Systematic Polarographic Metal Analysis

Characteristics of Arsenic, Antimony, Bismuth, Tin, Lead, Cadmium, Zinc, and Copper, in Various Supporting Electrolytes

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The polarographic characteristics in nine supporting electrolytes of the metals listed in the title have been studied, and complete data are presented for their half-wave potentials and diffusion current constants. The utility of diffusion current constants in practical analytical work is discussed; the use of these constants eliminates the need for calibrating each particular dropping electrode with known concentrations of the substances to be determined.

A PROGRAM has been started in this laboratory with the aim of developing systematic schemes of polarographic analysis that can be applied to the qualitative and quantitative analysis of any mixture of the commoner metallic elements. Soon after this program was initiated it became evident that its logical prosecution requires much more specific and quantitative information concerning the polarographic characteristics of the various metals than one can glean from the existing polarographic literature (*6*), and it was therefore decided to obtain such information before attempting to devise specific analytical procedures.

The present paper presents a compilation of the half-wave potentials, diffusion current constants, and other analytically pertinent characteristics of arsenic, antimony, bismuth, tin, lead, cadmium, zinc, and copper, in nine different supporting electrolytes. These metals were studied as a group because they are so commonly associated in nonferrous alloys and other commercial products, and also because, with the exception of zinc, they are usually separated as a group by hydrogen sulfide precipitation in common analytical schemes.

A simplified method of performing quantitative polarographic determinations, which eliminates the necessity of calibrating each dropping electrode with known concentrations of the substance being determined, is also described.

Experimental

A Model XI Heyrovský Polarograph, manufactured by E. H. Sargent and Co., Chicago, was used for recording polarograms according to the technique which has already been adequately described (*6*). The galvanometer of the instrument was calibrated frequently by the usual method (*6*), and with sufficient care so that the sensitivity factor was known with an accuracy of ±0.3 per cent. With the particular polarograph used the galvanometer deflection on the visual scale was 3.5 per cent larger than on the photographic paper for a given current, apparently because of a difference in the lengths of the two light paths, but both deflections were strict linear functions of the current (as required) within the limits of accuracy of the readings.

H-type cells like those described previously (*6, 13*) were used, with either a saturated calomel or mercury–mercurous sulfate reference working anode, and in all cases measurements were made with the cell in a water thermostat at 25.00° C. The importance of reasonably precise temperature control in polarographic measurements has been stressed elsewhere (*6*). Dissolved air was removed from the solutions by nitrogen which had been purified by passage over copper gauze at about 400° C.

The dropping electrode assembly was the same as that described by Lingane and Laitinen (*13*), and the capillary proper consisted of a 9-cm. length of 6-mm. outside diameter Corning "marine barometer tubing" with a uniform internal diameter of approximately 0.03 mm. The *m*-value was determined and checked daily by means of the simple volumetric instrument previously described (*10*). At the time of this writing the *m*-value of this capillary has remained constant at 2.57 ± 0.01 mg. per second at 25° C. for over eight months; this is a good example of the constant behavior that can be expected of such capillaries when they are accorded the simple maintenance care that has been recommended (*6*). The drop time was in the neighborhood of 3.5 seconds, the exact value depending on the nature of the supporting electrolyte and the potential of the dropping electrode. In all cases the exact drop time was determined at the particular potential at which the diffusion current was measured.

Stock solutions of the various metal salts were prepared from reagent quality materials, and when necessary they were standardized by the usual procedures. Particular care was taken in the preparation of the stock solutions of stannous tin to prevent the formation of stannic salt, because in some supporting electrolytes—e. g., dilute hydrochloric acid—stannic tin contributes to the diffusion current and hence its presence would lead to too high a value for the diffusion current constant of the stannous tin. A stock solution of stannous perchlorate in 1 *N* perchloric acid was prepared by dissolving pure tin in the acid solution in contach with a piece of platinized platinum wire to decrease hydrogen overvoltage; the solution was stored under a nitrogen atmosphere

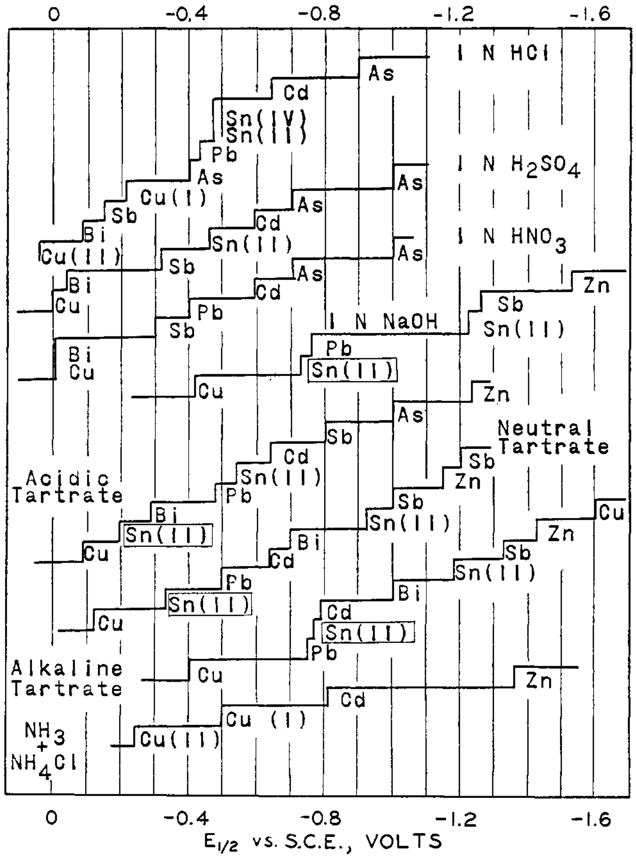

FIGURE 1. CHART OF HALF-WAVE POTENTIALS

Table I. Half-Wave Potentials

(Values listed are in volts *vs.* the saturated calomel electrode at 25° C. 0.01% gelatin is present in all cases.)

Supporting Electrolyte	As	Bi	Sb	Sn(II)	Sn(IV)	Pb	Cd	Zn	Cu
0.1 *N* KCl	...	Insoluble	Insoluble	Insoluble	Insoluble	−0.40	−0.60	−1.00	+0.04
1 *N* HCl	−0.4 −0.9	−0.09	−0.15	−0.47	−0.47	−0.43	−0.64	[a]	+0.04 −0.22
1 *N* H_2SO_4	−0.7 −1.0	−0.04	−0.32	−0.46	Insoluble	Insoluble	−0.59	[a]	−0.00
1 *N* HNO_3	−0.7 −1.0	−0.01	−0.30	−0.44	Insoluble	−0.40	−0.59	[a]	−0.01
1 *N* NaOH	N. R.[b]	Insoluble	−1.26	−0.73[c] −1.22	N. R.[b]	−0.76	Insoluble	−1.53	−0.42
Acidic tartrate	−1.0	−0.29	−0.8	−0.20[c] −0.54	N. R.[b]	−0.48	−0.64	−1.23	−0.09
0.5 *M* sodium tartrate	N. R.[b]	−0.7	−1.0 −1.2	−0.33[c] −0.92	N. R.[b]	−0.50	−0.64	−1.15	−0.12
Alkaline tartrate	N. R.[b]	−1.0	−1.32	−0.77[c] −1.18	N. R.[b]	−0.75	−0.79	−1.42	−0.4[d] −1.6
1 *N* NH_4Cl + 1 *M* NH_3	...	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	−0.81	−1.36	−0.24 −0.50

[a] Wave masked by final current increase.
[b] Not reduced at the dropping electrode.
[c] Anodic wave.
[d] See note under copper.

