THE SILVER–SILVER HALIDE ELECTRODES[1]

Preparation, Stability, Reproducibility, and Standard Potentials in Aqueous and Non-Aqueous Media

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I. INTRODUCTION

Although, in electromotive force measurements, all potentials are ultimately referred to the hydrogen electrode, secondary reference standards are frequently employed, since it is not always convenient to use the hydrogen electrode. The silver–silver halide electrodes as secondary reference standards offer the advantages of ease of preparation, reproducibility, compactness, and direct use in halide solutions, avoiding the uncertainty of liquid-junction potentials. These electrodes fall in the class of reversible electrodes of the *second kind*. In contrast to *electrodes of the first kind*, which are reversible with respect to ions of the electrode material, electrodes of the second kind have a solid phase in the form of a sparingly soluble salt in equilibrium with a saturated solution of this salt participating in the electrode process. A familiar example is the silver–silver chloride electrode,

$$\mathrm{Ag,\ AgCl(s)\ |\ Cl^-}(m)\mathrm{M^+}(m) \qquad (1)$$

which consists of solid silver chloride on silver and in contact with a solution of a soluble chloride. The reversible electrode reaction involves the passage of

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silver into solution as ions and combination with the chloride ions of the electrolyte to form the insoluble salt:

$$\begin{aligned} \mathrm{Ag(s)} &\leftrightharpoons \mathrm{Ag^+} + e \\ \mathrm{Ag^+} + \mathrm{Cl^-} &\leftrightharpoons \mathrm{AgCl(s)} \\ \hline \mathrm{Ag(s)} + \mathrm{Cl^-} &\leftrightharpoons \mathrm{AgCl(s)} + e \end{aligned}$$

This is virtually equivalent to the reaction at a chlorine gas electrode, except that the silver chloride can be regarded as the source of the chlorine. Many important reactions occur in halide solutions where such electrodes can be applied directly. The uncertainty of the liquid junctions generally introduced in using the hydrogen electrode, or a secondary standard such as the calomel half-cell, can often be avoided by use of the silver–silver halide electrodes as the reference standards. Of these electrodes, the silver–silver chloride electrode has been most extensively used and has achieved considerable individual importance as a reference standard.

The widespread use of these electrodes may be best illustrated by listing some of the many applications in the various fields of work. One of the principal applications has been in the investigation of the thermodynamics of electrolytes in aqueous (52, 62, 79) and non-aqueous solutions (84, 113) from the potentials of concentration cells. The advantages of the E.M.F. method over the other available methods are the wide temperature range available for study, and the fact that the precision of the measurements does not decrease rapidly as the concentrations of the solutions are lowered. A very powerful method for measurement of the thermodynamics of dissolved electrolytes is the isopiestic method of investigation (33, 97, 101). The absolute standards of reference for this method were established by E.M.F. measurements in concentration cells, using the silver chloride electrodes in sodium and potassium chlorides (60, 62). The modern theories of interionic interaction have been investigated in aqueous (52, 79) and non-aqueous (20, 21) media in similar E.M.F. cells. The silver–silver halide electrodes have been employed in E.M.F. cells for measurements of (*1*) the ionization constants of weak electrolytes (52, 54, 86), (*2*) the ion product of water in various solutions (37, 39, 47), (*3*) the solubility of sparingly soluble salts (20, 79), (*4*) standard electrode potentials (6, 98), (*5*) adsorption in acid protein solutions (57, 59), (*6*) transference numbers (2), (*7*) overlapping ionization constants (7), and (*8*) basic dissociation constants (86). The pH scale of the National Bureau of Standards is based upon the E.M.F. of cells with hydrogen and silver–silver chloride electrodes (8, 9, 10, 14, 105). In addition, the silver–silver chloride electrode has application (*1*) in high-precision direct-current conductance measurements, as a probe electrode (15, 34), (*2*) as a reference standard in corrosion studies (31, 32), (*3*) in heavy water (71), (*4*) in crystalloidal electrolytes (51), and (*5*) in buffers of the monobasic fatty acids (43).

The scope of the present work has been limited to matters concerning the reproducibility, stability, and methods of preparation for the various types and forms of these electrodes, in an attempt to resolve or settle some of the contradictions and conflicting opinions concerning this important type of electrode.

The silver–silver halide electrodes may be grouped into four types according to the methods of preparation: (*1*) *electrolytic*, the electrolytic deposition of both silver and silver halide, (*2*) *thermal*, the decomposition in a furnace of a paste of silver oxide, silver chlorate (or bromate, iodate), and water to form the silver–silver halide, (*3*) *thermal-electrolytic*, the electrolytic formation of the silver halide on thermally reduced silver oxide paste, and (*4*) *miscellaneous*, such as the use of precipitated silver halide in silver. The status of the silver–silver halide electrode will be considered in detail with reference to each of these types. The data on the standard electrode potentials and on the use of these electrodes as reference standards in aqueous, non-aqueous, and mixed solvents are also covered in this review.

II. PREPARATION OF THE SILVER–SILVER CHLORIDE ELECTRODE

A. Type A electrode: electrolytic

A review of the information and data concerning the preparation of the totally electrolytic silver–silver chloride electrode follows, starting with the work of Jahn (61), who first used this reference electrode in 1900 in place of the calomel electrode when studying the nature of strong electrolytes in solutions.

Little quantitative detail was given by Jahn (61) in describing the method of preparation. It was stressed that the electrodes must be carefully prepared and handled with caution. Pure silver wire, 2 mm. in diameter, was highly polished, repeatedly washed, and cemented into glass tubes. The bare wire was next electrolytically coated with a dense strong layer of silver, using as electrolyte a solution of potassium silver cyanide containing *excess* potassium cyanide, and as anode an electrode of pure silver. No data are given on the strength of this solution or the plating current and time. The silver-plated electrodes were washed several days in distilled water, changed frequently, and then electrolytically chloridized. For this purpose the electrodes were made anodes in a cell, using a platinum cathode and 25 per cent hydrochloric acid as electrolyte. The current was regulated with a rheostat to such a value that a small stream of hydrogen was noticed at the platinum electrode. A period of 4 hr. was used in this step, but after the first 2 hr. the current was briefly reversed until a weak evolution of hydrogen was seen at the silver electrode. The purpose of this was to obtain a porous silver deposit. The electrodes during this step, and after chloridizing, were protected from the influence of light. The freshly prepared electrodes were rinsed with distilled water and stored in dilute sodium chloride solution, which was frequently changed for several days. During storage they were externally short-circuited and also protected from light. Jahn reported that if the electrodes had been prepared with suitable care, the electromotive force measurements were constant to ± 0.02 mv. The electrodes could be used for several weeks in the same salt solution without the slightest change, if handled carefully.

MacInnes and Parker (81) and MacInnes and Beattie (80) gave more quantitative information for this type of electrode shortly after Jahn's work. The silver chloride electrode was required for reference in studying lithium chloride

and potassium chloride concentration cells. Rather than use the silver wire as the base for this electrode, these investigators started with fine platinum gauze, 1.5 or 3 cm.^{2} in area, which was welded to a platinum wire that was sealed through glass to make contact. This was coated with a thick layer of silver electrolytically from a potassium silver cyanide solution, using approximately 0.5 amp./dcm.^{2} of surface for 24 hr. The electrodes were thoroughly washed (in water for 1 day) and chloridized as anodes at 5–7 ma. per electrode for 10 to 20 min. A dilute solution of the halide salt to be studied was used for chloridizing the electrode, to minimize the possible inclusion of small amounts of electrolyte of unknown concentration. The color of the silver chloride layer thus formed was reddish brown, whether the electrolysis was carried out in the presence or the absence of light. The electrodes were prepared in sets of five to eight. Intercomparison showed that they were usually within 0.03 mv. of the same potential, the value increasing to 0.05 in the more dilute solutions. A slight aging effect was reported, older electrodes being positive to the newer ones. When two electrodes which had been chloridized in solutions of different strengths were placed in a common solution for intercomparison, they rapidly assumed the same potential to within 0.1–0.2 mv. This indicated that the same modification of silver chloride was present on all the electrodes. Scatchard (100) used this type of electrode in studying the activity of hydrochloric acid from E.M.F. measurements. Using the directions of MacInnes and Beattie (80), a set of six electrodes was prepared, all of which generally were quite well behaved (i.e., agreed in E.M.F. within 0.02–0.03 mv.). The electrodes were used 1 to 3 days after preparation. Nonhebel and Hartley (84) and Nonhebel (83) likewise followed the method of MacInnes and Beattie to prepare the silver–silver chloride electrodes for studying the properties of hydrochloric acid in aqueous medium and in anhydrous methanol. In the latter the electrodes were chloridized in 0.1 N sodium chloride in alcohol, and were reported reproducible to 0.1 mv.

Using the data given by MacInnes and associates, for the silver-plating and chloridizing steps it is estimated that the amount of silver deposited per square centimeter area of gauze was about 1.8×10^{-3} equivalents, of which 2.4×10^{-5} equivalents was converted to silver chloride in the next step or about 1.5 per cent of the silver layer. Two kinds of abnormal electrodes were reported but not explained. One type was an electrode that was attacked by a parasitic mould, and the other was a type in which a white allotropic form of silver chloride formed rather than the plum-colored form of silver chloride. This color was not changed by weeks of diffuse daylight, and the electrode was always negative in potential to the normal electrode by varying amounts. The latter may be interpreted thermodynamically (i.e., a negative free-energy change) as indicating that the normal electrodes (colored) exist in a state of lower free energy than the abnormal (white) electrodes. The reproducible, reversible, and stable properties of the normal colored electrodes indicate that this electrode exists in a state of stable thermodynamic equilibrium. From the above it seems that the state of the white allotropic form of silver chloride does not correspond to the standard state for crystalline silver chloride (i.e., unit activity). In a similar manner the aging

effect observed by these workers indicates, thermodynamically, an approach to the true equilibrium state (or ground state) of this electrode with time. An investigation of the aging effect will be discussed in a later section. No information, however, was given as to the period of useful life of the electrodes prepared in this manner.

The totally electrolytic silver chloride electrode was found by Smith (104) to be reproducible and stable, contrary to the report about that time by Randall and Young (95), who discarded this method of preparation as giving electrodes not reproducible or constant in potential. Smith proposed a modified procedure for the electrolytic chloridizing of the silver layer. The day prior to E.M.F. measurements, the electrodes, in sets of four, were coated electrolytically with silver chloride, using a large central silver–silver chloride electrode as cathode and a solution of the same composition as that in which the electrodes were to be used as electrolyte. In this way the silver chloride was formed without change in composition of the solution. The bias potentials (intercomparison E.M.F. using a common electrolyte) were measured the following day, after the electrodes had been standing in fresh solution overnight. Of 117 combinations, only one pair differed by as much as 0.1 mv., and the variations normally were only 0.02–0.03 mv. The freshly prepared electrodes were used in only one E.M.F. measurement. After each run the silver chloride on the electrodes was converted to silver by electrolysis, the chloride being plated out onto the central large silver–silver chloride electrode. The silver electrodes thus re-formed were ready for conversion into silver–silver chloride electrodes, using solutions of appropriate strength as before.

About this time, Carmody (22, 23) described an investigation undertaken to study the factors important for obtaining an electrode by the electrolytic method that would be reproducible and constant within 0.01 mv. Four factors that influence the potential were investigated: namely, (*1*) cyanide ion absorbed in the silver-plated electrode, (*2*) light, (*3*) time, and (*4*) concentration of the chloride solution.

Several series of electrodes were prepared by the method of MacInnes and Parker (81), but the time of washing of the silver layer was varied from 1 to 20 days in order to determine the importance of this step. According to the previous reports, electrodes of reddish brown color were obtained after 1 day of washing. Carmody found that, with continued washing of the silver layer, the color and potential of the silver chloride electrode did change, until after 14 days a pure white silver chloride electrode, constant in potential, was obtained. The electrodes chloridized after 24 hr. of washing, red-brown in color, checked well within each series but were usually about 0.2 mv. positive to the white silver–silver chloride electrodes. Carmody attributed the darkening in color to reduction of the silver chloride by traces of cyanide adsorbed during electrolysis and not removed by a short period of washing. To minimize this adsorption of cyanide, it was recommended that (*1*) the electrodeposition of silver on the platinum electrode be carried out in a two-compartment H type of cell so that the hydrogen cyanide formed at the anode is prevented from diffusing to the cathode, (*2*) the

time of electrolysis be decreased from 24 hr. to 8 hr. with a corresponding increase in current density, and (*3*) the potassium silver cyanide be prepared free from excess cyanide by precipitation and recrystallizations. After a washing period of 2 days, electrodes which had been silvered in this manner were pink in color, reproducible, and constant within 0.02 mv. After a 5-day washing period, the resulting electrodes were white and reproducible to within 0.01 mv.

