POTENTIOMETRIC ELECTRODE SYSTEMS IN NONAQUEOUS TITRIMETRY[1]

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Received July 11, 1957

CONTENTS

I. INTRODUCTION

The general field of nonaqueous titrimetry has been dealt with in monographs (8, 10, 53, 92, 146) and in the periodic reviews of Riddick (164, 165, 166). The present review, concerning the potentiometric aspects only, is extensive but not exhaustive and is further restricted by exclusion of the highly important Karl Fischer method for the determination of water.

In this rapidly advancing field the contributions of the Russian, and to a lesser extent of the Czechoslovak, workers have been somewhat overlooked.

The recently published work of Kolthoff and Bruckenstein (121) has put acid-base titrations in acetic acid on a firm theoretical basis, so that such titrations are no longer largely empirical.

II. THE CHLORANIL ELECTRODE

Commencing with the historic investigations of Conant and Hall (32, 33), use of the chloranil electrode has been confined almost completely to systems in glacial acetic acid. Hammett and Dietz (71) tried to use this electrode in the solvent formic acid but found it inferior to the quinhydrone electrode in definiteness and reproducibility.

Conant and Hall pointed out that an acid-base system similar to the water

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[1] This work was supported in part by the U. S. Atomic Energy Commission.

system exists in glacial acetic acid and succeeded in titrating numerous bases in the latter medium (32). They also studied the behavior of substances suitable for use as indicators in such solutions (33). An extensive study of the strength of organic bases in glacial acetic acid has been made by Hall (70). This solvent also proved suitable for the potentiometric titration of the basic groups in certain pyrrole and chlorophyll derivatives (31).

In 1935 Nadeau and Branchen (139) reported that, when dissolved in glacial acetic acid, amino acids act as bases strong enough to be titrated with perchloric acid. The pair *p*-toluenesulfonic acid and nitric acid can be separated by potentiometric titration in glacial acetic acid (180). The titration of weak bases and strong acids has been studied (16). The use of the chloranil electrode as a reference system in glacial acetic acid has been recommended (202).

The chloranil electrode has been used successfully for the titration of acid mixtures in dimethylformamide (117) and for the titration of weak bases in dichloroacetic acid (174). In the latter solvent, even water acts as a weak base. Acid-base equilibria in dichloroacetic acid have been studied by Prytz (160). The dissociation constants of hydrochloric and other acids and of a variety of bases have been determined in acetic acid (18).

III. THE QUINHYDRONE ELECTRODE

The potential of the quinhydrone electrode in absolute methanol has been determined by Ebert (48), who studied the dissociation constants of dibasic carboxylic acids in this solvent. The ratios of the dissociation constants of mono-, di-, and triphenylacetic acids in methanol, ethanol, and water have been measured using a concentration cell with quinhydrone–gold electrodes (114). The determination of the acidity of oils has been studied by titration in butanol (29, 50, 177) and in isoamyl alcohol (176). Ruehle (169) has shown that acetone, anisole, and dioxane can be used to enhance the solvent powers of butanol without interfering with the functioning of the quinhydrone electrode in this solvent. He also successfully employed methyl cellosolve. Izmaĭlov and his coworkers (86, 87, 90) have studied the application of the quinhydrone electrode to acid-base titrations in aqueous acetone medium. Shkodin (179) found that, in acetone or ethyl methyl ketone, sulfuric acid can be titrated in the presence of a large excess of lactic acid. Potentiometric titrations in benzene solution of trichloroacetic acid and diethylamine have been reported by LaMer and Downes (122). In their studies of acid-base indicators in benzene (123) these workers employed a cell consisting of two quinhydrone electrodes placed on either side of a gelatin-impregnated filter-paper membrane, as shown in figure 1. The square platinum electrodes proper were arranged to lie flat against either side of the membrane, the platinum connecting wires being brought out through capillary tubes I and II. Schaal (174) has titrated acetanilide in nitrobenzene solution with perchloric acid.

