stance amorphous silica was probably orientated within the network structure of the polymerized silicic acid gel.

(7) Unlike the inert acidic gels the basic opalescent forms were transitory in character. On gradually altering the *p*H value of the basic form by the addition of very dilute hydrochloric acid the passage of the gel through all degrees of opalescence could be attained, culminating in the partial or complete clearing and finally in an acidic gel. Acid extracts of such triturated basic gels were found on analysis to contain traces of iron, calcium and aluminum. Although the non-availability of pure water glass prevented the reproduction of the basic opalescent bands solely by the separation of amorphous silica, it may be assumed that the opalescence of the basic silicic acid from commercial water glass represented the combined effect of amorphous silica and mineral impurities. However, no such "salting out" of silica occurred with water glass, differing in the ratio of sodium to silicon. Thus, the acid-treated gels, when dissolved in the minimum quantity of pure sodium hydroxide and then subjected to the process of rhythmic re-gelation, yielded (in addition to the acidic gels) *clear* basic gelatinous silicic acid entirely free from cloudiness. Similarly non-opalescent basic gels were obtained by redissolving the clear poly-silicic acid gel from the upper acid region. The varying cloudiness of basic gels therefore appeared to be due to the impurities present in commercial water glass, namely, metallic hydroxides, and *not* the separation of amorphous silica. This conclusion is confirmed by the milkiness of the basic gels produced by the interaction of water glass with sulfuric acid.[5]

In view of these experiments the general course of the reaction could be reconstructed as follows: The contact of the acid with the alkaline surface led to the passage of the mobile silicic acid sol to a reactive basic mono-silicic acid gel (*p*H value 8.0–11.0),[3] which rapidly disintegrated into amorphous silica and water. The cloudy mass of silica particles became orientated to form radial and concentric patterns of the membrane structure, which aggregated ultimately into bands. In the meantime the locally liberated water created conditions favorable to peptization, and this resulted (in an acid medium) in the polymerization of some of the basic gel into inert acidic gelatinous silicic acid (*p*H value below 7.0).[3] Further diffusion brought about a repetition of conditions prevailing in the formation of the first silica membrane and this was again succeeded by peptization. Thus, the interaction of the acid with water glass under conditions specific to the Liesegang phenomenon produced an alternation of an anhydrous and hydrated state, in which the silica bands were separated by acidic poly-silicic acid gel. Yet this sequence of formations was maintained only under the limited experimental conditions given earlier. Consequently increased peptization, conditioned either by the exhaustion of the acid above the interface of the two liquids or by the impermeability of the growing number of silica bands, led to the permanency of basic gelatinous mono-silicic acid below the bands. With concentrations of water glass above 25% by volume the compact silica network formed a semi-permeable membrane through which no gelatinous silicic acid (though of lower specific gravity than the medium) could pass into the upper acid region; it thus remained in the interband spaces. With 25% solutions of water glass the silica bands became sufficiently porous to allow some of the silicic acid gel to rise into the acid region, where, at 17–18°, it coalesced into a clear, refractive, elastic poly-silicic acid gel (a case of thixotropy[6]). At 11–12°, however, the degradation of the basic silicic acid gel to silica and the orientation and consolidation of the latter were retarded, with the result that the upward current of poly-silicic acid carried with it a multitude of finely divided silica particles. These, orientating within its lattice structure, imparted an opalescence to the gel. By lowering the temperature to 3–5° the reaction was still further retarded, leading to an increased proportion of the dispersed silica to be carried away in the upward current of the silicic acid gel and giving rise to the opaque colloid. The difference between the opalescence and opaque gel must be attributed to one or more of such factors as number, size and orientation of silica particles.

Summary

In the present investigation the simpler basic-silicic acid gels, differing in *p*H value (between 8.0 and 11.0) and intensity of opalescence, are automatically reproduced as a rhythmic series under the conditions of the Liesegang Phenomenon.

The synthesis of the opalescent, opaque and clear polysilicic acid gels, recorded in this paper, is significance as a possible basis for the formation of opalite and hyalite.

[6] Pauli and Valkó, *Kolloid. Z.*, **38**, 289 (1926); Freundlich, *ibid.*, **46**, 289 (1928); Hurd and Thompson, Jr., *J. Phys. Chem.*, **45**, 1263 (1941).

MANCHESTER 16, ENGLAND RECEIVED MAY 24, 1945

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Coulometric Analysis

BY JAMES J. LINGANE

Recent experiments in this Laboratory have shown that it is relatively easy to attain 100% current efficiency in the electrolytic reduction of various metal ions,[1] and certain organic compounds,[2] when the electrolysis is performed with a mercury cathode whose potential is controlled precisely These results suggested the possibility of basing an electroanalytical method on the measurement of the quantity of electricity that must be passed through an electrolysis cell to achieve quantitative reaction at one of the electrodes of the substance being determined. The experiments described in the present paper demonstrate that such a procedure is feasible, and capable of general application, when the electrolysis is carried out with a mercury cathode at controlled potential.

