10^{-3} for the Pu-Be source; $-(1.16 \pm 0.04) \times 10^{-2}$ at 0.0326 e.v.; $-(8.26 \pm 0.17) \times 10^{-3}$ at 0.07 e.v.; $-(6.42 \pm 0.13) \times 10^{-3}$ at 0.273 e.v. The plots indicate that the cross section per hydrogen atom, at least for all the hydrocarbons studied, is constant at each of these neutron energies, but increases with decreasing energy. The total per cent hydrogen was determined with a lower limit of sensitivity corresponding to 0.1% with the Pu-Be source, and 0.05% at a neutron energy of 0.0326 e.v. (from the slopes in Figure 5).

The availability of more intense neutron sources, such as the high flux thermal beam from reactors and the 10^8 *n* per second per sq. centimeter from neutron generators may permit the measurement of scattered neutrons only (by measuring at angles other than 180°) rather than transmitted neutrons. The result should be increased precision and accuracy, and should permit attainment of the theoretical sensitivity of 0.01% hydrogen.

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Correction for the Inconstancy of the Chronopotentiometric Constant at Short Transition Times

ALLEN J. BARD
Department of Chemistry, The University of Texas, Austin, Texas

▶ An equation is presented to show the effect of charging of the electrical double layer, oxide film formation or reduction, and adsorption of the electroactive species, on the chronopotentiometric constant, $i_o\tau^{1/2}/C^\circ$. An estimation of the errors caused by these effects is given and a method proposed for correction of experimental data to yield the true chronopotentiometric constant. The method is applied to the chronopotentiometric oxidation of iodide and hydroquinone and the reduction of lead(II) and silver(I).

IN A PREVIOUS COMMUNICATION (*3*) the variation of $i_o\tau^{1/2}/C^\circ$, the chronopotentiometric constant, was investigated over a wide range of transition times. The inconstancy of this constant at long transition times (greater than 10 seconds), caused by nonlinear diffusion and natural convection due to density gradients, was eliminated by employing shielded electrodes of the proper orientation. All electrodes, however, showed an increase of $i_o\tau^{1/2}/C^\circ$ with decreasing τ (increasing i_o) at short transition times. For solid electrodes, this effect has been ascribed to contributions from the charging of the electrical double layer, oxide film formation or reduction, electrode roughness, and adsorption of the electroactive species. This paper attempts to give an approximate estimation of these effects and proposes a method of correction of experimental chronopotentiometric data at short transition times.

Correction Factor at Short Transition Times. The increase in $i_o\tau^{1/2}/C^\circ$ with decreasing transition time is most frequently caused by the distribution of the current between two different kinds of processes: the electrolysis of the electroactive species diffusing to the electrode, for which $\tau^{1/2}$ varies as $1/i_o$, and a complicating process for which τ varies as $1/i_o$. The relative contribution of this second process increases as τ approaches zero. Three such complicating processes of interest are charging of the electrical double layer (*4*), formation or reduction of oxide films on the electrode (*2*), and electrolysis of electroactive species adsorbed on the electrode (*1*, *7*, *9*). The exact derivation of an equation for a chronopotentiometric electrolysis taking these effects into account is complicated by several factors. The electrolysis of an oxide film or adsorbed species may precede, occur simultaneously with, or follow, the electrode reaction of interest. In many cases the potentials at which the two reactions occur are so similar that no definite transition between them is observed. Correction for the oxide film effect requires an estimation of the amount of oxide on the electrode, or the extent of oxidation of the electrode during electrolysis. Correction for the adsorption effect requires knowledge of the form of the adsorption isotherm for the electroactive species. Finally for the correction for double layer charging, the double layer capacity, which in general varies with potential, must be known. Even if all of this was known for a particular case, a closed form solution of the diffusion equation and a simple method of treating experimental data could not be obtained.

