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Introduction. 1. Electrochemical reactions — Qualitative treatment. 2. The equations of the current-potential curves — Quantitative treatment of electrochemical reactions. 3. Current-potential curves during chemical reactions — Fast electrochemical reactions. 4. Current-potential curves during chemical reactions — Slow electrochemical reactions. 5. Influence of physical factors on the electrochemical phenomena. 6. Experimental determination of the current-potential curves. 7. Potentiometry. 8. Amperometry. 9. The relationship between potentiometry and amperometry. 10. Coulometry. 11. Other applications of the current-potential curves. 12. Recent electrochemical methods. 13. Non-aqueous solvents. Appendix.

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by **LUIZ P. RIBEIRO**
EMILIO MITIDIERI
OTTILIA R. AFFONSO

of the Biochemical Laboratory, Instituto Oswaldo Cruz,
Rio de Janeiro, Brazil

This book is a completely revised and enlarged translation of the very successful Portuguese edition of 1958.
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c) Studies of non-macromolecular substances such as vitamins, hormones, nucleic acid fragments, sugars, inorganic ions etc.

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The book should prove of great practical and theoretical value to all scientists concerned with natural processes.

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ANODIC FORMATION AND CHEMICAL ANALYSIS OF OXYCHLORIDE FILMS ON PLATINUM ELECTRODES

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Considerable evidence has been obtained in recent years that platinum electrodes acquire oxide films when they are chemically or electrochemically oxidized in non-complexing media such as perchloric and sulfuric acids. ANSON AND LINGANE[1] demonstrated by direct chemical analysis that these films consist of both PtO and PtO_2. The paper by ANSON AND LINGANE and recent studies by LAITINEN AND ENKE[2] and by LINGANE[3] list most of the references on platinum oxide films and the effects of these films on other electrode reactions.

Although much attention has been devoted to platinum oxide films, there is a lack of similar information regarding the anodic behavior of platinum electrodes in aqueous media other than sulfuric and perchloric acids. This is true, for example, of hydrochloric acid solutions in which, owing to the stability of the chloro-complexes of +2 and +4 platinum, a platinum anode might be expected to lose its "noble" character. The potentials for the platinum–platinous and platinum–platinic couples in chloride medium are[4]

$$Pt + 4Cl^- = PtCl_4{}^{2-} + 2e; \quad E° = -0.73 \text{ V } vs. \text{ N.H.E.}$$
$$Pt + 6Cl^- = PtCl_6{}^{2-} + 4e; \quad E° = -0.72 \text{ V } vs. \text{ N.H.E.}$$
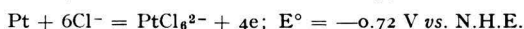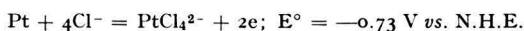
Hence, a platinum electrode could be expected to undergo free dissolution either in hydrochloric acid solutions of strong oxidants, e.g., chlorine, or in hydrochloric acid solutions in which the electrode is polarized anodically.

Among the workers who have studied the anodic behavior of platinum in hydrochloric acid, a primary concern has been the question of to what extent platinum anodes do undergo dissolution. Many of these studies have been carried out under conditions of high hydrochloric acid concentration, large current density, and elevated temperature. GRUBE[5] reported that during a prolonged electrolysis at 80° and at current densities up to 40 mA/cm² a platinum anode dissolves quantitatively as +4 platinum in 9–12 VF (volume formal) hydrochloric acid. However, the current efficiency for platinum oxidation decreases markedly as the temperature and electrolyte concentration decrease and as the current density is increased. Work by BRAN[6], HABER[7], and other authors agrees qualitatively with these observations.

More important from a practical point of view is the behavior of platinum electrodes

when they are used for various electroanalytical measurements. The conditions em-
ployed by the investigators cited above do not correspond to those which ordinarily
obtain in practical measurements, *i.e.*, room temperature, dilute hydrochloric acid
(0.1–1 VF), and low current density (100 $\mu A/cm^2$ to 20 mA/cm^2). That, under the
latter conditions, platinum electrodes suffer no, or only relatively slight, anodic
attack is a well-established fact. Among others, HABER AND GRINBERG[8] found that
when a platinum electrode is anodically polarized in 0.03–1 VF hydrochloric acid at
room temperature and a current density of 20 mA/cm^2 no platinum is dissolved. In
the coulometric titration of iodine to iodine monochloride with chlorine electro-gener-
ated at a platinum anode in 2 VF hydrochloric acid, WOOSTER, FARRINGTON AND
SWIFT[9] reported a positive error of 0.5–1.0%, which they attributed to oxidation of
platinum.

One possible explanation for this unexpected noble behavior of platinum is that the
rate of oxidation or dissolution is kinetically slow under the extant conditions.
Another may be found in an observation made by MARIE[10], that at room temperature
a platinum electrode immersed in 1 VF hydrochloric acid and anodized with current
densities of 20 to 740 mA/cm^2 became covered with a dark-brown to yellow-brown
protective layer. MARIE did not identify this film, however, and RUER[11] was unable to
reproduce these results. Finally, MÜLLER AND RIEFKOHL[12] hypothesized that the
passivity or nobility of a platinum anode in dilute hydrochloric acid might be attrib-
utable to the formation of a film of $PtCl_2$ on the electrode surface.

The present investigation was undertaken to learn more about the anodic behavior
of platinum in hydrochloric acid and in neutral and alkaline sodium chloride solutions.
Chronopotentiometry was employed as a tool because no previous similar study has
been made and because ANSON AND LINGANE[1] have shown that electrode phenomena
are particularly amenable to study by this technique. Evidence has been obtained
which indicates that in 1 VF hydrochloric acid there is formation of a film of $PtCl_2$
on the surface of the electrode. In neutral and alkaline 1 VF chloride media, mixed
films of +2 and +4 platinum oxychlorides are formed. The chronopotentiometric
measurements have been complemented by direct chemical analyses of these films.

<div align="center">EXPERIMENTAL</div>

Triply distilled water (specific conductance of $1.5 \cdot 10^{-6}$ ohm^{-1} cm^{-1} or less) was used
for the preparation of all solutions.

Constant boiling hydrochoric acid was prepared by distilling a mixture of equal
volumes of the triply distilled water and concentrated reagent acid in a quartz still.
The other chemicals were analytical reagent grade and were used without further
purification.

The essentials of chronopotentiometric technique and instrumentation have been
discussed by LINGANE[13]. The basic circuitry employed was the same as that used in
a previous study[14]. A Dumont 304-H cathode ray oscillograph was used to observe
and record the chronopotentiograms. The general technique employed in using the
oscillograph, particularly in respect to the methods for defining the time axis and
for measuring the transition times, has been described in detail in earlier communi-
cations[15,16].

The chronopotentiograms shown in this paper are photographic reproductions of
the original oscillographic traces. The chronopotentiograms appear as "broken"

curves. This is caused by the opening and closing of the motor-driven micro-switch used to define precisely the time axis. The construction and operation of this timing device are described in full detail in a previous study[17]. It is used because the sweep rate of the oscillographic trace becomes non-linear at long sweep times (3–8 sec). Thus, with this device in operation, the time elapsed from the beginning of one segment of a curve to the beginning of the next segment is exactly one-third second. (See curve 4 of Fig. 1.)
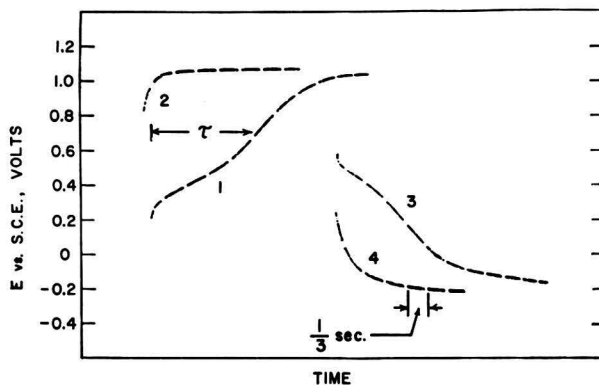
Fig. 1. Oxidation and reduction of platinum in air-free 1 VF hydrochloric acid at 30°. (1) Oscillo graphically recorded anodic chronopotentiogram for previously reduced platinum electrode. (2) Anodic chronopotentiogram recorded after curve 1. (3) Cathodic chronopotentiogram for a platinum electrode previously anodized in air-free 1 VF hydrochloric acid. (4) Cathodic chronopotentiogram taken after curve 3. In all cases the current was 35 μA and the electrode area was 0.370 cm². The broken curves are caused by the opening and closing of the motor-driven micro-switch used to define the time axis. The time from the beginning of one segment of a curve to the beginning of the next segment is exactly one-third sec. (curve 4). See also the discussion under EXPERIMENTAL.

The chronopotentiometric cell was of the type used previously[14]. For the majority of the experiments the reference electrode was a saturated calomel electrode (S.C.E.). However, for measurements involving the platinum oxide film where the exclusion of chloride ion from the test solutions was mandatory, a mercury–mercurous sulfate reference electrode was used; its potential was +0.408 V $vs.$ S.C.E. For convenience all the potentials quoted in this paper are referred to the S.C.E.

Two types of platinum working electrodes were used. For the chronopotentiometric measurements wire micro-electrodes (0.3–0.4 cm² area and 0.0255 cm radius) were made by sealing 99.99% pure platinum wire into 6-mm soft glass tubing. Electrical contact was made directly to the platinum electrode by extending the platinum wire all the way up the glass tubing.

For the chemical analyses of the platinum films, a platinum foil electrode with an area of 60 cm² (both sides) was employed.

The test solutions were de-aerated with high purity nitrogen and all measurements were made at a constant temperature of 30.0° ± 0.1°.

CHRONOPOTENTIOMETRIC STUDIES

Preliminary observations

If a previously cathodized platinum electrode is anodized in air-free, 1 VF hydrochloric acid, a chronopotentiogram is obtained which exhibits a distinct potential pause in the region from +0.3 to +0.6 V *vs.* S.C.E. (curve 1, Fig. 1). After this pause the potential increases until finally it becomes stabilized by steady chlorine evolution at *ca.* +1.1 V *vs.* S.C.E. When, following this first trial, a second one is made, but without pre-cathodization of the electrode, the potential rises rapidly to +1.1 V, and there is no potential pause (curve 2, Fig. 1). Characteristically, the open-circuit potential of the platinum electrode is *ca.* 0.5 V more positive (oxidizing) *after* the first trial than it is *prior* to the first trial. If, however, before each anodic trial, the electrode is given a reducing treatment, *e.g.*, cathodization to 0 V *vs.* S.C.E., the subsequent chronopotentiogram appears as in curve 1, Fig. 1.

After the platinum electrode has been anodized in air-free 1 VF hydrochloric acid, the solution stirred, and nitrogen bubbled through the solution to remove any chlorine, a cathodic chronopotentiogram is obtained as shown by curve 3, Fig. 1. When the cathodic trial is repeated (curve 4, Fig. 1) without re-anodizing, the electrode immediately assumes the potential at which hydrogen ion is reduced (*ca.* —0.2 V *vs.* S.C.E.).

Thus, the nature of the chronopotentiograms depends upon the initial state of the working electrode: the potential pause in the anodic chronopotentiogram occurs only when the electrode has been previously reduced, the cathodic wave only when the electrode has been pre-anodized. Two other preliminary observations, *viz.*, that stirring the solutions during a trial did not affect the anodic chronopotentiogram and that the quantity of electricity ($Q = i\tau$) for the anodic process is current-independent, indicate that the anodic process is not diffusion-controlled and that what must be involved is the formation of a film of an insoluble platinum compound on the electrode surface.

Constancy of quantity of film ($Q = i\tau$) in hydrochloric acid and comparison with the platinum oxide film

The importance of being able to bring a platinum electrode into a reproducible state as regards its surface oxidation cannot be over emphasized. In the present study it was imperative that a procedure for cathodic pre-treatment of the electrode be devised which would completely reduce or remove any previously formed film and yet which would avoid charging the electrode with hydrogen.

The following pre-treatment procedure was adopted. While the electrolyte was continuously stirred and de-aerated with nitrogen, the platinum working electrode was short-circuited through two saturated potassium chloride salt-bridges to a large (*ca.* 20 cm² area) saturated calomel electrode. Thus, the potential of the working electrode was maintained close to 0 V *vs.* S.C.E. until any previously formed film was reduced. The time required for the pre-treatment was established empirically. Various lengths of time from 1 to 35 minutes were allowed for this "spontaneous electrolysis". After each interval of time an anodic chronopotentiogram was recorded. The value of $i\tau$ increased for electrolysis times up to 15 minutes, but remained constant on longer electrolysis. The results of all experiments in 1 VF hydrochloric acid were obtained with an electrode pre-treated by 15 minutes' short-circuiting to the large saturated calomel electrode.

A series of experiments was performed to determine the effect of current on the transition time for the oxidation of platinum in air-free 1.00 VF hydrochloric acid. The chronopotentiograms appeared as in curve 1, Fig. 1. The transition times, τ, were measured from the instant the electrolysis circuit was closed to the moment the "transition potential" was reached. Measurements were made from enlarged photographs of the oscillographic traces, and the "transition potential" was taken to be +0.71 V vs. S.C.E. Typical transition time data are presented in Table I. The values of $i\tau$ are remarkably constant over the 35-fold range of current density. This constancy of $i\tau$ indicates that the oxidation of platinum under the extant conditions is not a diffusion-controlled process. Furthermore, it provides cogent evidence that a constant quantity of an insoluble platinum compound forms on the electrode surface. In chronopotentiometry a criterion for a strictly diffusion-controlled process is obeyance of the Sand equation, i.e., constancy of $i\tau^{1/2}$. In Table I, however, $i\tau^{1/2}$ varies from 28 μA sec$^{1/2}$ at a current of 15.8 μA to 171 μA sec$^{1/2}$ at 553 μA. Although, due to the cylindricity of the diffusion field[15], $i\tau^{1/2}$ could not be expected to be constant, its value actually should have decreased slightly in going from the smaller to the larger currents.

TABLE I

TYPICAL VALUES OF $i\tau$ AND $i\tau^{1/2}$

Electrode area = 0.328 cm^2; electrode radius = 0.0255 cm. Electrolyte was 1.00 VF hydrochloric acid. Temperature = 30.0°. Solution was de-aerated with pure nitrogen. Transition times were measured at +0.71 V vs. S.C.E.

i (μA)	τ (sec)	$i\tau$ (μC)	$i\tau^{1/2}$ (μA·sec$^{1/2}$)
15.8	3.21 ±0.12	51	28
24.3	2.11 ±0.03	51	35
34.7	1.48 ±0.03	51	42
68.9	0.77 ±0.04	53	61
138	0.37 ±0.00	51	84
278	0.18 ±0.00	50	117
553	0.095±0.007	53	171

Average 51±1

The average value of $i\tau$ of 51 μC (0.15 mC/cm^2) includes a contribution due to the charging of the electrical double layer. ROBERTSON[18] measured the capacitance of platinum micro-electrodes in 1 VF hydrochloric acid and found an average value of approximately 30 microfarads/cm^2 of geometric area between ca. +0.2 and +1.0 V vs. S.C.E. From this value for an electrode with an area of 0.328 cm^2, about 5 μC of electricity are required to charge the double layer between +0.2 and +0.7 V vs. S.C.E. Therefore, under present conditions the quantity of electricity needed to charge the double layer comprises only about 10% of $i\tau$. In the chemical analyses of the films described below, this conclusion is substantiated by the agreement between the values of $i\tau$ and the amounts of +2 and +4 platinum found chemically.

To compare the anodic behavior of platinum in hydrochloric acid with that for

sulfuric acid solutions in which the formation of a platinum oxide film is known to occur[1], some chronopotentiometric measurements were made with the same electrode (area 0.328 cm²) in a 1 VF sulfuric acid supporting electrolyte. Curves 1 and 2, respectively, in Fig. 2 are typical chronopotentiograms for the formation of a platinum oxide film (PtO and PtO₂) and for the subsequent reduction of this film. In sulfuric acid medium the chronopotentiogram for the oxidation of platinum (curve 1) is not very well developed, principally because of the more or less concomitant oxidation
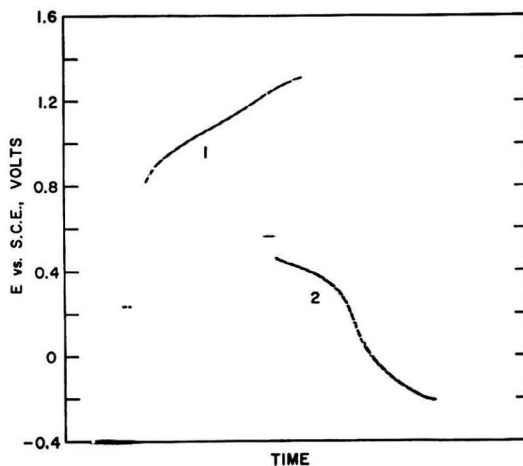
Fig. 2. Oxidation and reduction of platinum in air-free 1 VF sulfuric acid at 30°. (1) Anodic chronopotentiogram for oxidation of previously reduced platinum electrode. (2) Cathodic chronopotentiogram for reduction of the platinum oxide film (PtO and PtO₂). The current was 59 μA and the electrode area was 0.328 cm². The transition time for the anodic chronopotentiogram measured at +1.23 V vs. S.C.E. was 4.50 sec, and for the cathodic wave the transition time was 3.19 sec measured at +0.08 V vs. S.C.E. The short horizontal traces define the initial potential in each case. The timing device was not used in the recording of these chronopotentiograms.

of water. Also, this simultaneous oxidation of water decreases the current efficiency for platinum oxidation and causes the transition time to be greater than it should be for oxidation of platinum alone. On the other hand, the cathodic wave (curve 2, Fig. 2) for reduction of the oxide film is quite well-defined, and it is undoubtedly a more accurate measure of the quantity of oxide film. The quantity of oxide film formed in 1 VF sulfuric acid was measured chronopotentiometrically in exactly the same manner as ANSON AND LINGANE[1] described. The value of $i\tau/A$ obtained in the present study was 0.60 mC/cm². ANSON AND LINGANE[1] found 0.70 mC/cm² and LINGANE[14] obtained 0.74 mC/cm². These values are all in satisfactory agreement; the small disparity probably reflects differences in the microscopic areas of the electrodes employed.

The quantity of platinum oxide film (0.60 mC/cm²) is four times greater than the quantity of film formed in 1 VF hydrochloric acid (0.15 mC/cm²). In the hydrochloric acid medium the oxidation of the electrode (curve 1, Fig. 1) and the reduction of the film (curve 3, Fig. 1) proceed quasi-reversibly. However, the analogous processes in

sulfuric acid exhibit considerable irreversibility. Oxidation of a platinum electrode in 1 VF sulfuric acid (curve 1, Fig. 2) does not begin until its potential reaches +0.8 V vs. S.C.E., whereas reduction of the oxide film (curve 2, Fig. 2) occurs only below a potential of +0.5 V vs. S.C.E. In addition, there are some important differences between the stabilities of these films toward dissolution in the two media. ANSON[19] observed that a platinum electrode which had stood overnight in air-free 1 VF sulfuric acid still retained 80% of its original oxide film. In 1 VF hydrochloric acid, however, the transition time τ for the cathodic chronopotentiogram is much more dependent upon the length of time between the anodic trial and the subsequent cathodic one. The greater this elapsed time, the smaller is the cathodic τ. Such behavior is consonant with the fact that the film is slowly soluble in hydrochloric acid. Indeed if the filmed electrode is allowed to remain in the hydrochloric acid solution (vigorously stirred and air-free) long enough, all the film dissolves. In general with the cell geometry and wire electrodes employed in this study, approximately one-half of the film dissolved during the first ten minutes after the anodic trial. The last traces of film are very slow to dissolve and may require as long as one hour or more for complete solution. Interestingly, if the last traces of film are not removed, either by gradual dissolution or by cathodization, the subsequent anodic chronopotentiogram does not exhibit the well-defined potential pause between +0.3 and +0.6 V vs. S.C.E. (curve 1, Fig. 1).

Effect of pH

Chronopotentiometric measurements were made to determine the quantity of film ($i\tau$/A) as a function of pH at a constant chloride concentration of 1.00 VF. The test solutions contained hydrochloric acid and/or sodium chloride and had an ionic strength of 1.00 VF. No buffering agents were employed.

A method of electrode pre-treatment different from that described previously was used in these experiments. Prior to recording the anodic chronopotentiogram, the electrode was cathodically polarized just to the hydrogen evolution potential and the test solution was stirred, de-aerated with pure nitrogen to remove hydrogen, and al-
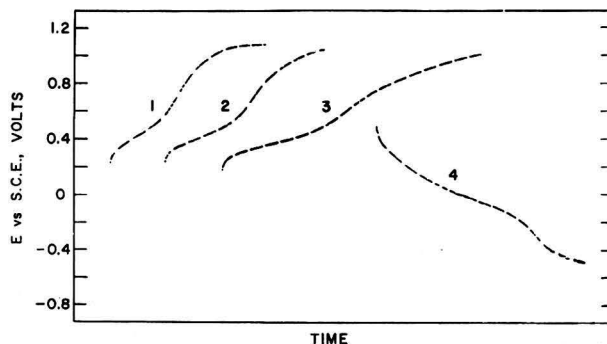
Fig. 3. Effect of pH on the chronopotentiometric behavior of platinum in 1 VF chloride medium. (1) Anodic chronopotentiogram in 1 VF hydrochloric acid (pH 0.1). (2) Anodic chronopotentiogram in 1 VF sodium chloride and 0.01 VF hydrochloric acid (pH 2.1). (3) Anodic chronopotentiogram in 1 VF sodium chloride (pH 5.1). (4) Cathodic chronopotentiogram for film reduction in 1 VF sodium chloride (pH 5.1) following curve 3. A current of 35 μA was used to record each chronopotentiogram, the electrode had an area of 0.370 cm², and the temperature was 30°.

lowed to become quiescent. For those experiments in which a cathodic chronopotentio-
gram for film reduction was to be recorded, the procedure was the same and the
electrode was then anodically polarized to film it. This anodization was interrupted
about 100 mV below the chlorine or the oxygen evolution potential and the solu-
tion was stirred, swept with nitrogen, and allowed to become quiescent before the
subsequent cathodic trial.
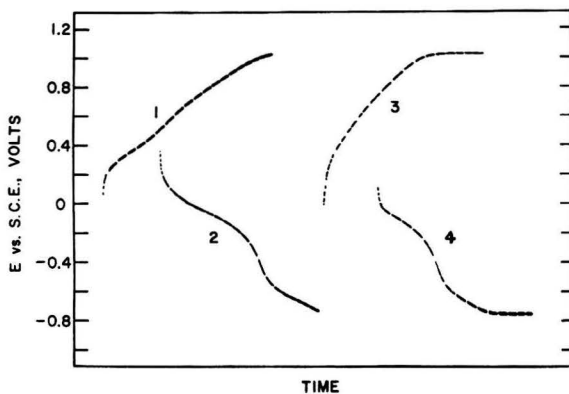
Fig. 4. Effect of pH on the chronopotentiometric behavior of platinum in 1 VF chloride medium·
Curves 1 and 2 show anodic and cathodic chronopotentiograms in 1 VF sodium chloride at pH 6.9
recorded with a current of 35 μA. Curves 3 and 4 are anodic and cathodic chronopotentiograms for
1 VF sodium chloride at pH 9.2 recorded with a 69 μA current. The electrode area was 0.370 cm^2
and the temperature was 30°.
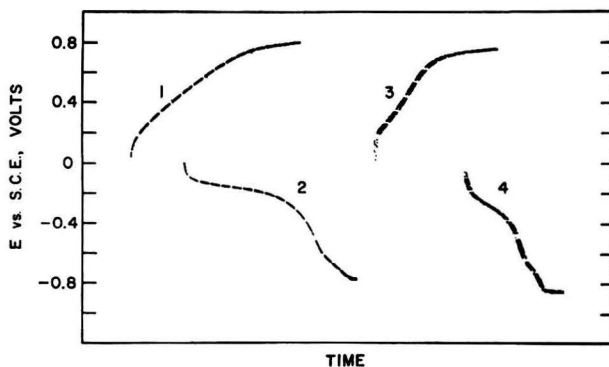
Fig. 5. Effect of pH on the chronopotentiometric behavior of platinum in 1 VF chloride medium.
Curves 1 and 2 are anodic and cathodic chronopotentiograms for 1 VF sodium chloride at pH 10.6
recorded with a current of 69 μA. Curves 3 and 4 are a similar pair of chronopotentiograms recorded
with a current of 137 μA for an electrolyte 1 VF in sodium chloride and 0.01 VF in sodium hydrox-
ide (pH 12.2). The temperature was 30° and the area of the electrode was 0.370 cm^2.

Chronopotentiograms for the oxidation of the platinum electrode and for the
reduction of the films in 1.00 VF chloride solutions at various pH's are shown in Figs.
3, 4 and 5. The transition time data obtained in the chloride media are presented in

Table II. Due to the relatively rapid solubility of the film at pH 0.1 and 2.1, the quantity of film $(i\tau/A)$ at these pH's was calculated from the anodic transition times. At pH 5.1 the film is not readily soluble and the anodic and cathodic chronopotentiograms (curves 3 and 4, Fig. 3) are both well-developed. The value of $i\tau/A$ reported in Table II for pH 5.1 is the average of several anodic and cathodic trials. At the higher pH's in 1 VF chloride medium, $i\tau/A$ was determined from measurements of the cathodic transition time for film reduction. From these results the plot of $i\tau/A$ versus pH

TABLE II

QUANTITY OF FILM AS A FUNCTION OF pH IN 1.00 VF CHLORIDE MEDIUM

Electrode area = 0.370 cm²; electrode radius = 0.0255 cm. Temperature = 30.0°.

Solution pH	i (μA)	τ (sec)	Transition potential V vs. S.C.E.	$i\tau/A$ (mC/cm²)
0.1	34.5	1.59	+0.71[a]	0.15
2.1	34.5	2.00	+0.69[a]	0.19
5.1	34.5	3.02	−0.28[b]	0.28
6.9	34.5	3.62	−0.40	0.34
9.2	68.6	1.88	−0.53	0.35
10.6	68.6	4.14	−0.58	0.77
12.2	137.3	2.15	−0.64	0.84

[a] At pH 0.1 and 2.1 the anodic transition times were measured because, in view of the relatively more rapid solubility of the film at these pH's, they were considered to be a more accurate measure of the quantity of film than the cathodic transition times.
[b] At pH 5.1 the anodic and cathodic chronopotentiograms are equally well-developed and the transition times are roughly equal. The transition potential given is for the cathodic curve; the transition potential for the anodic wave is +0.63 V vs. S.C.E. At the higher pH's the cathodic transition times were measured.
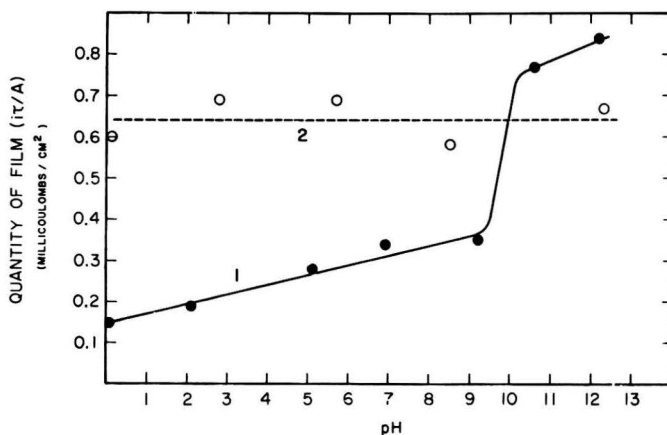
Fig. 6. Plot of the quantity of film $(i\tau/A)$ as a function of initial solution pH in chloride and sulfate media. Curve 1 shows the large variation of the quantity of film with pH in 1 VF chloride medium (data from Table II), and curve 2 shows the constancy of the quantity of platinum oxide film in 1 VF sulfate medium (data from Table III). Because unbuffered electrolytes were used, hydrogen ion produced during anodization (filming) of the electrode caused the pH *at the surface of the electrode* to decrease from its value in the bulk of the solution. The effect is especially important in the pH range from 5 to 9. The implications of this pH change are discussed in the text.

shown in curve 1 of Fig. 6 was constructed. As a further comparison with the platinum oxide film, a similar series of data was taken in sulfuric acid and/or sodium sulfate supporting electrolytes with a total sulfate concentration of 1.00 VF. As for the experiments in chloride media, no buffering agents were added. Cathodic chronopotentiograms for reduction of the platinum oxide film in sulfate solutions of pH 0.1, 2.8, 5.7, 8.5 and 12.3 are shown in Fig. 7. The oxide film data appear in Table III and the corresponding values of $i\tau/A$ are plotted in curve 2, Fig. 6. At each pH the value of $i\tau/A$ for the oxide film was determined from measurements of the cathodic transition time.

The variations in the quantities of film $(i\tau/A)$ formed in chloride and in sulfate media at different pH's are particularly interesting and important. For the platinum oxide film in sulfate media, $i\tau/A$ is more or less independent of the hydrogen ion concentration. This observation agrees qualitatively with that of ANSON AND LINGANE[1], who
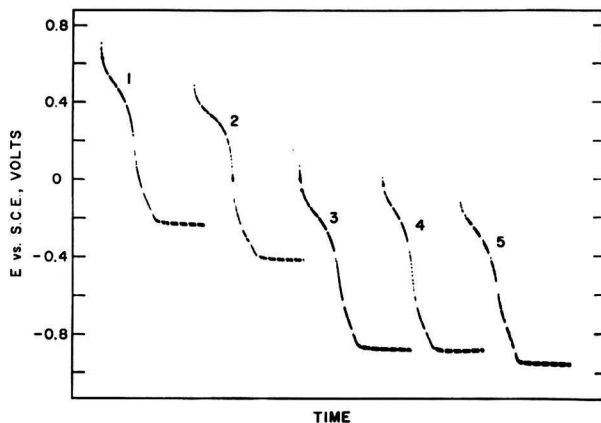
Fig. 7. Family of chronopotentiograms for the reduction of the platinum oxide film in 1 VF sulfate media of various initial solution pH's. (1) pH 0.1, (2) pH 2.8, (3) pH 5.7, (4) pH 8.5, and (5) pH 12.3. All the curves were recorded with a current of 138 μA, the area of the electrode was 0.370 cm², and the temperature was 30°.

TABLE III

QUANTITY OF PLATINUM OXIDE FILM AS A FUNCTION OF pH

Sulfuric acid and/or sodium sulfate solutions with a total sulfate concentration of 1.00 VF were used. Electrode area = 0.370 cm²; electrode radius = 0.0255 cm. Temperature = 30.0°.

Solution pH	i (μA)	τ (sec)	Transition potential[a] (V vs. S.C.E.)	$i\tau/A$ (mC/cm^2)
0.1	68.9	3.22	+0.08	0.60
2.8	137.7	1.86	—0.12	0.69
5.7	137.6	1.86	—0.60	0.69
8.5	137.4	1.56	—0.60	0.58
12.3	137.9	1.80	—0.70	0.67

[a] In all cases the transition times were measured from the cathodic chronopotentiograms.

made a similar study except that they used various buffer solutions. These authors found values for $i\tau/A$ from *ca.* 0.9 to 1.3 mC/cm^2, while in the present study $i\tau/A$ ranged from 0.58 to 0.69 mC/cm^2. Again the differences in these results most likely reflect variations in the "roughness factors" of the electrodes.

In contradistinction to the relatively constant quantity of platinum oxide film between pH 0 and 12 (Table III), the amount of film in chloride media over the same pH range shows considerable variation (Table II). From pH 0, where in 1 VF hydrochloric acid the quantity of film is only one-fourth that for the platinum oxide film in 1 VF sulfuric acid (*vide supra*), $i\tau/A$ increases roughly linearly until it attains at pH 7–9 (1 VF sodium chloride solution) the value 0.35 mC/cm^2, which is approximately one-half that for the platinum oxide film. Between pH 9 and 11, however, the value of $i\tau/A$ in the chloride medium increases very abruptly, and it reaches and even exceeds slightly the quantity of oxide film (Fig. 6).

Several points should be made in respect to the behavior just described. The use of buffering agents to maintain the pH constant was strictly avoided to prevent the ions of these buffers from becoming incorporated as anionic constituents of the films. That the test solutions were unbuffered does mean, however, that the pH of the electrolyte *at the electrode surface* changed during an anodic or cathodic trial because of the generation or consumption of hydrogen ions. This is especially significant in the pH range from about 5 to 9, since outside this range the pH was maintained more or less constant by the buffer capacity of the electrolyte itself. In 1 VF chloride medium at least above pH 5, oxide or hydroxide ion is a film constituent (*vide infra*). In the pH range from about 5 to 9, hydrogen ion produced during anodization (filming) of the electrode by the de-protonation of water causes the pH *at the electrode surface* to decrease relative to its value in the body of the solution. Therefore, the values of $i\tau/A$ listed in Table II for pH 6.9 and 9.2 must really correspond to $i\tau/A$ at *ca.* pH 5 or 6. Furthermore, the decrease in pH at the electrode surface *during* the filming process probably causes the ratio of hydroxide to chloride content in the film to decrease. However, once the electrode is filmed (anodized), the *increase* in pH *at the electrode surface* during the subsequent cathodic trial to measure the quantity of film will not affect the value of $i\tau/A$ (quantity of *reducible* platinum). Consequently, although the rapid increase of $i\tau/A$ in chloride medium observed to occur between pH 9 and 11 (curve 1, Fig. 6) is a real phenomenon, the actual pH range at the electrode surface wherein the increase occurs is probably between pH 5 and 7.

Over the pH range from about 5 to 9, the transition potentials for the anodic and cathodic chronopotentiograms in both chloride and sulfate media are, respectively, more oxidizing (positive) and more reducing (negative) than corresponds to the pH of the bulk of the solution. This is particularly noticeable, in the cathodic chronopotentiograms for platinum oxide film reduction at pH 5.7 and 8.5 (curves 3 and 4, Fig. 7). The reason for this behavior is again due to the fact that the test solutions were unbuffered. Hydroxide ion liberated (or hydrogen ion consumed) by the reduction of the platinum oxides, *e.g.*, $Pt(OH)_2 + 2 e = Pt + 2 OH^-$, causes the pH of the solution at the surface of the electrode to *increase* significantly. Thus in the experiment at initial pH 5.7 (Table III), approximately 200 μC of platinum oxides were reduced and, as a result, the pH of the solution *at the electrode surface* increased to about 10 by the time the transition potential was reached. An analogous situation prevailed in the experiments performed in chloride media between pH 5 and 9, but, because, as will be

shown below, the hydroxide (or oxide) content of these films is less than for the oxide films the effect of the pH change at the electrode surface was not so pronounced.

From the study of the quantity of film $(i\tau/A)$ vs. pH in chloride medium, some important conclusions were reached regarding the properties and composition of the films at various pH's.

In 1.00 VF chloride medium at pH 0.1 and 2.1, the general qualitative shapes of the anodic chronopotentiograms for electrode oxidation (curves 1 and 2, Fig. 3) are very similar. Furthermore, the transition potential for the anodic wave is in each case nearly the same (Table II). This latter observation suggests that little or no hydroxide (oxide) is present in the film, since if it were the transition potential should exhibit a definite pH dependence. The cathodic chronopotentiograms for film reduction in 1.00 VF chloride medium at pH 0.1 and 2.1 are as curve 3, Fig. 1, and there is no discernible difference in the values for the transition potentials. The solubility of the film at pH 2.1 in the electrolyte (0.01 VF hydrochloric acid and 1.00 VF sodium chloride) is about the same as it is in 1.00 VF hydrochloric acid.

At pH 5.1 (1.00 VF sodium chloride) the anodic and cathodic chronopotentiograms (curves 3 and 4, Fig. 3) are equally well delineated, and the anodic and cathodic transition times are equal. A series of experiments in which a cathodic chronopotentiogram was recorded at various times after initially filming (anodizing) the electrode indicated that at pH 5 the film is quite stable towards dissolution in the electrolyte. Even after the electrode had been in contact with the well-stirred and air-free electrolyte for 60 minutes, only ca. 20% of the film dissolved.

Anodic chronopotentiograms for film formation at pH's of 6.9 and higher (Figs. 4 and 5) do not exhibit a well-defined potential pause. Instead the potential increases more or less linearly with time. Contrarily, the cathodic chronopotentiograms are very well-defined and show definite transition times corresponding to reduction of the films. The films are also very stable towards dissolution at pH values above 7.

Quite evidently the films formed in chloride medium are not the same as the platinum oxide films studied by ANSON AND LINGANE[1]. The large variations in $i\tau/A$ versus pH for the films in chloride medium suggest that the composition as well as the quantity of film change as the pH varies. It appeared that at the lower pH's chloride ion is the chief anionic constituent of the films, and that what might occur as the pH increases from 0 to 12 is the transition from a wholly chloride-containing film ($PtCl_2$) to an oxychloride film, perhaps, finally to an oxide film.

CHEMICAL ANALYSES OF THE FILMS

The chronopotentiometric study of the quantity of film $(i\tau/A)$ versus pH in 1 VF chloride media revealed that at pH values greater than about 4 the film is not readily soluble in the electrolyte and, hence, that it should be possible to remove the filmed electrode, wash it free from the electrolyte, and analyze the film for its constituents. To obtain a sufficient quantity of film for analysis, a platinum foil electrode with an area of 60 cm² (both sides) was used. Even with this large electrode the total quantity of film was only about 0.03 mg.

Analysis of film in 1 VF sodium chloride at pH 7

(a) Platinum analysis

A chemical study of the film formed in an unbuffered 1.00 VF sodium chloride

solution at pH 7 proved especially fruitful because a complete analysis of the film could be obtained. The use of an unbuffered pH 7 medium has the disadvantage that during the electrolysis the pH of the solution near the electrode surface changes (*vide supra*). However, this objection is outweighed by the absence of any specific effects that might be caused by buffers. The use of an unbuffered medium at pH 7 serves as the basis of a method for determining the hydroxide (oxide) ion content of the film.

The quantities of +2 and +4 platinum in the film were determined by essentially the same technique employed by ANSON AND LINGANE[1] in their study of the platinum oxide film. A platinum electrode which has been filmed (anodized) in 1 VF sodium chloride at pH 7 may be washed free of the electrolyte without loss of the film. If this washed electrode is then placed in air-free 1 VF hydrochloric acid and the solution heated to boiling, the film dissolves with the consequent formation of $PtCl_4^{2-}$ and $PtCl_6^{2-}$. These species absorb in the near ultraviolet region of the spectrum; $PtCl_4^{2-}$ has an absorption peak at 230 mμ and $PtCl_6^{2-}$ at 262 mμ. By spectrophotometric analysis of the hydrochloric acid stripping solution, one can determine the amounts of +2 and +4 platinum in the film. The spectrophotometry of $PtCl_4^{2-}$ and $PtCl_6^{2-}$ has been described by KIRKLAND AND YOE[20].

Procedure for platinum analysis. Prior to each experiment the 60 cm² platinum electrode was cleaned of any residual film by placing it in boiling 1 VF hydrochloric acid for several hours. Following this treatment the electrode was immediately washed free of the acid with triply distilled water and placed into the chronopotentiometric cell containing the 1.00 VF sodium chloride electrolyte. The test solution was de-aerated with nitrogen for at least 30 minutes. The pH was then adjusted to 7.0 by electro-generation of hydroxide ion via reduction of water at the platinum electrode. This brief cathodization also served to reduce any traces of film which might have been formed during the various handling steps. The passage of nitrogen through the solution was continued for an additional 15–20 minutes to remove hydrogen. After the solution was allowed to become quiescent for about one minute, the electrode was anodized with a constant current until its potential reached about 100 mV below the chlorine and/or oxygen evolution potential (curve 5, Fig. 3). After the solution was stirred and de-aerated briefly and allowed to become quiescent again, the quantity of film formed was measured by recording a cathodic chronopotentiogram. Note that the anodization of the electrode in the unbuffered pH 7 medium produces hydrogen ions, so that after stirring the solution its pH drops to about 6. However, for the purpose of recording the subsequent cathodic chronopotentiogram to measure the quantity of film, there is no need to readjust the pH to 7.0.

After the chronopotentiometric measurement of the amount of film, the pH of the solution was again adjusted to 7.0 and the electrode was again anodized to form the film once more. Then the electrode was removed from the cell and washed free of the sodium chloride electrolyte with water. The electrode was replaced into the clean cell, and, while a continuous flow of nitrogen was maintained, air-free 1.00 VF hydrochloric acid was added. The acid solution was de-aerated for an additional ten minutes, then it was heated to boiling during the course of 60 minutes. During the heating a rapid flow of nitrogen was passed through the solution. Finally the solution was cooled to room temperature, the electrode removed from the solution, the nitrogen flow stopped, and the volume of the solution brought exactly to 100 ml by the addition of

fresh 1.00 VF hydrochloric acid. Subsequently, a cathodic chronopotentiogram of the stripped electrode was recorded in 1 VF sodium chloride solution to determine whether any undissolved film remained. No residual film was ever detected.

The stripping solution was analyzed spectrophotometrically against pure 1.00 VF hydrochloric acid as the comparison solution. A matched pair of 10-cm silica absorption cells and a Beckman DU spectrophotometer were used.

