

Journal of

ELECTROANALYTICAL CHEMISTRY

*International Journal Dealing with all Aspects
of Electroanalytical Chemistry,
Including Fundamental Electrochemistry*

EDITORS:

J. O'M. BOCKRIS (Philadelphia, Pa.)
G. MILAZZO (Rome)
C. N. REILLEY (Chapel Hill, N.C.)

EDITORIAL BOARD:

B. BREYER (Sydney)
G. CHARLOT (Paris)
B. E. CONWAY (Ottawa)
P. DELAHAY (Baton Rouge, La.)
A. N. FRUMKIN (Moscow)
L. GIERST (Brussels)
M. ISHIBASHI (Kyoto)
W. KEMULA (Warsaw)
H. L. KIES (Delft)
J. J. LINGANE (Cambridge, Mass.)
G. W. C. MILNER (Harwell)
J. E. PAGE (London)
G. SEMERANO (Padua)
M. VON STACKELBERG (Bonn)
I. TACHI (Kyoto)
P. E. WENGER (Geneva)
P. ZUMAN (Prague)

E L S E V I E R

GENERAL INFORMATION

Types of contributions

- (a) Original research work not previously published in other periodicals.
- (b) Reviews on recent developments in various fields.
- (c) Short communications.
- (d) Bibliographical notes and book reviews.
- (e) Abstracts of original papers from other journals (collected in a separate section).

Languages

Papers will be published in English, French or German.

Submission of papers

Papers should be sent to one of the following Editors:

Professor J. O'M. BOCKRIS, John Harrison Laboratory of Chemistry,
University of Pennsylvania, Philadelphia 4, Pa., U.S.A.

Professor G. MILAZZO, Istituto Superiore di Sanità,
Viale Regina Elena 299, Rome, Italy.

Professor C. N. RILEY, Department of Chemistry,
University of North Carolina, Chapel Hill, N.C., U.S.A.

Authors should preferably submit two copies in double-spaced typing on pages of uniform size. Legends for figures should be typed on a separate page. The figures should be in a form suitable for reproduction, drawn in Indian ink on drawing paper or tracing paper, with lettering etc. in thin pencil. The sheets of drawing or tracing paper should preferably be of the same dimensions as those on which the article is typed. Photographs should be submitted as clear black and white prints on glossy paper.

All references should be given at the end of the paper. They should be numbered and the numbers should appear in the text at the appropriate places.

A summary of 50 to 200 words should be included.

Reprints

Twenty-five reprints will be supplied free of charge. Additional reprints can be ordered at quoted prices. They must be ordered on order forms which are sent together with the proofs.

Publication

Since January 1st, 1962, the *Journal of Electroanalytical Chemistry* has appeared monthly and has six issues per volume and two volumes per year, each of approx. 500 pages (including the Abstracts Section).

Subscription price (post free): £ 10.15.0 or \$ 30.00 or Dfl. 108.00 per year; £ 5.7.6 or \$ 15.00 or Dfl. 54.00 per volume.

The Abstracts Section can be obtained separately (post free) at the following prices: £ 1.10.0 or \$ 4.20 or Dfl. 15.00 per volume.

Additional cost for copies by air mail available on request.

For advertising rates apply to the publishers.

Subscriptions

Subscriptions should be sent to:

ELSEVIER PUBLISHING COMPANY, P.O. Box 211, Spuistraat 110-112, Amsterdam-C., The Netherlands.

ABSTRACTS SECTION

of the

JOURNAL OF ELECTROANALYTICAL CHEMISTRY

Editor: **G. MILAZZO**, Rome

Because the abstracts section of the JOURNAL OF ELECTROANALYTICAL CHEMISTRY proved to be so useful to scientists all over the world, it was decided to make this section available separately from the Journal itself.

Our international team of abstractors examine literature from many countries in order to ensure that nothing of importance is missed. The section therefore provides a unique survey of up-to-date information, which considerably lightens the burden of literature searching which is the lot of any worker wishing to keep abreast of the latest developments in this field.

Subscribers to the Journal do, of course, receive the abstracts bound in with each issue. Those wishing to receive the abstracts alone may do so at the following modest rate:

30 s. **Dfl. 15.—** **\$ 4.20** per volume (post free)
Block subscriptions can be entered at a special rate - details on request.

From January 1962 both the Journal and the Abstracts Section will appear in monthly issues (2 volumes each consisting of 6 issues).

The abstracts are for convenience divided into ten sections as follows:

- | | |
|---------------------------------|--------------------|
| 1. Fundamental electrochemistry | 6. Electrolysis |
| 2. Apparatus and accessories | 7. Coulometry |
| 3. Polarography | 8. Electrophoresis |
| 4. Potentiometry | 9. Other methods |
| 5. Conductometry | 10. Related topics |



ELSEVIER PUBLISHING COMPANY
AMSTERDAM

PAPER ELECTROPHORESIS

A Review of Methods and Results

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.

The contents fall naturally into three sections:

- a) Theoretical principles, techniques and apparatus
- b) The determinations of proteins and the clinical applications
- c) Studies of non-macromolecular substances such as vitamins, hormones, nucleic acid fragments, sugars, inorganic ions etc.

Major emphasis has been placed on paper electrophoresis although many related methods are critically reviewed. New techniques are described in detail and the many illustrations demonstrate the principles and applications discussed in the text. There is a comprehensive list of more than 3200 references.

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

6 x 9" viii + 463 pages 130 figures 42 tables 3226 refs.

CONTENTS :

Introduction
Theoretical Considerations
Methods and Apparatus
Protein Determination
Human Serum Proteins
Animal Serum Proteins
Other Studies of Proteins
Proteins in Other Biological Fluids
Haemoglobins
Lipoproteins and Related Subjects

Glycoproteins and Mucoproteins
Enzymes and Related Substances
Hormones and Related Substances
Vitamins and Related Compounds
Carbohydrates and Polyalcohols
Nucleic Acids and Their Constituents
Amino Acids and Peptides
Inorganic Substances
Immunochemistry and Related Studies
Other Applications



ELSEVIER PUBLISHING COMPANY

Amsterdam

REVIEW

APPLICATION OF POLAROGRAPHY TO ORGANIC CHEMISTRY

P. ZUMAN

Polarographic Institute, Czechoslovak Academy of Science, Prague (Czechoslovakia)

(Received September 25th, 1961)

INTRODUCTION

Whereas the application of polarography in inorganic chemistry is well established for the solution of both theoretical and practical problems, organic chemists are rarely informed about the potential possibilities that polarography offers to them¹⁻⁹². The aim of the present article is to point out some examples of the applications of polarography in organic chemistry that have already been recognized.

SCOPE OF ORGANIC POLAROGRAPHY

To undergo polarographic electrolysis at a dropping mercury electrode (as well as at any other polarizable electrodes) the organic substance must be soluble in a solution which can be rendered conducting. Thus, in the main, aqueous solutions of organic compounds were studied, but also solutions in mixtures of organic solvents^{50,64} with water and solutions in polar organic solvents. Recently mixtures of nonpolar solvents (like benzene) with polar solvents (like ethanol) have also been successfully used⁹³. A buffer, an acid, a base or a neutral salt, possessing the function of the supporting electrolyte is normally present in the solution under investigation.

To obtain a wave on the polarographic curves, the organic substance should undergo either an electro-reduction giving a cathodic wave or an -oxidation giving an anodic wave under the galvanometer zero line. An anodic wave can also be observed in the presence of substances in solution that form slightly soluble or complex compounds with mercury. Finally numerous organic substances give catalytic waves that correspond in most instances to catalytic hydrogen evolution.

Reduction

Organic compounds that are reduced at the dropping electrode must contain a strongly polar or an unsaturated bond. Often the presence of such a group (corresponding to a chromophore group in the theory of spectra) is not sufficient to produce a reduction wave in the potential range from +0.4 V to -2.5 V (S.C.E.) to which polarography is usually restricted. The reduction can be facilitated by the presence of an activating group (analogous to an auxochrome in spectroscopy). Since the polarographic reduction of about 5000 organic substances has been described already it is impossible to give a detailed enumeration in this article. It can only be stated that the scope of reduction at the dropping mercury electrode is roughly parallel to those

substances reduced by metallic sodium. Furthermore, we can enumerate some of the more important types of polarographically reducible bonds.

Among the *single bonds* the reduction of the carbon-halogen bond is well established. Recently some examples of the reduction of activated single carbon-nitrogen, carbon-oxygen and carbon-sulfur bonds were observed^{92,94-99}. Single N—O and N—N bonds can also undergo reduction under polarographic conditions, as well as O—O and S—S bonds. Also several metal-organic bonds can be reduced.

The most important reducible *double bonds* are activated C=C and C=O bonds, and C=N, C=S and N=N bonds. Other important reducible groups are nitro-, nitroso and hydroxylamino groups.

In condensed aromatic hydrocarbons hydrogenation occurs whereas in several oxygen-, nitrogen- and sulfur-containing heterocyclics either hydrogenation or reductive ring-opening occurs.

Oxidation

Only the oxidations of phenolic compounds and enediols and a few other types of compounds occur at such negative potentials that a dropping mercury electrode can be used in their study. Numerous oxidations, like those of phenols, alcohols and amines, occur at potentials more positive than about +0.4 V requiring platinum or graphite electrodes.

Compounds with mercury causing anodic waves contain thiol, amino or sulphonic groups. Also some derivatives of urea and thiourea and certain heterocyclics belong to this group.

Catalytically active substances show catalytic waves either in pure buffer solutions or in the presence of salts of heavy metals such as cobalt or nickel.

To the former type belong some nitrogen containing compounds (mainly heterocyclics) and some O- and C-acids. To the latter type of catalytic waves belong waves often observed in the presence of compounds bearing a sulfur atom in the molecule.

POLAROGRAPHY IN ORGANIC ANALYSIS

A great share of papers, devoted to the polarography of organic substances, deals with the analytical applications of the method.

To draw general outlines of the applications of polarography in organic analysis, a comparison with applications in inorganic analysis may be used as the starting point.

However the approach to both these analytical divisions has been substantially different. Inorganic polarographic analysis has until recently used mainly an empirical approach. Several supporting electrolytes were tried in an effort to find one in which the substance to be analyzed would give a well developed wave unaffected by the presence of other components present in the electrolyzed solution. Only recently has the "renaissance" of inorganic chemistry in the last two decades, characterized mainly by studies of the behaviour of inorganic substances in solutions — mainly in connection with complex-formation — been reflected in the intensification of the studies of the theoretical foundations of inorganic polarography.

On the other hand, in polarographic organic analysis the recognized authors have already stressed for some time the importance of understanding the polarographic behaviour of a substance before an analytical method is developed.

Another important difference lies in the methodology of the chemical part of the

analytical problem, *i.e.*, that part concerning the preliminary treatment of the sample. In inorganic polarography it is possible to devise some general rules for the treatment of the sample; the dissolution, the choice of the supporting electrolyte, masking of unwanted common elements such as copper or iron, etc. In organic analysis the possibility of using analogous procedures is limited to a series of structurally very similar substances. Often the solution of an analytical problem represents a completely new approach, requiring individual consideration.

These complications and limitations have caused (among other factors) the present situation, where organic polarographic analysis is considerably less familiar in practical analysis in chemical and related industries. Whereas inorganic polarography is well established in several important branches of industry, polarographic analysis of organic substances is used as a standard method in pharmacy, pharmacology, medical sciences, the food industry and biochemistry. Applications in other fields of practical organic chemistry — *e.g.* in the heavy chemical industry, in dyestuffs chemistry, petrochemistry, explosives, plastics and rubber production etc., are still rather limited.

Another factor which, in industrial laboratories, limits the applicability of the polarographic method (especially polarography of organic compounds) is the fact that better qualified personnel are required with a broader knowledge of chemistry and instrumentation than is required *e.g.* with titrimetric or spectrophotometric methods. On the other hand, the greater specificity and objectivity of polarographic methods, allowing the exposure of errors made by technical personnel, represent an advantage of polarography.

During the last few years analysts have recognized the importance of fundamental studies. Thus in the literature the majority of papers dealing with organic polarography are devoted to studies of the general behaviour of organic substances, while only a minority deal with applications to a specific analytical problem.

The methods of polarographic analysis of organic substances can be divided into direct methods, where it is sufficient to dissolve the sample in an appropriate buffer solution, and indirect ones. In indirect methods the polarographically inactive substance is transformed by a chemical reaction into a substance which gives a wave on the polarographic curves in an appropriate supporting electrolyte. In another type of indirect determination the substance to be determined reacts with a reagent which gives a polarographic wave. After the reaction has occurred the wave of the reagent is measured. From the change in the height of this wave before and after reaction, the concentration of the analyzed substance is computed. This group includes polarometric (amperometric) titrations, in which case the equivalence-point is determined from the dependence of the wave height on the volume of titrant added.

A classical example of the first type of indirect method is the determination of polarographically inactive benzene and its homologues after transformation by means of nitrating agents into corresponding nitro-compounds¹⁰⁰⁻¹⁰². The waves corresponding to the reduction of the nitro-group to hydroxylamino- or amino-derivatives are measured. As examples of the second type, determination of some saturated ketones from the decrease of the waves for sulfurous acid¹⁰³ and of diols from the decrease of the waves of periodic acid¹⁰⁴⁻¹⁰⁵ can be quoted.

In numerous instances it is possible to submit the sample directly to polarographic analysis. For complex mixtures and mainly for samples of biological origin, it is sometimes necessary to use preliminary separation techniques such as extraction, dis-

tillation, precipitation etc. Great potentialities lie in the application of chromatographic methods using mainly ion-exchangers and paper chromatography. For analysis of protein fractions electrophoresis proved suitable. When the concentration of the analyzed substance is measured polarographically (and continuously) in the effluent from a chromatographic column and the dependence of the polarographic current on the volume of effluent followed, the method is called chromatopolarography¹⁰⁶⁻¹¹⁰. This combination allows *e.g.* the separation of mixtures of some isomers.

In mixtures of structurally similar substances polarography can be applied as functional analysis only if the substances bearing the functional grouping are actually of the same type. In this way it is possible to determine *e.g.* thiol groups or the total content of aldehydic substances in a mixture of higher aliphatic aldehydes. Similarly the sum of 3- or 17-ketosteroids can be determined after transformation into corresponding betainylhydrazones¹¹¹⁻¹¹³.