A similar method of "coulometric analysis" has already been described by Szebelledy and Somogyi,[3] but it differs in several important respects from the method described herein. Szebelledy and Somogyi employed an electrolysis cell with two platinum electrodes, and electrolyzed

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[1] J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **16**, 147 (1944).

[2] J. J. Lingane, C. G. Swain and M. Fields, THIS JOURNAL, **65**, 1348 (1943).

[3] L. Szebelledy and Z. Somogyi, *Z. anal. Chem.*, **112**, 313, 323, 332, 385, 391, 395, 400 (1938).

with approximately *constant current* until a suitable indicator in the solution indicated completion of the desired reaction, at which point the circuit was disconnected and the quantity of electricity passed determined by means of a silver weight coulometer in series with the cell. Although this method is capable of yielding very precise results, and is useful as a means of standardizing pure solutions, the fact that the electrode potentials are not controlled, as well as the requirement of a specific indicator to detect completion of the desired reaction, limit its application to relatively simple cases where only a single cell reaction is possible. The method described in the present paper, although inherently less exact than the Szebelledy–Somogyi method, has the advantage of being applicable to mixtures of reducible substances. In addition to its use as an analytical tool, the procedure described constitutes a valuable technique for establishing conclusively the reduction states that correspond to polarographic waves observed with the dropping mercury electrode in complicated cases where deductions from the Ilkovic equation are inadequate.

The great advantage of the mercury cathode for coulometric analyses lies in the fact that the polarographic method with the dropping mercury electrode serves as a convenient, reliable pilot technique to establish optimum conditions of cathode potential, and electrolyte composition and concentration, for a given determination. Thus the feasibility of a proposed determination can be ascertained, and the influence of various factors studied, with a minimum amount of laborious trial-and-error experimentation.[1,2]

It is not necessary for the analytical electrode reaction to be either chemically or thermodynamically reversible, provided that it is reproducible and exactly defined in a stoichiometric sense. The polarographic half-wave potential is as reliable a guide in irreversible as in reversible reductions.

To obtain a satisfactorily rapid electrolysis the potential of the mercury cathode during a coulometric determination should be controlled at a value that is at least 0.1 v. more negative than the polarographic half-wave potential of the substance concerned, but in most cases little is gained by employing a potential that is more than about 0.2 v. more negative than the half-wave potential. A difference of only 0.20 v. in the half-wave potentials usually is sufficient for the quantitative separation of two reducible substances if both undergo reversible reduction, but a larger difference may be required in irreversible reductions. In any case a polarogram of the solution will show the proper potential range.

Since oxygen is reduced at a mercury cathode, dissolved air must be displaced from the solution with an inert gas. For the same reason a platinum anode cannot be used for coulometric analyses. In solutions containing chloride ion, and no substances which form soluble complex ions with silver, a silver anode has proven to be as satisfactory for coulometric analyses as it was shown to be for simple separations.[1]

A hydrogen–oxygen volume coulometer was used in the experiments described below because it is uniquely suited to the measurement of the relatively small quantities of electricity involved, and, even more importantly, because it can be employed as a direct reading instrument to indicate continuously the progress of electrolysis.

Experimental

Electrolysis Cell.—The cell shown in Fig. 1 is quite similar to that previously described,[1] the chief differences being the use of a larger silver wire anode, and provision for removing air from the solution with a stream of nitrogen during electrolysis. The cell, which holds about 100 cc. of solution, has its top ground flat to fit flush against a thick Bakelite plate which serves as a cover. Air is removed by passing nitrogen through the inlet tube during the entire course of a determination. The nitrogen escapes via a loosely fitted glass sleeve through which the shaft of the glass stirrer passes.

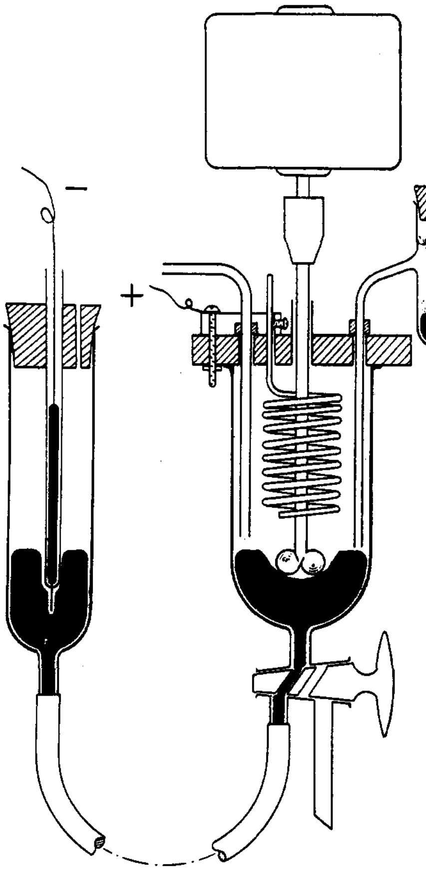

Fig. 1.—Cell for coulometric analysis.