Calibration curves for the spectrophotometric analyses were obtained with high purity K_2PtCl_4 and $(NH_4)_2PtCl_6$. In 1 VF hydrochloric acid both $PtCl_4^{2-}$ and $PtCl_6^{2-}$ obey Beer's law. The molar absorptivities for $PtCl_4^{2-}$ and $PtCl_6^{2-}$ in 1.00 VF hydrochloric acid were found to be 7510 and 22800 liter mole^{-1} cm^{-1}, respectively, at wavelengths of 230 and 262 mμ. Figure 8 shows spectra for $PtCl_4^{2-}$, $PtCl_6^{2-}$, and a mixture of both ions in 1 VF hydrochloric acid.
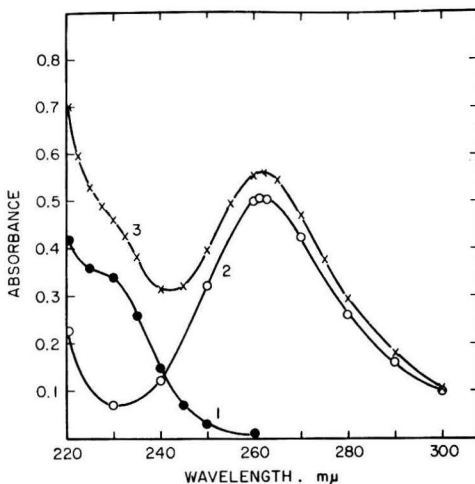
Fig. 8. Absorption spectra of $PtCl_4^{2-}$ and $PtCl_6^{2-}$ in 1.00 VF hydrochloric acid. (1) $4.52 \cdot 10^{-6}$ VF K_2PtCl_4. (2) $2.24 \cdot 10^{-6}$ VF $(NH_4)_2PtCl_6$. (3) $4.68 \cdot 10^{-6}$ VF K_2PtCl_4 and $2.30 \cdot 10^{-6}$ VF $(NH_4)_2PtCl_6$.

A wavelength of 230 mμ was used for the determination of $PtCl_4^{2-}$ and 262 mμ for $PtCl_6^{2-}$. At 230 mμ there is a contribution to the total observed absorbance due to absorption by $PtCl_6^{2-}$; however, since the amount of $+4$ platinum in this study was relatively much smaller than $+2$ platinum, this slight contribution could be neglected. For the concentrations of $PtCl_4^{2-}$ in this work, there was no significant absorption at 262 mμ.

Data presented by LATIMER[4] indicate that $PtCl_4^{2-}$ is slightly unstable in respect to disproportionation into metallic platinum and $PtCl_6^{2-}$. The net reaction is

$$2 \ PtCl_4^{2-} = Pt + PtCl_6^{2-} + 2 \ Cl^-$$

and one calculates from the free-energy data[4] that it has an equilibrium constant of about 50. However, the equilibrium expression for this reaction has such a form that the direction of reaction is dependent upon the concentrations of the species involved.

When all the species are at unit activity there will be considerable disproportionation of $PtCl_4^{2-}$. On the other hand, if a solution 1 VF in hydrochloric acid and 10^{-6} VF each in $PtCl_4^{2-}$ and $PtCl_6^{2-}$ is equilibrated in the presence of platinum metal (conditions which correspond very closely to the actual stripping experiments), the equilibrium concentration of $PtCl_4^{2-}$ will be *ca.* $3 \cdot 10^{-6}$ VF and that for $PtCl_6^{2-}$ only *ca.* $5 \cdot 10^{-10}$ VF. Thus, for the small concentrations of $PtCl_4^{2-}$ and $PtCl_6^{2-}$, *i.e. ca.* 10^{-6} VF, encountered in this work, $PtCl_6^{2-}$ was unstable to the extent that it should have undergone almost quantitative reduction by metallic platinum to $PtCl_4^{2-}$.

Quantitative measurements were made to determine what change does occur in the concentrations of the two oxidation states of platinum during an actual stripping experiment. Known solutions of $PtCl_4^{2-}$ and $PtCl_6^{2-}$ in 1 VF hydrochloric acid were boiled in contact with the platinum electrode according to the procedure for the stripping experiments (*vide supra*). A solution initially $4.68 \cdot 10^{-6}$ VF in $PtCl_4^{2-}$ (in 1 VF hydrochloric acid) showed no change in the $PtCl_4^{2-}$ concentration after one hour's boiling in contact with the platinum electrode; *i.e.*, there was no formation of $PtCl_6^{2-}$. When a $2.22 \cdot 10^{-6}$ VF solution of $PtCl_6^{2-}$ was similarly treated, the final concentration of $PtCl_6^{2-}$ was $1.82 \cdot 10^{-6}$ VF and the concentration of $PtCl_4^{2-}$ formed was *ca.* $0.5 \cdot 10^{-6}$ VF. When a solution containing both $PtCl_4^{2-}$ and $PtCl_6^{2-}$ at concentrations of $4.68 \cdot 10^{-6}$ and $2.22 \cdot 10^{-6}$ VF, respectively, in 1 VF hydrochloric acid was boiled with the platinum electrode for two hours, the final concentrations were $6.17 \cdot 10^{-6}$ VF for $PtCl_4^{2-}$ and $1.51 \cdot 10^{-6}$ VF for $PtCl_6^{2-}$.

Although $PtCl_6^{2-}$ should have undergone essentially quantitative reduction to $PtCl_4^{2-}$, the test experiments with known concentrations of $PtCl_4^{2-}$ and $PtCl_6^{2-}$ demonstrate that the rate of this reduction is actually relatively slow. In the test experiment with $PtCl_6^{2-}$, only 18% was reduced after *one* hours' boiling in contact with platinum, and in the experiment in which both $PtCl_4^{2-}$ and $PtCl_6^{2-}$ were present,
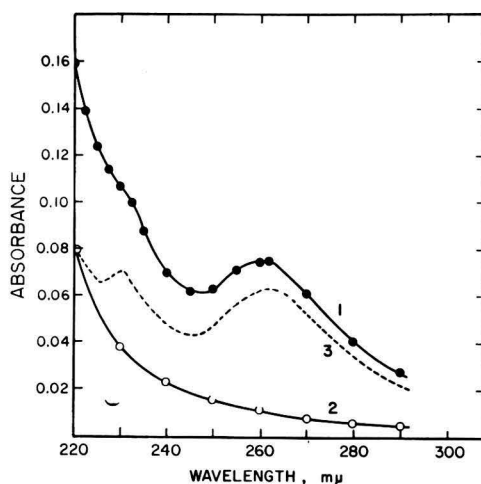
Fig. 9. Absorption spectra obtained in a typical stripping experiment. (1) Observed spectrum of 1 VF hydrochloric acid stripping solution. (2) Spectrum obtained in a "blank" stripping solution. (3) Spectrum of 1 VF hydrochloric acid stripping solution corrected for "blank" absorption (subtraction of curve 2 from curve 1).

about 33% of the $PtCl_6^{2-}$ was reduced during *two* hour's boiling. Anson[18] found that an approximately 15% decrease in the $PtCl_6^{2-}$ concentration occurred after one hour's boiling time. In the present study a correction has been made for the quantities of $PtCl_6^{2-}$ reduced and $PtCl_4^{2-}$ formed by the reduction reaction.

In some of the stripping experiments, extraneous absorption was observed in the wavelength region from 220 to 240 mμ; however, the source of this extraneous absorption was not discovered. Using fresh triply distilled water and constant boiling hydrochloric acid to prepare the stripping solution and cleaning the electrode by placing it in boiling $1\ VF$ hydrochloric acid for two or three hours prior to an experiment served to decrease this interfering absorption to a minimum.

The spectrum of a $1\ VF$ hydrochloric acid stripping solution obtained in an actual platinum analysis is reproduced in curve 1, Fig. 9. The electrode had been filmed (anodized) in an unbuffered $1\ VF$ sodium chloride solution of pH 7.0. The spectrum clearly shows the broad absorption peak at 262 mμ due to $PtCl_6^{2-}$, and the presence of $PtCl_4^{2-}$ is indicated as a shoulder at 230 mμ. As mentioned above, there is some extraneous absorption, particularly in the wavelength region of 220–240 mμ. The amount of this absorption was determined in "blank" experiments in which all the steps of the actual stripping procedure were repeated except for the anodization of the electrode. A typical spectrum obtained in one of these "blank" experiments is shown in curve 2 of Fig. 9. The reproducibility of this "blank" absorption spectrum was about 5–10% which was adequate for the present purposes. Curve 3 of Fig. 9 represents the spectrum of the stripping solution after correction for "blank" absorption (subtraction of curve 2 from curve 1). In curve 3 the two peaks due to the absorption of $PtCl_4^{2-}$ at 230 mμ and of $PtCl_6^{2-}$ at 262 mμ are clearly evident.

A further correction was made for the amount of $PtCl_6^{2-}$ which had undergone reduction by platinum metal and for the corresponding quantity of $PtCl_4^{2-}$ formed by this reduction. In accord with the earlier experiments, about 15–18% of the $PtCl_6^{2-}$ initially present was reduced, and, therefore, the concentration of $PtCl_6^{2-}$ determined spectrophotometrically must have been only about 85% of the quantity of $+4$ platinum initially present in the film. The "original" $PtCl_6^{2-}$ concentration, and, hence, the quantity of $+4$ platinum in the film, was calculated by multiplying the concentration of $PtCl_6^{2-}$ found spectrophotometrically by $1/0.85$ or 1.18. From the known stoichiometry of the reduction reaction (two moles of $PtCl_4^{2-}$ are formed for each mole of $PtCl_6^{2-}$ reduced), a correction was applied to obtain the quantity of $+2$ platinum in the film.

TABLE IV

ANALYSIS OF FILM FOR PLATINUM

The film was formed by anodizing the 60 cm^2 platinum foil electrode in an air-free, unbuffered $1.00\ VF$ sodium chloride solution initially at pH 7.0

Spectrophotometric determination of platinum in film			Chronopotentiometric measurement of quantity of film		
$+2$ platinum (mC)	$+4$ platinum (mC)	Total platinum (mC)	i (mA)	τ (sec. measd. at $-0.35\ V$ vs. S.C.E.)	$i\tau$ (mC)
16.0	12.4	28.4	2.16	14.4	31.1
19.1	10.4	29.5	2.16	14.8	32.0

Table IV presents results of two determinations of the platinum content of the film formed in unbuffered 1.00 VF sodium chloride solution at pH 7.0. The quantities of platinum tabulated have been corrected for the "blank" absorption and for the reduction of $PtCl_6^{2-}$ to $PtCl_4^{2-}$. The chronopotentiometric measurement of the quantity of film is included in Table IV for comparison. The agreement of the amount of platinum determined spectrophotometrically with the quantity of film measured chronopotentiometrically is remarkably good. This agreement proves conclusively that the anodic and cathodic chronopotentiograms observed above (curves 1 and 2, Fig. 4) are due to oxidation (filming) of the platinum electrode and subsequent reduction of the film. Both $+2$ and $+4$ platinum are present in the film at pH 7, and the molar ratio of $+2$ to $+4$ platinum is close to 3:1. ANSON AND LINGANE[1] found that for the platinum oxide film in 1 VF sulfuric acid the molar ratio of PtO to PtO_2 is 6:1.

(b) Chloride analysis

Chloride ion in the film at pH 7 was detected and determined by cathodically polarizing a thoroughly washed, previously filmed electrode in a chloride-free nitric acid solution and then analyzing this nitric acid solution for chloride ion liberated by the reduction of the film. The chloride concentrations to be determined in this study ranged from ca. $1 \cdot 10^{-6}$ to $5 \cdot 10^{-6}$ VF, so a very precise method of analysis was required. For this purpose a new method was devised for the determination of small concentrations of chloride ion. The details of this method are described elsewhere[21]. Briefly stated, the method takes advantage of the solubility product principle, that in a solution saturated with silver chloride the silver ion concentration is governed by the chloride ion concentration. The test solution is equilibrated with solid silver chloride, the silver ion concentration determined by potentiometric titration with iodide ion, and the chloride ion concentration calculated via the solubility product principle from the known solubility of silver chloride in the particular electrolyte alone.

Procedure for chloride analysis. The platinum foil electrode was filmed in exactly the same manner as described above for the platinum analyses. The filmed electrode was removed from the cell and washed free of the sodium chloride electrolyte by dipping it in a succession of ten beakers containing 10^{-3} VF nitric acid. When the effectiveness of this washing procedure was to be checked, the last beaker was replaced by one containing 0.0250 VF nitric acid. This solution was then analyzed for chloride by the method cited above[21].

After the washing sequence the electrode was replaced into the cleaned cell, 0.0250 VF nitric acid was added, and the solution was de-aerated for at least 30 minutes. A cathodic chronopotentiogram was recorded by the usual technique and the transition time was measured. Cathodization of a filmed electrode reduces $+2$ and $+4$ platinum to metallic platinum and liberates chloride ion into the nitric acid electrolyte. The nitric acid solution was brought to a known volume by the addition of fresh 0.0250 VF nitric acid, and chloride ion was determined via the procedure previously described[21]. The determination of chloride ion together with the transition time measurement allowed a correlation to be made between the quantities of platinum and chloride ions in the film.

A very important aspect of these experiments was the washing of the electrode after it had been filmed (anodized). It was necessary to remove all the electrolyte (sodium chloride solution) without at the same time dissolving any of the film or altering it chemi-

cally. It was possible to wash the electrode free of the sodium chloride solution by rinsing it thoroughly with distilled water. However, preliminary experiments showed that any chloride ion in the film was also removed, probably *via* replacement of chloride by hydroxide ion. Dilute $(10^{-3} VF)$ nitric acid proved to be an effective wash solution because this exchange of hydroxide for chloride was prevented. Chronopotentiometric measurements of the quantity of film both before and after the washing procedure revealed that none of the film dissolved. Note that such measurements do not indicate that the composition of the film remains constant, but only that the quantity of *reducible* platinum is unchanged.

TABLE V

CHLORIDE CONTENT OF THE FILM AT pH 7

The platinum foil electrode (area $= 60$ cm^2) was filmed by anodization in 1.00 VF sodium chloride solution initially at pH 7.0

Chloride (mmoles × 10⁴)	Quantity of film (mC)
2.22	37.4
2.07	33.0
2.13	36.3
Average 2.14	35.6

Results of three determinations of the chloride content of the film formed in 1.00 VF sodium chloride solution at pH 7.0 are listed in Table V. The chronopotentiometric measurements of the quantity of the film are also presented.

(c) *Hydroxide (oxide) analysis*

The hydroxide (oxide) content of the film at pH 7 was determined by measuring the quantity of hydroxide ion formed by the cathodization of a freshly filmed (oxidized) electrode. For an electrode filmed with platinous hydroxide, cathodization will liberate one mole of hydroxide ion for each equivalent of film reduced, *i.e.*

$$Pt(OH)_2 + 2 e = Pt + 2 OH^-$$
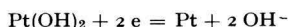
However, if a film of platinous hydroxide chloride (Pt(OH)Cl) is reduced, one-half mole of hydroxide ion will be formed for each equivalent of film, *i.e.*

$$Pt(OH)Cl + 2 e = Pt + Cl^- + OH^-$$
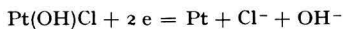
If the reduction of the film is accomplished chronopotentiometrically in an *unbuffered* solution, the quantity of film can be obtained from the transition time measurement and the amount of hydroxide ion can be determined by titration with standard acid.

Procedure for hydroxide analysis In precisely the same way as in the platinum and chloride analyses, the large (60 cm^2) foil electrode was filmed in an unbuffered 1.00 VF sodium chloride solution initially at a pH of 7.0. After the anodization the pH of the solution (which had decreased to about 6) was re-adjusted to pH 7 by elec-

tro-generating hydroxide ion with a small platinum wire electrode. The air-free solution was briefly stirred and the pH was measured to $\pm$ 0.001 pH unit. Then, after about one minute's time was allowed for the solution to become quiescent, the large (filmed) electrode was cathodized with a constant current until its potential just reached the inflection point of the cathodic chronopotentiogram. The solution (*ca.* 85 ml in volume) was stirred and titrated with standard 10^{-4} VF hydrochloric acid until the pH of the solution reached the same value to $\pm$ 0.001 pH unit that it had prior to cathodization of the electrode. The millimoles of standard acid added were equal to the millimoles of hydroxide ion present in the film. The pH measurements were made with a Beckman Model GS glass electrode pH meter which was readable to $\pm$ 0.001 pH unit.

The results of three determinations of the hydroxide ion content of the film in 1 VF sodium chloride solution at pH 7 are given in Table VI. The chronopotentiometric data for the quantity of film are also presented.

TABLE VI

HYDROXIDE ION CONTENT OF THE FILM AT pH 7

The platinum foil electrode (area = 60 cm²) was filmed by anodization in 1.00 VF sodium chloride solution initially at pH 7.0. The hydroxide ion formed on cathodization (see text) was titrated with 1.21 · 10^{-4} VF hydrochloric acid.

Hydroxide (mmoles · 10^4)	Quantity of film (mC)
2.17	45.7
2.24	50.0
2.42	45.1
Average 2.28	46.9

Note that the quantity of film at pH 7 for the platinum, chloride, and hydroxide analyses is variable. In the platinum analyses the quantity of film ($i\tau$) was about 32 mC for the electrode of area 60 cm² (Table IV). In the chloride and hydroxide analyses (Tables V and VI), $i\tau$ had values of 36 and 47 mC, respectively. These differences probably reflect changes in the "roughness factor" of the electrode. For the same reason the quantity of film ($i\tau/A$) formed on the large (60 cm²) electrode was different from $i\tau/A$ measured in 1 VF sodium chloride solution at pH 7 with the small (0.370 cm²) wire electrode (*vide supra*, Table II).

(d) Summary and discussion of results

In the interpretation of the data from the platinum, chloride, and hydroxide analyses (Tables IV, V, and VI), the analytical results have been expressed in terms of mmoles (of the particular ion) per mC (millicoulomb) of film. These values are summarized in Table VII.

The agreement of the amounts of $+2$ and $+4$ platinum found spectrophotometrically with the quantity of film (*reducible* platinum) measured chronopotentiometrically was pointed out earlier (*cf.*, Table IV). Therefore, we conclude that $+2$ and $+4$ platinum are the only cations present in the film. The probable error in the platinum analyses

is about $\pm$ 5–10%. From Table IV or from Table VII the sum of the mequiv. of +2 and +4 platinum per millicoulomb of film is calculated to be $9.6 \cdot 10^{-6}$. If the total quantity of film ($i\tau$) measured chronopotentiometrically corresponded only to oxidation of platinum, the sum of the mequiv. of +2 and +4 platinum per mC should be $10.4 \cdot 10^{-6}$. This latter figure is derived from the reciprocal of the Faraday constant (96,493 mC/mequiv.). The difference of about 8% between the two figures $9.6 \cdot 10^{-6}$ and

TABLE VII

SUMMARY OF ANALYTICAL DATA FOR FILM COMPOSITION IN 1.00 VF SODIUM CHLORIDE SOLUTION AT pH 7.0

Platinum:		
+2 state:	$2.9 \cdot 10^{-6}$	mmole/mC
+4 state:	$0.94 \cdot 10^{-6}$	mmole/mC
Chloride:	$6.0 \cdot 10^{-6}$	mmole/mC
Hydroxide:	$4.9 \cdot 10^{-6}$	mmole/mC

$10.4 \cdot 10^{-6}$ mequiv./mC falls within the expected range of error for the platinum analyses. However, the total quantity of electricity ($i\tau$) does include a contribution due to the charging of the electrical double layer. Consequently, one should expect that the quantity of platinum oxidized would be somewhat less than the chronopotentiometric quantity of electricity. Using the value of 30 μF/cm^2 reported by ROBERTSON[18] for the average capacitance of a platinum electrode in 1 VF hydrochloric acid and applying it to the present experiments in 1 VF sodium chloride solution, one calculates that of the 32 mC of film measured chronopotentiometrically (Table IV) approximately 3 or 4 mC were required to charge the double layer. This latter calculation suggests that the difference between the value for the mequiv. of platinum per mC of film found chemically ($9.6 \cdot 10^{-6}$) and the theoretical value ($10.4 \cdot 10^{-6}$) could be due almost entirely to the quantity of electricity needed to charge the double layer.

From Table VII the sum of the quantities of chloride and hydroxide ions is $10.9 \cdot 10^{-6}$ mmole/mC. Since each of these ions is singly charged, and provided these are the only anions present in the film, the theoretical sum should be $10.4 \cdot 10^{-6}$ mmole/mC (*vide supra*). The agreement between the experimental and theoretical values is remarkably good and proves that chloride and hydroxide are the only anionic constituents of the film. In a study of the accuracy of the method for the determination of chloride[21], known concentrations of chloride ion near $1 \cdot 10^{-6}$ VF were determinable with an error of about $\pm$ 5%. The error in determining the hydroxide content of the film was very probably of the same magnitude.

It should be emphasized that each of the analytical results (platinum, chloride, and hydroxide) is *independent* of the others. That the quantities of +2 and +4 platinum agree with the amounts of chloride and hydroxide ions and that these quantities account for all the chemical species in the film validate the methods of analysis used in this study.

It is known that +2 platinum forms a series of compounds of the type Pt(OH)$_x$-Cl$_{2-x}$, and a similar situation prevails for +4 platinum[22,23]. SIDGWICK[24] states that H$_2$PtOCl$_3$, a compound of +3 platinum, is stable in respect to disproportionation

into H_2PtOCl_2 (+2 platinum) and H_2PtOCl_4 (+4 platinum), but that the stability relations are reversed for the pure chloride complexes, *i.e.*, $PtCl_5^{2-}$ readily disproportionates into $PtCl_4^{2-}$ and $PtCl_6^{2-}$. Therefore, under the conditions of the present experiments at pH 7, it is conceivable that some +3 platinum is present in the film. It would have disproportionated, however, in the hydrochloric acid stripping solution. In the absence of more detailed information regarding the properties of these various platinum compounds, we conclude that anodization of a platinum electrode in an air-free, unbuffered 1.00 VF sodium chloride solution at pH 7 results in the formation of a film which consists of a mixture of +2 and +4 platinum oxychlorides in a molar ratio of about 3:1.

Analysis of film in 5 VF sodium chloride at pH 7

The effect on the film composition of increasing the chloride concentration to 5 VF at pH 7 was determined. The large (60 cm²) platinum electrode was filmed in a 5.00 VF sodium chloride electrolyte at pH 7 and was analyzed for platinum, chloride, and hydroxide in the same manner as described previously. A summary of these results is presented in Table VIII.

TABLE VIII

SUMMARY OF ANALYTICAL DATA FOR FILM COMPOSITION IN 5.00 VF SODIUM CHLORIDE SOLUTION AT pH 7.0

Platinum:		
+2 state:	$3.4 \cdot 10^{-6}$	mmole/mC
+4 state:	$0.8_5 \cdot 10^{-6}$	mmole/mC
Chloride:	$8.2 \cdot 10^{-6}$	mmole/mC
Hydroxide:	$2.9 \cdot 10^{-6}$	mmole/mC

The chloride content of the film in 5 VF sodium chloride is considerably larger than it is in 1 VF sodium chloride. The hydroxide content of the film is correspondingly smaller. The ratio of +2 to +4 platinum is 4:1. Again in these experiments the sum of the mequiv. of +2 and +4 platinum per mC ($10.2 \cdot 10^{-6}$) agrees well with the theoretical value of $10.4 \cdot 10^{-6}$ mequiv./mC. Also, the sum of the quantities of chloride and hydroxide ions ($11.1 \cdot 10^{-6}$ mmole/mC) is in satisfactory agreement with this theoretical figure.

As in 1 VF sodium chloride solution, the analytical data of Table VIII for 5 VF sodium chloride solution do not correspond uniquely to any specific platinum compounds. On the basis of the data in Table VIII, one can only state that at pH 7 in 5 VF sodium chloride, as in 1 VF sodium chloride solution, anodization of the electrode results in the formation of a mixture of +2 and +4 platinum oxychlorides. However, in the 5 VF sodium chloride electrolyte, the chloride content of the film is greater and the ratio of +2 to +4 platinum is somewhat larger than in 1 VF sodium chloride.

Analysis of film in 1 VF hydrochloric acid

The film formed in 1 VF hydrochloric acid is relatively much more readily soluble than the film formed in neutral sodium chloride solutions. Consequently, the simple

washing techniques employed in the analyses of the film at pH 7 could not be used, and, as a result, the film formed in 1 VF hydrochloric acid could not be analyzed for either chloride or hydroxide. No other straightforward analytical methods for accomplishing these analyses have been devised up to the present time. On the other hand, the analysis for platinum was simpler than at pH 7. After the electrode was anodized, the 1 VF hydrochloric acid electrolyte then served as the stripping solution for the platinum analysis. In its other details the procedure for the platinum analysis at pH 0 was the same as at pH 7 (*vide supra*).

The film was formed in 1.00 VF hydrochloric acid by anodization of the previously reduced (cleaned) 60 cm² electrode until its potential just reached + 0.71 V *vs.* S.C.E. Inasmuch as the film is relatively rapidly soluble in 1 VF hydrochloric acid, the transition time for the anodic chronopotentiogram is regarded as the more accurate measurement of the quantity of film. Table IX shows two results of the analysis for platinum and the pertinent chronopotentiometric data.

TABLE IX

PLATINUM ANALYSES FOR FILM FORMED IN 1 VF HYDROCHLORIC ACID

Spectrophotometric determination of platinum in film		Chronopotentiometric measurement of quantity of film		
+2 Platinum (mC)	Total platinum (mC)	i (mA)	τ (sec. measd. at +0.71 Vvs. S.C.E.)	iτ (mC)
8.9	8.9*	0.285	28.7	8.2
8.7	8.7*	0.284	26.0	7.4

* No +4 platinum was found.

The important result of these experiments is that only +2 platinum is formed by anodizing the electrode to +0.71 V *vs.* S.C.E. The absence of data for the chloride or hydroxide content of the film precludes its positive identification. However, all evidence obtained in the present study supports the conclusion that in 1 VF hydrochloric acid the film is $PtCl_2$.

That the film is neither $Pt(OH)_2$ nor $Pt(OH)Cl$ is demonstrated by the following observations. The potential range in which film formation occurs in 1 VF hydrochloric acid (*ca.* +0.3–0.7 V *vs.* S.C.E.) is approximately 500 mV more reducing than that in which platinum is oxidized to PtO and PtO_2 in 1 VF sulfuric acid (*cf.* curve 1, Fig. 1 and curve 1, Fig. 2). In addition, the quantity of film ($i\tau/A$) in 1 VF hydrochloric acid is 0.15 mC/cm², and this value is only one-fourth of that (0.60 mC/cm²) for the platinum oxide film in sulfuric acid medium (*cf.* curves 1 and 2, Fig. 6). Furthermore, between pH 0 and 2 the oxidation of platinum in 1 VF chloride medium occurs at very nearly the same potentials (Table II). The cathodic chronopotentiograms for film reduction at pH 0 and 2 also occur at the same potentials. For a platinous chloride ($PtCl_2$) film, no change in the values of the "transition potentials" for the anodic or cathodic chronopotentiograms should be observed when the pH of the electrolyte is varied. On the other hand, for films which contain hydroxide or oxide ion, the "transition potentials" do depend on the pH of the solution and become more reduc-

ing (less positive) as the pH is increased. In the case of Pt(OH)Cl the "transition potential" should decrease (become more reducing) by 30 mV for each unit increase in pH, and with Pt(OH)$_2$ a decrease of 60 mV should result. ANSON AND LINGANE[1] observed this pH dependence in their study of the platinum oxide film in various buffer solutions. The pH dependence of the "transition potential" for the platinum oxide film is also shown by the data in Table III.

Parenthetically, it should be mentioned that, in 1 VF chloride medium at pH 2.1, the increase in $i\tau/A$ and the slight decrease in the "transition potential" from the corresponding values at pH 0.1 (Table II) are evidence that there is a small quantity of hydroxide ion in the film at pH 2.1.

Analysis of film in 1 VF sodium chloride at pH 12

The chronopotentiometric measurements revealed that the quantity of film $(i\tau/A)$ in an electrolyte 1.00 VF in sodium chloride and 0.01 VF in sodium hydroxide (pH 12.2) is 0.84 mC/cm^2 (Table II). For the platinum oxide film, measurements of $i\tau/A$ in a 1.00 VF sodium sulfate and 0.01 VF sodium hydroxide solution at pH 12.3 gave the value 0.67 mC/cm^2 (Table III). The relative closeness of these two values indicated that the composition of the film in the chloride medium at pH 12 resembles the oxide film much more closely than at either pH 0 or pH 7.

The amounts of $+2$ and $+4$ platinum and of chloride ion in the film at pH 12.2 were determined. However, the direct determination of the hydroxide content of the film was not possible at pH 12 because changes occurred in the hydroxide content of the film when the electrode was washed to remove the electrolyte. Therefore, in the present experiments the hydroxide content of the film has been calculated by difference on the assumption that, as in the previous cases at pH 7, the sum of the quantities of chloride and hydroxide ions is $10.4 \cdot 10^{-6}$ mmole/mC. A summary of the analytical results is presented in Table X.

TABLE X

SUMMARY OF ANALYTICAL DATA FOR FILM COMPOSITION IN AN ELECTROLYTE 1.00 VF IN SODIUM CHLO-
RIDE AND 0.01 VF IN SODIUM HYDROXIDE (pH 12.2)

Platinum:		
$+2$ state:	$2.5 \cdot 10^{-6}$	mmole/mC
$+4$ state:	$1.3 \cdot 10^{-6}$	mmole/mC
Chloride:	$2.3 \cdot 10^{-6}$	mmole/mC
*Hydroxide:	$8.1 \cdot 10^{-6}$	mmole/mC

* Calculated by difference (see text).

These data show that at pH 12.2 the film contains a larger fraction of platinum in the $+4$ state than at the lower pH's. The ratio of $+2$ to $+4$ platinum at pH 12.2 is about 2:1. In addition, the chloride content of the film is considerably smaller than at pH 7. As for the previous studies at pH 7, the analytical data presented in Table X do not correspond to any definite platinum compounds, but very probably to a mixture of oxychlorides and oxides of $+2$ and $+4$ platinum.

Fig. 6 shows that at pH 12 (and at all pH's above about 10) the quantity of film, $i\tau/A$, in 1 VF sodium chloride solution is greater than the quantity of platinum oxide film in 1 VF sulfate medium. At lower pH's the presence of chloride in the film parallels the observation that $i\tau/A$ in chloride medium is smaller than the quantity of oxide film. Since the film in chloride medium at pH 12 is a mixture of platinum oxychlorides and oxides, one might expect that $i\tau/A$ would be smaller than the quantity of oxide film at the same pH. That, on the contrary, it is greater is undoubtedly caused by the much larger proportion of +4 platinum in the film formed in chloride medium (Table X) than in the platinum oxide film. ANSON AND LINGANE[1] only analyzed platinum oxide films formed in acidic solutions. These analyses showed that the molar ratio of PtO to PtO_2 was about 6:1. However, the constancy of $i\tau/A$ with pH observed by these authors and also in the present study (Table III) provides evidence that the composition of the platinum oxide film does not change under the prevailing experimental conditions.

SUMMARY

Chronopotentiometric studies and direct chemical analyses have established that platinum chloride and oxychloride films are formed on platinum electrodes which are anodically polarized in acid, neutral, and alkaline chloride media. A comparison of these films with the platinum oxide films formed in sulfate media has also been made.

Evidence has been obtained to support the conclusion that in 1 VF hydrochloric acid a $PtCl_2$ film is formed. The quantity of this film (0.15 mC/cm²) is only one-fourth that for the platinum oxide film formed in 1 VF sulfuric acid.

A film consisting of a 3:1 mixture of +2 and +4 platinum oxychlorides is formed in a 1 VF sodium chloride electrolyte at pH 7. A complete analysis of the film for +2 and +4 platinum, chloride, and hydroxide has been performed. When a platinum electrode is anodized in 5 VF sodium chloride solution at pH 7, a film is formed which, like the film formed in 1 VF sodium chloride, is a mixture of oxychlorides of +2 and +4 platinum. However, in 5 VF sodium chloride the ratio of +2 to +4 platinum is increased to 4:1 and the quantity of chloride ion in the film is larger.

Anodization of a platinum electrode in 1 VF sodium chloride solution at pH 12 produces a film of +2 and +4 platinum oxychlorides. The ratio +2 to +4 platinum was found to be about 2:1, and the amount of chloride in the film proved to be much smaller than at pH 7.

ACKNOWLEDGEMENT

REFERENCES

1 F. C. ANSON AND J. J. LINGANE, *J. Am. Chem. Soc.*, 79 (1957) 4901.
2 H. A. LAITINEN AND C. G. ENKE, *J. Electrochem. Soc.*, 107 (1960) 773.
3 J. J. LINGANE, *J. Electroanal. Chem.*, 2 (1961) 296.
4 W. M. LATIMER, *Oxidation Potentials*, Prentice-Hall, Inc., New York, 1952.
5 G. GRUBE, *Z. Elektrochem.*, 35 (1929) 703.
6 F. BRAN, *Z. Elektrochem.*, 8 (1902) 197.
7 F. HABER, *Z. anorg. Chem.*, 16 (1898) 442.

8 F. HABER AND S. GRINBERG, *Z. anorg. Chem.*, 16 (1898) 342.
9 W. S. WOOSTER, P. S. FARRINGTON AND E. H. SWIFT, *Anal. Chem.*, 21 (1949) 1457.
10 C. MARIE, *J. chim. phys.*, 6 (1908) 605.
11 R. RUER, *Z. Elektrochem.*, 14 (1908) 309.
12 F. MÜLLER AND A. RIEFKOHL, *Z. Elektrochem.*, 36 (1930) 181.
13 J. J. LINGANE, *Electroanalytical Chemistry*, 2nd edn., Interscience Publishers, Inc., New York, 1958.
14 J. J. LINGANE, *J. Electroanal. Chem.*, 1 (1960) 379.
15 D. G. PETERS AND J. J. LINGANE, *J. Electroanal. Chem.*, 2 (1961) 1.
16 J. J. LINGANE, *J. Electroanal. Chem.*, 2 (1961) 46.
17 J. J. LINGANE, *J. Am. Chem. Soc.*, 75 (1953) 788.
18 W. D. ROBERTSON, *J. Electrochem. Soc.*, 100 (1953) 194.
19 F. C. ANSON, *Ph.D. Thesis*, Harvard University, 1957.
20 J. KIRKLAND AND J. YOE, *Anal. Chim. Acta*, 9 (1953) 441.
21 D. G. PETERS AND J. J. LINGANE, *Anal. Chim. Acta*, in press.
22 J. W. MELLOR, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, Green, and Company, New York, 1937.
23 *Gmelin's Handbuch der anorganischen Chemie*, Verlag Chemie, G.m.b.h., Berlin, 1951.
24 N. V. SIDGWICK, *The Chemical Elements and their Compounds*, Oxford University Press, London, 1950.

KATALYTISCHE WASSERSTOFFWELLEN DER ÄTHYLENIMINO-BENZOCHINONE

III. DIE HYDROLYTISCHE ÄTHYLENIMINORINGSPALTUNG

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In den vorangehenden Mitteilungen[1,2] war gezeigt worden, dass eine elektroreduktive Spaltung der protonisierten Äthylenimino-Ringe im Potentialbereich der negativeren Welle erfolgt. Aus der pH-Abhängigkeit des Polarogramms von 2,5-Bis-(äthylenimino)-3,6-bis-(*n*-propoxy)-benzochinon-(1,4)[3] und anderer Äthylenimino-Chinone sowie den Elektronenspektren in saurer Lösung[3] musste andererseits auf eine hydrolytische Ringspaltung geschlossen werden. In vorliegender Arbeit wird ihre Kinetik polarographisch und spektrophotometrisch analysiert und aus den Aktivierungsparametern auf den Reaktionsmechanismus rückgeschlossen.

EXPERIMENTELLES

Zur polarographischen Verfolgung der Reaktion wurde diese direkt in einer temperierbaren polarographischen Zelle[4] durchgeführt. Die Temperatur wurde dabei auf ±0.05° konstant gehalten. Wegen der relativ schweren Löslichkeit des A_1 in Wasser enthielten alle Lösungen 10% Äthanol. Wässrige Pufferlösung und alkoholische Lösung des A_1 wurden vom gelösten Sauerstoff befreit und auf die gewünschte Reaktionstemperatur gebracht. Durch Mischen beider Lösungen wurde die Reaktion gestartet.

Zur polarographischen Registrierung wurde ein Polarograph System HEYROVSKÝ Typ V 301 bzw. ein LP 55 verwendet. Als Gegenelektrode diente eine Normal-Sulfat-Elektrode (NSE), die mit ihrem relativ positiven Potential in diesem Fall günstiger war. Die pH-Werte der verwendeten Acetat-Pufferlösungen wurden mit dem pH-Meter 4 der Firma Radiometer Kopenhagen gemessen.

Die Absorptionsspektren der Ausgangs- und Endprodukte wurden mit dem Universalspektrophotometer (C. Zeiss, Jena) gemessen und die zeitliche Änderung des Absorptionsspektrums der Reaktionslösung mit dem Beckmann DK 2 verfolgt.

An Substanzen wurden hauptsächlich das als Bayer E 39 bekannte 2,5-Bis-(äthylenimino)-3,6-bis-(*n*-propoxy)-benzochinon-(1,4), (Kurzbezeichnung A_1) als Reaktant verwendet und zum Vergleich die Verbindungen: 2,5-Bis-(äthylenimino)-3,6-(dichlor)-benzochinon-(1,4), (Kurzbezeichnung A_2); 2,5-Bis-(β-oxyäthylamino)-3,6-(dichlor)-benzochinon-(1,4), (Kurzbezeichnung C_1); 2-Äthylenimino-5,6-dimethyl-benzochinon-(1,4), (Kurzbezeichnung A_3) herangezogen.

ERGEBNISSE

Die hydrolytische Ringspaltung lässt sich sowohl aus einer Aufteilung der Chinonstufe als auch aus der Abnahme der diffusionsbegrenzten negativen Äthyleniminostufe
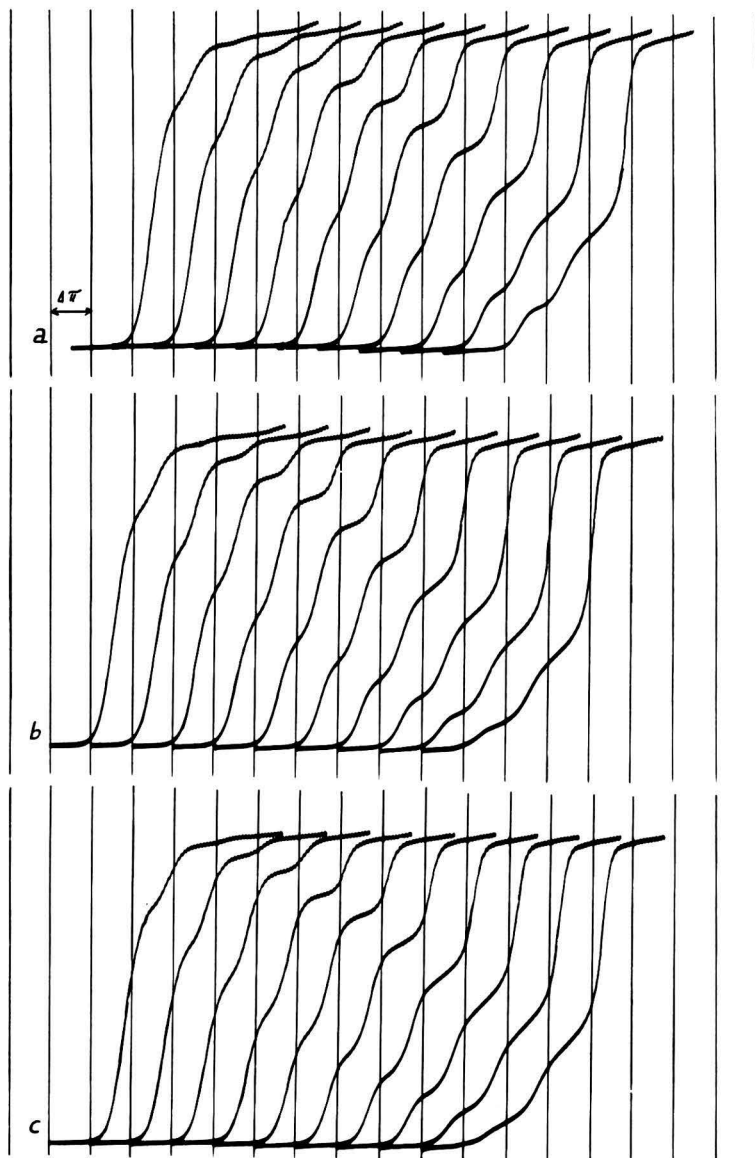
Fig. 1. Saure Hydrolyse von A_1: (a) Acetatpuffer pH 4.05, $\vartheta = 25°$, $\Delta\pi = 0.1$ V, NSE, $[A_1]_0 = 5 \cdot 10^{-4}$ mol l^{-1}, ab —0.15 V registriert nach: 6–12–18–24–30–36–42–50–58–65 min; (b) Acetatpuffer pH 4.26, $\vartheta = 25°$, $\Delta\pi = 0.1$ V, NSE, $[A_1]_0 = 5 \cdot 10^{-4}$ mol l^{-1}, ab —0.2 V registriert nach: 12–24–36–48–60–72–84–96–108–120 min; (c) Acetatpuffer pH 4.46, $\vartheta = 25°$, $\Delta\pi = 0.1$ V, NSE, $[A_1]_0 = 5 \cdot 10^{-4}$ mol l^{-1}, ab —0.2 V registriert nach: 17–34–51–71–85–102–119–136–153–170 min.

verfolgen. Beide Möglichkeiten sollen an dem Chinonderivat A_1 als Reaktant verglichen werden.