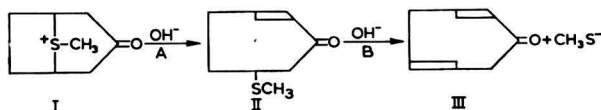
In elemental analysis polarography offers methods for the determination of sulfur¹¹⁴ and halogens^{115,116}; a method for the determination of nitrogen has also been devised.

HOMOGENEOUS REACTIONS

Polarography as an analytical method has found application in the studies of kinetics of several reactions in solutions^{40,44,65}. The measurement of the time-dependence of the wave height makes it possible to follow continuously the kinetic run, in several instances directly in the reaction mixture placed in the polarographic vessel. The application of polarography is advantageous mainly for reactions with a half-time of about 0.5-30 min. An additional advantage of the polarographic method is its sensitivity, permitting kinetic measurements in 10^{-5} - 10^{-3} M solutions. Thus with an amount, sufficient to construct a concentration-time curve using titrimetric methods, it is possible to record some 100 (or even more) complete and continuous concentration-time curves when polarography is applied.

In some instances the intermediates show a separate wave on the polarographic current-voltage curves. Thus by comparison with an appropriate model substance such intermediates can be identified. In a similar manner a final reaction product can also be detected.

In some instances it is possible to follow the change of the heights of several of the waves occurring on polarographic curves simultaneously and thus to verify the studied kinetics using different equations. In such a way individual rate constants of individual reaction steps can be determined in complex competitive reactions. This application of polarography can be demonstrated in the case of alkaline decomposition of the sulfur analogue of 3-tropinone, 8-thiobicyclo-(1,2,3)-octane-3-one (I), in which the reacting species, the final products (cycloheptadienone*(III) and methylmercaptane) as well as an intermediate, 6-methylthio-cyclohept-2-en-1-one(II), show separate polarographic waves¹¹⁷.



Here the rates of reactions A and B could be measured separately.

* A mixture of isomers.

Not only rate constants but also equilibrium constants can be detected polarographically. This is possible in such cases in which the equilibria are established slowly in comparison with the drop-time. The equilibrium constant can be computed from the measurement of the height of the wave for one component in the equilibrium which is dependent on the concentration of another component. As an example, the measurement of the equilibria between ketones and amines with the formation of ketimines¹¹⁸ can serve.

The potentialities of polarography in the detection and identification of intermediates, and further, the possibility of performing kinetic measurements in solutions of different pH-values at different ionic strengths and dielectric constants and over a wide range of temperatures, makes the application of this method advantageous in the detection of reaction mechanisms. As examples of reactions of organic substances studied in this way, reactions of isothiuronium salts with some bases described recently¹¹⁹, acid decompositions of dithiocarbamates^{120,121} and oxidation of diols by periodic acid can be quoted^{104,122,123}.

ORGANIC ELECTRODE PROCESSES

Based on studies of polarographic curves (mainly on the dependence of the form and height of polarographic curves and the half-wave potentials on pH and on the composition of the supporting electrolyte) it is often possible to distinguish the reactive form undergoing electro-reduction or -oxidation, the intermediates formed and possibly the products too. A half-wave potential measured in one deliberately chosen electrolyte usually does not yield sufficient information. From the dependence on composition of the supporting electrolyte, combined with the study of the role of the concentration of depolarizer and of the mercury pressure, we usually obtain information concerning the character of the electrode process and of the type of process governing polarographic currents (diffusion, reaction rate, catalysis, adsorption). For further understanding of the electrode process it is necessary to determine the number of electrons involved and possibly to identify the product of the electrolysis (after prolonged electrolysis at a constant potential). In addition to studies using classical polarographic methods several auxiliary methods are used, *e.g.* electrolysis at a hanging mercury drop, polarization by a periodically changing voltage, oscillographic and impulse polarography, measurement of instantaneous current (*i-t* curves) etc.

Using polarographic and related data it is possible to distinguish whether the electroactive form is already present in solution. For organic substances the reactions recognized as accompanying the electrode process can be classified as acid-base reactions, dehydration-hydration reactions and cyclization equilibria. In some instances it has been possible to determine the rate constants of these very fast reactions and sometimes their mechanisms, too. Such measurements will extend the field of reactions accessible for physical organic studies.

As intermediates in polarographic electrode processes, both unstable intermediates (mainly radicals and charged particles) and stable intermediates (which can be prepared by normal synthesis methods) can be detected. In some irreversible electrode processes the electron uptake occurs in successive steps (similar to those in reversible processes in which semiquinones are formed). On a polarographic curve, corresponding to a two-electron process, one two-electron wave occurs or two one-electron waves (which is the polarographic proof of radical formation). The stability of a radical at

the electrode depends on its electrophilic character and on the rate of a side reaction (dimerization, reaction with the solvent) which the radical might undergo.

The formation of stable intermediates was observed mainly with those substances which bear two polarographically active groups in the molecule.

There are two major contributions of the study of polarographic electrode processes to general organic chemistry. Firstly, electrode reactions, even when possessing their special features due to their heterogeneous character, follow principally the same rules (*e.g.* for structural effects) as homogeneous reactions in solutions. Thus an understanding of electrode processes presents a contribution to those reaction mechanisms that are already understood.

Secondly, a knowledge of the polarographic behaviour and the detection of the related mechanisms permits the choice of suitable conditions (potential, electrolyte, pH etc.) for preparative constant potential electrolysis. Thus *e.g.* from polarographic behaviour, we can conclude under which conditions an alcohol, and under which a pinacol is prepared by electrolysis of aldehydes and ketones, how hydroxylamine- and how amino-derivatives can be prepared from nitro-compounds, etc. In some α , β -unsaturated ketones, such as phenylvinylketone, a saturated ketone is formed in acid solutions, whereas at higher pH values the reaction proceeds at more negative potentials and an alcohol results¹²⁴. From 3-ketosteroids it is possible to prepare, according to the composition of the solution, two different stereoisomers of the pinacol formed¹²⁵. During the reduction of dibromosuccinic acid the product, according to the conditions, is either maleic or fumaric acid^{126,127}.

An understanding of polarographic curves for organic substances allows us to decide if the electrochemical method of preparation is possible at all. This is important as sometimes even structurally related substances undergo reduction by different mechanisms. For example, the electroreduction of 4-chloro-sydnones¹²⁸ produces hydrazine derivatives bearing a chlorine atom on a carbon (as the reductive ring opening occurs). For 4-bromo-sydnone a reductive substitution of the bromo atom (hydrogenolysis) occurs first (at more positive potentials). The product of the electroreduction can be either the parent sydnone or the hydrazine derivatives bearing no bromine atom. Another example is the reduction of aminoketones^{98,99,129}: electroreduction of β -aminoketones gives β -aminoalcohols, but reduction of α -aminoketones gives rise to a reductive substitution of the amino group for hydrogen resulting in formation of the parent ketone and the amine.

POLAROGRAPHY, REACTIVITY AND STRUCTURE

Half-wave potentials of quinoid systems are thermodynamic quantities, proportional to the change of standard free energy between the oxidized and reduced forms. For practically all other substances (where the electrode process is described as irreversible) the half-wave potential is a function of the free activation energy of the reduction process (or of the total rate of the electrode process). Changes of the half-wave potentials are thus functions of the changes in reactivity, as are the changes of the logarithms of the rate constants. Even when the electrode reactions are principally of a heterogeneous nature they are governed by similar structural effects like the rate constants of homogeneous reactions. Half-wave potentials are therefore a measure of reactivity and can be taken as measures of the influence of structure on reactivity like rate constants of homogeneous reactions.

This statement implies that we can compare the effects of structure on the half-wave potentials with those on rate constants. The most successful semi-empirical quantitative treatments are without doubt the linear free energy relationships and similar relations^{87-90,130,131}, the most important type of which is the HAMMETT AND TAFT equation. The effect of substituents on half-wave potentials in a series of structurally related substances can thus be expressed by

$$\Delta E_{1/2} = \rho_R \sigma_X$$

where ρ_R is a constant, characterizing the polarographically active group R and σ_X is a constant characterizing the polar effect of substituent X, derived from homogeneous reactions. These substituent constants can be tabulated.

Since the reacting agent in many instances is the electron (or the electrode, respectively) and since the reaction conditions of polarographic electrolysis (solvent, temperature, etc.) of different substances are not so markedly different as they usually are in homogeneous kinetics, it is possible to compare several electrode processes. This makes it possible to distinguish some generalizations that have not been apparent in homogeneous reaction kinetics so far^{130,131}.

The conditions necessary for a comparison of the reactivity in a given reaction series are the same mechanism of the electrode process for all members of the reaction series, and a constant value of the transfer coefficient α . In polarography we can distinguish in a much simpler way than in reaction kinetics, whether the deviations observed are due to a change in the mechanism or due to another type of structural influence than for the remaining members of the series under study.

Thus polarography enables us, in some series of compounds, to deduce *from the values of half-wave potentials the reactivity of these compounds in chemical reactions*.

The final goal of these studies on correlations between polarographic behaviour and structure of organic compounds is the interpretation of the structures of new substances using polarography. Only a few steps have been taken in this direction so far⁸⁹.

In the determination of the skeleton of organic substances polarography can only occasionally be applied. More important is the polarographic detection and proof of functional groupings attached to a known skeleton. The groupings must be either polarographically active showing a characteristic wave on polarographic curves* or a polarographically inactive substituent, present in the molecule studied next to an electroactive group. An example of the first type is the proof of carbonyl groups in several terpenes and the differentiation of ketonic and lactonic carbonyls, and the proof of disulfidic groups in some biologically important substances¹³². The second type is well represented by the identification of the kind of substituent and its position in quinolines⁸⁷, phthalimides⁸⁷ or pteridines¹³³.

The potentialities of polarography in this field are gradually being recognized.

APPLICATIONS IN SYNTHESIS AND ISOLATION

In addition to the possibility of studying polarographically the optimum conditions for electrochemical preparations, polarography offers some possibilities for improving

* A comparison of the analysed substance with an appropriate model should always be performed in several supporting electrolytes to exclude an accidental coincidence of half-wave potentials when one supporting electrolyte is used.

classical synthetic organic methods also. Namely it is possible sometimes to prove the presence in reaction mixtures of intermediates that otherwise would escape detection. Moreover, it is possible by application of polarographic analysis to find in a systematic manner the optimum conditions for the isolation of either the intermediates or the products. Thus during the study of the alkaline degradation of 3-tropinone and its sulphur analogue¹¹⁷ optimum conditions for the preparation of an intermediate II (see p. 160) were found from changes of the polarographic curves with pH and time. As another example, the synthesis of rethrolones can be mentioned¹³⁴. On the basis of a polarographic study of reaction conditions the yield could be increased from 20% to more than 70%.

Similarly in the isolation of natural products from biological material, polarography can be used to follow the progress of isolation and to find out the most effective methods of extraction etc. As examples, the procedures used in the isolation of anthocyanines¹³⁵, naturally occurring quinones¹³⁶ and tropolone¹³⁷ derivatives can be mentioned.

REFERENCES

I. General

(a) Textbooks

- 1 M. BŘEZINA AND P. ZUMAN, *Polarografie v lékařství, biochemii a farmácii* (Czech), Zdravotnické nakladatelství, Prague, 1952, 536 pp.; *Die Polarographie in der Medizin, Biochemie und Pharmazie*, Akademische Verlagsgesellschaft, Leipzig, 1956, 800 pp.; *Polarography in Medicine, Biochemistry and Pharmacy*, Interscience, New York, 1958, 883 pp.
- 2 J. HEYROVSKÝ, *Polarographie, theoretische Grundlagen, praktische Ausführung und Anwendungen der Elektrolyse mit der tropfenden Quecksilberelektrode*, Springer Verlag, Vienna, 1941, 514 pp., reprinted by Edwards, Brothers, Ann. Arbor, Mich., 1944.
- 3 J. HEYROVSKÝ AND P. ZUMAN, *Úvod do praktickéj polarografie (Introduction to Practical Polarography)*, (Slovak), Práca, Bratislava, 1950, 206 pp.; (Czech), Nakladatelství Českoslov. Akademie věd, Prague, 1953, 199 pp.; (Hungarian), Akadémiai Kiadó, Budapest, 1955, 204 pp.; (Polish), Panstwowe Wydawnictwo Naukowe, Warsaw, 1956, 252 pp.; (German), Verlag Technik, 1959, 236 pp.
- 4 I. M. KOLTHOFF AND J. J. LINGANE, *Polarography*, 2nd completely revised and augmented edition in 2 vols., Vol. I, *Theoretical Principles, Instrumentation and Technique*, Vol. II, *Inorganic-Biological Applications; Amperometric Titrations*, Interscience, New York, 1952, 990 pp.; (Chinese) Science Publ., Peking, 1955, 285 pp.; 1957, i-ix + 287-605 pp.
- 5 L. MEITES, *Polarographic Techniques*, Interscience, New York, 1955, xiii + 371 pp.
- 6 G. W. C. MILNER, *The Principles and Applications of Polarography and Other Electroanalytical Processes*, Longmans, London, 1957, 729 pp.
- 7 O. H. MÜLLER, *The Polarographic Method of Analysis*, Chemical Education Publ. Co., Easton, Pa., 1941; 2nd edn., revised and augmented, *ibid.* 1951, 209 pp.
- 8 K. SCHWABE, (Collab. H. J. BÄR, G. DIETZ AND R. TÜMMLER), *Polarographie und chemische Konstitution organischer Verbindungen*, Akademie Verlag, Berlin, 1957, 447 pp.
- 9 M. v. STACKELBERG, *Polarographische Arbeitsmethoden*, Walter de Gruyter, Berlin, 1950, 478 pp.
- 10 A. P. TERENT'EV AND L. A. YANOVSKAYA, *Polarograficheskii metod v organicheskoi khimii (Polarographic Method in Organic Chemistry) in Reakcii i metody issledovaniya organicheskikh soedinenii (Reactions and Investigation Methods of Organic Compounds)*, Vol. 5, Gosudarstvennoe nauch-tekhn. Izdatel'stvo khim. Literatury, Moscow, 1957, 388 pp.
- 11 Z. ZAGÓRSKI, *Metoda polarograficzna w analizie chemicznej (Polarographic Method in Chemical Analysis)*, (Polish), Panstwowe Wydawnictwo Naukowe, Warsaw, 1956, 594 pp.
- 12 P. ZUMAN, *Vliv konstituce na polarografické chování organických látek (The Influence of Structure on Polarographic Behaviour of Organic Substances)*, (Czech), Nakladatelství Čs. akademie věd, Prague, 1954, 64 pp.