The bridge (4 mm. tube) from the saturated calomel reference electrode is filled with a 3 to 4% agar gel in saturated potassium chloride, and its tip just touches the mercury cathode when the latter is stirred, so that the ohmic potential drop that is necessarily included in the measured cathode potential will be negligibly small.

The stationary silver anode consists of a closely wound helix of B. & S. gage no. 10 silver wire (*ca.* 2.6 mm. diam.) about 4 cm. long and 3 cm. in diameter, with a total surface of *ca.* 80 sq. cm. The solutions employed contain chloride ion, so that the reaction at the silver anode, $Ag + Cl^- = AgCl + e$, simply removes chloride ion from the solution in amount equivalent to the metal deposited in the cathode, and no foreign substances are introduced. The silver anode functions satisfactorily up to a current density of about 4 ma./sq. cm., and it can be used repeatedly for a number of determinations before the silver chloride coating becomes so thick that it must be removed. When the silver chloride coat is very thick, and the current density exceeds about 4 ma./sq. cm., chloride ion cannot penetrate rapidly enough to the silver surface to keep it depolarized, and the potential of the anode rises to the value at which oxygen is evolved. This vitiates a coulometric determination, because the evolved oxygen is reduced at the mercury cathode. Hence, the silver chloride coating should be reduced periodically by electrolysis, using either a dilute sulfuric acid solution and a platinum anode, or more conveniently by short-circuiting the silver chloride electrode with a piece of zinc in a dilute solution of zinc sulfate.

The mercury pool cathode (area *ca.* 30 sq. cm.) is stirred vigorously by a glass propellor stirrer, *immersed in the mercury-solution interface.* A smaller pair of blades near the middle of the stirrer shaft, operating inside the silver wire helix, serves to stir the solution. The importance of very efficient stirring of the mercury-solution interface has been emphasized in a previous paper,[1] which may be consulted for further details pertinent to the use of the mercury cathode.

Electrical Circuit.—The simple circuit previously used for electrolytic separations with the mercury cathode[1] can also be used for coulometric determinations. However, to eliminate the tedium of manually controlling the total applied e. m. f. in order to maintain a constant cathode potential, a device has recently been developed, and described elsewhere,[4] which performs this function automatically. With this apparatus a coulometric analysis proceeds automatically, without attention during the entire course of the electrolysis.

Hydrogen-Oxygen Coulometer.—After experimenting with a number of different designs the instrument shown in Fig. 2 proved to be most convenient. The volume of hydrogen and oxygen evolved in the electrolysis tube is measured in terms of the volume of the confining solution that is displaced into the adjoining buret. By simply choosing the proper size of buret the instrument is readily adapted to measuring diverse quantities of electricity.

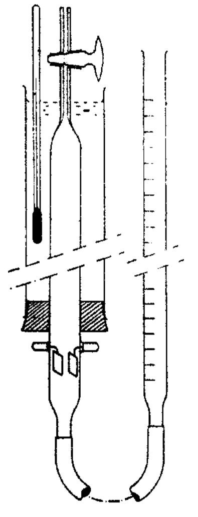

Fig. 2.—Hydrogen-oxygen coulometer.

The electrolysis tube, constructed from Pyrex glass, is about 40 cm. long and its internal diameter is about 20 mm., so that about 100 cc. of mixed hydrogen and oxygen (corresponding to about 500 coulombs) can be collected above the electrodes. To accurately define the temperature of the collected gas the electrolysis tube is surrounded by a glass mantle filled with water in which a 0.1° thermometer is suspended.

The electrodes consist of sheets of bright platinum with an area of about 1.7 sq. cm., welded to short lengths of stout platinum wire. The lead wires were welded to short lengths of tungsten wire which were covered completely with glass sleeves and then sealed through the wall of the tube. Metal caps, of the type commonly used on radio tubes, were cemented over the projecting tungsten leads. When filled with 0.5 *M* potassium sulfate the resistance of the coulometer was somewhat less than 5 ohms.

The buret is connected to the electrolysis tube by means of rubber pressure tubing (cleaned by boiling in concentrated sodium hydroxide and rinsing thoroughly with distilled water), and it is provided with an adjustable clamp so that it can be moved vertically through a distance about equal to its length to adjust the pressure of the confined gas to that of the atmosphere. The amount of solution in the instrument is adjusted so that when the buret is in its uppermost position the level in the electrolysis tube is within a centimeter or so from the exit tube.