Die zeitliche Änderung der Chinonstufe in saurer Lösung

In saurer Lösung teilt sich die A_1-Chinonreduktionsstufe mit der Zeit in drei Stufen auf (Fig. 1). Gleichzeitig wird eine Änderung des spektralen Verhaltens der wässrig-alkoholischen Lösung im Sichtbaren und UV beobachtet. Die im Polarogramm in Abhängigkeit der Zeit neu entstehenden Stufen liegen bei negativeren Potentialen als die Stufe der Ausgangsverbindung A_1. Die Gesamtstufenhöhe bleibt dabei in den Fehlergrenzen konstant. Dieses Verhalten zeigt, dass die Ausgangsverbindung im sauren Milieu unbeständig ist. Eine Reaktion ist an den beiden Äthyleniminringen zu erwarten.

Trägt man die relativen Stufenhöhen als Mass der Konzentrationen über der Zeit auf, so erhält man folgendes Bild (Fig. 2a). Das Ausgangsprodukt, allgemein als A
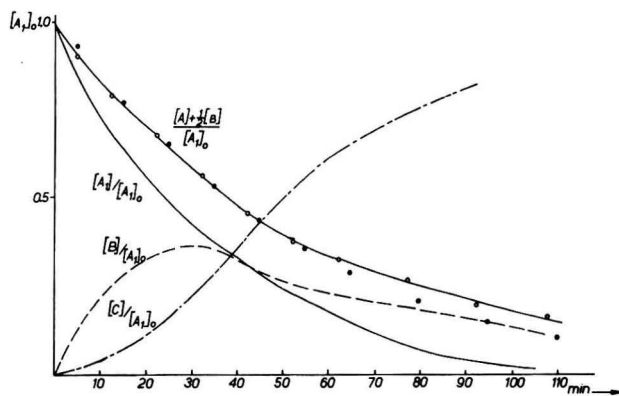
Fig. 2. (a) Die zeitliche Abnahme der relativen Konzentrationen $[A_1]/[A_1]_0$, $[B]/[A_1]_0$ und $[C]/[A_1]_0$; (b) Die Höhe der Äthyleniminwelle $\{[A_1] + \frac{1}{2}[B]\}/[A_1]_0$ als Funktion der Zeit: O, experimentell; ●, berechnet mit den Konstanten: $k_1 = 0.0275$ min^{-1}; $k'_1 = 0.033$ min^{-1} in Acetatpuffer pH 4.05; $[A_1]_0 = 7 \cdot 10^{-4}$ mol l^{-1}; $\vartheta = 25°$.

in den Diagrammen und Formeln bezeichnet, nimmt nach dem Zeitgesetz einer Reaktion 1. Ordnung (positivste Stufe) ab. Die entstehende zweite Stufe entspricht einem Zwischenprodukt B, dessen Konzentration bis zu einem Maximum wächst und mit fortschreitender Zeit wieder abnimmt. Die dritte Stufe entspricht dem Endprodukt C, das nach einer Induktionsperiode eine maximale Bildungsgeschwindigkeit erreicht, die mit fortlaufender Zeit wieder abnimmt. Dieses Verhalten ist charakteristisch für eine Folgereaktion nach dem Schema

$$A \overset{k_1}{\to} B \overset{k'_1}{\to} C \qquad (1)$$

Der einfachste Fall eines solchen Reaktionstyps ist gegeben, wenn ein Reaktant A irreversibel nach 1. Ordnung in ein Zwischenprodukt B übergeht, welches gleichzeitig irreversibel nach 1. Ordnung zum Endprodukt C reagiert.

Für die zeitliche Konzentrationsänderung der drei Komponenten gelten folgende Gleichungen[5]:

$$\frac{d[A]}{dt} = -k_1[A] \tag{2}$$

$$\frac{d[B]}{dt} = k_1[A] - k'_1[B] \tag{3}$$

$$\frac{d[C]}{dt} = k'_1[B] \tag{4}$$

Durch Integration erhält man unter Berücksichtigung der Randbedingungen:

$$[A] = [A]_0 e^{-k_1 t} \tag{5}$$

$$[B] = [A]_0 \frac{k_1}{k'_1 - k_1} (e^{-k_1 t} - e^{-k'_1 t}) \tag{6}$$

$$[C] = [A]_0 \left\{ 1 + \frac{1}{k_1 - k'_1} (k'_1 e^{-k_1 t} - k_1 e^{-k'_1 t}) \right\} \tag{7}$$

In vorliegendem Fall sind k_1 und k'_1 zusammengesetzte Brutto-Konstanten, weshalb sie als $\bar{k}_1$ und $\bar{k}'_1$ in den folgenden Erörterungen bezeichnet werden. Zur Ermittlung von $\bar{k}_1$ wurde die graphische Methode angewendet, die sich durch Einfachheit und Zuverlässigkeit auszeichnet. Aus Gleichung (5) folgt, dass $\ln [A]/[A]_0$ gegen die Zeit t aufgetragen eine Gerade mit der Steigung $-\bar{k}_1$ ergibt. Aus zwei Punkten der Geraden erhält man:

$$\bar{k}_1 = 2.303 \, \frac{\log \dfrac{[A]_1}{[A]_0} - \log \dfrac{[A]_2}{[A]_0}}{t_2 - t_1} \tag{8}$$

Die Ermittlung der Konstanten $\bar{k}'_1$ ist im vorliegenden Beispiel wesentlich vereinfacht, weil das Zwischenprodukt B eine getrennte Stufe verursacht. Für die maximale Konzentration von B gilt:

$$\frac{d[B]}{dt} = 0 \tag{9}$$

Wir erhalten dann aus Gleichung (6):

$$\bar{k}'_1 e^{-\bar{k}'_1 t} = \bar{k}_1 e^{-\bar{k}_1 t} \tag{10}$$

Eine spezielle Form dieser Gleichung ist:

$$[B]_{max} = [A]_0 \frac{\bar{k}_1}{\bar{k}'_1} e^{-\bar{k}_1 t} \tag{10.1}$$

Weiterhin gilt:

$$t_{max} = \frac{\ln \bar{k}_1 - \ln \bar{k}'_1}{\bar{k}_1 - \bar{k}'_1} \tag{11}$$

$[B]_{max}$ und t_{max} genügen zur Bestimmung von $\bar{k}'_1$. Aus den Gleichungen (10.1) und (11) erhalten wir:

$$\bar{k}'_1 = \frac{\ln [A]_0 - \ln [B]_{max}}{t_{max}} \tag{12}$$

Die zeitliche Änderung der Äthyleniminostufe in saurer Lösung

Vergleichende Untersuchungen am A_1 und anderen Äthyleniminochinonen sowie am 2,3,5,6-Tetraäthylenimino-benzochinon-(1,4) haben gezeigt, dass die negative Stufe durch eine reduktive Spaltung der Äthyleniminringe bedingt ist[2].

Im sauren Milieu erfolgt eine chemische Hydrolyse der Äthyleniminringe und die Äthyleniminwelle nimmt mit fortschreitender Reaktion ab. Bei einigen pH-Werten wurde die Aufspaltung der Chinonstufe gleichzeitig mit der Abnahme der negativen Welle zeitlich verfolgt (Fig. 3).
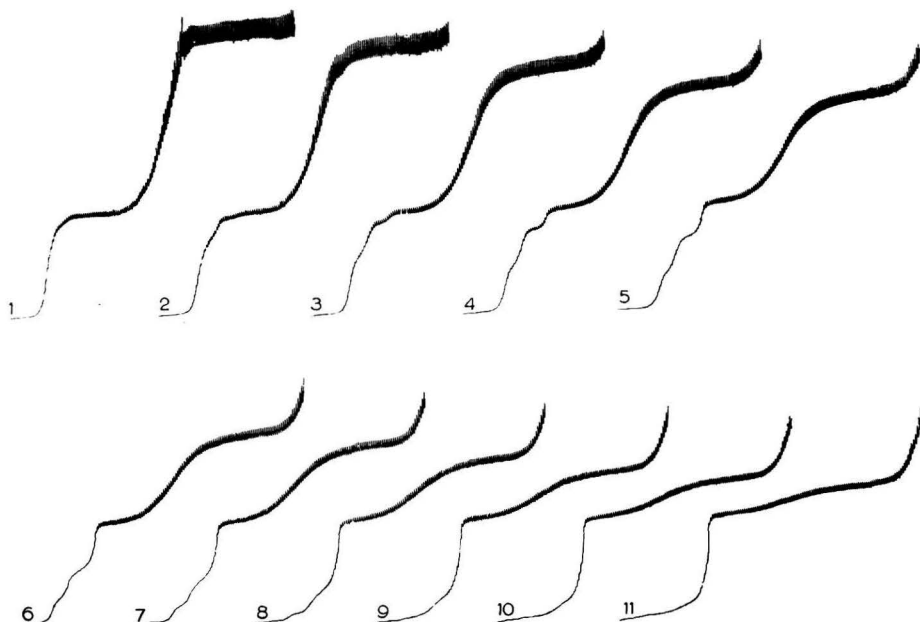
Fig. 3. Aufspaltung der Chinonreduktionsstufe und gleichzeitige Abnahme der Äthyleniminwelle während der sauren Hydrolyse von A_1: In Acetatpuffer pH 4.05, $[A_1]_0 = 7 \cdot 10^{-4}$ mol 1^{-1}, NSE; In der Reihenfolge 1,2,3... nach 3–10–20–30–40–50–60–75–90–105– und 120 min registriert.

Die Zeitgesetze der Aufspaltung der Chinonreduktionsstufe und der Abnahme der negativen Welle sollten für den Fall, dass die chemische Hydrolyse nach einem Folgemechanismus abläuft, einen Zusammenhang zeigen:

Die Höhe der negativen Welle ist in jedem Zeitpunkt t der Summe aus dem noch vorhandenen Ausgangsprodukt A und dem Zwischenprodukt B mit noch einem intakten Ring proportional. Dabei ist zu beachten, dass A mit noch zwei intakten Ringen den doppelten Beitrag zur Gesamtstufenhöhe leistet wie B, da jeder Ring unter Aufnahme von zwei Elektronen reduziert wird. Für die zeitliche Abnahme der negativen Welle gilt dann:

$$\frac{[A] + \tfrac{1}{2}[B]}{[A]_0} = e^{-\bar{k}_1 t} + \tfrac{1}{2} \left\{ \frac{\bar{k}_1}{\bar{k}'_1 - \bar{k}_1} (e^{-\bar{k}_1 t} - e^{-\bar{k}'_1 t}) \right\} \tag{13}$$

In Fig. 2(b) ist die zeitliche Änderung der relativen Stufenhöhe für ein Beispiel wiedergegeben. Bis zu einem Gesamtumsatz von etwa 75% ist gute Übereinstimmung zwischen der gemessenen und der aus den Konstanten k_1 und k'_1 der chemischen Hydrolyse berechneten Abnahme der negativen Welle vorhanden.

Eine weitere Stütze für den Folgemechanismus ist das polarographische Verhalten von Substanz A_3 (2-Äthylenimino-5,6-dimethyl-benzochinon-(1,4)). Diese Verbindung mit nur einem Äthyleniminring zeigt im sauren Gebiet nur eine Aufspaltung ihrer Reduktionswelle (Fig. 4).
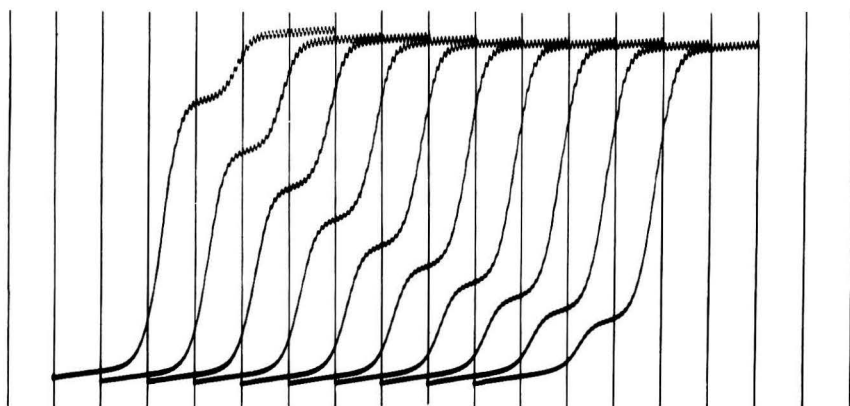
Fig. 4. Hydrolyse eines Mono-Äthylenimino-Chinons A_3: $[A_3]_0 = 5 \cdot 10^{-4}$ mol l^{-1}; Acetatpuffer pH 5.32, $\vartheta = 25°$, $\Delta\pi = 0.1$ V, NSE, $S = 1:30$, ab —0.1 V registriert nach: 25–50–75–100–125–150–175–200–225–250 min.

Das Ausgangsprodukt (erste Stufe) nimmt nach dem Zeitgesetz einer Reaktion 1. Ordnung ab. Die Reaktionsgeschwindigkeit ist unter vergleichbaren Bedingungen grösser als die beim A_1.

Bei pH 5.32 und $\vartheta = 25°$

$$A_1: k_1 = 0.002 \quad \text{min}^{-1}$$

$$A_3: k_1 = 0.0077 \quad \text{min}^{-1}$$

Die Abhängigkeit der Geschwindigkeitskonstanten von der Anfangskonzentration

In Acetatpuffer pH 4.27 mit der Ionenstärke $\mu = 0.1$ wurde die Reaktion bei verschiedenen Anfangskonzentrationen an A_1 verfolgt. In Tabelle I sind die Ergebnisse zusammengefasst.

TABELLE I

$[A_1]_0(mol\ l^{-1})$	$10^2 \cdot \bar{k}_1(min^{-1})$	$10^2 \cdot \bar{k}'_1(min^{-1})$
$6 \cdot 10^{-5}$	1.50	1.11
$1 \cdot 10^{-4}$	1.54	1.16
$2.5 \cdot 10^{-4}$	1.62	1.25
$5 \cdot 10^{-4}$	1.61	1.70

Die Geschwindigkeitskonstante k_1 ist in den Fehlergrenzen unabhängig von der Anfangskonzentration. Unter den gewählten Bedingungen verläuft demnach die Reaktion nach der 1. Ordnung. Die Werte für k'_1 zeigen keine so gute Konstanz. Der Grund dafür ist in der etwas schwierigeren Auswertung der Höhe der zweiten und dritten Stufe bei grösseren Gesamtkonzentrationen zu suchen.

Die Abhängigkeit der Geschwindigkeitskonstanten vom pH-Wert

Bei einer Substratkonzentration von $5 \cdot 10^{-4}$ mol l^{-1} wurde die Reaktionsgeschwindigkeit in Acetatpuffern von verschiedenem pH-Wert gemessen. Alle Puffer wurden durch Zusatz einer entsprechenden Menge NaNO$_3$ auf die Ionenstärke $\mu = 0.1$ gebracht.

Tabelle II und Fig. 5 zeigen die Ergebnisse.

TABELLE II

pH	$10^2 \cdot \bar{k}_1$ (min^{-1})	$10^2 \cdot \bar{k}'_1$ (min^{-1})
3.68	5.64	6.60
4.05	2.67	3.70
4.27	1.67	1.83
4.46	1.19	1.20
4.64	0.83	0.86
4.74	0.63	0.60
5.05	0.34	0.32
5.32	0.20	0.19

Die Untersuchung bei niedrigeren pH-Werten ist polarographisch durch fortlaufende Registrierung der Gesamtstufe wegen der schon relativ hohen Reaktionsgeschwindigkeit nicht mehr möglich. Da im sauren Gebiet die Potentialdifferenz zwischen der ersten und zweiten Stufe zu gering ist, konnte die potentiostatische Methode nicht mit ausreichender Genauigkeit angewendet werden (vgl. dazu ref.[11]).

Die Abhängigkeit der Geschwindigkeitskonstanten von der Pufferkonzentration

Die Versuche bei verschiedenen pH-Werten haben den Einfluss der Protonenkonzentration auf die Reaktionsgeschwindigkeit gezeigt. Es ist weiterhin von Interesse, ob nur die Säure H$_3$O$^+$, oder allgemein alle Säuren HA die Reaktion beschleunigen; d.h. ob sie spezifisch oder allgemein säurekatalysiert ist.

TABELLE III

HAc (mol l^{-1})	Ac$^-$ (mol l^{-1})	$10^2 \cdot \bar{k}_1$ (min^{-1})
HAc/Ac$^-$ = 4.0:		
0.032	0.008	2.58
0.080	0.020	2.67
0.160	0.040	2.85
0.320	0.080	3.20
HAc/Ac$^-$ = 2.33:		
0.014	0.006	1.60
0.056	0.024	1.67
0.140	0.060	1.90

Dazu wurde die Reaktion in verschiedenen Pufferlösungen untersucht, bei denen die Gesamtpufferkonzentration variiert wurde, das Verhältnis Säure/Base jedoch konstant blieb. Da die Dissoziationskonstante K_c der Säure sich mit der Salzkonzentration ändert (sekundärer Salzeffekt), wurde durch Zusatz entsprechender Mengen $NaNO_3$ für eine konstante Ionenstärke $\mu = 0.1$ gesorgt. K_c ist in erster Näherung nur
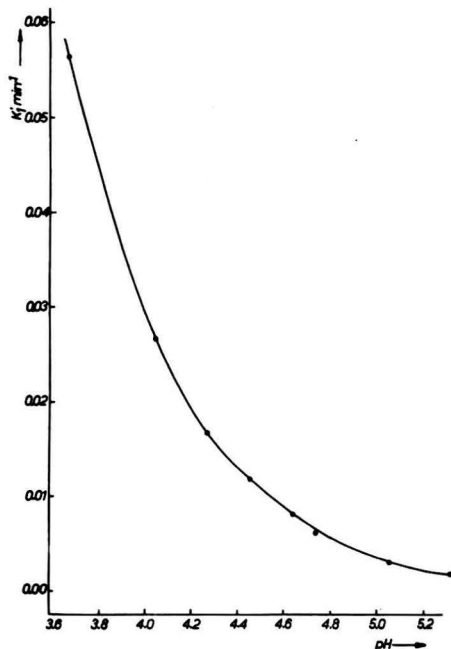
Fig. 5. Die Abhängigkeit der Brutto-Geschwindigkeitskonstanten k_1 vom pH-Wert.
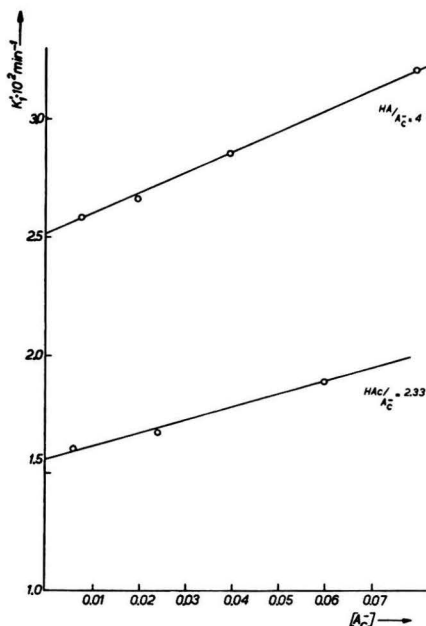
Fig. 6. Die Abhängigkeit der Brutto-Geschwindigkeitskonstanten k_1 von der Pufferkonzentration für zwei verschiedene Pufferreihen.

von der Ionenstärke und nicht von der Art der anwesenden Salze abhängig, somit sind diese Pufferlösungen isoprotonisch.

In Tabelle III sind die Ergebnisse für zwei Pufferserien wiedergegeben. Es wurde nur Teilreaktion 1 berücksichtigt, da k_1 genauer als k'_1 bestimmt werden kann.

Beide Versuchsreihen lassen eine geringe Abhängigkeit der Reaktionsgeschwindigkeit von der Pufferkonzentration erkennen. Die Unterschiede in k_1 liegen zum Teil noch innerhalb der Fehlergrenze, jedoch zeigen die Werte für k_1 einen deutlichen Gang mit steigender Pufferkonzentration. Fig. 6 zeigt, dass die Abhängigkeit zwischen k_1 und der Pufferkonzentration linear ist. Die für verschiedene Verhältnisse HAc/Ac⁻ erhaltenen Geraden zeigen einen Unterschied in ihrer Neigung. Dieser Befund deutet darauf hin, dass die Reaktion in geringem Mass auch von der Acetationenkonzentration beeinflusst wird.

Die Hydrolyse in alkalischer Lösung

Um entscheiden zu können, ob Basen allgemein die Reaktion beschleunigen, wurden Versuche in verdünnter wässriger NaOH durchgeführt.

Unter diesen Bedingungen wurde im Polarogramm ebenfalls eine doppelte zeit-abhängige Aufspaltung der Stufe des Ausgangsproduktes (Fig. 7) und eine gleich-zeitige Änderung des Spektrums beobachtet. Die Potentialdifferenz zwischen den einzelnen Stufen ist im alkalischen Gebiet grösser als bei pH < 7. Dies ist durch ver--
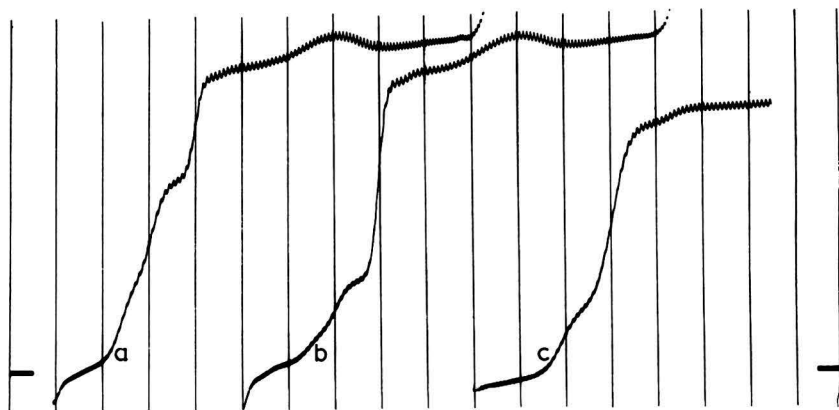
Fig. 7. Produkte der alkalischen Hydrolyse: $[A_1]_0$ $5 \cdot 10^{-4}$ mol l^{-1}; 0.05 N NaOH; $\vartheta = 25°$; NSE; $S = 1:30$; (a) und (b) $\Delta\pi = 0.2$ V; (c) $\Delta\pi = 0.1$ V; (a) nach 7 min; (b) nach 22 min Reaktions-dauer ab —0.4 V registriert; (c) nach 27 min Reaktionszeit neutralisiert (pH 6.90) und ab —0.3 V registriert.
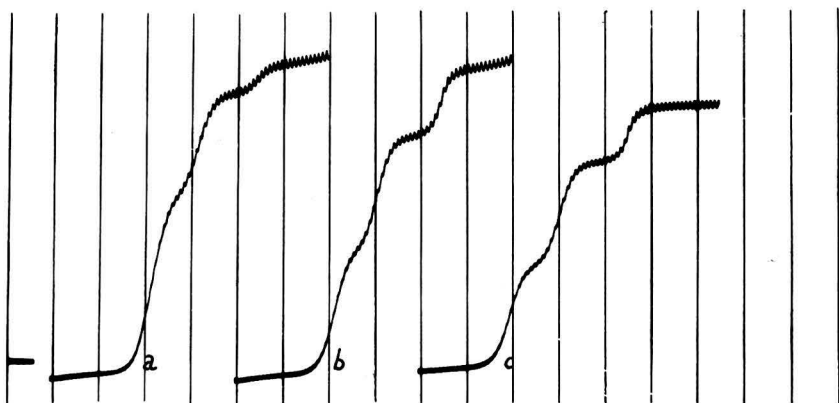
Fig. 8. Produkte der sauren Hydrolyse: $[A_1]_0$ $5 \cdot 10^{-4}$ mol l^{-1}; Acetatpuffer pH 4.05; $\vartheta = 25°$; $\Delta\pi = 0.1$ V, NSE; $S = 1:30$; (a) nach 20 min; (b) nach 35 min Reaktionsdauer ab —0.1 V registriert; (c) nach 39 min Reaktionszeit neutralisiert (pH 6.95) und ab —0.3 V registriert.

schiedene pH-Abhängigkeit der Halbstufenpotentiale der einzelnen Produkte bedingt. Die Stufen c in Figs. 7 und 8 sind bei gleichem pH-Wert registriert, nachdem einmal sauer und einmal alkalisch hydrolysiert wurde. Sie zeigen, dass in beiden Fällen die Produkte polarographisch gleich sind. Es kann noch qualitativ ausgesagt werden, dass

im alkalischen Milieu das Verhältnis k'_1/k_1 kleiner ist als bei pH < 7, das bedeutet eine grössere Stabilität des Zwischenproduktes B im alkalischen Gebiet. Die Reduktionsstufe des Ausgangsproduktes A wird im alkalischen Milieu aufgespalten. Das
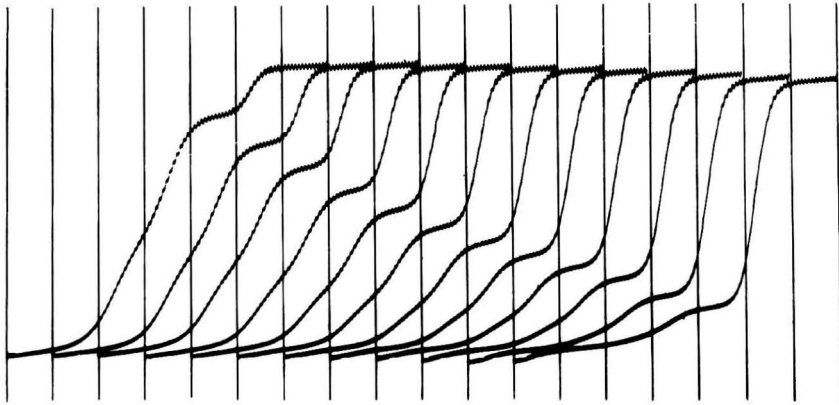
Fig. 9. Alkalische Hydrolyse, Semichinonstufe von $[A_1]_0$ $5 \cdot 10^{-4}$ mol l^{-1}; 0.02 N NaOH; $\vartheta = 25°$; $\varDelta\pi = 0.1$ V, NSE; $S = 1:30$; ab —0.45 V nach 7–14–21–28–35–42–49–56–63–70–85–100 min bis zum Diffusionsstrom des Zwischenproduktes registriert.

Verhältnis beider Stufen bleibt zeitlich konstant (Fig. 9). Diese Aufspaltung ist durch stufenweise Reduktion des Chinons über das Semichinon zum Hydrochinon bedingt, wie es beim Durochinon z.B. bekannt ist.

Die Teilgeschwindigkeitskonstanten der allgemeinen Säure–Basenkatalyse

Für die Geschwindigkeit einer allgemein säure--basenkatalysierten Reaktion gilt:

$$k = \sum_i k_{HA_i} \cdot [HA_i] + \sum_j k_{B_j} \cdot [B_j] \qquad (14)$$

HA und B sind Säuren bzw. Basen nach der Brönsted'schen Definition. Für die Reaktion in Acetatpuffer erhalten wir für die Gesamtgeschwindigkeit:

$$k = k_0 + k_{H_3O^+} \cdot [H_3O^+] + k_{OH^-} \cdot [OH^-] + k_{HAc} \cdot [HAc] + k_{Ac^-} \cdot [Ac^-] \qquad (14.1)$$

k_0 ist die Geschwindigkeitskonstante der durch Wasser katalysierten Reaktion. Es entsteht die Frage, unter welchen Bedingungen eine Ermittlung der einzelnen Konstanten möglich ist? Gleichung (14.1) kann zunächst vereinfacht werden zu

$$k = k'' + \alpha[Ac^-] \qquad (14.2)$$

wobei

$$k'' = k_0 + k_{H_3O^+} \cdot [H_3O^+] + k_{OH^-} \cdot [OH^-] \qquad (14.3)$$

und

$$\alpha = k_{Ac^-} + k_{HAc} \cdot HAc/Ac^- \qquad (14.4)$$

$k_{1;OH^-} = k_{OH^-}/[OH^-]$ wurde aus den Versuchen in verdünnter NaOH zu 0.85 l mol^{-1}

min^{-1} bestimmt. Unter den gewählten Bedingungen pH ~ 4.3 kann der Term $k_{OH^-}\cdot$ [OH$^-$] vernachlässigt werden. Die spontane Reaktion in 10%igem wässrigen Äthanol ergab eine Konstante $k_{1;0} = 1.0\cdot10^{-4}$ min^{-1}; dieser Term kann ebenfalls vernachlässigt werden. Eine Extrapolation der gemessenen Reaktionsgeschwindigkeiten bei verschiedenen Pufferkonzentrationen auf die Pufferkonzentration Null führt somit zu $k_{H_3O^+}\cdot$[H$_3$O$^+$]. Die wahre Geschwindigkeitskonstante für die Katalyse durch H$_3$O$^+$ wurde zu $k_{1;H_3O^+} = 286$ l mol^{-1}min^{-1} bestimmt. Für die verwendeten Pufferreihen sind x und k'' konstant und können bestimmt werden. Aus zwei Pufferreihen mit verschiedenem Verhältnis HAc/Ac$^-$ können die Konstanten k_{HAc} und k_{Ac^-} einzeln eɪmittelt werden. Es wurden folgende Werte gefunden:

$$k_{HAc} = 0.0186 \text{ l mol}^{-1}\text{min}^{-1}$$

$$k_{Ac^-} = 0.0124 \text{ l mol}^{-1}\text{min}^{-1}$$

Für die Gesamtgeschwindigkeit der Reaktion in wässrigem Acetatpuffer erhalten wir

$$k = 0.0001 + 286[\text{H}_3\text{O}^+] + 0.0186[\text{HAc}] + 0.0124[\text{Ac}^-] \tag{14.5}$$

In Tabelle IV sind die experimentellen Werte für k_1 und die nach Gleichung (14.5) berechneten Werte für Acetatpuffer bei verschiedenen pH-Werten gegenübergestellt.

TABELLE IV

pH	$10^2\cdot k_1$ (exp.) (min^{-1})	$10^2\cdot k_1$ (ber.) (min^{-1})
3.68	5.64	6.16
4.05	2.67	2.72
4.27	1.67	1.70
4.46	1.19	1.15
4.64	0.83	0.81
4.74	0.63	0.67
5.05	0.34	0.40
5.32	0.20	0.27

Die Abhängigkeit der Geschwindigkeitskonstanten von der Temperatur

Die Abhängigkeit der Reaktionsgeschwindigkeit von der Temperatur wird für ein nicht zu grosses Temperaturintervall durch die Arrhenius'sche Gleichung

$$k = Z\,e^{-E_A/RT} \tag{15}$$

wiedergegeben:

E_A = Arrhenius'sche Aktivierungsenergie;
Z = Frequenzfaktor.

Nach der Theorie der Übergangszustandes (Transition state) gilt für die Geschwindigkeit einer Reaktion

$$k = \frac{\mathcal{X}T}{h}\,e^{-\Delta G^\star/RT} \tag{16}$$

$\mathcal{X}$ = Boltzmann–Konstante;
h = Planck'sches Wirkungsquantum;
Da

$$\Delta G^\star = \Delta H^\star - T\Delta S^\star \tag{17}$$

gilt, ergibt sich aus einem Vergleich von Gleichung (15) mit Gleichung (16):

$$Z = \frac{e \varkappa T}{h} \ e^{\Delta S^{\star}/R}$$ (18)

Die Grössen $\Delta G^{\star}$, $\Delta H^{\star}$ und $\Delta S^{\star}$ beziehen sich auf das Gleichgewicht des Übergangs-zustandes nach der Theorie von LAIDLER. Sie sind mit den Grössen der Arrhenius'-schen Gleichung folgendermassen verknüpft:

$$\Delta H^{\star} = E_A - RT$$ (19)

$$\Delta S^{\star} = 4.576 \log \frac{Z}{T} - 49.203$$ (20)

Für eine allgemein säure–basenkatalysierte Reaktion ist unter Bedingungen, bei denen sowohl die saure als auch die basische Katalyse zur Geltung kommt, der
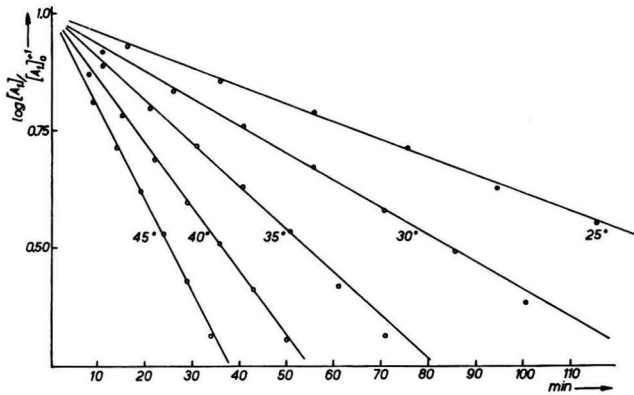
Fig. 10. Temperaturabhängigkeit der Startreaktion (A → B) in Acetatpuffer pH 4.64 von Reaktant A$_1$ (5·10^{-4} mol l^{-1}).

TABELLE V

T (°K)	$k_{1:H_3O^+}$ (l mol^{-1} sec^{-1})	Z	E_A (kcal mol^{-1})	$\Delta H^{\star}$ (kcal mol^{-1})	$\Delta S^{\star}$ (cal/Grad mol)	$\Delta G^{\star}$ (kcal)
298	4.76					
303	7.53					
308	11.35	7.5·10^{11}	15.4±1	14.8	—6.2	16.66
313	16.95					
318	24.40					

Richtungsfaktor der Arrhenius'schen Geraden nicht konstant. Die Hydrolyse des A$_1$ wurde in Acetatpuffer pH 4.64 bei Temperaturen zwischen 25° und 45° untersucht (Fig. 10). Da unter diesen Bedingungen die saure Katalyse überwiegt, ist die Arrhenius'sche Beziehung gültig (Fig. 11). Die Ergebnisse sind in Tabelle V zusammengefasst.

Reaktionsverlauf aus Elektronenspektren

Die Banden im sichtbaren und ultravioletten Bereich sind beim Endprodukt von A_1 (Fig. 12) gegenüber der Ausgangsverbindung bathochrom verschoben:

$$\text{Sichtbare Bande: } \Delta\tilde{\nu} = 3200 \text{ cm}^{-1};$$
$$\text{Ultraviolette Bande: } \Delta\tilde{\nu} = 1700 \text{ cm}^{-1}.$$

Die merkliche Verschiebung der energieärmsten Bande nach grösseren Wellenlängen wurde auch bei der Hydrolyse des 2-Äthylenimino-5,6-(dimethyl)-benzochinon-(1,4) und des 2,5-Bis-(äthylenimino)-3,6-(dichlor)-benzochinon-(1,4) beobachtet (vgl. Fig. 18).
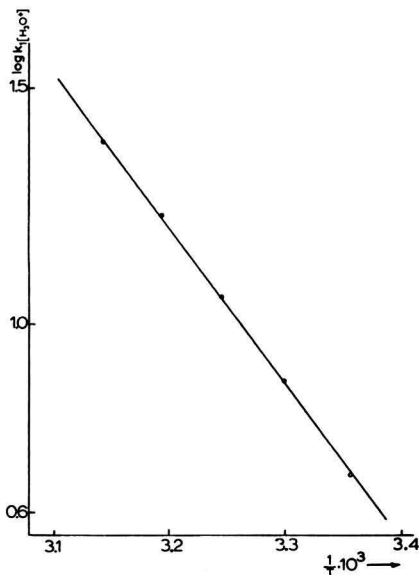
Fig. 11. Arrhenius'sche Gerade für die Start-
reaktion A → B.
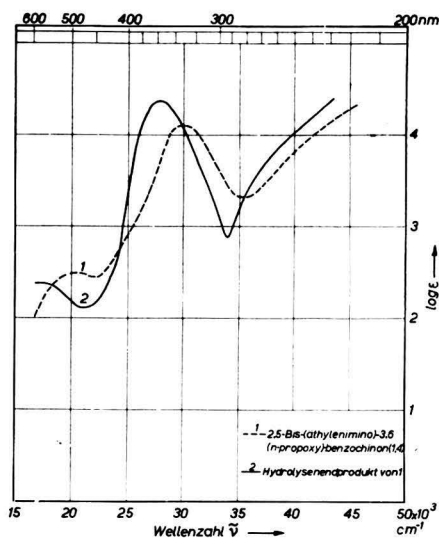
Fig. 12. Die Absorptionsspektren von A_1 (1)
und seines Hydrolysenendproduktes (2).

Die Änderung des Absorptionsspektrums eines Stoffes während einer chemischen Umsetzung desselben kann unter geeigneten Bedingungen zur quantitativen Verfolgung der Reaktion ausgenutzt werden, da die Extinktion nach dem Lambert-Beer'-schen Gesetz der Konzentration direkt proportional ist. Beim A_1 sind es drei Komponenten: Ausgangsprodukt, Zwischenprodukt und Endprodukt, deren zeitliche Konzentrationsänderungen während der Reaktion eine zeitliche Änderung der Gesamtextinktion bedingen. Für eine Lösung, die mehrere absorbierende Komponenten enthält, gilt allgemein:

$$E_{ges.} = \sum_i E_i = \sum_i \varepsilon_i c_i \tag{21}$$

E = Extinktion;
ε = Extinktionskoeffizient;
c = Konzentration des absorbierenden Stoffes in mol l^{-1};
für das vorliegende Beispiel gilt

$$E_{ges.} = \varepsilon_A c_A + \varepsilon_B c_B + \varepsilon_C c_C \tag{21.1}$$

Die Extinktionskoeffizienten von Ausgangsprodukt und Endprodukt sind einfach zugänglich. Da das Zwischenprodukt in keinem Zeitpunkt zwischen $t = 0$ und $t = \infty$ allein vorliegt, kann dessen Extinktionskoeffizient nur dann aus Gl. (21.1) berechnet werden, wenn im Zeitpunkt t die Gesamtextinktion und die Konzentrationen der drei Komponenten bekannt sind. Die Konzentrationen können aus der polarographischen Verfolgung der Reaktion entnommen werden.

Die zeitliche Änderung des Absorptionsspektrums des hydrolysierenden A_1 wurde in Acetatpuffer pH 4.46 und der Temperatur $\vartheta = 30°$ mit dem registrierenden Spek-
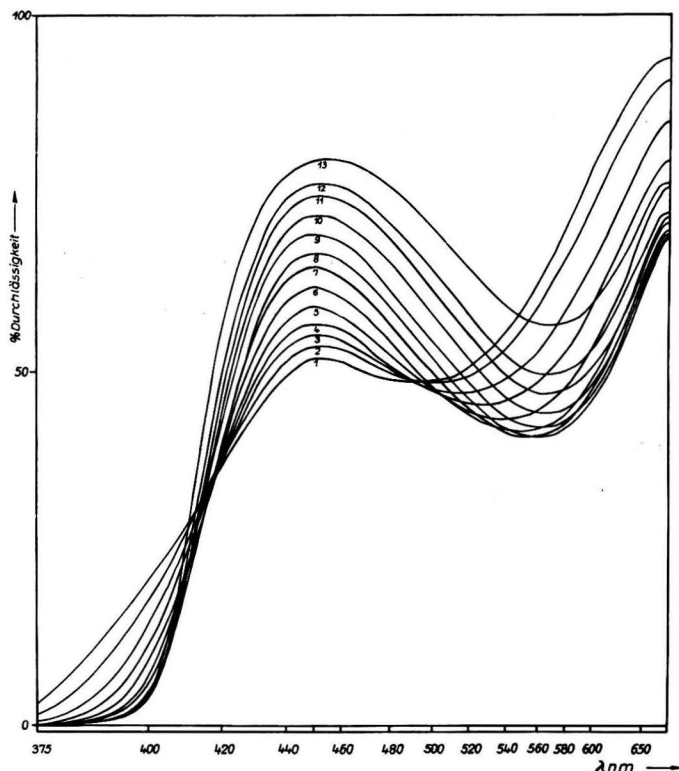
Fig. 13. Die zeitliche Änderung des sichtbaren Absorptionsspektrums von A_1 während der sauren Hydrolyse in Acetatpuffer pH 4.46 und $\vartheta = 30°$: 1 = Spektrum des Ausgangsproduktes; in der Reihefolge 2,3,4 . . . nach 5–12–20–30–45–60–75–95–120–150 und 180 min Reaktionszeit und am Reaktionsende registriert.

trophotometer Beckmann DK 2 verfolgt (Fig. 13). Zu Beginn der Reaktion wird bei 415 nm ein isosbestischer Punkt beobachtet, der im weiteren Verlauf der Reaktion auswandert[6]. Fig. 14 zeigt den Konzentrations–Zeit-Verlauf von A, B und C, der unter den gleichen Bedingungen polarographisch ermittelt wurde.