Hammett and Dietz (71) reported entirely satisfactory results in formic acid with the quinhydrone electrode, provided gold was used for the electrode proper. The reproducibility with platinum or gold-plated platinum electrodes was found

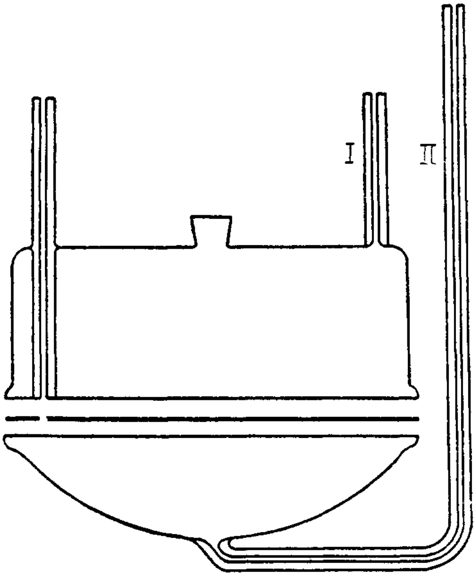


FIG. 1. Cell for potentiometric studies in benzene

to be poor. Shkodin, Izmaĭlov, and Dzyuba (181) have measured the strengths of bases such as sodium formate, pyridine, and aniline in anhydrous formic acid. The work was extended to the study of acid strengths in the same solvent (182). They showed that inorganic acids remain strong in formic acid and are not differentiated as in acetic acid, attributing this to the large difference in the dielectric constants of the solvents. Organic acids such as acetic, chloroacetic, and picric were reported to be so weak in formic acid that they could not be titrated. Acid-base titrations in this solvent have also been studied by Tomíček and Vidner (211). The potential of the quinhydrone electrode in anhydrous formic acid has been measured by Pinfold and Sebba (156), and the system has been recommended as a polarographic anode. In contrast to the results of Hammett and Dietz (71), these workers found platinum electrodes to be entirely satisfactory.

Shkodin and Izmaĭlov (180) studied the differentiating effect on the strengths of acids of anhydrous acetic acid containing some acetic anhydride. They found that the pairs perchloric acid plus sulfuric acid and perchloric acid plus hydrochloric acid could be readily separated in this medium, but found no such separation possible in water, ethanol, or acetone. The quinhydrone electrode has been used to study the response of glass electrodes in a variety of solutions in glacial acetic acid (84).

IV. THE HYDROGEN ELECTRODE

According to Izmaĭlov (82), the acidity of a nonaqueous solvent may be expressed on a universal "*PA*" scale. The relationship is

$$PA = -\log M\gamma\gamma_0$$

where M is the concentration of the solution, γ is its coefficient of activity referred to infinitely dilute solutions in the same solvent, and γ_0 is the ratio of the activity coefficient in the solvent to that in water, both at infinite dilution. The ratio γ_0 is obtained by comparing the cells:

$$H_2 \mid HCl \text{ (in the solvent)} \mid AgCl$$

and

$$H_2 \mid HCl \text{ (in } H_2O) \mid AgCl$$

The use of indicators of the nitrophenol series for the determination of pH in alcoholic solutions has been studied by means of a concentration cell involving two hydrogen electrodes (132). The dissociation constants of a series of acids and amines have been measured in ethanol and in methanol. Both platinized and palladized electrodes were used, the latter being more suitable for compounds containing the benzene ring (64, 65).

The potential of the hydrogen electrode has been determined in acetic and butyric acids in the presence of increasing quantities of sodium acetate or water (81). Kilpi (115, 116) has employed the hydrogen electrode in acetic acid medium for the determination of the dissociation constants of anthranilic acid.

In a study of acid-base titrations in anhydrous formic acid, Hammett and Dietz (71) found that hydrogen electrodes failed to agree with one another and were sluggish. On the other hand, Tomíček and Vidner (211) report that similar titrations were successfully carried out in 98–98.8 per cent formic acid.

A potentiometric study of clays in glycol has been reported (59). Examination of hydrogen chloride in pyridine solution showed that the hydrogen electrode is reversible with respect to the pyridinium ion (7).

V. THE GLASS ELECTRODE

A. Acidic solvents

The glass electrode has found extensive use in nonaqueous systems, especially for the titration of basic substances in glacial acetic acid. Examples are given in table 1. In the majority of cases perchloric acid, dissolved either in acetic acid or in dioxane (54, 151, 152, 153, 155, 183) is the titrant. Davis and Hetzer (41) investigated the use of diphenyl phosphate as a titrant in a number of solvents. However, they found that it was not strong enough to replace perchloric acid in titrations in acetic acid.

The work of Pifer and Wollish (152) made possible the potentiometric titration of the halide salts of organic bases. Mercuric acetate is added, binding the halide as the undissociated mercuric halide. This innovation has been used successfully by various other workers (2, 58, 110, 118, 178, 183).