With reference to the effect of daylight, Carmody tested several series of such white silver–silver chloride electrodes with exposure to direct sunlight, diffuse daylight, and incandescent electric light. After 1 min. the changes in potential noted were 0.2, 0.05, and 0.01 mv., respectively. The exposure to light caused the electrodes to become positive to the control electrodes and brown in color. No information, however, is given regarding the magnitude of the effect in the limit with excess exposure to light, nor was a study of this effect reported with the plum-colored electrodes normally obtained and used by previous investigators. In checking the effect of the concentration of the electrolytic solution, Carmody prepared two series of electrodes, one in 0.1 *M* and the second in 0.01 *M* hydrochloric acid. For intercomparison, 0.1 *M* hydrochloric acid was used. The electrodes acquired the same potential within 1 hr., showing that they may be used in solutions of different concentrations. The precaution observed by the earlier workers of chloridizing the silver electrodes in a solution of the same strength as that in which the electrode is to be used would seem unnecessary. Several white silver–silver chloride electrodes were also observed over a period of a month, some being stored in distilled water and others being in constant use. No difference in potential was found when these were compared with freshly prepared electrodes. It was suggested that the change in potential with time reported by previous investigators could thus be attributed to the effect of light on the electrodes. The specific directions formulated from this investigation by Carmody for the preparation of silver–silver chloride electrodes were: (*1*) the platinum gauze should be cleaned by boiling in concentrated nitric acid for a few minutes, (*2*) using the electrodes as cathodes with a solution of pure potassium silver cyanide (free of excess potassium cyanide) and an H-cell to minimize diffusion effects, silver should be plated at 8 ma. per electrode for a period of 8 hr., (*3*) the electrodes should next be washed 5 days in running distilled water, (*4*) the electrodes should be chloridized electrolytically in dilute hydrochloric acid at a current density of 3 ma. per electrode for 1 hr., (*5*) the electrodes should be protected from contact with direct or diffuse sunlight, and stored in distilled water until required for measurements. When carefully prepared in this manner, silver–silver chloride electrodes reproducible and constant to 0.01 mv. were obtained by Carmody.

Estimating each electrode as 1.5 cm.^{2} in area, about 3.6×10^{-3} equivalents of silver would be deposited and, of this, 1.7×10^{-4} equivalents would be chloridized using the directions recommended by Carmody, or about 5 per cent of the silver layer.

In further work, Carmody (23) prepared the silver–silver chloride electrode, modifying the procedure only in the plating step. Instead of using a current of

8 ma. for 8 hr., he plated with a current of 2 ma. per electrode for 30 hr. The total equivalents of silver deposited was thus about 9 per cent less, and the conditions in this step approximate more nearly those recommended by MacInnes and Beattie. These electrodes, when washed for three weeks and chloridized as before, also resulted in white silver–silver chloride electrodes, stable and reproducible to 0.01 mv. Carmody reported that light brown electrodes were obtained on several occasions, even though daylight was excluded. These electrodes were not used for the E.M.F. measurements, since they gave a potential 0.2–0.3 mv. higher than that of the white electrodes. In this work Carmody observed that if oxygen was present in the solutions, the potentials of the electrodes decreased rapidly, but if oxygen was excluded, a constant E.M.F. was obtained for periods as long as two weeks.

Very shortly after Carmody's first work appeared, Afanasiev (1) published the results of his investigations on the three types of silver–silver chloride electrodes, undertaken for much the same reasons. The totally electrolytic type was prepared in sets of 15–20 electrodes. Silver was plated on a platinum wire from a solution of potassium silver cyanide containing an *excess* of potassium cyanide, and with a current density of 0.9 ma./cm.^{2} for 5 or 6 days. The electrodes were protected from diffuse daylight, soaked in distilled water for 1 or 2 days, and immersed in dilute silver nitrate solution, each being connected externally to eliminate differences in potential. The silver chloride was formed electrolytically in 0.75 *M* hydrochloric acid for 5–6 hr. in complete darkness at a current density of 0.2 ma./cm.^{2} These electrodes were stored in total darkness in dilute potassium chloride and were connected externally (i.e., shorted). On testing, it was found that the reproducibility of these electrodes was only 0.1–0.2 mv. Afanasiev commented that the reproducibility of this type of electrode was dependent on many factors, either accidental or imperceptible, and dismissed the use of these in favor of the thermal-electrolytic type of silver–silver chloride electrode.

The fraction of the silver layer converted to silver chloride may be estimated from the data given by Afanasiev. Using the current densities and times recommended for each step as a guide, it would appear that only about 0.5 per cent of the silver layer was changed to silver chloride. This amount is less than that recommended by MacInnes and Beattie (80) and Carmody (22) for reproducible and constant electrodes.

A type of silver–silver chloride electrode suitable for use in dilute solutions has been described by Brown (18). This electrode consisted simply of a thin platinum wire, 0.040–0.045 cm. in diameter and of a smooth surface, sealed in Jena thermometer glass leaving a 1-cm. length of the wire outside for use as the electrode. The end of the wire was fused to remove sharp edges. This electrode thus has a small surface and bulk and may be expected to have the least disturbing effect on dilute solutions. For the silver deposition, a plating solution was prepared containing 10 g. of potassium silver cyanide per liter in which the free cyanide had been minimized by addition of dilute silver nitrate until a faint cloud of silver cyanide formed. It was recommended that the free cyanide be precipitated in this manner each time before use. The potassium silver cyanide

was carefully prepared and recrystallized for this solution as recommended by Carmody. Before silver plating, the platinum wire was cleaned with boiling concentrated nitric acid.

A beaker was used for the electrolyzing bath, fitted with a glass cover to hold six electrodes symmetrically about a central platinum anode. The latter was separated from the main portion of the bath by using an alundum porous diaphragm in a Pyrex tube 1 cm. in diameter and 8 cm. long. This was suspended in the central hole of the cover to provide the anode chamber. In this manner contamination of the main body of the solution by the hydrogen and silver cyanides formed at the platinum anode was minimized. When silver was used for the anode, this electrode polarized readily, possibly because of the absence of free cyanide. Each group of six electrodes was plated at a total current of 2–0.5 ma. for 2–6 hr. The electrodes were carefully rinsed and stored in distilled water (about 16 hr.). For chloridizing, 0.1 N hydrochloric acid was used with a platinum cathode in the same cell. A current of 2 ma. was used for 30 min.

According to these data, about 15×10^{-5} equivalents of silver was plated, of which 3.7×10^{-5} equivalents was changed to silver chloride, i.e., about 25 per cent. These electrodes were purplish brown in color and were not affected in color or electrical behavior by sunlight. Thus they could be prepared and used without the inconvenience of working in rooms with restricted illumination. A survey of about a thousand observations of bias potentials (intercomparison potentials of electrode pairs in neutral sodium chloride solutions at concentrations from 0.0002 to 0.2 N) established that the average reproducibility of the electrodes was 0.02 mv. Although differences as high as 0.05 mv. were sometimes noted, it was possible to select electrodes that agreed to within 0.01 mv. The reproducibility was found to be the same from group to group as within a group, and independent of the age of the electrode. In attempts to prepare white silver–silver chloride electrodes, the silver-plated wires were washed from periods of a few hours to several weeks. Each time, stable, reproducible, but colored electrodes were obtained on chloridizing the silver deposit. Brown has suggested that some factor other than this washing was responsible for the production of the Carmody white electrodes. Prolonged washing increases the chances of contamination of the silver by dust and fumes in the laboratory atmosphere, and thus may be disadvantageous.

The color of the Brown electrodes was found to be dependent on the current density used in chloridizing. With a current density of 0.6–2.5 ma./cm.^{2}, uniformly dark-colored electrodes were always formed. At lower current densities, electrodes resulted having grayish patches which did not darken on exposure to sunlight. These electrodes exhibited an unsteady potential when tested in silver nitrate solution. At very low current densities a white but insufficiently adherent layer of silver chloride is probably formed (80, 81).

Electrodes of the simple Brown type were very sensitive to mechanical shock or disturbances. A modification, providing protection for the active surface as shown in figure 1a, has been used by Brown and MacInnes (19) to study the physical chemistry of dilute sodium chloride solutions. A pair of wire electrodes

(e, e′) are mounted in inner and outer tubes (a, b). An extension of the outer tube (b) is used to protect the sensitive electrode surfaces. Free access of solution to the electrodes is provided by holes in this outer hood. This form also permits

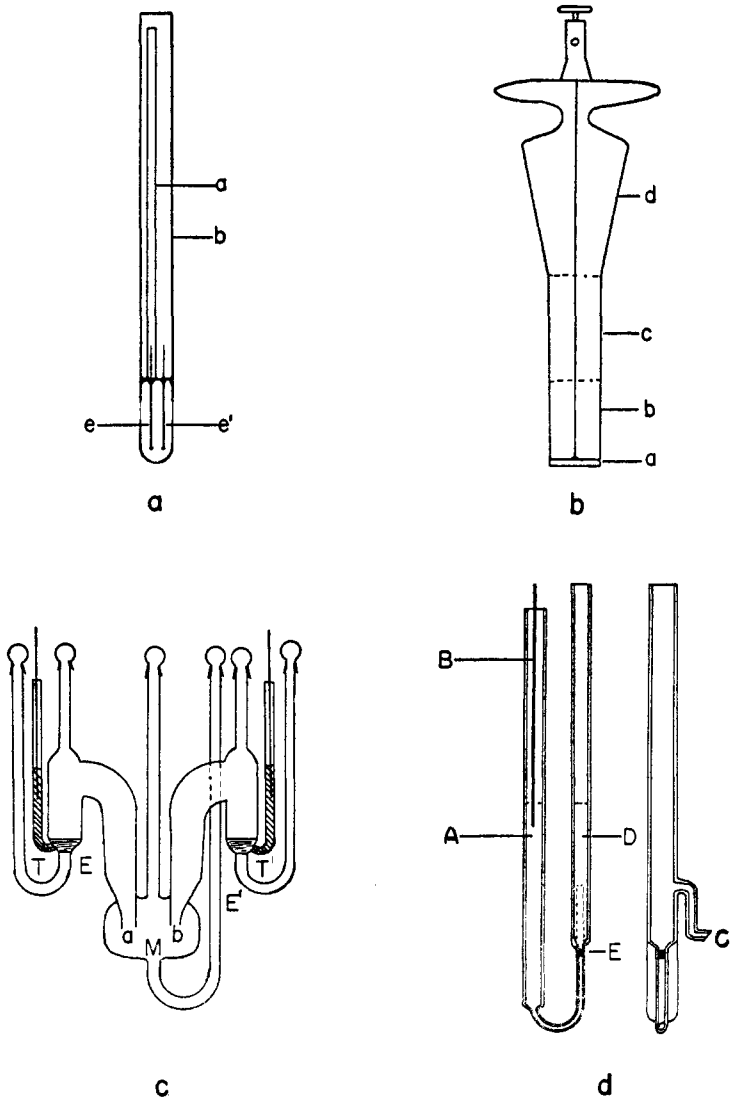

FIG. 1. Silver–silver chloride electrodes. (a) Brown–MacInnes wire pair electrodes; (b) Gordon disc electrode; (c) Shedlovsky cone electrodes and concentration cell; (d) Senderoff solid silver–molten silver chloride electrode.

preparation of electrode pairs under closely identical conditions and allows convenient intercomparison measurements.

Since a transfer of the electrodes to the cell was still necessary, the danger of

mechanical disturbance is real even with this modified Brown electrode. To overcome this difficulty, Shedlovsky and MacInnes (103) designed a new type of cell for use in studying the activities of electrolytes in dilute solution. In this cell, shown in figure 1c, two hollow truncated cones of platinum (E, E′) served for the silver–silver chloride electrodes. The outer surfaces were sealed to the glass cell wall, and the electrical contact was made through the mercury tubes (T, T′). The preparation of the electrodes was by the method of Brown, with the modification that the silver plate was first washed with strong ammonia and then with water. This was to ensure removal of the last possible traces of silver cyanide before chloridizing. A further novel feature of the cell was the method of making the liquid junction. With the two half-cells filled, the liquid junction was made by flowing the heavier of the two solutions into chamber M through tube H. The junction is thus made with a minimum of disturbance at the half-cell entrances (a, b). In addition to providing protection for the sensitive silver chloride surfaces, the possibility of contamination with grease through the sliding contact used by Brown and MacInnes to make the liquid junction was avoided. The design of this apparatus limits the number of electrodes to one per compartment. In the event of contamination or poisoning of an electrode, or breakdown in stability, exchange of the electrodes in the cell by a freshly prepared set is not possible.