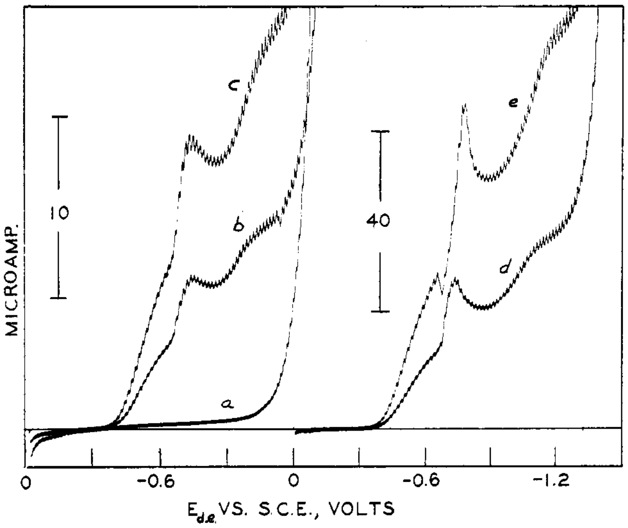

Figure 2. Polarograms of Arsenious Acid in 1 *N* Hydrochloric Acid in the Presence of 0.01 Per Cent Gelatin

Concentrations of As_2O_3: (*a*) 0, (*b*) 0.196, (*c*) 0.385, (*d*) 0.742, and (*e*) 1.53 millimolar

in contact with excess metallic tin, and it was standardized by titration against a ceric solution at each time of use by the procedure already described (*11*). In all cases the concentrations were known with an accuracy of ±0.3 per cent or better.

The supporting electrolyte solutions were also prepared from reagent quality materials, and in each case the purity of the solution was checked by running a residual current curve. The concentrations of the components of the supporting electrolytes were known to within ±10 per cent, which is a sufficiently rigorous tolerance as long as the concentration is large compared to that of the substance being determined.

The compositions of most of the supporting electrolytes are clearly shown in Tables I and II. The "acidic tartrate" solution (pH = *ca.* 4.5) comprised 0.4 *M* sodium tartrate and 0.1 *M* sodium hydrogen tartrate, and the "alkaline tartrate" solution (pH = *ca.* 13.0) was composed of 0.5 *M* sodium tartrate and 0.1 *N* sodium hydroxide.

Gelatin, at a concentration of 0.01 per cent, was present in all cases as a maximum suppressor. A 0.2 per cent stock solution was used, and it was preserved effectively against mold growth and bacterial decomposition by addition of a few drops of toluene per 100 cc.

The residual current of each supporting electrolyte was determined and proper correction for it was applied in evaluating the diffusion currents (*6*).

Half-Wave Potentials and General Wave Characteristics

Table I contains a summary of the half-wave potential data that have been gathered in this study, the values being referred to the saturated calomel electrode at 25° C. The theoretical significance and practical utility for purposes of qualitative analysis of data of this kind have been discussed in detail elsewhere (*6*, *9*).

The half-wave potential data of Table I are represented graphically in Figure 1, which is styled in accordance with V. Majer's "polarographic spectrum" (*8*). This chart will be found more convenient than a tabular listing of data for purposes of orientation in planning analytical procedures. For example, suppose an alloy of antimony and lead is to be analyzed. A glance at Figure 1 shows that sodium hydroxide or alkaline tartrate would be the most suitable supporting electrolytes if antimony predominates, because in these media the lead wave precedes that of the antimony, but if lead predominates a hydrochloric acid medium should be used, so that the antimony wave will precede that of the lead.

The characteristics of the waves that are of analytical importance are discussed in the following paragraphs. These brief remarks are limited chiefly to new facts discovered in this investigation, and will serve to supplement previous descriptions (*6*).

Arsenic. When present in the +5 state arsenic is not reduced at the dropping electrode under any conditions that have been tried to date.

Bayerle (*2*), Kacirkova (*5*), and Bambach (*1*) have shown that +3 arsenic produces complicated polarograms from strongly acid media. Some typical polarograms of arsenious

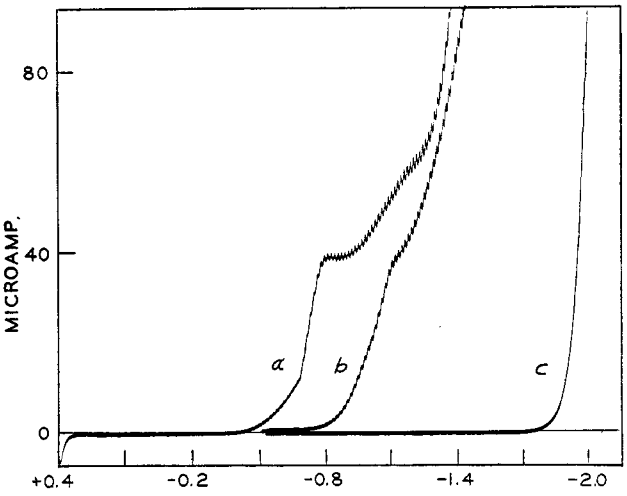

Figure 3. Polarograms of Arsenic

In (*a*) 1 *N* sulfuric acid, (*b*) 0.4 *M* sodium tartrate plus 0.1 *M* sodium hydrogen tartrate (pH = 4.5), and (*c*) 1 *N* sodium hydroxide. Concentration of +3 arsenic was 2.00 millimolar in each case, and 0.01% gel was present as a maximum suppressor.

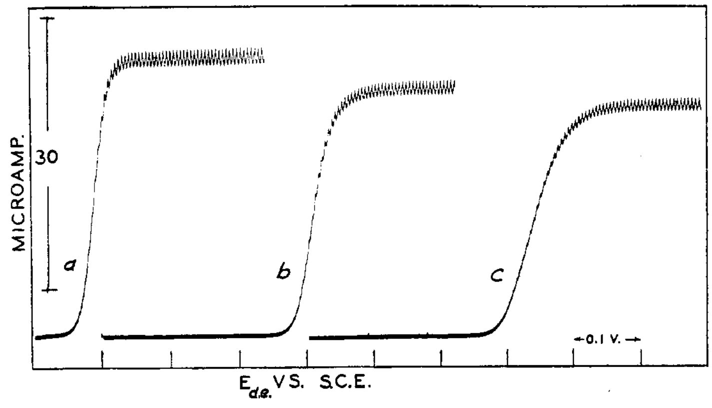

FIGURE 4. POLAROGRAMS OF 2.52 MILLIMOLAR BISMUTH

In (a) 1 *N* hydrochloric acid, (b) 1 *N* nitric acid, and (c) 1 *N* sulfuric acid, in the presence of 0.01% gelatin. Curve *a* starts at 0 volt, and curves *b* and *c* start at +0.3 volt; each voltage mark corresponds to 0.1 volt.

acid obtained with 1 *N* hydrochloric acid as supporting electrolyte, and in the presence of 0.01 per cent gelatin, are shown in Figure 2.