The removal of the last traces of water from acetic acid by the addition of excess acetic anhydride considerably sharpens the end point in the titration of most tertiary amines and alkali metal salts (56). No further improvement results with the use of a very large excess of acetic anhydride. The indirect determination of α,β-unsaturated compounds has been accomplished by their reaction with

TABLE 1

Titrations with the glass electrode in glacial acetic acid

Substances Titrated	References
Acetates, inorganic (differentiation of)*	(155)
Alkyl xanthogenates	(13)
Amines and other bases (large variety)	(49, 152, 178, 192)
Amines, microtitration	(113)
Amines, tertiary, in mixtures	(220)
Aminoacetic acid	(131)
p-Aminosalicylic acid and sodium salt†	(22)
"Antadril"	(58)
Antibiotics (aureomycin, etc.)	(183)
Antihistamine bases and salts	(105, 118)
Aniline, automatic titration	(127)
Antipyrine and related substances	(5, 104, 192)
Barbituric acid, derivatives of	(103)
Bases, in tobacco smoke‡	(222)
Bases, nitrogen (relative basicity)	(167)
Bases, organic	(52, 56, 128, 170)
Basic nitrogen in oils, etc	(42, § 134, 228)
S-Benzylthiuronium derivatives of carboxylic acids	(14)
Caffeine and related compounds	(3, 107)
Carbonyl compounds, indirect	(77)
Carboxymethylcellosolve, sodium derivative	(184)
Choline salts of carboxylic acids	(129)
Cocaine hydrochloride and related compounds	(110)
Diphenhydramine and its salts	(111)
"Elvetil"	(58)
Guanidine derivatives	(41)
Halides and other inorganic salts	(128, 153)
Isonicotinic hydrazide	(4,* 106)
Morphine and related compounds	(109, 214)
Nicotinic acid and related compounds	(106, 178)
Nitrogen-bearing compounds in shale oil¶	(136)
Oxine; indirect determination of copper	(80)
Oxirane oxygen	(47)
1-Phenyl-2-aminopropane, derivatives of	(108)
Picrates of substituted amides, etc	(11, 175)
"Proguanide"	(2)
Pyrazinamide	(171)
Pyrazolones	(215, 216)
Schiff bases	(51)
Sulfonamides	(200)
Thiamine salts	(151)

* Acetic acid–chloroform mixed solvent.
† Acetic acid–carbon tetrachloride mixed solvent.
‡ Acetic acid–cyclohexane mixed solvent.
§ Acetic acid–chlorobenzene mixed solvent.
¶ Acetic acid–toluene mixed solvent.

morpholine to form tertiary amines, which may be titrated with methanolic hydrochloric acid (34). Use of nitromethane–acetic anhydride (4:1) often gives sharper end points than acetic acid–acetic anhydride, e.g., in the titration of caffeine. Chatten, Pernarowski, and Levi (28) confirmed the results obtained with caffeine and attempted a differentiating titration of caffeine and codeine in mixtures. Gremillion (67) has used acetic anhydride as a solvent for the determination of the sulfuric acid used as catalyst in esterification mixtures. He also found that this solvent permitted very sharp end points to be obtained in the titration of some weak bases, e.g., glycine, pyridine, and urea. Bergamini and Mattei

(11) have used acetic anhydride, either alone or admixed with nitromethane, as a solvent for the titration of picrates of derivatives of 4-mercaptopyridine.

Shkodin, Izmaĭlov, and Dzyuba (182), in their studies of the strengths of acids in anhydrous formic acid, compared the glass electrode and the quinhydrone electrode. Streuli (195) has recommended the use of a mixture of nitromethane and formic acid as a medium for the titration of certain bases when copolymerized with acrylonitrile.

B. Basic solvents

Tomíček and Křepelka (207) performed acid-base titrations in pyridine using a glass electrode. This work established that the glass electrode will act as an indicator in pyridine. Anastasi and her coworkers (5) used this solvent for the assay of Barbital. In their studies on the suitability of tetrabutylammonium hydroxide as a titrant for acidic substances, Cundiff and Markunas (38) investigated a number of basic solvents, including pyridine. In the differentiating titration of phenol and acetic acid in pyridine, tetrabutylammonium hydroxide gave a larger inflection than was obtained with potassium hydroxide solution (74).The same titrant also permits the titration of phenol in piperidine solution.

Although the glass electrode is insensitive in ethylenediamine medium when titrants containing sodium are used, this electrode functions satisfactorily as an indicator when potassium hydroxide or a quaternary ammonium hydroxide is the titrant. Mineral acids are not differentiated from carboxylic acids; however, this solvent does distinguish very weak acids, such as phenol, from stronger acids. Dimethylformamide is used as the solvent to differentiate all three types of acids; namely, mineral, carboxylic, and very weak acids (43). This solvent has also been used for the titration of picrates using sodium methoxide as titrant (11).