For an approximate treatment of

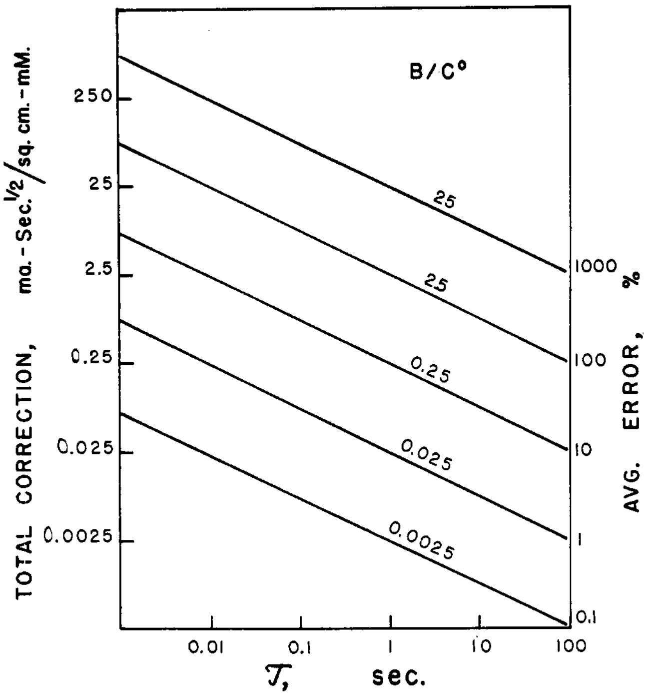

Figure 1. Variation of total correction $B/C^\circ\tau^{1/2}$ with τ for various values of B/C° and relative error in determination of substance with chronopotentiometric constant of 0.25 ma.-sec.$^{1/2}$/sq. cm.-m*M*

$$B = 10^3\Gamma + 10^{-3}(C_l)_{av.} + Q_{ox}$$

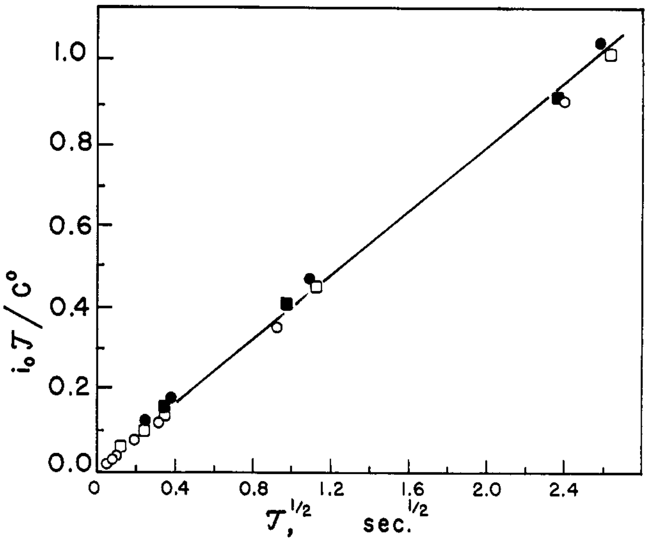

Figure 2. Variation of $i_o\tau/C^\circ$ (ma.-sec.$^{1/2}$/sq. cm.-m*M*) with $\tau^{1/2}$ for oxidation of iodide

○ Iodide concentration, 10m*M* in 1.0*M* H_2SO_4
□ 5m*M*
● 1m*M*
■ 0.5m*M*

these effects, we shall assume that the over-all current density, i_o, is made up of *constant* currents for electrolysis of the electroactive species in solution, i_e, charging of the double layer, i_c, oxidation of the electrode or reduction of the oxide film, i_{ox}, and electrolysis of the adsorbed species, i_{ads}. Then (*3*)

$$\frac{i_o\tau^{1/2}}{C^\circ} = 10^{-3}\,\frac{nFD^{1/2}\pi^{1/2}}{2} + \frac{10^{-3}(C_l)\text{ av. }\Delta E}{C^\circ\tau^{1/2}} + \frac{Q_{ox}}{C^\circ\tau^{1/2}} + \frac{10^3\,nF\Gamma}{C^\circ\tau^{1/2}} \quad (1)$$

where i_o is the current density (milliampere per square centimeter), τ is the transition time (seconds), C° is the concentration of the electroactive species (millimoles per liter), n is the number of faradays per mole of reaction, D is the diffusion coefficient (square centimeters per second), F is the faraday, (C_l)av. is the average double layer capacity (μfarads per square centimeter) in the potential interval ΔE (volts), Q_{ox} is the amount of electricity required for oxide film formation or reduction (millicoulombs) and Γ is the amount of electroactive species adsorbed on the electrode (moles per square centimeter). The first term on the right of Equation 1 is the true chronopotentiometric constant, while the additional correction terms are all of the same form, so that we can write

$$\frac{i_o\tau^{1/2}}{C^\circ} = 10^{-3}\,\frac{nFD^{1/2}\pi^{1/2}}{2} + \frac{B}{C^\circ\tau^{1/2}} \quad (2)$$