The *modus operandi* of the instrument is fairly obvious but a few precautions should be mentioned. In the first place it is essential to saturate the confining electrolyte solution with the hydrogen-oxygen mixture immediately prior to each experiment. This is done by opening the stopcock on the exit tube and raising the buret until the level of solution in the electrolysis tube is within a centimeter or two from the exit tube. A current of 50 to 100 ma. is then passed through the instrument for at least five minutes with the stopcock open. Immediately after the current is stopped the stopcock is closed, the buret is adjusted until the two liquid levels are equal, the buret is read, and the instrument is then ready for a determination. No special aids are required in adjusting the liquid levels to equality, because it would require an inequality of about 13 mm. of the solution to change the pressure of the gas by 1 mm. of mercury.

The temperature of the water jacket should be read to ±0.1° at the start and also at the conclusion of an experiment; ordinarily the two readings will not differ by more than a few tenths of a degree. The initial volume of the gas should be small compared to the volume to be collected; under this condition a small change in temperature during the course of an experiment will not cause any appreciable error, and the final temperature may be used in correcting the volume of the collected gas to standard conditions.

To avoid error due to the change in solubility of the hydrogen-oxygen mixture with pressure, and the slow attainment of solubility equilibrium after a change in pressure, the buret should be lowered periodically as the gas collects so that the liquid levels are maintained approximately equal; *i. e.*, within about 15 cm. as long as gas evolution is vigorous and the solution is well stirred, and within 1 or 2 cm. near the end of an experiment when gas is only slowly evolved.

The barometric pressure should be read either immediately prior or subsequent to an experiment, and the reading corrected to 0°. The pressure of the hydrogen-oxygen mixture is obtained by subtracting the partial pressure of water vapor over the confining solution from the corrected barometric pressure. When either 0.5 *M* potassium or sodium sulfate is used as electrolyte, the following data are applicable.

t °C.	20	21	22	23	24	25	26	27	28	29	30
Press.$_{aq.}$, mm.	17.2	18.4	19.4	20.6	22.2	23.3	24.7	26.2	27.8	29.4	31.2

Although the hydrogen-oxygen volume coulometer has long been a familiar instrument, the only systematic study of its accuracy that the writer has found in the literature is that of Lehfeldt.[5] Since Lehfeldt's admirably precise and painstaking investigation was carried out with a much more elaborate type of instrument, based on the weighing of mercury displaced by the evolved gas, and since no study of the accuracy of the simpler type of instrument used in the present investigation appears to have been made, it was necessary to establish the accuracy of the present instrument.

The accuracy of the hydrogen-oxygen coulometer is greatly dependent on the nature and purity of the elec-

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(4) J. J. Lingane, *Ind. Eng. Chem.. Anal. Ed.*. **17**, 332 (1945).

(5) R. A. Lehfeldt. *Phil. Mag.*. [6] **15**, 614 (1908).

trolyte used. Most electrochemical texts still recommend dilute sodium or potassium hydroxide solution, although Lehfeldt demonstrated conclusively that the yield of mixed hydrogen-oxygen from these solutions is 1 to 2% smaller than the theoretical, apparently because of the formation of some hydrogen peroxide at the anode (compare Table I). Strongly alkaline solutions are also unsuitable because they foam badly. Lehfeldt has shown that results accurate to 0.1% are obtained with sodium or potassium sulfate solution, and the writer's experience verifies this conclusion. The electrolyte solution must be made up from pure materials, and be completely free of impurities, such as iron salts, which can undergo cyclic reduction and oxidation at the electrodes. It is obvious that even a relatively small amount of such a substance can cause a large negative error. Mallinckrodt "Reagent Quality" potassium sulfate, made up to 0.5 *M* in a good quality distilled water, was completely satisfactory, but it is advisable to test the performance of the coulometer with each new lot of salt used if there is any question about its purity.

The accuracy of the coulometer was tested with known quantities of electricity as follows. A precision resistance box and a rough regulating resistance were connected in series with the instrument, and a total e. m. f. of about 6 volts was applied to the circuit from two large lead storage batteries connected in parallel (total capacity about 200 ampere hours). By adjusting the regulating resistance, currents ranging from 10 to 150 ma. were obtained. The current was determined by measuring with a potentiometer the potential drop across the precision resistance (10 to 100 ohms) and applying Ohm's law. Time was measured with an electric stop-clock.

By using large lead storage batteries (about half charged for maximum stability) and allowing the apparatus to run for two or three hours before an experiment was started, the rate of decrease of current during the course of each experiment was kept quite small; in most instances it did not exceed 0.5% per hour, and frequently was considerably smaller. Each calibration was started by simply closing the stopcock on the coulometer exit tube without interrupting the current. With these precautions the decrease of current was a linear function of time, which, coupled with the fact that the decrease was relatively small, permitted a simple and accurate integration to obtain the average current. This technique is much simpler than trying to maintain an exactly constant current, and it was easily possible to determine the average current with a precision and accuracy of 0.05%, or better.