The arsenic wave is seen to consist of two main parts with some semblance of a diffusion current plateau at −0.8 to −0.9 volt. The wave height at −0.8 volt is directly proportional to the concentration of arsenious acid, and the diffusion current constant, $i_d/(Cm^{2/3}t^{1/6})$, is equal to 8.6 at 25° C. This value is almost twice as large as the corresponding values for antimony and bismuth (compare Table II), but since it is to be expected that the diffusion coefficient of the uncharged arsenious acid molecule will be larger than the diffusion coefficients of the chloro complex ions of antimony and bismuth, it seems reasonable to conclude that this wave corresponds to reduction of arsenious acid to the elemental state rather than to arsine. The poorly defined wave that starts at about −0.9 volt is probably due to reduction to arsine, as Kacirkova concluded; the height of the wave indicates that this reduction does not proceed completely.

Curve *a* in Figure 3 is a typical polarogram of arsenious acid in 0.5 *M* sulfuric acid, and its character is similar to that obtained from hydrochloric acid. The development of the diffusion current is somewhat better than in hydrochloric acid, and it is linearly proportional to the concentration of arsenic. The wave obtained with 1 *N* nitric acid as a supporting electrolyte is virtually identical in all respects with that obtained from dilute sulfuric acid. The data in Table II indicate that the diffusion current constants in 1 *N* sulfuric and nitric acids are practically identical with that in 1 *N* hydrochloric acid.

Curve *c* in Figure 3 demonstrates that arsenite ion in 1 *N* sodium hydroxide is not reduced at the dropping electrode.

Arsenite ion is not reduced from neutral or alkaline tartrate media, but a poorly developed wave is produced from an acidic tartrate supporting electrolyte, as shown by curve *b* in Figure 3. It is obvious that this wave is not suitable for analytical purposes.

BISMUTH. In agreement with the results of Bayerle (*2*), Kacirkova (*5*), and Page and Robinson (*15*), the author found that the +3 bismuth wave is excellently defined in 1 *N* hydrochloric, nitric, or sulfuric acids, in the presence of 0.01 per cent gelatin as a maximum suppressor, as shown in Figure 4.

In 1 *N* hydrochloric acid $E_{3/4} - E_{1/4}$ was found to be 0.022 volt, compared to the theoretical value 0.019 volt (*6*). In 1 *N* nitric acid $E_{3/4} - E_{1/4}$ was equal to 0.026 volt, and in 1 *N* sulfuric acid it was equal to 0.050 volt. It follows from these data that the reduction of $BiCl_4^-$ from 1 *N* hydrochloric acid proceeds reversibly, but the reduction of BiO^+ from nitric or sulfuric acids is somewhat irreversible. However, all three supporting electrolytes are suitable for the determination of bismuth alone. In agreement with the conclusions of Page and Robinson (*15*) it was found that 1 *N* sulfuric acid is the best of these three supporting electrolytes for determination of bismuth in the presence of antimony (compare half-wave potential data in Table I).

Typical bismuth waves in acidic, neutral (pH = 8.8), and alkaline tartrate media are shown in Figure 5.

The bismuth wave is well developed only in an acidic tartrate medium (pH smaller than about 7), and in neutral or alkaline media (curves *b* and *c*) the waves are practically useless for quantitative purposes. Suchy (*17*) has stressed the use of a "neutral" tartrate supporting electrolyte, but since he added solutions of bismuth nitrate, which must have contained some free nitric acid, to a sodium tartrate solution, the solutions that he investigated must have actually had a pH value considerably smaller than that of a pure sodium tartrate solution. In the present experiments with "neutral tartrate" media the solutions were neutralized with sodium hydroxide to the pH of pure 0.5 *M* sodium tartrate (8.8 to 9.0) after the bismuth solution was added.

ANTIMONY. Antimony in the +5 state, like the corresponding compounds of arsenic, is not reduced at the dropping electrode from any of the supporting electrolytes so far studied.

Typical polarograms of +3 antimony in 1 *N* hydrochloric and 1 *N* nitric acids are shown in Figure 6 (see also Page and Robinson, *15*). Both media are suitable for the determination of antimony in the absence of interfering substances, and except for the peculiar irregularity near the top of the wave in hydrochloric acid, the wave forms are normal with excellent diffusion current plateaus.

The occurrence of the irregularity near the top of the wave (curve *a*, Figure 6) is dependent on the concentration of gelatin, and it disappears when the concentration of gelatin is increased above 0.01 per cent. It is significant that this irregularity was not observed by Page and Robinson (*15*), who used 0.1 per cent gelatin as a maximum suppressor.

The steep slope of the wave in 1 *N* hydrochloric acid corresponds closely to a reversible 3-electron reduction (probably of $SbCl_4^-$), but the smaller wave slopes in nitric acid (and in sulfuric acid) indicate that the reduction of SbO^+ is not perfectly reversible at the dropping electrode. Hydrochloric acid should be a

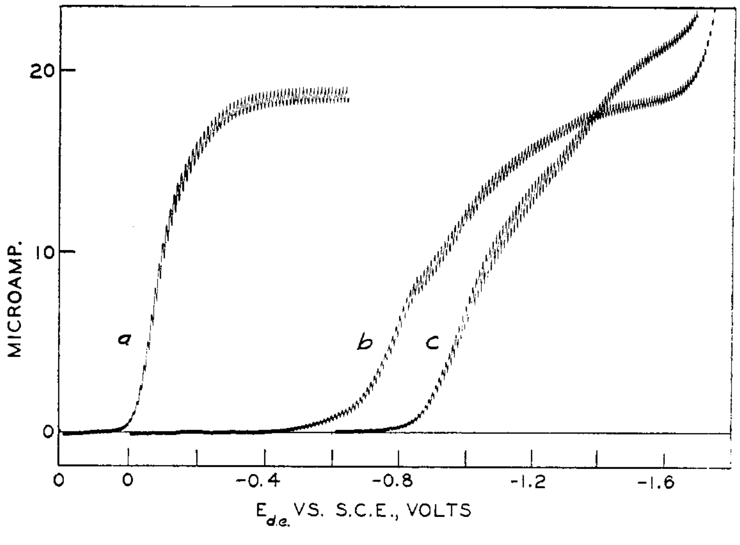

FIGURE 5. POLAROGRAMS OF 2.52 MILLIMOLAR BISMUTH

In (a) 0.4 *M* sodium tartrate plus 0.1 *M* sodium hydrogen tartrate (pH = 4.5), (b) 0.5 *M* sodium tartrate (pH = 8.8), and (c) 0.5 *M* sodium tartrate plus 0.1 *N* sodium hydroxide, in the presence of 0.01% gelatin.