The glass electrode does not respond in liquid ammonia (76).

C. Hydroxylic solvents

Izmaĭlov and coworkers (83, 88) have calibrated glass electrodes in ethanol, both anhydrous and admixed with water. In most cases, however, completely anhydrous ethanol has not been employed (68, 85, 168, 199, 208, 229). Thiers (199) gives titration curves in 95 per cent ethanol for a large number of organic acids and bases.

The behavior of various electrode glasses in solutions containing high proportions of methanol has been investigated by Izmaĭlov and coworkers (83, 88). Thermodynamic pK_A values for a series of carboxylic acids and anilinium ions in methanol–water mixtures containing up to 95 per cent (by volume) of methanol have been reported (9). Disubstituted benzaldehydes have been determined by addition to an excess of unsymmetrical dimethylhydrazine in methanol and back titration with methanolic hydrochloric acid (189). By modifying the solvent with ethylene glycol, aliphatic and other aromatic aldehydes were determined. Methanol–benzene has been used as a solvent for the titration of weak acids (11) and for the indirect determination of metals such as nickel by the alkaline titration of excess chelating agent, e.g., dimethylglyoxime (19).

Upon the addition of a mixture of aliphatic amines to a solvent consisting of methanol and salicylaldehyde, primary amines are converted to the azomethines. These are much less basic than are secondary and tertiary amines. The latter two may then be titrated with hydrochloric acid in 2-propanol (221). By using a solvent which is essentially chloroform, 2-propanol, and a little water, Jackson extended this method to the examination of mixtures of long-chain amines (91). Hydrogen bonding in phenolic resin intermediates has been studied by titration in a benzene–2-propanol medium (193). A mixture of 2-propanol and propylene glycol has been used for the titration of sodium *p*-aminosalicylate (194).

In the titration of weak acids in 1-butanol equilibrium is rapidly attained (217, 218). Although reducing the slope of the titration curve near the equivalence point, lithium chloride may be added to increase the conductivity of the medium.

Palit found that a mixture of glycol (ethylene or propylene) with any higher alcohol, hydrocarbon, or chlorinated hydrocarbon was a suitable medium for the titration of salts of weak acids (145). These media have been used for the titration of alkaloids, amino acids, and aminophenols (40), for the titration of the acetates of calcium, zinc, lead, etc. (39), and for the examination of mixtures of aromatic amines by the salicylaldehyde technique (187). By addition of aniline and back titration of the excess in a mixture of ethylene glycol and 2-propanol, carboxylic acid anhydrides can be determined in the presence of their acids (186). This same solvent can be used for the determination of aldehydes after treatment with primary amines (188).

The solvent mixture polyethylene glycol–chloroform has been used for the assay of barbiturates (197). Garvin and Karnovsky (61) have used the solvent system 0.001 *M* potassium chloride in 99 per cent cellosolve (2-ethoxyethanol) for the microtitration of long-chain fatty acids and phosphatides.

In media containing up to 99.8 per cent hydrogen peroxide the glass electrode behaves reversibly and reproducibly (119).

D. Other solvents

Examples of the use of the glass electrode in a variety of other solvents are given in table 2. The glass electrode has been calibrated in systems containing up to 90 per cent acetone (88). In nonaqueous titrimetry the end point may be improved by addition of an excess of a solvent of low dielectric constant, e.g., chloroform. A technique for potentiometric titration in aprotic solvents has been described (154).

The titration of amines and other bases in a wide variety of solvents, such as ethyl acetate, acetonitrile, nitromethane, ethylene dichloride, benzene, and chlorobenzene, has been studied (52, 69, 113). Differentiating titrations of acid mixtures in a variety of solvents, the most promising of which was ethyl methyl ketone, have been described (74).

VI. THE ANTIMONY (ANTIMONY–ANTIMONY OXIDE) ELECTRODE

The antimony electrode has proved most useful in titrations requiring basic solvents. There are a few cases, however, where the electrode has been used in