The Weston standard cell used to calibrate the potentiometer carried a Bureau of Standards certificate. The potentiometer was readable with a precision of ±0.1 mv., and the readings were believed to be accurate to at least ±0.5 mv. The precision resistance was adjusted so that the potential drop across it was between 1 and 2 volts.

The resistance box was calibrated carefully with direct current against a standard 10 ohm oil-immersed coil (Leeds and Northrup Type 4025), which carried a Leeds and Northrup Standardization Certificate. The author is indebted to Professor Grinnell Jones for the loan of this resistance standard.

The coulometer buret (50 cc.) was calibrated, and the observed gas volume was converted to standard conditions in the usual manner.

The data obtained in ten calibration runs with sodium and potassium sulfates, and six with sodium and potassium hydroxides as electrolytes, are shown in Table I, in terms of the volume of hydrogen plus oxygen per coulomb.

In agreement with the results of Lehfeldt,[5] the use of sodium or potassium hydroxide as electrolyte is seen to yield values that are about 1.2% lower, and much less concordant, than those obtained with sodium or potassium sulfate solutions.

The data obtained with either sodium or potassium sulfate as electrolyte are seen to be very concordant; the average deviation from the mean value is ±0.1%, which is about the limit of accuracy of the buret readings. Furthermore, the average value of 0.1739 cc. per coulomb at standard conditions agrees exactly with the value 0.17394 found by Lehfeldt with an entirely different type of instrument.

TABLE I

ACCURACY OF THE HYDROGEN-OXYGEN COULOMETER WITH VARIOUS ELECTROLYTES

Theoretical volume of the 2:1 hydrogen-oxygen mixture is 0.1741 cc./coulomb at 0° and 760 mm.

Electrolyte	Av. current, ma.	Time, sec.	$H_2 + O_2$, cc. S. T. P.	$H_2 + O_2$ cc. per coulomb
1 *M* Na_2SO_4	33.83	4984	29.32	0.1739
1 *M* Na_2SO_4	59.53	4243	43.96	.1740
1 *M* Na_2SO_4	69.52	2834	34.34	.1743
1 *M* Na_2SO_4	70.60	2702	33.21	.1741
1 *M* Na_2SO_4	98.81	2173	37.31	.1738
1 *M* Na_2SO_4	139.93	1579	38.35	.1736
0.5 *M* K_2SO_4	85.76	2391	35.51	.1740
0.5 *M* K_2SO_4	86.33	2251	33.58	.1736
0.5 *M* K_2SO_4	137.72	1546	37.03	.1740
0.5 *M* K_2SO_4	139.02	1325	32.02	.1738
			Av.	0.1739 ± 0.0002
2 *M* NaOH	16.18	4148	11.47	0.1710
2 *M* NaOH	49.30	2412	20.46	.1721
2 *M* NaOH	50.07	2464	21.16	.1715
3.5 *M* KOH	13.57	5724	13.25	.1706
3.5 *M* KOH	46.05	3063	24.35	.1727
3.5 *M* KOH	85.69	3051	45.46	.1739
			Av.	0.1720 ± 0.0009

From the densities of hydrogen and oxygen, 0.00008986 and 0.001429_0 g./cc. at standard conditions, the volume of the 2:1 hydrogen-oxygen mixture evolved should be 16,800 cc. per faraday at standard conditions, or 16,800/96,500 = 0.1741 cc. per coulomb, after allowance is made for the volume of water decomposed (10 cc. per faraday).[6] The average observed value with sodium or potassium sulfate as electrolyte (0.1739 cc.) is only 0.12% smaller than the theoretical value. It is evident that the hydrogen-oxygen coulometer deserves more consideration as a precise instrument than it has heretofore received.

General Technique.—The supporting electrolyte solution (*e. g.*, 50 to 90 cc.) is first placed in the electrolysis cell, and air is removed by passing a stream of nitrogen for about five minutes. The cathode mercury is then introduced by opening the stopcock in the bottom of the cell and raising the mercury reservoir. The stirrer is started and the tip of the bridge from the reference electrode is adjusted so that it just touches, or trails slightly, in the stirred mercury cathode. The coulometer, previously conditioned as described above, is connected in series with the cell, the applied e. m. f. is adjusted until the potential of the mercury cathode is 0.3 to 0.4 v. more negative than the value at which the determination is to be run, and electrolysis is allowed to proceed until the current becomes negligibly small. This preliminary electrolysis serves to remove traces of reducible impurities from the solution, and ordinarily the current decreases to 1 ma. or less after about ten minutes.