Because the silver–silver chloride electrode was finding increased use as a secondary reference electrode, Smith and Taylor (106, 111) undertook studies on the reproducibility of the various types of this electrode, and the aging in neutral salt and acid solutions. The factors investigated and the results follow in a later section of this paper. The totally electrolytic electrodes were prepared from platinum gauze (0.5 x 1 cm.), platinum foil, and wire bases. The silver-plating solution was prepared according to Brown (18), and the electrodes were plated in sets of six at 4 ma. per electrode for 24 hr. This corresponds to about 36×10^{-4} equivalents of silver deposited. To remove adsorbed contaminants, a 10-day washing period with frequent changes of distilled water was used. After this, the six electrodes were chloridized in series, using 1 *M* hydrochloric acid at 4–6 ma. for 1 hr. Thus about 1.5×10^{-4} equivalents of silver chloride was formed, i.e., about 5 per cent of the silver layer was changed to silver chloride. Electrodes were prepared both in the presence and in the absence of light. In all cases, intercomparison measurements established the same reproducibility within each set, and also with members of the other sets (0.02 mv.). No information is given as to the color of these electrodes. The influence of dissolved oxygen and the change in potential with time are discussed in the next section.

A silver–silver chloride electrode of somewhat different design has been developed by Gordon and associates (21, 60, 62, 82). The form of this electrode is shown in figure 1b. A platinum disc (a) was sealed into a hollow cylinder of soft glass (b) and used as the base for the silver–silver chloride electrode. The platinum disc was 1.1 cm. in diameter and 0.5 cm. thick and was highly polished before sealing into the glass. The soft-glass cylinder was sealed to a Pyrex standard-taper inner joint (d) through a graded seal (c). Electrical contact was made through a copper wire fused to a short platinum wire that had been welded

to the back of the disc. In this electrode the danger of mechanical disturbance of the sensitive silver–silver chloride layer was minimized by the rigid structure of the platinum base. A feature added through the use of the standard-taper cone was that this electrode could be interchanged readily, with no danger of contamination through rubber or grease in the E.M.F. cell, with a fresh electrode in the event of electrode failure. By intercomparison of a number of these, a suitable pair could be selected for the E.M.F. measurements. The platinum was cleaned by anodizing in concentrated nitric acid and washing with water before silver plating.

The set-up for silver plating consisted of two cells in series, each of two beakers serving as anode and cathode compartments, respectively. In each cell these compartments were joined by a bridge made of glass tubing in the shape of the letter M. This long bridge added resistance to the cell but decreased the possibility of contaminating the catholyte with the free cyanide being formed at the anode during electrolysis. In this manner, with two such cells in series, the electrodes were prepared in sets of two, using a plating time of 5–6 hr. at 0.65–0.70 ma. and a chloridizing time of 25–30 min. at the same current strength. Between these two steps, the electrodes were soaked in concentrated ammonium hydroxide, and subsequently washed with distilled water for at least 8 hr. The silver-plating solution was made from carefully purified potassium silver cyanide (10 g. per liter), noting the precautions of Brown (18). The silver plate was white, smooth, and velvet-like in appearance. Occasionally a set would be obtained in which the silver plate did not wet uniformly. If such were chloridized, they always resulted in erratic electrodes. The electrodes were chloridized using 0.1 N hydrochloric acid. Using the conditions above, uniform deep pink electrodes resulted, although at times a non-uniform coloring or freckling was noted. According to these data, about 1.6×10^{-4} equivalents of silver was deposited per electrode, of which 1.3×10^{-5} equivalents was changed to silver chloride, i.e., about 1 per cent. With electrodes of this type it was found that with higher current densities (e.g., 3 ma.) during the plating, the silver would deposit uniformly at first, but in a short time would tend to form "trees." The use of the lower plating currents and stirring in the cathode chamber ensured smooth, uniform silver plates. The electrodes thus obtained were found to have good reproducibility (0.02 mv.) and would not change in potential over a period of days.

More recently Gilbert (32) investigated the use of the silver–silver chloride electrode as reference standard for corrosion studies in dilute solutions. No experimental detail was given regarding the totally electrolytic type of electrode. Gilbert found the thermal-electrolytic electrode more satisfactory than both the electrolytic and the thermal types.

Kennard (67) in recent work has developed a form of the totally electrolytic silver chloride electrode suitable for biological and physiological investigations. A silver wire was sealed into a glass tube by polythene, which was fused to the terminal portion of the tube. The wire was then threaded through the appropriate size of ligature silk so that the latter projected beyond the end of the wire. The coated wire may then be bent to the desired shape and chloridized in the usual manner. When this electrode is stored in air, a small piece of cotton is placed

around the base of the wire and soaked in saline. This electrode is capable of maintaining good fluid contact with any structure. The projecting end of the sleeve can be used for contacting delicate surfaces and makes the electrode less polarizable, adding to its stability. The current between a bare wire electrode and a nerve passes largely at the point of contact only; with the sleeve a much larger area of the wire passes the current. The emerging wick may be made rigid by employing a glass fiber covered with silk. Details as to the plating and chloridizing currents or intercomparison E.M.F.'s were not given.

TABLE 1

Preparation of the electrolytic silver–silver chloride electrode

References	(80, 81)	(22, 23)	(1)	(19, 95, 103)	(60)
Electrode base	Platinum gauze	Platinum	Platinum wire	Platinum wire and cone	Platinum disc
Silver deposition:					
(i) Solution $KAg(CN)_2$		No excess cyanide	Excess cyanide	No excess cyanide	No excess cyanide
(ii) Time (hr.)	24	8	120	2–6	5–6
(iii) Current (ma.)	6	8	0.9	0.5–2	0.65
Silver washing:					
(i) NH_4OH				Yes	Yes
(ii) Water	1 day	5 days	2 days	16 hr.	8 hr.
Chloride deposition:					
(i) Solution	Dilute halide	Dilute HCl	0.75 *N* HCl	0.1 *N* HCl	0.1 *N* HCl
(ii) Time (hr.)	0.33	1	120	0.5	0.5
(iii) Current (ma.)	5–7	3	0.2	2.0	0.65
Silver as AgCl:					
Per cent	1.5	5	0.5	25	8
Color*	Plum	White		Plum	Plum
Reproducibility (mv.)	±0.02	±0.01	±0.1	±0.02	±0.02
Light	No effect	Unstable		No effect	No effect

* Plum: this shade embraces colors from deep pink to purple-brown.

With reference to the preparation of the totally electrolytic silver–silver chloride electrode, some of the data collected from the references giving sufficient detail are summarized in table 1. The white electrodes reported by Carmody have not been observed by later investigators and remain a topic of controversy. The factors important in the preparation of electrodes of good reproducibility (0.02 mv.) would seem to be as follows: (*1*) the silver plating solution (10 g. per liter) should be free of excess cyanide, (*2*) in the plating set-up the products formed at the anode should be kept from the catholyte by a suitable bridge or diaphragm, (*3*) the current (2–0.65 ma.) and time (2–24 hr.) for silver deposition

should be selected to give a smooth adherent layer of silver, (*4*) a concentrated ammonia wash should be used prior to water washing to decrease the time factor at this step, (*5*) the solution commonly used for chloridizing is dilute (0.1 *N*) hydrochloric acid, and (*6*) the current (0.65–7 ma.) and time (0.3–1 hr.) used for chloride deposition should be chosen sufficient to convert from 5 to 25 per cent of the silver layer to silver chloride. Electrodes prepared in this manner equilibrate rapidly with the solutions and have the stability and reproducibility desired for reference standards. The preparation of these electrodes in sets of two to twelve at one time seems a recommended procedure in order to ensure one or more pairs of electrodes suitable for use as reference standards.

B. Type B electrode: thermal

The thermal type of silver–silver chloride electrode is one in which the silver–silver chloride is formed as a mixture on the platinum base in one operation. Rule and LaMer (99) described and used this type of electrode for silver chloride. The coil of platinum wire, sealed into a Jena-glass supporting tube, was covered with an aqueous paste of 7 parts of silver oxide and 1 part of silver chlorate. This was heated in an electric furnace to decomposition, leaving the platinum spiral coated with an intimate mixture of silver and silver chloride. No appreciable differences were observed when the amount of silver chlorate was varied between 8 and 15 per cent. Rule and LaMer prepared and tested twelve electrodes. The average intercomparison E.M.F. was ± 0.02 mv., and after six weeks this had increased to not more than ± 0.04 mv. These investigators observed that this type of electrode was more stable than the thermal-electrolytic type. Smith and Taylor (106) tested the reproducibility of the thermal electrodes (table 2) and reported this to be of the same order as that of the electrolytic and thermal-electrolytic types.

The hazard present in the preparation of the electrolytic type of electrode—i.e., contamination of the silver layer by adsorbed or included cyanide—is not present in the preparation of the purely thermal type. However, the latter is more massive and spongy in nature and requires a longer period to come to equilibrium with the solutions than the other types. In addition, care must be taken to ensure that the platinum wire is completely coated, i.e., there are no minute spots or cracks. More recently this type of electrode was used by Patterson and Felsing (90, 91) in alcohol–water systems. The silver–silver chloride mixture was formed from a paste of 10 per cent silver chlorate and 90 per cent silver oxide by decomposition at 650°C. for 7 min. This method was first proposed for preparation of the silver bromide (68) and silver iodide (89) electrodes.

C. Type C electrode: thermal-electrolytic

The thermal-electrolytic silver–silver chloride electrode has been used by a number of investigators in preference to the totally electrolytic and the thermal electrodes. Lewis (72) described the method that has been found to be the only reliable one for coating the platinum wire with silver thermally. His procedure was simply to insert the platinum spiral into a tube containing a paste of silver

oxide and to heat this at 445°C. until all the oxide had decomposed. On removing the electrode, the platinum spiral was completely enclosed in a loosely coherent mass of finely divided silver. The success of this method is probably dependent on the fact that the silver thus deposited is annealed and strain-free. Noyes and Ellis (85) modified this procedure somewhat for the preparation of the thermal-electrolytic electrode. A platinum wire, 0.6 mm. in diameter and 5 cm. long, was wound to a helix 0.3 cm. in diameter. This was cleaned by boiling in strong nitric acid and washed thoroughly. A thin coat of silver was deposited on the spiral from a potassium silver cyanide solution, using 6 ma. for 4 hr. The electrode was washed with frequent changes of distilled water for 2 days to remove all cyanide. It was next completely covered with a paste of freshly prepared and washed silver oxide in such a manner as to fill the interstices of the helix with the paste as well as to coat the wire. After drying in a hot closet, the paste was decomposed in an electric oven for 6 hr. at 400°C., leaving a deposit of white, shining, porous silver. This was coated with chloride electrolytically in 0.75 *M* hydrochloric acid for 5 hr. at 4 ma. Four electrodes prepared in this manner agreed within ±0.05 mv. and maintained a constant potential for several days. Noyes and Ellis tested the effect of light on four electrodes that had been prepared in total darkness. On intermittent exposure to the light of a 6-amp. carbon arc, a small change in potential was observed. It was suggested that this may possibly be attributed to decomposition of the silver chloride to silver and chlorine. The effect, however, was small, and this type of electrode exhibited a definite potential whether used in light or in darkness. Harned and associates (38, 45, 46, 53, 55) have made extensive use of this type of electrode in studies of the physical chemistry of electrolytic solutions. In some instances it was recommended that the layer of electrolytic silver first deposited on the platinum spiral be omitted (38, 44, 89). The reproducibility of these electrodes has been reported as varying from 0.00 to 0.25 mv. Afanasiev (1), on studying the various types of silver chloride electrodes, had most success with the thermal-electrolytic electrodes, obtaining a reproducibility of 0.01 mv. The procedure of Noyes and Ellis was followed, but the silver was chloridized in 0.75 *M* hydrochloric acid using only 0.2 ma./cm.^{2} for about 6 hr. Owen (89) reported the use of 3 ma. for about 3 hr., using 0.5 *M* hydrochloric acid for this step.

A semimicro form of this electrode for pH titrations at constant ionic strength was used by Bates and associates (12, 13). The loops of platinum wire (16 mg.), 6 mm. in length, were covered with 0.16 g. of silver by thermal decomposition of silver oxide. The silver chloride was formed in 1 *M* hydrochloric acid for 15 min. at 1 ma. The agreement of these electrodes with each other was within 0.04 mv. Gilbert (32) found this type most satisfactory as a reference electrode for corrosion measurements. The silver oxide was decomposed on a platinum spiral (made of wire 1 mm. in diameter) at 350°C., and the silver was chloridized in 0.1 *M* hydrochloric acid with about 3 ma. for 2 hr. Rule and LaMer (99) preferred the thermal type of electrode to the thermal-electrolytic. It was reported that when the silver deposit was electrolyzed for 5 hr. at 1.8 ma. in 0.2 *M* hydrochloric acid, the electrodes obtained were not steady in potential and were, on

the average, about 0.04 mv. positive to the thermal type. The conflicting opinions and data concerning the reproducibility and constancy of the various types of silver chloride electrodes were resolved by the work of Smith and Taylor. The results, summarized in table 2, established that the three types are capable of the same reproducibility when sufficient time is allowed for equilibrium to be attained. This period may vary by 1 to 20 days, depending on factors such as stirring and porosity of the electrode surfaces.