TABLE 2

Titrations with the glass electrode in miscellaneous solvents

Solvent	Substances Titrated	Titrant	References
Acetone	Maleic acid-styrene polymer	NaOH in methanol	(60)
	Free acids in the presence of their anhydrides	Tertiary amines in acetone	(185)
	p-Aminosalicylic acid	KOH in methanol	(26)
	Organic acids, phenols, etc. (wide variety)	Tetraalkylammonium hydroxide in benzene-methanol	(55)
Acetonitrile	Amines; differentiating titration	$HClO_4$ in glacial acetic acid or dioxane	(54)
	Mineral acid mixtures; differentiating titration	Morpholine in acetonitrile	(35)
	Organic bases; coulometric titration	Generated H^+	(72, 196)
	Codeine phosphate*	$HClO_4$ in dioxane	(149)
	Salts of organic bases*	$HClO_4$ in dioxane	(25)
Chloroform	Ephedrine in nasal sprays	$HClO_4$ in glacial acetic acid	(27)
	Acetophenetidine after hydrolysis	$HClO_4$ in dioxane	(230)
	Tobacco alkaloids†	$HClO_4$ in glacial acetic acid	(37)
Isobutyl methyl ketone	Acid mixtures, resolution thereof	Tetrabutylammonium hydroxide in 2-propanol	(20)

* Acetonitrile admixed with chloroform and phenol.

† Chloroform admixed with excess benzene.

other media. The behavior of this electrode in aqueous ethanolic solutions has been investigated (89). An interesting application in a solvent mixture of ethanol and benzene is reported by Nakata and Kusaka (140). These workers determined sulfate by addition of a definite excess of barium ion, after which the mixture is evaporated almost to dryness. The residue is treated with an ethanolic solution of sodium palmitate, precipitating the excess barium ion. After removal of the precipitate and addition of benzene, the residual sodium palmitate is titrated with standard acid. Using the same solvent mixture as an eluent, the chromatography of mixed fatty acids has been followed (101). The potentiometric titration of substituted fatty acids in benzene–methanol solution has been performed with the antimony electrode (162).

The strongly basic solvent ethylenediamine has proved most valuable for the titration of phenols and other weak acids (44, 112, 130, 137, 193). Using a strip-chart recorder with a pH meter serving as an amplifier, Katz and Glenn (112) were able to obtain directly either the differential or the direct titration curves in the determination of phenols in the products of coal hydrogenation. Hydroxyanthraquinone derivatives (1) and phenolic constituents in tar distillation products (135) have been titrated in pyridine, while a solvent consisting of mixed pyridine bases has been used for the titration of derivatives of barbituric acid (75). A solvent consisting of 85 per cent pyridine and 15 per cent ethylenediamine has been recommended for the determination of phenolphthalein in chocolate preparations (45). Butylamine has been used as a solvent for the titration of phenols (57), including those present in tobacco smoke (222). The determination of isonicotinic hydrazide by acid-group titration in diethylamine as solvent has been reported (4). Nitroguanidine and related compounds (44) and phenolic groups in lignin preparations (23) have been titrated in dimethylformamide solution.

VII. THE PLATINUM ELECTRODE

The uses for the platinum electrode fall into the classes (*a*) acid-base and (*b*) oxidation-reduction. Gran and Althin (66) introduced the bright platinum electrode for the titration of phenols in ethylenediamine. The same electrode and solvent have been used for the determination of phenols in the products of coal hydrogenation (112) and for the titration of phenolic natural products (16) and of phenolic esters (63). Pretreatment of the electrode greatly affects its behavior; anodic prepolarization in dilute sulfuric acid is recommended (73). This electrode has been used for the titration of very weak acids in ethylenediamine, pyridine, and certain other solvents (74). Nitroguanidine and thiourea, which are not titratable in acetic acid, gave good results in trifluoroacetic acid when a platinum electrode was used (44). Neutralization studies in selenium oxychloride (150) and in anhydrous sulfuric acid have been reported (213). Automatic second derivative titration curves of benzoic acid in benzene–methanol and of aniline in acetic acid have been obtained with a platinum–10 per cent rhodium electrode (127). The platinum electrode (159) and the platinum–carbon electrode pair (163) have been used for the determination of acidity in oils.

Oxidation-reduction potentials of the systems cuprous–cupric chlorides and ferrous–ferric chlorides in pyridine have been measured (147). The observations were extended to other systems (e.g., cuprous–cupric bromides) in other solvents (e.g., acetonitrile) (148). Organic compounds such as phenols and naphthalene have been successfully titrated in glacial acetic acid with bromine solution, either directly or by back titration of excess bromine with arsenite (203). Sodium acetate was added as a buffer and the method was extended to the determination of unsaturation in essential and other oils (202, 203, 204) and to the titration of sulfanilamide and related compounds (46). The titrimetric applications of solutions in acetic acid of bromine, chromic acid, sodium permanganate, titanous chloride, etc. have been studied (206, 209). Tomíček has pioneered nonaqueous oxidation-reduction titrations and has reviewed his work and that of his collaborators (201). Iodine monobromide has been used for the determination of phenols, aniline, etc. (190).

