5}, 10^{-4}, and 10^{-3} normal. Similar measurements were carried out in solutions of tiap in benzene and in benzene-acetone mixtures varying in dielectric constant from 2.28 to 9.97.

Although we obtained quite satisfactory EO flow in nearly all our experiments, the ζ values, calculated from Q/V, turned out to be dependent on the applied voltage in a number of our solutions. This effect had already been observed by previous workers, but they reported only relatively small deviations from proportionality between Q_{EO} and V, whereas in our experiments the deviation often was quite considerable, as may be seen from the following:

V/l(volt/cm)	936	615	412	206	936
ζ (mv)	−75. 4	−62. 4	−57. 4	−39. 8	−71. 8.

These values were obtained for a 10^{-7} N solution of tiap in a dioxane-water mixture of $D=2.57$.

We, therefore, decided to turn back to the other class of electrokinetic effects in which a mechanical force is applied and an electric effect is obtained. In these solutions, measurements of SP are not feasible, because of the enormous electric resistance of the sytem. We, therefore, decided to measure streaming currents; for there, we have as long as the electric conduction current can be neglected in comparison with the convection current:

$$\mathrm{I}_{SC}=\frac{\rho}{\rho+\rho_1+\rho_2}\frac{D\zeta}{4\pi\eta}p\frac{\Omega}{l}. \qquad (8)$$

The streaming current was measured by the time in which a given capacity C was charged up to a certain voltage V:

$$\mathrm{I}_{SC}=CV/t. \qquad (9)$$

The results are given in figure 25.10 as a function of tiap concentration on a logarithmic and a linear scale and in figure 25.11 as a function of σ (which is roughly proportional to the ionic concentration). The maximum shown by all curves is very remarkable. Further, it seems that $\zeta=0$ when there are no ions in the solution. Results obtained in benzene-acetone mixtures are not shown.[3] Suffice it to say they show the same general characteristics.

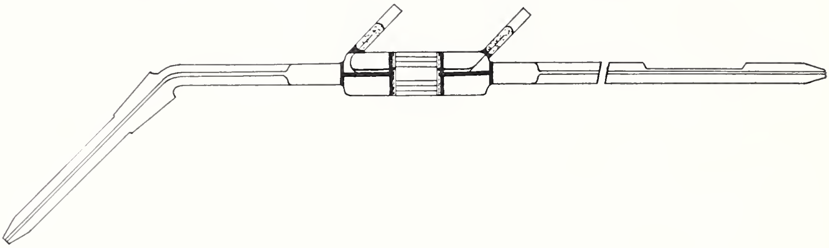

Figure 25.9. *Capillary system for measurements of electrokinetics in solvents of very low dielectric constant.*

$$Q=\frac{\rho}{\rho+\rho_1+\rho_2}\,\frac{D\zeta}{4\pi\eta}\,\frac{V}{l}\,\Omega.$$

Electrophoresis [4]

One of the difficulties in the microscopic measurements of the electrophoretic speed of particles in a colloid or in a suspension is the simultaneous movement of the liquid due to electrosmosis along the walls of the cell. This *EO* may set up a difference in hydrostatic pressure, giving rise to flow of the liquid for which the speed is given by

$$v(r)=v_{EO}-v_{\text{Pois.}}=v_{EO}-\frac{p}{4\pi l}(r_0^2-r^2).$$

If we work with a closed cylindrical capillary, in which the total flow is zero, then

$$v_{EO}\pi r_0^2=\frac{p}{8\eta l}\pi r_0^4;\quad \frac{p}{4\pi l}=\frac{2}{r_0^2}v_{EO},$$

and

$$v(r)=v_{EO}\left\{1-\frac{2}{r_0^2}(r_0^2-r^2)\right\}=v_{EO}\left(\frac{2r^2}{r_0^2}-1\right). \tag{10}$$

We see that $v(r)$ vanishes at $r=r_0/\sqrt{2}\simeq 0.71r_0$.

The electrophoresis of suspended particles is therefore measured at this distance from the axis. The drawback to this procedure, however, is that dv/dr is large at $r=0.71r_0$, so that a small error with respect to the depth at which the measurements are performed causes a considerable error in v_{EPh}. Since in the axis of the capillary, $dv/dt=0$, *EPh* should be measured in the axis. Accordingly, the capillary for *EPh* should be constructed in such a way that the speed of the liquid vanishes in the axis. This has been achieved by Smith and Lisse [3].[5] Their apparatus consisted, however, of two different capillaries

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[3] Copies of these results may be obtained from the authors.

[4] This work was done with Dr. van der Minne and Dr. Facq [3].

[5] Figures in brackets indicate the literature references on p. 279.

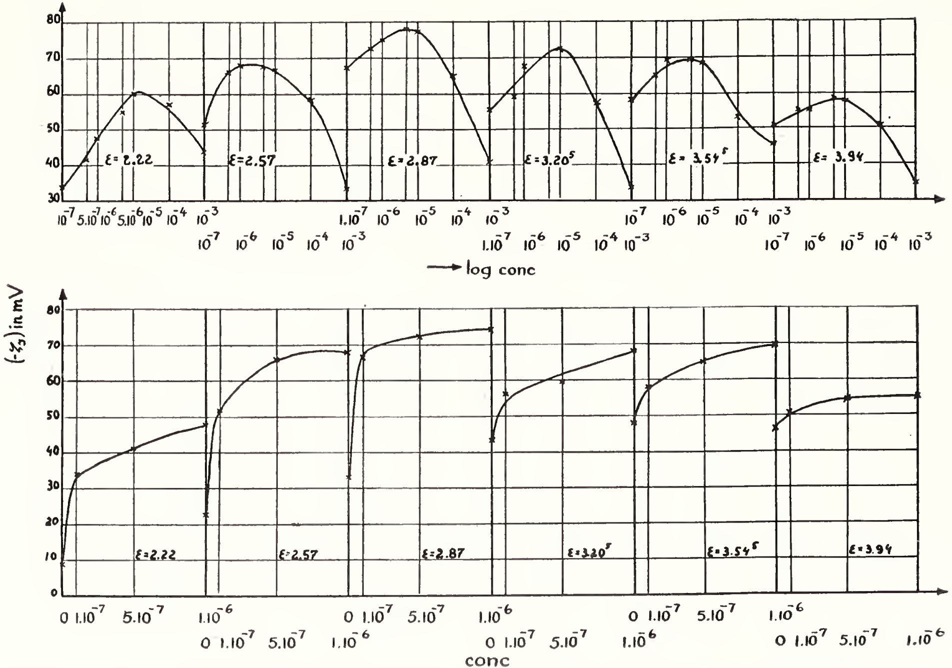

FIGURE 25.10. *Zeta potential for "tiap" in dioxane-water solutions of different dielectric constants as a function of concentration, on a logarithmic and a linear concentration scale, respectively.*

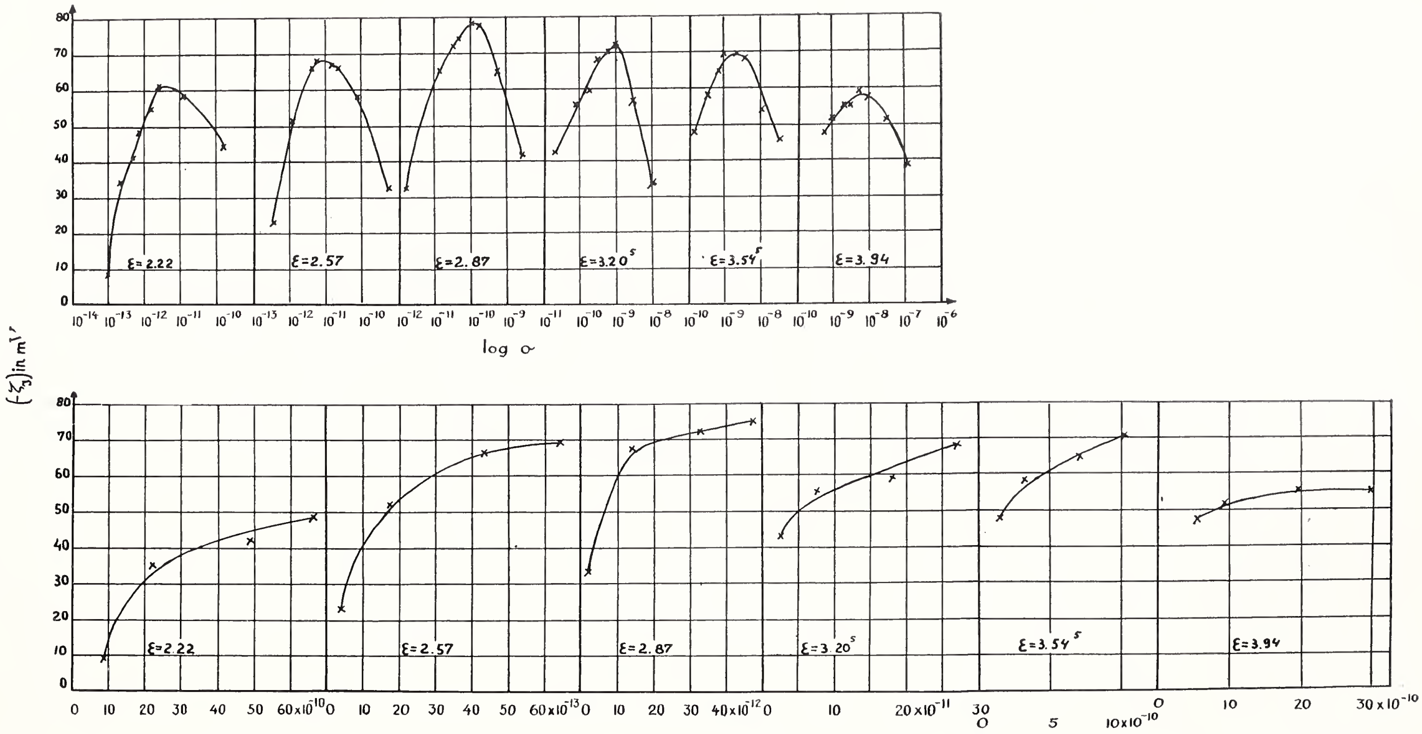

FIGURE 25.11. *Zeta potential for "tiap" in dioxane-water solution of different dielectric constants as a function of electric conduc coefficient of the solution.*

of which the glass-water interface had to have the same ζ-potential.

We have solved the problem in the following way. In the ordinary capillary, the Poiseuille flow is described by

$$v_{\text{Pois.}} = 2v_{EO}(1 - r^2/r_0^2).$$

In the axis

$$v_{\text{Pois.}} = 2v_{EO}.$$

We must have $v_{\text{Pois.}} = v_{EO}$ in the axis for then the speed of the liquid will vanish and accordingly $v_{\text{Pois.}}$ must be halved. This can easily be achieved as follows: Introduce two electrodes into a capillary one at the end and the other exactly in the middle. Then, when tension is applied, the liquid will move electrosmotically, say from left to right and the hydrostatic pressure in the middle bulb will increase (fig. 25.12).

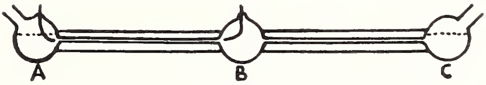

Figure 25.12. *Apparatus for measurement of electrophoresis; schematic drawing*

This pressure head will cause a Poiseuille flow of liquid from B to A and from B to C. These will be equal, hence the flow from B to A will be only half as large as the Poiseuille flow in the capillary cell. Hence

$$v(r) = v_{EO} - v_{\text{Pois.}} = v_{EO}\left\{1 - \left(1 - \frac{r^2}{r_0^2}\right)\right\} = v_{EO}\,\frac{r^2}{r_0^2}. \tag{11}$$

We see that with this $v(r)$ the speed of the liquid in the axis vanishes. Measurements with this cell, which had shape shown in figure 25.13, confirmed all expectations.