TABLE 2

Reproducibility of different types of silver–silver chloride electrodes in the presence of light and of dissolved air (106)

ELECTRODE NUMBER	ELECTRODE TYPE				
	Electrolytic			Thermal-electrolytic	Thermal
	Gauze	Foil	Wire		
	mv.	*mv.*	*mv.*	*mv.*	*mv.*
1–2	0.04	0.02	0.02	−0.03	−0.04
1–3	0.00	0.01	−0.01	−0.01	0.01
1–4	0.01	0.02	−0.02	−0.03	0.00
1–5	0.01	0.02	−0.01	0.02	−0.03
1–6	0.02	0.01	−0.03	−0.03	−0.03
1–7	0.03	0.01	−0.04	−0.04	−0.05
1–8	0.01	0.01	−0.01	−0.01	0.00
Average deviation	0.02	0.02	0.02	0.02	0.02

D. Other types of electrodes

In this section two types of silver–silver chloride electrodes, other than the electrolytic, thermal, and thermal-electrolytic, are described. The first may be termed a crystalline silver–precipitated silver chloride electrode, and the second a solid silver–molten silver chloride electrode. The former has been used by a number of investigators in aqueous solutions, while the latter is a form developed recently for use in molten salt systems at high temperatures.

Linhart (73, 74) investigated the applicability of the precipitated silver–silver chloride electrode to the measurement of the activity of hydrochloric acid in very dilute solutions. In this type of electrode the conventional silver–silver chloride layer was replaced by a mass of finely divided silver in intimate contact with silver chloride. The silver was deposited at a fine platinum wire from silver nitrate solution, using a current of about 7 amp. With this high current, the silver gathered about the platinum cathode in a loose spongy mass, easily loosened by light tapping of the wire. The fine silver crystals were washed and stored in distilled water until required for use. Silver chloride was precipitated from silver nitrate solution using hydrochloric acid. It was washed and stored under water in darkness until needed. The silver chloride remained white indefinitely. The electrode was simply prepared by first repeatedly washing the required amounts

of the silver and silver chloride with the solution to be investigated, and placing the silver chloride on the silver in the bottom of the E.M.F. vessel. Electrical contact was made through the glass to the silver crystals. No data were given as to the relative amounts of each present, but it is estimated that about equal weights of each were employed. The electrodes were slow to come to equilibrium. In some instances the dilute solutions of hydrochloric acid were in contact with the electrodes in glass for periods of one month, during which period the composition of such dilute solutions might have been affected through reaction with glass. The close agreement of the measurements using the totally electrolytic form of the electrode with the results of Linhart confirms the identity of the precipitated silver chloride electrode with the electrolytic silver–silver chloride electrodes. This type of electrode was selected by Gerke (30) in studying the temperature coefficient of galvanic cells and the entropies of reaction. Guntelberg (35) used the precipitated silver chloride electrode in a slightly modified form. The electrode consisted of a layer of crystalline silver with silver chloride. The latter rested on a cotton-wool plug in the bottom of the half-cell. Electrical contact was made through glass with a platinum spiral coated with silver deposited thermally from the decomposition of silver oxide. The solution to be investigated was introduced through a filling arm opening at the bottom of the half-cell under the cotton wool, so that on entering the compartment the solution washed through the silver–silver chloride electrode. The electrode came to equilibrium with the solution 1 or 2 days after washing and filling the cell in this manner. In many instances the electrodes were constant to 0.02 mv. for periods of three weeks. It was suggested that if the electrodes were protected from the action of light, such half-cells could be used for extended periods without suffering change. The silver chloride preferred by Guntelberg was a crystalline form prepared from an ammoniacal solution by slow evaporation (over sulfuric acid). Randall and Young (95) investigated the silver–silver chloride electrodes in acidic and neutral solutions. The totally electrolytic type was discarded in favor of the precipitated silver chloride electrode because of difficulties encountered in obtaining reproducibility. Three sets of six electrolytic electrodes were prepared on platinum foils 1 cm.^{2} in area. The potentials varied within the range of 0.1–2 mv. Details of the method of preparation used were not given. A silver spiral wire was used rather than the platinum spiral plated with silver, as recommended by Lewis (72), since it shortened the procedure. To obtain the crystalline silver in a state of high reproducibility, a solution of silver nitrate (0.1 *M*) was electrolyzed at about 90°C., using 6 amp. and a platinum-wire cathode. This yielded finely divided silver crystals rather than the large crystals used by Gerke (30), which were found to be far from reproducible. The silver chloride was prepared metathetically by precipitation from silver chlorate solutions. It was heated for 24 hr. at about 100°C. in dilute hydrochloric acid before being washed and used. A layer of the silver chloride was placed on a layer of silver in one limb of the E.M.F. cell, and electrical contact was made through the glass. Electrodes prepared in this manner never varied by more than 0.4 mv. This type of electrode

was also investigated by Harned (38), who employed three kinds of electrodes, i.e., the precipitated silver chloride electrode, and two forms of the thermal-electrolytic type, in studying the properties of alkali halides in E.M.F. concentration cells. This form of electrode has not been subject to recent investigations. From the data available it follows that three problems exist with the use of the precipitated electrode: (*1*) the length of time required for the electrode to come to concentration equilibrium with the solution, (*2*) the preparation of finely crystalline silver in a strain-free reproducible form, and (*3*) the susceptibility of this type of electrode to oxidation by air dissolved in the solutions. Guntelberg (35) and Randall and Young (95) found it necessary to use solutions freed of oxygen in order to obtain steady potentials with this type of electrode. The electrolytic, thermal, and thermal-electrolytic electrodes are also much more versatile and adaptable in physical form than the precipitated silver chloride type of electrode.

A form of the silver–silver chloride electrode suitable for E.M.F. measurements in molten salts has been described recently by Senderoff (102). The reference half-cell (figure 1d) was made of fused silica, and was designed for electrode polarization measurements in the temperature range of 600–900°C. Aten, den Hertog, and Westenberg (4), in studying the electrodeposition of metals from fused salts, found that silver deposited cathodically and dissolved anodically at 475°C., with the polarization voltage at a current density of 1 amp./dcm.^{2} being only 0.5 mv. The silver electrode was thus demonstrated to be reversible in molten silver chloride. The stability and reversibility of this cell have been demonstrated by Senderoff as follows:

Silver chloride (A) and silver rods (B) were placed in both legs of the cell, with capillary C sealed. The potential was measured before and after passing current through the cell. After 1 hr. at 600°C. equilibrium was reached with a small asymmetry potential of 0.4 mv. When 4 ma./cm.^{2} had been passed for 1 min., the cell returned to 0.4 mv. in less than 30 sec. on open circuit. The current was increased in these tests, until at 20 ma./cm.^{2} for 1 min. the open-circuit potential of the cell was changed to 1 mv. Since currents of this magnitude would not normally be used in potentiometric measurements, the likelihood of polarizing the electrode in a measurement is small. The criterion of attainment of equilibrium was the stability of potentials measured, i.e., within 1 mv. Once equilibrium was established, no difficulties were experienced with drift within these limits during the 3-hr. period required for the observations. For measurements of equilibrium potential Senderoff has indicated that the design of this reference half-cell can be simplified in that the capillary probe C on arm D would not be necessary.

This high-temperature Ag, AgCl (liquid) half-cell differs in one important aspect from the Ag, AgCl (solid), Cl^- (aq) half-cell. The latter is an example of an electrode of the "second kind," i.e., reversible to halide ions, whereas the former is an electrode of the first kind: namely, a metal immersed in a liquid containing its ions and reversible to the metal ion.

III. REPRODUCIBILITY AND STABILITY OF THE SILVER–SILVER CHLORIDE ELECTRODE

An examination of the literature reveals conflicting data and opinions concerning the reproducibility and constancy of the silver–silver chloride electrode. In the work of Noyes and Ellis (85), the totally electrolytic type of electrode, although it had already been used with success by MacInnes and Parker (81) and Jahn (61), was rejected in favor of the thermal-electrolytic type. It was suggested that electrolytically deposited silver could not be used with reliance unless the strains in it were removed in some manner. The coating of thermally deposited silver was probably nearly strain-free, since it was annealed during the process of deposition. MacFarlane and Hartley (78) in later work also reported that the potentials of electrodes having electrolytic silver on platinum were 1.7 mv. less than those of granular silver electrodes prepared by reduction of silver nitrate with ferrous sulfate. This may indicate that the energy content of the electrolytic electrode was higher, possibly owing to a state of strain of the surface. Very little information on this point has been reported. The large bias potentials observed by some investigators (1, 35, 74, 95) on intercomparison of the electrolytic type of electrodes may probably be attributed in part to strain in the electrode surface (due to the nature of the platinum base) or to the methods of silver deposition and chloridizing.

A further point which has been the subject of conflicting views concerns the sensitivity of the silver chloride electrodes to light. The electrodes have been used in darkness or subdued light by a large number of investigators (1, 22, 23, 35, 88), and the results of Carmody's studies on this point indicated that light did cause an appreciable change in potential of the silver–silver chloride electrode. On the other hand, there have been a number of reports to the effect that these electrodes were not appreciably sensitive to sunlight and could be used without the inconvenience of working in rooms with restricted illumination (18, 60, 93, 106). In the latter instances the electrodes were a plum shade in color, and on direct exposure to light did not appreciably change in potential or color. The electrodes that were reported by Carmody to be sensitive to light were white in color. On exposure to light these changed in potential and darkened to a brown color. The work of Carmody (white electrodes) has not been reproduced. The data of Harned (38), Brown (18), MacInnes and associates (19, 103), Gordon and associates (21, 60, 62), and Smith and Taylor (106) indicate that the shade of color of the silver chloride electrode had no effect upon its potential.

In addition, a drift in the potential of silver–silver chloride electrodes has been attributed to the effect of air dissolved in the solution (17, 76, 77, 95). The cause for this poor behavior in acid solutions was probably a slow primary oxidation reaction:

$$2Ag + 2HCl + \tfrac{1}{2}O_2 \rightarrow 2AgCl + H_2O$$

When oxygen was removed from the solutions by sweeping with nitrogen, the potential of the electrode was steady.

More recently Smith and Taylor (106, 111) have made a careful study of the silver–silver chloride electrode to evaluate the effect of light, dissolved air, and the change in potential of this electrode with time.

The results of the measurements (intercomparison or bias potentials) found for the three types of the silver–silver chloride electrode most commonly used are summarized in tables 2 and 3. The electrodes were tested in sets of eight prepared simultaneously in the presence or absence of light. A solution of 0.05 *M* potassium chloride was used for the intercomparisons. The reproducibility among individual electrodes when silver–silver chloride electrodes are prepared at the same time was found to be 0.02 mv.

The aging effect, i.e., change in potential with age, of the silver chloride electrode was noted by MacInnes and Parker (81). It was observed that older electrodes were slightly electropositive to newer electrodes, and that the effect was always in the same direction and of the same order of magnitude, within 0.05 mv.

TABLE 3

Comparison of electrodes, prepared in the presence and the absence of light, in air-saturated solutions (106)

ELECTRODE NUMBER*	POTENTIAL DIFFERENCE	ELECTRODE NUMBER*	POTENTIAL DIFFERENCE
	mv.		*mv.*
1–2	0.01	1–5	−0.02
1–3	0.01	1–6	0.02
1–4	−0.02		

* All electrodes were of the totally electrolytic gauze type. Electrodes 1, 3, and 5 were prepared in the absence of daylight; electrodes 2, 4, and 6 had been exposed to light during preparation.

Since in that work similar electrodes were always opposed to one another, this effect was partially compensated for, so that error from this source was minimized. The possibility of the occurrence of an aging effect may not have been recognized in some of the earlier work. This may have led some to discard the totally electrolytic type of electrodes in favor of the thermal-electrolytic (85), or to report the thermal-electrolytic type more positive to the thermal electrodes (99), and may account for differences reported for the standard electrode potential of the silver–silver electrode.