(b) Bibliographies

- 13 E. GAGLIARDO, *Bibliografia polarografica (1922-1951)*, (Italian, English, French, German), Suppl. No. 4, *Ricerca sci.*, 21 (1951) 63.

- 14 J. HEYROVSKÝ, Polarographic bibliography from 1922 to 1950, (English, French, German Russian), Part II of *Proc. 1st Intern. Polarog. Congr. Prague, 1951*, Přírodovědecké vydavatelství, Prague 1952, 194 pp.
- 15 J. HEYROVSKÝ, Bibliography of publications dealing with the polarographic method in 1953-1959, (English, French, German), *Collection Czechoslov. Chem. Commun.*, Suppl. I, 19 (1954) 38; 20 (1955) 61; 21 (1956) 76; 22 (1957) 79; 23 (1958) 79; 24 (1959) 96; 25 (1960) 94.
- 16 J. HEYROVSKÝ AND J. E. S. HAN, *Subject Index to Polarographic Literature*, Vol. II, 1951-1955, (English-Chinese), Academia Sinica, Peking, 1958, 519 pp.
- 17 J. HEYROVSKÝ AND O. H. MÜLLER, Bibliography of publications dealing with the polarographic method in 1951 and 1952, (English, French, German), *Collection Czechoslov. Chem. Commun.*, Suppl. I, 16/17 (1951-52) 31; 18 (1953) 46.
- 18 M. ISHIBASHI AND T. FUJINAGA, *Bibliography of Polarographic Publications, (A) Metallic Elements*, No. I, 1956, 8 pp.; No. II, 1957, 12 pp.; No. III, 8 pp.; No. IV, 6 pp.; Supplement to the former bibliographies: No. V, 10 pp.; No. VI, 6 pp.; published by Shimadzu, Kyoto, Japan.
- 19 Leeds Northrup Co., Philadelphia, *Bibliography of the Polarized Dropping Mercury Electrode, (1941) and (1943); Bibliography of Polarographic Literature (E-90)I, 1955*, 102 pp.
- 20 MARIA MENEGUS-SCARPA, Bibliografia polarografica (1922-1954), Suppl. No. 6, *Ricerca sci.*, 24 (1954) 6.
- 21 MARIA MENEGUS-SCARPA AND ELENA GAGLIARDO, Bibliografia polarografica (1922-1953), Suppl. No. 5, *Ricerca sci.*, 23 (1953) 94.
- 22 MARIA MENEGUS-SCARPA AND BIANCA TOSINI, Bibliografia polarografica (1922-1954), Suppl. No. 7, *Ricerca sci.*, 25 (1955) 49.
- 23 E. H. SARGENT AND COMPANY, *Bibliography of Polarographic Literature (1922-1946)*, 3 parts: 1922-1941; 1942-1945; 1946; Chicago, Ill.
- 24 C. L. SCHMITZ AND E. F. EVEN, *Bibliography of Polarographic Literature (1922-1955) (with subject index)*, E. H. Sargent & Co., Chicago, Ill., 1956, 192 pp.
- 25 O. SEMERANO, Bibliografia polarografica (1922-1949), Parte I: Elenco dei lavori e indica degli autori, Suppl. to *Ricerca sci.*, 19 (1949) 140.
- 26 BIANCA TOSINI, Bibliografia polarografica (1922-1957), Suppl. No. 9, *Ricerca sci.*, 26 (1956) 58; 27 (1957) 63; Suppl. No. 10, *ibid.*, 28 (1958) 79; Parte II: Indice per soggetti, Suppl. No. 10 A, *ibid.*, 28 (1958) 96, (in English).

(c) *Proceedings of Congresses and Special Issues of Journals*

- 27 *Acta Chim. Acad. Sci. Hung.*, [1-4] 9 (1956), (Hungarian-Czechoslovak Polarogr. Conf., Veszprém, 1955); [1-4] 18 (1959), (Conf. of the Society of Hungarian Chemists, Budapest, 1958).
- 28 *Advances in Polarography*, (Proc. of the 2nd Intern. Congr. of Polarog., Cambridge, 1959), edited by I. S. LONGMUIR, Vol. I-III, Pergamon Press, Oxford, 1960, 1204 pp.
- 29 *Chem. Listy*, 54 (1960), (70th Birthday of Professor Heyrovský).
- 30 *Chem. Zvesti*, 8 (1954), (Disc. Polarog. Meetg., Smolenice, 1954).
- 31 *Collection Czechoslov. Chem. Commun.*, 15 (1950), (60th Birthday of Professor Heyrovský); [12] 25 (1960), [1] 26 (1961), (70th Birthday of Professor Heyrovský).
- 32 Contributi teorici e sperimentali di polarografia, Suppl. to *Ricerca sci.*, Vol. I (1952), Vol. II (1956), Vol. III (1957), Vol. IV (1959), Vol. V (1960), (Proc. of the Confs. at Bressanone).
- 33 *Prace konferencji polarograficznej w Warszawie 1956*, (Proc. of the Polarog. Conf. in Warsaw), Państwowe wydawnictwo naukowe, Warsaw, 1957, 548 pp.
- 34 *Proc. Intern. Symposium on Microchemistry, Birmingham, 1958*, Pergamon Press, Oxford, 1960, 248 pp.
- 35 *Proc. 1st Intern. Congr. of Polarography, Prague, 1951*, Přírodovědecké vydavatelství, Prague, Part I 1951, 865 pp., Part III 1952, 774 pp.
- 36 *Z. anal. Chem.*, 173 (1960), (Intern. Polarog. Symp., Bonn 1958).
- 37 *Z. Elektrochem.*, 64 (1960), (Intern. Symp. on Fast Reactions, Hahnenklee 1959).
- 38 *Z. physik. Chem. (Leipzig)*, Sonderheft (1958), (Intern. Polarog. Symp., Dresden 1957).

(d) *Reviews*

- 39 H. BERG, Polarographie und Reaktionskinetik, *Chem. Technik*, 8 (1956) 5.
- 40 H. BERG, Polarographischen Reaktionsgeschwindigkeitsmessungen in Mikrobiologie und Biochemie, Suppl. to *Ricerca sci.*, 27 (1957) 184.
- 41 M. I. BOBROVA AND N. P. SOKOLOV, Tablica potencijalov vosstanovlenija organičeskich veščestev na rutnom kapelnom elektrode, (Tables of reduction potentials of organic compounds at the dropping mercury electrode), *Zavodskaya Lab.*, 15 (1949) 36.
- 42 R. BRDIČKA, Vlastnosti organických sloučenin ve světle polarografické elektrolýsy, (The

J. Electroanal. Chem., 3 (1962) 157-168

แผนกห้องสมุด กรมวิทยาศาสตร์

กระทรวงอุตสาหกรรม

- properties of organic compounds in the light of polarographic electrolysis), *Časopis Českého Lékárnictva*, 4 (1948) 53.
- 43 R. DABARD AND J. TIROUFLET, Quelques applications de la polarographie en cinétique organique, (Some applications of polarography in organic kinetics), *Advances in Polarography*, Vol. I, Pergamon Press, Oxford, 1960, p. 288.
 - 44 A. DELMARCO, Recenti applicazioni del metodo polarografico in cinetica chimica, (Recent applications of polarographic methods in chemical analysis), Suppl. to *Ricerca sci.*, 27 (1957) 134.
 - 45 P. J. ELVING, Application of polarography to organic analysis, in J. MITCHELL, JR., *Organic Analysis*, Vol. II, Interscience, New York, 1954, p. 195.
 - 46 P. J. ELVING, Mechanism of reduction of organic substances, Suppl. to *Ricerca sci.*, 30 (1960) 205.
 - 47 P. J. ELVING, *Progress in Polarography*, Vol. II, Interscience, New York, 1961, p. 625.
 - 48 F. FREESE, Polarografie van organische Verbindungen, (Polarography of organic compounds), *Chem. Weekbl.*, 50 (1954) 781.
 - 49 H. J. GARDNER AND L. E. LYONS, The polarographic reduction of organic compounds, *Rev. Pure Appl. Chem.*, 3 (1953) 134.
 - 50 P. H. GIVEN AND M. E. PEOVER, Some aspects of the polarography of organic substances in organic solvents, *Advances in Polarog.*, Vol. III, Pergamon Press, Oxford, 1960, p. 948.
 - 51 L. GRIGGIO, Indagini polarografiche su sistemi organici, (Polarographic investigations on organic systems), Suppl. to *Ricerca sci.*, 27 (1957) 79.
 - 52 V. HANUŠ, The polarographic behaviour of organic compounds, *Proc. I. Intern. Polarog. Congr. Prague, 1951*, Vol. III, Prague, 1952, p. 103.
 - 53 O. L. KAPCAN AND M. B. NEIMAN, Uspechi polarografii organičeskich sojedineniji, (Success in the polarography of organic substances), *Zhur. Anal. Khim.*, 5 (1950) 178.
 - 54 S. KOIDE, Recent applications of organic polarography, *Rev. Modern Polarog. (Japan)*, 11 (1950) 40.
 - 55 I. A. KORŠUNOV, Primenenie poljarografii v organitšeskom analize, (Application of polarography in organic analysis), *Zavodskaya Lab.*, 24 (1958) 543.
 - 56 O. H. MÜLLER, Polarography, in S. WEISSBERGER, *Physical Methods of Organic Chemistry*, Interscience, New York, 1949, p. 1785.
 - 57 O. H. MÜLLER, Oxidation and reduction of organic compounds at the dropping mercury electrode, *Chem. Revs.*, 24 (1939) 95.
 - 58 J. NAGATA, Recent polarographic studies on the carbonyl compounds, *Rev. Polarog. (Japan)*, 6 (1958) 124; 7 (1959) 12.
 - 59 H. W. NÜRNBERG, Die Anwendung der Polarographie in der organischen Chemie, (Applications of polarography in organic chemistry), *Angew. Chem.*, 72 (1960) 433.
 - 60 J. E. PAGE, Polarography of organic compounds, *Quart. Rev.*, 6 (1952) 262.
 - 61 J. E. PAGE, Application of polarography in pharmaceutical analysis, *J. Pharm. and Pharmacol.*, 4 (1952) 1.
 - 62 K. SCHWABE, Neuere Ergebnisse der Polarographie (New results in polarography), *Forsch. u. Fortschr.*, 28 (1954) 1, 48.
 - 63 K. SCHWABE, Neuere polarographische Untersuchungen, (New polarographic studies), *Chem. Techn.*, 9 (1957) 129.
 - 64 K. SCHWABE, Polarographie in nichtwässrigen Lösungen, (Polarography in non-aqueous solutions), *Progress in Polarography*, Vol. I, Interscience, New York, 1961, p. 333.
 - 65 G. SEMERANO, L'indagine polarografica in cinetica chimica, (Polarographic investigations on chemical kinetics), Suppl. to *Ricerca sci.*, 22 (1952) 197.
 - 66 P. SOUCHAY, *Proc. VI. Meeting Intern. Comm. of Electrochem. Thermodyn. and Kinetics, Liege 1954*, Butterworths, London, 1955, p. 425.
 - 67 M. v. STACKELBERG, Elektrochemische Potentiale organischer Stoffe, (Electrochemical potentials of organic substances), in HOUBEN-WEYL, *Methoden der organischen Chemie*, 4th edn., Vol. III/2, G. Thieme, Stuttgart, 1954, p. 257.
 - 68 M. v. STACKELBERG, Polarographie organischer Stoffe, (Polarography of organic substances), in HOUBEN-WEYL, *Methoden der organischen Chemie*, 4th edn., Vol. III/2, G. Thieme, Stuttgart, 1954, p. 297.
 - 69 I. TACHI, Polarographic analysis of organic compounds, *Recent Advances in Anal. Chem. (Japan)*, 4 (1952) 107.
 - 70 I. TACHI AND S. KOIDE, Applications of polarography in organic chemistry, *J. Org. Synthesis (Japan)*, 11 (1953) 244.
 - 71 J. TIROUFLET, Le mécanisme des réactions en chimie organique: les aspects de la polarographie, (Mechanism of reactions in organic chemistry: application of polarography), *Communs. 84e Congrès des Sociétés savantes, Dijon, 1959*, p. 215.
 - 72 J. TIROUFLET, Structure chimique et comportement polarographique en chimie hétérocyclique, *J. Electroanal. Chem.*, 3 (1962) 157-168

- (Chemical structure and polarographic behaviour in heterocyclic chemistry), *Advances in Polarography*, Vol. II, Pergamon Press, Oxford, 1960, p. 740.
- 73 J. TIROUFLET AND R. DABARD, L'analyse polarographique en série aromatique, (Polarographic analysis in aromatic series), Suppl. to *Ricerca sci.*, 29 (1959) 211.
- 74 J. TIROUFLET AND E. LAVIRON, L'analyse polarographique en séries hétérocycliques, (Polarographic analysis in heterocyclic series), Suppl. to *Ricerca sci.*, 29 (1959) 189.
- 75 J. TIROUFLET AND M. PERSON, Le mécanisme de la réduction polarographique en chimie organique, (Mechanisms of polarographic reduction in organic chemistry), *Communs. 84e Congrès des Sociétés savantes*, Dijon, 1959, p. 209.
- 76 H. VELDSTRA, On the use of the polarographic method in organic chemistry and in biochemistry, *Chem. Weekbl.*, 44 (1948) 245, 261.
- 77 J. VOLKE, Die Anwendung der Polarographie in der Pharmazie, *Leybold polarograph. Ber.*, 2 (1954) 175.
- 78 J. DE WAEL, Polarografie in de biochemie, (Polarography in biochemistry), *Chem. Weekbl.*, 50 (1954) 778.
- 79 S. WAWZONEK, Organic polarography, *Anal. Chem.*, 21 (1949) 61; 22 (1950) 30; 24 (1954) 65; 30 (1958) 661; 32 (1960) 1445.
- 80 P. ZUMAN, A list of half-wave potentials, *Collection Czechoslov. Chem. Commun.*, 15 (1950) 1107.
- 81 P. ZUMAN, Polarographie in der organischen Analyse, (Polarography in organic analysis), *Proc. Intern. Polarogr. Congr., Prague 1951*, Vol. III, Prague, 1952, p. 167.
- 82 P. ZUMAN, Polarographie in der Pharmazie, (Polarography in pharmacy), *Pharmazie*, 8 (1953) 903; *Českoslov. Farm.*, 2 (1953) 413.
- 83 P. ZUMAN, Vliv konstituce na polarografické chování organických látek, (The influence of structure on polarographic behaviour of organic substances), *Chem. Listy*, 48 (1954) 94.
- 84 P. ZUMAN, Pokroky polarografie ve farmácii, (Advances of polarography in pharmacy), *Českoslov. Farm.*, 5 (1956) 44; *Pharmazie*, 11 (1956) 449.
- 85 P. ZUMAN, A general equation for the effect of substituents on half-wave potentials, Suppl. to *Ricerca sci.*, 30 (1960) 229.
- 86 P. ZUMAN, Sterische Einflüsse in der organischen Polarographie, (Steric effects in organic polarography), *Acta Chim. Acad. Sci. Hung.*, 18 (1959) 141.
- 87 P. ZUMAN, Influence of substituents in aliphatic and heterocyclic series, *Advances in Polarography*, Vol. III, Pergamon Press, Oxford, 1960, p. 812.
- 88 P. ZUMAN, Studium vlivu konstituce na polarografické chování organických látek v polarografickém ústavu ČSAV, (Study of the influence of structure on polarographic behaviour of organic substances in Polarographic Institute ČSAV), *Chem. Listy*, 54 (1960) 1244.
- 89 P. ZUMAN, Použití polarografie k studiu konstituce organických látek a meziproductů, (Applications of polarography for the study of structure of organic substances and intermediates), *Chem. Listy*, 55 (1961) 261.
- 90 P. ZUMAN, Current trends in the study of the influence of structure on the polarographic behaviour of organic substances, *Progress in Polarography*, Vol. I, Interscience, New York, 1961, p. 319.
- 91 P. ZUMAN AND M. BŘEZINA, Polarographic analysis in pharmacy, *Progress in Polarography*, Vol. II, Interscience, New York, 1961, p. 687.
- 92 P. ZUMAN AND S. WAWZONEK, *Trends in organic polarography*, Vol. I, Interscience, New York 1961, p. 303.