Aus dem Spektrum nach 60 min Reaktionszeit wurde unter Verwendung der polarographisch bestimmten Konzentrationsverhältnisse die spezifische Extinktion des

Zwischenproduktes E'_B bei 560 nm berechnet; $E'_B = 0.330$. Die zeitliche Änderung der spezifischen Gesamtextinktion bei 560 nm ist in Fig. 15 dargestellt. Da das Zwischenprodukt bei 560 nm am stärksten absorbiert, hat diese Kurve einen ähnlichen Verlauf wie die Konzentrations–Zeit-Kurve des Zwischenproduktes (vgl. Fig. 14). Die
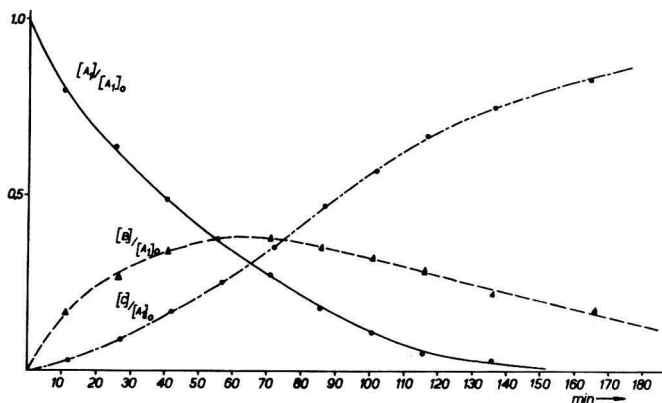
Fig. 14. Der polarographisch ermittelte relative Konzentrations–Zeit-Verlauf der Reaktanten A_1, B und C bei pH 4.46 und $\vartheta = 30°$.
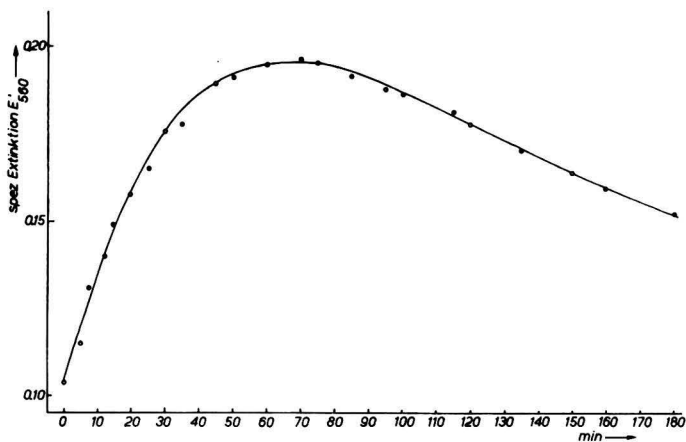
Fig. 15. Die zeitliche Änderung der spezifischen Extinktion E' bei 560 nm: ○, experimentell; ●, berechnet.

für bestimmte Zeiten berechneten spezifischen Gesamtextinktionen $E'_{ges.}$ sind in Fig. 15 ebenfalls eingetragen. Über den gemessenen Bereich zeigen polarographische und optische Messungen gute Übereinstimmung.

Das Spektrum des Zwischenproduktes B im sichtbaren Bereich wurde aus dem nach 60 min Reaktionszeit registrierten Mischspektrum berechnet. Fig. 16 zeigt die Spektren

der drei Komponenten zwischen 400 und 650 nm. Die energieärmste Bande des Zwischenproduktes ist gegenüber der des Ausgangsproduktes ebenfalls bathochrom verschoben; $\Delta \nu = 2500$ cm^{-1}. Ihre Intensität ist grösser als beim Ausgangsprodukt ($\Delta \log \varepsilon = 0.34$) und Endprodukt ($\Delta \log \varepsilon = 0.44$).
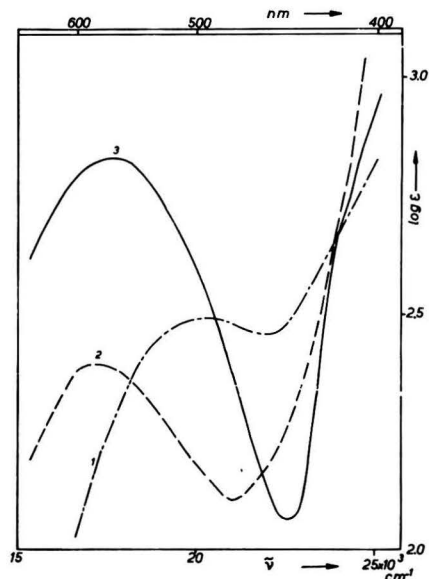
Fig. 16. Die sichtbaren Absorptionsspektren von A_1, seines Hydrolysenendproduktes und des Zwischenproduktes: 1, A_1; 2, Endprodukt; 3, Zwischenprodukt.

Die Identifizierung des Reaktionsproduktes C

Die Produkte der Hydrolyse von Äthyleniminoderivaten sind bekanntlich die entsprechenden Aminoalkohole. Das Hydrolysenendprodukt von A_1 wäre demnach 2,5-Bis-(β-oxyäthylamino)-3,6-(n-propoxy)-benzochinon-(1,4). Die Identität des unter den angewandten Bedingungen erhaltenen Reaktionsproduktes mit dem synthetisch hergestellten Äthanolaminderivat sollte bewiesen werden. Es wurde deshalb das Hydrolysenprodukt des A_2 mit synthetischem C_1 polarographisch und spektroskopisch verglichen. Diese analogen Verbindungen wurden herangezogen, weil das 2,5-Bis-(β-oxyäthylamino)-3,6-(n-propoxy)-benzochinon-(1,4) nicht als synthetisierte Verbindung vorlag. Substanz A_2 wurde sauer hydrolysiert.

Ein Zusatz von C_1 zur Reaktionslösung bewirkt eine Erhöhung der Reduktionswelle des Hydrolysenendproduktes (Fig. 17). Die Lösungen enthielten 40% Dioxan und 60% Phosphatpuffer pH 6.8. Die Äthyleniminoverbindung wurde in 0.2 N H_2SO_4–40% Dioxan hydrolysiert und anschliessend neutralisiert. In der Bandenlage stimmen das Hydrolysenprodukt und die synthetische Verbindung überein. Die Intensität der energieärmsten Bande des Hydrolysenproduktes ist grösser als bei der synthetisierten Verbindung, $\Delta \log \varepsilon = 0.26$. Dieser Befund kann folgendermassen erklärt werden. Polarographisch wurde festgestellt, dass die Hydrolyse der Äthyleniminoverbindung unter den angewandten Bedingungen nicht vollständig verläuft.

Das Spektrum ist deshalb ein Mischspektrum des Zwischen- und Endproduktes. Dei Intensität der energieärmsten Bande des Zwischenproduktes beim A_1 ist grösser als die des Endproduktes (vgl. Fig. 16). Wenn wir diese Verhältnisse auf die Hydrolysen-
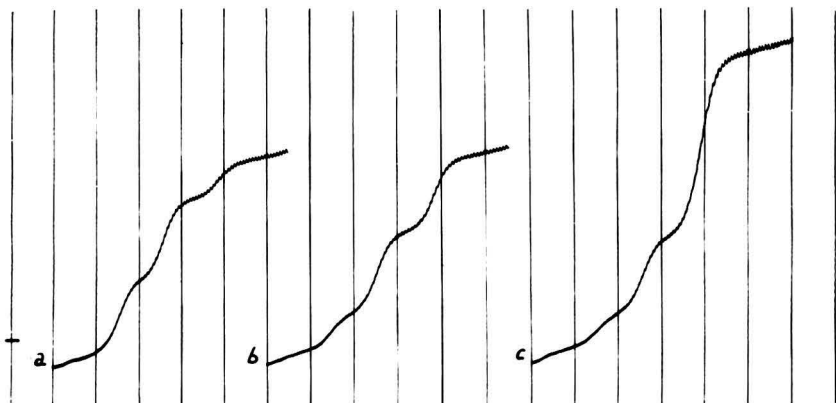
Fig. 17. 2,5-Bis-(äthylenimino)-3,6-(dichlor)-benzochinon-(1,4) $3 \cdot 10^{-4}$ mol l^{-1}: 30 % Aceton; 70 % Puffer pH 2; $\vartheta = 25°$; $S = 1:20$; $\Delta\pi = 0.1$ V; NSE; (a) nach 35 min; (b) nach 65 min; (c) nach 70 min und Zusatz von 0.5 ml $3 \cdot 10^{-3}$ mol l^{-1} 2,5-Bis-(β-oxyäthylamino)-3,6-(dichlor)-benzochinon-(1,4) ab 0.0 V registriert.
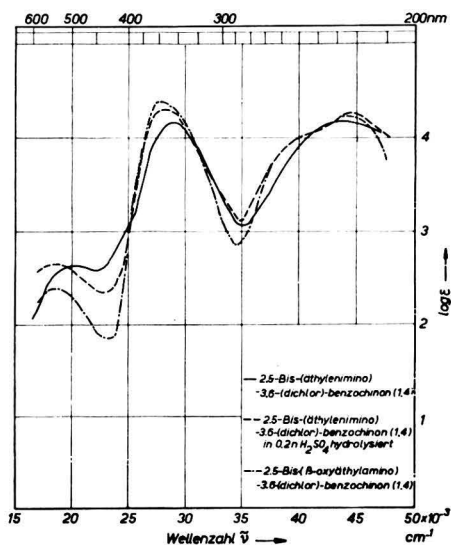
Fig. 18. Spektroskopische Identifizierung von Reaktionsprodukten von A_2, seines Hydrolysenproduktes und von C_1.

produkte des 2,5-Bis-(äthylenimino)-3,6-(dichlor)-benzochinon-(1,4) übertragen, ist die grössere Intensität der energieärmsten Bande des Mischspektrums im Sichtbaren verständlich.

DISKUSSION

Aus vorliegenden Messungen ergeben sich Hinweise auf den Mechanismus der Ringspaltung in saurer Lösung. Wie bei der Elektrolyse unterliegt die protonisierte Form der geschwindigkeitsbestimmenden Reaktion. Um zwischen S_N1- und S_N2-Mechanismus zu unterscheiden, lässt sich die Grösse der Aktivierungsentropie $\Delta S^\star$ heranziehen, welche im 2. Fall den höheren Zahlenwert aufweist. Verwandte Beispiele stellen die Hydrolysen von Äthylenimin und seiner C-Alkylderivate[7] dar, deren $\Delta S^\star$-Grenzwerte: S_N1: —1.9 cal/Grad mol und S_N2: —10 cal/Grad mol betragen. Der aus Tabelle V für Substanz A_1 ersichtliche Wert von —6.2 cal/Grad mol deutet auf den gleichzeitigen Ablauf beider Mechanismen hin, wovon der wahrscheinlichere formuliert sei:

$$R{-}N\!\!\begin{array}{c}\diagup CH_2 \\ \mid \\ \diagdown CH_2\end{array} + H_3^+O \rightleftarrows R{-}\overset{+}{N}\!\!\begin{array}{c}\diagup CH_2 \\ \mid \\ \mid \quad \diagdown CH_2 \\ H\end{array} + H_2O \qquad (22)$$

$$R{-}\overset{+}{N}\!\!\begin{array}{c}\diagup CH_2 \\ \mid \\ \mid \quad \diagdown CH_2 \\ H\end{array} \longrightarrow R{-}\underset{\mid}{N}{-}CH_2{-}C^+H_2 \qquad (23)$$

$$R{-}\underset{\mid}{\underset{H}{N}}{-}CH_2{-}\overset{+}{C}H_2 \xrightarrow{H_2O} R{-}\underset{\mid}{\underset{H}{N}}{-}CH_2{-}CH_2{-}OH + H^+ \qquad (24)$$
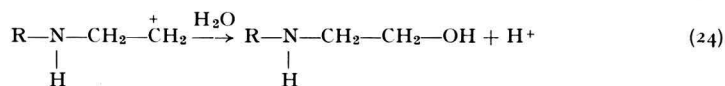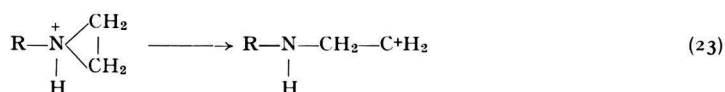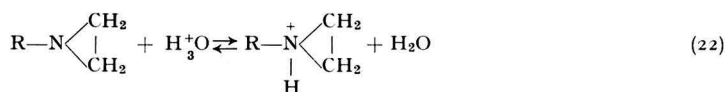
Gegenüber dem freien Äthylenimin, welches keine „Wasserstoffwelle" verursacht, reagiert der Dreiring am Chinon wesentlich schneller zum Iminoalkohol.

Damit erschliesst sich ein günstiger Reaktionsweg zu unsymmetrischen Mono-(β-oxyäthylamino)-Chinonen, da aus der direkten Reaktion zwischen Benzochinon und primärem Aminoäthanol überwiegend die symmetrischen 2,5-Bis-(β-oxyäthylamino)-benzochinone hervorgehen.

Die Ringspaltung führt somit in die Reihe der β-oxyäthyl-amino-Chinone, von denen die mit aussergewöhnlichen Eigenschaften, wie Thermochromie, Fluoreszenz und Gleichgewichts-Doppelstufen, an anderer Stelle[8,9] beschrieben sind.

Auch für die cytotoxische Wirkung der Äthylenimino-Chinone sind nach vorliegenden Messungen Rückschlüsse möglich geworden. Betrachtet man lediglich die pH-Abhängigkeit von k_1, so muss die Hydrolysengeschwindigkeit im Krebsgewebe ($\sim$pH 6.5) im Vergleich zu Normalzellen (pH $\sim$ 7.2) etwa 4 mal so hoch liegen, und zwar im Falle von A_1: $k_1 = 1.9 \cdot 10^{-4}$ min^{-1} (bei pH 6.5) zu $k_1 = 0.46 \cdot 10^{-4}$ min^{-1} (bei pH 7.2). Die damit verbundene Schädigung von Enzymen der Krebszelle[10] erfolgt dort also in höherem Masse.

ZUSAMMENFASSUNG

Ähnlich wie die Elektrodenreaktion verläuft auch die hydrolytische Lösungsreaktion unter Ringspaltung, und zwar beim Bis-Äthylenimino-Chinon mit einem nachweisbaren Zwischenprodukt. Eine allgemeine Säure–Basenkatalyse bewirkt die zeitliche Änderung der Stufenhöhe nach der 1. Ordnung. Die Aktivierungsentropie lässt Rückschlüsse auf den Reaktionsmechanismus zu.

Bei dieser Folgereaktion ergänzen sich polarographische und spektrophotometrische Messungen so gut, dass die Absorption des reinen Zwischenproduktes:

$$
\begin{array}{c}
\text{O} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{O} \quad\quad \text{N} \overset{\text{CH}_2}{\underset{\text{CH}_2}{<}} \\
\text{HOCH}_2\text{CH}_2\text{—N} \quad\quad \text{O—CH}_2\text{CH}_2\text{CH}_3 \\
\text{H} \quad \text{O}
\end{array}
$$
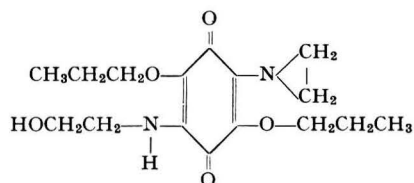
ermittelt werden konnte und beide Methoden gleiche Geschwindigkeitskonstanten k_1 ergeben. Auch konnte das Endprodukt der Hydrolyse identifiziert werden.

Zur Theorie der cytotoxischen Wirksamkeit bringen vorliegende Messungen einen quantitativen Beitrag.

SUMMARY

Like the electrode reaction, the hydrolytic solution reaction also occurs with ring cleavage, and in the case of bis-ethyleneiminoquinone with formation of a detectable intermediate. A general acid–base catalysis brings about the modification with respect to time of the wave-heights according to the first order. The entropy of activation allows conclusions to be drawn regarding the reaction mechanism.

In this sequence of reactions the polarographic and spectrophotometric measurements are supplementary to one another in so excellent a way that it has been possible to determine the absorption of the pure intermediate,

$$
\begin{array}{c}
\text{O} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{O} \quad\quad \text{N} \overset{\text{CH}_2}{\underset{\text{CH}_2}{<}} \\
\text{HOCH}_2\text{CH}_2\text{—N} \quad\quad \text{O—CH}_2\text{CH}_2\text{CH}_3 \\
\text{H} \quad \text{O}
\end{array}
$$
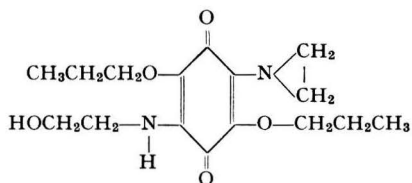
and to find that both methods furnish the same velocity constants k_1. Moreover, the end-product of the hydrolysis could be identified.

The above measurements represent a quantitative contribution to the theory of the cytotoxic activity.

LITERATUR

[1] H. WAGNER UND H. BERG, *J. Electroanal. Chem.*, 1 (1959/60) 61.
[2] H. WAGNER UND H. BERG, *J. Electroanal. Chem.*, 2 (1961) 452.
[3] H. BERG UND K.-H. KÖNIG, *Z. Krebsforsch.*, 62 (1958) 495.
[4] H. BERG, *Chem. Techn.*, 7 (1955) 679.
[5] A. FROST UND R. PEARSON, *Kinetics and Mechanisms*, New York, John Wiley, 1953.
[6] H. SCHLÄFER UND O. KLING, *Angew. Chem.*, 68 (1956) 667.
[7] J. E. EARLEY, C. E. O. ROURKE, L. B. CLAPP, J. O. EDWARDS UND B. C. LAWES, *J. Am. Chem. Soc.*, 80 (1958) 3458.
[8] H. BERG, K.-H. KÖNIG, D. TRESSELT UND H. WAGNER, *Ricerca sci.*, 30 (1960) 277; Suppl. 5.
[9] H. BERG, E. BAUER UND D. TRESSELT, *Advances in Polarog.*, 1 (1960) 382.
[10] H. HOLZER, G. SEDLMAYER UND A. KEMNITZ, *Biochem. Z.*, 328 (1956) 163; H. HOLZER UND H. KRÖGER, *Biochem. Z.*, 330 (1958) 579.
[11] H. BERG, *Chem. zvesti*, 1962 (im Druck).

FARADAIC ADMITTANCE AND ADSORPTION: A DIFFUSION MODEL

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RANDLES[1] (and ERSHLER independently[2]) showed that the behaviour of micro-electrodes under the action of a small alternating potential gives a powerful tool for measuring the rates of fast electrodes reactions. It was shown that: (a), the change in the concentration of the oxidant lags behind the anodic current by $\pi/4$; (b), the phase angle, ϕ, between the alternating components of the voltage and the current is given by the relation

$$\cot \phi = 1 + \frac{1}{k_s} \sqrt{\frac{\omega D}{2}}$$

so that ϕ is always $\leq \pi/4$, and (c), the electrode reaction

$$\text{ox} + ne \rightleftharpoons \text{red}$$

giving rise to faradaic current, can be considered as equivalent to an electrical circuit comprising a resistance R_r in series with a capacitance C_r; these values are given by

$$R_r = \frac{RT}{n^2 F^2 A C} \left[\sqrt{\frac{2}{\omega D}} + \frac{1}{k_s} \right]$$

$$C_r = \frac{n^2 F^2 A C}{RT} \sqrt{\frac{D}{2\omega}} \quad \text{and} \quad \omega R_r C_r = \cot \phi$$

In obtaining these, it has been assumed that the only mode of mass transport is diffusion, the diffusion coefficient D for the electroactive species being a constant, *i.e.* independent of the distance from the electrode, time or concentration. Consequently, the boundary condition used is

$$nFAD \left(\frac{\partial C}{\partial x} \right)_{x=0} = \pm i(t)$$

RANDLES[1], RANDLES AND SOMERTON[3], LAITINEN AND RANDLES[4] and BAUER AND ELVING[5], among others, have observed that ϕ can *exceed* $\pi/4$. LAITINEN AND RANDLES[4] have traced this to the presence of adsorbed reactants, which would make their own contribution to the faradaic current. They have also given a formula for

the contribution of adsorbed reactants to the current, in addition to those of the reactants in solution. These additional elements R_a and C_a so obtained are

$$R_a = \left(\frac{RT}{n^2 F^2 A k_a x' \Gamma}\right)$$

and

$$C_a = \frac{n^2 F^2}{RT} A x'^2 \Gamma$$

so that $R_a C_a = x'/k_a$. It can be noted that, whereas the plots of R_r and C_r vs. $1/\sqrt{\omega}$ should give straight lines, R_a and C_a are *independent* of the angular frequency ω. The expressions cited above for R_a and C_a are obtained under the assumption[4] "that it is the loss or gain of an electron by ions of the reactant *which remain adsorbed on the electrode surface* which is postulated as the source of an additional current, not the adsorption and desorption of these ions". Hence, a boundary condition $i = nFA$ $d\{(1-x)\Gamma\}/dt$ is used, where Γ is the total surface excess concentration (moles/cm^{-2}) of the species and x is the fraction of coverage of the oxidant.

A diffusion model is suggested in this paper which is similar to a mathematical model suggested by the authors previously[6] (Appendix I) and which will *correspond* to the model adopted by LAITINEN AND RANDLES[4].

Diffusion layers of thicknesses ν_i ($i = 0$, ox or R, red) and associated with these, the diffusion coefficients D'_{i1}, are assumed. The initial concentrations are taken as $^{\circ}C_0{}^{ad}$ and $^{\circ}C_R{}^{ad}$, and the conditions that determine the instantaneous concentration for the oxidant at any point in this layer are

(i) $\quad D'_{01} \dfrac{\partial^2 C_0{}^{ad}}{\partial x^2} = \dfrac{\partial C_0{}^{ad}}{\partial t}$

(ii) $\quad C_0{}^{ad}(x,0) = {}^{\circ}C_0{}^{ad}$

(iii) $\quad D'_{01} \left(\dfrac{\partial C_0{}^{ad}}{\partial x}\right)_{x=\nu_0} = 0$

(iv) $\quad D'_{01} \left(\dfrac{\partial C_0{}^{ad}}{\partial x}\right)_{x=0} = i(t)/nFA$

Denoting the Laplace Transformation of any function $f(t)$ by

$$\bar{f} = p \int_0^\infty e^{-pt} f(t)\, dt$$

we obtain

$$D'_{01} \frac{d^2 \bar{C}_0{}^{ad}}{dx^2} - p\bar{C}_0{}^{ad} = -p{}^{\circ}C_0{}^{ad}$$

so that,

$$\bar{C}_0{}^{ad}(0,p) - {}^{\circ}C_0{}^{ad} = A e^{\sqrt{p/D'_{01}}\, x} + B e^{-\sqrt{p/D'_{01}}\, x}$$

The boundary conditions (iii) and (iv) imply that

$$(A - B) = \bar{i}(p)/nFA\sqrt{D'_{01}p}$$

and

$$(A - B e^{-2\sqrt{p/D'_{01}}\, \nu_0}) = 0$$

hence

$$B = -[\bar{i}(p)/nFA\sqrt{D'_{01}p}][1 - e^{-2\sqrt{p/D'_{01}}\, \nu_0}]^{-1}$$

and

$$A = - [\bar{i}(p)/nFA\sqrt{D'_{01}p}] \; \frac{e^{-2\sqrt{p/D'_{01}} \; v_0}}{1 - e^{-2\sqrt{p/D'_{01}} \; v_0}}$$

so that

$$\bar{C}_0{}^{ad}(o,p) - {}^{\circ}C_0{}^{ad} = A + B$$

$$= - \frac{\bar{i}(p)}{nFA\sqrt{D'_{01}p}} \; \frac{1 + e^{-2\sqrt{p/D'_{01}} \; v_0}}{1 - e^{-2\sqrt{p/D'_{01}} \; v_0}}$$

$$= - \frac{\bar{i}(p)}{nFA\sqrt{D'_{01}p}} \coth (\sqrt{p/D'_{01}} \; v_0)$$

It can be incidentally noted that as $v_0 \to \infty$

$$(\bar{C}_0{}^{ad}(o,p) - {}^{\circ}C_0{}^{ad}) \to \frac{-\bar{i}(p)}{nFA\sqrt{D'_{01}p}}$$

which is a result derived already for the familiar model[7]. When $i(t)$ is sinusoidal, say $i(t) = I \cos(\omega t + \phi)$, (when $V(t) = V \cos \omega t$), the steady state concentration at the interface is given by:

$$C_0{}^{ad}(o,t) = {}^{\circ}C_0{}^{ad} - \text{Real part of} \left[\frac{Ie^{j(\omega t + \phi - \pi/4)}}{nFA\sqrt{D'_{01}\omega}} \coth \left(\sqrt{\frac{\omega}{2D'_{01}}} v_0(1 + j) \right) \right]$$

where $j = \sqrt{-1}$. For small values of $v_0\sqrt{\omega/2D'_{01}}$ such that $v_i\sqrt{\omega} \ll \sqrt{D_i}$, we get:

$$\Delta C_0{}^{ad} = C_0{}^{ad}(o,t) - {}^{\circ}C_0{}^{ad}$$
$$= - I \cos(\omega t + \phi - \pi/2)/nA F\omega v_0$$
$$= I \cos(\omega t + \phi + \pi/2)/nA F\omega v_0.$$

A similar result holds for $C_R{}^{ad} (o,t)$. This shows that $\Delta C_0{}^{ad}$, considered as a vector, leads the net current (cathodic current taken as positive) by $\pi/2$. Similarly, $\Delta C_R{}^{ad}(o,t)$ lags behind the net current (same convention) by $\pi/2$. It is interesting to note that the *same results* are obtained by LAITINEN AND RANDLES by using a *different model*. Substituting these values for the interfacial concentrations in the rate equation:

$$i^{ad} = i_0{}^{ad} \left[\frac{C_0{}^{ad}(o,t)}{{}^{\circ}C_0{}^{ad}} e^{-\alpha nFv/RT} - \frac{C_R{}^{ad}(o,t)}{{}^{\circ}C_R{}^{ad}} e^{(1-\alpha)nFr/RT} \right]$$

and, linearising the exponentials, we get

$$i^{ad} = i_0{}^{ad} \left[\frac{C_0{}^{ad}(o,t)}{{}^{\circ}C_0{}^{ad}} - \frac{C_R{}^{ad}(o,t)}{{}^{\circ}C_R{}^{ad}} - \frac{nFv}{RT} \right]$$

approximately, so that

$$I \cos(\omega t + \phi) = -i_0{}^{ad} \left[\frac{I \sin(\omega t + \phi)}{nA F\omega v_0{}^{\circ}C_0{}^{ad}} + \frac{I \sin(\omega t + \phi)}{nA F\omega v_R{}^{\circ}C_R{}^{ad}} + \frac{nFV\cos\omega t}{RT} \right]$$

i.e.

$$\frac{I}{i_0{}^{ad}} \cos(\omega t + \phi) + \frac{I \sin(\omega t + \phi)}{nA F\omega v_0{}^{\circ}C_0{}^{ad}} \left(1 + \frac{{}^{\circ}C_0{}^{ad}v_0}{{}^{\circ}C_R{}^{ad}v_R} \right) = - \frac{nFV}{RT} \cos \omega t$$

or

$$\frac{RT}{nFi_0{}^{ad}}(i(t)) + \frac{RT}{n^2F^2} \left(1 + \frac{{}^{\circ}C_0{}^{ad}v_0}{{}^{\circ}C_R{}^{ad}v_R} \right) \frac{\int i(t) dt}{A v_0{}^{\circ}C_0{}^{ad}} = -V\cos \omega t.$$

Hence,

$$|R_a| = \frac{RT}{n\,Fi_0{}^{ad}} \quad \text{and} \quad |C_a| = \frac{n^2F^2A\,v_0{}^{\circ}C_0{}^{ad}}{RT\left(1 + \dfrac{{}^{\circ}C_0{}^{ad}v_0}{{}^{\circ}C_R{}^{ad}v_R}\right)}$$

(The negative signs for the elements arise from the fact that $i(t)$ denotes 'net cathodic current' while $v(t)$ denotes 'the potential of the electrode with respect to the solution'.) Thus, we deduce that, for this model, the equivalent circuit elements R_a and C_a corresponding to this 'perturbation' near the interface, are independent of frequency. Another significant aspect is the *non-dependence* of R_a and C_a on the 'superposed' diffusion coefficient D. A transition to the adsorption model of LAITINEN AND RANDLES can thus be made — or more correctly — a comparison of this model with that of LAITINEN AND RANDLES[4] can bring out some striking similarities (refer to Table I).

TABLE I

COMPARISON OF THE DIFFUSION MODEL WITH THAT ADOPTED BY LAITINEN AND RANDLES[4]

Laitinen and Randles[4]	Diffusion
(a) Surface concentrations, initially $x_0\Gamma$; $(1-x_0)\Gamma$	(a) 'Smeared out' surface concentrations, ${}^{\circ}C_0{}^{ad}v_0$; ${}^{\circ}C_R{}^{ad}v_R$
(b) Total initial surface concentration: Γ	(b) ${}^{\circ}C_0{}^{ad}v_0 + {}^{\circ}C_R{}^{ad}v_R$
(c) Total instantaneous surface concentration: Γ: a constant with time.	(c) $v_0 C_0{}^{ad}(0,t) + v_R C_R{}^{ad}(0,t)$ $= $ constant with time $= v_0{}^{\circ}C_0{}^{ad} + v_R{}^{\circ}C_R{}^{ad}$
(d) $x(t)\Gamma$ and $[1-x(t)]\Gamma$	(d) $v_0 C_0{}^{ad}(0,t)$ and $v_R C_R{}^{ad}(0,t)$
(e) The condition that the 'loss or gain of an electron by ions of the reactant *which remain adsorbed* on the electrode surface contribute to the additional current'. $i(t) = nAF\dfrac{d}{dt}[(1-x)\Gamma]$	(e) No flux across the layer at $x = v_i[i = 0,R]$ $D'_{i1}\dfrac{\partial C_i{}^{ad}}{\partial x} = 0 \text{ at } x = v_i$ $i(t) = nFA\left[-D'_{R1}\dfrac{\partial C_R{}^{ad}}{\partial x}\right]_{x=0}$
(f) $R_a = \dfrac{RT}{n\,Fi_0{}^{ad}}$	(f) $R_a = \dfrac{RT}{n\,Fi_0{}^{ad}}$
(g) $C_a = \left(\dfrac{n^2F^2A}{RT}\right)x_0(1-x_0)\Gamma$	(g) $C_a = \dfrac{n^2F^2A}{RT}\dfrac{v_0{}^{\circ}C_0{}^{ad}v_R{}^{\circ}C_R{}^{ad}}{(v_0{}^{\circ}C_0{}^{ad}+v_R{}^{\circ}C_R{}^{ad})}$

It must be mentioned that the value for R_a, as given by LAITINEN AND RANDLES, is apparently different from that given above, *viz.*, $RT/nFi_0{}^{ad}$. But one can see that the expression for R_a as given by LAITINEN AND RANDLES is obtained under the assumption that $\alpha = 0.5$ and hence gives only an approximate expression for $RT/nFi_0{}^{ad}$. If the rate equation, as given for their model, is re-written in the form

$$i = i_0{}^{ad}\left[\frac{x}{x_0}\,e^{-\alpha nFv/RT} - \left(\frac{1-x}{1-x_0}\right)e^{(1-\alpha)nFv/RT}\right]$$

the above expression alone will result.

APPENDIX I

To explain the anomalous behaviour of the phase angle ϕ between the alternating components of the faradaic current and the potential, another model — essentially mathematical — is suggested. This assumes that there are two diffusion layers with different diffusion coefficients. The thicknesses ν_i of the first layers (those nearer the electrode) are assumed to be very small, and the formal diffusion coefficients defined therein are different from those of the bulk. These assumptions are expected 'to simplify' the mathematical formulation and are expected to account for (at least as a perturbation effect) the complex phenomena that may exist adjacent to the interface. Such a model clearly showed that a value greater than $\pi/4$ for ϕ *is not impossible*. The expressions for the elements R'_r and C'_r are also different from those obtained already[1,2]. It showed that, as a first approximation $((\nu_i \sqrt{\omega/2D_{i_1}})^2$ and higher powers being neglected), for

$$R'_r = R_r + \text{a term independent of frequency } (\omega)$$
$$C'_r = C_r$$

indicating that the difference in the model has not changed the C_r values much (except in the neighbourhood of very small $1/\sqrt{\omega}$ where a non-linearity is predicted). R'_r itself differs from R_r only by a constant (independent of frequency), and, hence, with these approximations, a plot of R'_r vs. $1/\sqrt{\omega}$ will still be a straight line[4], but the intercept on the R'_r axis will no longer be RT/nFi_0. The details of these and other results arising out of this *general* formulation will be published later[6].

SUMMARY

When diffusion alone is the mode of mass transfer, expressions derived previously[1,2] for the elements of the faradaic admittance predict that its phase angle cannot exceed $\pi/4$. Several systems[3,4,5] show the possibility of the phase angle being greater than $\pi/4$. LAITINEN AND RANDLES had suggested that such anomalous behaviour can be explained by taking into account the correction for the contribution of the adsorbed reactants. A different model, based on diffusion, is presented in this paper and shows how the conclusions of LAITINEN AND RANDLES (*e.g.*, the elements of the equivalent circuit, R_a and C_a, which are independent of frequency) can be obtained through this model as well. A detailed comparison between the parameters used in the two different models is made. Results for a generalised diffusion model are cited.

REFERENCES

[1] J. E. B. RANDLES, *Discussions Faraday Soc.*, 1 (1947) 11.
[2] B. V. ERSHLER, *ibid.*, 1 (1947) 269.
[3] J. E. B. RANDLES AND K. W. SOMERTON, *Trans. Faraday Soc.*, 48 (1952) 937.
[4] H. A. LAITINEN AND J. E. B. RANDLES, *Trans. Faraday Soc.*, 51 (1955) 54.
[5] H. H. BAUER AND P. J. ELVING, *J. Am. Chem. Soc.*, 82 (1960) 209.
[6] S. K. RANGARAJAN AND K. S. G. DOSS, in press.
[7] S. K. RANGARAJAN, *J. Electroanal. Chem.*, 1 (1960) 396.

POLAROGRAPHIC DETERMINATION OF RUTHENIUM*

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The analytical chemistry of ruthenium is complicated, and as a result satisfactory methods of analysis are still needed. This is primarily because of the many oxidation states of the element and the many complexes formed by the various oxidation states. Also the absence of an easily purified and isolatable compound has helped prevent the development of reliable analytical methods.

The classical procedure for the determination of ruthenium involves the distillation of RuO_4 and subsequent reduction of the distillate by hydrogen to the metal[1]. The tedious nature of this procedure plus its lack of sensitivity has prompted many other studies. CONNICK AND HURLEY[2] have proposed the spectrophotometric determination of RuO_4 after prior oxidation with KIO_4. More recently two additional spectrophotometric procedures for ruthenium have been proposed; one involving the oxalate complex[3] and the other the thiocyanate complex[4]. The latter work gives references to other spectrophotometric studies as well as to the review by BEAMISH AND McBRYDE[5].

Several polarographic procedures have been proposed for the determination of ruthenium; SILVERMAN AND LEVY[6] studied ruthenium(VI, VII, VIII) in basic solutions with a platinum electrode, BRANICA AND MESARIĆ used citrate and tartrate solutions[7] as well as oxalate solutions[3] for reduction of a ruthenium species thought to be Ru(IV), and NIEDRACH AND TEVEBAUGH[8] reduced ruthenium(IV) in perchloric acid media.

In a recent study of the ruthenium(III) gluconate complexes[9] we observed a well defined polarographic wave which appeared potentially useful for the quantitative analysis of ruthenium. The possibility of an improved polarographic method for ruthenium together with the need for better analytical methods in general for this element has led to the present study.

EXPERIMENTAL

Equipment

Polarograms were recorded with a Sargent Model XV Polarograph; a modified H-cell was used to prevent attack by basic solutions of the agar in the salt bridge[10]. All measurements were made at $25.0 \pm 0.1°$ and the solutions were deaerated with prepurified nitrogen. Diffusion currents were measured using the tops of the oscil-

lations (maximum current) and were corrected for residual current by extrapolation. All potentials were measured *versus* the saturated calomel electrode. The characteristics of the capillary gave a value of 1.95 for $m^{2/3}t^{1/6}$ at -0.68 V applied potential, where m is milligrams of mercury flowing per second and t is the drop time in seconds. pH measurements were made with a line-operated Leeds and Northrup pH meter (using a wide range electrode for high pH's).

Reagents

Ruthenium solutions were prepared from ruthenium chloride (Fisher Scientific Company, purified). This material was found to contain approximately 85% of the ruthenium as Ru(IV) and 15% as Ru(III) (using the iodometric method of CROWELL AND YOST[11] for the Ru(IV) determination). The total ruthenium concentration was determined gravimetrically by reduction to the metal[1].

Ruthenium(III) solutions were prepared by boiling the above stock solutions with concentrated hydrochloric acid; such treatment reduced any Ru(IV) to Ru(III). Solutions of ruthenium(III) were also prepared determinately from $(NH_4)_2[Ru(H_2O)Cl_5]$ (Johnson, Matthey and Co., Limited; 99.995% pure). Chloride-free solutions of ruthenium(III) were prepared by electrolytic reduction of ruthenium(IV) solutions (0.03 F in ruthenium and 1 F in sulfuric acid) at a mercury pool cathode[9]. The latter solutions were prepared by fuming ruthenium chloride with sulfuric acid for approximately 20 minutes.

Solutions of palladium chloride and of platinum chloride were prepared from $PdCl_2.2H_2O$ and K_2PtCl_4, respectively (both salts from Fisher Scientific Company, purified). The iridium and rhodium solutions were prepared from $(NH_4)_2IrCl_6$ and $(NH_4)_3RhCl_6.1\frac{1}{2}H_2O$, respectively (Johnson, Matthey and Co., Limited). The osmium solutions were prepared from OsO_4 (Mallinkrodt Chemical Works, reagent grade).

Sodium gluconate solutions were prepared determinately from D-glucono-δ-lactone (Chas. Pfizer and Co., Inc.) which had been recrystallized twice from ethylene glycol monomethyl ether. The purity of the lactone was determined by back-titrating, with standard acid, a sample to which excess standard base had been added. The lactone was found to be 99.7% pure. All other materials were reagent grade.

RESULTS AND DISCUSSION

The previous study[9] of the ruthenium gluconate system indicated that a reversible reduction wave is obtained for ruthenium(III) above pH 12 in the presence of a sodium gluconate supporting electrolyte. Below pH 12 the wave becomes an irreversible double wave. The half-wave potential for the reduction is -0.67 V and is independent of pH from pH 12 to pH 14.3. Similarly the half-wave potential is independent of gluconate concentration from 0.02F to 0.20F sodium gluconate. These characteristics are desirable conditions for a quantitative polarographic method of analysis. However, ruthenium(III) solutions have been found to be unstable, particularly in the presence of sulfuric acid. If an acidic ruthenium(III) solution is freshly prepared by electrolytic reduction of ruthenium(IV), curve a of Fig. 1 is obtained after adding gluconic acid and adjusting to pH 14. After 24 hours the acidic stock solution gives, upon preparing a fresh basic ruthenium(III) gluconate solution, curve b of Fig. 1. This latter solution gives curves c–f as a function of time. Obviously such behavior as indicated by Fig. 1 precludes accurate quantitative polarographic analyses for ruthenium. The

probable sequence of reactions represented by this figure has been discussed previous-ly[9].

In developing a useful polarographic method for ruthenium it is essential to develop a procedure and conditions which prevent the phenomena shown in Fig. 1. One method, although impractical, is to prepare a basic ruthenium gluconate solution and allow it to stand for 48 hours before running the polarogram. If this is done, curve *f* in Fig. 1 results, which is an analytically useful polarogram. In the interest of practicality a more rapid procedure has been sought. Because one can never be certain what oxidation state a ruthenium sample will be in, the procedure should be applicable to any oxidation state of the element.
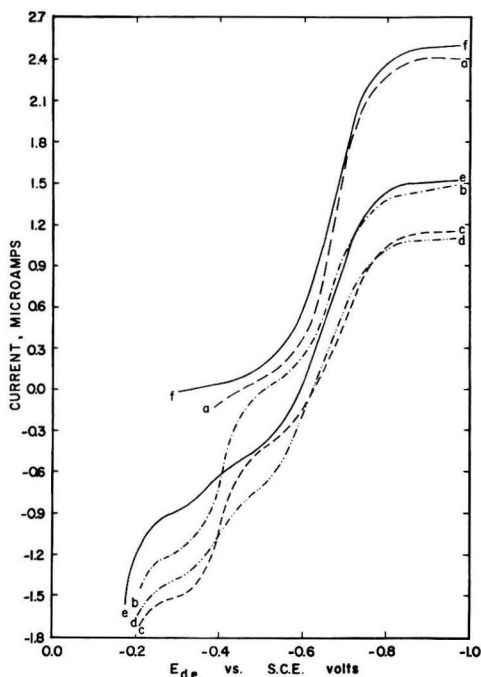
Fig. 1. Polarograms of ruthenium in the presence of sodium gluconate: Ru(III), $1.0 \cdot 10^{-3} F$; sodium gluconate, $0.2 F$; pH 14. Curve (a) fresh Ru(III) stock solution, sample run immediately. (b) Solution *b*, 24 hour-old Ru(III) stock solution; sample run immediately. (c) Solution *b*, 45 minutes later. (d) Solution *b*, 6 hours later. (e) Solution *b*, 19.5 hours later. (f) Solution *b*, 37.5 hours later.

A number of sample treatments have been tried with varying degrees of success. A stock solution of ruthenium chloride in hydrochloric acid when added to sodium gluconate and adjusted to pH 14 gives a polarographic wave for which 5–10% of its height is anodic. After 24 hours this gluconate solution has a wave which is essentially all anodic, and after 48 hours is entirely cathodic (curve *f*, Fig. 1). If the sample solution is boiled in concentrated hydrochloric acid for approximately 15 minutes before preparing a basic-gluconate sample solution, 30–40% of the wave is anodic. Under

these conditions a well defined wave is not obtained even after several days. Fuming the sample with perchloric acid or with sulfuric acid gives equally poor results. Although boiling the sample with nitric acid before adjusting to a basic gluconate solution only gives a cathodic wave, the catalytic nitrate wave interferes with the ruthenium wave. Several variations of the above procedures were also tried before a satisfactory method of sample preparation was evolved.