Smith and Taylor (106) investigated the change in potential with age of the silver chloride electrode to ascertain the factors important to this effect. The data obtained on the aging effect in the case of the electrolytic type of electrode in 0.05 *N* potassium chloride, oxygen-free (a) and saturated with air (b), are shown in figure 2. Each point represented the difference in potential between the average potential of four electrodes which had been aged at least one week before use, and the average potential of four newer electrodes, plotted against time in hours. The new electrodes were generally placed in the cell about 2 hr. after chloridizing. In this manner it was shown that the aging effect occurred practically to the same extent for light-protected and for light-exposed electrodes, in

dilute sodium chloride as well as potassium chloride, and in the presence or absence of dissolved oxygen in the solutions. That the approach to equilibrium was more rapid in the oxygen-free solutions was due to the stirring action of

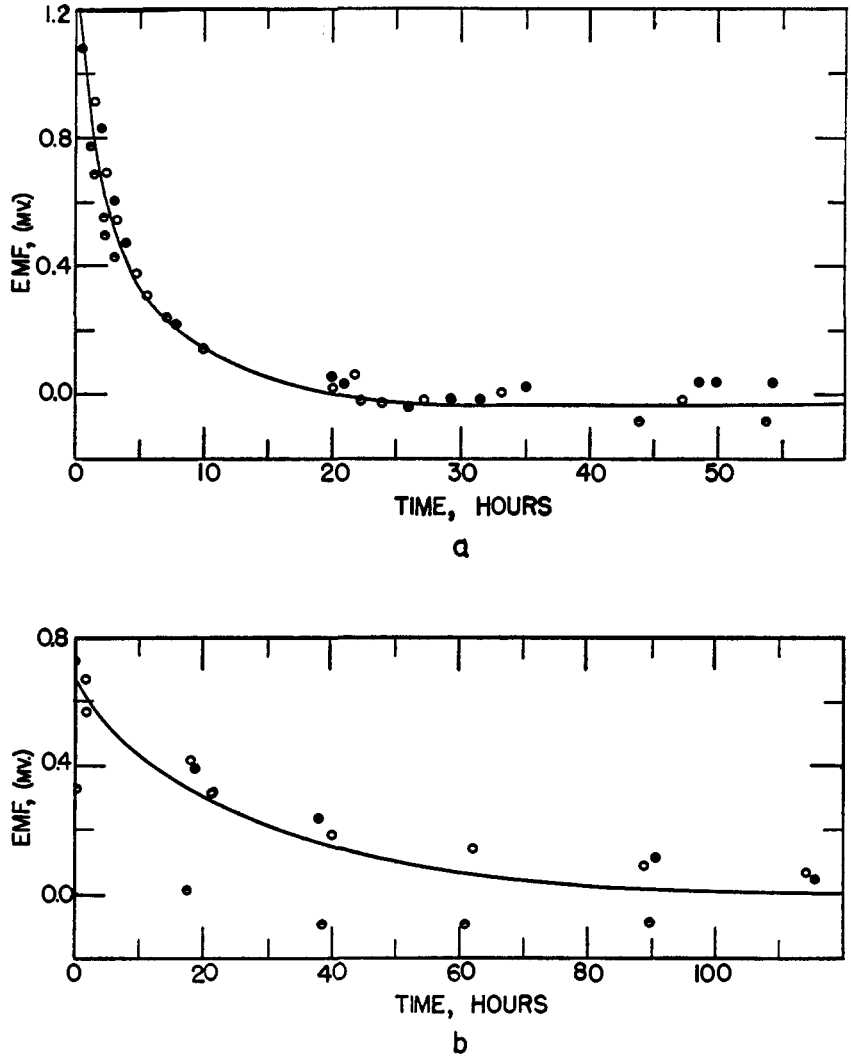

FIG. 2. Aging effect of the silver–silver chloride electrode in (a) oxygen-free and (b) air-saturated solutions of 0.05 *N* potassium chloride.

nitrogen bubbling through the solutions. The possibility that this effect might be attributed to dissolved traces of bromide impurities was eliminated by very careful purification of the potassium chloride. Only in dilute hydrochloric acid solutions, the presence of dissolved oxygen was confirmed to have a disturbing effect on the potential of the silver chloride electrode (111), as reported earlier

by Guntelberg (35). Both the thermal-electrolytic and the thermal electrodes were tested in a similar manner. While the overall change in potential was less than for the electrolytic type, the same aging effect was observed.

Having eliminated the factors above with reference to the aging effect, Smith and Taylor investigated concentration-polarization within the silver chloride layer as possibly causing this effect. Thus, when silver electrodes are chloridized electrolytically, the solution in the pores of the silver chloride becomes more dilute than the surrounding solutions. Freshly prepared electrodes should then act as cathodes towards electrodes previously aged in the solution, since the latter have had the electrolyte within their pores replenished. Agreement of electrodes within a set prepared at a given time is no criterion that their potential has come to equilibrium, since the aging effect is different from the fluctuating bias potential of a few hundredths of a millivolt. The latter would be present in both equilibrium and non-equilibrium electrodes. The role of concentration-polarization was clearly shown in oppositely polarizing a set of two thermal-electrolytic electrodes that had been at equilibrium. A small current for a short period of time produced mutually opposite concentration-polarization in the electrodes. The electrode which had been the anode during the passage of the current behaved as the cathode, and the other as the anode, to aged electrodes. A period of approximately 24 hr. was required, with nitrogen stirring, for these electrodes to regain equilibrium. In dilute hydrochloric acid, an oxidation occurs in the presence of dissolved air, which causes a slight decrease in the concentration of the acid within the interstices of the silver chloride layer. This decrease in concentration causes an oxygen-saturated solution to act as a cathode to an oxygen-free electrode. From the change in potential (0.21 mv.) Taylor and Smith have estimated the change in effective concentration of the acid within the pores of the electrode to be about 0.5 per cent.

Smith and Taylor (106) have pointed out that the aging period of freshly prepared electrodes may vary from a negligible time of a few minutes to appreciable times, such as 1–20 days. Hornibrook, Janz, and Gordon (60) had found no indication of aging after periods of 25–40 min., and questioned the extremely long periods (20 days) in the light of the concentration-polarization explanation of Smith and Taylor. For the simple case of the plane diffusion, the concentration differences would disappear with exp. $(-\pi^2 kt/x^2)$, where k is the diffusion constant, t the time, and x the distance where the plane is constant. For $x = 0.1$ cm. in potassium chloride at 25°C., about 10 min. would be required for the concentration difference to fall to 10^{-4}. The question was resolved by recognizing the difference in electrode preparation used in these two investigations. The thickness of coating and current densities used by Smith and Taylor were 13.4 and 5.6 times as large as those used by Gordon and associates. Assuming a period of 10 min. for the aging effect for the thinly coated electrodes, it follows that for a layer thirteen times this thickness about 28 hr. would elapse before the effect was over. Thus for a small thickness of silver chloride deposited at a low current density, the aging effect would be over in a very short (negligible) time.

The random drift frequently observed in the bias potential of an electrode

pair (60), and the aging effect observed with the thermal type of electrodes, which are dry and completely free from electrolyte before immersion in the solution (106), may indicate that other factors in addition to concentration-polarization are operative in causing this drift of potential with time. A change in the nature of the sensitive silver chloride surface of the electrode, e.g., solution of the smaller silver crystals or uncovering of "hot spots" on silver crystals, may well contribute to this effect (60).

Pinching and Bates (93) have recently investigated the effect of impurities in chloride solutions on the potential of the silver–silver chloride electrode. A

TABLE 4

Effect of small concentrations of foreign salts on the potential of the silver–silver chloride electrode in halide solutions at 25°C. (93)

FOREIGN SALT	MOLALITY OF		MOLE PER CENT OF FOREIGN SALT	ΔE*
	Halide	Foreign salt $\times 10^5$		
Sodium chloride solutions				
KBr	0.02	1.3	0.064	0.87–1.08
	0.05	25	0.5	1.90
KI	0.05	2.5	0.05	0.05
	0.05	25	0.5	0.17†
KCN	0.05	2.5	0.05	0.23
Potassium chloride solutions				
KBr	0.05	2.5	0.05	0.50
	0.05	6	0.12	0.73–2.30
Hydrochloric acid solutions				
KBr	0.05	2.5	0.05	0.46–3.64

* Positive ΔE signifies that the electrode in the solution of salt was negative with respect to the electrode in the pure halide salt solutions.

† The electrode was yellow at the end of the experiment.

summary of the results is given in table 4. Thermal-electrolytic silver–silver chloride electrodes were used in a modified H-type cell. The electrodes were brought to equilibrium in a solution of the pure chloride. Each arm was then filled with carefully deaerated portions of the chloride solution, to one of which the small quantity of foreign salt had been added. Hydrogen was used in the filling process to displace the solutions, each arm being filled two or three times before the final filling. The potential difference, ΔE, in general reached a constant value within an hour, but when the electrodes were immersed in solutions containing bromide as impurity, the E.M.F. rose slowly during 24–48 hr. In table 4 the lower value of ΔE is the value reached after 1 hr., and the higher value is the constant value, or that noted after 24 hr. In addition to the foreign salts listed, sodium sulfate, sodium oxalate, disodium hydrogen phosphate, and sodium

sulfide were tested. Of these the latter caused the largest change in potential (a value of 0.71 mv.), and the electrodes were black at the end of the experiment. With certain impurities, such as iodide and sulfide, the effect on the electrode potential may be explained through the formation of a salt of lower solubility than silver chloride on the surface of the electrode. An accurate computation of the molality of bromide or iodide ion necessary to form solid silver bromide or iodide on the surface of a silver–silver chloride electrode was made with the aid of the standard electrode potentials: namely, −0.2224 (AgCl), −0.0713 (AgBr), and +0.1522 (AgI) in volts at 25°C. The relation between these and the standard potential of the silver electrode is given by:

$$E^0_{AgX} = E^0_{Ag} - \frac{RT}{F} \ln K_{sp(AgX)}$$

$$= E^0_{Ag} - 0.05914 \log (f_{Ag} f_X)(m_{Ag} m_X)$$

where K_{sp} is the solubility product constant of the respective silver halide salt. Thus, for the silver electrode in equilibrium with a solution saturated with both silver chloride and silver bromide, this expression becomes

$$E^0_{AgBr} - E^0_{AgCl} = 0.05914 \log (m_{Cl}/m_{Br})$$

since f_{Cl} and f_{Br} are nearly equal. The value for m_{Br} in equilibrium with solid silver bromide is 0.00279 m_{Cl} or 0.28 mole per cent of m_{Cl}. In a similar manner, m_I is $4.63 \times 10^{-7} m_{Cl}$ or 5×10^{-5} mole per cent of m_{Cl}. Small traces of bromide (table 4) have an abnormally large effect on the potential of the silver–silver chloride electrode. The cause of this is as yet unexplained.

In view of the magnitude of the error due to the small amounts of bromide present frequently in commercial samples of potassium chloride, the removal of bromide is important in purification of the salt for precise electrochemical work. Pinching and Bates have made a thorough study of this problem, describing a sensitive colorimetric test to determine bromide in the presence of chloride, evaluating the various methods of purifying sodium chloride and potassium chloride relative to removal of bromide impurity, and developing an apparatus of simple design for diminishing the hydrolysis of sodium and potassium chlorides during fusion. Precipitation with hydrogen chloride was found to be the best method for purifying sodium and potassium chlorides. The recommended procedure was as follows. For a period of 10 min. chlorine is passed at a moderate rate through a filtered solution of the salt, saturated at room temperature. The free halogens are next removed by boiling for 5 min. From this solution, saturated at room temperature, the salt is precipitated using hydrogen chloride, collected in a filter (sintered glass), and carefully washed with pure water. After a second precipitation with hydrogen chloride, the washed salt is dried at 180°C. and finally fused to remove occluded water and hydrochloric acid. This procedure should yield a product meeting the most exacting requirements of electrochemical work.

The problem of the drift in potential of the silver–silver chloride electrode is

generally resolved in experimental work by preparing a set of several electrodes at one time, and using from two to four electrodes in each compartment of the cell. The stability of the electrode potential may be readily observed by using a number of combinations of these in any measurements (35, 60, 88, 90, 103, 104). In addition to a direct measurement of bias potential, a check on the difference in the potentials of the electrodes may be obtained by making two measurements with the same solutions under investigation, but with a reversal of positions of the solutions within the cell for the second measurement. If the apparatus is designed symmetrically, the difference in E.M.F. should be twice the directly measured difference of potential of the electrodes. This has been found true within a few microvolts (60, 103).

IV. THE SILVER–SILVER BROMIDE AND SILVER–SILVER IODIDE ELECTRODES

The silver–silver bromide and silver–silver iodide electrodes have not been subject to as much study as the silver–silver chloride electrode. The preparation, reproducibility, and stability of these electrodes are treated in this section, the references being discussed in chronological order.