II. Specific

- 93 W. R. LEWIS, F. W. QUACKENBUSCH AND T. DE VRIES, *Anal. Chem.*, 21 (1949) 762.
- 94 R. M. POWERS AND R. A. DAY, JR., *J. Org. Chem.*, 24 (1959) 722.
- 95 S. WAWZONEK AND J. D. FREDERICKSON, *J. Electrochem. Soc.*, 106 (1959) 325.
- 96 P. KABASAKALIAN AND J. MCGLOTTEN, *Anal. Chem.*, 31 (1959) 1091.
- 97 H. LUND, *Acta Chem. Scand.*, 14 (1960) 1927.
- 98 P. ZUMAN AND V. HORÁK, *Advances in Polarography*, Vol. III, Pergamon Press, Oxford, 1960, p. 804.
- 99 P. ZUMAN AND V. HORÁK, *Collection Czechoslov. Chem. Commun.*, 26 (1961) 176.
- 100 S. ŠKRAMOVSKÝ AND J. TEISINGER, *Časopis Lékařů Českých*, 82 (1943) 621; 83 (1944) 1435; 84 (1945) 523.
- 101 J. ROUBAL AND J. ZDRAŽIL, *Pracovní Lékařství*, 1 (1949) 26; *Časopis Lékařů Českých*, 89 (1950) 761.
- 102 A. S. LANDRY, *Anal. Chem.*, 21 (1949) 674.
- 103 F. ŠTRNAD, *Chem. Listy*, 43 (1949) 16.
- 104 P. ZUMAN AND J. KRUPÍČKA, *Collection Czechoslov. Chem. Commun.*, 23 (1958) 598.
- 105 K. TAKIURA AND K. KOIZUMI, *Yakugaku Zasshi*, 78 (1958) 961; 79 (1959) 809.

- ¹⁰⁶ W. KEMULA, *Roczniki Chem.*, 26 (1952) 281, 639.
¹⁰⁷ W. KEMULA, *Przemysl Chem.*, 10 (1954) 453.
¹⁰⁸ W. KEMULA, *Chem. Zvesti*, 8 (1954) 740.
¹⁰⁹ W. KEMULA, *Proc. Intern. Symp. Microchem.*, Birmingham 1958, Pergamon Press, Oxford, 1960, p. 248.
¹¹⁰ W. KEMULA, *Progress in Polarography*, Vol. II, Interscience, New York, 1961.
¹¹¹ J. K. WOLF, E. B. HERSBERG AND L. F. FIESER, *J. Biol. Chem.*, 136 (1940) 653.
¹¹² V. PRELOG AND O. HÄFLIGER, *Helv. Chim. Acta*, 32 (1949) 2088.
¹¹³ M. BŘEZINA, V. VOLKOVÁ AND J. VOLKE, *Collection Czechoslov. Chem. Commun.*, 19 (1954) 894.
¹¹⁴ C. RULFS AND A. A. MACKELA, *Anal. Chem.*, 25 (1953) 660.
¹¹⁵ V. ŠAPARA, *Časopis Českého Lékárnictva*, 62 (1949) 132.
¹¹⁶ J. V. A. NOVÁK, in J. HEYROVSKÝ, *Polarographie*, Springer Verlag, Vienna, 1941, p. 361.
¹¹⁷ V. HORÁK AND P. ZUMAN, *Tetrahedron Letters*, in the press.
¹¹⁸ P. ZUMAN, *Collection Czechoslov. Chem. Commun.*, 15 (1950) 839.
¹¹⁹ P. ZUMAN AND M. FEDOROŇKO, *Z. physik. Chem. (Leipzig)*, 209 (1958) 376.
¹²⁰ P. ZUMAN AND R. ZAHRADNÍK, *Z. physik. Chem. (Leipzig)*, 208 (1957) 135.
¹²¹ R. ZAHRADNÍK AND P. ZUMAN, *Collection Czechoslov. Chem. Commun.*, 24 (1959) 1132.
¹²² P. ZUMAN, J. SICHER, J. KRUPÍČKA AND M. SVOBODA, *Nature*, 178 (1956) 1407.
¹²³ P. ZUMAN, J. SICHER, J. KRUPÍČKA AND M. SVOBODA, *Collection Czechoslov. Chem. Commun.*, 23 (1958) 1237.
¹²⁴ P. ZUMAN AND J. MICHL, *Nature*, 192 (1961) 655.
¹²⁵ H. LUND, *Acta Chem. Scand.*, 11 (1957) 283.
¹²⁶ I. ROSENTHAL AND P. J. ELVING, *J. Am. Chem. Soc.*, 73 (1951) 1880.
¹²⁷ P. J. ELVING, A. J. MARTIN AND I. ROSENTHAL, *Anal. Chem.*, 25 (1953) 1082.
¹²⁸ P. ZUMAN, *Collection Czechoslov. Chem. Commun.*, 25 (1960) 3252.
¹²⁹ P. ZUMAN AND V. HORÁK, *Collection Czechoslov. Chem. Commun.*, 27 (1962) 187.
¹³⁰ P. ZUMAN, *Collection Czechoslov. Chem. Commun.*, 25 (1960) 3225.
¹³¹ P. ZUMAN, *Suppl. to Ricerca sci.*, 30 (1960) 229.
¹³² P. ZUMAN, unpublished results.
¹³³ J. KOMENDA, *Collection Czechoslov. Chem. Commun.*, in the press.
¹³⁴ J. KRUPÍČKA, private communication.
¹³⁵ P. ZUMAN, *Collection Czechoslov. Chem. Commun.*, 18 (1953) 36.
¹³⁶ P. ZUMAN, *Collection Czechoslov. Chem. Commun.*, 19 (1954) 1140.
¹³⁷ F. ŠANTAVÝ AND T. REICHSTEIN, *Helv. Chim. Acta*, 33 (1950) 1606.

ANWENDUNG VON AMINOVERBINDUNGEN IN
DER POLAROGRAPHIE ANORGANISCHER STOFFENXI. DAS POLAROGRAPHISCHE VERHALTEN VON MANGAN UND EISEN
IN MEDIEN VON BIS-(2-HYDROXYPROPYL)-2-HYDROXYÄTHYLAMIN,
BIS-(2-HYDROXYBUTYL)-2-HYDROXYÄTHYLAMIN UND ALKALISCHEM
HYDROXYD

JAN DOLEŽAL, VLADIMÍR PETRUS UND JAROSLAV ZÝKA

Lehrstuhl für analytische Chemie der Karlsuniversität, Prag (Tschechoslowakei)

(Eingegangen den 25. März 1961)

Bei dem Verfolgen des polarographischen Verhaltens von Kationen in Lösungen von Bis-(2-hydroxypropyl)-2-hydroxyäthylamin (weiter A_2) und Bis-(2-hydroxybutyl)-2-hydroxyäthylamin (weiter A_3) wurde gefunden¹, dass das zweiwertige Mangan in Medien einiger Aminopolyalkohole bei pH 10.5 durch Luftsauerstoff oxydiert wird, unter Bildung eines smaragdgrün gefärbten Mn(III)-Komplexes. Die Reduktion dieses Komplexes an der Quecksilbertropfenelektrode macht sich durch zwei Wellen kenntlich, von denen die eine ($Mn(III) \rightarrow Mn(II)$) in 0.5 M A_3 und 0.5 M NaOH $E_{1/2} = -0.53$ V hat. Die zweite Welle, die der Reduktion $Mn(II) \rightarrow Mn(0)$ entspricht, ist zweimal so hoch als die erste und ihr $E_{1/2}$ ist stark negativ (-1.7 V). Das Halbwellenpotential der ersten Welle in dem gegebenen Medium ist um etwa 500 mV mehr positiv als das Halbwellenpotential der Welle, die der Reduktion des Fe(III)-Komplexes entspricht. Bei den meisten der bisher benutzten Elektrolyten liegt aber die Welle des dreiwertigen Eisens vor der Manganwelle, und erschwert deshalb die Bestimmung des Mangans. Deshalb zeigten sich die Aminoalkohole A_2 und A_3 als vorteilhafte Medien für die gleichzeitige Bestimmung von Mangan und Eisen.

In der vorliegenden Arbeit wird das polarographische Verhalten von Mangan, Eisen und einigen anderen Kationen in Medien von A_2 und A_3 in Gegenwart von alkalischem Hydroxyd untersucht. Auf Grund der erreichten Ergebnisse wurde die Bestimmung von Mangan und Eisen neben einigen störenden Elementen ausgearbeitet; die Gebrauchsfähigkeit dieser Methode wird an praktischen Beispielen gezeigt.

EXPERIMENTELLER TEIL UND RESULTATE

Reagenzien und Apparatur

Die Molarität des 0.1 M Mn(II)-Sulfats ($MnSO_4 \cdot 4 H_2O$ p.a. Merck) das zugleich als Standard bei der Erzanalyse diente, wurde durch komplexometrische Titration mit Eriochromschwarz T als Indikator bestimmt. Die Fe(II)-Sulfat Lösung wurde durch Lösen der notwendigen Menge Mohrschen Salzes in 0.1 M H_2SO_4 bereitet. Die Molarität

der Lösung wurde durch Titration mit Kaliumbichromat kontrolliert. Die übrigen verwendeten Reagenzien und die Apparatur waren dieselben wie in der vorgehenden Mitteilung¹ beschrieben.

Das polarographische Verhalten von Mangan

Wenn zu einer Lösung von zweiwertigem Mangan eine verdünnte A_2 - oder A_3 -Lösung zugegeben wird, entsteht zuerst ein weisser Niederschlag von Manganhydroxyd, der schnell in braunes hydratisiertes Mn(IV)-Oxyd übergeht. Wenn die Lösung noch vor dem Entstehen des braunes Niederschlages alkalisch gemacht wird (entweder durch erhöhen der Aminoalkohol-Konzentration, oder besser durch alkalisches Hydroxyd oder Ammoniak), entsteht durch Oxydation mit Luftsauerstoff ein smaragdgrüner Komplex von dreiwertigem Mangan. Der Komplex ist in alkalischem Medium sehr beständig, er wird nur durch sehr starke Oxydationsmittel zerstört. Die Höhe der symmetrischen kathodischen Welle, die seiner Reduktion entspricht, ist durch Diffusion begrenzt und ist der Mangankonzentration in der Lösung direkt proportional. Das graphische Bild der Abhängigkeit der Höhe von der Quadratwurzel der Reservoirhöhe ist eine Gerade, die durch den Ursprung des Koordinatensystems geht (Abb. 1).

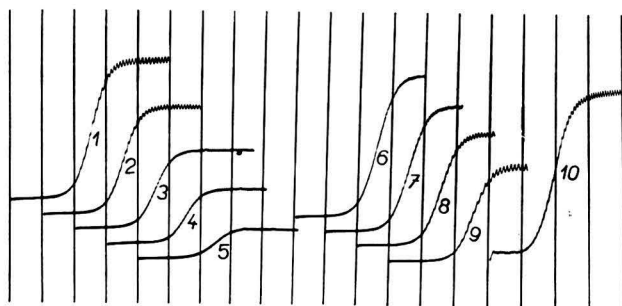


Abb. 1. Abhängigkeit der Wellenhöhe des Mn(III)-Komplexes von der Mangankonzentration in der Lösung, und von der Reservoirhöhe: $0.5 M A_2$; $0.5 M NaOH$; (1), (6), (7), (8) und (9), $10^{-3} M Mn^{3+}$; (2) $8 \cdot 10^{-4} M Mn^{3+}$; (3), $6 \cdot 10^{-4} M Mn^{3+}$; (4), $4 \cdot 10^{-4} M Mn^{3+}$; (5), $2 \cdot 10^{-4} M Mn^{3+}$. Kurve (10) $5 \cdot 10^{-4} M Tl^+$ in $0.1 M NH_3$ und $0.1 M NH_4Cl$. Alle Kurven ab $-0.2 V$ registriert. Kurven (1) bis (5), (7) und (10), $h = 64$ cm; Kurve (6), $h = 81$ cm; (8), $h = 49$ cm; (9), $h = 36$ cm. Gesättigte Kalomelektrode, kathodische Polarisation, $100 mV/Abz.$ Empf. $1/15$.

Durch Mischung einer Lösung von zweiwertigem Mangan mit Lösungen von A_2 oder A_3 in Gegenwart von alkalischem Hydroxyd wird ein farbloser Komplex von zweiwertigem Mangan gebildet, dessen Oxydation an der Tropfelektrode durch eine symmetrische anodische Welle gekennzeichnet wird. Dieser Komplex wird an der Luft sofort zu dem grünem Mn(III)-Komplex oxydiert. Die Halbwellenpotentiale der anodischen und kathodischen Welle sind unter den gegebenen Bedingungen dieselben.