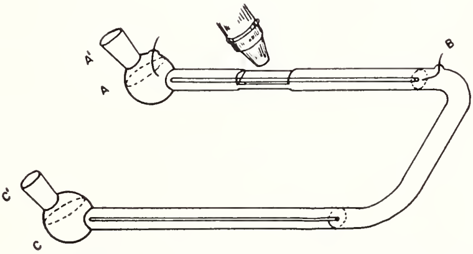

Figure 25.13 *Definitive apparatus for measurement of electrophoresis.*

Centrifugation Potentials [6]

If a colloidal solution is centrifuged the suspended particles, which we will assume to be heavier than water, will move toward the periphery. This motion of speed v_0 represents, as can easily be deduced, an electric current, the density of which is given by

$$i = nD\zeta a v_0, \tag{12}$$

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[6] This work was done with Dr. G. Jacobs [4].

where a is the radius of colloidal particles and n their number per cubic centimeter. Now

$$v_0 = \text{force}/\rho = m'g'/\rho,$$

where m' is the apparent mass of the particles, ρ the frictional coefficient ($=6\pi\eta a$ according to Stokes) and g' their acceleration, due to rotation. Hence $g'=\omega^2 r$, where r is the distance from the axis of rotation. This electric current will set up a potential difference, so large, that the current of conduction, caused by it, is equal to the current of convection. Hence

$$\left.\begin{aligned} i &= nD\zeta a \frac{m'\omega^2 r}{\rho} = \sigma \\ \epsilon &= \frac{nm'}{\sigma}\,\frac{D\zeta a}{\rho}\, m'\omega^2 r \\ V_{CP} &= \int_{r_1}^{r_2} \epsilon\, dr = \frac{nm'}{\sigma}\,\frac{D\zeta a}{\rho}\, m'\,\frac{\omega^2}{2}\,(r_2^2 - r_1^2) \end{aligned}\right\} . \qquad (13)$$

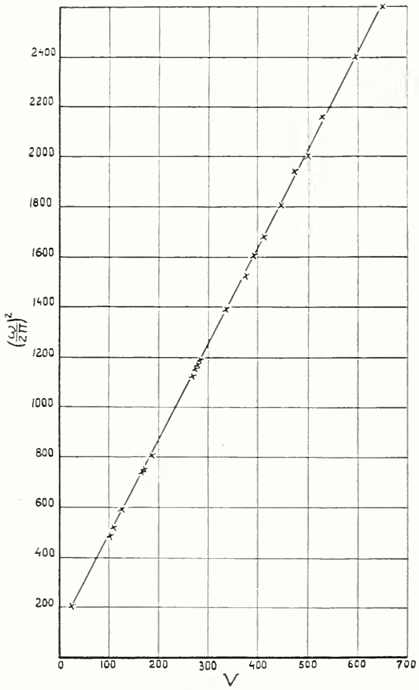

FIGURE 25.14. *Proportionality of centrifugation potential and the square of the angular speed of rotation.*

This proportionality of V_{CP} with ω^2 was confirmed by experiment as shown in figure 25.14. V_{CP} must be measured during rotation. Therefore, it must be conveyed from the rotating system to the potentiometer, which is at rest. This is achieved by a box filled with mercury in which a disk could rotate (fig. 25.15). The rotor is shown

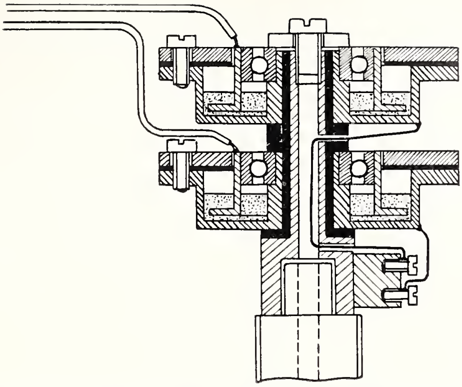

Figure 25.15. *Box filled with mercury containing a rotating disk for measurements of centrifugation potentials*

in figure 25.16. For symmetry and to increase the magnitude of the effect, 16 tubes were connected in series. The tubes were connected by a platinum wire, the ends of which were immersed in the ultrafiltrate, to which chinhydron had been added. This was separated from the sol by a thin cellophane foil as shown in figure 25.17.

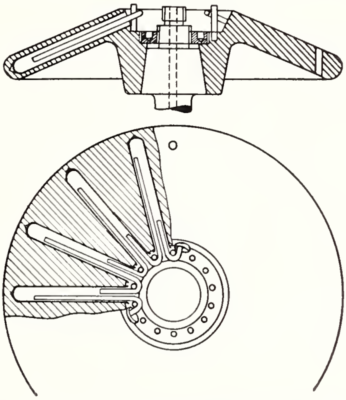

Figure 25.16. *Rotor used in measurements of centrifugation potentials.*

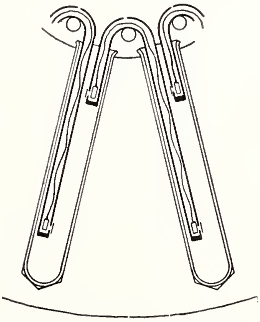

Figure 25.17. *Details of apparatus used in rotor showing connection between two consecutive tubes, accomplished by a platinum wire immersed in ultrafiltrate to which quinhydrone has been added.*

The determination of ζ potentials of colloidal particles has always been a difficult problem. Most results obtained by various authors generally do not agree. In figure 25.18 our results for KCl are shown. There is a pronounced bend in the ($\zeta - c$) curve at $c=3$ millimole/liter, which cannot be explained by the usual theory of the double layer. In fact, this theory predicts a consistent change of ζ as a function of concentration. The bend might be caused by a secondary process, e.g., a conglomeration of the colloidal particles, when ($-\zeta$) has fallen below a certain value. This conglomeration then might prevent a further decrease of ($-\zeta$). Measurements of the scattering of light have failed, however, to bring any support for this explanation. Measurements have also been made for $K_4Fe(CN)_6$, HCl, Na_2S, Na_2SO_4, $BaCl_2$, and $[Co(NH_3)_5Cl]Cl_2$ but are omitted here.[7]

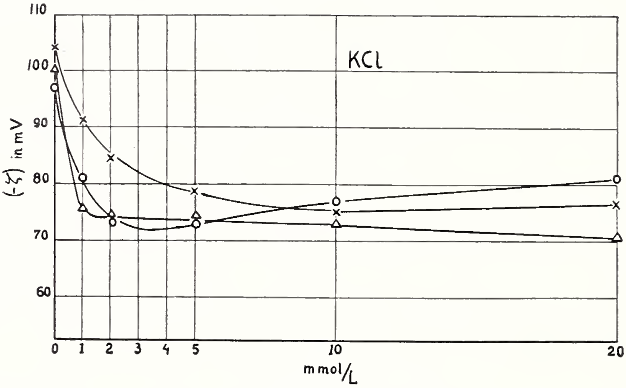

FIGURE 25.18. *Zeta potentials in sols of As_2S_3 with KCl added, obtained from centrifugation experiments.*

Ultrasonic Vibration Potentials [7,8]

Debye [5] in 1933 pointed out that an ultrasonic wave will generate an alternating potential difference in the solution of an asymmetric electrolyte. In 1938 it was pointed out [6] that this effect would be a thousand times larger in colloids. The amplitude of the positive and the negative current densities, accompanying the oscillating motion of the colloidal particles and their counter ions in the ultrasonic wave, are again given by eq (12). If they were exactly in phase, they would counterbalance each other exactly. There is, however, a phase lag for the colloidal particles, due to their inertia. The resulting current density will be proportional to

$$\frac{F_{in}}{F_{fr}}=\frac{m'\omega v}{\rho v}=\frac{m'\omega}{\rho}$$

hence

$$i=n\frac{D\zeta a}{\rho}m'\omega v=\sigma\epsilon$$

$$=\frac{nm'}{\sigma}\frac{D\zeta a}{\rho}\omega v.$$

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[7] Copies of graphs for these may be obtained from the authors.
[8] This work was done with Dr. J. Vidts [8].

Now, in the sound wave

$$v = v_0 \sin \frac{2\pi z}{\lambda} \sin \omega t.$$

Hence, we find for the electric potential amplitude

$$\phi_0 = 2 \int_0^{\lambda/4} \epsilon d = 2 \frac{nm'}{\sigma} \frac{D\zeta a}{\rho} v_0 w,$$

where w is the speed of sound in the liquid. Also by replacing a factor 6 in the denominator by a factor 4 we have

$$\phi_0 = 2 \frac{nm'}{\sigma} \frac{D\zeta}{4\pi\eta} w v_0,$$

In an As_2S_3 sol of 100 g/liter we have, if $v_0 = 1$ cm sec^{-1}, $nm' = 0.1 \times (2.46/3.46) = 0.07$ g/cm^3 $\sigma = 4 \times 10^{-4} \Omega^{-1}$ cm$^{-1} = 36 \times 10^7$ esu; $\zeta = -100$ mv, $w = 1.5 \times 10^5$ cm sec^{-1}, $v_0 = 1$ cm sec^{-1}, whereby $\phi_0 = 3.1$ mv.

We detected the effect in 1946 in a sol of AgI [7, 8]. Yeager, Bugosh Hovorka, and McCarthy [9] detected the effect in 1949 for electrolytic solutions. The main difficulty for a quantitative interpretation of experimental results is the absolute measurement of the velocity amplitude of the ultrasonic wave, v_0; work is now underway in this direction.

References

[1] M. de Smet, Electro-Endosmose I–V; Meded. Kon. Vl. Akad. v. Wetensch. III, 12, 14 (1941), IV, 4, 8 (1942).

[2] A. J. Rutgers and M. de Smet, Trans. Faraday Soc. **41,** 758 (1945); **43,** 102 (1947); **48,** 635 (1952).

[3] A. J. Rutgers, J. L. van der Minne, and L. Facq, Nature **166,** 100 (1950); M. E. Smith and M. W. Lisse, J. Phys. Chem. **40,** 399 (1936).

[4] G. Jacobs, Centrifugation potentials, Thesis (Ghent, 1951); Trans. Faraday Soc. **48,** 355 (1952).

[5] P. Debye, J. Chem. Phys. **1,** 13 (1933).

[6] J. J. Hermans, Phil. Mag. [7], **25,** 426 (1938); **26,** 674 (1938).

[7] A. J. Rutgers, Physica **5,** 46 (1938), Nature **157,** 74 (1946).

[8] A. J. Rutgers and J. Vidts, Nature **165,** 109 (1950).

[9] E. Yeager, J. Bugosh, F. Hovorka, and J. McCarthy, J. Chem. Phys. **17,** 412 (1949).

Discussion

DR. J. TH. G. OVERBEEK, University of Utrecht, Utrecht, The Netherlands: Dr. Rutgers has argued that the ζ-potential and the absolute potential are not identical but are similar. We find with silver iodide that for low potentials there is a definite similarity and for higher potentials they go away from each other. I will just make a small sketch of it on the board. I think there is a clear parallel between the two objects, glass and silver iodide.

DR. A. J. RUTGERS: I agree with Dr. Overbeek.

26. Electromotive Force From Proton Transfer Reactions

By Theodore Shedlovsky[1]

Introduction

Galvanic cells derive their electrical energy in large part from oxidation-reduction reactions. However, for electrical work to result from such a reaction the site at which oxidation occurs, the anode, must be separated from the site at which reduction takes place, the cathode. Moreover, metallic conductors must be present at these sites to provide for the required *electron* transport involved in oxidation-reduction processes.

In living cells there are found electric potentials, as high as 0.1 v per cell, which are capable of operating low-power galvanometers for relatively long periods of time, and which, therefore, cannot be purely electrostatic in nature. But since metallic (electron) conductors, which are required for the electrodes in galvanic cells, do not appear to exist in biological materials oxidation-reduction reactions cannot serve as the immediate energy precursors for bioelectric phenomena. It has consequently been frequently assumed that such electrical potentials arise from ionic diffusion mechanisms, and, in fact, many electrical activities of living cells can be satisfactorily explained on this basis. However, in the case of the algae, *Halicystis Osterhoutii*, containing a large vacuole filled with a sap that is not very different in composition from the sea water in which it is found, an outwardly directed potential of about 65 mv.[2] exists across the membrane separating these two solutions. If the sea water is replaced by sap, so that both internal and external solutions are alike, the potential is about 45 mv (see footnote 2). In another marine plant cell, Valonia, which is similar in appearance to Halycistus, but whose sap contains considerably more potassium than does sea water, there exists an inwardly directed potential of about 10 mv. If the sea water is replaced with sap, in this case the potential rises to about 90 mv in the opposite direction. It is difficult to attribute such phenomena to simple ionic diffusion processes.