where B is an over-all correction factor. The magnitude of B for various values of Γ, (C_l)av. and Q_{ox} assuming contribution from only one of these at a time, is given in Table I. A platinum electrode contains about 1.5 × 10^{15} atoms per sq. cm., so that a monolayer of adsorbed material would yield a Γ of about 2.5 × 10^{-9} moles per sq. cm. Q_{ox} can vary up to about 0.8 millicoulomb per sq. cm. and depends upon the potential range and the particular solution under investigation. Estimation of Q_{ox} for various potential changes, can be obtained from curves such as those given by Laitinen and Enke [Figure 5 in (*6*)]. (C_l)av. is usually about 25 μfarads per sq. cm. for a smooth platinum electrode. The variation of the total correction, $B/C^\circ\tau^{1/2}$, as a function of τ and B/C°, and an estimation of the relative error caused by this correction for average chronopotentiometric constants is shown in Figure 1. That these corrections can be quite large is shown by the fact that only one hundredth of a monolayer of adsorbed substance or only 2.5 μcoulombs of an oxide film, can cause an error of about 1% for the electrolysis of a 1 millinormal solution of an electroactive substance at a transition time of 1 second.

It is fruitful to consider how well the above approximation conforms to what would be expected of a more rigorous treatment under different experimental conditions. The assumption of constant currents for the several processes during the electrolysis implies the simultaneous occurrence of the electrode reaction of interest and the complicating reaction. A more rigorous method of treating simultaneous reactions, assuming a linear adsorption isotherm and not requiring the partial currents to remain constant, has been described (*7*), but the results do not lead to a method of correction which is easily applicable to experimental data. The more rigorous treatment apparently does not lead to an $i_o\tau^{1/2}/C^\circ$ *vs.* $1/\tau^{1/2}$ plot which differs very significantly from results of the more approximate treatment [compare p_3 and p_4 in work of Lorenz (*7*)]. If the complicating reaction occurred before electrolysis of the electroactive species

Table I. Variation of *B* with Different Contributions from Adsorption, Double Layer Charging, and Electrode Oxidation

B, mcoulombs	Γ, moles per sq. cm.	$(C_l)_{av.}$ (μf. per sq. cm.) for ΔE of 0.1 volt	$(C_l)_{av.}$ (μf. per sq. cm.) for ΔE of 0.5 volt	Q_{ox}, mcoulombs
2.5	2.5 × 10^{-8}	25,000	5,000	2.5
0.25	2.5 × 10^{-9}	2,500	500	0.25
0.025	2.5 × 10^{-10}	250	50	0.025
0.0025	2.5 × 10^{-11}	25	5	0.0025

in solution, the correction factor would be somewhat larger, and could be calculated by assuming the total transition time was composed of a τ for diffusion and a τ for each complicating reaction. On the other hand, a complicating reaction following the diffusion controlled electrode reaction would lead to a smaller correction factor, the transition time being lengthened even further by electroactive species diffusing to the electrode during the subsequent complicating reaction. This type of behavior can be treated by a method developed by Lingane and Anson (*1*, *2*), but it is not easily used for correcting experimental i_o–τ data. The proposed method makes corrections which are intermediate to the two extremes of a preceding or following complicating reaction and is quite simple to apply.

Correction of Experimental Results. There are several ways of applying Equation 2 to experimental data. We have found it convenient to rearrange it to

$$\frac{i_o\tau}{C^\circ} = \frac{10^{-3}nFD^{1/2}\pi^{1/2}\tau^{1/2}}{2} + \frac{B}{C^\circ} \qquad (3)$$

A plot of $i_o\tau/C^\circ$ *vs.* $\tau^{1/2}$ yields a straight line with a slope of the true chronopotentiometric constant and an intercept of B/C°. Each individual value of $i\tau/C^\circ$ can then be corrected by subtraction of B/C° and dividing by $\tau^{1/2}$. This technique was used on chronopotentiometric data for the oxidation of iodide ion and hydroquinone and the reduction of lead(II) and silver(I) at short transition times. The experimental procedure and the apparatus used in obtaining these data have been described (*3*).

A plot of $i_o\tau/C^\circ$ *vs.* $\tau^{1/2}$ for the oxidation of iodide for transition times of 2 milliseconds to 7 seconds and concentrations of 0.1 to 10mM is shown in Figure 2. Actually a series of lines, one for each concentration of iodide, with the same slope and slightly different intercepts, should result, but on the scale used for plotting these data, the intercepts are so close together that the points appear to fit a single line. Data in Table II for this system show the slopes and intercepts for each concentration calculated numerically by the method of averages from the data, and show the apparent and corrected values of the chronopotentiometric constant. The agreement among the corrected values, representing a 100-fold range in concentration and a 3000-fold range in transition time is within the accuracy of measurement of τ from photographically recorded oscilloscope traces. Table III contains similar data for several other systems. Note that the apparent chronopotentiometric constant for the reduction of silver(I) at a shielded platinum electrode varies from 0.472 to

Table II. Variation of $i_o\tau^{1/2}/C^\circ$ with τ for the Oxidation of Iodide Ion

Solution was 1M H_2SO_4. Platinum electrode had projected area of 0.212 sq. cm.