Bei dem Studium des oszillopolarographischen Verhaltens des Mangans mittels der Untersuchung der Abhängigkeit $dV/dt = f(V)$ wurde gefunden, das die Lage des kathodischen und anodischen Einschnittes an der oszillographischen Kurve gegenüber der Potentialachse identisch ist (Abb. 2). Der negativ gelegene Einschnitt, der schon im Elektrolyt selbst zum Vorschein kommt, ist wahrscheinlich durch Verunreinigung des Elektrolyten verursacht.

Eine Erhöhung der Aminoalkoholkonzentration bei konstant bleibender Konzentration der Hydroxylionen in der polarographierten Lösung hat zur Folge eine Herabsetzung der Wellenhöhe des komplex gebundenen Mangans (die Viskosität der Lösung wird erhöht), das Halbwellenpotential wird um ein wenig zu den negativen

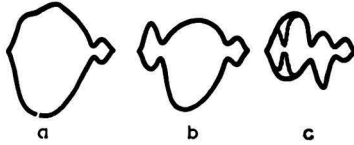


Abb. 2. Das oszillographische Verhalten der Mn(III)- und Fe(III)-Komplexe in einer Lösung von $0.5 M A_3$ und $0.5 M NaOH$: (a), (b) und (c), $0.5 M A_3$ und $0.5 M NaOH$; (b), $+10^{-3} M Mn^{3+}$; (c), $+10^{-3} M Fe^{3+}$ und $10^{-3} M Mn^{3+}$ (gestrichelt). Quecksilbertropfenelektrode, gesättigte Kalomel-elektrode, Wechselstromkomponente 0.2.

Werten verschoben. Bei A_2 - und A_3 -Konzentrationen niedriger als $5 \cdot 10^{-2}$ ($0.5 M NaOH$, $10^{-3} M Mn(II)$) sind die Resultate nicht reproduzierbar, denn aus den Lösungen wird braunes hydratisiertes Mn(IV)-Oxyd ausgeschieden. Die optimale Aminoalkoholkonzentration ist $0.5 M$.

Die Bildung des Mn(II)- und Mn(III)-Komplexes und seine Reduktion oder Oxydation an der Quecksilbertropfenelektrode ist stark von der Hydroxylionenkonzentration in der Lösung abhängig. Alkalisierung der Lösung verursacht ein Verschieben der Halbwellenpotentiale in Richtung von mehr negativen Werten. Die minimale Konzentration von alkalischem Hydroxyd (bei $0.5 M$ Aminoalkoholkonzentration und $10^{-3} M Mn$), wobei der Mn(III)-Komplex noch quantitativ entsteht, ist $0.01 M$. Um zweiwertiges Mangan in Lösung zu erhalten (ohne Zutritt von Sauerstoff) ist unter denselben Bedingungen sogar $0.1 M NaOH$ nötig. Kleinere Hydroxylionenkonzentrationen in der Lösung verursachen im ersten Fall wieder das Ausscheiden von braunem hydratisiertem Mn(IV)-Oxyd, im zweiten das Entstehen eines weissen Niederschlages von Mn(II)-Hydroxyd. Das Verschieben des Halbwellenpotentials, sowie das Entstehen des $Mn(OH)_2$ Niederschlages, dem eine Erniedrigung der anodischen Welle

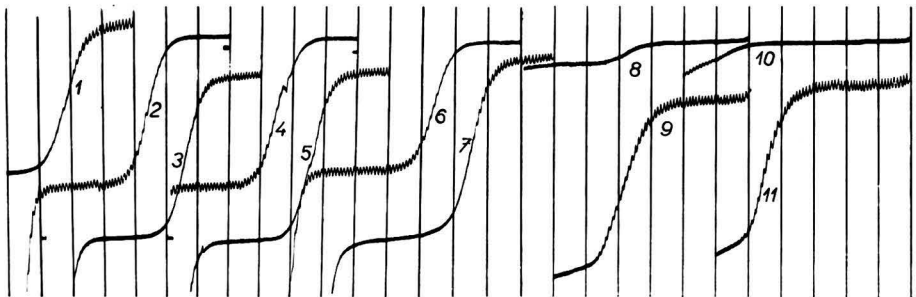


Abb. 3. Anodische und kathodische Wellen von Komplexen des zwei- und dreiwertigen Mangans mit A_3 . Abhängigkeit von der NaOH Konzentration: $0.5 M A_3$; $2 \cdot 10^{-3} M Mn^{2+}$; Kurven (2) und (3), $1 M NaOH$; (4) und (5), $0.5 M NaOH$; (6) und (7), $0.1 M NaOH$; (8) und (9), $0.01 M NaOH$; (10) und (11), $0.002 M NaOH$. Kurve (1), $5 \cdot 10^{-4} M Tl^+$ in $0.1 M NH_3$ und $0.1 M NH_4Cl$. Anodische Wellen (2), (4), (6), (8) und (10) in Stickstoffatmosphäre; kathodische Wellen (3), (5), (7), (9) und (11) nach Oxydation mit Luftsauerstoff. Kurven (2), (3), (4) und (5) ab $-0.1 V$, die übrigen ab $0 V$. Gesättigte Kalomelektrode, kathodische Polarisation, $100 mV/Abz.$, $h = 64 cm$, Empf. $1/20$.

entspricht, sind aus Abb. 3 (Kurve 8, 10) gut ersichtlich. Werte der Halbwellenpotentiale bei verschiedenen Konzentrationen des alkalischen Hydroxyds sind in Tabelle I angegeben.

TABELLE I

ABHÄNGIGKEIT DES HALBWELENPOTENTIALS DER MANGANWELLE IN 0.5 M A₂ ODER A₃ VON DER KONZENTRATION DES ALKALISCHEN HYDROXYDS

NaOH (M)	E _{1/2} (V)	
	0.5 M A ₂	0.5 M A ₃
1	-0.53	-0.55
0.5	-0.51	-0.535
0.1	-0.48	-0.51
0.05	-0.25	-0.27

pH-Werte der Aminoalkohol-Lösungen in Gegenwart von alkalischem Hydroxyd bewegen sich von etwa 10.2 (0.1 M A₃, 0.002 M NaOH) bis 12.5 (0.1 M A₃, 2 M NaOH). Die genauen pH-Werte konnten nicht ermittelt werden, denn das Messen in alkalischen Lösungen wurde durch den alkalischen Fehler der Glasselektrode stark beeinflusst. Höhere Konzentrationen des alkalischen Hydroxyds als 1 M (bei 0.5 M A₃) konnten nicht angewendet werden, denn Aminoalkohol und Natriumhydroxyd-Lösung sind gegenseitig nicht unbegrenzt mischbar.

In 0.5 M Aminoalkohol und 0.5 M NaOH kann die Mangankonzentration höchstens 0.01 M sein, bei höheren Konzentrationen wird Mangan ausgeschieden.

Es wurde gefunden, dass die kathodische Welle, die der Reduktion des Mn(III)-Komplexes entspricht, um etwas höher ist als die anodische Welle, die der Oxydation des Mn(II)-Komplexes entspricht. Die Erhöhung der kathodischen Welle kann dadurch erklärt werden, dass die Oxydation des zweiwertigen Mangans durch Luft-sauerstoff zu dem grünem Mn(III)-Komplex, die sofort nach Alkalisierung der Lösung auftritt, durch die Bildung von Wasserstoffperoxyd begleitet wird. Ein Teil des Sauerstoffs wird dementsprechend nur zu Peroxyd reduziert, das aus der Lösung durch Kochen entfernt werden kann, durch Zugabe von Sulfit (Abb. 4, Kurve 3) oder

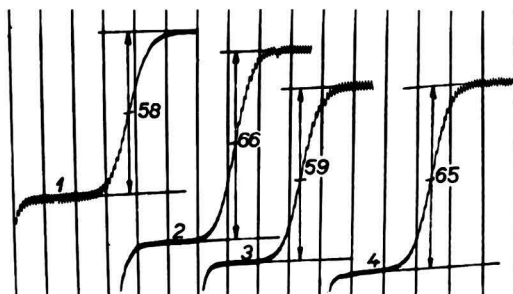


Abb. 4. Erhöhung des Grenzstromes des Mn(III)-Komplexes durch Wasserstoffperoxyd, Entfernung des Peroxyds durch Sulfit: Kurve (1), 0.5 M A₃, 0.5 M NaOH, $2 \cdot 10^{-3}$ M Mn²⁺, Stickstoffatmosphäre; (2), Lösung (1) nach Luftoxydation; (3), Lösung (2) + 0.2 g Na₂SO₃; (4), Lösung (1) + 3 Tropfen 0.5% H₂O₂; Kurve (3) ab -0.2 V, die übrigen ab -0.1 V. Gesättigte Kalomelektrode, kathodische Polarisation, 100 mV/Absz., h = 64 cm, Empf. 1/20.

durch längeres Stehen der Lösung. Werden zu dem Mn(III)-Komplex mehrere Tropfen einer höchstens 0,5% H_2O_2 Lösung zugegeben (bei Anwendung von stärkerem Peroxyd wird der grüne Mn(III)-Komplex zu einer violetten Lösung des Mn(III)-Salzes zersetzt, die unbeständig ist und schnell zu Mn(II)- und Mn(IV)-Ionen disproportioniert), wird die Welle ebenfalls erhöht (Abb. 4, Kurve 4). Das Peroxyd nimmt an der Elektrodenreaktion teil, indem es die nachfolgende Oxydation des von der Elektrode wegdiffundierenden Mn(II)-Komplexes verursacht, und demnach auch eine Erhöhung des Grenzstromes herbeiführt. Die Erhöhung der kathodischen Welle durch Wasserstoffperoxyd beträgt gegenüber der anodischen Welle etwa 10%.

Das polarographische Verhalten des Eisens

Dreiwertiges Eisen bildet in Lösungen der Aminoalkohole A_2 und A_3 verhältnismäßig wenig beständige, braun gefärbte Komplexe, die an der Quecksilbertropfelektrode in zwei Wellen reduziert werden. Die erste Welle, die der Reduktion des Fe(III)-Komplexes zu dem Fe(II)-Komplex entspricht, hat (entsprechend der Aminoalkoholkonzentration in der Lösung) ein Halbwellenpotential von etwa $-0,7$ V. Der Reduktion des Fe(II)-Komplexes entspricht die zweite Welle, die zweimal so hoch ist als die erste, mit $E_{1/2} = -1,5$ V. Mit der Zeit wird aus diesen Komplexen braunes Fe(III)-Hydroxyd ausgeschieden.

Wird zu der braunen Lösung des Komplexes von dreiwertigem Eisen mit dem Aminoalkohol eine Lösung von alkalischem Hydroxyd zugegeben (über $\text{pH} = 10,5$), entsteht ein anderer Fe(III)-Komplex, der farblos und viel mehr beständig ist als der erste. Seine Reduktion an der Tropfelektrode verläuft bei mehr negativen Potentialen: für die Reduktion des Komplexes $\text{Fe(III)} \rightarrow \text{Fe(II)}$ ist $E_{1/2} = -1,08$ V (bei $0,5$ M A_3 und $0,5$ M NaOH), die Reduktion des Komplexes $\text{Fe(II)} \rightarrow \text{Fe(0)}$ verläuft bei so negativen Potentialen, dass in dem gegebenen Medium eine polarographische Welle überhaupt nicht gebildet wird. Weiter wurde nur das Verhalten der Komplexe von Eisen mit Aminoalkoholen in Gegenwart von alkalischem Hydroxyd untersucht.

Wie aus der Abhängigkeit der Wellenhöhe von der Eisenkonzentration und von der Quadratwurzel der Reservoirhöhe hervorgeht, ist die kathodische Welle, die der Reduktion des Fe(III)-Komplexes entspricht, durch Diffusion begrenzt (Abb. 5).

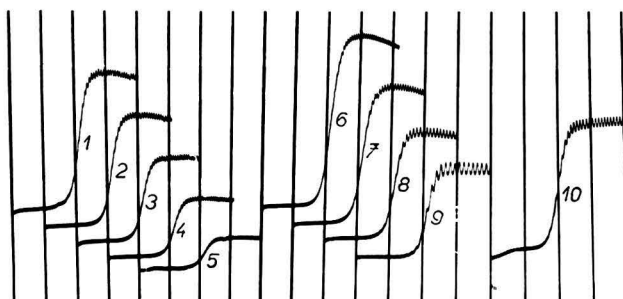


Abb. 5. Abhängigkeit der Wellenhöhe des Fe(III)-Komplexes von der Eisenkonzentration in der Lösung und von der Reservoirhöhe: $0,5$ M A_3 ; $0,5$ M NaOH; Kurve (1), (6), (7), (8) und (9), 10^{-3} M Fe^{3+} ; (2), $8 \cdot 10^{-4}$ M Fe^{3+} ; (3), $6 \cdot 10^{-4}$ M Fe^{3+} ; (4), $4 \cdot 10^{-4}$ M Fe^{3+} ; (5), $2 \cdot 10^{-4}$ M Fe^{3+} ; Kurve (10), $5 \cdot 10^{-4}$ M Ti^+ in $0,1$ M NH_3 und $0,1$ M NH_4Cl . Kurve (1) ab 0 V, die übrigen ab $-0,6$ V. Kurven (1) bis (5), (7) und (10), $h = 64$ cm; (6), $h = 81$ cm; (8), $h = 49$ cm; (9), $h = 36$ cm. Gesättigte Kalomelektrode, kathodische Polarisation, 200 mV/Absz., Empf. $1/30$.

Auch zweiwertiges Eisen bildet in vollkommen inerte Atmosphäre mit alkalischen Lösungen der Aminoalkohole A_2 oder A_3 farblose Komplexe. Ähnlich wie die $Mn(II)$ -Komplexe sind auch diese an der Luft unbeständig, und werden sofort zu $Fe(III)$ -Komplexen oxydiert.

Die anodische Welle, die der Oxydation des $Fe(II)$ -Komplexes entspricht, hat unter denselben Bedingungen dasselbe Halbwellenpotential wie die kathodische Welle, die der Reduktion des $Fe(III)$ -Komplexes entspricht.