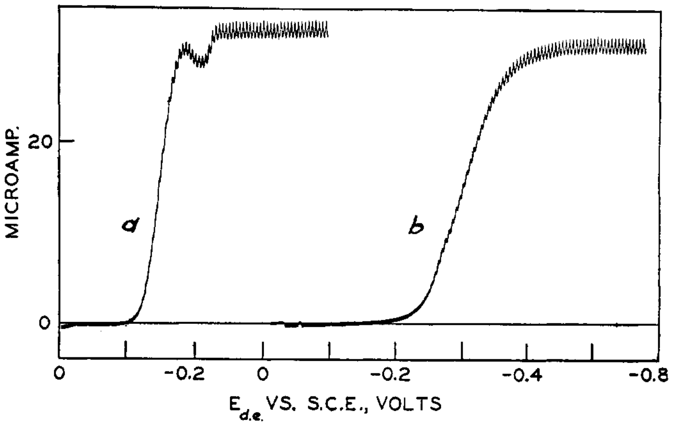

Figure 6. Polarograms of 2.50 Millimolar +3 Antimony
In (a) 1 N hydrochloric acid and (b) 1 N nitric acid, in the presence of 0.01% gelatin

useful supporting electrolyte for determining antimony in the presence of lead—e. g., in battery plate and other antimonial lead alloys—provided, of course, that interfering elements are either absent or have been removed. Page and Robinson (*15*) have shown that a hydrochloric acid medium is very suitable for determining antimony in various organic antimonial medicinals.

Polarograms of +3 antimony in 1 N sulfuric acid and 1 N sodium hydroxide are shown in Figure 7; the wave forms and diffusion currents in both media are very satisfactory.

The second small wave at −1.0 volt in 1 N sulfuric acid (curve *a*) may be due to partial reduction of the antimony to stibine; the smallness of this wave indicates that this reduction does not take place completely, and its presence precludes the determination in the presence of antimony of other metals whose half-wave potentials in dilute sulfuric acid are more negative than about −0.8 volt.

The polarograms of antimony in tartrate media of various pH values, shown in Figure 8, demonstrate that only in an alkaline tartrate supporting electrolyte containing excess hydroxide ion is the diffusion current sufficiently well defined to be used for exact quantitative purposes (curve *d*), although the wave in acidic tartrate medium (curve *c*) may be useful for semiquantitative work when other conditions preclude the use of an alkaline tartrate solution. The wave in neutral sodium tartrate solution in the absence of gelatin (curve *a*, pH about 9) is seen to comprise three distinct parts. Since reduction to oxidation states between +3 and the metal is highly improbable, this triple wave probably corresponds to the existence of the +3 antimony in three different ionic and/or molecular states in a sodium tartrate solution, with the antimonyl tartrate ion predominating.

Stannous Tin. Excellently defined waves are obtained with 1 N hydrochloric acid, 1 N nitric acid, or 1 N sulfuric acid as supporting electrolyte when 0.01 per cent gelatin is present as a maximum suppressor, and as far as polarographic characteristics alone are concerned, all three media are equally suitable for the determination of stannous tin. In 1 N hydrochloric acid an indication of an anodic wave, corresponding to the oxidation of tetrachlorostannite ion to hexachlorostannate ion, was observed at about −0.1 volt *vs.* the saturated calomel electrode, but the wave was too poorly developed to be of any analytical use.

Smrz (*16*) claimed that stannite ion in 1 N sodium hydroxide produced two cathodic waves at about −1.2 and −1.55 volts, and that when a stannite solution was allowed to stand, the height of the first wave increased while that of the second decreased. He concluded that the first wave at −1.2 volts was due to the reduction of stannate ion produced by the slow disproportionation of stannite ion, but this conclusion is erroneous because stannate ion is not reduced at the dropping electrode (see below). The author's experience is considerably at variance with Smrz' results in other respects.

The polarogram of stannite ion in 1 N sodium hydroxide comprises a very well developed anodic wave at −0.73 volt, and only a single cathodic wave at −1.22 volts, as shown in Figure 9. The cathodic and anodic diffusion currents are exactly equal, and it is evident that the cathodic wave results from the reduction of stannite ion to the metallic state and the anodic wave corresponds to oxidation of stannite ion to stannate ion. The polarograms in Figure 9, and several others that have been obtained, show no indication of the second cathodic wave at −1.55 volts that Smrz reported. From the fact that the anodic half-wave potential is −0.73 volt, whereas the reversible potential of the stannite-stannate couple is −1.21 volts *vs.* the S. C. E., it is clear that the oxidation of stannite ion proceeds irreversibly at the dropping electrode. The cathodic half-wave potential is several tenths of a volt more negative than one would predict from the reversible potential of the stannite-tin couple and a reasonable estimate of the free energy of formation of tin amalgam, from which it must be concluded that the reduction of stannite ion also takes place irreversibly. This irreversibility of the electrode reactions is of no importance in practical analytical work, since the diffusion currents are so well defined.

Stannite ion in 1 N sodium hydroxide is unstable to the extent of about 7.7 kcal. per mole with respect to disproportionation into stannate ion and metallic tin (*8*), and therefore when it is used as a determining form of tin the solution must be freshly prepared and protected carefully from air oxidation. However the author observed no change in any of the characteristics of the stannite wave after a solution stood for one hour protected from atmospheric oxygen, and hence with pure solutions the disproportionation evidently takes place slowly. This may not be true with impure solutions, or in the presence of metallic tin.

The polarogram of stannite ion in sodium hydroxide medium is very similar to that of stannous tin in an alkaline tartrate solution (*11*), and the cathodic and anodic half-wave potentials in the two media are almost identical (compare Table I). Furthermore, inspection of the data in Table II shows that the diffusion current constant in an alkaline tartrate solution (2.86) is about midway

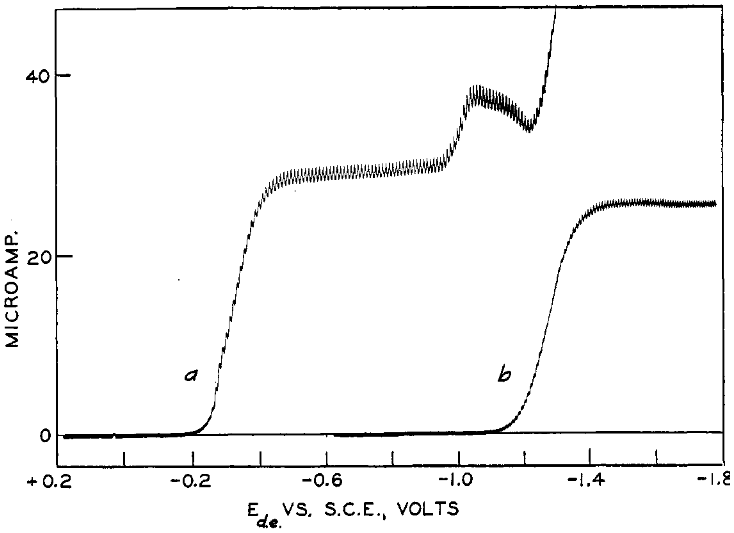

Figure 7. Polarograms of 2.50 Millimolar +3 Antimony
In (a) 1 N sulfuric acid and (b) 1 N sodium hydroxide, in the presence of 0.01% gelatin

between the value in an acidic tartrate solution (2.41) and that of stannite ion (3.45). It may be concluded that a considerable proportion, although not all, of the stannous tin in an alkaline tartrate solution actually exists as stannite ion.