Theoretical

The electric forces due to the charges of the fundamental particles, protons and electrons, are so great at the small distances at which they can interact with matter that neither can exist free in material media. Unlike ions, which conduct an electric current by simple migration superimposed on their Brownian motion, electrons undergo displacement transitions from atom to atom in metallic conduction. Similarly, the abnormally high conductance of the hydrogen and the hydroxyl ions in water is most readily explained, as has been shown

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[1] The Rockefeller Institute for Medical Research, New York, N. Y.

[2] W. J. V. Osterhout, J. Gen. Physiol. **23**, 53 (1939); L. R. Blinks, J. Gen. Physiol. **18**, 409 (1934).

by Hückel,[3] Bernal and Fowler,[4] and Wannier,[5] by proton transitions between neighboring water dipoles. If the hydrogen and hydroxyl ions in water were normal, one would expect their equivalent conductances to be about the same as K^+ and Cl^-,[6] i. e., at 25° C 73.5 for K^+ and 76.3 for Cl^-. However the observed values are 350 for H_3O^+ and 198 for OH^-. Thus, over 70 percent of the conductance of pure water appears to be due to proton conductance.

Let us consider a system, containing acidic or basic substances, in which simple ionic conductance is sufficiently impeded by appropriate binding forces so that it becomes negligible in comparison with the proton displacements. These can be represented by proton reactions of the type

$$(H_2O)H^+ + (H_2O)' = (H_2O)'H^+ + (H_2O),$$

or

$$(OH^-)H^+ + (OH^-)' = (OH^-)'H^+ + (OH)^-,$$

in which the proton displacement requires passage over an energy barrier. And these may well continue to take place under conditions that virtually abolish ionic migration. In this case conductance becomes entirely protonic. It has been shown that in pure H_2SO_4 proton displacement appears to account for all the electrical conductance.[7] This may be expected to be generally so for other pure acids (and bases), particularly in the solid state.

A glass "electrode" cell, it is well known, does not give potentials that are a function of the hydrogen-ion concentration until the glass has been aged in water. Binding of the solvent in the glass then may well take place, at least in the surface layers, so that the conductance may be practically all protonic.

In looking for alternative explanations for such bioelectric behaviour I have been led to the question: Is it possible for electrical work to arise *directly* from acid-base rections, that is, from *proton* transfer in a manner analogous to the *electron* transfer mechanism of the galvanic cell? It is the purpose of this communication to show that this is possible, and to present supporting experimental evidence.

The conditions for deriving electrical work from the free energy of an electron, e^-, transfer (oxidation-reduction) reaction $Me^- + N = Ne^- + M$ are that (1) the reaction be resolved into two steps $Me^- = M + e^-$ and $N + e^- = Ne^-$, and (2) that these take place simultaneously, at two separate sites where metallic conductance is available to receive or release electrons.

As a specific example let us consider a typical electrochemical cell (E) consisting of a (platinum) hydrogen electrode (a) and a silver–silver-chloride electrode (b), both in contact with solution containing hydrogen and chloride ions. The electrochemical reactions which take place at (a) and at (b) when the cell operates are shown below:

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[3]. E. Z. Huckel, Electrochem. **34**, 546 (1928).

[4] J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515 (1933).

[5] G. Wannier, Ann. Physik **24**, 545, 569 (1935). See also, A. E. Stearn and H. Eyring, J. Chem. Phys. **5**, 113 (1937).

[6] The crystallographic radii, *r*, of the "unsolvated" spherical H_3O^+ and K^+ ions are both 1⅓A. Since the ionic equivalent conductances of symmetrical cations follow a smooth function of $1/r$, the value for H_3O^+ should be similar to that for K^+ if the former behaved as a normal ion. For symmetrical anions such as the halides, and even (½)$SO_4^=$, the equivalent ionic conductances are not very different from the value for Cl^-. Consequently, if OH^- were a normal ion it should conduct to a degree comparable with Cl^-.

[7] L. P. Hammett and F. A. Lowenheim, J. Am. Chem. Soc. **56**, 2620 (1934).

Reactions of galvanic cell E

(c)	Electrode	(a)	Solution (S)	(b)	Electrode	(c)
	Pt, (H_2)		H_3O^+, Cl^-,---		AgCl, Ag	

(a) $(1/2)H_2+H_2O \rightleftharpoons H_3O^+ + e^-_{(Pt)}$.

(b) $Ag^+ + e^-_{(Ag)} \rightleftharpoons Ag^+e^-$ (solid); or Ag^+Cl^- (solid) $+ e^-_{(Ag)} \rightleftharpoons Ag^+e^-$ (solid) $+ Cl^-$.

(c) $e^-_{(Pt)} \rightleftharpoons e^-_{(Ag)}$.

Alternate galvanic cell E

(Electrode)	(d)	Solution (S)	(b)	Electrode	(c)	Electrode	(a)	Solution (S)	(d)	(Electrode
Ag, AgCl		HCl (aq)		AgCl, Ag		Pt, (H_2)		HCl (aq)		AgCl, Ag

On closed circuit, electrons also pass from platinum to silver according to reaction (c) at the site of a Volta potential. On combining (a), (b), and (c) the electrons in the platinum, $e^-_{(Pt)}$, and in the silver, $e^-_{(Ag)}$, cancel and we obtain,

$$(1/2)H_2+H_2O+Ag^+ = Ag^+e^- \text{ (solid silver)} + H_3O^+$$

or

$$(1/2)H_2+H_2O+Ag^+Cl^- \text{ (solid)} = Ag^+e^- \text{ (solid silver)} + H_3O + Cl^-$$

The second form of this equation, which represents the change in state accompanying the electrical operation of the cell, includes the fact that the activity of the silver ion is determined by that of the chloride ion through the solubility product of AgCl, which is present in solid phase. It is the Gibbs free energy of this reaction that determines the electromotive force of cell E. This emf will depend on the activities of the hydrogen ion and of the chloride ion, since the chemical potentials of the solids are constant. The emf of this cell is usually measured by connecting electrodes Pt and Ag to copper wires that make connection to the appropriate measuring instruments. The copper junctions introduce no additional net potential since, under isothermal conditions, the sum of the metal junctions still add up to (c). However, as is shown by the alternate galvanic cell E above one could connect the Pt and Ag at (c) and divide the solution in two by using separate vessels each containing a Ag-AgCl electrode (d). This procedure also would not change the potential since the electrodes at (d) are alike and are bathed by solutions of identical composition.

A cell, P, corresponding to the electrochemical cell E just discussed, but involving *proton* rather than *electron* transfers is shown below:

Reactions of galvanic cell P

(c)	Protode	(a)	Solution (S)	(b)	Protode	(c)
	Glass, (H_2O)		H_3O^+, Cl^-, Ba^{++}----		BaL_2, HL	

(a) $H_3O^+ \rightleftharpoons H_2O + H^+_{G(H_2O)}$.

(b) $L^- + H^+ \rightleftharpoons H^+L^-$; or $(1/2)Ba^{++}L_2^-$ (solid) $+ H^+_{HL} \rightleftharpoons H^+L^-$ (solid) $+ (1/2)Ba^{++}$.

(c) $H^+_{G(H_2O)} \rightleftharpoons H^+_{HL}$.

Alternate galvanic cell P

(Electrode)		Solution (S)		Protode	
Ag, AgCl	(a)	Buffered $BaCl_2(aq)$	(b)	BaL_2, HL	(c)

Protode		Solution (S)		(Electrode)
Glass, (H_2O)	(a)	Buffered $BaCl_2(aq)$	(d)	AgCl, Ag

It consists of a buffered $BaCl_2$ solution in contact with a glass "electrode" on the left and solid lauric acid, HL, and barium laurate, BaL_2, on the right.

At (a) proton conductance is provided from the bound water in the glass surface, $G(H_2O)$, and at (b) it occurs in the solid acid, HL, while at (c) protons pass from the state $H^+_{G(H_2O)}$ to $H^+_{(HL)}$. On combining (a), (b), and (c) the protons cancel, and we obtain

$$H_3O^+ + L^- = H_2O + HL$$

or

$$H_3O^+ + (1/2)Ba^{++}L_2^-(\text{solid}) = H^+L^-(\text{solid}) + H_2O + (1/2)Ba^{++},$$

since the activity of the laurate ion is determined by that of the barium ion through the solubility product of barium laurate which is present in solid phase. Just as in the analogous case of AgCl and Ag, which behaves as a chloride electrode, BaL_2 and HL should behave as a barium "electrode." Here the acid HL, or laurate "protonide," corresponds to the metal Ag, or silver "electronide." The free energy of the reaction $HL + H_2O = H_3O^+ + L^-$, which is an acid-base reaction in the Brønsted-Lowry sense,[8] determines the emf of cell P. It will depend on the activities of the hydrogen and laurate ions, since the chemical potentials of the solids are constant. In the electrochemical cell E, the metals at (a) and (b), where electron transfer takes place, are the *electrodes*. It may be well to call the sites (a) and (b) in cell P, where proton transfer takes place *protodes*, in order to distinguish clearly between the two mechanisms each of which involves a different *fundamental* particle.

Experimental Results

For an experimental test of the theory that emf can result directly from an acid-base reaction in a manner completely analogous to the emf resulting from an oxidation-reduction reaction in a galvanic cell, a study of the alternate cell P shown above was carried out.

The experimental arrangement is shown in figure 26.1. It consists of a soft glass tube, T, of about ¼-in. diameter, on the bottom of which is fused a thin membrane of Corning 015 glass.[9] To the inner surface of this membrane is fused reagent grade lauric acid, which extends into the space between tube T and an inner tube, T′, of slightly smaller diameter, in order to reduce the possibility of solution creeping in and dislodging the acid from the glass. A thin layer of molten barium laurate covers the lauric acid layer to a total thickness of

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[8] J. N. Brønsted, Rec. Trav. Chim. **42**, 718 (1923); T. M. Lowry, Chem. Ind. **42**, 43 (1923).
[9] D. A. MacInnes and M. Dole, J. Am. Chem. Soc. **52**, 29 (1930).

2 or 3 mm. This procedure is carried out in an electric oven at 50° to 60° C with dry materials. The top is sealed with paraffin to assure adequate electrical insulation. The tube is then filled with water and allowed to stand in water before use.

The measurements were carried out with the aid of two similar Ag-AgCl electrodes, E,[10] one of which dipped into the solution, s, in the beaker and the other inserted into the tube, which also contained the solution, s, as shown in figure 26.1. The tube and electrodes were held firmly with insulating Lucite supports (not shown in the figure). The beaker rested on a block of paraffin. The entire assembly was housed in a grounded metal case for electrostatic shielding, and the measurements of emf were made in a constant-temperature room at 25°±0.2° with a vacuum-tube, high-resistance amplifier potentiometer.[11]

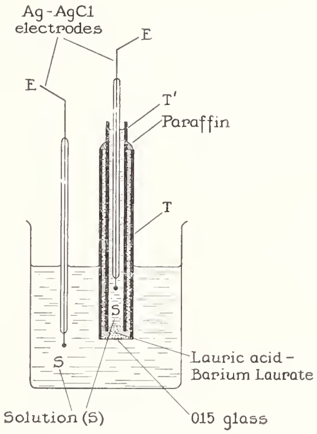

FIGURE 26.1. *Apparatus to test theory that electromotive force can result directly from an acid-base reaction.*

The solutions studied were buffered $BaCl_2$ covering a barium concentration range from 0.005 to 0.5 M and a pH range between about 1.0 and 8.5. In making the buffered solutions HCl or $Ba(OH)_2$ partially neutralizing acetic acid, cacodylic acid, or di-ethyl-barbituric acid were used. The buffers were prepared so that 90 percent of the total barium was supplied by the $BaCl_2$, except in the solutions that contained only $BaCl_2$ and HCl.

The results of a series of measurements obtained with the cell, figure 26.1, are summarized in table 1, in which the total barium concentration in moles per liter is given in column 1. The corresponding mean ion-activity coefficients, γ, for the acetate, cacodylate, and diethyl barbiturate buffered $BaCl_2$ solutions are listed in the second column. The corresponding values of γ for the $BaCl_2$-HCl solutions are shown in the last column. These values of γ were obtained from the emf data of Tippetts and Newton [12] for $BaCl_2$ at 25°, at the same ionic strength.

In columns 3 and 4, 5 and 6, 7 and 8, and 9 and 10 are listed the measured pH values and the corresponding potentials, E, in millivolts,

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[10] A. S. Brown, J. Am. Chem. Soc. **56**, 646 (1934).