Shortly after the work of Jahn (61) with the chloride electrode, Halla (36) published his investigation of the silver bromide and silver iodide electrodes. The silver deposition was carried out according to the method described by Jahn for the chloride electrodes, using a current of 0.5 amp./dcm.^{2} For the formation of silver bromide and silver iodide, Halla recommended the use of 0.07 M potassium bromide or iodide rather than the halogen acid. These solutions were made weakly acidic with the appropriate acid to prevent the formation of per- and hypo-halogens. The electrodes were anodized in such solutions at 1 v., using the commutator described by Jahn to obtain a porous electrode layer. Halla claimed that the electrodes thus formed in darkness were very dependable. The electrodes were reported almost white when brought into the light.

Jones and Hartmann (65) have described the following procedure to form good silver–silver iodide electrodes: A small platinum spiral, after careful cleaning, was coated electrolytically with silver from silver nitrate in potassium cyanide at 0.005 amp. per electrode for 2 hr. Six electrodes were prepared simultaneously. After washing to remove adsorbed cyanide, the spiral was coated with a very thin coherent layer of silver iodide from dilute potassium iodide, using 1 ma. for about 2 hr. The electrodes were stored in fresh potassium iodide, of the same strength as that to be studied, saturated with silver iodide until required for use. The maximum intercomparison potential was 0.04 mv., and the average deviation from the mean was 0.01 mv. in a set of six electrodes.

H. S. Taylor (110) reported that after a little experience, the procedure of Jones and Hartmann yielded constant and reproducible silver iodide electrodes. In a set of five electrodes, the maximum and average deviations were 0.08 and 0.02 mv., respectively. This type has also been used by Gelbach (29) and by Harned and Douglas (42).

A precipitated form of the silver–silver iodide electrode has been described by Pearce and Fortsch (92) and by Gerke (30). The latter observed that the electro-

motive force of cells with electrolytically formed silver iodide was much higher than that of those with chemically precipitated silver iodide. Gerke suggested that therefore the chemically precipitated iodide was a more stable form of silver iodide than that formed electrolytically, since it is known that this substance does exist in two forms (28). The precipitated form of this electrode was prepared by tightly packing a platinum wire with fine, electrolytically deposited crystals of silver. This was covered with a layer of silver iodide. The latter was carefully prepared by precipitation from solutions of purified potassium iodide and silver nitrate. After washing with conductance water until no test for iodide was obtained, it was stored in darkness under conductance water. The time required for this electrode to attain equilibrium varied from 4 to 8 days, depending on the concentrations of the solutions.

Afanasiev (1) prepared the totally electrolytic type of silver bromide electrode, using the silver-plating conditions already described for the chloride electrodes. The electrodes were coated with silver bromide in 0.75 *M* hydrobromic acid at 0.2 ma./cm.^{2} for 5–6 hr. in darkness. Like his electrolytic chloride electrodes, these were found to be of poor reproducibility (0.1–0.2 mv.). Afanasiev found the thermal-electrolytic type similar to the thermal-electrolytic chloride electrodes, but bromidized as above, to be more dependable (0.01 mv.).

In the work of Macfarlane and Hartley (77) in ethanol, a totally electrolytic type of silver bromide electrode was used. Silvered platinum grids were bromidized for 1 hr. at 0.01 amp. per electrode in 0.1 *M* potassium bromide. The potentials were constant to 0.2 mv.

The preparation of a thermal type of silver–silver bromide electrode suitable for work in dilute solutions was described by Keston (68) shortly after the work of Carmody (23) on the electrolytic silver halide electrodes. The decomposition of an intimate mixture of silver oxide and silver bromate at 650°C. was used to form this type of electrode. The amount of silver bromate in the paste varied from 8 to 12 per cent, the time of heating varied from 4 to 15 min., and the temperatures of decomposition ranged from 575° to 750°C. The electrodes prepared within this range had the same potential. It was noted that if a large amount of silver bromate was used in the paste, the electrodes were not satisfactory. Silver bromide could be used in place of silver bromate. The latter, however, is preferred since it is more easily purified, and the oxygen liberated in the thermal decomposition tends to increase the porosity of the electrode.

These electrodes would come to equilibrium in 5–6 hr. The reproducibility was 0.05 mv., and the electrodes were capable of potentials constant to 0.02 mv. for long periods of time. Keston pointed out that the advantages of this electrode over the totally electrolytic electrode were the ease and speed of preparation, no possibility for the electrolyte to be occluded or adsorbed during its preparation, a lower sensitivity to light, and the lower solubility of fused silver bromide as compared with electrolytic silver bromide. In addition, by virtue of the thermal treatment, these electrodes should be very nearly strain-free. This type of electrode has been used by Kanning and Campbell (66) in methanol and by Stokes and Stokes (109) in zinc bromide solutions.

Two types of silver–silver iodide electrodes, thermal-electrolytic and thermal, were prepared by Owen (87) in his investigation of the electrode potential from 0° to 40°C. The thermal-electrolytic type was prepared by the method of Jones and Hartmann (65). Silver oxide paste on a platinum spiral was decomposed at 450°C. to form about 0.75 g. of silver per electrode. This was electrolyzed for about 2 hr. at 1.5 ma. in dilute potassium iodide to form the silver iodide layer. It was found that protection from short exposure to diffuse daylight or to direct light by a red bulb was not necessary. These electrodes were usually kept in the cell about 12 hr. before use. The thermal type was prepared by heating a paste of silver iodate (1 part) and silver oxide (9 parts) at 650°C. for 7–8 min. A coprecipitated mixture of oxide and iodate was satisfactory, but a coprecipitated mixture of oxide and iodide was less reliable. The electrodes were usually stored dry, but were allowed to stand in the cell solution about 12 hr. to hasten attainment of equilibrium and to minimize the risk of introducing air. The electrodes were used in diffuse daylight. The reproducibility was ±0.05 mv.

TABLE 5

Reproducibility of different types of silver–silver bromide electrodes exposed to light in neutral air-free 0.05 N potassium bromide solution (111)

ELECTRODE PAIR	ELECTRODE TYPE		
	Electrolytic	Thermal-electrolytic	Thermal
	mv.	*mv.*	*mv.*
1–2	0.00	−0.03	0.01
1–3	0.04	0.02	0.00
1–4	0.05	0.00	0.00
1–5	−0.01	0.01	−0.04
1–6	−0.02	0.00	−0.04
1–7	−0.02	0.02	0.00
Average deviation	0.02	0.01	0.02

The silver–silver bromide electrodes used by Owen and Foering (89) for measurement of the normal electrode potential from 0° to 40°C. were of the thermal type. Similar to the thermal silver iodide electrodes, these were prepared by decomposition of a paste of 1 part of silver bromate and 9 parts of silver oxide at 650°C. for 7 min. Protection from diffuse daylight was not necessary. It was shown that the thermal silver–silver bromide electrode is highly reproducible by using silver bromate of various sources and different degrees of purification. This type of electrode was kept dry until required for use.

The stability and reproducibility in potential of the three types of electrodes (electrolytic, thermal-electrolytic, and thermal) for silver bromide and silver iodide, as well as for silver chloride, were investigated by Taylor and Smith (111). The tests were closely similar to those described in their studies of the silver chloride electrode. The results for the reproducibility of the different types of silver bromide electrodes are shown in table 5, and the intercomparison of the

three types in table 6. The electrolytic silver–silver bromide electrodes were prepared by depositing silver on platinum gauze (0.5 x 1 cm.), washing for 10 days with frequent changes of distilled water, and bromidizing in 1 *N* hydrobromic acid at 4 ma. for 1 hr. The thermal-electrolytic types were made by decomposition of silver oxide–water paste, and bromidizing the silver from a large silver bromide electrode in a solution of the strength to be used in the tests. The thermal electrodes were prepared by the method of Keston. All electrodes were aged for one week in 0.05 *N* potassium bromide solution free of oxygen and with stirring before the intercomparisons were made. It is seen from tables 5 and

TABLE 6

Intercomparison of three types of silver–silver bromide electrodes in neutral air-free 0.05 N potassium bromide solution (111)

ELECTRODE PAIR	TYPE*	*E*
		mv.
1-2	TE-TE	0.00
1-3	TE-TE	−0.01
1-4	TE-TE	−0.01
1-5	TE-TE	−0.01
1-6	TE-E	0.00
1-7	TE-E	0.04
1-8	TE-E	0.05
1-9	TE-E	0.01
1-10	TE-E	0.02
1-11	TE-E	0.02
1-12	TE-T	0.01
1-13	TE-T	0.00
1-14	TE-T	0.00
1-15	TE-T	−0.04
1-16	TE-T	−0.04
1-17	TE-T	0.00

* E, TE, and T represent electrolytic, thermal-electrolytic, and thermal electrodes, respectively.

6 that the equilibrium potential is independent of the type for the silver–silver bromide electrode (within 0.02 mv.). No significant differences were observed on comparison of light-protected and light-exposed electrodes. An aging effect with each type was found in air-free potassium bromide solutions very similar to that reported for the silver chloride electrode. It was also noted that an oxygen-saturated set acted as cathodes towards an oxygen-free set of electrodes, as with silver chloride, in dilute hydrobromic acid solutions. The effect of oxygen is as would be expected from the reaction:

$$2Ag + 2HBr + \tfrac{1}{2}O_2 = 2AgBr + H_2O$$

which would cause an effective decrease in the concentration of the electrolyte within the silver bromide layer.

In the same study, a number of sets of the electrolytic, thermal-electrolytic, and thermal types of silver–silver iodide electrodes were prepared for similar tests. It was found that the thermal and electrolytic types were unsatisfactory.[2] The thermal-electrolytic electrodes, however, were capable of a reproducibility of about 0.02 mv. Also, on intercomparison of the three types, the former two were always positive (i.e., anodic) to the thermal-electrolytic type by 0.1 to 0.2 mv. In view of this, only the thermal-electrolytic type was tested for the effect of light, aging, and dissolved air. The effect of oxygen was very marked in both neutral and acid solutions, causing, on the average, a change of 1.5 mv. positive relative to the electrodes in the air-free cell. The aging effect, demonstrated for the silver chloride and silver bromide electrodes, was also present in the silver iodide electrode. By comparison of electrodes exposed and not exposed to light, it was found that the silver–silver iodide electrodes are not affected appreciably by light.

MacWilliam and Gordon (82) used totally electrolytic silver–silver bromide electrodes of the disc type, as described for silver chloride (60). It was found that steadier electrodes were obtained by bromidizing for 40 min. at 0.4 ma. rather than for 25 min. at 0.65 ma. Potassium bromide (0.1 *N*) was the electrolyte. The silver layer had been electrodeposited as for the silver chloride electrodes. An acceptable electrode pair was one giving a bias potential of 0.02–0.03 mv. It was observed that the silver–silver bromide electrode, in general, was much more erratic than the corresponding silver–silver chloride electrode.

The work of Pinching and Bates (93) concerning the effect of dissolved impurities on the potential of the silver–silver chloride electrode was extended to similar observations for the silver bromide and silver iodide electrodes. The silver bromide electrode was prepared by the method of Keston, except that a temperature of 550°C. rather than 650°C. was used to decompose the silver oxide–silver bromate paste. The silver iodide electrode was also the thermal type, prepared by decomposition of a paste of silver oxide (9 parts) and silver iodide (1 part) at about 450°C. It was found that neither traces of chloride nor traces of bromide affected the potential of the silver iodide electrode in potassium iodide. With the silver bromide electrode in sodium bromide solution, traces of chloride had no effect, but traces of iodide had a large effect on the electrode

[2] A thermal type of silver–silver iodide electrode has been used with success by Bates (J. Am. Chem. Soc. **60**, 2983 (1938)) in the study of the thermodynamics of bi-univalent iodides. The electrodes were formed on small platinum spirals by the thermal decomposition of a paste of 90 per cent silver oxide and 10 per cent silver iodide by heating at 450°C. for 10–15 min. The silver iodide was prepared by precipitation and was digested for 3 days under water at about 80°C. These electrodes were found to be more reproducible in the more concentrated solutions, where 20–25 per cent silver iodide was used, than those prepared by the method of Owen, using silver iodate. Bates has suggested that the relatively low decomposition temperature of silver iodide may account for the decreased stability of electrodes prepared from silver iodate, which decomposes at about 390°C. but requires 1–2 hr. for complete decomposition. Silver iodide has a decomposition temperature of 550°C. An appreciable loss of silver iodide may thus result when mixtures are heated in the temperature range of 400°C. for extended periods of time.

potential. Decomposition of silver iodide on the silver bromide in this case caused a change in potential of 2.2 mv. A change of 0.10 mv. was predicted by calculation from the standard electrode potentials of these electrodes and that for silver. The effect seems abnormally high and has not been explained.