Die minimale Aminoalkoholkonzentration (für $0.5 M NaOH$ und $10^{-3} M Fe$), bei welcher die Komplexe noch entstehen, ist $0.01 M$. Bei Erhöhung der Aminoalkoholkonzentration wird infolge der erhöhten Viskosität der Lösung die Wellenhöhe herabgesetzt. Bei niedrigeren Aminoalkoholkonzentrationen wird aus der Lösung des $Fe(III)$ -Komplexes braunes $Fe(III)$ -Hydroxyd gefällt, und aus Lösungen des $Fe(II)$ -Komplexes in inerte Atmosphäre weißes $Fe(II)$ -Hydroxyd.

Die Erhöhung der Alkalinität der Lösung durch Zugabe von alkalischem Hydroxyd hat zur Folge ein Verschieben des Halbwellenpotentials zu mehr negativen Werten (Abb. 6). Die Komplexe entstehen noch bei $0.01 M NaOH$ ($0.5 M A_2$ oder A_3 und $10^{-3} M Fe^{3+}$ bzw. Fe^{2+}). Die Werte der Halbwellenpotentials sind in Tabelle II

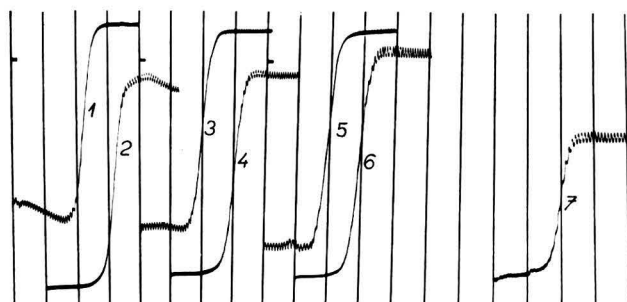


Abb. 6. Anodische und kathodische Wellen der $Fe(II)$ - und $Fe(III)$ -Komplexe mit A_3 . Abhängigkeit von der $NaOH$ -Konzentration: $0.5 M A_3$; $10^{-3} M Fe^{2+}$; (1) und (2), $1 M NaOH$; (3) und (4), $0.1 M NaOH$; (5) und (6), $0.05 M NaOH$; (7), $5 \cdot 10^{-4} M Ti^+$ in $0.1 M NH_3$ und $0.1 M NH_4Cl$. Anodische Wellen (1), (3) und (5) in Stickstoffatmosphäre; kathodische Wellen (2), (4) und (6) nach Oxydation mit Luftsauerstoff. Kurve (7) ab $0 V$, die übrigen ab $-0.6 V$. Gesättigte Kalomelektrode, kathodische Polarisation, $200 mV/Absz.$, $h = 64 cm$, Empf. $1/20$.

TABELLE II

ABHÄNGIGKEIT DES HALBWELLENPOTENTIALS DER EISENWELLE IN $0.5 M A_3$ VON DER KONZENTRATION DES ALKALISCHEN HYDROXYDS

$NaOH$ (M)	$E_{1/2}$ (V)
1	-1.10
0.5	-1.08
0.1	-1.06
0.05	-1.04

angegeben. Bei Hydroxydkonzentrationen niedriger als $0.01 M NaOH$ wird das Halbwellenpotential schnell zu mehr positiven Werten verschoben, unter gleichzeiti-

gem Braunfärben der Lösung. (Wahrscheinlich wird im schwach alkalischen Gebiet ein Komplex gebildet, der von dem in stark alkalischem Gebiet gebildeten Komplex verschieden ist.)

Die Eisenkonzentration in einer 0.5 M A₃ und 0.5 M NaOH Lösung (d.h. unter den optimalen Bedingungen) darf höchstens 0.01 M sein.

Wenn der Fe(III)-Komplex durch Oxydation des Fe(II)-Komplexes mit Luft-sauerstoff bereitet wird, beobachtet man, ganz analog dem Falle des Mangans, eine Erhöhung des Grenzstromes des dreiwertigen Eisens. Diese Erhöhung ist der Eisenkonzentration in der Lösung proportional und fällt mit dem Stehen der Lösung ab, sowie mit Kochen oder Zugabe von Sulfit. Die Erhöhung ist durch die Gegenwart von Wasserstoffperoxyd, das bei der Oxydation des Fe(II)-Komplexes entsteht, verursacht. Wasserstoffperoxyd oxydiert wahrscheinlich in einer nachfolgenden Reaktion den von der Elektrode diffundierenden Fe(II)-Komplex und erhöht damit die Welle des Eisens. Es wird aber viel weniger Peroxyd gebildet als bei der Oxydation von zweiwertigem Mangan, deshalb ist auch die Erhöhung der Welle verhältnismässig klein (etwa 5%). Wenn aber zu dem Fe(III)-Komplex eine kleine Menge verdünnter Wasserstoffperoxydlösung zugegeben wird, wächst der Grenzstrom des Eisens bis zum mehrfachen. (Für 0.5 M A₃, 0.5 M NaOH und 10⁻³ M Fe³⁺ wird durch Zugabe von 1 ml 0.5% H₂O₂ zu 100 ml Lösung die Welle 2.5 mal erhöht.)

Das polarographische Verhalten der anderen Ionen

Das Verhalten der übrigen Kationen in Lösungen der Aminoalkohole A₂ und A₃ in Gegenwart von alkalischem Hydroxyd (ausser Bi und In) ist im Grunde nicht verschieden von dem Verhalten der Ionen in Lösungen, die nur die Aminoalkohole enthalten, wie schon früher beschrieben wurde.¹ Alkalisierung der Lösung führt in allen Fällen zu einem Verschieben der Halbwellenpotentiale zu mehr negativen Werten.

Bi³⁺-Ionen werden durch Zugabe von alkalischem Hydroxyd aus Aminoalkohol-Lösungen als weisse Niederschläge ausgeschieden. Andererseits bilden die In³⁺-Ionen mit dem Aminoalkohol allein weisse Niederschläge, die sich in Gegenwart von alkalischem Hydroxyd auflösen.

TABELLE III.

DIE HALBWELLENPOTENTIALE EINIGER IONEN IM MEDIUM VON 0.5 M A₃ UND 0.5 M NaOH

Ion	E _{1/2} (V)	Ion	E _{1/2} (V)
Pb ²⁺	-1.23	Sb ³⁺	ca. -1.4
Cu ²⁺	-0.92	Fe ³⁺	-1.08
Cd ²⁺	-1.19	Mn ³⁺	-0.535
Bi ³⁺	Nlg.	Ni ²⁺	-1.50
Tl ⁺	-0.48	Zn ²⁺	-1.60
In ³⁺	-1.57	VO ₃ ⁻	-1.65
As ³⁺	-0.2**		

Ag⁺, Hg²⁺ Der Strom steigt von Null des Galvanometers sofort nach Auflösen des Quecksilbers.

Sn^{2+,4+}, Al³⁺, Cr³⁺, MoO₄²⁻, WO₄²⁻ Im erreichbaren Potentialbereich ist keine Welle zu beobachten.

^a Anodische Welle. Nlg., es wird ein Niederschlag gebildet.

* Nur die Andeutung einer Welle.

Die Halbwellenpotentiale einiger Ionen in Medium von 0.5 M A_3 und 0.5 M NaOH sind in Tabelle III angeführt.

Die gleichzeitige polarographische Bestimmung von Mangan und Eisen

Eisen und Mangan sind sehr oft in Legierungen, Erzen und anderem Material zusammen anwesend. Aus dem, was in den vorgehenden Absätzen gesagt wurde geht hervor, dass Mangan in Lösungen der Aminoalkohole A_2 oder A_3 in Gegenwart von alkalischem Hydroxyd zugleich mit Eisen neben einer Reihe von Elementen bestimmt werden kann. Der grüne Komplex des dreiwertigen Eisens ist in alkalischem Medium sehr beständig (sofern nicht starke Oxydationsmittel anwesend sind), und weder die Höhe der Diffusionswelle die der Reduktion dieses Komplexes entspricht, noch das Halbwellenpotential werden durch die Gegenwart von Sulfaten, Nitraten, Chloriden, Phosphaten, Chromaten und Sulfiten beeinflusst. Durch Cyanide wird der Komplex in einer Weile zersetzt. EDTA verschiebt das Halbwellenpotential in Richtung der mehr positiven Potentiale (in 0.5 M A_3 und 0.5 M NaOH ist bei 10^{-3} M Mn $E_{1/2} = -0.53\text{ V}$; in Gegenwart von $5 \cdot 10^{-3}\text{ M EDTA}$ ist $E_{1/2} = -0.49\text{ V}$), der Mn(III) -Komplex wird durch EDTA selbst nach längerer Zeit nicht zersetzt). Es ist also die Möglichkeit gegeben den störenden Einfluss einiger Elemente, die in dem gegebenen Medium Niederschläge bilden, zu eliminieren (Kalzium, Magnesium u.a.).

Unter den geläufigeren Kationen stört besonders Kupfer, denn seine langegezogene Welle koinzidiert in Gegenwart von höheren Konzentrationen mit der Manganwelle. Mangan kann noch dann bestimmt werden, wenn die Kupferkonzentration in der Lösung zweimal so hoch ist als die Mangankonzentration.

Die übrigen Kationen stören nicht, sofern sie nicht in einer solchen Konzentration anwesend sind, dass sie in der Mischung von Aminoalkohol und Hydroxyd gefällt sein würden. Bei der Bestimmung von $5 \cdot 10^{-4}\text{ M Mn}$ in 0.5 M A_3 und 0.5 M NaOH stören Eisen, Aluminium, Zink, Kobalt und Blei nicht in einem hundertfachen (molaren) Überschuss, Kadmium in fünfzigfachem Überschuss gegenüber dem Mangan.

Bei der gleichzeitigen Bestimmung von Mangan und Eisen ist die Höhe der Wellen von dreiwertigem Mangan und Eisen durch Gegenwart von Wasserstoffperoxyd beeinflusst. Wollen wir bei der Manganbestimmung richtige und reproduzierbare Re-

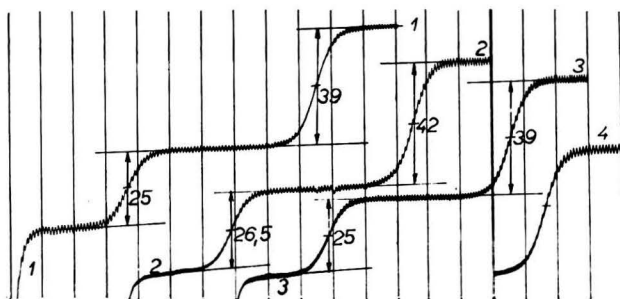


Abb. 7. Erhöhung des Mn und Fe Grenzstromes durch Wasserstoffperoxyd, Entfernung des Peroxyds durch Sulphit. Kurve (1), 0.5 M A_3 , 0.5 M NaOH , 10^{-3} M Mn^{2+} , 10^{-3} M Fe^{2+} ; (2), Lösung (1) nach Oxydation mit Luftsauerstoff; (3), Lösung (2) + $0.2\text{ g Na}_2\text{SO}_3$; (4), $5 \cdot 10^{-4}\text{ M Tl}^+$ in 0.1 M NH_3 und $0.1\text{ M NH}_4\text{Cl}$. Kurve (1) ab 0 V , (2) und (3) ab -0.1 V ; Kurve (4) ab -0.2 V . Gesättigte Kalomelektrode, kathodische Polarisation, $h = 64\text{ cm}$, 100 mV/Absz. , Empf. $1/20$.

sultate erzielen, bzw. bei der Bestimmung von Eisen neben Mangan, muss Wasserstoffperoxyd aus der zu analysierenden Lösung durch längeres Stehen (etwa 4 Stunden) der Lösung oder durch Zugabe von Sulfid entfernt werden. Die Erhöhung des Eisen und Mangan-Grenzstromes, sowie die Wasserstoffperoxydentfernung sind aus Abb. 7 ersichtlich.

Die optimalen Bedingungen für die Bestimmung von Mangan (bzw. Eisen) in alkalischen Lösungen der Aminoalkohole A_2 oder A_3 sind die folgenden: 0.5 M Aminoalkohol, 0.5 M NaOH, Konzentration der zu bestimmenden Elemente $10^{-3} M$. Die Bestimmung kann noch in $5 \cdot 10^{-2} M$ Aminoalkohol (bei 0.5 M NaOH) durchgeführt werden. Die Konzentration der zu bestimmenden Elemente darf 0.01 M nicht überschreiten. Die Mangan enthaltende Lösung muss gut an der Luft durchgeschüttelt werden, um die Sicherheit zu erlangen dass alles Mangan in dreiwertiger Form vorliegt. Um eine Erhöhung des Mangan- und Eisen-Grenzstromes durch Wasserstoffperoxyd zu verhindern wird zu 10 ml der polarographierten Lösung nach der Oxydation mit Luftsauerstoff etwa 0.2 g Natriumsulphit zugegeben, oder lässt man die Lösung wenigstens 4 Stunden stehen. Die Lösung wird durch 5 Minuten Stickstoffzufuhr von Sauerstoff befreit.

PRAKTISCHE ANWENDUNG

Die Bestimmung von Mangan in Erzen

Arbeitsvorschrift. Ein genau abgewogene Menge des Manganerzes (etwa 1 g) wird in HCl (2 + 1) gelöst, zum Trockenem abgedampft, und der Rest wird mit H_2SO_4 bis zum Erscheinen von weissen Dämpfen abgeraucht. Der Rückstand wird mit Wasser ausgelaugt und filtriert. Der Filter mit Kieselsäure, an die eventuell die zu bestimmenden Komponenten des Erzes adsorbiert sein können, wird in einem Platintiegel verbrannt. Der Inhalt des Tiegels wird mit konz. H_2SO_4 angefeuchtet und die Kieselsäure wird mit HF als flüchtiges Siliziumfluorid abgedampft. Der Rückstand wird mit $KHSO_4$ geschmolzen, mit heissem Wasser ausgelaugt und die Lauge zu dem ursprünglichen Filtrat zugegeben. Sofern die Schmelze nicht vollkommen in Lösung geht, muss die ganze Arbeit von dem Abrauchen der Kieselsäure angefangen wiederholt werden. Das Filtrat wird mit 5 M NaOH neutralisiert bis eine Trübung des ausgeschiedenen Eisenhydroxyds erscheint, die in einem geringen Überschuss an H_2SO_4 gelöst wird. Die solcherweise bereitete klare Lösung wird in einen Masskolben gebracht (100 ml) und mit destilliertem Wasser bis zur Marke aufgefüllt. Zu der eigentlichen polarographischen Bestimmung wird ein aliquoter Teil (1 bis 2 ml, je nach dem Mangangehalt des Erzes) in einen 10 ml Masskolben pipettiert. Zu der Lösung, die Eisen und Mangan enthält, werden 5 ml 1 M A_3 und 1 ml 5 M NaOH und etwas destilliertes Wasser zugegeben und die Lösung wird in dem Masskolben gut durchgeschüttelt. Dann wird 0.2 g Na_2SO_3 zugegeben und die Lösung mit destilliertem Wasser aufgefüllt. Die klare grüne Lösung wird nach 5 Minuten langem Durchführen von Stickstoff polarographiert. Die Manganwelle wird von 0 bis -0.8 V registriert (Akkumulator 4 V). Bei der Auswertung des Mangangehaltes des Erzes ist die Methode der Standardzugabe vorteilhaft. Im gegebenen Falle wurde als Standard Mn(II)-Sulphat von bekannter Molarität verwendet.