[11] M. Dole, Glass electrode, p. 58 (John Wiley & Sons, New York, N. Y., 1941).

[12] E. A. Tippetts and R. F. Newton, J. Am. Chem. Soc. **56** 1675 (1934).

for the acetate, cacodylate, diethyl barbiturate, and HCl buffered $BaCl_2$ solutions, respectively, in alternate cell P. The same protodepair membrane was used for all the measurements of E, except those given in parentheses for $m=0.10$, which were obtained with a different membrane. The difference in the values of E corresponding to the two membranes probably are due largely to their "assymetry potential" differences.

TABLE 1. *Results obtained with apparatus shown in figure 1*

M (Ba^{++})	γ	Acetate		Cacodylate		Diethyl barbiturate		HCl		γ
		pH	E	pH	E	pH	E	pH	$-E$	
0.005	0.794	4.74	72	6.28	178	----	----	----	----	------
.01	.723	4.69	77	6.23	188	8.51	309	1.06	130	0.543
.02	.661	4.64	85	6.20	192	8.61	318	----	----	------
.05	.559	4.58	85	6.16	195	8.65	337	1.04	120	.507
.10	.492	4.56	95	6.12	200	8.67	339	1.03	110	.473
"	"	"	(20)	"	(102)	"	(260)	"	(180)	"
.25	.422	4.46	100	6.06	212	8.67	355	----	----	------
.50	.390	4.35	105	6.00	218	8.65	365	0.94	90	.389

It will be recalled that the potential, E, of alternate cell P depends on the reaction

$$(1/2)BaL_2+H_3O^+=HL+(1/2)Ba^{++}+H_2O$$

and, therefore, on

$$\frac{2.3\ RT}{\mathbf{F}}\log\frac{(HL)(Ba^{++})^{1/2}(H_2O)}{(BaL_2)^{1/2}(H_2O^+)},$$

in which the parentheses refer to activities. At 25° C this quantity is

$$0.059\left[\log\frac{(HL)}{(BaL_2)^{1/2}}+(1/2)\ \log(Ba^{++})-\log\frac{(H_3O^+)}{(H_2O^+)}\right].$$

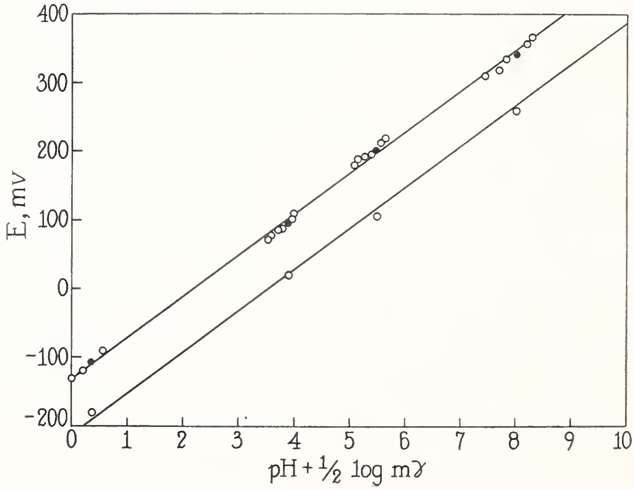

FIGURE 26.2. *Plots showing linear relation between emf and* pH+1/2 log $m\gamma$ *and validity of postulated reaction for alternate cell P.*

The first term in the bracket is constant, due to the fact that both HL and BaL_2 are present in the solid state, and the term, $-\log(H_3O^+)/(H_2O)$ will be assumed to be linear with pH.[13] Thus, a plot of the emf data in table 3 against $pH + \frac{1}{2} \log m\gamma$ should be linear with a slope of 0.059. This is found to be the case, as shown in figure 26.2, in which the two lines refer to data obtained with two different membranes, as stated above.

Evidently we are dealing here with a barium-ion protode and a hydrogen-ion protode in confirmation of the theory outlined in this paper.

Discussion

Dr. W. F. K. Wynne-Jones, University of Durham, Newcastle, England: Mr. Chairman, I think we have listened to a very brilliant exposition of a brilliant idea, and I could only wish that Brønsted were here today to listen to Shedlovsky. I think this idea of the chemical reaction is an extremely important one, and, as Shedlovsky has indicated, it can be of considerable biological value. I would like to say, although it does not really contribute anything to Shedlvosky's point of view, that I think there is little doubt that we can treat the electrode as a strict protode. Over the last 2 years we have been making measurements with the glass electrode in solutions, and we find, contrary to the ideas prevalent, that electrodes respond strikingly to proton activity (the hydrogen activity and not to water), and that actually one can go right up to a completely nonaqueous solvent and find the glass electrode behaving simply as a protode. I think Shedlovsky's mechanism there is well justified.

Dr. O. H. Müller, State University of New York, Medical Center, Syracuse, N. Y.: I think the ideas proposed by Dr. Shedlovsky are very good, but I still would like to see him maintain a place for the oxydation reduction systems. They are very important in there, too. After all, it is not necessary to have a wire to oxidize one ion by another.

Dr. T. Shedlovsky: Certainly not. Chemists do that every day. You can titrate ferrous ions with a permanganate solution. But to get electric energy from it you have to have the metals. Of course, oxidation-reduction processes take place in all living cells and, of course, they provide the energy, but not directly. If you want to go a step back, it is the sun that provides the energy. However, in the language of the biochemists, the oxidation reduction system cannot be the immediate energy precursor for the electrical phenomena.

Dr. A. J. Rutgers, University of Ghent, Ghent, Belgium: Dr. Shedlovsky brought up, and there was also a certain amount of discussion here, whether water should be considered as a liquid or more or less as a jelly. There is, however, quantitative argument that water is not a structure and not a jelly. Einstein, in 1910, calculated Avogadro's number in a quantitative way by assuming Stokes' law for the diffusion of sugar molecules. It seems to me that that cannot be reconciled with the idea of an interconnected structure for water.

Dr. Shedlovsky: I think that what people mean is that when there are protons around, there may be hydrogen bonding. Water is a curious substance, of course, in that it shows all sorts of deviations

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[13] This assumption amounts to considering the variations in the liquid junction potentials berween saturated KCl and the solutions in question to be within the experimental error in the measurements of *E*.

from normal behavior, such as a temperature of maximum density above the freezing point, etc. But I am tempted to agree with you that it is a question of degree of this structure, certainly loose enough to swim in.

Dr. Wynne-Jones: With regard to the structure of water, I think the point is, that whereas the strength of each hydrogen bond is small (it is only between 4 and 6 kcal), nevertheless, you have four bonds per molecule, and consequently you cannot have any large fraction of the bonds broken because the kinetic energy that will be required is not adequate to break any high proportion of the bonds. That does not mean that one must imagine that it is quite strict with every single bond throughout the structure, but that it is a continuing structure with bonds making and breaking throughout.

Dr. R. E. Gibson, Johns Hopkins Appplied Physics Laboratory, Silver Spring, Md.: I don't think we can get too far with this discussion. As we approach an electrolyte with supersonic speed, you would find those bonds a little stronger.

27. Development of Constants in Polarography: A Correction Factor for the Ilkovic Equation

By Otto H. Müller[1]

Introduction

One of the most fundamental relations in polarography with the dropping Hg electrode is the Ilkovic [1][2] equation

$$i = knD^{1/2}Cm^{2/3}t^{1/6}. \tag{1}$$

Here i is the diffusion controlled current; k, a numerical constant;[3] n, the number of electrons involved per mole substance reacting at the electrode; D, the diffusion coefficient of that substance; C, its concentration; m, the rate of flow of Hg from the dropping electrode capillary; and t, the drop time. In his derivation, Ilkovic [1] applied Fick's first and second laws for linear diffusion to the case of the dropping Hg electrode where the decrease in current due to the decreasing concentration gradient at its surface is more than compensated by the increase in area of the growing drop. Because of this, he assumed that the diffusion layer around the electrode is so thin that its curvature did not significantly differ from that of the Hg drop.

Since the appearance of the Ilkovic equation several more derivations [2, 3, 4], leading to the same end result, have been published. Also numerous experiments proved the Ilkovic equation to be essentially correct. Even diffusion currents calculated on the basis of diffusion coefficients at infinite dilution were found, on the average, to differ only by about ±3 percent from those actually observed [4]. Hence it seemed promising to investigate the possibility of the introduction of absolute instead of comparative methods. However, these efforts have not been successful, but rather have proved the superiority of the comparative methods. A valuable contribution resulting from these studies was the clear demonstration that an additional factor was needed in the Ilkovic equation to account for variations in the diffusion current with major changes in drop time.

Proposed Modifications of the Ilkovic Equation

Rearrangement of the Ilkovic equation,

$$i_d/Cm^{2/3}t^{1/6} = knD^{1/2} = I, \tag{2}$$

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[1] Department of Physiology, State University of New York Medical Center, Syracuse, N. Y.

[2] Figures in brackets indicate the literature references on p. 303.

[3] k is equal to 607 when i is the mean current during the life of a drop, expressed in microamperes: D is in cm²/ sec; C, in millimols per liter; m, in mg/sec; and t, in seconds.

shows that $knD^{1/2}$, or I, should be constant for a given reactant. This quantity I has been called "diffusion current constant" [4] by Lingane [5]. A variation of I with changes in drop time could either mean a failure of the Ilkovic equation or a current controlled by factors other than diffusion.

Buckley and Taylor [7] from many experiments found that a "critical drop time" existed below which diffusion control ceased.

Lingane and Loveridge [8] also found that slight changes in the values of I occurred with an increase in drop time which were real and not caused by experimental or instrumental peculiarities. They attributed this to Ilkovic's assumption in his derivation of a spherical drop with its entire surface exposed to the solution. However, the lumen of the capillary may screen off a considerable portion of the area of a very young drop and a fully grown large drop may lose its sphericity and become slightly pear shaped. Since no good practical or theoretical procedure was available for the determination of the effect of these factors individually, they [9] proposed the empirically modified Ilkovic equation

$$i_d = knD^{1/2}Cm^{0.64}t^{1/6}, \tag{3}$$

which fitted their experimental data obtained with lead ion.

In January 1950 two papers appeared from widely separated laboratories with almost identical conclusions concerning the nature of the discrepancy in the Ilkovic equation, but differing in a numerical constant.

In one of these Lingane and Loveridge [10] followed Ilkovic's procedure but applied it to the equation for symmetrical diffusion to a spherical electrode, rather than for linear diffusion to a plane electrode, and obtained

$$I = \frac{i_d}{Cm^{2/3}t^{1/6}} = 607nD^{1/2}(1 + KD^{1/2}m^{-1/3}t^{1/6}), \tag{4}$$

in which K is a numerical constant equal to 39. This equation differs from the Ilkovic eq (1) by the term $(1+39D^{1/2}t^{1/6}m^{-1/3})$, which represents the influence of the curvature of the electrode surface. A slight discrepancy between this equation and their experimental data on lead ion in 1 N KCl was attributed to the use of the diffusion coefficient at *infinite dilution*, whereas the results showed that a value about 16-percent smaller should have been employed.

In the other paper Strehlow and v. Stackelberg [11] attempted a rigorous mathematical treatment but found it necessary to make certain approximations. Nevertheless, they arrived at a most probable solution and obtained an equation similar to eq (4) except that K in the second term is 17 instead of 39, as claimed by Lingane and Loveridge.

In good agreement with this, a K value of 17.6 was found experimentally for thallium ions in 0.1 N KCl. Similarly, from less uniform measurements for cadmium ions in 0.1 N KCl, 20.1 was found for K.

Strehlow and v. Stackelberg also evaluated Lingane and Loveridge's data for lead ions in 1 N KCl. The graph reproduced in figure 27.1 shows two straight lines drawn through the points past the minimum.

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[4] This term should not be confused with the formerly used "diffusion current constant" of Kolthoff and Lingane which is i_d/C [6].