The silver–silver bromide electrode has been investigated in anhydrous hydrogen cyanide by Coates and Davies (24) for reversibility and reproducibility. All tests were made in 0.02 *M* potassium bromide in hydrogen cyanide. Electrodes of the thermal type (Keston) showed some erratic fluctuations but were capable of agreement within 1 mv. An aging effect of about 1 mv. was observed in 8–10 days. Electrodes of the thermal-electrolytic type agreed within themselves to 1–2 mv. initially, and after 14 days, to 0.5 mv. In aqueous solution the electrodes returned to the original bias potential of 0.2 mv. A slight aging effect was noted. When this type was bromidized in a hydrogen cyanide solution of potassium bromide, the reproducibility was 0.5 mv. Electrodes of the electrolytic type were prepared by the method of Brown (17). Initially this type was found to be 2 mv. positive to the thermal-electrolytic type, but this difference decreased on long standing. The aging effect was short (less than 24 hr.) for this type, and reproducibility was 1 mv. within the set.

V. THE STANDARD POTENTIALS OF THE SILVER–SILVER HALIDE ELECTRODES

A. The silver–silver chloride electrode

The determination of the standard electrode potential for the silver–silver chloride electrode offers an opportunity for comparison of the independent measurements of various investigators from the time of the work of Noyes and Ellis (85) in 1917 to date. Three different types of this electrode, the thermal-electrolytic (44, 85, 96), the totally electrolytic, and the precipitated type (23, 83, 100), have been used; the data from these measurements have been treated by graphical methods (74, 95) and by the method of least squares (94). A critical treatment of the many attempts to determine this electrode potential has been made by Harned and Owen (52).

The standard electrode potential for the silver–silver chloride electrode is obtained from E.M.F. measurements for the cell without liquid junction:

$$H_2 \mid HCl(m) \mid AgCl, Ag \qquad (A)$$

for which the reaction occurring and the E.M.F. are given by the expressions

$$\tfrac{1}{2}H_2(g, atm) + AgCl(s) = Ag(s) + HCl(m)$$

and

$$E_m = E^0 - \frac{2RT}{F} \ln (m_\pm \gamma_\pm)_{HCl} \qquad (1)$$

In the graphical treatment of the data (52, 58, 79) equation 1 is rearranged to the form:

$$E_m + \frac{2 \times 2.3026RT}{F} (\log m_\pm - A\sqrt{m}) = E^0 + Bm \qquad (2)$$

since at moderate concentrations the Debye–Hückel limiting law with an additional term:

$$\log \gamma_{\pm} = -A\sqrt{m} + Bm \tag{3}$$

may be used to eliminate the activity coefficient in the first expression. Accordingly, the data can be represented by straight lines at lower concentrations, and the extrapolation can be made with high precision. The method has been criticized as being subjective in treatment, the values being influenced by the choice of the Debye–Hückel limiting slope. The least-squares method of treating these data is completely objective, and has been used by Prentiss and Scatchard (94) to determine the standard potential for this electrode from the data treated graphically for the same purpose. In table 7 the results of these investigations

TABLE 7

The standard potential of the silver–silver chloride electrode at 25°C.

REFERENCE	STANDARD ELECTRODE POTENTIAL		REMARKS
	Graphical	Least squares (94)	
	international volts	*international volts*	
Noyes and Ellis (85)	−0.2238		Thermal-electrolytic electrode
Linhart (74)	−0.2234	−0.22253	Precipitated electrode
Scatchard (100)	−0.2226		Electrolytic electrode
Nonhebel (83)	−0.2228		Electrolytic electrode
Randall and Young (95)	−0.2221		Precipitated electrode
Carmody (23)	−0.2223	−0.22222	Electrolytic electrode
Roberts (96)	−0.22240	−0.22241	Thermal-electrolytic electrode
Harned and Ehlers (44)	−0.22239	−0.22244	Thermal-electrolytic electrode
Scatchard (100)	−0.2226		Data of Linhart
Hitchcock (58)	−0.2224		Data of Linhart
Spencer (108)	−0.2222		Data of Carmody
MacInnes (79)	−0.2225		Data of Harned and Ehlers

are listed, with the type of electrode or source of data given in each case. The results obtained graphically are in good agreement with the values calculated by the least-squares method. Harned and Wright (56) calculated the value of E^0, using the data of Harned and Ehlers (44) with (*1*) the *International Critical Tables* constant data, and (*2*) the values of Birge (16) to evaluate the term $(2.3026R)T/F$. The values for E^0 were 0.22239 and 0.22223 v., respectively, at 25°C. This indicates clearly the influence of the choice of numerical values for the constant terms on the values for the standard potential.

The standard potential of the silver–silver chloride electrode was determined by Harned and Ehlers from 0° to 60°C. at 5° intervals. In a cell of the type A, a thermal-electrolytic electrode was used, and the values of E^0 were evaluated graphically. The standard potential of this electrode has been redetermined quite recently by Harned and Paxton (53) from 0° to 50°C., and by Bates and Bower (11) up to 95°C. The results of these investigators, using the physical constants

of Birge (16) in the first two investigations and the physical constants of the National Research Council Report (Washington) of 1950 in the third, are listed in table 8.

Harned and Paxton used a cell without liquid junction but having solutions of strontium chloride and hydrochloric acid as electrolyte:

$$H_2 \mid HCl(0.01), MCl_2(m) \mid AgCl, Ag \qquad (B)$$

The overall cell reaction is the same as for type A, but the ionic strength must be used in place of molality in treating the data graphically.

TABLE 8

The standard potential of the silver–silver chloride electrode as a function of temperature

t	INVESTIGATION		
	Harned and Ehlers (44)	Harned and Paxton (51)	Bates and Bower (11)
°C.	*volts*	*volts*	*volts*
0	0.23642	0.23652	0.23655
5	0.23400	0.23405	0.23413
10	0.23134	0.23137	0.23142
15	0.22854	0.22849	0.22857
20	0.22558	0.22549	0.22557
25	0.22246	0.22239	0.22234
30	0.21919	0.21908	0.21904
35	0.21570	0.21570	0.21565
40	0.21207	0.21207	0.21208
45	0.20828	0.20833	0.20835
50	0.20444	0.20449	0.20449
55	0.20042		0.20056
60	0.19627		0.19649
70			0.18782
80			0.1787
90			0.1695
95			0.1651

Bates and Bower (11) investigated the E.M.F. of a cell of type A, using solutions all more dilute than 0.113 m to determine the standard potentials up to 95°C. A large number of cells, varying from twenty-four at 45° and 50°C. to eighty at 60°C., were used. The least-squares method was used to establish the extrapolation lines. The standard deviation of the individual E^0 values ranged from 0.05 mv. at 10°C. and 15°C. to 0.28 mv. at 95°C. The agreement of results (table 8) with the more recent investigations leaves little to be desired.

An attempt has been made by Gilbert (32) to find a basis for direct comparison of potential measurements made at different temperatures. The value of the standard potential of an electrode at any temperature is, by convention, always referred to the standard potential of the hydrogen electrode, taken as zero at all temperatures. For the direct comparison of potential measurements made at different temperatures, allowance must be made for the effects of a possible

temperature coefficient of the hydrogen electrode. Gilbert studied two types of cells:

$$\underset{(20°C.)}{\text{Ag, AgCl} \mid \text{MCl}(m)} \;\|\; \underset{(T°C.)}{\text{MCl}(m) \mid \text{Ag, AgCl}} \qquad \text{(C)}$$

and

$$\underset{\substack{\text{(plus other ions to}\\ \text{give electroneu-}\\ \text{trality) (20°C.)}}}{\text{Ag, AgCl} \mid \text{H}^+(a = 1)\text{Cl}^-(m)} \mid \text{H}_2, \text{Pt–Pt}, \text{H}_2 \mid \underset{\substack{\text{(plus other ions to}\\ \text{give electroneu-}\\ \text{trality) (}T°\text{C.)}}}{\text{H}^+(a = 1)\text{Cl}^-(m)} \mid \text{AgCl, Ag} \qquad \text{(D)}$$

for which the potential of the former was measured directly, but was calculated for the latter from the data of Harned and Ehlers (44). The results are summarized in table 9.

TABLE 9

Absolute temperature dependence of electrode potentials (*32*)

(Difference in temperature of cell compartments, 65°C.)

ELECTROLYTE	OBSERVED E.M.F. (Cell C)	CALCULATED E.M.F. (Cell D)	DIFFERENCE (C − D)
	volts	*volts*	*volts*
0.0115 *N* KCl	0.014	−0.052	0.066
0.00115 *N* KCl	0.050	−0.016	0.066
1.0 *N* NaCl	0.014	0.051	0.065
0.001 *N* NaCl	0.045	0.016	0.061
0.0875 *N* HCl	0.0	0.024	0.024
0.000875 *N* HCl	0.023	0.015	0.038

The electrode in the hot end was found to be always positive. From the calculations, the hot end should be more negative in all cases. This discrepancy may be attributed to several factors. Transport occurs in cell C and not in D, and the E.M.F.'s should differ by a factor involving transference numbers of the ions. There is a liquid junction in cell C, and various thermo-effects, since the electrodes and conductors are at different temperatures. Finally, the discrepancy would include effects due to any temperature coefficient of the hydrogen electrode. For a difference of 65°C. in temperature the thermoelectric effects are probably too small to account for an appreciable part of this discrepancy. Gilbert thus points out the need for a thermodynamic treatment of a cell of type C to find out if information could be gained with reference to the possibility of referring electrode potentials to any standard other than that of the hydrogen electrode at the temperature of measurement. If the above effects could be calculated with certainty, it would be possible to deduce whether or not a temperature coefficient of the hydrogen electrode exists and to make absolute comparison of electrode potentials at different temperatures.

B. The silver–silver bromide electrode

The standard electrode potential of the silver–silver bromide electrode has been well established through measurements on cells similar to the two types described for silver chloride, and a third type in which the silver bromide electrode and silver chloride electrode are directly compared in borax solutions containing the corresponding halides. Owen (87, 89) developed the latter method for the standard potentials of the silver bromide and silver iodide electrodes. The use of borax solutions under certain prescribed conditions has the advantage of eliminating the need for an extrapolation to infinite dilution. The method is recommended for the study of electrodes for which the determination of the standard potentials by direct extrapolation is impracticable.

For silver–silver bromide, Owen and Foering (89) measured the following cells:

$$H_2 \mid HBO_2(m), NaBO_2(m), KX(m) \mid AgX, Ag \qquad (E)$$

where X was bromide or chloride and m was approximately 0.005 molal. The E.M.F. of these cells is given by:

$$E^m_{HBr} = E^0_{HBr} - \frac{RT}{F} \ln \gamma_H \gamma_{Br}(m_H m_{Br}) \qquad (5)$$

$$E^m_{HCl} = E^0_{HCl} - \frac{RT}{F} \ln \gamma_H \gamma_{Cl}(m_H m_{Cl}) \qquad (6)$$

The term $\gamma_H m_H$ may be eliminated from these expressions by using the thermodynamic equilibrium equation for boric acid:

$$K_A = \frac{\gamma_H \gamma_{BO_2}}{\gamma_{HBO_2}} \times \frac{m_H m_{BO_2}}{m_{HBO_2}} \qquad (7)$$

This gives the expression:

$$E^0_{HBr} - f(\gamma) = E^m_{HBr} + \frac{RT}{F} \ln K_A + \frac{RT}{F} \ln (m) \qquad (8)$$

$$E^0_{HCl} - f(\gamma) = E^m_{HCl} + \frac{RT}{F} \ln K_A + \frac{RT}{F} \ln (m) \qquad (9)$$

where $f(\gamma)$ is simply

$$\frac{RT}{F}\left(\log \frac{\gamma_x \gamma_{HBO_2}}{\gamma_{BO_2}}\right)$$

and is practically uninfluenced by substitution of similar ions at the concentrations studied. By using all three electrolytes at the same concentration, this leads to the simple expression for the standard potential:

$$E^0_{HBr} = E^0_{HCl} + E^m_{HBr} - E^m_{HCl} \qquad (10)$$

whereby $E^0_{Ag,AgBr}$ (i.e., $-E^0_{HBr}$) is obtained from a knowledge of E^0_{HCl} and one measurement of E^m_{HBr} and E^m_{HCl}, respectively. The results of Owen and Foering

for the temperature range up to 40°C. are compared with the values obtained by Harned and Donelson (40) in table 10. The latter were established from measurements on cells having mixtures of lithium bromide and the acid as electrolyte. The results are in agreement within 0.05 mv. over the whole temperature range. These data differ from the earlier values reported by Harned, Keston, and Donelson (48) for the cell containing the acid only by amounts varying from 0.1 to 0.3 mv.

TABLE 10

The standard potential of the silver–silver bromide electrode as a function of temperature

t	INVESTIGATION		t	INVESTIGATION	
	Owen and Foering (89)	Harned and Donelson (40)		Owen and Foering (89)	Harned and Donelson (40)
°C.	*volts*	*volts*	°C.	*volts*	*volts*
0		−0.08165	30	0.06876	0.06872
5	−0.07986	0.07991	35	0.06600	0.06602
10	0.07800	0.07801	40	0.06306	0.06300
15	0.07596	0.07593	45		0.05995
20	0.07374	0.07377	50		0.05666
25	0.07134	0.07127			

TABLE 11

The standard potential of the silver–silver bromide electrode at 25°C.