C°, mM	i_o, ma. per sq. cm.	τ, sec.	$i_o\tau^{1/2}/C^\circ$ (ma./sec.$^{1/2}$)/(sq. cm./mM) Observed	Corrected	Slope	B/C°, mcoulombs per sq. cm. per mM	B, mcoulombs per sq. cm.
10	1.594	5.74	0.383	0.381			
	4.173	0.853	0.385	0.384			
	12.39	0.0998	0.392	0.387			
	20.64	0.0382	0.403	0.397			
	40.19	0.00963	0.394	0.379			
	51.96	0.00590	0.399	0.381			
	87.45	0.00215	0.406	0.376			
			Av.	0.383	0.380	0.0014	0.014
5	0.7335	6.97	0.387	0.383			
	1.783	1.28	0.403	0.394			
	5.901	0.1208	0.411	0.377			
	8.986	0.0578	0.433	0.384			
	20.83	0.0141	0.497	0.400			
	27.75	0.00836	0.507	0.382			
			Av.	0.387	0.383	0.0113	0.056
1	0.1584	6.65	0.409	0.396			
	0.3975	1.188	0.433	0.403			
	1.272	0.1435	0.482	0.396			
	2.107	0.0584	0.509	0.374			
			Av.	0.392	0.398	0.0325	0.032
0.5	0.08090	5.65	0.385	0.373			
	0.2180	0.950	0.425	0.399			
	0.6415	0.122	0.449	0.373			
			Av.	0.382	0.381	0.0259	0.013
0.1	0.009198	20.5	0.417	0.381			
	0.01561	7.85	0.437	0.381			
			Av.	0.381	0.382	0.160	0.016

Table III. Variation of $i_o\tau^{1/2}/C^\circ$ With τ for Various Substances

i_o, ma. per sq. cm.	τ, sec.	$i_o\tau^{1/2}/C^\circ$, ma./sec.$^{1/2}$ (sq. cm./mM) Observed	Corrected	Slope	B/C°, mcoulombs per sq. cm. per mM	B, mcoulombs per sq. cm.
10 mM Hydroquinone, NBS Buffer pH 7[a]						
2.407	5.20	0.547	0.528			
5.632	1.028	0.575	0.532			
11.85	0.278	0.623	0.532			
20.81	0.106	0.679	0.527			
		Av.	0.530	0.532	0.0486	0.49
5 mM Hydroquinone, NBS Buffer pH 7[a]						
0.7226	14.71	0.557	0.536			
1.287	4.74	0.561	0.529			
3.439	0.809	0.618	0.543			
9.807	0.134	0.717	0.533			
		Av.	0.535	0.534	0.0679	0.34
5 mM Lead(II), 0.20M $NaNO_3$[a]						
0.7849	13.81	0.584	0.576			
1.272	5.14	0.572	0.565			
2.772	1.156	0.596	0.573			
4.929	0.400	0.624	0.583			
9.557	0.116	0.652	0.575			
30.39	0.0160	0.759	0.574			
		Av.	0.574	0.576	0.0255	0.13
5 mM Silver(I), 0.20M KNO_3, 0.01M HNO_3[b]						
0.1146	303.0	0.399	0.398			
0.1656	145.2	0.398	0.398			
0.2486	63.5	0.397	0.395			
0.4292	21.6	0.398	0.397			
0.7190	7.57	0.396	0.391			
1.905	1.198	0.415	0.405			
6.480	0.114	0.440	0.398			
14.51	0.0263	0.472	0.391			
		Av.	0.396	0.391	0.0129	0.065

[a] Platinum electrode, projected area = 0.212 sq. cm.

[b] Platinum electrode, shielded horizontal disk, diffusion upwards, projected area = 1.00 sq. cm.

0.399 for transition times of 0.026 to 303 seconds, whereas the corrected values show a variation of only 0.391 to 0.398 over this 12,000-fold transition time range.