Line *a* is that used by Lingane and Loveridge; line *b*, that drawn by Strehlow and v. Stackelberg calculated by the method of least squares for all points where $m^{-1/3}t^{1/6}$ is greater than 0.6. The slope of this line yielded a K value of 17.4, in very good agreement with that theoretically derived by them. Also the diffusion coefficient for lead in 1 N KCl obtained in this way (see eq (5)) is only 4 percent less than that found at infinite dilution. There is thus seen a real discrepancy between the conclusions of the two groups of workers even when the same data are used for proof.[5]

Independently, but following along the lines of v. Stackelberg [3], Kambara, Suzuki, and Tachi [12] arrived at an equation, essentially that of Lingane and Loveridge [10], with a K value of 39.1. Their experimental verification for this did not permit a quantitative evaluation of K; it merely demonstrated the need for a correction of the old Ilkovic equation.

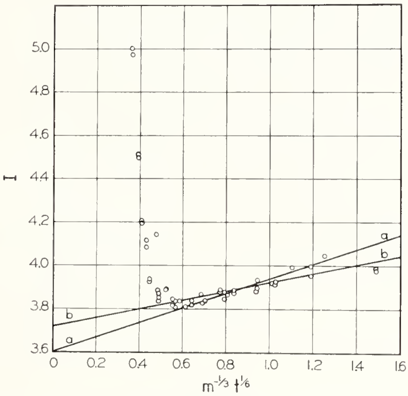

FIGURE 27.1. *Effect of $m^{-1/3}t^{1/6}$ on the diffusion current constant I of lead in 1 N potassium chloride containing 0.01 percent of gelatine.*

Data of Lingane and Loveridge [8]. Straight lines drawn to represent results past the minimum of the curve *a* by Lingane and Loveridge [10], *b* by Strehlow and v. Stackelberg [11].

Meites and Meites [13] have added extensive experimental data with unusual effects which do not seem to be consistent with the findings of either Lingane and Loveridge or Strehlow and v. Stackelberg, and will, therefore, not be considered here. On the other hand, Strehlow, Mädrich, and v. Stackelberg [14] recently gave additional experimental evidence pointing to a K value near 17. They worked with a variety of depolarizers, differing in D, in charge, and in n, and behaving reversibly (Tl^+, Cd^{++}, Pb^{++}), or irreversibly ($Ni(H_2O)_6^{++}$, IO_3^-) at the dropping Hg electrode. The experiments were done with different capillaries at varying pressures of Hg so that many points were obtained for each solution. When these were plotted (fig. 27.2), a straight line could be calculated by the method of least squares whose point of crossing the I axis at $m^{-1/3}t^{1/6}=0$ yields $I_0=607nD^{\frac{1}{2}}$. As suggested by Strehlow and v. Stackelberg [11], *this value alone is the true diffusion current constant* and should replace the older terms.

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[5] It may be pointed out that the last two points on the graph appear to be mainly responsible for the difference.

On the basis of this constant the correct diffusion coefficient in the medium in which the experiments are performed can be calculated

$$D=\left(\frac{I_0}{607n}\right)^2. \qquad (5)$$

Once D is known, the value of K can be determined from the slope I/Y where $Y=m^{-1/3}t^{1/6}$. For instance, in the case of Pb in 0.1 N KCl shown in figure 27.2 the straight line crosses the I axis at $I_0=3.681$ and has a slope $I/Y=0.1928$. Hence it can be defined by: $I=3.681+0.1928Y=3.681(1+0.0523\ Y)$. From $I_0=3.681$, we get $D=(3.681/607\cdot 2)^2=0.92\times 10^{-5}$ cm^2 sec^{-1}. The quantity $0.0523\ Y$ is equal to $KD^{\frac{1}{2}}Y$; hence, $K=(I/Y\cdot 607n)/I_0^2=(0.0523\cdot 607\cdot 2)/3.681=17.27$. Other results obtained by Strehlow, Mädrich, and v. Stackelberg [14] are shown in table 1. Note the magnitude of n which shows its influence on I_0. The slopes of the straight lines are given in column 4, and the diffusion coefficients calculated by eq (5) in column 5. Calculations of K show a satisfactory uniformity and yield a mean value of 16.8, which implies that a simple technique for the determination of diffusion constants is available by which one can calculate D from a single measurement [14]. In view of the need for such a method and the discrepancies mentioned above, it was considered worth while to present here a somewhat different approach.

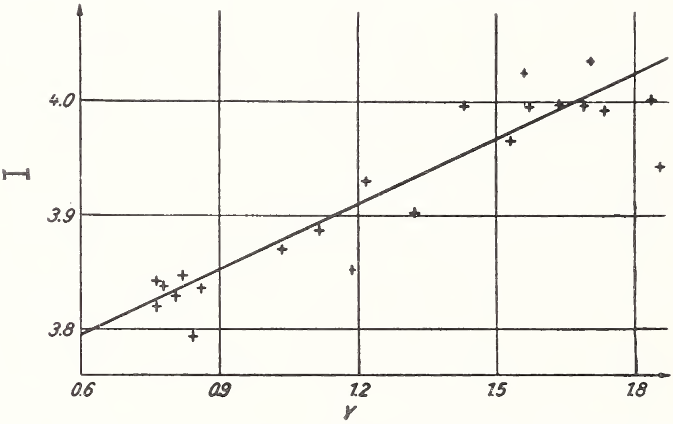

FIGURE 27.2. *Effect of* $m^{-1/3}t^{1/6}(Y)$ *on the diffusion current constant I of lead in 0.1 N potassium chloride containing 0.01 percent of gelatine, according to Strehlow, Mädrich and v. Stackelberg* [14].

General Treatment of Diffusion-Controlled Currents

In the presentation of a more general treatment of diffusion-controlled currents we refer to references [1, 10, 11], and add a novel graphical representation of the phenomena described. The cases discussed will be currents controlled by
(I) linear diffusion to a plane electrode,
(II) symmetrical diffusion to a stationary spherical electrode,
(III) linear diffusion to a growing mercury electrode (sphere with hypothetically plane surface),

(IV) symmetrical diffusion to a growing spherical mercury electrode.

For all these we consider a solution containing reacting material of concentration, C, in excess of indifferent electrolyte. The electrode has an area, q, at any particular time, t. The current intensity at that time, i_t, is a function of the concentration gradient nearest the electrode, i. e., where the distance from the electrode, x, approaches zero. This gradient, δ, is expressed as:

$$\delta=\left(\frac{\partial C}{\partial x}\right)_{x=0}. \tag{6}$$

The current intensity is then

$$i_t=n\mathbf{F}qD\delta, \tag{7}$$

where n is the number of faradays required per mole of electrode reaction, **F**, the faraday (96,500 coulombs) and D, the diffusion coefficient of the reacting substance (in $\mathrm{cm}^2\ \mathrm{sec}^{-1}$).

There is also a volume of solution near the electrode which, as the result of the electrode reaction, has undergone a change in concentration. For convenience, we may calculate that hypothetical volume of solution, V, which has been "completely exhausted", so that the rest of the solution is left unchanged at the original concentration, C. This exhausted volume originally contained the amount of material which has reacted and can hence be found by integration of current between starting time, 0, and final time, t,

$$V=\frac{1}{n\mathbf{F}C}\int_0^t idt \text{ or } V=\frac{D}{C}\int_0^t \delta q dt. \tag{8}$$

We shall use these equations in discussing the four cases mentioned above.

TABLE 1. *True diffusion current constants, (I_0), K values and diffusion coefficients of different ions in 0.1 N potassium chloride solutions* [14]

Ion	n	I_0	I/Y	$D\times10^5$ in 0.1 N KCl	K	$D_0\times10^5$
Tl^+	1	2.551	0.1866	1.78	17.4	2.00
Ca^{++}	2	3.284	.1454	0.73	16.4	0.72
Pb^{++}	2	3.681	.1928	.92	17.3	.98
Ni^{++}	2	3.121	.1341	.66	16.7	.69
IO_3^-	6	11.495	.5835	1.00	16.1	1.09
					Mean 16.8	

To illustrate the physical meaning of these different types of diffusion, it is advantageous to picture analogous situations for cylinders and frustums of inverted cones or corresponding cuboids and pyramids. However, scale drawings become somewhat involved and we prefer the following simplified treatment wherein we plot area versus distance, or second order versus first order terms.

To make comparisons easy, we start in each case with a line of unit length which represents the area q of the electrode at a given time t. This area is determined by the shape of the electrode. For convenience we shall consider only a circular plane electrode and a spherical electrode, both with radius r. Their surface areas can then grow at any rate which we may impose on them. For instance the area q in case III may grow at the same rate as the surface area of a Hg drop. Any such growth will be indicated by an increase in the length of the line representing q. (Since this represents a square term, it will always be positive.)

In addition to area q we shall draw the outermost area, Q of a "completely exhausted" volume of solution in contact with the electrode. Q will be identical with the electrode area as long as we deal only with linear diffusion, but for symmetrical diffusion to a spherical electrode it will be larger than q by an amount that depends in part on the distance, ϑ, between it and the electrode. The volume of the "completely exhausted" solution, V, is thus found as the area enclosed by the lines q and Q, separated by ϑ, the thickness of the exhausted layer. However, to simplify our drawings, we shall use a somewhat larger thickness of the exhausted layer, Δ, defined as

$$\Delta = \frac{\pi}{2}\vartheta, \tag{9}$$

and a correspondingly larger volume. We shall start each case with the condition that at time t_1 the exhausted layer has a thickness Δ_1 equal to unity. Having fixed these starting conditions we can calculate outermost diffusion areas, exhausted volumes of solution and their thickness for any other time, e. g., a second later, at time t_2.

Case I. Current controlled by linear diffusion to a plane electrode. Consider the electrode to be at one end of a cylinder filled with solution. Its area must be $q=\pi r^2$, where r is the radius of the cylinder. From Fick's laws one can find for linear diffusion [1, 2, 3]

$$\delta_{\mathrm{I}} = \frac{C}{\sqrt{\pi D t}} \tag{10}$$

wherefore $i_t = (n\mathbf{F}qDC)/(\sqrt{\pi D t})$, i. e., the current decreases with the square root of time. The exhausted volume then is, according to eq (8),

$$V_{\mathrm{I}} = \frac{D}{C}\int_0^t \frac{qC}{\sqrt{\pi D t}}\,dt = \frac{2q}{\pi}\sqrt{\pi D t} = \frac{2q}{\pi}\frac{C}{\delta_{\mathrm{I}}}. \tag{11}$$

Part I of figure 27.3 demonstrates this graphically. The electrode area q remains constant; since we deal only with linear diffusion, $Q=q$. The exhausted volume V_{I} must be given by $q\,\vartheta$; hence, according to eq (11), and eg (9),

$$\vartheta = \frac{2}{\pi}\sqrt{\pi D t} = \frac{2}{\pi}\Delta \quad \text{or} \quad \Delta = \sqrt{\pi D t}. \tag{12}$$

$\Delta_1 = \sqrt{\pi D t_1}$ has been taken as unity, and has been drawn into figure 27.3 for all four cases. The volume $(\pi/2)V$ is thus represented as a unit volume. A second later, at time t_2, the corresponding value for Δ_2 must be $(\Delta_1\sqrt{t_2})/\sqrt{t_1}$. With $t_1=1$ sec and $t_2=2$ sec, Δ_2 becomes equal to $\sqrt{2}\,\Delta_1 = 1.4\Delta_1$. This value, correct for cases I and II, has been drawn in figure 27.3 with an interrupted line. It represents only a first approximation for cases III and IV.

Case II. Current controlled by symmetrical diffusion to a stationary spherical electrode. Here the electrode area is $q=4\pi r^2$, where r is the radius of the sphere. In eq (6) for the concentration gradient δ, the quantity x represents now the radial distance from the surface of the sphere. Again Fick's laws can be applied to yield [2, 3]

$$\delta_{\text{II}}=C\left(\frac{1}{\sqrt{\pi Dt}}+\frac{1}{r}\right)=\frac{C}{\sqrt{\pi Dt}}\left(1+\frac{\sqrt{\pi Dt}}{r}\right). \qquad (13)$$

According to eq (7) the current $i_t=nFqDC[(1/\sqrt{\pi Dt})+(1/r)]$. Thus a constant value of current, proportional to r, is superimposed in this instance on the linear diffusion current found for case I.