Without disconnecting the circuit, the applied e. m. f. is reduced until the cathode potential decreases to the desired value, and the coulometer buret is read. Usually the current decreases completely to zero when this adjustment is made. A known volume (*e. g.*, 10 to 50 cc.) of the solution to be analyzed is then pipetted into the cell. This produces a positive shift of the cathode potential. The applied e. m. f. is then increased until the desired cathode potential is reached, and the electrolysis is carried out with

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(6) D. A. MacInnes, "Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1939, p. 36.

either manual or automatic control, until the current decreases practically to zero (*i. e.*, to 1 ma. or less).

Results and Discussion

Results obtained in the determination of various amounts of copper from an acidic tartrate supporting electrolyte are shown in Table II. In this supporting electrolyte the polarographic half-wave potential of copper is −0.09 v. *vs.* the S. C. E.,[1,7] and the coulometric determinations were carried out with the potential of the mercury cathode at −0.24 ± 0.02 v., *i. e.*, 0.15 v. beyond the half-wave potential. The electrolyses required from forty to sixty minutes, and the final current was usually considerably smaller than 1 ma. The average error of ±0.3 mg., or ±0.009 milliequivalent, compares favorably with the accuracy of the classical electrogravimetric determination of copper.

TABLE II

COULOMETRIC DETERMINATION OF COPPER

Supporting electrolyte consisted of 0.4 *M* sodium tartrate plus 0.1 *M* sodium hydrogen tartrate plus 0.1 to 0.3 *M* sodium chloride. Mercury cathode at −0.24 ± 0.02 v. *vs.* S. C. E. Air removed from the solutions with nitrogen. Total volume of solution *ca.* 50 cc.; 1 mg. Cu = 0.5285 cc. hydrogen–oxygen at std. conditions.

Copper taken, mg.	Coulometer reading S. T. P., cc.	Copper found, mg.	Error	
			Mg.	Meq.
73.7	39.00	73.8	+0.1	+0.003
49.1	26.22	49.6	+ .5	+ .016
49.1	25.90	49.0	− .1	− .003
49.1	26.22	49.6	+ .5	+ .016
24.6	12.90	24.4	− .2	− .006
24.6	13.22	25.0	+ .4	+ .013
12.3	6.18	11.7	− .6	− .019
6.15	3.19	6.04	− .11	− .003
6.15	3.28	6.21	+ .06	+ .002
		Av.	±0.3	±0.009

Table III summarizes results obtained in the determination of bismuth. In the acidic tartrate supporting electrolyte used the half-wave potential of +3 bismuth is −0.29 v.,[1,7] and the determinations were performed with the potential of the mercury cathode at −0.35 ± 0.02 v., only 0.06 v. more negative than the half-wave potential. Although the average error of the bismuth determination in milligrams is a little more than twice as great as that in the determination of copper, the error in milliequivalents is seen to be virtually the same in the two cases.

TABLE III

COULOMETRIC DETERMINATION OF BISMUTH

Supporting electrolyte consisted of 0.4 *M* sodium tartrate plus 0.1 *M* sodium hydrogen tartrate plus 0.1 to 0.3 *M* sodium chloride. Mercury cathode at −0.35 ± 0.02 v. *vs.* S. C. E. Total volume of solution *ca.* 50 cc. and air removed with nitrogen. 1 mg. Bi = 0.2411 cc. hydrogen–oxygen at std. conditions.

Bismuth taken, mg.	Coulometer reading S. T. P., cc.	Bismuth found, mg.	Error	
			Mg.	Meq.
105.3	25.46	105.8	+0.5	+0.007
105.3	25.25	104.9	−0.4	− .006
105.3	25.12	104.2	−1.1	− .016
52.7	13.08	54.2	+1.5	+ .021
52.7	12.75	52.9	+0.2	+ .003
26.3	6.17	25.6	−0.7	− .010
13.2	3.08	12.8	−0.4	− .006
		Av.	±0.7	± .010

From the data in Tables II and III, and the results previously described,[1] it is evident that the determination of copper in the presence of bismuth, and the successive determination of the two in a mixture, should be relatively easy by the coulometric method. The same determination and separation is very difficult by classical electrogravimetric procedures.[8,9]

Table IV presents data obtained in the determination of various amounts of lead (added as lead nitrate) in 0.5 *M* potassium chloride as supporting electrolyte. The half-wave potential of lead in these solutions is −0.42 v. *vs.* the S. C. E.[1,7] and the determinations were carried out with the potential of the mercury cathode at −0.50 ± 0.02 v., only 0.08 v. beyond the half-wave potential. The results obtained are quite satisfactory, and it will be noted that the average error expressed in milliequivalents is practically identical with the average errors in the copper and bismuth determinations. From the results obtained in these three cases it appears that the coulometric method in its present stage of development yields results accurate to about ±0.01 milliequivalent, regardless of the metal being determined.