REFERENCE	STANDARD ELECTRODE POTENTIAL	REMARKS
	volts	
Harned and Hamer (47)	−0.0717	Cell type B; T-E electrodes*
Jones and Baekstrom (64)	−0.0712	Comparison of bromide with calomel and T-E electrodes; chloride electrodes
Keston (68)	−0.0711	Cell type A; T electrodes
Harned, Keston, and Donelson (48)	−0.0710	Cell type A; T electrodes
Owen and Foering (89)	−0.0713	Cell type E; T electrodes
Harned and Donelson (40)	−0.0713	Cell type B; T electrodes

* T-E and T represent the thermal-electrolytic and thermal types of the silver-silver bromide electrode.

At 25°C. closely agreeing results for the standard electrode potential have been obtained by different investigators. These are summarized in table 11. The value -0.07115 ± 0.00015 v. includes all these values. The close agreement is very satisfactory, since the data were obtained by independent investigations, with different materials and different electrodes, and using different types of cells.

C. The silver–silver iodide electrode

The standard electrode potential of the silver–silver iodide electrode has been more difficult to establish by direct means (cells of types A and B), owing to the

uncertainty in the activity coefficients of hydrogen iodide which made the graphical extrapolation impracticable. It was also shown in the work of Taylor and Smith (111) that of the electrolytic, thermal-electrolytic, and thermal types of this electrode, only the thermal-electrolytic is satisfactory from the viewpoint of reproducibility and stability.

Owen (87) has measured the standard potential of the silver–silver iodide electrode, using the thermal-electrolytic type of electrode and the borax-buffered cell technique (cells of type E). The results of this work are listed in table 12. No further data or studies on the standard electrode potentials of silver iodide have been reported.

TABLE 12

The standard potential of the silver–silver iodide electrode as a function of temperature (89)

T	E^0	T	E^0
°C.	*volts*	°C.	*volts*
5	0.14712	25	0.15225
10	0.14805	30	0.15396
15	0.14920	35	0.15586
20	0.15062	40	0.15787

D. In non-aqueous media

In non-aqueous media, the hydrogen electrode has been accepted as the ultimate standard of reference, the electrode potential being defined as equal to zero at a mean ion activity of unity for the hydrogen-ion component. Owing to the high molecular weights of organic solvent media, the differences in the activity coefficients referred to the three concentration scales, m, c, and N (molal, molar, and mole-fraction, respectively) are no longer negligible, as in the case of aqueous solutions. Accordingly the definitions of the molal, molar, and mole-fraction standard electrode potentials (i.e., E_m^0, E_c^0, and E_N^0) are given by:

$$\begin{aligned} E &= E_m^0 - \frac{2RT}{F} \ln (m_{\mathrm{H}} m_{\mathrm{Cl}}) \gamma_{\mathrm{H}} \gamma_{\mathrm{Cl}} \\ E_c^0 &= E_m^0 + 0.1183 \log (d_0) \\ E_N^0 &= E_m^0 + 0.1183 \log (1000/M) \end{aligned} \tag{11}$$

where E is the measured potential for a cell of type A, and d_0 and M are the density and molecular weight of the solvent. As a practical standard, the hydrogen electrode is inconvenient; the silver–silver halide electrodes have been proposed as secondary reference standards.

The use of the silver–silver chloride electrode as reference standard in pure methanol (D = 31.5) has been investigated by Nonhebel and Hartley (84) and by Austin and coworkers (5), in pure ethanol (D = 24.31) by Woolcock and Hartley (113), and in pure acetonitrile (D = 38.8) by Ulich and Spiegel (112) and by Janz and Taniguchi (63). In the former two solvents the electrode is of

good stability and reproducibility, whereas in the latter instability is observed, probably owing to the tendency to complex formation of silver chloride in this solvent. MacInnes (79) and, more recently, Harned and Owen (52) have recalculated the early work in methanol and ethanol, taking into account the effect of the molecular weights of these solvents on the standard potentials.

At 25°C. the values of E^0_m are 0.0101 and 0.0740 v. in methanol and ethanol, respectively, for the silver–silver chloride electrode. According to the data of Austin and coworkers (5), the temperature dependence of this electrode potential is given by the equation:

$$E^0_t = 0.0103 + 12.080 \times 10^{-4}(t - 25) + 4.00 \times 10^{-6}t^2 \qquad (12)$$

The standard potentials of the silver–silver bromide electrode at 25°C. have been measured in pure methanol by Kanning and Campbell (66), using a cell of type A and thermally prepared electrodes. The values for E^0_m and E^0_c are 0.1328 and 0.1451 v., respectively. The silver bromide electrodes came to equilibrium rapidly and were constant for periods as long as 24 hr. (maximum deviation, ±0.07 mv.).

Traces of moisture in these solvents result in an increase of the electromotive force of the cell; e.g., 0.01 per cent by weight of water added to a 0.1 *m* solution of hydrogen chloride in methanol and ethanol increased the E.M.F. by about 1 mv.

Measurements for the standard potential of the silver–silver iodide electrode in non-aqueous media have not been reported. A recent compilation of the data for the silver halide electrodes in non-aqueous media is that of Conway (25). A critical presentation and discussion of the work in non-aqueous media is found in the work of Harned and Owen (52).

E. In mixed solvents

In addition to the measurements described in the previous sections on the type A cell in aqueous and non-aqueous media, a number of investigations have been made in which the hydrogen chloride was dissolved in various mixed solvents, i.e.,

$$H_2 \mid HCl(m) \text{ in solvent } (X), H_2O(Y) \mid AgCl, Ag \qquad (F)$$

where X and Y give the weight percentage of the organic liquid and water, respectively, present in the mixture. Selecting miscible solvents, this offers a method of studying medium effects on the solute as the dielectric constant varies continuously from the value of water to that of the organic liquid. The Hitchcock method of extrapolation has been used to obtain the standard potentials of the silver–silver chloride electrode in these media. However, as the dielectric constant decreases, the effect of the higher-order terms of the interionic attraction theory must be taken into account. In media of dielectric constant of 10 or greater, Harned and associates (46, 49, 50, 52) have shown that the standard potential of this type of cell may be obtained from the function:

$$E' = E + 2k \log m - \frac{2kA\sqrt{c}}{1 + \mathring{a}B\sqrt{c}} - 2k \log (1 + 0.002M_{xy}m) = E^0 + f(m) \qquad (13)$$

where E' is the apparent molal potential, E is the observed electromotive force corrected to 1 atm. of hydrogen, m is the molality of the acid, A and B are the Debye–Hückel constants, $\mathring{a}$ is the ion size parameter, C is the concentration in moles per liter, k equals $2.3026RT/F$, and M_{xy} is the mean molecular weight of

TABLE 13

The standard potential (molal) of the silver–silver chloride electrode as a function of temperature in organic solvent–water mixtures (52)

ORGANIC SOLVENT	$E^0_m = a + b(t - t_r) + c(t - t_r)^2$		
	a	$b \times 10^4$	$c \times 10^6$
Dioxane–water, t_r = 25°C. (0–50°C.)			
weight per cent			
20	−0.20303	7.605	3.70
45	−0.16352	11.35	3.70
70	−0.06395	17.67	3.70
82	−0.0413	23.70	8.80
Methanol–water, t_r = 20°C. (0–40°C.)			
10	−0.21818	55.563	4.128
20	−0.21151	52.910	4.706
Methanol–water, t_r = 25°C. (5, 25)			
43.3	−0.1941	7.262	6.594
64.0	−0.1764	9.512	1.739
84.2	−0.1319	13.241	4.303
94.2	−0.0840	14.064	5.435
Ethanol–water, t_r = 20°C. (0–40°C.)			
10	−0.21900	5.03	3.82
20	−0.21025	4.19	6.00
2-Propanol–water, t_r = 20°C. (0–40°C.)			
5	−0.22110	5.7425	3.8357
10	−0.21666	5.3324	4.7405
20	−0.20905	4.9001	6.8362
Glycerol–water, t_r = 25°C. (0–40°C.)			
10	−0.21650	6.52	3.3
30	−0.20221	6.68	3.4
50*	−0.18392	7.45	3.0

* Valid from 0° to 90°C., inclusive.

the solvent. The graphical extrapolation of this function, and the evaluation of the standard potential in solutions with dielectric constant less than 10, have been recently discussed in detail by Harned and Owen (52) and need not be developed here.

The first comprehensive series of measurements of this kind was made by Harned and associates (41, 49) for solutions of hydrogen chloride in dioxane–water. The possible range of the solvent dielectric constant was from 2.1 (dioxane) to 78.54 (water). Similar investigations have been reported for methanol–water (3, 55), ethanol–water (90), and glycerol–water (19, 50, 70, 75) over temperature

TABLE 14

The standard potential (molal) of the silver–silver chloride electrode in organic solvent–water mixtures at 25°C.

Dioxane–water (49)

Dioxane*	20.00	45	70	82
Dielectric constant, D	60.8	38.5	17.7	9.5
Standard potential, E_m^0	−0.20303	−0.16352	−0.06395	0.0413

Methanol–water (5, 55)

Methanol*	10	20	43.3	64.0	84.2	94.2
D	74.0	69.2	58.0	48.0	38.2	33.9
E_m^0	−0.21535	−0.20881	−0.1941	−0.1764	−0.1319	−0.0840

Ethanol–water (90)			2-Propanol–water		
ROH*	10	20	ROH*	5	10	20
D	72.8	67.0	D	74.9	71.4	65.7
E_m^0	−0.21442	−0.20736	E_m^0	−0.21807	−0.21383	−0.20637

Ethylene glycol–water (26)

Ethylene glycol*	5	10	15	20	30	40	60
D	76.9	75.7	74.2	72.8	69.8	66.6	59.4
E_m^0	−0.21905	−0.21635	−0.21330	−0.21020	−0.20360	−0.19720	−0.18070

Glycerol–water (50, 69, 75)

Glycerol*	3.06	10	21.2	30	50
D	77.7	75.7	72.2	70.0	64.0
E_m^0	−0.2196	−0.21650	−0.2082	−0.20221	−0.18392

* The concentration is given in weight per cent.

ranges from 0° to 90°C. The standard potentials as a function of temperature were found to fit a simple three-parameter type of equation:

$$E^0 = E^0_{t_r} + b(t - t_r) + c(t - t_r)^2 \qquad (14)$$

in each case, where $E^0_{t_r}$ is the standard potential of this electrode at the reference temperature. The results of these investigations are expressed in this manner in table 13. Except for the most recent work (26, 69), more detailed tabulations and discussions of the results of these investigations may be found in papers by Conway (25) and Harned and Owen (52).

Crockford, Knight, and Staton (26) have extended such measurements to ethylene glycol–water solutions at 25°C. These data, together with the standard

potentials (molal) at 25°C. of this electrode in aqueous solutions of dioxane, methanol, ethanol, 2-propanol, ethylene glycol, and glycerol, are listed in table 14 with the dielectric constants for these media.

In the mixed solvents, the standard electrode potentials of the silver–silver chloride electrode exhibit pronounced individual behavior in each system studied. A feature common to all systems, however, is the general behavior as the dielectric constant of the medium was decreased. In each case, the values of the standard electrode potentials also decreased. In some systems (ethanol–water, methanol–water) a very rapid decrease of E^0_m, as a function of $1/D$, was noted in the range of very low water content. It has been suggested that this rapid decrease of the standard potential takes place under conditions where the oxonium ion, H_3O^+, is being replaced by (solvent)H^+ according to the reaction:

$$H_3O^+ + (\text{solvent}) = H_2O + (\text{solvent})H^+$$

The order of magnitude of this change can be predicted by the Born equation of electrostatic theory (13), although it cannot be relied upon for accurate calculations. This subject awaits a more general theoretical treatment. For the aqueous glycerol solutions, over the region investigated (up to 50 weight per cent), Knight, Crockford, and James (69) found that E^0_m decreased linearly when plotted *versus* $1/D$, the region of rapid decrease of E^0_m apparently not yet being reached within these limits. Harned and Owen investigated the expression $(E^0_N - 0.05915 \log N_1)$ as a function of $1/D$. In this N_1, the mole-fraction of water, is used as a first approximation of the activity of the water in the solutions. The points for all the solvents (table 14) fall very nearly on the same line in this instance. Further work seems necessary to verify this interesting result, which may be of considerable importance in organizing data of this type.

Similar investigations for the silver–silver bromide and silver–silver iodide electrodes in mixed solvents have not been reported.

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