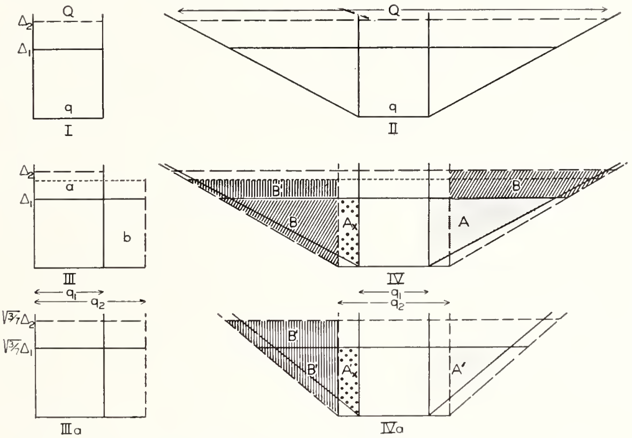

FIGURE 27.3. *Graphical representation of diffusion processes.*

Horizontal axis represents areas (q that of the electrode, Q that of the periphery of the diffusion layer), vertical axis the thickness Δ, or $\sqrt{3/7}\Delta$, of the diffusion layer so that the enclosed area on the graph represents a function of the "exhausted volume" ($\pi/2V$). (I) linear diffusion to a plane electrode; (II) symmetrical diffusion to a stationary spherical electrode; (III) and (IIIa) linear diffusion to a plane electrode whose surface is growing at the same rate as that of a mercury drop; (IV) and (IVa) symmetrical diffusion to a growing spherical drop of mercury. For explanation see text.

The substitution for δ_{II} in eq (8) yields for the exhausted volume:

$$V_{\text{II}}=\frac{D}{C}\int_0^t qC\left(\frac{1}{\sqrt{\pi Dt}}+\frac{1}{r}\right)dt=\frac{2q}{\pi}\sqrt{\pi Dt}+\frac{qDt}{r}, \qquad (14)$$

which may be written

$$V_{\text{II}}=\frac{2q}{\pi}\sqrt{\pi Dt}\left(1+\frac{\sqrt{\pi Dt}}{2r}\right), \qquad (15)$$

showing that in symmetrical diffusion to a spherical electrode one has to consider two components. One is the same linear component as seen in case I, the other has been called a "wedge effect" by Strehlow and v. Stackelberg [11] and will be discussed in greater detail along with case IV. The important thing to notice is that this wedge effect can be expressed as a function of the linear component $(2q/\pi)\sqrt{\pi Dt}$, which has already been defined.

For the graphical representation, given as part II of figure 27.3, we start with area q which here represents $4\pi r^2$. After substituting from eq (12) we can rewrite eq (15) as follows:

$$\frac{\pi}{2}V_{\text{II}}=\Delta q\left(1+\frac{1}{2}\frac{\Delta}{r}\right). \tag{16}$$

This gives us the necessary information for the construction of the graph. Since q is unity, $r=\sqrt{1/4\pi}=0.282$ so that at time t_1, $\Delta_1/r=1/0.282=3.55$. This quantity 3.55 added to $q(=1)$ gives us $Q=4.55$ at a distance of Δ_1 from q. (To balance the graph and to suggest the cross section of a cone or pyramid, as well as for purposes of clarifying case IV later on, we have drawn a symmetrical picture.) If we now connect the ends of q and Q, we enclose an area (on paper) of (a) linear diffusion, as in case I, plus (b) "wedge effect" equal to $\frac{1}{2}\Delta/r$. Because of the coordinate system chosen, these areas really represent volumes and hence are a pictorial representation of eq (16).

Conditions at time t_2 are found by substituting $\Delta_2=1.4\Delta_1$ in eq (16). The corresponding volumes ($\times\pi/2$) are shown in figure 27.3. One can see that the area through which diffusion occurs increases rapidly because of the wedge effect and that the constant linear component of the diffusion area constitutes only a negligible fraction of the total. This is the condition when the "steady state" current is reached.

Case III. Linear diffusion to a growing electrode (sphere with hypothetically plane surface). This is the case originally considered by Ilkovic in the derivation of his equation. He assumed linear diffusion to an electrode surface which grew with time at the same rate as the surface of a sphere. One might also think of this as an electrode at the base of a cylinder which is getting thicker at this same rate. Although diffusion to the new area is going on all the time while it is being added, nevertheless the total exhausted diffusion layer gets slightly thinner than otherwise. Consequently, one may expect the gradient δ_{III} at the electrode to be somewhat larger than δ_{I}. The factor y by which δ_{I} is increased is given by

$$\delta_{\text{III}}=y\delta_{\text{I}}=y\frac{C}{\sqrt{\pi Dt}}. \tag{17}$$

There are two relations which express the exhausted volume and which can be combined. First, we get from eq (11) and (17)

$$V_{\text{III}}=\frac{2q}{\pi}\frac{C}{\delta_{\text{III}}}=\frac{2q}{\pi}\frac{C}{y\delta_{\text{I}}}. \tag{18}$$

Second, eq (8) and (17) yield

$$V_{\text{III}}=\frac{D}{C}\int_0^t\frac{yC}{\sqrt{\pi Dt}}\,qdt. \tag{19}$$

Since q in this instance is assumed to grow as the surface of a drop we can write $q=4\pi r^2=4\pi\gamma^{2/3}t^{2/3}$. (In the case of the dropping Hg electrode, r is given by the equation $4/3\pi r^3=mt/13530$, where m is the flow of Hg (in milligrams per second) and 13530 its density; hence, $r=\sqrt[3]{3mt/4\pi 13530}$ or $\text{r}=(\gamma t)^{1/3}$, where $\gamma=3m/4\pi 13530$).

Combining (18) and (19) we get

$$\frac{2q}{\pi y}\sqrt{\pi Dt}=\frac{4\pi yD\gamma^{2/3}}{\sqrt{\pi D}}\int_0^t \frac{t^{2/3}}{t^{1/2}}\,dt=\frac{4\pi yD\gamma^{2/3}t^{7/6}}{(\sqrt{\pi D})\cdot 7/6}=3/7y\,\frac{2q}{\pi}\sqrt{\pi Dt}. \quad (20)$$

Hence,

$$y^2=\frac{1}{3/7}\text{ or }y=\frac{1}{\sqrt{3/7}}, \quad (21)$$

from this we find

$$\delta_{\mathrm{III}}=y\delta_{\mathrm{I}}=\frac{C}{\sqrt{3/7\pi Dt}} \quad (17a)$$

and

$$V_{\mathrm{III}}=\frac{2q}{\pi}\sqrt{3/7\pi Dt}, \quad (18a)$$

which leads directly to the Ilkovic equation, when substituted into (7):

$$i_t=\frac{n\mathbf{F}qDC}{\sqrt{3/7\pi Dt}}=knD^{\frac{1}{2}}Cm^{2/3}t^{1/6}, \quad (1)$$

where

$$k=\frac{(96500)\,4\pi}{\sqrt{3/7\pi}\,(4/3\,\pi 13530)^{2/3}1000}=709,$$

when i_t is expressed in microamperes; D, in cm^2/sec; C, in millimoles/liter; m, in mg/sec; and t, in seconds. For the mean current during the life of a drop,

$$i_d=\frac{1}{t}\int_0^t 709nD^{\frac{1}{2}}Cm^{2/3}t^{1/6}dt,$$

we get

$$i_d=(6/7)\,i_t=607nD^{\frac{1}{2}}Cm^{2/3}t^{1/6}, \quad (1a)$$

which is the most common form in which the Ilkovic equation has been used.

The correction factor $y=1/\sqrt{3/7}$ can also be approximated by graphical means, shown as part III of figure 27.3. At time t_1 we have an area $q_1=4\pi r_1^2=4\pi\gamma^{2/3}t_1^{2/3}$ and a thickness of the diffusion layer Δ_1, both equal to unity. During the next second, up to time t_2, the electrode area has grown 0.59 unit to $4\pi\gamma^{2/3}t_2^{2/3}=(2^{2/3})4\pi\gamma^{2/3}t_1^{2/3}$, or to $q_2=1.59q_1$. As a first approximation, during the same time interval the thickness of the original exhausted layer above q_1 has increased from Δ_1 to Δ_2, while over the new area q_2-q_1 another exhausted layer was formed whose thickness can have reached only the value Δ_1. Thus the exhausted volumes a and b of figure 27.3 were added. Since there must be a uniform thickness over the whole electrode surface, the volume a has to be spread over the area q_2. This results in the thinner layer indicated by a dotted line in figure 27.3. This line is about 0.625 times the distance from Δ_1 to Δ_2, which is in good agreement with the theoretical value of $\sqrt{3/7}$, or 0.655, if one considers the assumptions made for the growth of the exhausted volume b. Besides illustrating the Ilkovic correction, this treatment enables us to see more clearly the conditions in case IV.

Case IV. Symmetrical diffusion to a growing spherical electrode. In this instance we may expect that a combination of the effects described under cases II and III will hold. We should see a decrease in the thickness of the exhausted diffusion layer because of the increase in surface area of the electrode, as in case III. We should also expect a contribution from the symmetrical component which was shown to be proportional to r in case II. These considerations alone would lead to the expressions of Lingane and Loveridge [10] and of Strehlow and v. Stackelberg [11] whose treatment will now be briefly discussed.

Since Ilkovic [1] could evaluate linear diffusion to an expanding drop of Hg by the introduction of the factor $1/\sqrt{3/7}$ into the equation for linear diffusion to a plane surface, Lingane and Loveridge [10] thought it logical that the same correction factor, if introduced into the diffusion current equation for a stationary spherical electrode, would yield an equation which would take into account the curvature of the electrode surface. Hence they started with the known equation for instantaneous current governed by symmetrical diffusion to a stationary spherical electrode (see under case II) and multiplied the first term in parentheses by $1/\sqrt{3/7}$ to obtain

$$i_t = n\mathbf{F}DCq\left(\sqrt{\frac{7}{3\pi Dt}} + 1/r\right). \tag{22}$$

This, upon proper substitution of units and numerical values leads to

$$i_t = 709nD^{\frac{1}{2}}Cm^{2/3}t^{1/6} + 31560nDCm^{1/3}t^{1/3}. \tag{23}$$

Integration over the drop life yields for the average current

$$i_d = 607nD^{\frac{1}{2}}Cm^{2/3}t^{1/6} + 23670nDCm^{1/3}t^{1/3}, \tag{24}$$

or

$$\frac{i_d}{Cm^{2/3}t^{1/6}} = 607nD^{\frac{1}{2}}\left(1 + 39\,\frac{D^{\frac{1}{2}}t^{1/6}}{m^{1/3}}\right). \tag{4a}$$

Lingane and Loveridge saw no reason to question the correctness of this equation since they felt that it was substantiated by their experimental results already mentioned.

The treatment of Strehlow and v. Stackelberg [11] consisted in a series of approximations that eventually led to eq(4) with a K value of 17, in good agreement with the mean experimental value of 16.8. This finding was apparently fortuitous because the authors neglected to integrate the correction term to get its mean value for the life of a drop. Had that been done, the K value would have been $\frac{3}{4}\times 17 = 12.8$ so that the agreement between theory and experiment is considerably less satisfactory.

Another procedure of Strehlow and v. Stackelberg is also open to question. In the derivation of their eq (37) they assume that the term $\sqrt{\pi Dt}/2r_0$, being a small correction term, has a constant mean value e' during the time interval 0 to t. After using this parameter e' to good purpose, they substitute for it the quantity $\sqrt{\pi Dt}/2r_0$. It seems more logical to have substituted the mean value of this factor, namely,

$$\frac{l}{t}\int_0^t \frac{\sqrt{\pi Dt}}{2r_0}\,dt = 3/7\sqrt{\pi Dt}/r$$

which, however, would have led to a different final result.

In a different approach to the problem, given to illustrate the physical meaning of this phenomenon, Strehlow and v. Stackelberg [11] obtained additional relations almost identical to those of Lingane and Loveridge [10]. Their reasoning is best explained by means of figure 27.4 which shows an electrode with radius r, surrounded by a diffusion layer with thickness, d. If this diffusion layer is very thin, or d is infinitely small, the diffusion is linear and essentially that to a plane surface so that Ilkovic's assumption holds. However, as d grows, there is a volume C from which an appreciable amount of diffusion occurs. This is neglected in the old Ilkovic equation which considers diffusion only through volume B. Since C looks like a wedge in cross section, Strehlow and v. Stackelberg have called this effect the "wedge effect." One could anticipate on the basis of figure 27.4 that

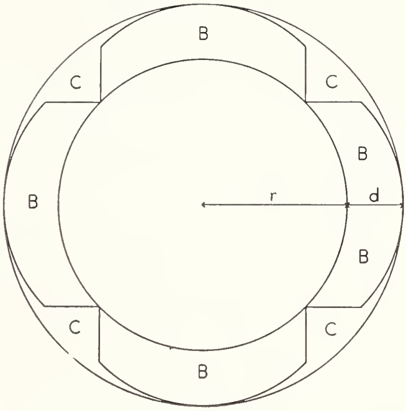

Figure 27.4. *Schematic illustration of the "wedge effect".*

For explanation, see text.

$$i_d = 607 n D^{\frac{1}{2}} C m^{2/3} t^{1/6} (1+x), \tag{25}$$

where x is the ratio of volumes C to B.