The characteristics of the stannous waves in various tartrate media have been discussed in a previous paper (*1*).

STANNIC TIN. Curve *a* in Figure 10 is a typical polarogram of stannic tin in 1 *N* hydrochloric acid; the character of the wave leaves much to be desired. Since the limiting current is not well developed, but increases uniformly with increasing negative potential, the wave cannot be recommended for exact quantitative work.

The small pre-wave starting at about −0.05 volt, whose height does not correspond to any integral electron requirement, indicates that in addition to the predominating $SnCl_6^{--}$ ion the solution also contains stannic tin in another form that is more easily reducible. Furthermore, the fact that two separate waves are obtained shows that the equilibrium between the two species is established very slowly. In view of the well-known tendency of stannic chloride solutions to hydrolyze slowly, even in the presence of a relatively high concentration of hydrogen ion, it is likely that the more easily reducible species is a hydrolysis product of some sort. The half-wave potential of the main stannic wave in a hydrochloric acid medium is identical with that of the stannous wave (compare Table I).

Stannic tin in either 1 *N* sulfuric or nitric acids is too greatly hydrolyzed, with the precipitation of basic salts, to permit the use of these media as supporting electrolytes.

Stannic tin is not reduced from its solutions in sodium hydroxide (curve *b*, Figure 10), nor from any of the three tartrate solutions. Although this is rather disappointing from the standpoint of determining tin itself, it will probably prove to be advantageous in connection with the determination of other metals, such as antimony, bismuth, or lead, in the presence of stannic tin.

LEAD. The lead waves from 0.1 *N* potassium chloride, 1 *N* hydrochloric or nitric acids, and 1 *N* sodium hydroxide are very well developed with excellently defined diffusion currents. All these media can be recommended for the determination of lead.

Normal well developed waves are also obtained from the various tartrate media, except that in an alkaline tartrate solution the wave requires a fairly great voltage span (*ca.* 0.4 volt) for full development of the diffusion current.

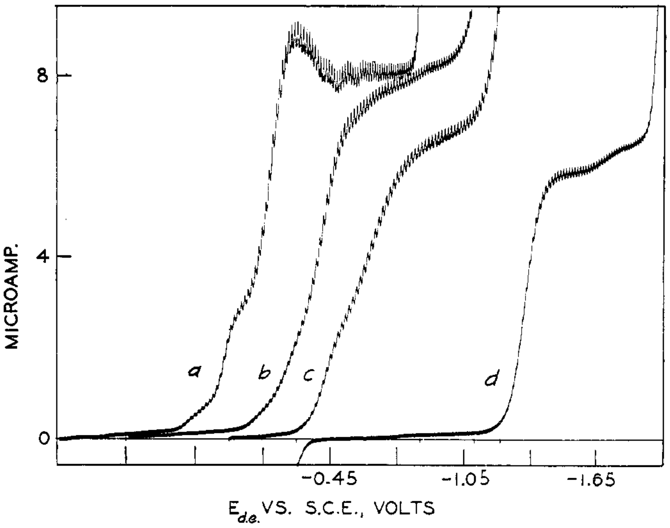

FIGURE 8. ANTIMONY IN TARTRATE MEDIA

a. 0.91 millimolar potassium antimonyl tartrate in 0.5 *M* sodium tartrate. *b.* Like *a* except 0.01% gelatin present. *c.* 0.86 millimolar potassium antimonyl tartrate in 0.4 *M* sodium tartrate plus 0.1 *M* sodium hydrogen tartrate plus 0.01% gelatin. *d.* 0.71 millimolar potassium antimonyl tartrate in 0.5 *M* sodium tartrate plus 0.1 *N* sodium hydroxide plus 0.01% gelatin. Each curve starts at −0.3 volt.

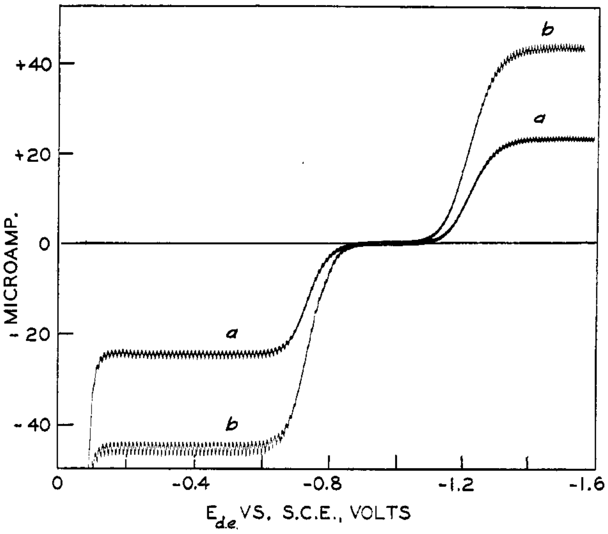

FIGURE 9. POLAROGRAMS OF STANNITE ION

In 1 *N* sodium hydroxide in the presence of 0.01% gelatin. Concentrations of tin: (*a*) 3.04, (*b*) 5.59 millimolar.

CADMIUM. With either 1 *N* hydrochloric or nitric acid as supporting electrolyte the cadmium wave is excellently defined and both media are suitable for quantitative purposes.

The wave obtained from 1 *N* sulfuric acid can be recommended only for qualitative or rough quantitative measurements because the diffusion current does not reach a perfectly constant value, but increases gradually with increasing negative potential up to the potential of hydrogen discharge. It may be possible to obtain a better diffusion current in a more dilute sulfuric acid solution, but this has not been investigated.

With either an acidic or neutral tartrate supporting electrolyte the wave form is entirely normal with a very good diffusion current plateau, and both media can be recommended for the quantitative determination of cadmium.

On the other hand, an alkaline tartrate supporting electrolyte is not suitable for the determination of cadmium. In such a medium the wave itself is well enough defined, but the limiting current is abnormally small and it is not directly proportional to the concentration of cadmium. For example, in a typical series of experiments the quantity $i_d/(Cm^{2/3}t^{1/6})$ decreased from 1.36 to 0.33 when the cadmium concentration was increased from 1 to 18.6 millimolar. These data show that the limiting current is not diffusion controlled, and hence it has little analytical value.

The wave obtained from an ammoniacal supporting electrolyte is normal in all respects with an excellent diffusion current plateau.

ZINC. Zinc cannot be determined in the presence of a large concentration of hydrogen ion, because the wave is masked by hydrogen evolution.