A wave with a much smaller anodic portion results if air is bubbled through the polarographic cell while the components in the sample solution are mixed. By bubbling oxygen through the cell instead of air a totally cathodic wave is obtained, which remains entirely cathodic for at least $2\frac{1}{2}$ hours. After this time an anodic portion
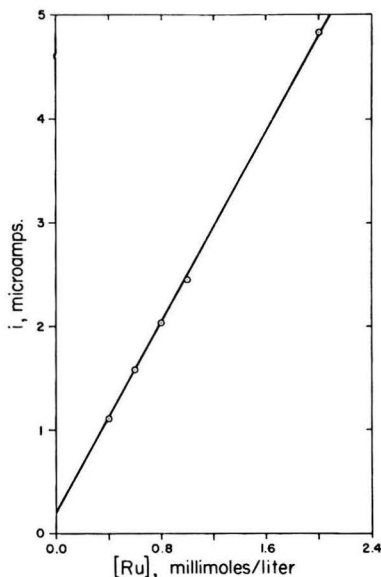
Fig. 2. Calibration curve for polarographic diffusion currents as a function of ruthenium concentration. The curve intercepts the ordinate at 0.20 microampere. From the slope, the diffusion current constant, I, is 1.18. All solutions were 0.1 F in sodium gluconate and adjusted to pH 14.

appears. These observations have led to a procedure which has proven satisfactory for a wide range of ruthenium samples, regardless of their oxidation state. The sample treatment may be summarized as follows: bring the ruthenium sample into solution with hydrochloric acid and add to sufficient sodium gluconate solution to give a final concentration of 0.1 F gluconate. Neutralize and add sufficient base to bring the final solution to pH 14. After diluting to volume, add the solution to the polarographic cell and bubble oxygen vigorously through the solution for 15–20 minutes (a fritted bubbler is desirable). Deaerate the solution for 5 minutes with nitrogen, then introduce the dropping mercury electrode into the cell, and run the polarogram.

Using the above procedure the diffusion current remains constant for two hours, but the best defined wave is obtained within 15 minutes after the oxygen treatment. It is important not to introduce the dropping mercury electrode into the cell solution

until the polarogram is to be recorded. Mercury apparently reduces ruthenium(III) slowly and causes an anodic portion on the wave.

Figure 2 gives a calibration curve for a series of known concentrations of ruthenium and indicates the linearity of the diffusion current with concentration. Actually the linearity continues to concentrations of ruthenium above 5 mM. Reference to Fig. 2 indicates that the curve does not go through zero. We have reproduced the same result with several other calibration studies and must conclude that this deviation is real. The diffusion currents are measured by drawing parallel lines through the plateau of the top of the wave and the extrapolation of the residual current at the foot of the wave. This is by far the most reproducible method for measuring the diffusion currents. Apparently there is either some impurity which adds to the residual current or the true diffusion current is represented by a measurement other than the one used. In either case the reproducibility of the curve in Fig. 2 permits an analytically useful expression to be written.

$$i_d = Im^{2/3}t^{1/6}C + 0.20 \tag{1}$$

where i_d is the diffusion current in microamperes (corrected for residual current), I is the diffusion current constant (using maximum current rather than average current), m is the rate of flow of mercury in milligrams per second, t is the drop time in seconds, and C is the ruthenium concentration in millimoles per liter. From Fig. 2 and eqn. (1) it is possible to determine that the value of I is 1.18 ± 0.02.

To test the validity of eqn. (1) and the outlined procedure a series of ruthenium samples have been analyzed. The results of these analyses are tabulated in Table I.

TABLE I

POLAROGRAPHIC ANALYSES OF RUTHENIUM SAMPLES

Concentrations		% deviation
Taken, millimoles/liter	Found, millimoles/liter	
0.106	0.107	+1.2
0.211	0.201	−4.7
0.423	0.415	−1.9
1.06	1.04	−1.6
1.58	1.60	+1.1
2.11	2.15	+1.8
2.64	2.52	−4.5
5.28	5.28	0.0
	Average % deviation	2.1

These data indicate that the average deviation is 2.1% and that the method is applicable for the concentration range from 0.1 mM – 5 mM ruthenium. Each of the samples tabulated in Table I was run five times and the value tabulated represents the average. The average of the average deviations for the five replicates at each concentration was 1.5%.

The polarographic procedure for ruthenium is subject to a number of interferences.

Obviously any ion reduced in the vicinity of —0.67 V will interfere. Essentially all such interferences can be eliminated by first oxidizing the ruthenium to RuO_4 and distilling it[1]. The volatile character of RuO_4 permits its separation from most metals other than osmium. The RuO_4 is collected in a hydrochloric acid solution where it is reduced to ruthenium(III).

Because the six platinum metals frequently occur together their interference in the procedure for the ruthenium determination is of interest. The tedious nature of the distillation process makes a procedure without a separation desirable. The presence of platinum is a serious interference and this element must be absent from the ruthenium sample if meaningful results are to be obtained. Palladium ion may be present up to concentrations of $1 \cdot 10^{-4}$ F without affecting the ruthenium results significantly. Iridium and rhodium ions do not interfere at all because of their extremely negative reduction potentials. Although osmium(VI) is reduced at approximately —0.5 V in basic gluconate solutions, pretreatment of the acidic sample solution with hydrogen peroxide reduces most of the osmium to Os(IV). By such a procedure it is possible to have osmium concentrations equimolar, or less, relative to the ruthenium concentration without significant interference. A complete report of the osmium gluconate complexes and their polarographic behavior is in preparation[11].

SUMMARY

A method for the polarographic determination of ruthenium is discussed using basic sodium gluconate as the supporting electrolyte. The half-wave potential is —0.67 V *versus* the saturated calomel electrode for 0.1 F sodium gluconate at pH 14. For these conditions the diffusion current constant, I, is 1.18 (maximum rather than average current). This constant is applicable for ruthenium concentrations from $1 \cdot 10^{-4} F$ to $5 \cdot 10^{-3} F$; analyses in this concentration range have an average deviation of 2.1%. The procedure and precautions for sample preparation are discussed. Platinum causes serious interference, but low concentrations of palladium and osmium can be tolerated. Iridium and rhodium do not interfere.

REFERENCES

1 W. F. HILLEBRAND AND G. E. F. LUNDELL, *Applied Inorganic Analysis*, 2nd edn., John Wiley and Sons, New York, N.Y., 1953, p. 334–383.
2 R. E. CONNICK AND C. R. HURLEY, *J. Am. Chem. Soc.*, 74 (1952) 5012.
3 S. MESARIĆ AND M. BRANICA, *Croat. Chem. Acta*, 30 (1958) 81.
4 W. L. BELEW, G. R. WILSON AND L. T. CORBIN, *Anal. Chem.*, 33 (1961) 886.
5 F. E. BEAMISH AND W. A. E. McBRYDE, *Anal. Chim. Acta*, 9 (1953) 349; 18 (1958) 562.
6 M. D. SILVERMAN AND H. A. LEVY, *J. Am. Chem. Soc.*, 76 (1954) 3319.
7 M. BRANICA AND S. MESARIĆ, *Croat. Chem. Acta*, 30 (1958) 89.
8 L. W. NIEDRACH AND A. D. TEVEBAUGH, *J. Am. Chem. Soc.*, 73 (1951) 2835.
9 D. T. SAWYER, R. S. GEORGE AND J. B. BAGGER, *ibid.*, 81 (1959) 5893.
10 R. L. PECSOK AND R. S. JUVET, JR., *Anal. Chem.*, 27 (1955) 165.
11 D. T. SAWYER AND D. TINTI, unpublished results, in preparation.

Short communications

Reaction layer concept applied to rotating disk electrodes

The rotating disk electrode (RDE) is very convenient for investigating the kinetics of chemical processes coupled with electrochemical reactions[1]. Several such cases were studied by LEVICH AND KOUTECKY[2] and suitable equations were given for processes which can be described by the relations

$$A \overset{k}{\to} B \overset{ne}{\to} C \tag{1}$$

$$2\,A \overset{k}{\to} B \overset{ne}{\to} C \tag{2}$$

$$A \overset{ne}{\to} B + X \overset{k}{\to} A \tag{3}$$

We noticed that using the reaction layer concept it is easy to obtain for process (1) an equation identical with that given by LEVICH AND KOUTECKY.

Because the reaction layer treatment gave results similar to more rigorous treatments in the case of polarography[3] and chronopotentiometry[4] for electron transfer followed by chemical reaction:

$$Ox + ne \to Red \overset{k}{\to} A \tag{4}$$

we used this method to describe process (4) in the case of the RDE.

The concentration C_{Ox} can be calculated approximately from the equation for the RDE[1]

$$C_{Ox}(o,t) = C_{Ox}^{b} - \frac{i}{0.62 n F A D_{Ox}^{2/3} \nu^{-1/6} \omega^{1/2}} \tag{5}$$

where C^b is the bulk concentration Ox,

   $C_{Ox}(o,t)$ is the concentration Ox at the surface of the electrode,

   ν is the kinematic viscosity,

   ω is the angular velocity,

   A is the surface area of electrode.

The other symbols have their usual meaning.

If the chemical reaction Red $\overset{k}{\to}$ A is fast, according to the reaction layer concept, the concentration Red can be written[5]

$$i = \frac{n F A D_{Red} C_{Red}(o,t)}{\mu} \tag{6}$$

where μ is the reaction layer thickness.

Introducing (5) and (6) in the Nernst equation and with the reaction layer thickness given by[6]:

$$\mu = \left(\frac{D_{Red}}{k}\right)^{1/2}$$

one can obtain

$$E = E^\circ + \frac{RT}{nF} \ln \frac{i_L - i}{i} + \frac{RT}{nF} \ln \frac{D_{Red}^{2/3}}{D_{Ox}^{2/3}} + \frac{RT}{nF} \ln \frac{k^{1/2}}{0.62\nu^{-1/6}\omega^{1/2}D_{Red}^{1/6}} \qquad (7)$$

When $i = i_L/2$ the potential is given by the formula

$$E_{1/2}^K = E^\circ + \frac{RT}{nF} \ln \frac{D_{Red}^{2/3}}{D_{Ox}^{2/3}} + \frac{RT}{nF} \ln \frac{k^{1/2}}{0.62\nu^{-1/6}\omega^{1/2}D_{Red}^{1/6}} \qquad (8)$$

because for the rotating disk electrode

$$E_{1/2}^{Red} = E^\circ + \frac{RT}{nF} \ln \frac{D_{Red}\delta_{Ox}f_{Ox}}{D_{Ox}\delta_{Red}f_{Red}} \qquad (9)$$

where δ, the thickness of the diffusion layer is given by: $\delta = 1.62D^{1/3}\nu^{1/6}\omega^{-1/2}$. Assuming $f_{Ox} = f_{Red}$, we have the final equation:

$$E_{1/2}^k = E_{1/2}^{Red} + \frac{RT}{nF} \ln \frac{k^{1/2}}{0.62\nu^{-1/6}\omega^{1/2}D_{Red}^{1/6}} \qquad (10)$$

In the same way we can treat the process

$$2\ Ox + ne \rightarrow 2\ Red \xrightarrow{k} C \qquad (11)$$

But in this case the thickness of the reaction layer is given by the equation[5]:

$$\mu = \frac{D^{1/2}}{k^{1/2}C_{Red}^{1/2}} \qquad (12)$$

The final result for (11) will be

$$E_{1/2}^k = E^\circ + \frac{RT}{nF} \ln \frac{k^{1/3}(C^b)^{1/3}}{0.91\omega^{1/3}\nu^{-1/9}D^{1/9}} \qquad (13)$$

where C^b is the bulk concentration of Ox.

The relation (10) predicts that the half-wave potential of the kinetic process (9) is, in the case of reduction, shifted towards more positive potentials with respect to the potential which would be noticed if, in (9), Red did not undergo transformations. The shift is higher, the higher k and the smaller ω and D. In the case of the process (11) the kinetic half-wave potential is also dependent on bulk concentration Ox. Both relations are true if charge transfer is fast. It was not possible to check this equation by experiments. Only a few processes are known so far which go according to equations (9) and (11) with fast charge transfer. The best example of reaction (9) in polarography is the oxidation of ascorbic acid. On rotating platinum and carbon paste disk electrodes this reaction behaves irreversibly and cannot be treated in the fashion given.

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[1] V. G. LEVICH, *Fiziko-khimicheskaya gidrodinamika (Physico-Chemical Hydronydamics)*, Gosu-darstvennoe, Izdatel'stvo Fizikomatematicheskoi Literatury, Moscow, 1959, p. 348.
[2] V. G. LEVICH AND J. KOUTECKY, *Zhur. Fiz. Khim.*, 32 (1958) 1565.
[3] D. M. H. KERN, *J. Am. Chem. Soc.*, 75 (1953) 2473; 76 (1954) 1011.
[4] Z. GALUS, *Ph.D. Dissertation*, Warsaw University, 1960.
[5] V. HANUS, *Chem. Zvesti*, 8 (1954) 702.
[6] J. KOUTECKY AND R. BRDICKA, *Collection Czechoslov. Chem. Communs.*, 12 (1947) 337.

The influence of pen response time on recorded a.c. polarograms

A heretofore unreported limitation of MILLER's[1,2,3] modification of the Sargent Model XXI Polarograph for recording a.c. polarograms, with the dropping mercury electrode (DME), is the effect of the relatively slow pen response time of the Brown recorder used in this instrument (10 sec for full scale pen excursion) upon the observed a.c. currents.

The pen response time does not unduly influence the recording of d.c. polarograms (cf. DELAHAY AND TRACHTENBERG[4]). Recording polarographs with rapid pen response (0.5 sec full scale) can follow faithfully almost the entire current transient during the life of a mercury drop[5]. Those instruments with slower pen speeds do not respond rapidly enough to track the current during the early stages of drop life, yet "catch up" prior to detachment of the drop and indicate the maximum current. SUZUKI AND ELVING[6] recently demonstrated the validity of using the maximum of the Sargent XXI pen excursions as a measure of true maximum current.
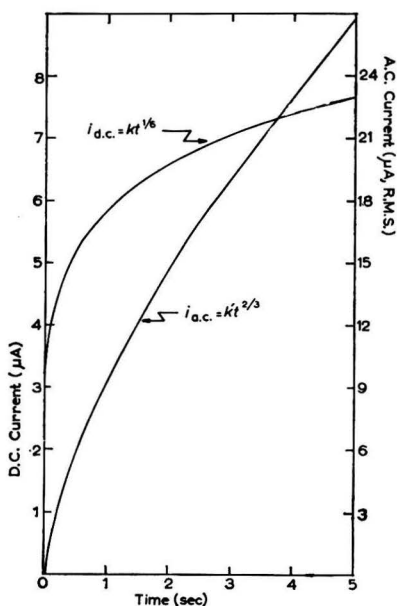
Fig. 1. Comparison of theoretical d.c. and a.c. current–time curves for a single mercury drop.

The theoretical current–time curves for both d.c. and a.c. polarographic diffusion controlled reversible processes at the DME are shown in Fig. 1. The instantaneous d.c. currents were calculated using the Ilkovič equation,

$$i_{d.c.} = 706 n D^{1/2} C_{ox} m^{2/3} t^{1/6}$$

The instantaneous a.c. currents were calculated, at the summit potential, using the equation reported by SENDA AND TACHI[7],

$$i_{a.c.} = \frac{n^2 F^2 (D\omega)^{1/2} A C_{ox} v}{4RT} \sin (\omega t + \pi/4)$$

For these calculations the following substitutions were made in the equations:

$D_{ox} = D_{red} = D = 1.0 \cdot 10^{-5}$ cm^2 sec^{-1}

$n \quad = 2$

$t \quad = 0-5$ sec

$C_{ox} = 1.0$ mmol l^{-1}

$m \quad = 1.5$ mg sec^{-1}

$F \quad = 96,493$ C

$R \quad = 8.314$ VC deg^{-1}

$T \quad = 298°$K

$v \quad = 0.005$ V

$\omega \quad = 2\pi f$, where $f = 60$ c/sec

$A \quad = 85.15$ m$^{2/3}t^{2/3}$ (area of drop).

The equations can be simplified, after proper substitution, to the following: $i_{d.c.} = kt^{1/6}$, and $i_{a.c.} = k't^{2/3}$.

The theoretical currents at 80% of drop life are 85.8% and 96.3% of the maximum currents for the a.c. and d.c. processes respectively; at 90% of drop life the values are 92.9% and 98.3%. It is apparent that the a.c. current is more dependent upon the age of the drop than is the d.c. current. We might suspect, therefore, that recorder response time would significantly influence the measurement of a.c. currents at the DME.

The effect of pen speed was first observed in this laboratory by noting that, for a given a.c. polarographic process measured on a Sargent Model XXI Polarograph modified for a.c. use, doubling the recorder sensitivity did not double the a.c. current at the peak. When a resistance box was substituted for the cell, perfect correspondence between recorded current output and recorder sensitivity was observed. The apparent
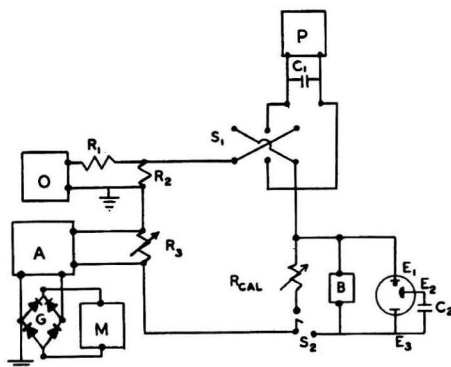
Fig. 2. Scheme of alternating current polarograph. A, amplifier; B, Beckman Model G pH meter; E$_1$, DME; E$_2$, mercury pool; E$_3$, S.C.E.; M, recorder; O, oscillator; S$_1$, DPDT switch; C$_1$, C$_2$, 2000 μF 15 WV electrolytic capacitor; G, copper oxide rectifier; P, direct current polarizing bridge; R$_1$, 200 Ω; R$_2$, 5 Ω; R$_3$, 50 Ω; R$_{cal}$ 10,000 Ω decade resistance box; S$_2$, DPST switch.

loss of signal for the polarographic process was related to the relative position of the recorder pen on the chart, *i.e.*, the greater the required pen excursion, the greater the signal loss.

In order to measure the effect of pen response time, a.c. polarograms for a reversible redox system, Cd(II), recorded on the Brown recorder of the Sargent Model XXI Polarograph and on a Photovolt Varicord Model 43 laboratory recorder (1 sec pen speed) were compared. The a.c. instrumentation employed in this work was of conventional design (Fig. 2)[8]. The polarizing voltage was supplied by a Sargent Model XII polarograph at a rate of 0.39 mV sec^{-1}. The a.c. signal from the cell thermostated at 25° was recorded as a voltage drop across a 50 ohm resistor after amplification and rectification. Two different DME's were employed for experiments, one of which had a drop time of 2.71 sec and an *m* value of 2.16 mg sec^{-1} (DME #1) and the other a drop time of 2.58 sec and an *m* value of 3.15 mg sec^{-1} (DME #2) in an oxygen-free 1.0 *M* KNO$_3$ solution, under a mercury pressure of 64 cm and open circuit. The applied a.c. voltage was 20 mV r.m.s. and its frequency was 100 c/sec. A.c. current at the summit potential (0.59 V *vs.* S.C.E.) was expressed in terms of the equivalent reciprocal resistance required to reproduce the observed recorder deflection. The equivalent resistance of the supporting electrolyte, 1.0 *M* KNO$_3$, was 1500 ohms. Table I summarizes the data obtained in this experiment.

TABLE I

EFFECT OF RECORDER RESPONSE TIME ON A.C. CURRENTS FOR
4.2 · 10^{-4} *M* Cd(II) IN 1.0 *M* KNO$_3$, DME #1

Full scale sensitivity (μA d.c.)	Recorder response (ohms^{-1} · 10^3)	
	1 sec speed	*10 sec speed*
2.8	—	1.48
4.2	—	1.55
5.6	—	1.59
8.4	—	1.66
10.0	1.90	—
11.2	—	1.72
16.8	—	1.75
25.0	1.87	—
50.0	1.82	—

The peak currents, even at the lowest sensitivity employed in these experiments, were less than the peak response of the 1 sec recorder. A significant loss in sensitivity was observed when the "slow" recorder was used, as the a.c. currents were actually being measured at different stages of drop growth, depending upon the degree of excursion of the recorder pen. Recorder outputs for different redox processes will only be comparable if measured under conditions of identical pen excursions. Furthermore, a different empirical concentration–current calibration curve must be determined for each recorder sensitivity setting. The variations in the observed a.c. currents for the 1 sec recorder can be attributed to a combination of several effects: (1), the loss of sensitivity experienced in measuring resistance on the 50 μA scale as compared to the 10 μA scale; (2), the variations in dropping rate of the DME, ("no two drops are identical") due to capillary noise[9], and (3), the influence of polarization rate on a.c. recorded waves as described by TANAKA *et al.*[10]. In the latter case, the

true peak current may be skipped, if the drop time is long compared to the scanning rate.

The effect of drop time on the a.c. peak was also studied using the "slow" recorder. Currents were measured at the summit potential by permitting the recorder to come to a constant value, in order to eliminate any influence of potential scanning rate on the a.c. polarogram. The results are summarized in Table II. They confirm the previous study, indicating that increased sensitivity results if drop time is slowed as well as if recorded response time is decreased. The peak current is still increased when the sensitivity of the recorder is reduced.

TABLE II

EFFECT OF DROP TIME ON A.C. CURRENTS OBSERVED WITH 10 SEC RECORDER

FOR $3.960 \cdot 10^{-4}$ M Cd(II) IN 1.0 M KNO_3, DME #2

Full scale sensitivity (μA d.c.)	Recorded response (ohms$^{-1} \cdot 10^3$)	
	2.81 sec drop	5.36 sec drop
4.2	1.96	2.28
5.6	1.99	2.34
8.4	2.04	2.44
16.8	2.13	2.63
28.0	2.38	2.70

It should be noted that the measurements of impedances in this experiment were made with a DME having a larger peak area than the DME used in the previous study, i.e., 0.028 cm^2 (DME #1) vs. 0.034 cm^2 (DME #2), accounting for the higher currents observed. The differences obtained at different drop times in this experiment cannot be attributed to differences in drop area, since the product $m^{2/3}t^{2/3}$ was a constant independent of the mercury pressure.

The results of this investigation indicated that a 1 sec recorder is capable of measuring instantaneous current at maximum drop size. This conclusion was verified using an oscilloscope in an experimental arrangement similar to that employed by DELAHAY AND ADAMS[11]. A.c. polarograms obtained using slower recorders must be interpreted with care. Modifications of commercial d.c. polarographs, especially the Sargent Model XXI, may have severe limitations built into them. The considerable loss of signal compared to the theoretically attainable value and the large variation in response observed at different recorder sensitivities perhaps negate the use of such instruments in most a.c. polarographic studies. Furthermore, the suggestion of TANAKA et al.[10], that the rapidly dropping mercury electrode (drop time < 1 sec) be employed in order to record true a.c. currents will only be of value if a "fast" recorder is also used.

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1 D. M. MILLER, *Can. J. Chem.*, 34 (1956) 942.
2 *ibid.*, 35 (1957) 1589.
3 W. F. HEAD JR., *Anal. Chim. Acta*, 23 (1960) 207.
4 P. DELAHAY AND I. TRACHTENBERG, *J. Am. Chem. Soc.*, 80 (1958) 2100.
5 I. M. KOLTHOFF AND J. J. LINGANE, *Polarography*, Vol. I, 2nd edn., Interscience Publishers, Inc., New York, 1952, p. 318–319.

6 M. SUZUKI AND P. J. ELVING, *J. Phys. Chem.*, 65 (1961) 391.
7 M. SENDA AND I. TACHI, *Bull. Chem. Soc. Japan*, 28 (1955) 632.
8 G. BUCHANAN AND R. L. WERNER, *Australian J. Chem.*, 6 (1953) 439.
9 W. D. COOKE, M. T. KELLY AND D. J. FISHER, *Anal. Chem.*, 33 (1961) 1209.
10 N. TANAKA, R. TAMAMUSHI AND M. KODAMA, *Anal. Chim. Acta*, 20 (1959) 573.
11 P. DELAHAY AND T. J. ADAMS, *J. Am. Chem. Soc.*, 74 (1952) 5740.

Book Reviews

Scientific Reports of the Istituto Superiore di Sanità, 1st Vol., Elsevier Publishing Co., Amsterdam, 1961, 591 pages, 1 volume annually, £ 8.10.0, or $ 24, or Dfl. 90 per volume.

When a new scientific publication is reviewed, the following three questions can be asked: (1), Is the new publication really necessary?; (2), What is its purpose?; (3), What is the quality of the scientific articles which it contains? *Scientific Reports of the Istituto Superiore di Sanità* has just completed its first year, and can now be evaluated on the basis of these questions.

It should be made clear that the Istituto Superiore di Sanità is a government institution, primarily concerned with matters of public health, and setting standards for the manufacture and marketing of foods and drugs. Within its complex of different departments and laboratories there are many scientists who, apart from the routine work mentioned above, are engaged on different basic research projects. Because the extent of their research has now been developed so considerably, it was felt that publications concerning their work and results merit access to the scientific world at large, and an English-language publication has therefore been launched.

As the Istituto Superiore di Sanità is also the venue of many scientific meetings and symposia, and well-known personalities of the scientific world regularly give lectures there, the new journal has been planned to include reports of the proceedings and discussions arising from these activities.

The journal is published quarterly. Of the four issues which appeared in 1961, nos. 2 and 3 are devoted entirely to publication of the papers presented, and subsequent discussions, at the First International Fermentation Symposium, held at the Istituto Superiore di Sanità from 9–14th May, 1960, in which scientists from 21 nations participated. The three main topics considered were: (1), Fermentation Technology; (2), Fermentation Biology, and (3), Special Fermentation, together with a panel discussion on microbial genetics and its application to fermentation. Those interested in fermentation will find many excellent articles of general and technical interest, oriented mainly towards the problems and demands of the pharmaceutical and chemical industries. The section on genetics, apart from its basic scientific interest, indicates new possibilities of improving and increasing the use of moulds, micro-organisms, etc. for the benefit of man. The Proceedings are well edited, and discussions following some of the papers are both interesting and provocative.

Issues nos. 1 and 4 contain articles relevant to the work done in different departments of the Istituto. These cover the fields of chemistry and biochemistry, therapeutic chemistry, physics and microbiology. Two papers deal with the fractionation of alkaloids; three publications present devices and techniques for conditioning laboratory animals in the testing of psychotropic drugs, and the Department of Physics presents papers on its work in the fields of experimental and biophysics, and electron microscopy. In issue no. 4, the lectures delivered at the Istituto by four distinguished visitors are on "Advances in Quantum Chemistry", "Theoretical Considerations of Paper Chromatography", "Structure of Lycopodium Alkaloids", and "Comparison of the Action of Ionizing Radiations and Biological Alkylation Agents at the Cellular and Sub-cellular Level."

On the first anniversary of the *"Scientific Reports"* the reviewer would like to wish the new periodical continued success, and to make two suggestions; articles should be kept brief, whenever possible, and they should be grouped together in their relevant fields, rather than spread about haphazardly.

PETER BEACONSFIELD, University of Chicago

Spectrochemical Analysis, a Treatise on d-c Arc Analysis of Geological and Related Materials, 2nd edn., by L. H. AHRENS AND S. R. TAYLOR, Addison-Wesley Publishing Company, Inc., Reading, Mass., U.S.A., 1961, xxiv + 454 pages, 6 plates, 75 figs., 136 tables, $15.00.

As indicated by the sub-title, the purpose of this book is twofold; (1), to present the basic knowledge of d-c arc spectrochemical methods essential for their comprehension; (2), their application to geochemical problems in the widest sense.

The work is divided into a general and a specialized part and contains a large reference section, which consists of a 50 page bibliography with *ca.* 1000 titles, and some 70 pages of wavelength tables of the elements alphabetically grouped, indicating a small number of analysis lines together with the lines of elements which could interfere.

The first part consists of a rather short discussion of phenomena underlying the physical theory of the d-c arc, and indeed, of spectral emission and spectrum analysis in general. This is achieved without the use of much theoretical discussion. Although this brings about a slightly inexact terminology, the wealth of practical details interwoven with this general discussion is an extremely valuable source of information. This method of presentation will appeal to scientists primarily interested in the potentialities of the method, rather than in the method as such.

The special part is a useful discussion of practical emission characteristics of the elements. From the point of view of the general chemist, the grouping of the elements is somewhat unorthodox, being related to the ways in which elements are associated in inorganic nature. A chapter dealing with the determination of major elements is included in this edition.

Instrumentation, as such, has not been dealt with, and this, together with the almost exclusive stress on photographic methods of registration, gives this otherwise stimulating text a decidedly conservative flavour. But this scarcely affects the value of this beautifully produced book.

In view of the favourable properties of the d-c arc for general spectrochemical analysis, this book should be available to everyone either using, or considering the application of, these methods in analytical problems.

W. VAN TONGEREN, University of Amsterdam

J. Electroanal. Chem., 4 (1962) 256

Atomic Absorption Spectrophotometry, by W. T. ELWELL AND J. A. F. GIDLEY, Pergamon Press, Oxford, 1961, 102 pages, 30 sh.

This booklet (with an index and references) is a very short introduction to the theory of atomic absorption spectra, in which some objections could be made to the mathematical part. The chapter on equipment describes only equipment which is already commercially available. For example, nothing is said about demountable hollow-cathode lamps. Chapters 4 and 5 contain some general and specific discussions, concerning various questions approached mainly from a practical point of view. The second half of the book gives detailed procedures for analyzing the most common metals, *i.e.* Zn, Pb, Mg, Mn, Fe, Ca, Na, K, Cu and Cd. Other elements are mentioned. As a practical guide in the laboratory, this short monograph can be useful.

J. Electroanal. Chem., 4 (1962) 256

Méthodes Sélectionnées de Microanalyse Organique Quantitative, von R. LEVY UND B. COUSIN, Band 1, Dunod, Paris, 1961, x + 122 Seiten, 15 N.F

Gegenstand der *Méthodes sélectionnées de microanalyse organique quantitative* ist ausführliche Anleitung zur Einrichtung eines Mikrolaboratoriums, sowie die quantitative Erfassung der Elemente und der Gruppen mit erprobten Arbeitstechniken. Dieses Büchlein gibt ausreichende Hinweise zur selbständigen Aneignung mikroanalytischer Arbeitsmethoden.

Das erste Kapitel dieses 1. Teiles enthält die allgemeine Beschreibung eines Laboratoriums für quantitative organische Mikroanalyse, die nötigen Vorkenntnisse des Personals und die organisation eines Mikrolabors. Das Aufstellen und Überprüfen einer Mikrowaage von Bunge, sowie das Wägen und die Berechnung der Wägefehler, werden ausführlich im zweiten Kapitel behandelt. Das letzte Kapitel befasst sich mit der Probenahme und Einwaage fester, flüssiger, zähflüssiger und hydroskopischer Substanzen.

Die Abbildungen sind sehr klar und übersichtlich und tragen zum besseren Verständnis gut bei. Das Büchlein hat wohl eine sehr gute Inhaltsübersicht, enthält aber leider kein Inhaltsverzeichnis. Man vermisst auch eine ausführlichere Literatur, denn es werden nur einige klassische Werke genannt.

Dieses Buch ist auch bezüglich des Taschenformates, besonders als Nachschlagewerk für die praktische Arbeit sehr zu empfehlen.

M. MARZADRO, Istituto Superiore di Sanità, Roma

J. Electroanal. Chem., 4 (1962) 256

1. Fundamental electrochemistry

592 – Preliminary observations of a peculiar effect of nuclear radiations on electrode processes (in Italian). L. Busulini (Institute of Physical Chemistry and School of Applied Nuclear Physics, C.N.E.N., University of Padua, Italy). *Atti accad. naz. Lincei. Rend. Classe Sci. fis. mat. e nat.*, 30 (1961) 53–54.

Pairs of microelectrodes (vibrating or stationary platinum or mercury electrodes) having the same surface were used. One electrode in each couple was "radioactivated" by electrochemical deposition of polonium. The reduction of an aqueous solution of ferric ions at the electrode was followed by means of oscillographic polarography. During the experiments, a marked increase of current was observed at the electric tensions corresponding to each reduction step. This phenomenon disappeared, or was greatly reduced, after some time, due to superficial ageing phenomena. This ageing can be temporary or permanent, depending on the nature of the electrode and operating conditions. A tentative hypothetical interpretation is suggested, relating the observed facts with the oxidising effect of the α- and β-radiations, and with the oxygenated water effect on the mechanism of reduction of the iron(II) produced.   [Su.Mo.Ce.]

593 – The effect of the exponential distribution function on the electrophoretic contribution to the conductance of 1–1 electrolytes (in English). D. J. Karl and J. L. Dye (Kedzie Chemical Laboratory, Michigan State University, East Lansing, Mich., U.S.A.). *J. Phys. Chem.*, 66 (1962) 477–481.

It was found after the examination of calculations by a digital computer for a number of salts in dioxane–water and in ethanol–water mixtures, that much of the deviation from conductance theory, usually attributed to ion-pair formation, could arise from neglect of the higher terms in the distribution function.   [D.S.Ru.]

594 – Electrode kinetics by hydrodynamic voltammetry. Study of ferrous–ferric, ferrocyanide–ferricyanide and iodide–iodine systems (in English). J. Jordan and R. A. Javick (Department of Chemistry, Pennsylvania State University, University Park, Pa., U.S.A.). *Electrochim. Acta*, 6 (1962) 23–33.

Using rotated and circulatory electrolysis cells, rate parameters of electrode processes have been determined at stationary conical and cylindrical platinum microelectrodes in flowing solutions, under judiciously controlled hydrodynamic conditions. Virtually ideal laminar flow was maintained at velocities up to 700 cm/sec. Normally reversible d.c. current–voltage waves were made "irreversible in shape", due to enhancement of convective mass transfer. Thus, specific electron-transfer rate constants, ranging up to an estimated limit of 10 cm/sec could be evaluated by a simple, unambiguous "wave analysis" procedure. The electro-oxidation of iodide to iodine, in perchloric acid in the absence of triiodide is governed by second-order kinetics. A mechanism is proposed to account for this remarkable finding.   [Author]

595 – Electrochemical properties of powders (in French). W. Tomassi (The Polytechnic, Warsaw, Poland). *Electrochim. Acta*, 6 (1962) 91–99.

We have observed that powder electrodes made with activated carbon powder or platinum black, immersed in the Cl_2/Cl^-_{aq} system, take up a potential which is permanently much below that of a platinum wire electrode in the same system. This observation has been utilized to construct a cell that gives electrical work, on account of the adsorption energy. The cell can be charged and discharged and has the properties of an accumulator.

Powder electrodes can also be used in electrolytic processes of gas evolution, of chlorine, hydrogen and oxygen. A very advantageous lowering of the electrolysing voltage can be obtained, below the "reversible" voltage, and overpotential is eliminated; the gas is obtained adsorbed on the powder of the electrode. To maintain the lowered electrolysing voltage, the powder surface must be renewed.   [Author]

596 – The dielectric constant and conductance of ion pairs; an extension of Onsager's field effect to relaxation of ion pairs in an alternating field (in English). W. R. Gilkerson (Department of Chemistry, University of South Carolina, Columbia, S.C., U.S.A.). *J. Phys. Chem.*, 66 (1962) 669–673.

A solution was obtained for Onsager's expression for the distribution function of ion pairs in an

external field in the form of a definite integral and expressed as an infinite series which reduces to the zero-field distribution and a term linear in the field for low field strengths. This is used to calculate the displacement current in the field direction in an alternating field, and equations are derived for the resulting increase in dielectric constant and conductance as a function of frequency.

[D.S.Ru.]

597 – A conjecture concerning the electrical conductance of metal–molten salt mixtures (in English). S. A. Rice (Department of Theoretical Chemistry, University Chemical Laboratory, Cambridge, Great Britain). *Discussions Faraday Soc.*, 32 (1961) 181–187.

A theoretical discussion of the electronic contribution to the electrical conductance in terms of rapid resonant transfer, possibly but not necessarily through bridging anions. It is suggested that the basic mechanism of the excess electrical conduction of atomically dispersed metals in molten parent salts involves a random walk of the electron, and not excitation to a conduction band in the sense used in the theory of crystalline metals. Both the qualitative nature of the concentration dependence of the excess conductance and the order of magnitude of the calculated electron mobility are in accordance with experimental data. Results obtained do not permit a definitive decision concerning the role of the anion in the conduction process.   [Su.Mo.Ce.]

598 – Study of the impedance of a platinum electrode in the system Br_2-Br^- ($HClO_4$, aq.). **I. Influence of the surface state** (in English). L. Llopis and M. Vàzquez (Instituto de Quimica Fisica "Rocasolano", Madrid, Spain). *Electrochim. Acta*, 6 (1962) 167–176.

Impedance measurements, over a wide range of frequencies, of a platinum electrode immersed in a solution of Br_2-Br^- ($HClO_4$, aq.), allow us to obtain the values of the exchange current j_0, it being also possible to study its variation with the experimental conditions. The results thus obtained depend on the state of the electrode surface. With activated electrodes the Randles circuit explains well enough the electrochemical behaviour of this system. With poisoned electrodes the circuit is inadequate, but it can be shown that the exchange current is decreased by the poisoning effect. Decrease of the exchange current with increase of surface oxidation of the electrode has also been observed.

As a first approximation the poisoning effects can be explained by a diminution of the effective area concerned with electron transfer, but the inadequacy of the Randles circuit indicates that adsorption processes have to be taken into account.   [Authors]

599 – Study of the impedance of a platinum electrode in the system Br_2-Br^- ($HClO_4$, aq.). **II. Mechanism of the electrode reaction** (in English). J. Llopis and M. Vàzquez (Instituto de Quimica Fisica "Rocasolano", Madrid, Spain). *Electrochim. Acta*, 6 (1962) 177–183.

The Randles circuit well represents impedance measurements carried out with activated Pt electrodes. This enables us to study the variation of j_0 for redox reactions with concentration of the reactants, at constant potential (electric tension), and also the variation of j_0 with potential, keeping the concentration of one of the reactants constant. The results thus obtained indicate that the step, $Br_2 + e^- = Br_2^-$ is rate-determining; it is followed or preceded by the rapid equilibria, $Br_2^- \rightleftharpoons Br^- + Br$, and $2 Br \rightleftharpoons Br_2$. The mechanisms proposed hitherto for the electrochemical behaviour of the halogen–halide systems at inert electrodes are discussed, and it is reasoned that the "reversibility" of these systems increases in the order, $Cl_2-Cl^- > Br_2-Br^- > I_2-I^-$.   [Authors]

See also abstract no. 677.

2. Apparatus and accessories

600 – Electrostatic methods of zone location for paper chromatographs. V. A chromatograph humidiser (in English). G. G. Blake (Chemistry Department, Sydney University, Sydney, Australia). *Anal. Chim. Acta*, 22 (1960) 38–40.

A "humidiser" or chromatograph conditioner is described in this paper. It is employed for sensitive chromatographic spots of weakly conductive solute. It can be used in conjunction with either rectified radio-frequency or electrostatic discharge methods of zone location. The spot edge effect, observed during spot localization, is recorded.   [P.Me.]

601 – A titration coulometer (in English). V. Subrahmanyan and N. Lakshminarayanaiah

(Physical Chemistry Laboratory, University of Madras, India). *Current Sci. (India)*, 30 (1961) 13–14.

The apparatus consists of an H-shaped cell, divided in the middle of the horizontal limb by an ion exchange membrane. After equilibration of the membrane with the electrolyte (NaCl from 1 N to saturated) a current of 20–30 mA is passed for 20–30 min. The cathode compartment is emptied and washed, and the combined solution and washings are titrated with standard acid solution using methyl orange as indicator. The results are in agreement with those obtained using a silver coulometer.   [Gio.Ser.]

602 – Device for measuring the resistance of solutions linearly and continuously (in English). P. V. Avizonis, F. Fritz and J. C. Wriston, Jr. (Department of Chemistry, University of Delaware, Newark, Del., U.S.A.). *Anal. Chem.*, 34 (1962) 58–61.

The circuit, calibration curve and a detailed description are given of a new servo-mechanical monitor of high stability and linearity, which is used for continuous measurements of resistance in solutions. In theory, the instrument should be able to measure solution resistances at high as well as low concentrations; in practice, some sensitivity is lost at high concentration (0.2 M). The way to overcome this inconvenience is indicated. The instrument has excellent stability and reproducibility: no deviation was observed with a 0.005 M phosphate solution flowing through the cell at various flow rates over a period of 24 h.   [Su.Mo.Ce.]

603 – A pH-stat (in English). L. Josefsson, C. E. Ryberg and R. Svensson (Department of Physiological Chemistry, University of Lund, Lund, Sweden). *Anal. Chem.*, 34 (1962) 173–174.

A pH-stat equipment developed in the author's laboratory is described. It is especially suited for the study of reaction systems having low concentrations during long time periods. The pH is kept constant within ± 0.01 pH unit for one or more days. A wiring diagram for burette control is given. The apparatus permits studies of both rapid and extremely slow reactions, with small concentrations of reactants.   [Su.Mo.Ce.]

604 – An automatic-recording titration apparatus for use with slow reactions (in English). L. R. Leake and G. F. Reynolds (Chemical Inspectorate, War Office Royal Arsenal, Woolwich, London, Great Britain). *Talanta*, 9 (1962) 421–425.

An automatic-recording apparatus for titrations involving slow reactions is described in connection with a potentiometric method for acid–base titrations in acetone–water solutions of nitrocellulose, published by the authors in a previous paper (*Talanta*, 9 (1962) 413). Trials with the new apparatus showed that very satisfactory results can be obtained.   [Su.Mo.Ce.]