Volume B for the whole drop is not quite correctly presented in figure 27.4, but it is given accurately by

$$B = 4\pi r^2 d, \tag{26}$$

whereas volume $B+C$ is

$$B+C = 4/3\pi[(r+d)^3 - r^3], \tag{27}$$

so that

$$1+x = \frac{B+C}{B} = \frac{(r+d)^3 - r^3}{3r^2 d} = 1 + d/r + d^2/3r^2. \tag{28}$$

Since d must be small compared to r in polarography, $d^2/3r^2$ can be neglected. However, d as diffusion layer is proportional to $\sqrt{Dt}$ while r is proportional to $(mt)^{1/3}$, wherefore

$$d/r = K D^{\frac{1}{2}} m^{-1/3} t^{1/6} = C/B = x. \tag{29}$$

Thus in a simple way the correction factor for the Ilkovic equation can be obtained. To get an approximation for K, Strehlow and v. Stackelberg proceeded as follows: Let $d=\sqrt{3/7\pi Dt}$ and $4/3\pi r^3=mt/13530$, then

$$d/r=\sqrt{3/7\pi}\sqrt[3]{\frac{4\pi 13530}{3}}\,D^{\frac{1}{2}}m^{-1/3}t^{1/6}=44.4D^{\frac{1}{2}}m^{-1/3}t^{1/6}. \tag{30}$$

This value of 44.4 for the constant K is identical with that found by Lingane and Loveridge in eq (23) before integration over the drop life. Strehlow and v. Stackelberg never made this integration; instead, they argued that a mean value for d was necessary since the solution nearest the electrode contributes more to the current. For reasons not clear, they thus obtain $K=1/3\cdot 44.4=14.8$ on the assumption of a linear concentration decrease. This they considered in fair agreement with their more rigorous mathematical treatment which gave a value of $K=17$.

It seems, however, that both treatments of Strehlow and v. Stackelberg, as well as that of Lingane and Loveridge, have neglected the fact that as the electrode area grows, the linear component of diffusion increases to a certain extent at the expense of the symmetrical component (the wedge). This wedge effect therefore gets smaller per unit of time not only because of the change in the value of Δ/r, but also because part of any existing wedge is wiped out by the spreading of the area available for linear diffusion. In other words, in place of the term $1/r$ as in eq (13), we should expect a factor z/r where z is smaller than unity.

The gradient δ_{IV}, patterned after eq (13) and (17a), must then be as follows

$$\delta_{\text{IV}}=\delta_{\text{III}}\left(1+\frac{C}{\delta_{\text{III}}r}\,z\right)=\frac{C}{\sqrt{3/7\ \pi Dt}}\left(1+\frac{z\sqrt{3/7\ \pi Dt}}{r}\right). \tag{31}$$

The exact mathematical evaluation of z is difficult and has consequently been carried out by the following method of approximation. From V_{II} (eq 14) we can calculate the average linear and wedge components for time t, assuming r and q to grow as in a Hg drop. These are

$$\frac{1}{t}\int_0^t \frac{qDt}{r}\,dt=(3/7)\left(\frac{2q}{\pi}\sqrt{\pi Dt}\right)\frac{\sqrt{\pi Dt}}{2r}, \tag{32}$$

and

$$\frac{1}{t}\int_0^t \frac{2q}{\pi}\sqrt{\pi Dt}\,dt=(6/13)\,\frac{2q}{\pi}\sqrt{\pi Dt}\cong(1/2)\,\frac{2q}{\pi}\sqrt{\pi Dt}. \tag{33}$$

If we may now introduce the Ilkovic correction factor of $\sqrt{3/7}$ (see case III, eq (17a)) into each of the $\sqrt{\pi Dt}$ terms, we get the following ratio of average wedge to average linear components which should hold for values other than average, as well,

$$\frac{(3/7)\left(\frac{2q}{\pi}\sqrt{3/7\ \pi Dt}\right)\frac{\sqrt{3/7\ \pi Dt}}{2r}}{1/2\,\frac{2q}{\pi}\sqrt{3/7\ \pi Dt}}=\frac{3/7\sqrt{3/7\ \pi Dt}}{r}=\frac{3}{7}\,\frac{C}{\delta_{\text{III}}r}. \tag{34}$$

In other words, $z=3/7$, so that

$$\delta_{\mathrm{IV}}=\delta_{\mathrm{III}}\left(1+\frac{3C}{7\delta_{\mathrm{III}}r}\right)=\frac{C}{\sqrt{3/7\ \pi Dt}}\left(1+\frac{3/7\sqrt{3/7\ \pi Dt}}{r}\right). \tag{35}$$

The corresponding value for V_{IV} is

$$V_{\mathrm{IV}}=\frac{2q}{\pi}\sqrt{3/7\ \pi Dt}\left(1+\frac{3/7\sqrt{3/7\ \pi Dt}}{2r}\right). \tag{36}$$

We may now examine the graphical representation of these phenomena given as part IV of figure 27.3, which should lead to an essentially identical correction factor. Our starting conditions are the same as in case II. The wedge effect for time t_1 is the volume $\Delta_1(\Delta_1/2r_1)$ represented by the two symmetrical triangles, one of which is marked as A. The linear diffusion component is given by $\Delta_1 q_1$. In the present case, r grows as well as Δ during the next second. The growth of r produces the same increase in linear component as given for case III; this growth of 0.59 unit in q has been drawn symmetrically in case IV. The new wedge effect is given by $\Delta_2(\Delta_2/2r_2)$, where Δ_2/r_2 is equal to $1.4/\sqrt{1.59/4\ \pi}$, or 3.9. In figure 27.3 this effect has been divided equally between the two time intervals of one second each. Triangle B on the left would have formed in the first second had we started with an electrode area q_2. The section of a triangle B on the right is identical in area with the triangle just discussed and represents one half of the uncorrected wedge effect added in the second time interval to the wedge effect A of the first second. However, from a consideration of case III we know that, because of the growing surface, the exhausted layer will grow in thickness by $\sqrt{3/7}(\Delta_2-\Delta_1)$. Thus only area B' shown on the left (or the exhausted volume represented by it) need by expected. But, while this area B' has been growing between time t_1 and t_2, some of the existing wedge effect, represented by area A_x, has been wiped out by the simultaneous growth of the area available to linear diffusion. The net gain in wedge effect is thus the difference between the areas B' and A_x. Expressed in terms of B' we find graphically that $(B'-A_x)/B'$ is approximately 3/7, as theoretically expected.

This graphical representation of the conditions described by eq (36) may be also be given in a slightly different form. In examples IIIa and IVa the coordinate system has been changed from Δ to $\sqrt{3/7}\Delta$. Hence the increases in diffusion layer thickness need no longer be corrected for $\sqrt{3/7}$. Note, however, that here the wedge effect is given by $\sqrt{3/7}\Delta(\sqrt{3/7}\Delta/r)$; hence during the first second it will be A'. Here the two areas B' are obtained directly and the ratio of $(B'-A'_x)/B'$ is again near 3/7.

Having thus given a graphical and a mathematical treatment, both of which lead to a value of 3/7 for the correction of the wedge effect, we can write the modified Ilkovic equation as follows:

$$i_t=n\mathbf{F}DCq\left(\frac{i}{\sqrt{3/7\pi Dt}}+\frac{3/7}{r}\right). \tag{37}$$

Upon proper substitution of units and numerical values, this leads to

$$i_t = 709 n D^{\frac{1}{2}} C m^{2/3} t^{1/6} + 13525 n D C m^{1/3} t^{1/3}. \tag{38}$$

Integration over the drop life yields for the average diffusion current

$$i_d = 607 n D^{\frac{1}{2}} C m^{2/3} t^{1/6} + 10144 n D C m^{1/3} t^{1/3}, \tag{39}$$

or

$$\frac{i_d}{C m^{2/3} t^{1/6}} = 607 n D^{\frac{1}{2}} \left(1 + 16.7 \frac{D^{\frac{1}{2}} t^{1/6}}{m^{1/3}} \right). \tag{39a}$$

The numerical value of 16.7 for K is in excellent agreement with the experimentally found mean value of 16.8 (see table 1).

Determination of Diffusion Coefficients

Equation (4) can be rearranged to give a value for $D^{\frac{1}{2}}$,

$$D^{\frac{1}{2}} = \frac{-1}{2KY} + \sqrt{\frac{I}{607nKY} + \frac{1}{4K^2Y^2}}, \tag{40}$$

where $Y = m^{-1/3} t^{1/6}$. Having a constant value for K, we can thus calculate D from a single measurement. Because the accuracy of single measurements may not be good enough, it is best to determine a mean value for D from several determinations of I and Y with the same dropping Hg electrode at different pressures.

Using a value of $K = 17$, Strehlow, Mädrich, and v. Stackelberg [14] found by this method the diffusion coefficients for Tl in KCl of varying normality, given in table 2. If corresponding values for D had been calculated either on the basis of K equal to 16.7 as demanded by eq (39a), or 17.4 (table 1) as determined by the elaborate method of least squares, they would have been 0.2 percent higher and lower, respectively, or the small variations between actual and theoretical K values would mean an uncertainty in the values for the diffusion coefficient of at most ±0.5 percent. This is of the same order of magnitude as the uncertainty in the determination of m, t, C, and i.

Thus we may have considerable confidence in the D values of tables 1 and 2 and can expect that the polarographic method will yield valuable information concerning diffusion in a variety of media. Table 2 clearly demonstrates the diminution of D with increase in the concentration of the indifferent electrolyte KCl. The use of D_0 values at infinite dilution, calculated on the basis of the Nernst equation, in the Ilkovic equation has always been considered merely a first approximation. From table 1 we can see that use of D_0 in the case of 0.1 N KCl solutions involves an error of about 5 to 6 percent on the average. As Strehlow and v. Stackelberg [11] have pointed out, this error was largely compensated in the old Ilkovic equation by neglect of the wedge effect. The outstanding exception is Cd, the diffusion coefficient of which actually increases with increasing concentration of indifferent electrolyte [14].

Table 2. *Diffusion coefficient of thallium in potassium-chloride solution* [14]

Normality of KCl	$D \times 10^5$
------------	$(2.00 = D_0)$
0.1	1.78
1	1.56
2	1.44
3	1.35

References

[1] D. Ilkovic, Collection Czechoslov. Chem. Commun. **6,** 498 (1934).
[2[D. MacGillavry and E. K. Rideal, Rec. trav. chim. **56,** 1013 (1937).
[3] M. v. Stackelberg, Z. Elektrochem, **45,** 466 (1939).
[4[I. M. Kolthoff and J. J. Lingane, Polarography. (Interscience Publishers, Inc., New York, N. Y., 1941.)
[5] J. J. Lingane, Ind. Eng. Chem., Anal. Ed. **15,** 583 (1943).
[6] I. M. Kolthoff and J. J. Lingane, Chem. Rev. **24,** 1 (1939).
[7] F. Buckley and J. K. Taylor, J. Research NBS **34,** 97 (1945) RP1631.
[8] J. J. Lingane and B. A. Loveridge, J. Am. Chem. Soc. **66,** 1425 (1944.).
[9] J. J. Lingane and B. A. Loveridge, J. Am. Chem. Soc. **68,** 395 (1946).
[10] J. J. Lingane and B. A. Loveridge, J. Am. Chem. Soc. **72,** 438 (1950).
[11] H. Strehlow and M. v. Stackelberg, Z. Elektrochem. **54,** 51 (1950).
[12] T. Kambara, M. Suzuki, and I. Tachi, Bul. Chem. Soc. (Japan), **23,** 219 (1950); T. Kambara and I. Tachi, **23,** 225 (1950).
[13] L. Meites and T. Meites, J. Am. Chem. Soc. **72,** 3686 (1950); **73,** 395 (1951); L. Meites, **73,** 1581 and 3724 (1951).
[14] H. Strehlow, O. Mädrich, and M. v. Stackelberg, Z. Elektrochem. **55,** 244 (1951).