The reduction of zincate ion from 1 *N* sodium hydroxide produces a well developed wave; the diffusion current is reached just before the discharge of sodium ion.

Well defined waves are also obtained from neutral or alkaline tartrate media. The voltage span of these waves is rather large (*ca.* 0.4 volt), from which it is evident that the reduction of the tartrate zinc complexes is not thermodynamically reversible, but in both cases a satisfactory diffusion current plateau

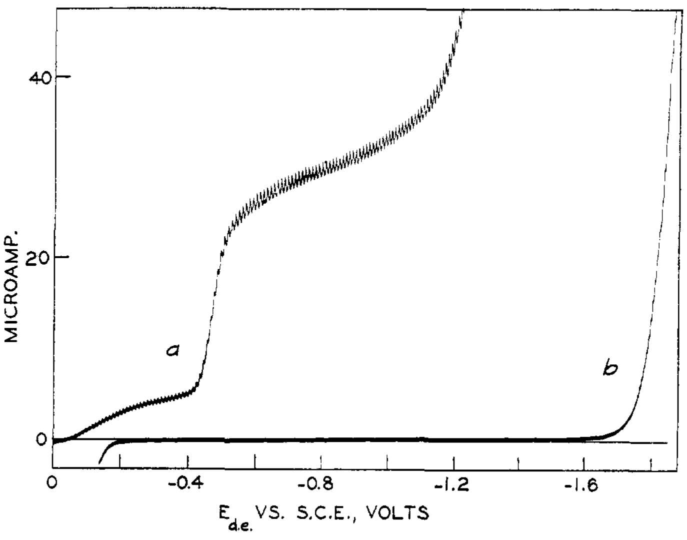

FIGURE 10. POLAROGRAMS OF 2.60 MILLIMOLAR STANNIC CHLORIDE

In (*a*) 1 *N* hydrochloric acid and (*b*) 1 *N* sodium hydroxide, in the presence of 0.01% gelatin

is developed. A distinct wave is also produced in an acidic tartrate medium, but the diffusion current is masked by hydrogen discharge and the wave can be used only for qualitative purposes.

The wave of the tetramminozinc ion from an ammoniacal supporting electrolyte is beautifully developed, and its slope corresponds closely to the value expected for a reversible 2-electron reduction.

COPPER. Typical polarograms of cupric copper in 1 *N* hydrochloric, nitric, and sulfuric acids are shown in Figure 11.

The double wave in a concentrated chloride solution is similar to the characteristic double wave produced in the presence of ammonia, pyridine, and other substances that stabilize the +1 state of copper by complex formation (*6*, *9*). In 1 *N* hydrochloric acid the first wave results from reduction of the +2 copper (probably present as $CuCl_4^{--}$) to the dichlorocuprite ion, $CuCl_2^-$, and the second wave corresponds to further reduction of the dichlorocuprite ion to the metal. The exact half-wave potential of the first stage of the reduction in 1 *N* hydrochloric acid cannot be accurately measured, since it is more positive than the anodic dissolution potential (calomel electrode potential) of mercury, and the wave starts from zero applied e. m. f. From the instability constant of $CuCl_2^-$ (2.9×10^{-6}) quoted by Latimer (*8*) and the standard potential of the cuprous ion–copper amalgam couple (+0.144 volt *vs.* the S. C. E.), and by relations that have already been described (*6*, *9*), the half-wave potential of the second wave should be −0.183 volt *vs.* the S. C. E. for the reversible reduction of $CuCl_2^-$. The observed value (−0.22 volt) agrees sufficiently closely with the theoretical value to indicate that the reduction is reversible at the dropping electrode. From the character of the first wave, and also from a visible amalgam formation, it is evident that +2 copper is reduced by mercury in 1 *N* hydrochloric acid, and hence a separate anode, rather than a quiet pool of mercury as anode, should be used in practical analytical work in order to minimize contact of the solution with mercury. It is usually most convenient to measure the total height of the double wave.

In both 1 *N* nitric and 1 *N* sulfuric acids the reduction of +2 copper produces only a single wave, the reduction proceeding directly to the metallic state. The wave form in 1 *N* nitric acid is normal (curve *b*, Figure 11), but in 1 *N* sulfuric acid a peculiar semblance of a minimum is noted in the diffusion current (curve *c*, Figure 11) and this is followed by a gradually increasing current. Therefore, 1 *N* sulfuric acid cannot be recommended for the quantitative determination of copper, except when it is present at very small concentrations, nor for the determination in the presence of copper of more difficultly reducible substances.

In 1 *N* sodium hydroxide the +2 copper wave is perfectly normal and the diffusion current is very well defined. However, since the solubility of cupric hydroxide in 1 *N* hydroxide ion is small (*ca.* 0.001 *M*), sodium hydroxide possesses only limited usefulness as a supporting electrolyte for the determination of copper in practical analytical work.

The characteristics of the cupric wave in tartrate media have been discussed in a previous paper (*11*). The waves from acidic or neutral tartrate solutions are excellently developed. In an alkaline tartrate solution a small "pre-wave" occurs at about −0.4 volt, and the diffusion current of the main wave at −1.6 volts is masked by the final increase in current from the reduction of sodium ion. It may be possible to eliminate the pre-wave by employing a more alkaline tartrate solution than that used in this study; if this is successful, it will provide a more convenient means than a prior chemical separation of eliminating the interference of copper in the determination of other metals in copper-base alloys.

Diffusion Current Constants and Their Application to Practical Analyses

An ideal polarographic procedure would permit the determination of a substance from a single polarogram, or even from a single measured value of the diffusion current, without the necessity of calibrating the particular dropping electrode that is used with known concentrations of the substance in question. In addition to placing polarographic analysis on a relatively "absolute" basis, such a procedure possesses the important practical advantage of saving the considerable amount of time that must otherwise be spent in preparing standard solutions of each substance to be determined and in obtaining calibration polarograms. Chiefly as a result of the fundamental studies that were made by Ilkovič in Professor Heyrovský's laboratory in Prague (*4*), the factors which govern a polarographic diffusion current are now so well known that the application of this simplified technique to practical analyses is perfectly feasible, when certain fundamental data are available.

It was first demonstrated by Ilkovič (*4*), and later confirmed by others (*6*, *12*), that the diffusion current is expressed completely and quantitatively by the following equation:

$$i_d = knD^{1/2}Cm^{2/3}t^{1/6} \qquad (1)$$

in which i_d is the diffusion current in microamperes, n is the number of electron equivalents per molar unit of the electrode reaction, D is the diffusion coefficient (sq. cm. per second) of the reducible or oxidizable substance, C is its concentration in millimoles per liter, m is the rate of mercury flow from the dropping electrode in mg. per second, and t is the drop time in seconds. The theoretical significance and general practical utility of this relation have been discussed in detail by Kolthoff and Lingane (*6*), and its validity has been definitely established, particularly as regards the linear dependence of i_d on C and on the quantity $m^{2/3}t^{1/6}$. Since k, n, and D are independent of the characteristics of the dropping electrode capillary, the quantity $knD^{1/2}$, which is experimentally determinable as $i_d/(Cm^{2/3}t^{1/6})$, is a fundamental constant for any given substance, and is referred to below as the "diffusion current constant". This term has previously been applied to the ratio i_d/C (*6*), but since this ratio depends on the properties of the dropping electrode capillary—i. e., on $m^{2/3}t^{1/6}$—it is recommended that this usage be discontinued in favor of the more fundamental quantity $i_d/(Cm^{2/3}t^{1/6})$.