Die mit dieser Methode erzielten Resultate sind vollkommen reproduzierbar, und stimmen mit dem wirklichen, durch die Procter-Smith Methode ermittelten, Mangangehalt gut überein. Die Resultate einiger Analysen sind in Tabelle IV angegeben.

TABELLE IV

RESULTATE DER ANALYSEN VON PRAKTISCHEN PROBEN

Probenbezeichnung	Wirklicher Gehalt (%)	Gefunden (%)			Relativer Fehler (%)
		I	II	III	
Mn-Erz	2.30	2.23	2.25	2.35	2.6
Siderit I	2.17	2.06	2.11	2.11	3.6
Siderit II	1.83	1.75	1.78	1.78	2.6

DISKUSSION DER RESULTATE

Aus den durchgeführten Experimenten geht hervor, dass im Medium von Bis-(2-hydroxypropyl)-2-hydroxyäthylamin (A_2) und Bis-(2-hydroxybutyl)-2-hydroxyäthylamin (A_3) drei- und zweiwertiges Mangan in Gegenwart von alkalischem Hydroxyd Komplexe bildet, die sich in der Quecksilbertropfelektrode als reversible Redox-Systeme verhalten (im Konzentrationsbereich 0.05 bis 1 M A_2 oder A_3 und 0.5 M NaOH, eventuell 0.01 bis 1 M NaOH und 0.5 M A_2 oder A_3 bei Mangankonzentrationen der Lösung bis 10^{-2} M). Die Reversibilität des Redox-systems wurde durch logarithmische Analyse der polarographischen Kurven bestätigt, die der Reduktion oder Oxydation der Mangankomplexe entsprechen. Die graphische Darstellung der Abhängigkeit des $\log(i_d - i)/i$ vom Potential ist eine Gerade mit einer Neigung von etwa 58 mV (Abb. 8). Die Halbwellenpotentiale der anodischen und kathodischen Welle sind unter denselben Bedingungen identisch (für 0.5 M A_3 und 0.5 M NaOH ist $E_{1/2} = -0.535$ V). Ein weiterer Beweis für die Reversibilität wurde durch die Übereinstimmung der Depolarisationspotentiale der Einschnitte bei der polarographischen Verfolgung der Kurven $f(V) = dV/dt$ geliefert (Abb. 2).

Ähnliche Komplexe des zwei- und dreiwertigen Eisens mit den entsprechenden Aminoalkoholen in Gegenwart von alkalischem Hydroxyd bilden ein reversibles Redox-System (0.01 bis 1 M A_2 oder A_3 bei Eisenkonzentrationen in der Lösung bis 10^{-2} M), was durch Identität der Halbwellenpotentiale (für 0.5 M A_3 und 0.5 M NaOH

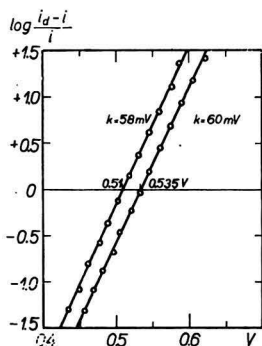


Abb. 8. Logarithmische Analyse der Kurven: links, 0.5 M A_2 , 0.5 M NaOH, 10^{-3} M Mn^{2+} oder Mn^{3+} ; rechts, 0.5 M A_3 , 0.5 M NaOH, 10^{-3} M Mn^{2+} oder Mn^{3+} .

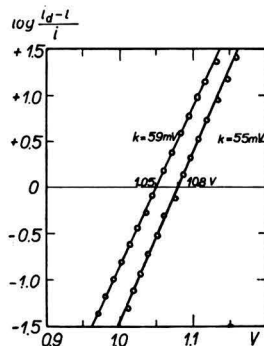


Abb. 9. Logarithmische Analyse der Kurven: links, 0.5 M A_2 , 0.5 M NaOH, 10^{-3} M Fe^{2+} oder Fe^{3+} ; rechts, 0.5 M A_3 , 0.5 M NaOH, 10^{-3} M Fe^{2+} oder Fe^{3+} .

ist $E_{1/2} = -1.08$ V), logarithmische Analyse beider Kurven (Abb. 9) und oszillopolarographisches Studium (Abb. 2) bestätigt wurde.

Analogische Komplexe wie die untersuchten Aminoalkohole bildet auch Triäthanolamin (weiter TEA). Ihr polarographisches Verhalten hat JESSOR³ untersucht, und MOJŽIŠ⁴ hat in diesem Medium in Gegenwart von alkalischem Hydroxyd eine Bestimmung von Mangan und Eisen ausgearbeitet. Die Bildung von ähnlichen Komplexen ist hier durch die Ähnlichkeit der Molekülstruktur von TEA und den untersuchten Aminoalkoholen A₂ und A₃ bedingt. In allen diesen Medien werden in Gegenwart von alkalischem Hydroxyd smaragdgrüne Komplexe des dreiwertigen Mangans gebildet, während dem 1-Aminopropanol-3 mit Mangan kein Komplex bildet. Es ist also wahrscheinlich, dass die Struktur des tertiären Amins, das an allen drei Kohlenstoffatomen in der β -Lage gebundene Hydroxygruppen enthält, für die Bildung der genannten Mn(III)-Komplexe spezifisch ist.

Der Fe(III)-TEA Komplex wurde eingehend von ŘÍHA *et al.*^{5,6} beschrieben. Die Struktur der Komplexe der untersuchten Aminoalkohole mit dreiwertigem Eisen wird wahrscheinlich ganz analogisch sein.

CHABEREK *et al.*⁷ die die komplexbildenden Eigenschaften der β -Hydroxyäthyliminodiessigsäure und des β , β' -Dihydroxyäthylenglycins verfolgten sind der Meinung, dass die Ionisation der Gruppe $-\text{CH}_2-\text{CH}_2-\text{OH}$ nur in alkalischem Medium vorkommt, in Gegenwart einiger Ionen von Schwermetallen, insbesondere Fe³⁺, für die diese Gruppe spezifisch ist. Triäthanolamin, sowie die untersuchten Aminoalkohole enthalten die Gruppe $-\text{CH}_2-\text{CH}_2-\text{OH}$, und bilden deshalb, in Einklang mit CHABEREK's Erkenntnissen, feste Komplexe mit dreiwertigem Eisen.

Die Abhängigkeit der Wellenhöhen und der Halbwellenpotentiale der Komplexe des zwei- und dreiwertigen Mangans mit Triäthanolamin von der Konzentration des alkalischen Hydroxyds sowie von der Konzentration des Triäthanolamins ist analogisch der Abhängigkeit bei diesen Komplexen mit A₂ oder A₃. Der Komplex des zweiwertigen Mangans mit TEA ist aber bei niedrigeren Hydroxydkonzentrationen (unter 0.1 M NaOH bei 0.5 M TEA) wahrscheinlich nicht so beständig wie die Komplexe mit A₂ und A₃, wie aus Abb. 10, Kurve 6 ersichtlich ist (die anodische Welle wird herabgesetzt). Im allgemeinen genügt weniger alkalisches Hydroxyd, um Mangan

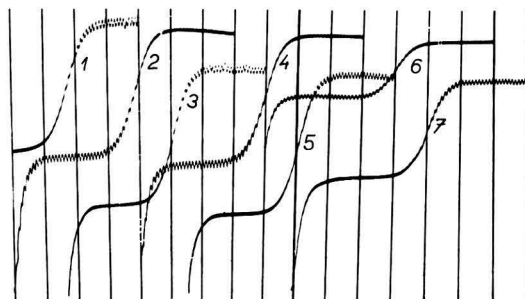


Abb. 10. Anodische und kathodische Wellen der Komplexe von zwei- und dreiwertigem Mangan mit TEA — Abhängigkeit von der NaOH-Konzentration: 0.5 M TEA; $2 \cdot 10^{-3}$ M Mn²⁺; (2) und (3), 1 M NaOH; (4) und (5), 0.5 M NaOH; (6) und (7), 0.1 M NaOH. Kurve (1), $5 \cdot 10^{-4}$ M Tl⁺ in 0.1 M NH₃ und 0.1 M NH₄Cl. Anodische Wellen (2), (4) und (6) in Stickstoffatmosphäre; kathodische Wellen (3), (5) und (7) nach Oxydation mit Luftsauerstoff. Kurven (1), (2), (4), (6) und (7) ab 0 V, (3) und (5) ab -0.1 V. Gesättigte Kalomelektrode, kathodische polarisation, $h = 64$ cm, 100 mV/Absz., Empf. 1/30.

und Eisen in den Lösungen der untersuchten Aminoalkohole zu erhalten, als es in der TEA-Lösung nötig ist. Dies wird vermutlich dadurch verursacht, dass Triäthanolamin-Lösungen selbst weniger alkalisch sind, als ebenso konzentrierte Lösungen von A_2 oder A_3 .

In Tabelle V sind die Halbwellenpotentiale des Fe(III)- und Mn(III)-Komplexes mit 0.5 M TEA, A_2 und A_3 bei 0.5 M NaOH verglichen.

TABELLE V

VERGLEICH DER HALBWELLENPOTENTIALE VON MANGAN- UND EISEN-KOMPLEXEN MIT 0.5 M TEA, A_2 UND A_3 (0.5 M NaOH)

Ion	Halbwellenpotentiale gegen G.K.E., (V)		
	0.5 M TEA	0.5 M A_2	0.5 M A_3
$Mn^{3+} \rightleftharpoons Mn^{2+}$	-0.49	-0.51	-0.53s
$Fe^{3+} \rightleftharpoons Fe^{2+}$	-1.01	-1.05	-1.08

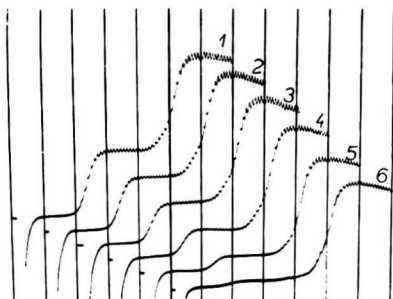


Abb. 11. Einfluss der Manganmenge (und dadurch auch der Menge des entstandenen H_2O_2) auf die Höhe der Eisenwelle in 0.5 M A_3 und 0.5 M NaOH: 0.5 M A_3 ; 0.5 M NaOH; 10^{-3} M Fe^{3+} ; Mn^{2+} wurde in der Lösung mit Luftsauerstoff zu Mn^{3+} oxydiert; (1), 10^{-3} M Mn^{2+} ; (2), $8 \cdot 10^{-4}$ M Mn^{2+} ; (3), $6 \cdot 10^{-4}$ M Mn^{2+} ; (4), $4 \cdot 10^{-4}$ M Mn^{2+} ; (5), $2 \cdot 10^{-4}$ M Mn^{2+} ; (6), ohne Mangan in der Lösung. Ab 0 V, kathodische Polarisation, $h = 64$ cm, 200 mV/Abz., Empf. 1/30.

Analogisch wie bei den Aminoalkoholen A_2 und A_3 macht sich der Einfluss von Wasserstoffperoxyd auch bei TEA geltend⁵. Bei den Aminoalkoholen A_2 und A_3 ist der Einfluss des Peroxyds viel kleiner als bei TEA, wie aus Abb. 11 zu sehen ist. Die Änderung der Höhe der Eisenwelle bei der höchsten und bei der kleinsten Menge Mangan in der Lösung ist sehr klein.

ZUSAMMENFASSUNG

Es wurde das polarographische Verhalten von Mangan, Eisen und einigen anderen Ionen im Medium von Bis-(2-hydroxypropyl)-2-hydroxyäthylamin, Bis-(2-hydroxybutyl)-2-hydroxyäthylamin und alkalischem Hydroxyd untersucht. Es wurde gefunden, dass Komplexe von zwei- und dreiwertigem Mangan und Eisen sich an der Quecksilbertropfenelektrode unter bestimmten Bedingungen als reversible Redoxsystem verhalten. Das besagte komplexbildende Elektrolyt kann zur polarographischen

Bestimmung von Mangan und Eisen neben einer ganzen Reihe von anderen Ionen verwendet werden. Die Methode wurde an Hand der Analyse von Manganerzen und Siderit überprüft.

SUMMARY

The polarographic behaviour of manganese, iron and several other ions has been investigated in a medium consisting of bis-(2-hydroxypropyl)-2-hydroxyethylamine, bis-(2-hydroxybutyl)-2-hydroxyethylamine and alkaline hydroxide. It was found that complexes of bi- and trivalent manganese and iron behave under certain conditions at the dropping mercury electrode as reversible redox systems. The complex-forming electrolyte mentioned can be used for the polarographic estimation of manganese and iron in addition to a whole series of other ions. The method is tested by the analysis of manganese ore and siderite.

LITERATUR

- ¹ J. DOLEŽAL, V. PETRUS UND J. ZÝKA, *J. Electroanal. Chem.*, 3 (1962) 91.
- ² R. PŘIBIL, *Komplexone in der chemischen Analyse*, NCSAV, Praha, 1957, S. 271.
- ³ G. JESSOP, *Nature*, 158 (1946) 59.
- ⁴ J. MOJŽIŠ, *Vortragssammlung des I. internationalen polarographischen Kongresses, Praha 1951*.
- ⁵ J. ŘÍHA, *Kandidatsdissertation*, Praha, 1955.
- ⁶ J. V. A. NOVÁK, J. KŮTA UND J. ŘÍHA, *Chem. Listy*, 47 (1953) 649.
- ⁷ S. CHABEREK, R. C. COURTNEY UND A. E. MARTELL, *J. Am. Chem. Soc.*, 77 (1955) 1477.