605 – Comparison electrodes for high temperatures (in French). G. Danner and M. Rey (Société Electrochimique d'Ugine, Laboratoire de Recherches, Saint Ouen, France). *Electrochim. Acta*, 4 (1961) 274–287.

A reference electrode based on the system $Ag–Ag^+$, capable of functioning very satisfactorily up to 960°, the melting point of silver, is described. Modifications permit the electrode to be applied up to 1300°. Its principal properties are reviewed, and some anodic polarization curves are presented to illustrate its application.   [Authors]

606 – A potentiostat for amperometric kinetic studies (in English). J. M. Matsen and H. B. Linford (Department of Chemical Engineering, Columbia University, N.Y., U.S.A.). *Anal. Chem.*, 34 (1962) 142–145.

An electronic instrument that incorporates a potentiostat technique into amperometric titration investigations of redox systems is described, with details. In the study of the kinetics of a redox reaction, if the reduced ion is anodically reoxidized at such a rate as to keep the redox electric tension of the solution constant, the current consumed for the electrolysis is proportional to the reaction rate. The apparatus described automatically produces electrolysis current to maintain a constant electric tension in the solution. Application to the study of the kinetics of oxidation of coal by iron(III) is reported: reaction rates from 1 to 60 mA have been followed. A typical current–time curve is reproduced; estimated error of the procedure is about 5%. The instrument can be operated continuously for periods of as long as one week. Main advantage of the potentiostatic technique is that it eliminates reaction rate dependence on the redox electric tension. [Su.Mo.Ce.]

607 – Microcell for voltammetry with the hanging mercury drop electrode (in English). W. L. Underkofler and I. Shain (Department of Chemistry, University of Wisconsin, Madison, Wis., U.S.A.). *Anal. Chem.*, 33 (1961) 1966–1967.

Details of construction and diagrams of a new type of microcell containing a hanging mercury drop electrode (HMDE) and a comparison electrode are given. The reproducibility of the procedure used

to form the HMDE was tested by replicate determinations using fast-sweep polarography on a solution containing $2 \cdot 10^{-4}$ M Cd^{2+} in 0.1 M potassium chloride; average deviation of five replicate determinations was less than 0.6%. Results obtained in the stripping analysis of cadmium solutions (10^{-6} to 10^{-8} M) indicated that the analysis can be performed with very small volumes of solution with a remarkable sensitivity.   [Su.Mo.Ce.]

608 – High precision comparative polarography (in English). H. I. Shalgosky and J. Wathing. (U.K.A.E.A. Research Group, Chemistry Division, Royal Arsenal, Woolwich, London, Great Britain). *Anal. Chim. Acta*, 26 (1962) 66–74.
This paper describes a new cell assembly for use with the differential cathode ray polarograph. An entirely new stand was constructed in which two matched cells are permanently mounted in a box which contains an oxygen-free atmosphere. No further manipulations of the cells or electrodes was required after the initial setting up operation. A detailed description of the design and construction of the stand is given. Results obtained show that the coefficient of variation of a polarographic determination can be as low as 0.04%.   [P.Me.]

609 – Rotating disk electrodes (in English). Z. Galus, C. Olson, H. Y. Lee and R. N. Adams (Department of Chemistry, University of Kansas, Lawrence, Kan., U.S.A.). *Anal. Chem.*, 34 (1962) 164–166.
Applications of rotating disk electrodes developed by some of the authors (R. N. Adams, *Anal. Chem.*, 30 (1958) 1576; C. Olson and R. N. Adams, *Anal. Chim. Acta*, 22 (1960) 582) are summarized. Applications to routine analysis, to the determination of diffusion coefficients and to the studies of electrode mechanisms are considered.   [Su.Mo.Ce.]

610 – Platinization of an electrode for tracing intensity –electric tension curves in acetonitrile (in French). J. Desbarres (Laboratoire de Chimie Analytique, E.P.C.I., 10 rue Vauquelin, Paris, France). *Bull. soc. chim. France*, (1962) 727–729
L'auteur précise les conditions de platinage conduisant à un fonctionnement correct de l'électrode à hydrogène dans l'acétonitrile. Le platinage en solution aqueuse fournissant des résultats peu reproductibles est à proscrire. Le tracé de la courbe intensité–tension électrique relative au bain de platinage dans l'acétonitrile permet de préciser les conditions d'électrolyse. Le système H_2–HPy^+ (HPy^+ = ion pyridinium) est rapide à une électrode de platine platinée, comme l'indique le tracé de la courbe intensité–tension électrique correspondante.   [An.Sn.]

See also abstracts nos. 670, 711, 731, 734.

3. Polarography

611 – Faradaic admittance: sign conventions (in English). S. K. Rangarajan and K. S. G. Doss (Central Electrochemical Research Institute, Karaukudi, India). *Electrochim. Acta*, 7 (1962) 201–204.
The conventions for positive and negative current and electric tensions at electrodes carrying a.c. are discussed.   [Authors]

612 – Polarography in molten systems. I. Oscillographic a.c. polarography of reversible depolarisators on solid electrodes (in German). E. Schmidt (Institut für anorganische Chemie der Universität, Bern, Schweiz). *Electrochim. Acta*, 7 (1962) 179–200.
In the Heyrovský–Forejt method of oscillographic polarography the electrode is polarized with a.c. and the resulting voltage–time curve is recorded with an oscillograph. In contrast to d.c. polarography, this method can be readily applied to solid electrodes and appears therefore to be a suitable means for the polarographic investigation of molten salts. Depending on the properties of the reduced species we may distinguish between: (a) polarography in homogeneous solutions, where all species taking part in the electrode reaction dissolve in the electrolyte (or the electrode); (b) polarography of a depolarizer, the reduced form of which is deposited as metal at the electrolyte–solid electrode interface without dissolution in appreciable amounts in any one of the two phases. E–t relationships for both cases have been derived, and are discussed under the assumption of a reversible electrode reaction.   [Author]

613 – A simple method of solving Ilkovič's differential equation for the transfer of depolarizer to the dropping mercury electrode (in English). R. S. Subrahmanya (Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India). *Can. J. Chem.*, 40 (1962) 296–300.

The method developed by Ilkovič for solving the differential equation:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial \chi^2} + \frac{2\lambda}{3t}\frac{\partial C}{\partial \chi}$$

governing the diffusion of the depolarizer to the surface of the dropping mercury electrode is very difficult. A simple method is presented. By introducing two variables, $S = \chi t^{2/3}/2\sqrt{3/7\ D}$ and $T = 1/4t^{7/3}$, the above equation is transformed into $\partial C/\partial T = \partial^2 C/\partial S^2$. The boundary conditions for the transformed differential equation are formulated and the equation is solved by the Laplace transformation method.   [D.S.Ru.]

614 – Modification of the Ilkovič equation (in English). R. S. Subrahamanya (Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India). *Can. J. Chem.*, 40 (1960) 289–295.

The expression for the flux obtained by Ilkovič has been obtained by replacing A with a function of t in Stachelberg's integral and considering the effect which the moving surface will have on the thickness of the diffusion layer. This new approach, when applied to the case of the spherical diffusion of the dropping mercury electrode, has lead to the following equation:

$$i_d = 607\ nD^{1/2}Cm^{2/3}t^{1/6}\ (45.1\ D^{1/2}m^{-1/3}t^{1/6} + 1)$$ [D.S.Ru.]

615 – Studies on the vibrating dropping mercury electrode. Effect of frequency and magnitude of the alternating field on the polarographic limiting current (in English). R. Narayan (Central Electrochemical Research Institute, Karaikudi, India). *Electrochim. Acta*, 7 (1962) 225–232.

A detailed study of the vibrating dropping mercury electrode was made. Electrocapillaryphoresis is shown to be primarily responsible for the increased diffusion current due to the application of a transverse alternating field. A few typical results of the investigation of the effect of the magnitude and frequency of a transverse alternating field on the polarographic limiting current in a solution of 0.001 M Cd^{2+} and 0.001 M Hg^{2+} respectively in 0.1 M KCl and on the polarographic maximum in a solution of 0.001 M Hg^{2+} in 0.1 M KCl are presented.   [Author]

616 – The limiting current at mercury drop electrodes at low concentrations of foreign electrolytes (in German). Z. Zembura, A. Fulínski and B. Bierowski (Lehrstuhl für Physikalische Chemie und Elektrochemie an der Akademie für Berg- und Hüttenwesen zu Kraków, Polen). *Z. Elektrochem.*, 65 (1961) 887–891.

Eine Gleichung, mit deren Hilfe man den Grenzstrom an einer Quecksilber-Tropfelektrode mit guter Annäherung für Drei-Ionen-Elektrolyte berechnen kann, wird abgeleitet. Es wird hierbei vereinfachend vorausgesetzt, dass die Konzentration der Ionen vor der Tropfelektrode gleich derjenigen in ruhenden Systemen ist. Die Gleichung wird anhand experimenteller Ergebnisse von Lingane und Kolthoff nachgeprüft.   [He.We.]

617 – A.c. polarographic wave — modified equation (in English). S. K. Rangarajan and K. S. G. Doss (Central Electrochemical Research Institute, Karaikudi, India). *J. Electroanal. Chem.*, 3 (1962) 217–218.

Results obtained in a detailed analysis of the equation that relates the variation of the summit electric tension (d.c. electric tension at which Δi is a maximum for a given ΔV) with the frequency, for the a.c. polarographic wave, are reported. Observations made during the study of the characteristics of the summit electric tension are also included. Details of the derivation of the equation will be published.   [Su.Mo.Ce.]

618 – The a.c. polarographic wave. III. Amended treatment (in English). H. H. Bauer (Faculty of Agriculture, University of Sydney, Australia). *J. Electroanal. Chem.*, 3 (1962) 150–152.

The equation previously published (H. H. Bauer, *J. Electroanal. Chem.*, 1 (1959) 2; 2 (1961) 66) that relates interface and bulk concentrations, used to obtain expressions to characterize the a.c. polarographic waves, and the derived equations, were valid only for the case where the diffusion coefficients of the oxidized and reduced species are equal. In this short communication, the equations are amended to be valid also in the case of inequality of the diffusion coefficient.

[Su.Mo.Ce.]

619 – The role of adsorption in constant current transition time studies. The hydrogen

electrode (in English). R. A. Munson (Research Laboratory, General Electric Company, Schenectady, N.Y., U.S.A.). *J. Phys. Chem.*, 66 (1962) 727–729.
The influence of a pre-electrochemical first-order adsorption step upon galvanostatic transition times was considered in a mathematical treatment. The results observed with a platinum electrode in an aqueous solution saturated in hydrogen conformed over three orders of magnitude and a factor of 10^4 in transition time. The first order rate of adsorption was calculated to e greater than 10^{-1} cm/sec with the corresonding rate of desorption greater than 30 cm/sec.   [D.S.Ru.]

620 – Voltammetric determination of metals in low concentrations (in English). W. W. Ullman, B. H. Pfeil, J. D. Porter and W. W. Sanderson (Division of Laboratories and Research, New York State Department of Health, Albany, N.Y., U.S.A.). *Anal. Chem.*, 34 (1962) 213–216.
The use of a mercury pool cathode with a silver–silver chloride anode, recently designed by some of the authors, improves the sensitivity of the voltammetric method, allowing its application to stream pollution problems. Quantitative results for copper, zinc, cadmium lead, and nickel, in trade wastes are reported. The lower concentration determined with a satisfactory accuracy is 1 μg per 10 ml of cell solution; by a tenfold concentration of the sample, an original concentration of 0.01 mg/l can be determined. The method is not suitable for chromium and iron determinations.
    [Su.Mo.Ce.]

621 – Amperometric determination of gold with certain organic reagents in the presence of some associated elements (in English). L. S. Retshakrit and N. S. Sukhobokova. *Uchenye Zapiski Leningrad. Gosudarst. Univ. im. A. A. Zhdanova*, (1960) 150–154.
The titration of Au in the presence of Se, Te, Pd, Ir, Rh and Ru with organic reagents such as quinol, *p*-methylaminophenol, *p*-aminophenol, and *p*-phenylenediamine, was carried out amperometrically in H_2SO_4 using a rotating platinum electrode. The titration was carried out at 1 V *vs.* the S.C.E. at a temperature of 50°. None of the above mentioned elements was oxidised at the electric tension used. At the end-point the current was proportional to the concentration of the reagent used. The results obtained agreed with those given by the mercury method. The error was $\pm$ 10% for concentrations of 20–80 mg/l.   [Gio.Ser.]

622 – Polarographic behaviour of indium in the presence of chloride (in English). E. D. Moorhead and W. M. MacNevin (McPherson Chemical Laboratory, Ohio State University, Columbus, Ohio, U.S.A.). *Anal. Chem.*, 34 (1962) 269–271.
The polarographic behaviour of indium at the dropping mercury electrode in perchlorate base solutions and in chloride supporting electrolytes was investigated. The results reported for the reduction behaviour of In(III) in the presence of chloride cast considerable doubt on the significance of accepted polarographically obtained dissociation constants of $InCl_n^{(3-n)}$ reported in the literature.   [Su.Mo.Ce.]

623 – Square wave polarograph amperometric titrations of indium with EDTA (in English). R. E. Hamm and C. T. Furse (Chemistry Department, University of Utah, Salt Lake City, Utah, U.S.A.). *Anal. Chem.*, 34 (1962) 219–221.
Square wave polarography at the dropping mercury electrode is used to follow the amperometric titration of species at concentrations lower than those usually reported for amperometric techniques and to separately determine pairs of ions with a small half-wave electric tension difference. Results are reported for the amperometric titration of indium, in concentrations down to $8 \cdot 10^{-6}$ mole/l with EDTA, and for the separate titration of indium–cadmium and indium–lead mixtures, over a range of In : Cd molar ratios of 0.016 : 40 and In : Pb of 0.016 : 80. When indium is contained in the mixture in quantities as large as 1–70 mg per 50 ml of solution, the accuracy of the titration averaged about 0.5%. The accuracy for the second figure is generally within 2%.   [Su.Mo.Ce.]

624 – Semimicro iodometric determination of thallium(III) by an amperometric method with two polarisable electrodes (in English). Rita Bhatnagar, M. L. Bhatnagar and N. K. Mathur (Department of Chemistry, Jaswant College, and M. B. M. Engineering College, Jodhpur, India). *Talanta*, 9 (1962) 455–456.
An amperometric iodometric titration of thallium(III) is described, using a system of two similar platinum electrodes across which an electric tension of 20–30 mV was applied. Results obtained in the titration of amounts of thallium ranging from 0.8–40 mg of thallium(III) in 20 ml of solution are tabulated. Relative error is not larger than 1%. The method can be extended to the determination of thallium in industrial preparations after extraction of thallium trichloride with ether.
    [Su.Mo.Ce.]

625 – Velocity constants and activation energy of fast electrode reactions: $Tl^+ – Tl$ amalgam

(in Italian). G. Gavioli and P. Papoff (Institute of Physical Chemistry, University of Modena, Italy). *Ricerca sci.*, [II A] 31 (1961) 193–203.

The authors investigated the system: Tl^{+}–0.33 M K_2SO_4 + 0.01 N H_2SO_4–Tl (Hg) by the method of oscillographic polarography. Scanning speeds were 0.3–2300 V/sec. The following kinetic parameters were computed at 25°: α = 0.18 and $k_{s,h}$ = 1.25. The activation energy was found to be 1.9 kcal. A similar investigation was carried out on Zn^{2+} solutions. [Fr.Pan.]

626 – Polarographic determination of thallium in ores in the presence of bismuth. D. Weiss (Institute for Research in Ores, Prague, Czechoslovakia). *Rudy (Prague)*, 9 (1961) 15.

Thallium is extracted from a medium containing tartrate and cyanide by $CHCl_3$ containing diethyldithiocarbonate. The extracted thallium is determined polarographically after separation of lead as $PbSO_4$ and Bi as 8-hydroxyquinolinate. The method is suitable for very small amounts of Tl. [Gio.Ser.]

627 – Direct amperometry of cyanide at extreme dilution (in English). J. A. McCloskey (U.S. Army Chemical Corps Biological Laboratories, Fort Detrick, Frederick, Md., U.S.A.). *Anal. Chem.*, 33 (1961) 1842–1843.

The direct anodic response of a system composed of a rapidly rotating (1550 r.p.m.) silver anode and a stationary platinum cathode to extremely small concentrations of cyanide ion at an electric tension of 150 mV was taken as an indication of cyanide concentration; no titration was involved. When a certain volume of the sample solution was introduced into 10 ml of 0.03 M NaOH, the current increases, remains at a peak value for several seconds, then slowly decays. Peak response of the galvanometer over the residual current was proportional to the cyanide concentration. The lower limit of linear response is about $1 \cdot 10^{-8}$ g of cyanide when the volume of the sample introduced is 7 ml; for very small sample volumes (in the range of 0.0005 ml) the lower limit of linear response is $5 \cdot 10^{-10}$ g of cyanide. Interference studies were carried out for 16 anions; each one contained in a thousandfold excess. [Su.Mo.Ce.]

628 – Polarography of tin(IV) – pyrogallol complexes (in English). A. J. Bard (Department of Chemistry, The University of Texas, Austin, Tex., U.S.A.). *Anal. Chem.*, 34 (1962) 266–269.

Stannic tin gives a reversible, two-step reduction wave in acidic pyrogallol. The effect of pyrogallol and hydrogen ion concentrations is investigated with the aim of finding the best conditions for analytical purposes and to study the composition of the tin(IV)–pyrogallol complex. Good analytical results are obtained in a solution 0.1 M $HClO_4$, 1 M $NaClO_4$, 0,1 M pyrogallol and 0.002% Triton X-100. Ratio i_d/C in this solution is constant for both waves for tin concentrations up to 1 mM. The polarographic reduction wave is characterized by the presence of a minimum; a mechanism for this effect is suggested. [Su. Mo.Ce.]

629 – Simultaneous determination of tin and indium using anodic stripping voltammetry (in English). R. D. DeMars (Thomas J. Watson Research Center, International Business Machines Corp., Yorktown Heights, N.Y., U.S.A.). *Anal. Chem.*, 34 (1962) 259–262.

A method is proposed for determining concentrations of indium as low as 10 p.p.m. in tin, the method being suitable for the simultaneous determination of both tin and indium in binary alloys. The technique described includes a pre-electrolysis step in an electrolyte system consisting of pyrogallol and ammonium thiocyanate. Pre-electrolysis of the sample takes only 5 min at −0.800 V *vs.* S.C.E. The electric tension is then scanned in the anodic direction and the current–electric tension curve is recorded. The accuracy and precision are comparable to those given by cathodic voltammetry with linearly varying electric tension. [Su.Mo.Ce.]

630 – Application of stripping analysis to the trace determination of tin (in English). S. L. Phillips and I. Shain (Chemistry Department, University of Wisconsin, Madison, Wis., U.S.A.). *Anal. Chem.*, 34 (1962) 262–265.

Stoichiometry of the stripping analysis of tin is investigated and a method is proposed for the determination of tin in steel, for concentrations of the order of 0.001% tin. To avoid contamination by reagents, the tin is directly determined after dissolution of the sample in hydrochloric acid; ferric ion is reduced with ascorbic acid. Pre-electrolysis is carried out at −0.60 V *vs.* S.C.E. using the hanging mercury drop electrode; tin amalgam formed is subsequently analyzed by anodic stripping using linear electric tension scan voltammetry (fast sweep polarography). A standard addition technique is used to simplify the procedure and reduce the effect of any interference. [Su.Mo.Ce.]

631 – Cathodic action of the lead–glutamate complex at the dropping mercury electrode (in English). Tsai-Teh Lai and Teh-Liang Chang (Analytical Chemistry Laboratory,

Cheng Kung University, Tainan, Taiwan, China). *Anal. Chem.*, 33 (1961) 1953–1955. The polarographic characteristics of lead–glutamate complex are investigated; glutamic acid is used as a chelating agent. The effect of pH on the polarographic wave was studied over the pH range 5.0–10.0; well defined reversible waves were obtained in this pH range in a base solution of 0.498 M glutamic acid. In the pH region 5.0–7.2 a constant $E_{1/2}$ of -0.476 V *vs*. S.C.E. was obtained. At higher pH values the $E_{1/2}$ became pH dependent and shifted to the negative side as the pH increased. Equations for the electrode reaction are proposed. Complexes, formulae and dissociation constants were determined. A linear relationship between lead ion concentration and diffusion current was found over the lead concentration range of $1.0 \cdot 10^{-4}$ to $1.8 \cdot 10^{-3}$ M with an average error of 1.5%.   [Su.Mo.Ce.]

632 – Iron(II) as an indicator ion for amperometric titrations with ethylenedinitrilotetraacetic acid. Application to the determination of thorium (in English). G. Goldstein, D. L. Manning and H. E. Zittel (Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A.). *Anal. Chem.*, 34 (1962) 358–361.
Ferrous ion is used as indicator for the amperometric titration of thorium(IV), in the presence of U^{6+}, Zr and other cations, with ethylenedinitrilotetraacetic acid (EDTA), using a platinum electrode. Complexing Fe^{2+} with EDTA shifts the standard reduction electric tension from $+0.77$ to $+0.12$ V (*vs*. S.C.E.). Titrations are carried out at an electric tension of $+0.4$ V (*vs*. S.C.E.), most of them in a buffered medium at pH 4.5. The method is also applicable to the titrations of those elements that form EDTA chelates having a stability constant greater than 10^{18}; results obtained for 34 different cations in solutions of pH 2.5 and 4.5 are reported. The relative standard deviation for Th^{4+} titrations is about 1% at pH either 2.5 or 4.5.   [Su.Mo.Ce.]

633 – Polarometric titration of thorium in monazite (in English). Shao-Chun Tung and Er-Kang Wang (Institute of Applied Chemistry, Academia Sinica, Peking, China). *Sci. Sinica (Peking)*, 19 (1961) 403–410.
Decomposition of the sample and polarometric titration of thorium in monazite are thoroughly investigated. The method of thorium determination presented includes fusion of the dried sample with potassium hydrogen bifluoride followed by polarometric titration at -0.75 V, using as supporting electrolyte 1.5 N $AlCl_3$, 7% CH_3COOH and CH_3COONa (pH 1.7) and ammonium molybdate as reagent. The determination can be carried out in three hours with a precision of 2%.   [Su.Mo.Ce.]

634 – Amperometric titration of thorium in monazite sands (in English). J. J. Burastero and R. W. Martres (Administración Nacional de Combustibles, Alcohol y Portland, División Investigaciones Científicas, Pando, Uruguay). *Anal. Chem.*, 34 (1962) 378–381.
A reliable method for the determination of thorium in monazite sands, that can easily be performed in a few hours is described. The sample can be decomposed by the classical sulphuric acid treatment; thorium and rare earths are separated by a single precipitation with oxalic acid, followed by oxalate decomposition with nitric acid and conversion to chloride. Final amperometric titration is carried out using ammonium paramolybdate as titrant. The agreement with results obtained by the iodate chemical method and other more complicated amperometric techniques is good.   [Su.Mo.Ce.]

635 – The effect of surface-active agents on the polarograms of pyro- and triphosphate complexes (in English). P. R. Subbaraman, P. S. Shetty and J. Gupta (Inorganic Chemistry Division, National Chemical Laboratory, Poona, India). *Anal. Chim. Acta*, 26 (1962) 179–184.
Many cathodic polarographic waves are affected by camphor and gelatin. This is the case for the reduction of metal complexes with pyro- and -triphosphate. Camphor displaces the waves to more negative electric tensions and gelatin (0.1%) virtually obliterates all the waves, while lower concentrations distort them. Of eleven cations studied, only thallium(I) and silver(I) reduction are not affected.   [P.Me.]

636 – Amperometric determination of phosphorus in food. E. Szyszko (State Institute of Hygiene, Warsaw, Poland). *Roczn. Zakl. Hig. (Warsaw)*, 12 (1961) 267–277.
The sample is ignited at 550° and the residue is dissolved in HNO_3. After evaporation to dryness, the residue is dissolved in 1.5 ml of 50% acetic acid + 1 ml of 1% methyl cellulose. The solution is brought to pH 6 with 10% NaOH and made up to 100 ml with water. The titration is carried out with 0.03 M lead acetate, after deaeration, with a dropping mercury electrode at 18°. The half-wave electric tension is -0.59 V *vs*. the S.C.E. Fe, Na and K do not interfere. Ca interferes if the ratio Ca : P is greater than 1 : 2. The error is within ± 0.4%.   [Gio.Ser.]

637 – Redox titrations in glacial acetic acid. 1. Oxidations with bromine solutions (in Italian). G. Piccardi (Institute of Analytical Chemistry, University of Florence, Italy). *Ann. chim. (Rome)*, 52 (1962) 201–207.
A standard Br_2 solution in glacial acetic acid is used to oxidize several reducing substances in the same medium, the end-point being determined by dead-stop (diamperometric) titrations. Sb^{3+} is oxidized at room temperature, while As^{3+} and Hg^+ should be titrated at 60°. When oxidizing Fe^{2+} care must be taken to avoid the presence of O_2. In the reactions between SO_3^{2-}–Br_2 and CNS^-–Br_2 the molar ratios are, respectively, $1 : 1$ and $1 : 3$.   [Fr.Pan.]

638 – A particular influence of the supporting electrolyte on the limiting current of the first polarographic wave of oxygen (in English). R. Cornelissen and L. Gierst (Laboratory of Analytical Chemistry, Free University of Brussels, Belgium). *J. Electroanal. Chem.*, 3 (1962) 219–221.
The first limiting current of the polarographic waves of oxygen obtained in certain base solutions is definitely larger than half of the second. Polarograms obtained in three supporting electrolytes (0.05 M NaF, 0.1 M $N(C_2H_5)_4Cl$ and 0.01 M $N(C_3H_7)_4Cl$) are reproduced as typical examples of this phenomenon. A theoretical explanation of the observed facts is given, as well as some conclusions that can be inferred.   [Su.Mo.Ce.]

639 – A polarographic study of dissolved oxygen. I (in English). V. S. Griffiths and M. I. Jackman (Battersea College of Technology, London, and The Gas Council, London Research Station, Fulham, London, Great Britain). *Talanta*, 9 (1962) 205–211.
Results are reported of an investigation on the two polarographic oxygen waves covering a range of dissolved oxygen concentrations from 0.1–10 p.p.m. Polarograms were obtained in a base solution of 0.1 N potassium chloride, using a dropping mercury electrode and with an electric tension sweep from 0 to -0.5 or to -1.7 V *vs.* S.C.E. It was noticed that, although both waves give linear plots of i_d against dissolved oxygen concentration, the slopes are unequal, being 0.229 μA/p.p.m. for the first wave and 0.200 μA/p.p.m. for the second one. It is suggested that the probable reason for this changing ratio between the wave heights is a disproportionation reaction of the hydrogen peroxide. The diffusion coefficient of oxygen in KCl solution is obtained from polarographic data.   [Su.Mo.Ce.]

640 – New platinum electrode system measures oxygen and B.O.D. (in English). J. D. Eye, L. H. Reuter and K. Keshavan (University of Cincinnati, Cincinnati, Ohio, U.S.A.). *Water and Sewage Works*, 108 (1961) 231–236.
A plastic covered platinum electrode has been used to measure dissolved oxygen and B.O.D. in water and domestic sewage. The results are highly reproducible and accurate and compare favourably with standard methods. The cell can be operated with KOH or KCl in different concentrations as internal electrolytes. Polyethylene is a good material for the membrane, but any material inert to biological oxidation may be used. The system must be standardised at least every day and the battery replaced every 10–15 days.   [Gio.Ser.]

641 – Determination of minute amounts of water in insulating oils (in German). H. Kawinski (Transformatorenwerk Lepper, Bad Honnef, Deutschland). *Erdöl u. Kohle*, 14 (1961) 271–275.
By using the direct method, it is possible to achieve a sensibility of 1 p.p.m. with Karl Fischer reagent, using dead-stop indication.   [E.Pun.]

642 – Polarographic investigation of H_2O_2 (in French). A. Rius and A. Sacristàn (Instituto de Quimica Fisica "Rocasolano", Madrid, Spain). *Electrochim. Acta*, 6 (1962) 155–165.
The polarographic behaviour of hydrogen peroxide was studied at dropping and jet electrodes. For both electrodes, the half-wave potential (electric tension), $E_{1/2}$, is constant for pH values of 11.5. Beyond this value $E_{1/2}$ becomes more and more negative as pH increases. The jet electrode gives a single wave, even in strongly alkaline solution, and i_a is proportional to hydrogen peroxide concentration over the whole range of pH. The dropping electrode gives two waves at pH 13.4. In this pH region the height of the second wave is proportional to $[H_2O_2]$ whereas that of the first is not. With varied dropping rate, the height of the first wave remains constant, but that of the second varies more sharply. The height of the two waves depends on the dropping rate.
It is proposed as a working hypothesis that the first wave is due to the adsorption of one of the products that appears during the overall reduction process of the hydrogen peroxide.   [Authors]

643 – Behaviour of oxides and metallic sulphides in the eutectic LiCl–KCl melt. Chemical reactions resulting in formation of the ions O^{2-} and S^{2-} (in French). G. Delarue (Institut

National des Sciences et Techniques Nucléaires, Gif-sur-Yvette, S. et O., France). *Chim. anal.*, 44 (1962) 91–101.

Cet article concerne la mise en évidence dans l'eutectique KCl–LiCl fondu à 450° d'un certain nombre de réactions chimiques mettant en jeu les particules O^{2-} et S^{2-}. Parmi les méthodes utilisées par l'auteur pour suivre ces réactions, le tracé des courbes intensité–tension électrique a permi de suivre les concentrations des ions O^{2-} et S^{2-}. L'appareillage utilisé pour ce tracé est décrit. La réaction électrochimique, $2\ O^{2-} + C - 4\ e \rightarrow CO_2\uparrow$, prend naissance à une électrode de graphite et est caractérisée par une vague anodique dont la tension électrique de demi vague $E_{1/2}$ dépend de la concentration des ions O^{2-} : $E_{1/2} \# + 0.2\ V/Pt\downarrow - PtCl_2$ pour $O^{2-} = 10^{-1}\ M$. La réaction, $S^{2-} - 2\ e \rightarrow S(o)$ est caractérisée à une électrode de platine par une vague anodique dont le $E_{1/2}$ (voisin de $0.45\ V/Pt\downarrow - PtCl_2$) dépend de la concentration des ions S^{2-}. L'auteur indique également la tension électrique de demi vague cathodique relatif à la réaction $Ca^{2+} + 2\ e \rightarrow Ca\downarrow$, $E_{1/2} = -2.25\ V/Pt\downarrow - PtCl_2$. Deux diagrammes, $E = f(pO^{2-})$ $[pO^{2-} = \text{colog}\ C_{O^{2-}}]$ et $E = f(pS^{2-})$ $[pS^{2-} = \text{colog}\ C_{S^{2-}}]$ sont présentés et permettent de prévoir un certain nombre de réactions chimiques dans l'eutectique fondu.   [An.Sn.]

644 – Polarography of solutions containing elemental sulfur and metal ions (in English). R. E. Humphrey (Ethyl Corporation Research Laboratories, Detroit, Mich., U.S.A.). *Anal. Chem.*, 34 (1962) 167–168.

The effect of metal ions on the polarographic wave of sulfur was investigated. Polarograms were obtained in 0.1 M methanol as solvent with a sulfur concentration of 0.2 mmole/l. Diffusion currents for sulfur decreased linearly with increase in silver ion concentration. When silver ions were removed by addition of chloride ion, the sulfur wave attained its normal height. The effect of other metal ions that form insoluble sulphides was also studied.   [Su.Mo.Ce.]

645 – A scheme for the rapid analysis of uranium ore acid leach solutions. Determination of Al, As, Ca, Cd, Co, Cu, Mg, Ni and Zn in the presence of excess Fe and Mn (in English). Lyn Jarman and M. Matic (Chamber of Mines Biological and Chemical Research Laboratory, Johannesburg, S. Africa). *Talanta*, 9 (1962) 219–225.

A scheme of analysis for effluents from uranium mines has been evolved, the emphasis being on rapidity and simplicity. Determination of As, Ce, Co, Cu, Ni, and Zn, is made by polarography, determination of Al, Fe and Mn by colorimetry, and titration with EDTA was used for Ca and Mg estimation. The scheme includes a method for the separation of Al, Cd, Ca, Co, Mg, and Zn, from Fe and Mn and from each other by anion-exchange chromatography and solvent extraction of oxinates. Results obtained in the analysis of a synthetic mixture containing Al, As, Ca, Co, Cu, Fe, Mg, Mn, Ni and Zn are tabulated.   [Su.Mo.Ce.]

646 – Amperometric determination of fluoride in relation to the formation of iron(III) – fluoride complexes (in Dutch). E. M. Aarts (Pharmaceutical Laboratory, State University, Utrecht, The Netherlands). *Pharm. Weekblad*, 96 (1961) 373–379.

The amperometric titration of F^- in the range of concentration from 0.0003–0.0008 M can be carried out with $FeCl_3$ in 50% ethanol solution saturated with NaCl. A blank determination is necessary. The ratio of F^- to F^{3+} at the end-point is 3.8 because of the formation of different $Fe^{3+}-F^-$ complexes. The determination must be carried out at pH 2.7–3, since the residual current and the complexes formed are strongly dependent on the pH.   [Gio.Ser.]

647 – High-precision volume titrimetry (in English). G. A. Dean (Department of Chemistry, Dalhousie University Halifax, Nova Scotia, Canada). *Can. J. Chem.*, 40 (1962) 545–556.

The use of the bulb burette is discussed along with various factors which influence the precision. Several end-point systems with sensitivity better than 1 p.p.m. are considered. The titration of iron(II) dichromate was carried out using an amperometric end-point with precision of 0.7–1.1 p.p.m. The ultimate limit of precision of any titrimetric operation, either by weight or by volume, is shown to be about 0.1 p.p.m.   [D.S.Ru.]

648 – The coulometry and polarography of iridium (in English). J. A. Page (Department of Chemistry, University of Toronto, Canada). *Talanta*, 9 (1962) 365–369.

The reduction of iridium can be carried out at a mercury or platinum cathode controlled at a suitable electric tension, and can be used for coulometric or polarographic determination of iridium. In a 0.2 M hydrochloric acid base solution, iridium(IV) gives a well defined polarographic wave at electric tensions negative enough to prevent mercury oxidation. Results obtained demonstrated that the process is diffusion controlled. The polarographic method must be standardized against solutions of known iridium content. Coulometry in the 0.2 M HCl electrolyte provides a mean for the absolute assay of a pure iridium(IV) solution. The formal electric tension for the couple $IrCl_6^{2-}-IrCl_6^{3-}$ in 0.2 M HCl is $+1.05$ V *vs.* N.H.E. Reproducibility for twenty titrations of

aliquots of the standard iridium solution is good: the mean value obtained is 0.332 mg of iridium, with an average deviation of 0.002 mg. Gold(III), palladium(II), platinum(IV) and rhodium(III), among others, would be expected to interfere. [Su.Mo.Ce.]

649 – Polarography in food chemistry. IV. Polarographic determination of free formaldehyde in plastic articles (in German). H. W. Ardelt, P. H. Opel and W. Steindorf (V.E.B. Stickstoffwerk Piesteritz, Lutherstadt, Wittenberg-Piesteritz, Deutschland). *Pharmazie*, 16 (1961) 128–131.
The sample is extracted with water so as to have 0.02 to 10 mg of formaldehyde in 50 ml. After adding 10 ml of 1 N NaOH and 5 ml of 1% NaCl the solution is made up to 100 ml with water. After deaeration the polarogram is recorded between -1 and -2 V *vs.* the S.C.E. The $E_{1/2}$ is -1.73 V. The accuracy for 0.5 mg is $\pm 4\%$. The method compares favourably with the colorimetric determination with chromotropic acid or fuchsin. [Gio.Ser.]

650 – Polarographic method for determination of chlorbutol (in English). J. Birner (Commonwealth Serum Laboratories, Parkville, Victoria, Australia). *Anal. Chem.*, 33 (1961) 1955–1957.
Tetramethylammonium bromide, benzethonium chloride and zephiran were examined as supporting electrolytes for the polarographic determination of chlorbutol (1,1,1-trichloro-2-methyl-2-propanol). Good results were obtained with 0.0045 M benzethonium chloride and 0.072 M sodium sulphite base solution; the $E_{1/2}$ was -1.0 V. Polarographic wave height is directly proportional to chlorbutol concentration within the range of 5–500 μg per ml. The method is useful for the determination of chlorbutol in chemical preparations and biological products. [Su.Mo.Ce.]

651 – Coulometric determination of hexaethylplumbane in tetraethyl lead with ammetric indication (in Italian). G. Tagliavini, U. Belluco and L. Riccoboni (Institute of General Chemistry, University of Padua, Italy). *Ricerca sci.*, [II A] 31 (1961) 338–345.
Hexaethylplumbane can be determined in a microanalytical range in a 1:1 benzene–methyl alcohol solution, satured with KI, by electrolytically generated iodine. A constant current coulometric apparatus can be used, operating at $-5°$. The end-point is determined by the dead-stop method. The accuracy of such determination is 1–2%, for a hexaethylplumbane content of 0.1% in tetraethyl lead. [Fr.Pan.]

652 – Polarography and reduction of hydroxylamine-*o*-sulfonic acid (in English). H. Lund (Department of Chemistry, University of Aarhus, Aarhus, Denmark). *Acta Chem. Scand.*, 16 (1962) 524.
It was found that hydroxylamine-*o*-sulfonic acid gives rise to a well-defined polarographic wave from pH 2.5–14. The half-wave electric tension of the compound is 1.28 V *vs.* S.C.E. and is independent of pH. The height of the wave suggests a two-electron reduction. Reduction at controlled electric tension at pH 9 shows the electrode reaction to be a two-electron reduction, and the reduction products are ammonia and sulfate. [G.Ekl.]

653 – Polarographic characteristics and controlled potential electroreduction of dimethylglyoxime (in English). M. Spritzer and L. Meites (Department of Chemistry, Polytechnic Institute of Brooklyn, N.Y., U.S.A.). *Anal. Chim. Acta*, 26 (1962) 58–65.
At pH values below 3.5, solutions of dimethylglyoxime in an ethanol 15% v/v water mixture give a well-defined polarographic wave, corresponding to an 8-electron reduction to 2.3 diaminobutane. The effects of pH and ethanol concentration on the characteristics of the wave are described, and an equation is advanced for its rate-determining step. This rate-determining step involves only one electron. The mechanism of the process is discussed on the basis of coulometric evidence. [P.Me.]

654 – Voltammetric studies of phenol and aniline ring substitution (in English). J. C. Suatoni, R. E. Snyder and R. O. Clark (Gulf Research and Development Co., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 33 (1961) 1894–1897.
An investigation was made of the effect of ring substitution on the half-wave electric tension of phenol and aniline using anodic voltammetry at an impregnated graphite electrode. Substituents in the *p*- and *m*-position of the phenol ring produced a comparable effect on the half-wave electric tension of the aniline analogue. Substitution in the *o*-position did not produce the same effect. It was demonstrated that half-wave electric tensions of *m*- and *p*-monosubstituted rings are linearly related to Hammett's substituent constant. Using this relationship, together with the additivity of substituent constants, values of $E_{1/2}$ for disubstituted phenols and anilines have been predicted. The calculated values are in good agreement with the experimental ones; exceptions were found with the 2,6-disubstituted phenols and with dichloro compounds. [Su.Mo.Ce.]

655 – Tensammetric studies of resorcinol and phloroglucinol (in English). R. Narayan (Central Electrochemical Research Institute, Karaikudi, India). *Electrochim. Acta,* 7 (1962) 111–120.

A tensammetric study of resorcinol and phloroglucinol was made. The results indicate that these substances are adsorbed at the mercury–solution interface. A sharp desorption peak is obtained with phloroglucinol in alkaline solutions, whereas resorcinol appears to be desorbed over a range of potentials. The effects of these substances on polarographic reduction processes (electric tensions) have been studied. Resorcinol suppresses the polarographic maximum, whereas phloroglucinol depresses only the limiting current in a solution containing 0.5 mM Cu^{2+}, indicating the different natures of the adsorption films of these substances.   [Author]

656 – Oscillography and influence of structure in the ferrocene series (in French). J. Komenda and J. Tirouflet (Laboratoire de chimie générale, Faculté des Sciences, Dijon, France, et Faculté des Sciences de Brno, Tchécoslovaquie). *Compt. rend.,* 254 (1962) 3093–3095.

Les auteurs présentent une étude oscillopolarographique (tracé des courbes $dE/dt = f(E)$ selon Heyrovský-Forejt, à l'électrode à jet de mercure ou à lélectrode de platine) des dérivés substitués (FcX) du ferrocène (FcH). Les 17 dérivés étudiés sont des systèmes rapides: la rapidité des systèmes est caractérisée par la position relative des "pointes" anodique et cathodique de l'oscillopolarogramme. La tension électrique de chaque système est définie par le paramètre Q de Heyrovský et Kalvoda. Les différences de tension électrique, $\Delta Q(X) = Q$ (FcH) $- Q$(FcX) sont reliées linéairement aux termes $\sigma_p(X)$. Une étude détaillée de la série FcCOX' [X' = OH, CH_3, CH_2COCH_3, C_6H_5, $CH_2C_6H_5$, C_4H_3S-2 (thiényl), C_4H_3O-2 (furyl)] montre que le substituant X' n'apporte pas de modifications appréciables sur l'effet polaire du carbonyle, exception faite pour X' = C_4H_4N-2 (pyrryl).   [An.Sn.]

657 – Electrochemical investigation of ninhydrin (in German). L. Holleck and O. Lehmann (Institut für physikalische Chemie der Universität, Hamburg, Deutschland). *Monatsh. Chem.,* 92 (1961) 499–509.