According to theoretical considerations (*6*), constant k in Equation 1 should be equal to 605 at temperatures between about 15° and 40° C., when the other quantities are expressed in the units indicated above. The approximate correctness of this value has been verified experimentally in the few cases where sufficiently accurate values of diffusion coefficients are available to permit a comparison (*6*). In most cases, however, it is not possible to employ this theoretical constant to calculate diffusion

Table II. Diffusion Current Constants

[Values listed are $i_d/(Cm^{2/3}t^{1/6})$ at 25° C. Values in italics are uncertain because of poorly defined diffusion currents. In all cases 0.01% gelatin was present as a maximum suppressor.]

Supporting Electrolyte	As	Bi	Sb	Sn(II)	Sn(IV)	Pb	Cd	Zn	Cu
0.1 *N* KCl	...	Insoluble	Insoluble	Insoluble	Insoluble	3.80	3.51	3.42	3.23
1 *N* HCl	*8.6*	5.23	5.54	4.07	*4.8*	3.86	3.58	[a]	3.39
0.5 *M* H_2SO_4	*8.4*	4.31	4.94	3.54	Insoluble	Insoluble	*2.6*	[a]	*2.12*
1 *N* HNO_3	*8.8*	4.64	5.10	4.02	Insoluble	3.67	3.06	[a]	3.24
1 *N* NaOH	N. R.[b]	Insoluble	4.54	3.45	N. R.	3.39	Insoluble	3.14	2.91
Acidic tartrate	[c]	3.12	*3.4*	2.41	N. R.	2.37	2.34	[a]	2.37
0.5 *M* sodium tartrate	N. R.	*3.0*	*3.9*	2.48	N. R.	2.30	2.34	2.30	2.24
Alkaline tartrate	N. R.	[c]	3.54	2.86	N. R.	2.39	[d]	2.65	[a]
1 *N* NH_4Cl + 1 *M* NH_3	...	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	3.68	3.99	3.75

[a] Diffusion current masked by final current increase (discharge of hydrogen or sodium ion).
[b] N. R., not reducible.
[c] No definite limiting current.
[d] Diffusion current not well developed, and not proportional to concentration of cadmium.

current constants with any degree of accuracy, because diffusion coefficient data under the conditions existing in polarographic measurements are not to be found in the literature; therefore these constants must be determined experimentally.

Table II contains a summary of the diffusion current constants of the metals with which the present investigation is concerned. Except for the values in italics, which are more or less uncertain because of imperfectly developed diffusion currents, the values are believed to be generally accurate to ±2 per cent. The values for lead, cadmium, and zinc in 0.1 *N* potassium chloride are taken from a previous compilation (*6*, *12*), and that for copper in the same medium is based on the measurements of Kolthoff and Orlemann (*7*). All other values were determined in the present study.

The data in Table II can be applied directly to the analysis of unknown solutions of these metals in these particular supporting electrolytes. If we represent the diffusion current constant by *I*, then the concentration in an unknown case will be given by

$$C = \frac{i_d}{Im^{2/3}t^{1/6}} \tag{2}$$

In addition to a knowledge of the diffusion current constant, this method requires that the quantity $m^{2/3}t^{1/6}$ be known for the capillary that is used, but the determination of *m* and *t* by a technique that has already been described (*10*) requires only a very few minutes' time, and obviously it is much simpler than the preparation of a standard solution for each substance.

The reliability of this technique depends primarily on the existence of a linear relation between i_d and $m^{2/3}t^{1/6}$. Basing their opinion on the excellent work of Maas (*14*), Kolthoff and Lingane (*6*) have concluded that this relation is obeyed with an accuracy of at least ±1.5 per cent. From more recent experience the author is convinced that with *m*-values in the usual range from about 1 to 3 mg. per second, and drop times between about 2 and 4 seconds, the accuracy of this relation is as good as the accuracy with which one can measure a diffusion current.

Although *m* is independent of the potential of the dropping electrode and the medium in which the mercury drops form, the drop time, and hence $m^{2/3}t^{1/6}$, changes appreciably with changing potential and also with the medium (*6*, *7*). Therefore, *m* can be determined with the mercury drops forming in air (*10*), but it is essential that the drop time be determined in the same medium and at the same potential at which the diffusion current is measured (*6*, *7*).

Although the diffusion current constant is independent of the properties of the dropping electrode, it does depend on temperature and on the composition of the supporting electrolyte, because the diffusion coefficient is a function of these factors (*6*). In most cases the temperature coefficient is in the neighborhood of 1.5 per cent per degree, which requires that the temperature be controlled to at least ±0.5°, preferably at 25° C. Usually the composition of a supporting electrolyte is of more importance than its exact concentration, provided that the concentration is relatively large; in many instances the concentration can be varied by as much as a factor of 2, or even more, without seriously changing the diffusion current constant, although this should never be taken for granted without experimental verification. As a general rule the diffusion current constant of a substance is not influenced by the simultaneous reduction or oxidation of other substances at the dropping electrode, and the values listed in Table II are applicable to mixtures of the various metals.

Gelatin, which is commonly used as a maximum suppressor, frequently has a marked influence on the diffusion current constant, and hence its concentration must be controlled carefully and should not be larger than is actually necessary; 0.01 per cent is usually ample.

In addition to their practical analytical value, the data in Table II are also of theoretical interest because they lead directly to values for the diffusion coefficients, and hence constitute a measure of the apparent sizes, of the various ions. The diffusion current constants of cadmium, zinc, and copper are largest in ammoniacal medium, from which it follows that the ammino complex ions of these metals must be smaller, and perhaps also less subject to the restraining effects of interionic attraction, than the complexes present in the other media. The values for lead, cadmium, zinc, and copper in 1 *N* hydrochloric acid are only slightly larger than in 0.1 *N* potassium chloride, and the difference is of the same order of magnitude in each case.