By addition of excess lithium aluminum hydride and back titration with a standard benzene solution of 1-propanol, alcohols and phenols may be titrated in tetrahydrofuran. Although this is actually a redox reaction, it is closely related to acid-base systems (124). Potential chemical indicators for this titrant have also been studied (79). Lithium aluminum amides have been substituted for lithium aluminum hydride in the titration of alcohols and phenols (78).

The platinum electrode has proved successful for titration in liquid ammonia (223, 224, 225, 226).

VIII. THE SILVER ELECTRODE

Under this heading are included second-class electrodes, e.g., the silver–silver chloride electrode. In the determination of alcohols by the lithium aluminum hydride technique, a silver electrode is effective, being somewhat more stable than a platinum one (79, 124). Highly accurate argentometric titrations in absolute ethanol have been performed using a silver electrode in combination with a glass or antimony electrode (15). The titration of halogens in certain organic compounds in aqueous ethanol medium may be followed by a silver-amalgamated silver electrode system (30). The silver electrode has been used for the determination of low concentrations of chloride in systems containing 80 per cent or more of formamide (12).

Tomíček has reported that chloride, bromide, and iodide, either separately or in admixture, can be titrated in acetic acid with thallous acetate (201). The use of the silver–silver chloride electrode in anhydrous methanol, ethanol, and acetonitrile and of the silver–silver bromide electrode in methanol has been reviewed (100). Purlee and Grunwald (161) give directions for the preparation of a very satisfactory silver–silver chloride electrode for use in 95 per cent methanol solutions. The dissociation constants of some organic and inorganic chlorides in glacial acetic acid have been determined (18). In arsenious chloride solution "bases" such as tetramethylammonium chloride have been titrated with "acids" such as ferric chloride (6).

The silver–silver sulfide electrode has been used in the titration of mercaptans in gasoline with alcoholic silver nitrate (102, 125, 198). Back titration of excess mercaptan permits the indirect potentiometric titration of acrylonitrile (99). The same electrode has been used for the titration of carbonyl sulfide in petroleum gases after absorption in alcoholic monoethanolamine (21).

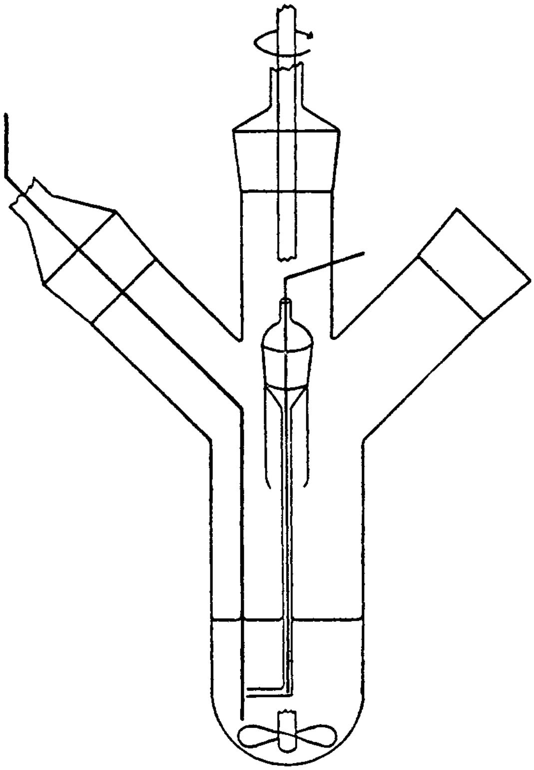
IX. OTHER PRECIOUS METAL ELECTRODES

A special type of the "retarded" electrode system, originally introduced by Müller (138), has been used by Jander and Klaus for the titration of pyridine in acetic acid (95). The titration cell, which incorporates the recommended gold electrodes, is shown diagrammatically in figure 2. It appears that gold electrodes can be used to follow acetate-ion concentration in studies in glacial acetic acid (96). The ionic product for anhydrous acetic acid has been measured (97). A gold electrode has been used for the titration of aliphatic amines in solvents such as acetic acid, acetonitrile, and alcohols (231). The gold electrode also gives reproducible potentials in molten mercuric bromide (93, 94).

Sandved and Harang (172) have employed the palladium hydride electrode in the titration of a variety of bases in ethanol or acetone. The palladium electrode appears to be satisfactory for acid-base titrations in 1-butanol (219). The behavior of the palladium electrode in nonaqueous systems is now being studied in this laboratory.