In order to obtain an explanation of the complex polarographic behaviour at varying pH of ninhydrin (1,2,3-indantrione monohydrate), and to get information about the reaction mechanism of the different waves, the products formed at the D.M.E. were prepared by potentiostatic reduction or oxidation of ninhydrin at different pH values. The reaction products were subjected to polarographic, spectroscopic and chemical analysis, and in some cases to chemical reactions and further potentiostatic electrolysis. From these experiments it was found that, in the two-electron reduction of ninhydrin which occurs at pH values > 1.5, one of the two non-hydrated keto groups is reduced. At pH 4.5 this colourless benzoid reduction product is transformed into a tautomeric quinoid compound. This compound itself is colourless, but at pH values between 4.5–8 it splits off a proton and a molecule of water. A red compound is formed, whereas at pH > 11 two protons are split off, resulting in a blue compound. The colourless benzoid two-electron reduction compound, primarily obtained at pH 10, differs from the one primarily obtained at pH 4.5–8 by the ionisation of one of the two OH groups on the 2-carbon atom.

At pH > 8 the ninhydrin itself splits off a proton. At high pH values this leads to the formation of o-carboxy mandelic acid. Because this is polarographically inactive, its formation accounts for the lowering of the total wave height at pH > 11. The two-electron oxidation wave of ninhydrin which appears at pH > 8 gives o-carboxyphenyl glyoxylic acid as the reaction product.
                    [C.I.Moo.]

658 – Electro-organic preparations. X. Polarography and reduction of α-naphthoic acid (in English). H. Lund (Department of Chemistry, University of Aarhus, Aarhus, Denmark). *Acta Chem. Scand.,* 16 (1962) 525–526.

α-Naphthoic acid yields a polarographic wave only in unbuffered or alkaline solutions. Only solutions containing lithium or tetraalkylammonium ions as supporting electrolyte can be used. By a reduction at controlled electric tension it was shown that the reduction consumed 2 electrons per molecule, and a product with m.p. 150° and an analysis corresponding to $C_{11}H_{11}NO$ was obtained. The analysis suggested a reduction in the naphthalene ring rather than in the amide group.
                    [G.Ekl.]

659 – Polarographic standardization of aqueous histamine solutions (in English). D. E. Sellers, K. L. Greenlee and R. E. Van Atta (Department of Chemistry, Southern Illinois University, Carbondale, Ill., U.S.A.). *Anal. Chem.,* 34 (1962) 441–442.

Solutions of histamine salts (or histamine) and acetaldehyde, maintained at pH 10.0 by a buffer, which also serves as the supporting electrolyte give a polarographically reducible imine. The imine wave appears at approximately -1.4 V *vs.* S.C.E., while the acetaldehyde wave occurs at -1.7 V *vs.* S.C.E. Two separate calibration curves having different slopes are obtained for histamine dihydrochloride and for histamine phosphate, respectively, each one showing a linear

relationship between concentration and diffusion current up to 2 mM in histamine content. The average relative errors in the determination of the histamine dihydrochloride and the histamine phosphate are $\pm$ 1.9 and $\pm$ 2.5%, respectively.   [Su.Mo.Ce.]

660 – Influence of adsorption on the polarographic behaviour of reducible organic compounds: autoinhibition of the discharge reaction (in French). E. Laviron (Laboratoire de Chimie Générale, Faculté des Sciences de Dijon, France). *Bull. soc. chim. France*, (1962) 418–422.
Les polarogrammes de l'acétyl-3 pyridine, de la diformyl-2,6 pyridine et de cinq dipyridyléthylènes-1,2, permettent aux auteurs d'émettre l'hypothèse d'une autoinhibition de la réaction de décharge. Ces composés ou l'une des formes réduites de ceux-ci sont adsorbés sur l'électrode et inhibent la réduction par la formation d'un film. Cette réduction ne peut se poursuivre qu'à partir de la tension électrique où cesse l'adsorption. Cette hypothèse est confirmée par le tracé des courbes électrocapillaires ainsi que par des études chronoampérométriques et oscillopolarographique à variation linéaire de tension électrique (0.15 V/sec). La forme réduite finale serait responsable de l'autoinhibition dans le cas de l'acétyl-3 pyridine, alors qu'un produit intermédiaire de réduction provoquerait l'inhibition de la décharge de la diformyl-2,6 pyridine. L'adsorption des dipyridyléthylènes eux-mêmes explique les anomalies de leurs polarogrammes.   [An.Sn.]

661 – Polarographic determination of 3-methyl chromone. S. Arizan and M. Sterescu (Institute of Chemistry and Pharmaceutical Research, Bucharest, Rumania). *Rev. chim. (Bucharest)*, 12 (1961) 177.
The chromone derivative shows a diffusion wave ($E_{1/2} = -1.72$ V) in aqueous methanol in the presence of lithium chloride as electrolyte, at pH 6.2   [E.Pun.]

662 – Polarographic determination of flavone-7-ethyl glycolate. M. Sterescu and S. Arizan (Institute of Chemistry and Pharmaceutical Research, Bucharest, Rumania). *Rev. chim., (Bucharest)*, 12 (1961) 178.
The flavone derivative gives a polarographic diffusion wave in aqueous methanol solution in the presence of lithium chloride as electrolyte at pH 6.36, having $E_{1/2}$ — 1.49 V.   [E.Pun.]

663 – Determination of proteolytic activity by adsorption polarography (in Russian)·
I. D. Ivanov (Institute of Biochemistry, Academy of Sciences, Moscow, U.S.S.R.)·
Biokhimiya, 26 (1961) 575–580.
A polarographic method is described, based on the reduction of the maximum of the Co-8-hydroxy-quinoline system. Different amounts of *B. subtilis* proteinase are added to tubes containing 5 ml of 0.5% substrate (gelatin, casein or haemoglobin). After incubation for 15–20 min at 35°, up to 3 ml of 6% $CuSO_4 \cdot 5 H_2O$ and up to 3.5 ml of 1.25% NaOH are added. The solution is filtered, 1 ml is added to 18 ml of reagent and the polarogram is recorded. The reagent is prepared by dissolving 2 g of NH_4Cl, 4 ml of $2 \cdot 10^{-3}$ M 8-hydroxyquinoline, 0.8 ml of 30% NH_3, and 5–10 ml of 0.5 % starch in 70–80 ml of water. Just before use, 166 mg of $CoCl_2 \cdot 6 H_2O$ are added and the volume is made up to 100 ml.   [Gio.Ser.]

664 – Polarographic reduction of 1,2,4-benzothiadiazine-1,1-dioxides and related compounds (in English). A. I. Cohen, B. T. Keeler, N. H. Coy and H. L. Yale (Squibb Institute for Medical Research, New Brunswick, N.J., U.S.A.). *Anal. Chem.*, 34 (1962) 216–219.
Polarographic reduction of trifluoromethylaryl compounds both in aqueous (pH 8.5 with borate buffer) and in N,N-dimethylformamide (DMF) solutions was investigated. The reduction in DMF took place in one, two or three steps; the number of waves obtained and half-wave electric tensions were influenced by the number and type of substituents on the aryl ring. The study covered various sulfamyl-, carboxyl-, and aminotrifluoromethyl-benzenes, and 6-(trifluoromethyl)-1,2,4-benzothiadiazine-1,1-dioxides. Correlation between structure and polarographic behaviour is considered.   [Su.Mo.Ce.]

665 – Some applications of the oxidimetric determination of morphine (in Dutch). J. A. C. van Pinxteren and M. E. Verloop (Pharmaceutical Laboratory, State University, Utrecht, The Netherlands). *Pharm. Weekblad*, 97 (1962) 1–10.
The oxidimetric determination of morphine with biamperometric or potentiometric end-point indication described in the same journal (*Pharm. Weekblad*, 97 (1962) 545) is not influenced by the presence of lactose, atropine, scopolamine, heroin, acetylsalicylic acid, phenacetin, hydrocodeine, narceine, codeine, thebaine, papaverine and narcotine. Consequently, opial and pantopon preparations can be analysed without any separation.
On the other hand, phenolic alkaloids, such as narcotoline, present in some opium extracts, are

also oxidizable, and this makes separation necessary. This can be performed by extraction with chloroform, after acidification with dichloroacetic acid. The aqueous layer contains the morphine, which can subsequently be estimated in the usual way.   [H.L.Ki.]

666 – Polarographic characteristics of carbohydrates. The aldose oximes and semicarbazones (in English). J. W. Haas, Jr., J. D. Storey and C. C. Lynch (Grove City College, Grove City, Pa. (first two authors), University of Delaware, Newark, Del., U.S.A. (third author)). *Anal. Chem.*, 34 (1962) 145–147.
Polarographic waves for aldose oximes and semicarbazones are investigated in buffered aqueous media, using a dropping mercury electrode. The range of pH covered by the study is from pH 1–6. Over certain concentration ranges a linear relationship is obtained between diffusion current and concentration of electroactive compounds. The polarographic characteristics appear to be influenced by three factors: acid strength of the compound, position of the equilibrium (non-reducible cyclic form $\rightleftarrows$ reducible acyclic form) and transformation rate of the cyclic to the acyclic form.
                                                                                                      [Su.Mo.Ce.]

667 – Polarographic determination of tyrosine in wool (in German). L. Benišek (Research Institute for the Wool Industry, Brno, Czechoslovakia). *Faserforsch. u. Textiltech.*, 12 (1961) 74–78.
Tyrosine in wool hydrolysates can be determined by polarography, after nitration to 2,3-dinitrotyrosine, using the method previously described for cystine and cysteine (*ibid.*, 12 (1961) 23). Other amino-acids do not interfere since they are decomposed during the nitration or they are not nitrated. Wool damage due to Cl is shown by the decrease in tyrosine content, while other damage is shown by the decrease in cysteine and cystine content. The wool hydrolysate is filtered and 10 ml are heated for 2 h under reflux with 20 ml of 0.3 N HNO$_3$. The solution is cooled, neutralised with 20% KOH and diluted to 250 ml. A 2 ml aliquot is diluted with 20 ml of McIlvain buffer at pH 5 and, after deaeration, the polarogram is recorded between 0 and −0.5 V. Quantitative determination is carried out by the method of standard additions.   [Gio.Ser.]

668 – Investigations of drug preparations by paper chromatography and paper electrophoresis (in English). H. Schriftman and R. C. Shultz (Wyeth Laboratories Inc., Radnor, Pa., U.S.A.). *J. Pharm. Sci.*, 50 (1961) 332–336.
The method was succesfully used in the case of phenylephrine-HCl, chlorpheniramine maleate, dextrometarphan-HBr, N-acetyl-*p*-aminophenol, meperidin-HCl, atropine, ethinyloestradiol, procaine-HCl, tetracaine-HCl, and their mixtures.   [E.Pun.]

669 – Rifomycin. XXIII. The polarographic behaviour of rifomycin B, rifomycin O, rifomycin S, and rifomycin SV (in English). Gian Gualberto Gallo, Luigi Chiesa and Piero Sensi (Research Laboratories of Lepetit S.p.A., Milan, Italy). *Anal. Chem.*, 34 (1962) 423–426.
Polarographic behaviour of rifomycin B, O, S and SV is described. Well defined polarographic waves are obtained; proportionality between concentration and diffusion current is checked. Dependence of the half-wave electric tension on pH is examined. Conjectures on the number of electrons involved in the electrode processes are made. The irreversibility of the electrode process is confirmed for the reduction wave of rifomycin B and for the two reduction waves of rifomycin O; rifomycin S and SV are the oxidized and reduced forms of a reversible redox system. Quantitative applications for the determination of the four substances are proposed.   [Su.Mo.Ce.]

See also abstracts nos. 592, 606, 607, 608, 699, 725, 757.

4. Potentiometry

670 – A simple potentiostat for general laboratory use (in English). A. Hickling (University of Liverpool, Great Britain). *Electrochim. Acta*, 5 (1961) 161–168.
In this paper the author describes a very simple electronic potentiostat for general laboratory use. This apparatus will maintain the electric tension of a working electrode within ±0.01 V of a set value over any desired period, the output current supplied being automatically controlled in the range 0–0.3 A. By combining this instrument with a saturable reactor, currents of any magnitude

can be controlled without appreciable waste of electrical power. Applications and further possible developments of the potentiostat are discussed.   [Fr.Cla.]

671 – Comparative investigations of the electromotive properties and of the chemical behaviour of glass electrodes using radio-active indicators. I. Experiments to find the alkali error (in German). K. Schwabe und H. Dahms (Institut für Electrochemie und physikalische Chemie der Technischen Hochschule, Dresden, Deutschland). *Z. Elektrochem.*, 65 (1961) 518–526.

Der Austauschmechanismus zwischen der Quellschicht von Glaselektroden und Alkalisalzlösungen wurde untersucht, und zwar im pH-Bereich 8–13. Dazu wurden diese Lösungen radioaktiv markiert und auch die Elektrodengläser durch Neutronenfluss im Reaktor aktiviert. Die Herstellung der Glaselektroden wird beschrieben. Unter der Annahme einer mit der Zusammensetzung der Quellschicht veränderlichen Aktivität der Wasserstoff- und Natriumionen in dieser Quellschicht wird für den Alkalifehler die Gleichung:

$$\Delta p_H + n \log(1 - 10^{-\Delta p_H}) = p_H + \log a_{Na} + \log K$$

aufgestellt und gezeigt, dass sie für Gläser verschiedener Zusammensetzung gültig ist. Hierbei bedeutet a die Natriumaktivität in Lösung; K die Ionenaustausch-Konstante, und n die Konstante, die das Verhältnis der Ionenaktivitäten in der Quellschicht charakterisiert. n wird gewonnen aus der Beziehung:

$$a'_{Na} = (1 - a'_H)^n \qquad \text{(vereinfacht)}$$

wobei a'_{Na} und a'_H die Aktivitäten der Natrium- und Wasserstoffionen in der Quellschicht bedeuten.   [He.We.]

672 – Note on "Reference electrodes and tensions" (in English). G. Milazzo, G. Bombara and A. J. de Bethune (Chemical Laboratory, Istituto Superiore di Sanità, Rome, Italy (first author); Laboratori Riuniti Studi e Ricerche (E.N.I.), S. Donato Milanese, Italy (second author); Chemistry Department, Boston College, Mass., U.S.A. (third author)). *J. Electroanal. Chem.*, 2 (1961) 340–341.

Some points in a paper published by Milazzo and Bombara (*J. Electroanal. Chem.*, 1 (1960) 265) are clarified.   [Su.Mo.Ce.]

673 – Where is the minimum of the buffer capacity in potentiometric titrations? (in German). F. L. Hahn (Angel Urraza 718–303, Mexico D.F., Mexico). *Anal. Chim. Acta*, 26 (1962) 258–264.

The minimum of the buffer capacity, *i.e.*, the differential quotient dv/dE where v is the volume of reagent, coincides with the equivalence point in all symmetrical potentiometric titrations. This is not the case for asymmetrical titration. The author has established the numerical values in this case.   [P.Me.]

674 – Behaviour of the aluminum electrode in alkaline solution (in Italian). M. Forina and E. Scarano (Institute of Analytical Chemistry, University of Rome, Italy). *Rass. chim. per chim. e ind.*, [5] 13 (1961) 17–20.

A previously reported investigation on the behaviour of aluminum electrodes of high purity (99.99%) in pure, oxygen free 0.1 M NaOH solutions (E. Scarano and I. Letizia, *Ricerca sci.*, 30 (1960) 1384), is extended to a range of alkalinity of 0.01–1 M NaOH. Diagrams of the apparatus and electric tension–time graphs are given. The electrodes, kept for several hours in strongly alkaline solutions in stationary conditions, maintain a constant electric tension. In 0.01, 0.1 and 1 M NaOH, the electric tension of the electrodes showed a marked increase during the first 5–10 min, a small variation (0–10 mV) during the next hour, and good stability for some hours afterwards. The time needed to reach stability depends on the preparation and pretreatment of the electrode, and is also related to the purity of the solution. The electric tension is quickly affected by pH changes in the range of NaOH concentration investigated.   [Su.Mo.Ce.]

675 – Differential arrangement of antimony electrodes for pH measurement (in English). A. E. Simchen (Scientific Department, Ministry of Defence, Tel Aviv, Israel). *J Electroanal. Chem.*, 3 (1962) 286–287.

The essential points of the method of differential pH measurements with antimony electrodes are summarized. Reported data are taken from the work of F. Vlès and his pupils, published between 1925 and 1935 in the *Archives de Physique Biologique*.   [Su.Mo.Ce.]

676 – The cell Hg/Hg₂Cl₂(s), HCl/H₂ (1 atm.) Pt in organic solvents and their mixtures with water. V. Hg/Hg₂Cl₂(s), HCl(M) *isopropanol*(x), H₂O(100 − x) Pt, H₂ (1 atm.) (in German). (Institut für Elektrochemie und physikalische Chemie der Technischen Universität, Dresden, Deutschland). *Z. Elektrochem.*, 65 (1961) 891–894.

Die elektrische Spannung der Kette $Hg/Hg_2Cl_2(s)$, HCl (M), Isopropanol (x), $H_2O(100-x)$ / Pt, $H_2(1$ atm.) wurde bei 25° gemessen. Die Konzentration an Chlorwasserstoff und der Anteil des Isopropanols am Lösungsmittelgemisch wurden variiert. Über die Versuchsanordnung wurde bereits in vorangegangenen Arbeiten berichtet. Nach Verfahren von McInnes und Brown und von Hitchcock wurden die Standard-Spannung-Werte durch Extrapolation ermittelt. Die primären, sekundären und totalen Mediumeffekte wurden berechnet und diskutiert. Ein Anstieg der primären Medium-effekte mit wachsendem Alkoholgehalt der Lösungsmittel wurde festgestellt. Die Theorien verschiedener anderer Autoren über den Einfluss des Lösungsmittels auf die Standard-Spannung wurden im Zusammenhang mit den eigenen Ergebnissen erörtert.   [He.We.]

677 – Thermodynamic treatment of the electrocapillary curve for reversible electrodes and properties of the double layer (in English). D. M. Mohilner (Coates Chemical Laboratory, Louisiana State University, Baton Rouge, La., U.S.A.). *J. Phys. Chem.*, 66 (1962) 724–726.
The equation of the electrocapillary curve for a reversible electrode has been derived thermodynamically. This equation and the theory of the diffuse double layer indicate that in certain cases it should be possible to determine the potential difference across the diffuse double layer.
                                                                                      [D.S.Ru.]

678 – Direct potentiometric estimation of the apparent activity of the sodium ion. Use of a salt bridge (in English). E. S. Hyman (Department of Biochemical Research, Touro Infirmary, New Orleans, La., U.S.A.). *Anal. Chem.*, 34 (1962) 365–370.
The apparent activity of sodium ion is potentiometrically determined using a glass membrane, selectively sensitive to sodium ions, and a modified comparison electrode with a special liquid junction. A mixed $KCl-KNO_3$ salt solution appears to be more useful than the usual saturated KCl solution. A diagram of the apparatus is given. Application of this electrode system to determinations in blood and other biological fluids is suggested.   [Su.Mo.Ce.]

679 – Potentiometric titration of very weak acids. Effect of potassium on the glass electrode (in English). G. A. Harlow (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 34 (1962) 148–151.
The peculiar inverted inflections observed occasionally in the potentiometric titrations of very weak acids are due to the presence of potassium ion. Traces of potassium can completely change the shape of the potentiometric curve shifting the midpoint electric tension by several hundred millivolts. This phenomenon is the result of two simultaneous titrations: one is the expected reaction between the weak acid and the titrant, the other is the titration of the surface of the glass electrode with traces of potassium ion contained in the titrant solution. Curves are given for the effect of the different factors affecting this potassium interference on the titration curves.
                                                                                      [Su.Mo.Ce.]

680 – Formation of complex compounds between uranyl nitrate and alkaline earth nitrates. V. The system: $Ba(NO_3)_2-UO_2(NO_3)_2-H_2O$ (conductivity, pH and spectrophotometry) (in English). C. S. Pande and S. S. Gupta (University of Lucknow, India). *J. prakt. Chem.*, 13 (1961) 121–126.
The existence of $Ba(NO_3)_2 . UO_2(NO_3)_2$ in solution is confirmed by experiments carried out on the $Ba(NO_3)_2-UO_2(NO_3)_2-H_2O$ system. pH, conductivity and spectrophotometric measurements were used.   [Su.Mo.Ce.]

681 – Formation of complex compounds between uranyl nitrate and alkaline earth nitrates. VI. The system: $Sr(NO_3)_2-UO_2(NO_3)_2-H_2O$ (conductivity, pH and spectrophotometry) (in English). C. S. Pande and S. S. Gupta (University of Lucknow, India). *J. prakt. Chem.*, 13 (1961) 127–133.
The existence of a definite complex $Sr(NO_3)_2 . UO_2(NO_3)_2$ was confirmed by conductivity, pH and spectrophotometric measurements carried out on $Sr(NO_3)_2-UO_2(NO_3)_2-H_2O$ systems
                                                                                      [Su.Mo.Ce.]

682 – Direct potentiometric titration of Hg with thioacetamide in the presence of several elements (in Italian). M. Piazzi (Institute of Chemistry, Naval Academy, Leghorn, Italy). *Ann. chim. (Rome)*, 52 (1962) 45–50.
0.05–8 mg of Hg^{2+} are dissolved in 50–100 ml EDTA solution, which is in excess with respect to Hg^{2+}. After addition of ammonia buffer at pH 10, a potentiometric titration can be performed at 35° by using standard thioacetamide solution with a silver–silver sulphide indicating electrode. A sharp end-point is obtained, corresponding to the precipitation of HgS; Cu, Pb, Bi, Cd, Ni, Co and Fe do not interfere. In the presence of Ag^+, both silver and mercury are determined at the same time.   [Fr.Pan.]

683 – Potentiometric analysis of Al_2O_3 in molten cryolite by means of an insoluble oxide electrode (in French). M. Rolin and J. J. Gallay (Institut National des Sciences Appliquées, Lyon-Villeurbanne, France). *Electrochim. Acta*, 7 (1962) 153–178.

An oxide electrode, insoluble in a given molten salt medium, should be suitable for the potentio-metric determination of the oxygen ion activity of the medium. The medium investigated here is molten cryolite, in which alumina is soluble up to 11% by weight, but in which Cr_2O_3 and SnO_2 are practically insoluble. The sintered oxide electrode of Cr_2O_3 or SnO_2 is associated with an auxiliary electrode, such as molten Al, or W or Fe. Under these conditions one obtains an e.m.f. which is a function of the concentration of alumina in the bath. The reference state chosen for the activity being pure alumina, a standard e.m.f., equivalent to the free energy of formation of the oxide, can be obtained for Cr_2O_3 by extrapolation. An expression for the activity as a function of concen-tration can also be obtaned, but is not yet interpretable. It may ultimately constitute a guide for the application of the ionic theory of salt melts. [Authors]

684 – Significance of electrochemical titration methods in food investigations (in German). H. Bolling. *Mitt. Deutsch. Chem. Lab.*, 15 (1961) 30–32.

Determination of nitrogen in foods by formaldehyde titration, with potentiometric end-point indication. 1 g of the sample is boiled with 15 ml of concentrated sulphuric acid containing 3–4 g of potassium sulphate (free of nitrogen) for 20 min, then for a further 5 min with 5 ml of hydrogen peroxide, until the mixture becomes colourless. The solution is then made up to 250 ml with water. 50 ml of this solution are diluted with 100 ml of water and adjusted with 30% sodium hydroxide to pH 7.6, using an adequate pH-meter. The solution is treated with 20 ml of formaldehyde, adjusted to pH 8.1, and titrated with 0.05 N sodium hydroxide to pH 8.1.
Determination of water with Karl Fischer's reagent by a dead-stop method. Both the direct, and the dissolution and extraction methods proved to be suitable. [E.Pun.]

685 – Potentiometric determination of phosphates with a lead electrode. J. Woźniak (State Institute of Hygiene, Warsaw, Poland). *Roczniki Państwowego Zakładu Hig.*, 12 (1961) 33–39.

Using a lead electrode and a S.C.E., lead acetate can be titrated with Na_2HPO_4. Details for pre-paring the lead electrode are given. The titration is best carried out at pH 8.8 and 18°. The error is within $\pm 1.5\%$. No interference is observed from Ca, Mg, SO_4^{2-} or Cl^- when present in amounts not exceeding 7, 3, 0.2 or 0.6 times the amount of phosphorus. [Gio.Ser.]

686 – The oxidimetric determination of uranium(III) and (IV) with lead(IV) acetate (in German). A. Berkà, J. Doležal, I. Nemeč and J. Zýka (Institut für analytische Chemie der Karlsuniversität, Praha, Tschechoslovakei). *Anal. Chim. Acta*, 26 (1962) 148–154.

It is not possible to titrate uranium(III) or (IV) directly with lead tetraacetate. Therefore, a method has been established where uranium(III) and (IV) are oxidized with iron(III) chloride, the excess of iron(III) being potentiometrically titrated with lead tetraacetate solution. As little as 20 μg of uranium(IV) can be determined accurately in a volume of 30 ml. [P.Me.]

687 – High temperature electrochemical study of uranium oxides in the $UO_2 – U_3O_8$ region (in English). K. Kiukkola (Metallurgical Laboratory, Institute of Technology, Otaniemi, Finland). *Acta Chem. Scand.*, 16 (1962) 327–345.

Electric tension measurements on galvanic cells involving solid electrolytes were made at tem-peratures of 800°–1200° in order to obtain standard thermodynamic data for the mixing of UO_2 and oxygen gas. Values for the partial molar heat and entropy of mixing and the corresponding relative integral quantities were calculated for the whole composition and temperature range investigated. Non-stoichiometry in the homogeneous UO_{2+x} phase is discussed. The solubility of oxygen in this phase was found to be higher than was previously known. [G.Ekl.]

688 – Volumetric determination of uranium in the presence of niobium using a bismuth me-tal reductor (in English). R. J. Jaworowski and W. D. Bratton (Pratt and Whitney Air-craft, Canel, Middletown, Conn., U.S.A.). *Anal. Chem.*, 34 (1962) 111–112.

Uranium determination in the presence of niobium was investigated. Granular bismuth metal contained in a reductor column was used for the quantitative reduction of the uranium(VI) to uranium(IV); no formation of uranium(III) or niobium(III) was observed and no niobium hydro-lysis problems were encountered. Determination of uranium(IV) was made indirectly by reaction with an excess of iron(III), the excess being back titrated with standard cerium(IV) solution. Visual determination of the end-point of titration with ferroin as indicator was not suitable, due to the difficulty in obtaining a stable end-point. This difficulty was eliminated by determining the end-point by potentiometry. Standard deviation for the determination of pure uranium or of ura-

nium in the presence of 100.0 mg of niobium is 0.2%. The effect of various sources of interference are considered.   [Su.Mo.Ce.]

689 – Titration of uranium with potassium dichromate. Determination of disproportionality effects (in English). J. E. A. Toni (Atomic Energy Commission, Buenos Aires, Argentina). *Anal. Chem.*, 34 (1962) 99–102.
Potentiometric determination of the end-point in the titration of uranium with potassium dichromate eliminates, within certain limits, the disproportionality observed between mg of uranium titrated and ml of potassium dichromate used. Such discrepancy, observed in the titration when the end-point is determined visually, is ascribed to the diphenylaminesulphonic acid used as indicator. The effects of some variables on the indicator were investigated. Optimum conditions for the potentiometric titration of uranium, down to as little as 10 mg of uranium, were established.
                                                                                                      [Su.Mo.Ce.]

690 – Perchloric acid titrations with a commercially available electrode (in English). J. J. Hefferen and H. M. Koehler (Division of Chemistry, American Dental Association, Chicago, Ill., U.S.A.). *J. Pharm. Sci.*, 50 (1961) 583–585.
Potentiometric titrations in non-aqueous, water-miscible or -immiscible solvents may be carried out with $HClO_4$ in glacial acetic acid or dioxane as titrant. Satisfactory results, even in high resistance solvents and in the presence of mercuric acetate, may be obtained by using a calomel–glass electrode pair (Beckman No. 39142). The electrodes should not be exposed for long periods to glacial acetic acid, because diffusion of electrolyte from the calomel electrode may produce a less sharp change of the electric tension at the end-point.   [Gio.Ser.]

691 – Determination of halogens in polymers and other petroleum products by a two-furnace combustion method (in English). E. W. Seefield and J. W. Robinson (Esso Research Laboratories, Esso Standard, Division of Humble Oil and Refining Co., Baton Rouge, La., U.S.A.). *Anal. Chim. Acta*, 23 (1960) 301–305.
A method for the determination of chloride and bromide in organic liquids and solids was developed. The procedure uses a two-stage furnace which allows rapid and controlled combustion of samples up to 20 g in weight. After combustion in an oxygen stream, the free halide is collected and titrated with standard 0.01 N silver nitrate. An automatic recording titrator is used in conjunction with glass and silver electrodes. The lower limit of the method is about 0.1%. The upper range is unlimited.   [P.Me.]

692 – New method for determining small concentrations of chloride ions (in English). D. G. Peters and J. J. Lingane (Department of Chemistry, Harvard University, Cambridge, Mass., U.S.A.). *Anal. Chim. Acta*, 26 (1962) 75–80.
A new method for the determination of concentrations of chloride ions from approximately 10^{-6}– $2 \cdot 10^{-4}$ M was established. The test solution is equilibrated with excess silver chloride, and the silver ion concentration determined by potentiometric titration with iodide ions. The chloride concentration is calculated by the solubility product principle. The accuracy is about $\pm 5\%$ for chloride concentrations near $10^{-6} M$ and $\pm 0.5\%$ at 10^{-5} M. The formation of $AgCl_2^-$ limits the possibility of determining concentrations above $2–3 \cdot 10^{-4}$ M.   [P.Me.]

693 – Non-compensating potentiometric method for determining manganese in steel, cast iron, manganese ores, ferromanganese and blast furnace slags (in Russian). L. N. Kurannaya. *Trudy Voroshilovsk. Gorn. Met. Inst.*, 1 (1960) 133–137.
In the presence of $Na_4P_2O_7$ at pH 4.4–7, Mn^{2+} is oxidised by $KMnO_4$, and the titration of the first salt with the latter can be followed using a platinum–tungsten electrode pair. The sample is dissolved in hot HCl; carbides are oxidised with HNO_3 and the nitrogen oxides are removed by boiling. An aliquot of the solution is added to 100–125 ml of 11% $Na_4P_2O_7 \cdot 10H_2O$ (another 20 ml are added if the solution is turbid). The solution is neutralised to the required pH with HCl and the titration is carried out with 0.002–0.01 M $KMnO_4$. The whole procedure requires about 20 min.
                                                                                                      [Gio.Ser.]

694 – Redox titrations in glacial acetic acid. II. Oxidation of ferrous perchlorate with ceric nitrate (in Italian). G. Piccardi and P. Cellini (Institute of Analytical Chemistry, University of Florence, Italy). *Ann. Chim. (Rome)*, 52 (1962) 208–212.
Potentiometric and diamperometric (dead stop) titrations were performed to investigate the reaction between ferrous perchlorate and ceric nitrate in glacial acetic acid. Fe^{2+} is at first oxidized to Fe^{3+} by the NO_3^- ions, which are added at the same time as Ce^{4+}. NO, which is formed in such a reaction, is re-oxidized to NO_3^- by Ce^{4+}. The influence of H_2O on the Fe^{2+}/NO_3^- reaction is also investigated.   [Fr.Pan.]

695 – Mixed ligand complexes of iron(II) as non-aqueous acid–base and aqueous oxidation–reduction indicators (in English). A. A. Schilt (Department of Chemistry, University of Michigan, Ann Arbor, Mich., U.S.A.). *Anal. Chim. Acta*, 26 (1962) 134–143.
Mixed ligand complexes of iron(II), such as dicyano- bis(1, 10-phenanthroline)–iron(II) and dicyano-bis(2,2'-bipyridine)–iron(II) react rapidly and reversibly with strong acids to give stable mono- and diprotonated species. Since the visible absorption characteristics, as well as the basicities, of the protonated and neutral species differ markedly, the neutral complexes are able to function as acid–base indicators. This paper shows that the complexes are applicable as indicators for titrating certain bases in various non-aqueous solvents, or for certain redox titrations in aqueous solutions. Their applicability in determining primary aromatic amines is especially noteworthy.
[P.Me.]

696 – The transference number and activity coefficient of tris(ethylene-diamine)–cobalt (III) chloride in water at 25° (in English). D. J. Karl and J. L. Dye (Kedzie Chemical Laboratory, Michigan State University, East Lansing, Mich., U.S.A.). *J. Phys. Chem.*, 66 (1962) 550.
The cell with transference, represented by:

$$\text{Ag, AgCl/Co(en)}_3(\text{Cl}_3(C_1) \vdots \text{Co(en)}_3 \text{ Cl}_3 \ (C_2)/\text{AgCl, Ag}$$
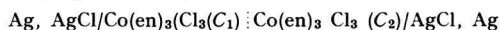
was used to obtain data concerning tris(ethylenediamine)–cobalt(III) chloride. The electric tensions, transference numbers, conductances and calculated mean molar activity coefficients are given for concentrations of $0.68–23.6 \cdot 10^{-3}$ moles/l. Extrapolation gave $T_{+}^{\circ} = 0.4945$.
[D.S.Ru.]

697 – Potentiometric titration of weak acids in non-aqueous solvents. IV. Titration of acids in bitumen (in English). D. H. Mathews, J. R. Brown and T. R. Welch (Road Research Laboratory, D.S.I.R., Middlesex, Great Britain). *J. Appl. Chem.*, 12 (1962) 64–73.
The acidic substances in bitumen were determined by potentiometric titration with potassium methoxide. The titration of carboxylic acids and other strong acids is carried out in a mixture of benzene and methanol.
[D.S.Ru.]

698 – Potentiometric titration of weak acids in non-aqueous solvents. III. Determination of the neutralisation value of road tar (in English). D. H. Mathews and G. M. Buglass (Road Research Laboratory, D.S.I.R., Harmondsworth, Middlesex, Great Britain). *J. Appl. Chem.*, 12 (1962) 48–52
A new method is described for determining the phenol content of road tar using a potentiometric titration with potassium methoxide. The "neutralisation value" (*i.e.* the weight of potassium methoxide required to neutralise the phenols in one g of tar) of tars from various sources has been determined. The results are considered more reliable than those obtained by the benzoylation method.
[D.S.Ru.]

699 – Direct titration of phenols by bromination (in English). C. O. Huber and J. M. Gilbert (Rockford College, Rockford, Ill., U.S.A.). *Anal. Chem.*, 34 (1962) 247–249.
A method for the direct titration of phenols in glacial acetic acids is proposed. A good reaction rate is obtained by the addition of a certain amount of pyridine, a solution of $0.15 \ M$ bromine in glacial acetic acid being used as titrant. Constant current potentiometry with two identical platinum foil electrodes is used for the end-point indication. The relative titration error for several different phenols is not bigger than 1.2%. The titration curve is interpreted from voltammetric data: current–electric tension curves are obtained at a platinum foil electrode, identical to those used in the titration *vs.* S.C.E.
[Su.Mo.Ce.]

700 – Determination of primary aromatic amines and compounds containing reactive methylene groups by diazotization and C-nitrozation using alkyl nitrite (in English). N. K. Mathur, S. P. Rao and D. Narain (Department of Chemistry, Jaswant College, Jodhpur, India). *Anal. Chim. Acta*, 23 (1960) 312–316.
Diazotization of primary aromatic amines and C-nitrozation of compounds containing a reactive methylene group by means of alkyl nitrite can be used for the determination of these compounds with potentiometric end-point detection. The electrode system used consists of a bright platinum spiral as indicator electrode and a saturated calomel comparison electrode. The accuracy was better than in the usual visual titration with nitrous acid using starch iodide paper as external indicator.
[P.Me.]

701 – Ionization constant of 2,2'-dihydroxybiphenyl in light and heavy water (in English).

J. E. Gordon and S. L. Johnson (Mellon Institute, Pittsburgh 13, Penn., U.S.A.). *J. Phys. Chem.*, 66 (1962) 534–536.

Measurements of the first ionization constant of 2,2'-dihydroxybiphenyl were made in light and heavy water at 25° giving values $pK_1^H = 7.56$ and $K_1^H/K_1^D = 6.34$, while K_1^H/K_2^H was estimated to be 10^6 or higher. This large isotope effect on pK_1 and the large separation between pK_1 and pK_2 indicate the formation of a strong hydrogen bridge in the mono-anion.   [D.S.Ru.]

702 – Potentiometric acid–base titration in acetone–water solutions of nitrocellulose (in English). L. R. Leake and G. F. Reynolds (Chemical Inspectorate, War Office, Royal Arsenal, Woolwich, London, Great Britain). *Talanta*, 9 (1962) 413–419.

A satisfactory method for acid–base titration of solutions of nitrocellulose with acetone concentrations greater than 90% is described. It gives an instrumental technique for showing that equilibrium has been attained after each addition of reagent. Optimum conditions are a maximum concentration of 0.5% nitrocellulose in a 99.5% acetone–water solution; under these conditions titration curves of surprisingly good shape are obtained using a glass electrode and a calomel comparison electrode, in the titration of sulphuric acid. The main drawback is the length of time required for each titration.   [Su.Mo.Ce.]

703 – Potentiometric non-aqueous semimicro titration of papaverine and narcotine (in English). H. Sakurai (Shinagawa Plant, Sankyo Co., Nishishinagawa, Shinagawa-ku, Tokyo, Japan). *J. Pharm. Soc. Japan*, 81 (1961) 164–165.

Papaverine or narcotine, respectively, present in a solution of acetone, methyl*iso*butyl ketone or chloroform, can be titrated as a base with *p*-toluene sulphonic acid, with potentiometric end-point indication.   [E.Pun.]

See also abstracts nos. 595, 603, 604, 605.

5. Conductometry

704 – The electric conductance of simple molten electrolytes (in English). J. O'M. Bockris, E. H. Crook, H. Bloom and N. E. Richards (John Harrison Laboratory of Chemistry, University of Pennsylvania, Philadelphia, Pa., U.S.A.). *Proc. Royal Soc., Series A*, 255 (1960) 558–578.

Measurements of electric conductance as a function of temperature (from melting point to a maximum of 1100°), with an accuracy of 0.2–0.3%, are reported for the following molten halides of groups IIA and IIB of the Periodic System: $MgCl_2$, $MgBr_2$, MgI_2, $CaCl_2$, $CaBr_2$, CaI_2, $SrCl_2$, $SrBr_2$, SrI_2, $BaCl_2$, $BaBr_2$, BaI_2, $ZnCl_2$, $ZnBr_2$, ZnI_2, $CdCl_2$, $CdBr_2$, CdI_2, $HgCl_2$, $HgBr_2$, and HgI_2. The combination of these results with those concerning the halides of Group IA, reported in the literature, allows the authors to draw certain conclusions on the molecular constitution of pure liquid electrolytes of groups IA, IIA and IIB.   [Su.Mo.Ce.]

705 – Electroanalytical instrumentation (in English). S. Z. Lewin (New York University, Washington Square, New York, N.Y., U.S.A.). *J. Chem. Educ.*, 39 (1962) A261–A272.

The principles, characteristics and limitations of commercially available instruments used in analytical work are discussed. Approximate price quotations are given, together with circuits and other general information.   [D.S.Ru.]

706 – Reaction kinetics from conductivity data — an apparatus for the student laboratory (in English). D. B. Greenberg (Engineering Department, United States Naval Academy Annapolis, Md., U.S.A.). *J. Chemical Educ.*, 39 (1962) 140–144.

The electrical circuit and details of construction are given for a relatively simple instrument which is used to follow the progress of a reaction conductometrically. The formation of acetic acid from acetic anhydride and water is given as an example.   [D.S.Ru.]

707 – The conductance of molten lithium chlorate and the effect of additions of traces of non-electrolytes on the conductance (in English). A. N. Campbell, E. M. Kartzmark and D. F. Williams (Chemistry Department, University of Manitoba, Winnipeg, Manitoba, Canada). *Can. J. Chem.*, 40 (1962) 890–895.

The specific conductance of pure molten lithium chlorate between 130–145° was determined and an activation energy of conductance deduced. Additions of substances having various dielectric constants were made to the molten lithium chlorate and the conductances determined. Additions were: (a) water, 0–6% by weight; (b) nitrobenzene, 0–0.4%; and (c) methyl alcohol, 0–1.25%.

[D.S.Ru.]

708 – Ionic melts as solvents for electronic conductors (in English). A. S. Dworkin, H. R. Bronstein and M. A. Bredig (Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A.). *Discussions Faraday Soc.*, 32 (1961) 188–196.

Results obtained for measurements of the electrical conductivity of solutions of Ca, Sr, La and Nd metals in their molten chlorides are reported. An all metal, parallel electrode conductivity apparatus, already described by one of the authors in a preceding paper, is used to avoid corrosion by the molten solutions. Results further illustrate the variety of electrical behaviour, that implicates differences of electronic and molecular structure, found in metal–metal halide systems.

[Su.Mo.Ce.]

709 – Electromigration in ionic melts (in English). A. Klemm (Max-Planck-Institut für Chemie, Otto-Hahn-Institut, Mainz, Deutschland). *Discussions Faraday Soc.*, 32 (1961) 203–209.