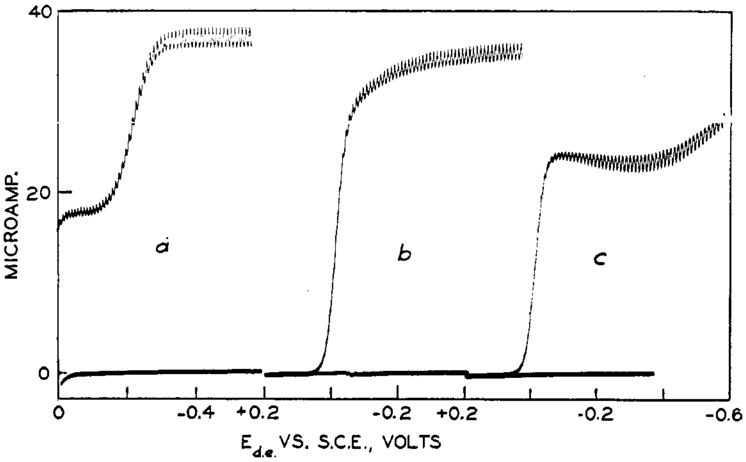

Figure 11. Polarograms of 4.71 Millimolar Copper

In (*a*) 1 *N* hydrochloric acid, (*b*) 1 *N* nitric acid, and (*c*) 1 *N* sulfuric acid, in the presence of 0.01% gelatin

In all cases, except that of copper, the diffusion current constants in the three mineral acids and in sodium hydroxide decrease in the order hydrochloric acid > nitric acid > sulfuric acid > sodium hydroxide, which indicates that the chloro complexes in hydrochloric acid are smaller than the aquo complexes that predominate in nitric and sulfuric acids, and that these in turn are smaller than the hydroxo complex ions present in sodium hydroxide solution.

The values in the tartrate media are smaller than in the other media, which is to be expected in view of the relatively large size of a tartrate complex ion. Furthermore, the diffusion current constants correspond to practically identical values for the diffusion coefficients of the tartrate complexes of the various metals. This leveling effect is doubtless due to the fact that the coordinating tartrate ions are so large compared to the size of the central metal ion, that differences in the size of the central ion, and even in the type and orientation of the bonds, have only a slight influence on the effective sizes of the different complexes.

Literature Cited

(1) Bambach, K., Ind. Eng. Chem., Anal. Ed., 14, 265 (1942).
(2) Bayerle, V., *Rec. trav. chim.*, 44, 514 (1925).
(3) Heyrovský, J., and Ilkovič, D., *Collection Czechoslov. Chem. Commun.*, 7, 198 (1935).
(4) Ilkovič, D., *Ibid.*, 6, 498 (1934); *J. chim. phys.*, 35, 129 (1938).
(5) Kacirkova, K., *Collection Czechoslov. Chem. Commun.*, 1, 477 (1929).
(6) Kolthoff, I. M., and Lingane, J. J., "Polarography", New York, Interscience Publishers, 1941.
(7) Kolthoff, I. M., and Orlemann, E. F., *J. Am. Chem. Soc.*, 63, 2085 (1941).
(8) Latimer, W. M., "Oxidation Potentials", New York, Prentice-Hall, 1938.
(9) Lingane, J. J., *Chem. Rev.*, 29, 1–36 (1941).
(10) Lingane, J. J., Ind. Eng. Chem., Anal. Ed., 14, 655 (1942).
(11) Lingane, J. J., *J. Am. Chem. Soc.*, 65, 866 (1943).
(12) Lingane, J. J., and Kolthoff, I. M., *Ibid.*, 61, 825 (1939).
(13) Lingane, J. J., and Laitinen, H. A., Ind. Eng. Chem., Anal. Ed., 11, 504 (1939).
(14) Maas, J., "De Polarografische Methode met de Druppelende Kwikelectrode ten Dienste van het Pharmaceutisch Onderzoek", Amsterdam, 1937.
(15) Page, J. E., and Robinson, F. A., *J. Soc. Chem. Ind.*, 61, 93 (1942).
(16) Smrz, J., *Rec. trav. chim.*, 44, 580 (1925).
(17) Suchy, K., *Collection Czechoslov. Chem. Commun.*, 3, 354 (1931); *Chem. News*, 143, 213 (1929).

An Apparatus for Quantitative Catalytic Hydrogenation

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THE apparatus for catalytic hydrogenation recently described by Noller and Barusch (*3*) is very useful when not more than 50 ml. of hydrogen are to be absorbed; however, it is not suitable for the many occasions when it is necessary to meter with some degree of accuracy as much as several hundred milliliters of hydrogen. The apparatus pictured (Figure 1) fills the entire gap between a strictly micro apparatus and the standard Adams (Burgess-Parr) machine.

This apparatus is a combination, with certain modifications, of features previously reported. The buret system is similar to that described by Fieser and Hershberg (*2*) and the reaction flask together with the stirring device is a slight modification of the one used by Noller and Barusch (*3*). The 50-ml. buret is for small-scale work and the 500-ml. buret is used for larger runs. If more than 500 ml. of hydrogen are to be absorbed, the stirring is slackened or momentarily stopped while the buret is quickly refilled with hydrogen. All the stopcocks are the oblique-bore high-pressure type manufactured by Eck and Krebs, New York, N. Y., who fabricated the glass parts of this apparatus. For those who wish to construct their own apparatus, attention is called to the pressure stopcock recently described by Connelly (*1*). A somewhat less elegant, although reasonably satisfactory, method is to use rubber bands to keep the stopcocks seated firmly. Ordinary stopcocks with none of these precautions will leak hydrogen, especially if extra internal pressure is applied during the hydrogenation as described below.

Flasks of the three sizes indicated afford flexibility in the volume of liquid that can be used, and small coil springs keep the greased ground-glass joint tightly sealed. This joint is reversed to minimize the danger of contamination of the flask contents with grease. A critical dimension is the height of the apparatus, which should not be less than 1 meter, in order that the system may be subjected to either a vacuum or the pressure of an extra atmosphere without forcing mercury out of the manometer.

Some experimenters will prefer using water or the solvent being employed in the hydrogenation as the displacing fluid instead of mercury, especially in view of the current limited availability of mercury. Increased accuracy can probably be obtained if the amount of dead space is reduced by using capillary tubing of about 3-mm. bore in place of the 10-mm. outside diameter standard tubing indicated for the manometer and connections. Unless care is exercised, the stirring may become vigorous enough to drive the stirrer through the wall of the flask, but encasing the iron core in a material such as Saran, instead of glass, may be at least a partial solution of this difficulty.

The air can be displaced from the apparatus by opening the flask stopcock and sweeping with hydrogen; however, unless care has been taken to trap hydrogen in the buret by closing the buret stopcock at the end of the previous hydrogenation, mere sweeping may leave a pocket of air in the buret. It is prudent, therefore, to open the buret stopcock, raise the mercury to a point near the top of the buret, close the screw clamp, and, with the flask stopcock closed, successively evacuate and flood the system with hydrogen three or four times by manipulating the three-way stopcock. Any addition of catalyst or compound after the system has been filled with hydrogen is made by washing the material through the cup into the flask with a little solvent after the internal pressure has been reduced by lowering the mercury in the buret. A small amount of solvent is allowed to remain in the cup, so that air is not admitted to the system. The sequence of addition of catalyst and reagents can be left to the discretion of the investigator; in many cases it is convenient to have the sample in the flask before attaching it to the buret system, but where a highly volatile substance is to be hydrogenated, it is preferable to introduce it through the cup after the sweeping or evacuation procedure has been completed. The catalyst can be reduced in the presence of the sample or the catalyst can be reduced first, a reading