X. MISCELLANEOUS INDICATOR ELECTRODES

Tomíček has reported that chloride and bromide can be titrated in acetic acid with mercuric acetate using a mercury electrode (201, 210, 212). The mercury electrode, shown in figure 3, has been used for the titration of aniline, brucine,



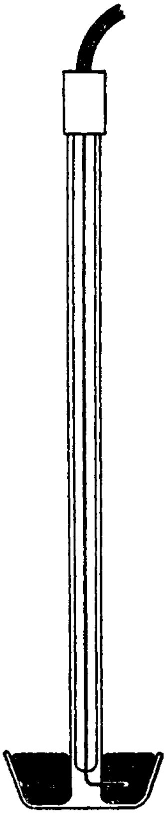
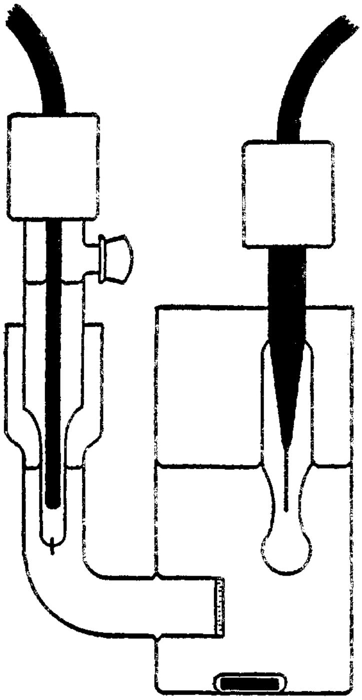


FIG. 2 (left). Gold-electrode cell for titrations in acetic acid
FIG. 3 (right). Ohlweiler and Meditsch mercury electrode

etc. in the same solvent (144). Formed on a gold wire, the mercury–mercury acetate electrode is suitable for neutralization titrations in acetic acid (173). This electrode has been used for the determination of xylocaine and stovaine hydrochloride (20). A much earlier use was in nonaqueous argentometric titrations (198).

A tellurium (or antimony) electrode in conjunction with a palladized platinum electrode is suitable for neutralization titrations in anhydrous acetic acid (205). A tellurium–graphite combination is also reported to be satisfactory (141). The tellurium electrode has also been used for the titration of benzoic acid in 1-butanol solution (219).

The molybdenum electrode has been used for titrimetric studies in thionyl chloride (191). Various other metals, such as platinum, copper, or nickel, proved unsuitable in this medium. In his classical work Jander (92) used a variety of metals, e.g., copper, tin, and silver, as electrodes for titrations in such solvents as liquid hydrogen sulfide, liquid hydrogen cyanide, and molten iodine. Virasoro (219) has briefly studied the behavior of more than twenty metals as indicators



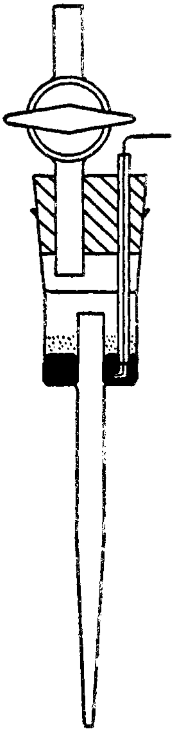


FIG. 4 (left). Warner and Haskell titration cell
FIG. 5 (right). Calomel electrode for use in ethylenediamine solutions

in 1-butanol. Novák (141, 142) has examined various combinations of elements as "bimetallic" electrode pairs for neutralization titrations in acetic acid and methanol.

XI. REFERENCE ELECTRODES

A. The saturated calomel electrode

By far the most commonly used of all the reference electrodes for nonaqueous titrimetry is the commercial saturated calomel electrode. This form of electrode incorporates its own salt bridge and, since junction with the sample is either through a ground-glass sleeve, a thin asbestos thread, or a palladium annulus, little water is introduced into the sample. In some cases the junction between the aqueous and nonaqueous phases may cause difficulties, such as irregularities in and slow stabilization of E.M.F. (120, 222). Wolff (229) employed a salt bridge of buffered acetic acid to connect the calomel electrode to the nonaqueous system. Warner and Haskell (222) used a similar method, the arrangement being shown in figure 4. In the titration of salts of organic bases in acetic acid, Pifer and Wollish (151, 152) found that the mercuric acetate added to bind the halogen anions readily contaminated the calomel electrode, causing fluctuations in voltage. This difficulty was not encountered in the titration of the salts of antihistamine bases (118). When this difficulty is found, however, Pifer and Wollish