An experimental study of electromigration in ionic melts is described. Part 1 covers the separation of the isotopes of Mg, Ca, Sr and Ba by electromigration in their molten halides. The mass effects (μ) were measured from mobilities (b) of the cations by putting the salt between two carbon electrodes, the corresponding halogen gas being always present at the cathode to prevent deposition of metal. Formulae for calculations, and diagrams of the cell are given. Part 2 concerns the electromigration of Cd in molten $CdCl_2$ and Pb in molten $PbCl_2$. The mobility of dissolved Cd at 600° with respect to Cl^- is slower by only 8% than that of Cd^{2+}. The velocity of migration of the boundary $Pb–PbCl_2$ increases with decreasing concentration of Pb; this fact, and the direction of migration, leads to the conclusion that free electrons are substantially involved in $Pb + PbCl_2$. In part 3, electromigration with respect to a diaphragm was investigated for molten $ZnCl_2$ and $TiCl$. External transport numbers and their temperature dependence were determined.   [Su.Mo.Ce.]

710 – Structural influences on ion migration in crystals and melts (in English). B. Cleaver, E. Rhodes and A. R. Ubbelohde (Department of Chemical Engineering and Chemical Technology, Imperial College of Science and Technology, London, Great Britain). *Discussions Faraday Soc.*, 32 (1961) 210–217.

Two possible extensions of the Wagner effect were experimentally investigated: the Wagner effect in crystalline potassium nitrate, and the conductances of mixtures of molten nitrates. A marked increase in conductivity was found on introducing calcium ions, in solid solution in crystalline KNO_3, of up to 0.01 mole fraction of $Ca(NO_3)_2$. In contrast with the Wagner effects, addition of divalent cations to both NaCl and KNO_3 melts decreased the electrical conductivity. Such melts are normally more compressible than the corresponding solid crystals; the cause which hinders ion migration appears to be a shrinkage produced by the greater electrostatic forces associated with the higher charges.   [Su.Mo.Ce.]

711 – Self-diffusion and electrical conductance measurements on solutions of cadmium in molten cadmium chloride (in English). C. A. Angell and J. W. Tomlinson (Nuffield Research Group in Extraction Metallurgy, Royal School of Mines, London, Great Britain). *Discussions Faraday Soc.*, 32 (1961) 237–249.

Results of measurements of the diffusion coefficients of cadmium and chlorine in solutions of cadmium in molten cadmium chloride, by the open capillary technique, are reported. Description and design of an apparatus for diffusion, conductance and solubility measurements are included. In this apparatus the filling, diffusion and sampling can be carried out under an inert atmosphere in a single chamber that can be sealed to prevent the loss of the volatile component (Cd) from the melt. Values for the electrical conductance and solubility have also been obtained. The results support the view that solutions of cadmium in cadmium chloride are ionic conductors, in which association occurs with formation of $CdCl^+$ and Cd_2Cl^+ ions, polymerization to more complex structures seeming unlikely.   [Su.Mo.Ce.]

712 – The constitution of cadmium–potassium chloride melts (in English). M. A. Bredig (Chemistry division, Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A.). *Electrochim. Acta*, 5 (1961) 299–300.

Against the conclusions drawn by Bockris and Angell from measurements of the self-diffusion coefficient, D_{Cd}, of Cd(II) in $CdCl_2–KCl$ melts, measurements of conductance and Raman spectroscopic data show the existence of $CdCl_4{}^{2-}$, rather than $CdCl_3{}^-$, ions.   [Fr.Cla.]

713 – The conductances of dilute aqueous cadmium perchlorate solutions at 25° (in English).
R. A. Matheson (Chemistry Department, University of New England, Armidale, N.S.W.,
Australia). *J. Phys. Chem.*, 66 (1962) 439–441.
The equivalent conductances of aqueous cadmium perchlorate solutions are reported from 0.1–
10^{-3} N. An estimation of the contribution made by the hydrolysis products is made. No evidence
was found for incomplete dissociation of cadmium perchlorate in dilute aqueous solution.

[D.S.Ru.]

**714 – Conductometric method for the determination of dichromate ions in the presence of
chromate.** S. Ivăscanu, N. Ciureanu and I. Ciochină (Institutul Politechnic Iaşi, Rumania).
Bul. inst. politeh. Iaşi, 6 (1960) 99–106.
The method described should have some advantages over the methods previously used.

[Gio.Ser.]

**715 – The electrochemical behaviour of the metals of the iron group (Fe, Co, Ni) electrolytic-
ally deposited on mercury** (in French). J. Mindowicz (Laboratoire d'Electrochimie et
Métallurgie, Université Libre de Bruxelles, Belgique). *Electrochim. Acta*, 5 (1961) 202–215.
The electrodeposition of the metals of the iron group on mercury, using their 0.1 M aqueous chloride
solutions, was studied. This paper deals only with the observations made at low current densities
by the galvanostatic method, recording the cathodic tension as a function of time. A new method
for measuring electric tensions was used to demonstrate that the process of electrodeposition of the
metals of the iron group on mercury is accompanied neither by diffusion of the metal in the mer-
cury nor by the formation of amalgams. These metals cover the surface of mercury as if they
had been deposed on a solid cathode. The surface of the mercury cathode, more or less covered by
the metals of this group, has the same behaviour as a heterogeneous poly-electrode on which spon-
taneous electrochemical corrosion takes place.   [Fr.Cla.]

**716 – Conductances of aqueous solutions of sodium octanoate at 25° and 35° and the limiting
conductance of the octanoate ion** (in English). A. N. Campbell, E. M. Kartzmark and G. R.
Lakshminarayanan (Department of Chemistry, University of Manitoba, Winnipeg,
Manitoba, Canada). *Can. J. Chem.*, 40 (1962) 839–844.
The equivalent conductances, densities and viscosities of aqueous solutions of sodium octanoate
were determined at 25° and 35° at concentrations ranging from 0.0002–2.8 M. The limiting con-
ductances of the octanoate ion were determined as 23.08 and 29.09 mhos at 25° and 35°, respec-
tively.   [D.S.Ru.]

6. Electrolysis

717 – Identification of metals and alloys by the "electrotest" method (in French). L. Guitton.
Mém. sci. rev. mét., 58 (1961) 331–334.
The metals were dissolved electrolytically in a drop of reagent. The apparatus and procedure used
to control the electrolysis are described. Electrolysis was carried out in 10–20 sec using a few mA.
The method was applied to Cr, Ni, Mn, Ti, Cu, Mo, W, Co, Zn, Sn, Al, Mg, C and Si. The elec-
trolysis reagent may be used in some cases for qualitative detection and semi-quantitative colori-
metric determination.   [Gio.Ser.]

**718 – Mass transfer in the electrolysis of CuSO$_4$–H$_2$SO$_4$ in aqueous solutions under limiting
current and forced convection employing a cylindrical cell with rotating electrodes** (in
English). A. J. Arvia and J. S. W. Carrozza (Instituto Superior de Investigaciones, Fa-
cultad de Química y Farmacia, Universidad Nacional de La Plata, La Plata, Argentina).
Electrochim. Acta, 7 (1962) 65–78.
The rate of mass transfer for the electrodeposition of copper ions was investigated using different
rates of stirring. The reaction occurs on the cathode of a cylindrical cell, where the anode is the
stirring device. The following correlation was obtained:

$$j' = 0.0791 \ (Re)^{-0.30}(D_1/D_2)^{-0.70}$$

which also holds for other transfer processes in cylindrical cells. The peripheral velocity of the anode, V, was a measure of the rate of stirring. The mass transfer rate constant, K, is a function of $V^{0.70}$. Figures for the effective dependence of the rate constant follow an equation of the Arrhenius type. The apparent energy of activation is 450 ± 250 cal/mole, independent of the rate of stirring.
[Authors]

719 – Stability of condensed monolayers of palmitic acid on gold (in English). H. A. Laitinen and M. S. Chao (Noyes Chemical Laboratory, University of Illinois, Urbana, Ill., U.S.A.). *Anal. Chem.*, 33 (1961) 1836–1838.
The stabilities of condensed monolayers of palmitic acid on oxidized and reduced gold surfaces are compared. A gold foil electrode was slowly withdrawn through a solution–air interface containing a condensed monolayer of C^{14}-labelled palmitic acid. A controlled electric tension was applied previously to the electrode surface to oxidize or reduce it. The stabilities of the monolayers obtained were determined by observing the double layer capacity as a function of time. At the end of each experiment, the absolute measure of the adsorbed palmitic acid was performed by a radio-chemical method. The best monolayer stability was obtained when reduced conditions prevailed.
[Su.Mo.Ce.]

720 – Application of internal electrolysis to the determination of Au, Bi, Sb (in French). P. Deschamps and Y. Bonnaire (Laboratoire de chimie, Faculté des Sciences, Paris, France). *Mikrochim. Acta*, (1962) 463–474.
After a good explanation of the underlying principles, details are given of the following separations: Au from Bi, Pb, Sb and Cu; Bi from Cu and Sb (Pb eliminated by adding thiourea); Sb from Sn. The metals deposited were present in amounts from 1–3 mg. The accuracy is a few %. [H.L.Ki.]

721 – A peculiar phenomenon in the electrolysis of a flowing system (in English). S. R. Palit (Indian Association for the Cultivation of Science, Calcutta, India). *Indian J. Phys.*, 36 (1962) 55–57.
When a constant electric tension is applied between two electrodes immersed in a flowing solution of an electrolyte, a constant decrease of current is noticed. Above a critical velocity of flow, the current drops to a steady value independent of any further increase of velocity for the flowing electrolyte. This behaviour is shown both by a.c. and d.c. The Δi magnitude seems to be governed by the distance between the electrodes and the electrolyte conductivity. Current–electric tension curves, with a.c., for 0.2 and 0.1 M $MgSO_4$ are given for both "stationary" and flowing electrolyte. The two flowing electrolyte curves are also linear and pass through the origin, indicating that the flowing electrolyte behaves as an ohmic resistance over quite a large range of electric tensions. A correct interpretation of the observed facts is not yet possible; the experiments are still in progress.
[Su.Mo.Ce.]

722 – Electrodeposited thallic oxide (in English). W. T. Foley (Chemistry Department, St· Frances Xavier University, Antigonish, Nova Scotia, Canada). *Can. J. Chem.*, 40 (1962) 408–412.
Thallium oxide, electrolytically deposited at the anode, has a defective oxide structure and the thallium(I) content is about 1% by weight. The conductivity of the oxide is $(1.54 \pm 0.04) \cdot 10^3$ ohm^{-1} cm^{-1}, and the conductivity is of the n-type. The oxide contains variable amounts of water, which it retains very tenaciously.
[D.S.Ru.]

723 – Analysis of the main constituents of lead- and tin-base alloys by controlled potential electrolysis (in English). B. Alfonsi (Research and Control Laboratory, Fiat, Torino, Italy). *Anal. Chim. Acta*, 26 (1962) 316–322.
Electrolysis methods at controlled electric tension have been developed for the determination of antimony, lead (+ copper) and tin in lead- or tin-base alloys and of bismuth-base alloys. Antimony and bismuth, if present, are separated as a preliminary by electrolysis at controlled electric tension in hot hydrochloric acid solution. The bismuth and antimony deposit is redissolved, and bismuth may be re-deposited, while maintaining antimony in solution with a complexing agent. Copper and lead are electrolysed below -0.65 V *vs.* S.C.E., and tin at -0.65 V *vs.* S.C.E. [P.Me.]

724 – Electrochemical reduction of U(VI) to U(IV) in hydrochloric acid in conjuction with cation-exchange membranes (in Russian). B. N. Laskorin and N. M. Smirnova. *Atomnaya Energ.*, 10 (1961) 530–531.
Results obtained in a kinetic study of the reduction of U^{6+} to U^{4+} in hydrochloric acid solution are reported. A 100% reduction was obtained with a graphite cathode for a solution containing 90 g/l uranium and with current densities of 40 and 20 μA/cm^2; the corresponding reduction times were 70 min and 40 min. Results obtained with solutions containing 140 g/l uranium were similar.

When the current density exceeded 40 $\mu A/cm^2$ the cathode electric tension became negative.
[Su.Mo.Ce.]

725 – The use of acetonitrile in organic electrochemistry, and use of a smooth platinum electrode (in French). J. P. Billon (Laboratoire de chimie analytique, E.P.C.I., Paris, et Société Rhône-Poulenc, Laboratoires de Recherches de Vitry, Seine, France). *Bull. soc. chim. France*, (1962) 863–870.

L'auteur précise le domaine d'électroactivité dont on peut disposer dans l'acétonitrile lorsqu'on emploie un perchlorate comme électrolyte indifférent et une électrode de platine poli. En oxydation, la formation à partir des perchlorates d'un radical ClO_4^- réagissant plus ou moins rapidement sur le solvant limite ce domaine vers $+ 2.4$ V/Ag$\downarrow$–Ag$^+$ 10^{-2} M. Cette oxydation du solvant par l'intermédiaire du radical ClO_4^- conduit à la production d'ions H$^+$, c'est-à-dire d'acide perchlorique anhydre dans le solvant. En réduction, la nature du cation de l'électrolyte indifférent joue un rôle prépondérant dans l'étendue de la tension électrique disponible: limitation vers -2 V avec le sodium, vers -3 V avec le lithium et le tetrabutylammonium: dans ce cas la présence d'une petite quantité d'eau réduit considérablement le domaine (-2 V avec 3% d'eau). L'auteur indique ensuite l'analogie entre la réduction électrochimique de CH_3CN et la réduction chimique par le sodium ou le lithium métallique: formation de cyanures alcalins peu solubles, de méthane et de la base CH_2CN^- peu stable qui se polymérise en composés moins basiques.   [An.Sn.]

726 – The electrolytic oxidation of oxalate ion in the determination of calcium and magnesium (in English). J. Martin and W. Wagner (Department of Chemistry, University of Detroit, Mich., U.S.A.). *Talanta*, 9 (1962) 265–269.

In limestone analysis the excess oxalate ion, added to precipitate calcium, must be eliminated prior to the determination of magnesium as phosphate or quinolate. A satisfactory electrolytic method of oxalate removal is proposed. The solutions are electrolysed, with stirring for 25 min at 4A, using a sixteen rod graphite electrode assembly. A diagram of the electrode assembly is given, as well as graphs of the oxalate oxidation efficiency at graphite electrodes in hydrochloric acid, and at platinum electrodes in acetic acid. The electrolysed solutions were filtered to remove any carbon particles, and magnesium determination by precipitation as phosphate or quinolate was then carried out. Magnesium in concentrations as low as 5 mg in 250 ml of solution can be recovered and weighed as pyrophosphate.   [Su.Mo.Ce.]

See also abstracts nos. 595, 611, 672.

7. Coulometry

727 – Determination of very small quantities of electricity by means of an ultramicrotitration coulometer (in German). W. Helbig (Zentralinstitut für Kernphysik, Dresden-Rossendorf, Deutschland). *J. Electroanal. Chem.*, 3 (1962) 146–149.

Es wird ein Titrationscoulometer beschrieben, das auf der Titration von anodisch erzeugtem Jod durch Thiosulfat beruht. Durch Anwendung ultramikroanalytischer Arbeitsverfahren können Strommengen von etwa 10^{-2}–10^{-5} A/sec mit guter Genauigkeit bestimmt werden.   [Author]

728 – Microchemical methods in radiochemical analysis. II. Determination of chemical yields by microcoulometry (in English). R. G. Monk and K. C. Steeds (Atomic Weapons Research Establishment, U.K.A.E.A., Aldermaston, Berks., Great Britain). *Anal. Chim. Acta*, 26 (1962) 305–315.

Two titration methods are described for the microcoulometric determination of several elements using the Reilley and Portefield method of generating EDTA by electrolysis of its mercuric chelate. The first one used a mercury–calomel electrode system to detect the end-point. The drawback of this method was the length of time taken for the mercury indicator electrode to reach a stable electric tension after switching off the current. In the second one, polarized mercury electrodes were used to detect the end-point. This procedure was much more rapid than the first one. The methods described are designed for determining chemical yields of radiochemical procedures using 100–1000 μg amounts of carriers.   [P.Me.]

729 – A new method for the study of intermetallic compound formation in mixed amalgams

(in English). H. K. Ficker and L. Meites (Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, N.Y., U.S.A.). *Anal. Chim. Acta*, 26 (1962) 172–179.
The authors tried to determine zinc in the presence of many other metals by coulometry at controlled electric tension using the anodic stripping of zinc, after deposition on this metal, into a mercury cathode. They obtained a number of other co-deposited metals. They describe a chrono-amperometric method for the study of the mixed amalgam obtained in the case of cobalt and zinc containing solutions. It reveals the presence of five distinct species containing zinc, one of which is pure zinc.   [P.Me.]

730 – Coulometric titration of hydroxylamine and hydrogen peroxide by electrogenerated ceric ion (in English). T. Takahashi and H. Sakurai (Institute of Industrial Science, University of Tokyo, Chiba City, Japan). *Talanta*, 9 (1962) 189–194.
Coulometric cerimetry was applied to the determination of hydroxylamine and hydrogen peroxide. Determination of hydroxylamine was carried out indirectly by reaction with ferric ion, and subsequent coulometric titration of the ferrous ion produced with electrogenerated ceric ion. Titration error was about 1%. Hydrogen peroxide reacts instantaneously and quantitatively with cerium(IV); the determination can be directly carried out by coulometry using 0.01 N cerous sulphate–1 N sulphuric acid as electrolytic solution and carrying out the electrolytic oxidation at a constant current of about 10 mA. For quantities of hydrogen peroxide larger than 10^{-4} equiv. the error is $\pm$ 0.5%; the error increases to about 2% in the determination of about $5 \cdot 10^{-5}$ equiv. of hydrogen peroxide.   [Su.Mo.Ce.]

731 – Completely automatic coulometric titration apparatus for process use. Determination of sulphur dioxide in gases with concentrations ranging from 0.1 to 100% by volume (in English). E. Barendrecht and W. Martens (Central Laboratory, Staatsmijnen in Limburg, Geleen, The Netherlands). *Anal. Chem.*, 34 (1962) 138–142.
An electric circuit, diagram of the modified coulometric cell, scheme of titration apparatus and operative details of an automatic coulometric titration apparatus are given. Sulfur dioxide in concentrations ranging from 0.1–100% by volume can be determined every 5 min. Sulfur dioxide was quantitatively absorbed in a diluted solution of NaOH; this solution was added to an acidic solution of bromide. Titration of the sulphur dioxide was made with electrolytically generated bromine. The potentiometric system was preferred to the amperometric system for the determination of the end-point. Reproducibility is good; standard deviation is less than 0.8%. No calibration is needed, in general. The method can also be useful in the titration of hydrogen sulfide, mercaptans, etc.   [Su.Mo.Ce.]

732 – Continuous coulometric titration of micro-quantities of iron in water (in English). T. Takahashi and H. Sakurai (Institute of Industrial Science, University of Tokyo, Chiba City, Japan). *Talanta*, 9 (1962) 195–203.
A continuous coulometric method for the determination of iron(II) using electrogenerated bromine is described, as well as a continuous coulometric titration of total iron, which includes a prior reduction of iron(III) to iron(II) by zinc amalgam. For the total iron determination, the test solution is made to flow continuously through a Jone's reductor column (0.2 ml per sec). The reduced solution, flowing at 0.16 ml per sec, is continuously titrated by coulometry; the electrolytic solution contains potassium bromide in a buffer solution of acetic acid–sodium acetate. The applied electric tension is 0.73–0.75 V *vs.* S.C.E., and the electrolytic current is recorded on the chart of the recording milliammeter. The end-point is determined potentiometrically with platinum–calomel electrodes. A schematic diagram of the automatic continuous coulometric titrator, as well as records of titration and curves of electrolytic current–iron concentration, are given.   [Su.Mo.Ce.]

See also abstracts nos. 601, 648.

8. Electrophoresis

733 – The disturbing effect of electro-osmosis in electrophoresis (in French). J. Gilbert et Mlle R. Goutille (Laboratoire de chimie, Ecole Nationale Supérieure des Mines de Saint-Etienne, France). *Compt. rend.*, 254 (1962) 2756–2758.
Les auteurs mettent en évidence le rôle perturbateur de l'électroosmore en électrophorèse. Un

tube en U contenant une solution diluée d'acide fort est parcouru par un courant constant. La différence de potentiel ΔV_{ij} existant entre deux sondes situées respectivement aux distances i et j de la cathode varie en fonction du temps t. L'interprétation de la courbe expérimentale $\Delta V_{ij} =$ f(t) a conduit l'auteur à faire appel aux phénomènes d'électroosmose.   [Bad.Lam.]

734 – Separation of inorganic ions in fused salts by electrophoresis on glass fiber paper (in English). G. Alberti, G. Grassini and R. Trucco (Istituto di Chimica Generale ed Inorganica della Università, Laboratorio di Chimica delle Radiazioni e Chimica Nucleare del C.N.E.N., Rome, Italy). *J. Electroanal. Chem.*, 3 (1962) 283–285.
The possibility of a simple and fast separation of various inorganic ions by means of electrophoresis in fused salts on strips of glass fiber paper is examined. Diagrams of the apparatus are given. From the results reported it can be seen that some separations, such as Co–Pb–Ag and Zn–Cu, are possible. Results of a number of preliminary tests on the mobilities of Pb(II) and Cd(II) using different salts of these ions are also tabulated: values obtained showed that the anion does not influence the mobility of the cation.   [Su.Mo.Ce.]

735 – Separation of francium by paper electrophoresis (in French). J. P. Adloff and R. Bertrand (Centre de recherches nucléaires de Strasbourg, Départment de Chimie nucléaire, France). *Comptes rend.*, 254 (1962) 2575–2577.
La préparation du francium 223 de courte durée de vie ($T = 21$ min) nécessite l'emploi d'une méthode de séparation rapide. Les éléments gênants (actinium 227, qui l'engendre, et les membres de la série radioactive de l'actinium) peuvent être complexés par les sels d'ammonium des acides oxalique, citrique, nitrilotriacétique et éthylènediaminetétracétique. Une électrophorèse sur papier effectuée dans ces milieux avec une tension aux bornes de 80 V/cm permet d'obtenir une bonne séparation du francium 223 (émigrant seul vers la cathode) en 30 sec.   [Bad.Lam.]

736 – Continuous electrophoretic separation of the radioactive mixture ^{115}cadmium–^{114}indium (in English). Z. Konrad-Jakovac and Z. Pučar (Institute Rudjer Boškovič, Zagreb, Croatia, Yugoslavia). *Croat. Chem. Acta*, 33 (1961) 33–34.
The electrophoresis is carried out in 0.1 N KI–0.01 N HBr with the apparatus described by Pučar (*Croat. Chem. Acta*, 28 (1956) 195). The complete separation of 172 mg of ^{114}In from 108 mg of ^{115}Cd, and of 396 mg of ^{114}In from 4 g of ^{115}Cd requires 24 h.   [Gio.Ser.]

737 – Quantitative chromatographic analysis using rectified radio frequency methods. II. Fluoride, chloride, bromide and iodide (in English). V. A. Broomhead and N. A. Gibson (Chemistry School, University of Sydney, Australia). *Anal. Chim. Acta*, 26 (1962) 265–268.
A paper chromatographic separation of sodium fluoride, chloride, bromide and iodide was developed with a new solvent consisting of a 4 : 2 : 1 mixture (by volume) of acetone, pyridine and water. The separated ion zones were located by the Blake Zone Detector, and the quantity of halide ion present was determined by measuring the impedance of their respective aqueous extracts.   [P.Me.]

738 – Paper electrophoresis of metal ions in bivalent acids and their salts. II (in English). H. C. Chakrabortty (Institute of Radium, Paris, France). *J. Electroanal. Chem.*, 2 (1961) 261–262.
Results obtained in the determination of the iso-electric point of Fe(III) in mixtures of Na$_2$SO$_4$–H$_2$SO$_4$ are reported, as well as those obtained in the investigation on the electromigration of metal ions in oxalic acid and sodium oxalate.   [Su.Mo.Ce.]

739 – Buffer solution for paper electrophoretic investigations (in Russian). B. N. Usakov (Kirov Academy for Military Medicine, S.S.S.R.). *Lab. Delo*, 7 (1961) 22–23.
On using a 1.2% solution of sodium diethylbarbiturate (pH 10.6 and ionic strength 0.06) the changes of the parameters empirically established after each individual electrophoresis are corrected by the author.   [E.Pun.]

740 – Separation of C$_2$–C$_{10}$ fatty acids by paper electrophoresis (in English). A. S. Bhown and J. C. Gaur (Chemical Laboratories, Jaswant College, Jodhpur, India). *Indian J. Appl. Chem.*, 23 (1960) 156.
After electrophoresis on Whatman No. 1 paper in a 0.1 N solution of sodium chloride, the C$_2$–C$_4$ fatty acids did not separate. Higher fatty acids, in turn, could be separated from each other. The paper was developed with bromocresol green.   [E.Pun.]

741 – Paper chromatographic and electrophoretic separation and identification of some naturally occurring tetronic acids (in English). N. Spencer (Department of Biochemistry,

King's College, University of London, London, Great Britain). *J. Chromatog.*, 6 (1961) 498–504.

A sensitive spray reagent is described for the detection of some naturally occurring tetronic acids on paper chromatograms and electrophoretic strips. New chromatography solvents are also described, and R_F values are reported. The high voltage electrophoresis of tetronic acids is reported, and their electrophoretic mobilities are recorded. The identification of tetronic acids by means of their u.v. spectra is discussed; some relevant new data are recorded. A paper chromatographic procedure is described for the partial characterisation of tetronic acids.   [Author]

742 – Proteins of milk serum. Note 1 (in Italian). C. Ambrosino, J. Liberatori and A. Ubertalle (Institute of Physical Chemistry, University of Torino, Italy). *Ricerca sci.*, (II B) 31 (1961) 83–86.

The behaviour of cow milk serum was investigated by means of moving boundary electrophoresis in a veronal–citrate buffer at pH 7.8. Electrokinetic alterations in the protein content were found when heating from 75° up to boiling. A comparison was made with raw, pasteurized and sterilized milk.   [Fr.Pan.]

743 – Proteins of milk serum. Note 2 (in Italian). C. Ambrosino, J. Liberatori, A. Ubertalle and M. Pianarosa (Institute of Physical Chemistry, University of Torino, Italy). *Ricerca sci.*, [II B] 31 (1961) 141–150.

Cow milk serum was investigated by means of electrophoresis on agar gel. Seven different buffers were used, with pH values ranging from 6–9. Four new components were found, compared with data in a previous work.   [Fr.Pan.]

744 – Proteins of milk serum. Note 3 (in Italian). C. Ambrosino, J. Liberatori and A. Ubertalle (Institute of Physical Chemistry, University of Torino, Italy). *Ricerca sci.*, [II B] 31 (1961) 151–156.

Following the previous papers, a few data are reported concerning immunoelectrophoretic research on cow milk serum. A different antigen activity was found for the various serum components.   [Fr.Pan.]

745 – Separation of the copper complexes of neutral amino acids and oligopeptides by paper electrophoresis (in English). P. R. Carnegie and R. L. M. Synge (Rowett Research Institute, Bucksburn, Aberdeen, Scotland, and Ruakura Animal Research Station, Department of Agriculture, Hamilton, New Zealand). *Biochem. J.* 78 (1961) 629–696.

The amino acids and the products, respectively, obtained by shaking with a suspension of copper phosphate in sodium tetraborate, were allowed to run by electrophoresis on a Whatman 3 MM paper into a phosphate–borate buffer solution of pH 9.2. On the basis of the electropherograms developed with ninhydrin and rubeanic acid, respectively, the literature data, the mobility, and the distribution of amino acids were critically investigated.   [E.Pun.]

746 – New method for the electrophoretic study of the lipoproteins of blood serum by preliminary colouring (in Russian). D. B. Zil'berman and A. A. Moibenko. *Lab. Delo*, 7 (1961) 18–18.

The serum is treated with a solution of acetylated Sudan IV (C. I. Solvent Red 24) in diacetin. Sudan IV is acetylated by the method of Schuette (*J. Am. Chem. Soc.*, 48 (1926) 3161). The coloured serum is centrifuged to remove the excess of colour, and applied to a strip of paper. A barbiturate buffer of μ 0.05 and pH 8.6 is used. The electrophoresis is carried out for 5 h at 400 V. The lipids are separated in three orange bands, which can be eluted by 20% acetic acid and determined photometrically with a blue filter.   [Gio.Ser.]

747 – Treatment of horse serum cholinesterase with sialidase (in English). E. Heilbronn (Research Institute of National Defence, Sundbyberg 4, Sweden). *Acta Chem. Scand.*, 16 (1962) 516.

With an electrophoretic method it was found that horse serum cholinesterase, as well as some of the impurities of the used preparations, are sialoproteins.   [G.Ekl.]

748 – Analysis of serum esterases of adult and embryo hens by immuno-electrophoresis (in French). Y. Croisille (Laboratoire d'Embryologie expérimentale du Collège de France et du C.N.R.S., Paris, France). *Compt. rend.*, 254 (1962) 2253–2255.

L'analyse immunoélectrophorétique permet d'étudier les estérases du serum de poulet adulte et embryonnaire et de distinguer trois estérases différentes présentes au stade adulte alors que le stade embryonnaire ne semble posséder que deux de ces estérases.   [Bad.Lam.]

749 – Immuno-electrophoretic study of liver esterases of adult and embryo hens (in French). Y. Croisille (Laboratoire d'Embryologie expérimentale du Collège de France et du C.N.R.S., Paris, France). *Compt. rend.*, 254 (1962) 2103–2105.
L'analyse par électrophorèse en gel d'amidon de l'extrait de foie de poulet adulte met en évidence deux estérases immunochimiquement différentes.   [Bad.Lam.]

750 – A method of lipoprotein electrophoresis (in English). N. Ressler, R. Springgate and J. Kaufman (Department of Medicine, Wayne County General Hospital, Eloise, Mich., U.S.A.). *J. Chromatog.*, 6 (1961) 409–415.
An electrophoretic method is described for the routine analysis of lipoproteins. Use of a semi-fluid medium for the migration minimizes adsorption of lipoproteins by the medium. α_1-, α_2-, and β-lipoproteins are separated by this procedure. Little working time per sample is required when a number of sera are analyzed together.
The lipoprotein bands can be quantitated by isolation and spectrophotometric measurement. It is also possible to quantitate the bands by direct photometry. The use of light at wavelengths of both 200 and 590 mμ permits comparison of the relative mobilities of the lipoproteins to other proteins in the serum.
The separation allows recovery of the lipoprotein fractions in quantities which may be sufficient for further uses or investigations.   [Authors]

751 – Starch gel electrophoresis of prostata serum in order to localize the acid phosphatase. B. Estborn (Department of Clinical Biochemistry, Karolinska Sjukhuset, Stockholm, Sweden). *Clin. Chim. Acta*, 6 (1961) 22–24.
The electrophoresis of starch gel in a borate buffer solution at 4° proved that acid phosphatase ranges between the zones of albumine and α_2-globuline, while alkaline phosphatase ranges between those of α_2-globuline and transferrin.   [E.Pun.]

752 – Starch gel electrophoresis of basic water-soluble barley grain proteins (in English). T. Enari, J. Mikola and M. Nummi (Laboratory of Brewing, Helsinki, Finland). *Acta Chem. Scand.*, 16 (1962) 517–518.
The experiment was performed by a vertical method using a starch gel, and it was found that the basic fraction of water-soluble barley grain proteins can be resolved reproducibly into 16 bands of significant intensity, which appear to be native components of barley grain.   [G.Ekl.]

753 – Paper-electrophoretic determination of morphine, papaverine and atropine in the presence of amidopyrine, phenazone and barbiturates (in English). A. Liukkonen (Apteek-kitavaraintarkastuslab., Helsinki, Finland). *Farm. Aikakauslehti*, 69 (1960) 286–292.
Electrophoresis is carried out on Whatman paper using a citric acid–phosphate buffer, pH 5.6. The strips are dried at 100° and sprayed with Dragendorff's reagent. The separated bands of morphine, atropine and papaverine are quantitatively determined by photometry. The method is suitable for determination in tablets and suppositories.   [Gio.Ser.]

754 – Identification of sugars in urine by electrophoresis on paper. D. Jušič and M. Fišer-Herman (Institute of Clinical Chemistry, Faculty of Pharmacy, Zagreb, Yugoslavia). *Clin. Chim. Acta*, 6 (1961) 472–474.
Electrophoresis is carried out on Whatman No 1 paper at 4–5 V/cm for 5–6 h, using a buffer of 0.1 M H_3BO_3–0.025 M NaCl–0.025 M $Na_2B_4O_7$, pH 8.4, $\mu = 0.1$. After electrophoresis the paper is dried and sprayed with the usual reagents for the detection of sugars.   [Gio.Ser.]

755 – Investigation of hybrid haemoglobins by starch gel electrophoresis (in English). D. B. Gammack, E. R. Huehns, H. Lehmann and E. M. Shooter (Department of Biochemistry, University College, London, and Department of Pathology, St. Bartholomew's Hospital, London, Great Britain). *Biochem. J.*, 76 (1960) 55–56.
By using the starch gel technique, it is possible to detect 1 mg quantities of haemoglobins having an anomalous chain. G,D$_{Cyprus}$, D$_{Frankfurt}$, Dγ,J$_{Trinidad}$, N and O proved to possess anomalous β-chains, while K and Norfolk have anomalous α-chains.   [E.Pun.]

756 – Standard ionophoretic mobilities of various biochemicals, in amaranth units, at several pH values from 3.3 to 9.3 (in English). W. W. Thornburg, L. N. Werum and H. T. Gordon (Biological Research Laboratory, California Packing Corporation, Emeryville, Calif., and Department of Entomology and Parasitology, University of California, Berkeley, Calif., U.S.A.). *J. Chromatog.*, 6 (1961) 131–141.
The *Am* values of many known compounds in 30% formamide organic buffers at several pH values have been tabulated to aid in comparison and identification of unknowns. The pK and

molecular weight values calculable from ionophoretic data sometimes differ considerably from expected values because of unusually strong molecular interaction with the formamide buffer. The mobility–pH pattern nevertheless gives significant information about molecular structure of unknowns.   [Authors]

9. Other methods

757 – Electronic triangular wave generator for use in linear chrono-amperometry and oscillo-recording voltammetry (in French). G. Davolio, W. Guerzoni and P. Papoff (Institut de chimie physique de l'Université Modena, Italie). *Electrochim. Acta*, 5 (1961) 291–298.

An electronic triangular wave generator is described, for use at controlled electrode electric tensions. The control gives an initial stability of ± 1 mV and ensures, during scanning, a linear time variation of the electric tension imposed on the electrode, for currents up to 10 mA, in spite of an ohmic drop in the circuit. The speed of scanning is variable from 0.01 to 1500 V/sec; the initial electric tension and the width of voltage scan can be varied from $+1.5$ V to -1.5 V, and from 0 to 1.5 V respectively. Reduction curves for Tl$^+$ on a pool electrode of mercury, obtained with a scanning rate between 0.05 and 1500 V/sec are analysed, and compared with those calculated from the theoretical equation of Randles, Sevčik and Matsuda. For scanning rates > 100 V/sec the agreement is very good. The reproducibility is ± 2mV.   [Fr.Cla.]

758 – Concentration polarization in electrodialysis. III. Practical electrodialysis systems (in English). B. A. Cooke and S. J. Van der Walt (National Chemical Research Laboratory, South African Council for Scientific and Industrial Research, Pretoria, Union of South Africa). *Electrochim. Acta*, 5 (1961) 216–228.

Concentration overtension was measured in systems having mass transfer by forced convection caused by flow through a compartment bounded by ion-exchange membranes. The dependence upon current density of the difference between the bulk solution concentration and the apparent interfacial concentration derived from the measured overtension is not linear. This is ascribed to the changing nature of current distribution with increasing current, together with the presence of a diffusion layer of varying thickness. Interposition of a perforated corrugated spacer between the membranes, besides assisting depolarization, widens the range of layer thicknesses to an extent which increases with increasing flow velocity.   [Fr.Cla.]

759 – Chronopotentiometry of cerium(IV) (in English). D. G. Davis (Department of Chemistry, Louisiana State University, New Orleans, La., U.S.A.). *Anal. Chem.*, 33 (1961) 1839–1842.

Results of a study on the chronopotentiometry of cerium(IV) are reported. The plane, working platinum electrode is shielded to prevent disturbance of the diffusion layer during electrolysis. Constancy of $i\tau^{1/2}/C$ for the reduction of Ce(IV) is established over a concentration range of 2–20 mM in both 1 M sulfuric and 3 M perchloric acids. The chronopotentiometry of Ce(IV) and Fe(III) mixtures is described, including a correction for the reduction of the platinum oxide film. Indirect chronopotentiometric methods for the analysis of reducing agents are considered; results of determinations of arsenic(III) and oxalic acid are reported.   [Su.Mo.Ce.]

760 – Effect of surface oxidation and platinization on the behaviour of platinum electrodes. Reduction of vanadium(V) and iodate (in English). F. C. Anson and D. M. King (California Institute of Technology, Pasadena, Calif., U.S.A.). *Anal. Chem.*, 34 (1962) 362–365.

Results of chronopotentiometric studies on the behaviour of vanadium(V) and iodate at platinum electrodes subjected to a variety of pretreatment procedures are presented. The experimental evidence supports the author's previous proposal (F. C. Anson, *Anal. Chem.*, 33 (1961) 934) that platinization of the electrode, resulting from reduction of the oxide film on oxidized platinum electrodes, is the major factor contributing to an increase in the reversibility of subsequent electrode reactions.   [Su.Mo.Ce.]

761 – Estimation of tributyl phosphate in kerosene: an oscillometric method (in English). A. K. Sundaram (Coates Chemical Laboratory, Louisiana State University, Baton Rouge, La., U.S.A.). *J. Electroanal. Chem.*, 2 (1961) 490–492.

A method for the determination of tributylphosphate (TBP) in kerosene is reported, based on the differences in dielectric constants. Values for % TBP are obtained from a calibration curve that gives % TBP *vs.* oscillometer readings. A scale reading of 10 corresponds to about $0.2\% \pm 0.02\%$ TBP.   [Su.Mo.Ce.]

See also abstracts nos. 600, 729.

10. Related topics

762 – A new electrochemical D–H separating column (in German). A. Winsel (Institut für technische Physik der Technischen Hochschule, Braunschweig, Deutschland). *Z. Elektrochem.*, 65 (1961) 168–177.

Ein neues Verfahren zur elektrochemischen Deuterium-Gewinnung wird beschrieben. Dazu wird eine Trennsäule verwendet, die aus mehreren Anreicherungszellen und einer Elektrolysenzelle besteht. Erstere enthalten je eine Wasserstoffanode und -kathode. An der Anode wird D-reicher Wasserstoff gelöst, die gleiche Menge, jedoch D-ärmer, an der Kathode abgeschieden und der nächsten Anreicherungszelle zugeführt. Der Wasserstoff wird also an Deuterium abgereichert. Das längs der Trennsäule entstandene Konzentrationsgefälle an Deuterium und der stationäre Betrieb als technisch interessierender Spezialfall werden mathematisch betrachtet, die Trennwirkung in erster Näherung berechnet. Die optimalen Betriebsbedingungen werden untersucht und ein Zahlenbeispiel wird durchgerechnet. Geeignete Elektroden werden beschrieben und deren Stromdichte–Polarisations-Kennlinien gezeigt. Das Verfahren ist thermodynamisch weitgehend reversibel.   [He.We.]

763 – Electrochemical adsorption of organic bases and their conjugate acids. I. Adsorption of neutral bases on mercury (in English). B. E. Conway and R. G. Barradas (Department of Chemistry, University of Ottawa, Ottawa, Canada). *Electrochim. Acta*, 5 (1961) 319–348.

Electrocapillary measurements are reported for the adsorption of a series of heterocyclic and aromatic bases (and their ions) at the mercury electrode. The adsorption isotherms and $\overline{\Delta G^\circ}$ of adsorption are deduced from electrode electric tensions and are related to molecular and electronic structure of the adsorbates. Specific π-orbital interaction effects are indicated which determine the orientation of the bases at the electrode. It is shown that dipole interaction effects lead to variations of $\overline{\Delta G^\circ}$ (adsorption) with the 3/2 power of surface coverage θ; this prediction is confirmed experimentally. The variation of $\overline{\Delta G^\circ}$ with $\theta^{3/2}$ has two distinct linear regions, the range of the slope $(\partial \overline{\Delta G^\circ}/\partial \theta^{3/2}) - E$ being related to molecular orientation at high fields and coverages. The effects are closely related to the shifts of the potential of the electrocapillary maximum (e.c.m.) observed in the solutions of the bases. The observed $\overline{\Delta G^\circ}$ values at the e.c.m. are related to those found for adsorption of two bases at the air–water interface.   [Fr.Cla.]

764 – Electrochemical adsorption of organic bases and their conjugate acids. II. Comparison of adsorption of the bases and their ions on mercury (in English). R. G. Barradas and B. E. Conway (Department of Chemistry, University of Ottawa, Canada). *Electrochim. Acta*, 5 (1961) 349–361.

Free energies of adsorption $\overline{\Delta G^\circ}$ of several heterocyclic and aromatic bases and their conjugate ionic acids were evaluated from the adsorption isotherms reported in part I. The authors calculated the hydration effects. The role of π-orbital interactions with the electron-deficient metal surface on the positive branch of the electrocapillary curve is discussed. From previous work, an estimation of energies of π-orbital interaction of hydrocarbons with mercury electrodes is given, and they are compared with the free energies of adsorption calculated for the organic ions. Ionic interaction effects in the surface layer are investigated. Deviations from an expected linear relation between $\overline{\Delta G^\circ}$ and $\theta^{1/2}$ are found, and are consistent with van der Waals attractive forces. Changes of the potential of the electrocapillary maximum were evaluated, and appeared to be related to the degree of interaction of the ions of the bases with the mercury surface through π-bonding.   [Fr.Cla.]

See also abstract no. 595.

CONTENTS

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