Discussion

Dr. F. E. W. Wetmore, University of Toronto, Toronto, Canada: I would like to point out that all of this is on the integrated equation. We did some work on the instantaneous curve; it is a sixth-order parabola.

Dr. O. H. Müller: I certainly agree with you. For the instantaneous current the equations become more complicated. For instance, the third term in eq (28), $d^2/3r^2$, can no longer be neglected.

Dr. Wetmore: It is more than that. Perhaps I could draw the picture on the board and show you. The actual experimental current-time curves, which we found with a high-speed oscilloscope, start underneath the Ilkovic curve and cross it here (about two-thirds of the drop life). So there is a cancellation of difference in integrated form. The new theories lead to curves that are higher than either of these. There is one favorable point for the new theories, however. The log I—log t curve turns out experimentally to have a slight concavity upward and to be bent downward very markedly at low time. Clearly, one could not expect too good results in the first part of the drop life. On the whole, the parabola is of order 4.5 rather than 6. I think that this represents more than the other possibility suggested. Incidentally, our runs were taken in solutions from 5- to 30-percent sulfuric acid, which made a real change in the diffusion coefficient of the reducible ion.

Incidentally, in the diffusion coefficient taken up to concentration of two or three normal we ran it in 30-percent sulfuric acid, which really changed the results.

28. Some Electrode Properties of Mild Steel in Sea Water

By T. P. May and F. L. LaQue [1]

Abstract

Reversible electrode potentials of metals indicate the probable direction of the galvanic current when dissimilar metals are connected, but they fail to indicate the intensity of attack which may result. Accordingly, they are of secondary interest to the corrosion engineer. The irreversible "corrosion potentials" of metals provide a more useful index of the probable behavior of the metals and are of more practical significance. Nevertheless, they have limitations and must be used with caution. For example, galvanic currents in bimetallic systems may be more or less strongly affected by the polarization which they cause at the anode and cathode surfaces. A knowledge of the polarizing characteristics of metals and alloys would complement the information available from their "corrosion potentials."

The behavior of many engineering metals and alloys is being studied at the Marine Corrosion Laboratory at Harbor Island, N. C. Of the data obtained to date, the electrode behavior of mild steel is of special interest because of its wide use in marine applications. The potential of freely corroding steel is reported for several conditions of exposure to sea water, namely, quiescent, several velocities, and alternate immersion at the tidal zone. Cathodic and anodic polarization curves have been determined for these same conditions of exposure. Behavior in the tidal zone is particularly interesting because it is shown galvanic coupling of submerged steel to a more noble alloy, such as Monel, causes less corrosion than when coupled to steel in the tidal zone.

Cathodic polarization of steel in sea water is considerably enhanced by the deposition of a calcareous coating as a result of electrolysis of the sea water by the galvanic current. This coating sometimes exhibits the crystal structure of the mineral aragonite. The effects of aging are discussed.

The treatment of Mears and Brown is applied to the polarization data to estimate the polarization curves of the local anodes and cathodes on the steel surface.

Discussion

Dr. H. H. Uhlig, Massachusetts Institute of Technology, Cambridge, Mass.: Dr. May, do I understand that you use the same electrode to measure anodic and cathodic polarization?

Dr. T. P. May: No, they were measured on different occasions. We used the same type of electrode. It was always changed to the appropriate position while working on the anode and cathode.

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Dr. Uhlig: That probably explains the peculiar shape because the extrapolation makes certain assumptions.

Dr. May: There is some question there. As I said, we do not know what effect the current has on redistribution of the local areas.

Dr. W. M. Latimer, University of California, Los Angeles, Calif.: It would seem to me that peroxide is a possibility. I would like to see some explanation of that polarization on the various surfaces. I would not give up and say it was hopeless; I would like to know what was actually going on.

Dr. May: I am inclined to think it is hopeless from a reversible potential viewpoint, and I might add that our treatment of these data has certainly been superficial. We are still working on it and we hope to develop some more information about it. At this point I do not think we can.

Dr. W. J. Hamer, National Bureau of Standards: Are your corrosion potentials reproducible? A series of such potentials implies that they are.

Dr. May: That depends upon the method preparation of the sample. We can get variations of 100 mv very easily.

Dr. Hamer: That means a displacement of 1 mv in your series of corrosion potentials.

Dr. May: Yes. The general characteristics are the same. We get the same performance at different velocities.

Dr. Hamer: A series of corrosion potentials is independent of the velocity?

Dr. May: Well, I am not prepared to say that, because we have not done this sort of thing. We expect to do that for other material.

Dr. M. Bloom, Naval Research Laboratory, Washington, D. C.: Have you any idea of the mechanism by which you get this tremendous drop in the potential in the direction of the tide? If I gathered correctly, in one of the slides you showed a very large drop in the potential of the steel with changes in tide. This drop was such that the potential of the steel at that point was far outside of the region that you represented as being normal. Have you any idea what the mechanism was by which this large drop occurred?

Dr. May: Not at this time.

Dr. F. L. LaQue: I can offer a suggestion. Bear in mind this experiment was started with the waves just barely lapping the piece so as to produce a deflection on the galvanometer of the instrument. You may be surprised that as soon as you could get a reading at all, the current measured was of the order of 25 ma. The area wet was maybe ⅛ by 24 in.; the current density was terrific. As the tide came in and wet a larger area of the piece, the current did not rise anywhere in proportion to the area wetted so that what we were getting there was not simply a change in current but a violent change in current density—not upward but downward.

29. Electrolyte-Solvent Interaction

By Robert C. Miller [1] and Raymond M. Fuoss [1]

Abstract

The conductance of electrolytes in mixed solvents can often be computed from the conductance in one of the components, by use of Walden's rule for Λ_0 and of the Fuoss-Kraus theory for K. But Sadek and Fuoss [2] found that the theory broke down completely for tetrabutylammonium bromide in methanol-nitrobenzene mixtures. Subsequent work in mixtures of nitromethane and of benzene with methanol give the same result: the salt is a much stronger electrolyte in the mixtures than in either pure solvent. The conductance is so high that no association is demonstrable, even in mixtures with a dielectric constant as low as 25; the conductance curves approach the Onsager tangent from above.

Discussion

Dr. G. Scatchard, Mass. Institute of Technology, Cambridge, Mass.: I would like to ask, does it recover? Does the slow one ever get fast, or the fast one ever get slow?

Dr. R. M. Fuoss: One of these three solutions where we added the 1 Cm^3 of benzene to the methanol was refluxed for an hour and let stand for 3 months and still stayed up. The other one I cannot answer for. It does look as if we get fairly stable properties. One solution actually has stood for 4 months. The other one is about a week old now.

Dr. R. E. Gibson, Johns Hopkins Applied Physics Laboratory, Silver Spring, Md.: People who work with benzene and nitro compounds learn to expect trouble. In my laboratory it has been the case. Your instrument wanders off the line, and things happen that you do not expect.

Dr. S. E. Wood, Illinois Institute of Technology, Chicago, Ill.: It appears that any time aromatics are used as solvents, peculiar properties may arise. I think it has been shown that complexes of iodine and the aromatic ring increase in stability with increased methylation of the ring. I know of some work, which has not been published, in which the ionization constants of HF in BF_3 change remarkably in the presence of aromatic compounds. There is the well-known complex between silver ion and the aromatic group. I think that this paper is more corroboration of the complexities involved. Only Professor Fuoss has complicated the problem still further by adding a nitro group.

Dr. Fuoss: Do not believe what you read in the textbooks and not even what you read in the journals.

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[1] Department of Chemistry, Yale University, New Haven, Conn.

[2] J. Am. Chem. Soc., **72**, 301 (1950).

30. Significance of Ionization Constants

By W. F. K. Wynne-Jones[1]

Abstract

The extent of dissociation of an electrolyte is determined by its own ionization energy and by the properties of the medium in which it is dissolved. The separation of these two factors is important if ionization constants are to be related to the properties of the molecules. In the past many attempts have been made to obtain such a relation, but in all such attempts it has been assumed that the solvent can be regarded either as playing no part at all, or merely acting as an inert dielectric. In attempting a more thorough examination of the significance of ionization constants there are four aspects of the effect of solvent which should be taken into account: (1) The specific chemical interaction between solvent and electrolyte which is most clearly shown by the effect of basicity of the solvent upon the ionization of acids, (2) the effect of variation in dielectric constant upon the degree of ionization, (3) the effect of temperature upon ionization constants, and (4) the hydrogen bonding between acids and bases which occurs in solvents which do not themselves readily form hydrogen bonds.

The importance of the first effect has been realised for many years and more especially since the work of Goldschmidt and Lapworth, culminating in the theory of acids and bases advanced by Brønsted. Brønsted himself showed how it was possible to discuss the dependence of acidity upon solvent and his treatment was carried further by Conant and especially by Hammett.

The treatment of the second effect has always been based on Born's equation, the applicability of which has been discussed in detail by Bjerrum and which has been applied in various forms to ionization constants.

The study of the third effect began with Arrhenius and was greatly advanced by the careful study made by Harned over a number of years.

The importance of the fourth effect has not been fully appreciated, but there seems little doubt that in certain solvents the significance of ionization constants is profoundly modified by hydrogen bonding.

Analysis of the data shows that, while to a rough approximation, the simple electrostatic theory advanced by Gurney is able to describe the temperature dependence of ionization constants, it is inadequate for any exact description and that the separation of the electrostatic and nonelectrostatic contributions to dissociation constants is a problem which cannot be solved without a much more adequate theory of the liquid state. The recent attempt by Lennard-Jones and Pople to formulate a theory for water seems very promising and it is hoped that a similar treatment can be extended to other ionizing media.

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Discussion

Dr. W. J. Hamer, National Bureau of Standards: What was your ordinate in that last graph?

Dr. W. F. K. Wynne-Jones: That is the extinction coefficient plotted against wavelength. That was just an absorption spectrum.

Dr. A. J. Rutgers, University of Ghent, Ghent, Belgium: I was very much interested in the explanation by Gurney of this parabola. Is this parabola strictly confirmed by experiment?

Dr. Wynne-Jones: I think the answer is essentially that it is parabolic just near the peak. It is not to be regarded as a strict expression, holding at a long distance from the temperature maximum. In other words, it is a convenient way of representing the results rather than an exact relation.

Dr. H. S. Harned, Yale University, New Haven, Conn.: Well, it was admittedly approximation and done that way to show a graph. We used other functions to calculate the thermodynamic properties. But it is surprisingly good for 25 degrees on either side of that maximum. The first statement was admittedly an approximation. We knew it was not good enough. It makes a beautiful illustration and then at the ends you saw the exact parabola and the experimental points disagreed. This uncertainty causes big differences in estimating ΔC_p. As a matter of fact, there is no function I know that will tell us whether ΔC_p increases or decreases or remains constant with temperature.

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$Fe \rightarrow Fe^{++} + 2e \quad E_1 = 0.440$

$2Fe^{++} \rightarrow 2Fe^{+++} + 2e \quad E_2 = -0.771$

Subtract 2 from 1

$Fe + 2Fe^{+++} \rightarrow 3Fe^{++} \quad E_3 = +1.982$

$\therefore \Delta F_3 = \ominus$

$\Delta F_1 - 2\Delta F_2 = \Delta F_3$

$-n_1E_1F - 2(-n_2E_2F) = -n_3E_3F$

$-1(+.440) - 2(-1 \times -.771) = -1E_3$

$-.440 - 1.542 = -E_3$

$E_3 = +1.982$

$Cu^{+} \rightarrow Cu^{++} + e \quad E_1 = -.167$

$Cu \rightarrow Cu^{+} + e \quad E_2 = -.55$

Subtract 2 from 1

$2Cu^{+} \rightarrow Cu^{++} + Cu \quad E_3 = +0.383$

$\therefore \Delta F_3 = \ominus$

$\Delta F_1 - \Delta F_2 = \Delta F_3$

$-n_1E_1F - (-n_2E_2F) = -n_3E_3F$

$-1(-.167) - [- -.55] = -1E_3$

$+.167 - .55 = -E_3$

$-.383 = -E_3$

$E_3 = +0.383$