TABLE IV

COULOMETRIC DETERMINATION OF LEAD AND SEPARATION FROM CADMIUM

Supporting electrolyte consisted of 0.5 *M* potassium chloride. Air removed from solutions with nitrogen. Total volume of solution *ca.* 100 cc. Mercury cathode at −0.50 ± 0.02 v. *vs.* S. C. E. 1 mg. Pb = 0.1622 cc. of hydrogen–oxygen at standard conditions.

Lead taken, mg.	Coulometer reading S. T. P., cc.	Lead found, mg.	Error	
			Mg.	Meq.
207.2	33.80	208.4	+1.2	+0.012
207.2	33.10	204.3	−2.9	− .028
103.6	16.82	103.8	+0.2	+ .002
103.6	16.92	104.3	+ .7	+ .007
41.3	6.63	40.9	− .4	− .004
41.3	6.82	42.0	+ .7	+ .007
103.6	16.88	104.1[a]	+ .5	+ .005
41.3	6.74	41.5[b]	+ .2	+ .002
		Av.	±0.9	±0.009

[a] 50 mg. of cadmium present. [b] 135 mg. of cadmium present.

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(7) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 583 (1943).

(8) W. Böttger, "Physikalische Methoden der analytischen Chemie," Teil II, Akad. Verlagagesellschaft, Leipzig, 1936.

(9) H. J. S. Sand, "Electrochemistry and Electrochemical Analysis," Blackie and Son, Ltd., London and Glasgow, 1940.

The last two experiments in Table IV demonstrate that it is possible to determine lead in the presence of either a smaller or considerably larger amount of cadmium with the same accuracy as in its absence. The half-wave potential of cadmium in 0.5 *M* potassium chloride is −0.62 v. *vs.* the S. C. E.,[1,7] only 0.20 v. more negative than that of lead in these solutions.

Current–Time Relationship.—A typical current–time curve obtained in the determination of lead is shown by curve *a* in Fig. 3. The experimental points for this curve were obtained in three separate experiments, in each of which the solution contained 5 mM. lead ion (103.6 mg./100 cc.) in 0.5 *M* potassium chloride, and the potential of the mercury cathode was kept constant at −0.50 v. Curve *b* in Fig. 3 is a plot of the logarithm of the current against time, using the data of curve *a*, and the points are seen to fall very well on a straight line. Hence the current is an exponential function of the time and may be expressed by

$$i = i_0\,10^{-kt} \qquad (1)$$

where t is time measured from the beginning of electrolysis, and i_0 is the initial current at zero time. It is seen that the current approaches zero asymptotically, and, strictly speaking, the electrolysis will require an infinite time for completion. This relationship is the chief limitation to the accuracy of the coulometric method. Practically, however, the electrolysis is more than 99% complete after the current drops to 1% or less of its initial value, and little is gained by prolonging the electrolysis much beyond this point. In the experiments described above the time required was found to be practically independent of the concentration of metal ion being determined. With the particular cell used the initial currents ranged from about 30 to 300 ma., depending on the concentration of metal ion, and the current usually decreased to less than 1 ma. after forty to sixty minutes.

Lines *c* and *d* in Fig. 3 are log plots obtained with two other concentrations of lead ion, 41.3 and 207.2 mg./100 cc., respectively. The slopes of all three log plots are the same within the precision of the data, the average slope ($-k$ in eq. 1) being -0.037 ± 0.001 min.$^{-1}$.

From the intercepts of the log plots, it is found that the initial currents are approximately directly proportional to the concentration of lead ion. The intercepts correspond to initial currents of 56, 151, and 251 ma., or a ratio 1/2.7/4.5, compared to the ratio 1/2.5/5 of the concentrations. It follows that the current at any time must be proportional to the concentration C_t at that time, and hence the current ratio in eq. 1 may be replaced by the concentration ratio C_t/C_0, so that

$$C_t = C_0\,10^{-kt} \qquad (2)$$

From this equation the extent of reduction after any given time may be computed. For example, the time required for 99% reduction, corresponding practically to $C_0/C_t = 100$, will be equal to $2/k$ min. Since with the particular cell used $k = 0.037$ min.$^{-1}$, reduction was 99% complete after $2/0.037 = 54$ min., independent of the concentration of lead ion.