(151, 152) recommend that the potassium chloride solution inside the electrode be replaced. In the titration of *p*-aminosalicylic acid in the mixed solvent acetic acid–carbon tetrachloride, Butler and Ramsey (22) used an agar-saturated potassium chloride salt bridge between the calomel electrode and the nonaqueous solution. This affords a larger interface than the capillary openings of a commercial calomel electrode and is claimed to eliminate erratic potentials. A calomel electrode containing sodium chloride in absolute methanol has been used as a reference in studies of dissociation constants in methanol (64). For titrations of tobacco alkaloids in a benzene–chloroform–acetic acid medium Cundiff and Markunas (37) found that more satisfactory titration curves were obtained if the aqueous potassium chloride in the calomel electrode was replaced with methanolic potassium chloride. This modification of the calomel electrode has proved useful for the titration of a wide variety of acidic compounds in a number of basic solvents (38). Fritz (55) has used this electrode for differentiating titrations of acid mixtures in acetone. For titrations in ethylenediamine, a saturated calomel electrode in which the liquid filling is ethylenediamine saturated with mercurous chloride and lithium chloride has been recommended (66) (see, for example, figure 5). With mercury–mercurous halide electrodes made up in acetonitrile or cyclohexanol, constant readings were obtained only in some cases and after long times (36). It has been found that a modified calomel electrode can be prepared in anhydrous acetic acid with a reproducibility of ±0.25 mv. (18).

An ethanolic or methanolic mercury–mercuric iodide electrode has been used as a reference in studies of dissociation constants (65).

B. Other reference systems

In his studies on electrode potentials in acetonitrile, Pleskov (157) used as a reference a silver electrode immersed in a solution of silver nitrate in this solvent. The silver–silver chloride electrode behaves reversibly in formamide (12), while the same electrode in acetonitrile saturated with silver chloride and trimethylethylammonium chloride has been used as a polarographic reference electrode (158).

To eliminate use of a salt bridge, Fritz (52) substituted a silver–silver chloride electrode immersed directly in the solution to be titrated. This modification was also reported by Ohlweiler and Meditsch (143). A much earlier use of this reference electrode was for the determination of acidity of oils by titration in 1-butanol saturated with lithium chloride (50, 177). Erratic readings have been reported in the region of the end point in acetic acid. These are eliminated by isolating the reference electrode in a separate compartment containing acetic acid saturated with potassium chloride (62, 133). For titrations with alkali methoxide, a filling of 10 per cent lithium chloride in methanol proved successful (133).

Advantage may be taken of the lack of response of the glass electrode in strongly basic solvents in the presence of sodium ion to utilize this electrode as a reference (1, 4, 21, 45, 57, 75). It has also been employed in nonaqueous argentometry (15, 125). This principle can obviously be extended for use with other indicator electrodes.

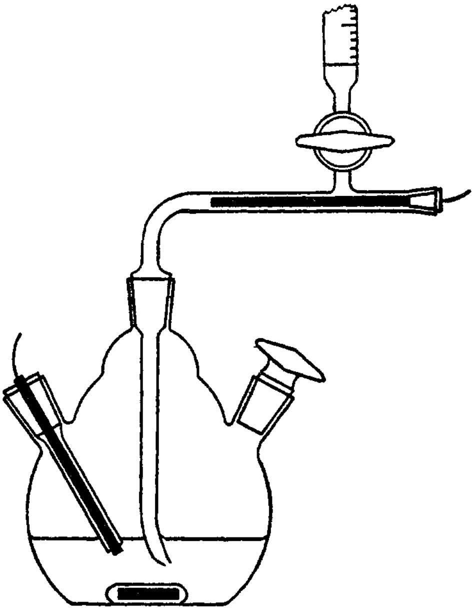


FIG. 6. Double antimony electrode system for titrations in ethylenediamine

In principle, any indicator can serve as a reference if the activity of the ion to which the electrode responds is kept constant. One method of achieving this is to insert the electrode in a small isolated portion of the solution to be titrated (138). Extensive use of this technique in nonaqueous systems has been made by Jander (92, 98). Another method is to insert the electrode in the titrant stream. This technique, first introduced for aqueous systems by Willard and Boldyreff (227), was applied by Moss, Elliott, and Hall (137) to the antimony electrode for titrations in ethylenediamine with sodium ethoxide (see figure 6). This innovation has been used by other workers (112, 130, 193). Brockmann and Meyer (17) extended this technique to the platinum electrode for titrations in benzene–methanol and ethylenediamine. This modification has also been utilized for the potentiometric titration of very weak acids in ethylenediamine and other basic solvents (73, 74).

Since it employs identical electrodes without a salt bridge, the differential electrode technique of MacInnes and Jones (126) should be valuable in nonaqueous titrimetry (117). This aspect is at present under study in this laboratory.

XII. REFERENCES

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