It is difficult to determine what fraction of B is made up of the various factors it contains. In all of the cases examined the contribution from charging of the double layer was probably within 0.01 millicoulomb. Oxidation of the electrode was very important during the electro-oxidation of hydroquinone. Oxidation in a pH 7 buffer alone shows that a platinum electrode starts to oxidize in the potential range where hydroquinone oxidation occurs, and contributes at least 0.1 millicoulomb to B. The additional contributions to B for the other substances may reflect adsorption of the electroactive species of about 2×10^{-10} moles per sq. cm. (about one tenth of a monolayer), although only small amounts of contribution from oxide film effects would make this estimation seriously in error.

Laitinen has recently suggested (*5*) that chronopotentiometric measurements may be useful in determining the amount of adsorbed electroactive species on an electrode. The method of treating the data which he suggests, plotting $i_o\tau$ *vs.* $1/i_o$, which implicitly assumes that the electrolysis of the adsorbed species occurs first, can also be used in correcting experimental data. Plotting our experimental data according to this scheme yielded straight lines with a slope giving essentially the same value of the chronopotentiometric constant, but with resulting B values about twice as large. The obvious difficulty with this type of measurement, as illustrated by the results given here, is that it is difficult to determine what contribution is made by oxide film effects to B. Chronopotentiometric measurement of adsorption by this technique would probably be more useful on mercury electrodes, and the most fruitful approach on solid electrodes is probably that taken by Lorenz and coworkers (*7*, *8*), which involves heavy platinization of the electrode, increasing the adsorption effect, and yielding variations of $i_o\tau^{1/2}/C^\circ$ of up to 800%.

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Thin Layer Chromatography of the Mixed Neomycin Sulfates on Carbon Plates

T. F. BRODASKY

Research Laboratories, The Upjohn Company, Kalamazoo, Mich.

▶ To facilitate the analysis of commercial preparations of neomycin sulfate, a novel method for the chromatography of neomycins A, B, and C sulfates has been developed. The procedure is based on the application of thin layer chromatography on carbon black, using aqueous acid as the mobile phase. The separation has been carried out on carbon pretreated with H_2SO_4 and on untreated carbon. Both substrates are effective when using an acidic mobile phase; however, water as the mobile phase fails to resolve the B, C sulfate complex. The effects of treatment of the carbon and varying the nature of the mobile phase are discussed in relation to their influence on the separation of the antibiotics. The biological activity on the thin layer plates was detected using the agar diffusion technique with *Bacillus pumilus*, and the quantitation of the neomycins on the organism is described. The quantitation of the neomycin sulfates proved to be difficult because of stimulation of the organism due to certain experimental techniques. This problem was partially resolved by adjustment of the inoculum rate and incubation temperature.

SINCE THE DISCOVERY of neomycin by Waksman in 1949, a direct technique for the analytical separation of two stereoisomeric forms, neomycin B and neomycin C, has not been available. For some time, workers separated neomycin B from its degradation product, neomycin A (neamine), by paper chromatography without effecting a separation of the stereoisomers (*5*, *6*) although there was evidence for the presence of these compounds in the neomycin complex (*8*, *10*). In 1951, Dutcher *et al.* (*2*) separated the hydrochloride salts of neomycin B and neomycin C on an alumina column, eluting with 80% methanol. Ford *et al.* (*3*) were successful in separating the two isomeric sulfates on an acid-treated carbon column, using water as the eluent. Although the antibiotics had been separated on preparative adsorption columns, an analytical procedure using paper chromatography was not readily developed. Saito and Schaffner reported the separation of neomycins A, B, and C on paper saturated with 1.0*M* sodium sulfate, using aqueous methanol containing sodium chloride as a developing solvent (*9*). However, the method proved less than satisfactory. The conversion of the antibiotics to their *N*-acetyl derivatives did result in a satisfactory separation of the three compounds and to date has been the only analytical procedure for the separation of the neomycins (*7*). This paper introduces a novel qualitative method of chromatographing the neomycin sulfates based on the application of thin layer chromatography on carbon black. The quantitative aspects of this technique have presented considerable difficulty. Measures designed to overcome some of these problems are described.

EXPERIMENTAL

Preparation of Carbon. Thirty grams of Nuchar (C-190-N) vegetable carbon black and 1.5 grams of $CaSO_4 \cdot 1/2\ H_2O$ were slurried with 220 ml. of distilled water or distilled water adjusted to pH 2 with H_2SO_4. The carbon prepared with distilled water was applied to the glass plates immediately; however, the acidified carbon must stand a minimum of 16 hours prior to preparation of the plates. Using these quantities it is possible to coat 35 plates.

Preparation of Thin Layer Plates. Single-strength glass plates (100- by 200-mm.) were degreased by washing with acetone. The carbon was applied with a Camag thin layer ap-