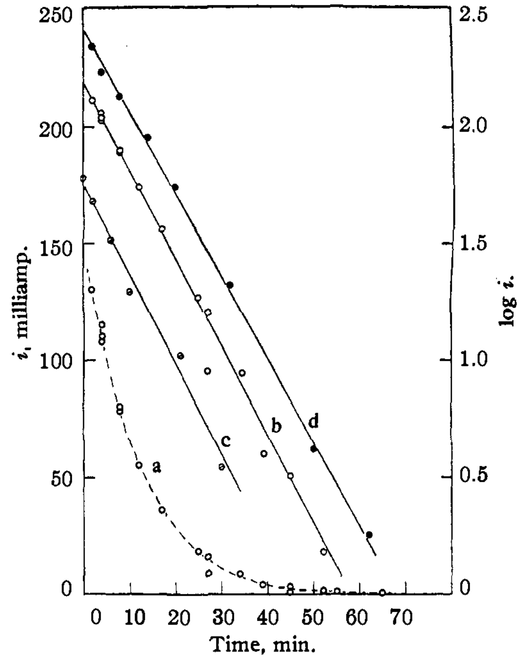

Fig. 3.—Current–time relationship during coulometric electrolyses. Curve a is the current–time curve from electrolysis of 5 millimolar lead ion in 0.5 *M* potassium chloride, and line b is the corresponding plot of log *i* *vs.* time. Lines c and d are log plots from electrolysis of 2 and 10 millimolar lead ion, respectively. Potential of the mercury cathode at −0.50 ± 0.02 v. *vs.* S. C. E. in all cases.

In experiments described below, in which picric acid was reduced, the same value of *k* was found as in the experiments with lead ion. This indicates that *k* is independent of the substance being reduced, but it doubtless does depend on the geometry of the cell, the area of the mercury cathode, the rate of stirring, the temperature, and similar factors.

Determination of Polarographic Reduction States by Coulometric Analysis.—Although the reduction states that correspond to polarographic waves observed with the dropping mercury electrode are deducible from observed diffusion current constants by means of the Ilkovic equation,[10] this procedure requires a knowledge of the diffusion coefficient of the substance concerned, which more often than not will be unknown. In simple cases, involving only a few electrons per molar unit of reduction, estimated values of diffusion coefficients can be used satisfactorily,[10] but such approximations become increasingly uncertain as *n* increases. In such cases, which are fre-

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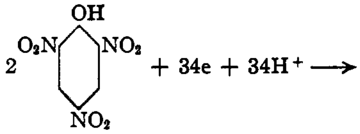
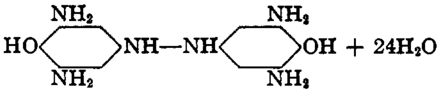
[10] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

quently encountered with organic compounds, the coulometric technique serves as a reliable method to determine reduction states.

The reduction of picric acid (2,4,6-trinitrophenol) serves as a good example. In a supporting electrolyte composed of 0.4 M potassium chloride and 0.1 M hydrochloric acid picric acid produces a rather complicated polarogram. Reduction starts almost at zero applied e. m. f., with several poorly defined stages noticeable, and the polarogram displays a prominent maximum. However, a well developed diffusion current is obtained over the range from -0.6 to about -1.5 v. *vs.* the S. C. E. The diffusion current constant $i_d/(Cm^{2/3}t^{1/6})$ was found to be 27.0 microamp./millimolar/mg.$^{2/3}$/sec.$^{1/2}$ at 25°, indicating that a relatively large number of electrons is involved in the reduction, but since the diffusion coefficient of picric acid under these conditions is not known accurately the Ilkovic equation cannot be applied with any degree of certainty.

One hundred cc. of a solution containing 0.0399 mmole. of picric acid in the same supporting electrolyte as above was subjected to coulometric analysis with the potential of the mercury cathode at -0.65 v. Complete reduction to a perfectly colorless solution was obtained after sixty-five minutes. The coulometer reading, corrected to standard conditions, was 12.70 cc., corresponding to 0.681 milliequivalents. Hence the value of n is $0.681/0.0399 = 17.07$, corresponding to 17 electrons per mole of picric acid reduced, whereas complete reduction of the three nitro groups to amino groups would require 18 electrons. Hence it is most probable that reduction under these conditions yields di-(4-hydroxy-3,5-diaminophenyl)-hydrazine as a product rather than triaminophenol, according to the equation





The foregoing simple technique is limited to irreversible reductions, because in reversible reactions the reduction product will be re-oxidized at the silver anode. To apply the coulometric technique to reversible reductions a cell must be used in which the anode and cathode compartments are separated by a diaphragm.

Summary

An electroanalytical method is described, based on the exact measurement of the quantity of electricity that must be passed through an electrolysis cell to obtain quantitative reaction at one of the electrodes of the substance being determined. The electrolysis cell comprises a thoroughly stirred mercury cathode and a silver–silver chloride anode. The electrolysis is performed at a carefully controlled cathode potential, whose optimum value is deducible from the polarographic characteristics of the substance concerned, and the quantity of electricity passed is determined with a hydrogen–oxygen coulometer in series with the cell.

Data obtained in the determination of copper, bismuth, and lead, show that the accuracy of the method compares favorably with classical electrogravimetric procedures. It is demonstrated that sharp separations of metals, such as lead and cadmium, whose reduction potentials differ by only 0.20 v., can be performed relatively easily with a mercury cathode.

Using the reduction of picric acid as an example, it is shown that the coulometric method can be applied advantageously to the determination of the reduction states that correspond to polarographic waves observed in complicated cases where the Ilkovic equation is inadequate.

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