J. Electroanal. Chem., 3 (1962) 169–181

CHRONOPOTENTIOMETRY WITH PROGRAMMED CURRENT

II. RESPONSE FUNCTION ADDITIVITY PRINCIPLES APPLIED TO CURRENT PROGRAMMING AND MULTICOMPONENT SYSTEMS

ROYCE W. MURRAY AND CHARLES N. REILLEY

Department of Chemistry, University of North Carolina, Chapel Hill, N.C. (U.S.A.)

(Received August 12th, 1961)

INTRODUCTION

Much progress in the development of chronopotentiometric theory for a variety of fundamental and analytical cases has been seen in the past decade. For diffusion-controlled mass transport, linear diffusion relations for single step¹, step-reverse-step², multi-step³, single square root of time⁴⁻⁶, single ramp^{5,7}, ramp-reverse-ramp⁸, and single general power of time⁹ current impulses have appeared. Spherical and cylindrical relations are available for single step¹⁰⁻¹², single square root of time¹³, step-reverse-step⁸, and multi-step⁸ current impulses. Limited theoretical work has been done in the area of periodic current impulses¹⁴. Because the development of new chronopotentiometric techniques and applications is greatly facilitated by the availability of the proper theoretical relationships, procedures by which these relations may be derived are of no small interest.

An important consideration in the treatment of theoretical chronopotentiometric relations is the presence of discontinuities in the electrode reaction process. These discontinuities may be changes in the species reacting at the electrode (more than one electroactive species present), the addition of new current impulses to the original one(s) at some time, or both. The result is changes at the time of the discontinuity in the equations describing the concentration gradients and surface concentrations of the reacting species. Mathematical complexities are more likely when discontinuities occur, and such cases are of most concern in the present work.

There are three basic approaches to the development of theoretical chronopotentiometric relations for cases in which discontinuities in the electrode reaction process occur:

1. *Step-wise application of initial conditions.* In this approach, at each discontinuity the equations describing the concentration gradients of reacting species at the time of the discontinuity are used as initial conditions in formulating the new relations for the concentration gradients of reactants after the discontinuity. Thus, in a two component system, a discontinuity arises at the first transition time because of the commencement of the reaction of the second component. The concentration gradient of the first component at that time is used as an initial condition to describe the continued influx of the first component, and a separate solution of Fick's second law is effected under this condition to obtain the second transition time. This approach was

first used by BERZINS AND DELAHAY for the two-component case with a step current impulse and for the step-reverse-step impulse case². Because of the generally involved nature of these initial conditions, the mathematical complexity in solving for the new relations becomes excessively large if more than one discontinuity occurs, or if the current impulse employed is not of a simple type.

2. *Zero time shift.* In any chronopotentiometric experiment in which the discontinuity arises from the addition of a new current impulse at time greater than zero, use of the zero shift theorem of the Laplace transform calculus¹⁵ enables a simple mathematical shifting of the relations describing the new current impulse to the time of the discontinuity with little resulting additional complexity in the mathematical derivations. This allows a single derivation to suffice for the obtaining of concentration gradient relations for any time and any current impulse(s). KAMBARA AND TACHI¹⁶ first suggested the use of the zero shift method; it has been employed by KING AND REILLEY¹⁷ in a step-reverse-step case. A general discussion of the use of the zero shift method with applications to a number of new chronopotentiometric cases has been reported⁸.

The zero shift approach may be applied to situations in which the kinetics of chemical reactions must be considered, but yields only the relations for the total transition time when more than one electroactive species is present.

3. *Use of response function additivity principles.* In any situation in which the supply of electroactive species is limited solely by the rate of diffusion, the fact that individual members of the *true current impulse response functions* and the *surface concentration response functions* may be additively combined and their sums equated to each other, may be used to provide an expedient route to chronopotentiometric relations. This new method of derivation may almost be said to be a *non-mathematical* approach, as it does not necessitate the solution of the differential equation given by Fick's law in order to obtain the relation for each new case in which a discontinuity occurs. Thus, in multi-component systems, the surface depletion (or enhancement) of all reactants, properly weighted for differing values of n and D , may be directly added to yield a surface concentration response function that describes the total current-producing flux of reactant in the case of linear diffusion. In programmed current chronopotentiometry, current impulse response functions, resulting from the application of simple current impulses at any time, may be directly added provided the differing times of usage of each current impulse are taken into account.

Equations which contain this principle of response function additivity (although on a limited basis) have been derived for multicomponent systems with single step current impulses¹⁹, for multi-component systems with single power of time current impulses⁹, and for multi-component systems with multi-step impulses³; however, in none of these cases has the basic additivity idea inherent in the derived equations been pointed out.

It is the purpose of the present discussion to describe fully the use of the response function additivity principle in the formulation of theoretical relations for chronopotentiometry. The treatment of multi-component systems with single current impulses will be considered first. Programmed current relations (including the relatively untouched area of periodic current impulses) as applied to single component systems and to multi-component systems will follow. A variety of known chronopotentiometric cases will be reviewed throughout for purposes of illustration.

MULTI-COMPONENT SYSTEMS, SINGLE CURRENT IMPULSES

Consider first a single-component system in which the electrode reaction is



A single current impulse is used:

$$i = \beta i(t) \quad (2)$$

where $i(t)$ denotes the type (step, ramp, etc.) of current impulse and β describes the magnitude of the impulse in amperes cm^{-2} . The current impulse defines the flux of electroactive species at the electrode surface; this condition may be written as

$$\left(\frac{\partial A}{\partial x} \right)_{x=0} = \frac{\beta i(t)}{nFD} \quad (3)$$

The extent of depletion of A at any time, t , and any distance, x , from the electrode, *i.e.* $A^* - A_{(x,t)}$, is a function of n , D , β , $i(t)$, and the geometry of the electrode. The relationship describing the diffusion gradient of A may be obtained by standard mathematical procedures from the solution of the form of Fick's law appropriate to the electrode geometry under the conditions of $A_{(x,0)} = A^*$, $A_{(\infty,t)} = A^*$, and eqn. (3). The resultant solution describing the depletion of the concentration at any point is of the form

$$A^* - A_{(x,t)} = Z(x,t) \quad (4)$$

where $Z(x,t) = f(x, t, n, D, \beta, i(t))$. The mathematical form of $Z(x, t)$, and thus the shape of the diffusion gradient of A , is characteristic of the particular type of current impulse, $i(t)$, used.

For the case of linear diffusion, the surface depletion quantity, $A^* - A_{(0,t)}$, has been found to be inversely proportional to $nFD^{\frac{1}{2}}$ for all types of current impulses which have been studied. These include current impulses which vary with any power of time⁸ and exponentially with time¹⁸. Thus, for linear diffusion eqn. (4) is modified to give

$$nFD^{\frac{1}{2}}[A^* - A_{(0,t)}] = Z(0,t) \quad (5)$$

where $Z(0,t) = f(t, \beta, i(t))$. The quantity $Z(0,t)$ is independent of the diffusion characteristics of A and may thus be termed a true *current impulse response function*, dependent only on the nature of the applied current impulse. The left side of eqn. (5) is similarly called the *surface concentration response function*. The current impulse response functions for a variety of simple current impulses are shown in Table I. At the *transition* time, $A_{(0,t)} = 0$, eqn. (5) yields

$$nFD^{\frac{1}{2}}A^* = Z(\tau) \quad (6)$$

where $Z(\tau) = Z(0,t)$ at $t = \tau$.

Consider now a multi-component system in which the electrode reactions are



TABLE I

Current impulse	Current impulse response function ^{a,b}
<i>Linear Diffusion</i>	
step ($i = \beta_p$)	$\frac{2\beta_p(t-t_p)^{1/2}}{\pi^{1/2}}$
square root of time ($i = \beta_p t^{1/2}$)	$\frac{\beta_p \pi^{1/2}(t-t_p)^{3/2}}{2}$
ramp ($i = \beta_p t$)	$\frac{4\beta_p(t-t_p)^{3/2}}{3\pi^{1/2}}$
squared time ($i = \beta_p t^2$)	$\frac{16\beta_p(t-t_p)^{5/2}}{15\pi^{1/2}}$
general power of time ($i = \beta_p t^r$)	$\frac{\beta_p(t-t_p)^{r+1} \Gamma(r+1)}{\Gamma(r+3/2)}$
<i>Spherical Diffusion</i>	
step ($i = \beta_p$)	$\frac{\beta_p r_0}{D^{1/2}} \left\{ 1 - \exp \left[\frac{D(t-t_p)}{r_0^2} \right] \operatorname{erfc} \left[\frac{D^{1/2}(t-t_p)^{1/2}}{r_0} \right] \right\}$
square root of time ($i = \beta_p t^{1/2}$)	$\frac{\beta_p \pi^{1/2} r_0}{2D} \left\{ \frac{2D^{1/2}(t-t_p)^{1/2}}{\pi^{1/2}} - r_0 + r_0 \exp \left[\frac{D(t-t_p)}{r_0^2} \right] \operatorname{erfc} \left[\frac{D^{1/2}(t-t_p)^{1/2}}{r_0} \right] \right\}$
<i>Cylindrical Diffusion</i>	
step ($i = \beta_p$)	$\frac{2\beta_p(t-t_p)^{1/2}}{\pi^{1/2}} \left[1 - \frac{D^{1/2}(t-t_p)^{1/2}}{4r_0} + \frac{D(t-t_p)}{4r_0^2} - \dots \right]$
square root of time ($i = \beta_p t^{1/2}$)	$\frac{\beta_p \pi^{1/2}(t-t_p)^{3/2}}{2} \left[1 - \frac{2D^{1/2}(t-t_p)^{1/2}}{3\pi^{1/2} r_0} + \frac{3D(t-t_p)}{16r_0^2} - \dots \right]$

^a Response function = $nFD^{1/2}(A^* - A(0,t)) = -nF(D')^{1/2}(B^* - B(0,t))$

^b Time t_p corresponds to the time of application of the current impulse. (Application of the impulse at zero time yields $t_p = 0$).

In this case, the supply of electroactive species to the surface of the electrode is described by the total current-producing flux of reacting species at the surface:

$$\sum_{m=1,2}^j n_m D_m \left(\frac{\partial A_m}{\partial x} \right)_{x=0} = \frac{\beta i(t)}{F} \quad (8)$$

If the species $A_1, A_2 \dots A_j$ are equally electroactive, *i.e.* they react at the same potential, a single transition time is observed and only a measurement of the total concentration of all species present is possible.

The more usual case, however, is that reactions of the various species occur at different electrode potentials. A series of transition times is then expected, and, if the transition time relations are known, the concentration of each of the species may be evaluated. Assuming A_1 to be the most electroactive, and no other species to react before the transition time, τ_1 , of A_1 , the relations above (eqns. (4) (5) and (6)) for a single-component system are valid up to $t = \tau_1$. After the transition time for A_1 , the species A_2 begins to react. The shape of the diffusion gradient for A_2 is not the same as that found for A_1 before τ_1 , as the continued influx of A_1 decreases the efficiency of the current for A_2 and lengthens the time, τ_2 , required for the complete surface depletion of A_2 . Treatment of this case by previous methods would require at this point a new solution of Fick's law.

The diffusion gradient additivity principle of eqn. (8) leads one to the conclusion that this situation may be readily handled by considering the summation of the diffusion gradients of all species so as to yield a total current-producing flux of reactive species. While the external observer notes changes in the electron density of the electrode by measuring its potential, thus deducing what species are reacting at various times, the rate of flow of electrons, or current, is defined from the start of the experiment by the nature of the applied current impulse. Because all species have a common reactant, electrons, a view from the electrode into the surrounding solution would see simply a total requisite influx of electron acceptors (or donors) to support the applied current. The contribution of each reactant to the total current-producing flux is determined by the extent of its depletion from its original concentration ($A_m^* - A_m(x,t)$), its value of n (or effectiveness as an electron acceptor), and its inherent rate of diffusion as given by D_m . The summation of contributions from all species reacting must yield a total flux which is defined by the nature of the current impulse. At the surface, the depletion of any species, A_m , at any time is inversely proportional to $n_m F D_m^{1/2}$, thus the summation of all surface depletions multiplied by this term must be equal to the current impulse response function. The solution to the two-component linear diffusion system above may thus be written immediately as

$$n_1 F D_1^{1/2} \{A_1^* - A_{1(0,t)}\} + n_2 F D_2^{1/2} \{A_2^* - A_{2(0,t)}\} = Z(0,t) \quad (9)$$

This relation applies at any time; before τ_1 , the middle term is zero and the simple case of eqn. (5) results. At the second transition time, the surface concentrations of all species considered have fallen to zero and eqn. (9) becomes

$$n_1 F D_1^{1/2} A_1^* + n_2 F D_2^{1/2} A_2^* = Z(\tau_1 + \tau_2) \quad (10)$$

The quantity on the left is given by eqn. (6) as $Z(\tau_1)$ and substitution yields

$$Z(\tau_1 + \tau_2) - Z(\tau_1) = n_2 F D_2^{1/2} A_2^* \quad (11)$$

which permits a solution for A_2 from measurement of τ_1 and τ_2 .

For the multi-component system containing j species, the surface concentration response functions of all reactants are again summed to yield a total surface concentration response function. The summation for all species is given by a more general form of eqn. (9):

$$\sum_{m=1,2}^j n_m FD_m^{\frac{1}{2}} \{A_m^* - A_{m(0,t)}\} = Z(0,t) \quad (12)$$

The time corresponding to the complete surface depletion of all species is the sum of the transition times for all species. The values of the individual concentrations are obtained through successive substitution of the preceding transition time relations as was done above in eqn. (10). The general relation results:

$$Z \left[\sum_{m=1,2}^j \tau_m \right] - Z \left[\sum_{m=1,2}^{j-1} \tau_m \right] = n_j FD_j^{\frac{1}{2}} A_j^* \quad (13)$$

It is important to note in the response additivity approach that it is only necessary to mathematically obtain the response function, $Z(0,t)$, from a solution of Fick's law for a *single* species. This response function may then be used for any multi-component system without the need for further derivation by simply setting it equal to the sum of the n - and D -weighted surface depletion terms for the species present.

The additivity of surface concentration response functions may be likewise applied to other types of diffusion, such as spherical and cylindrical diffusion. The current impulse response function as defined above for linear diffusion becomes dependent in these cases on the values of r_0 , the spherical or cylindrical radius, and the diffusion coefficient of the reacting species. The current impulse response function is written in these cases as $Z(r_0,t)$; response functions for step and square root of time current impulses are given in Table I. The treatment of these forms of diffusion for multi-component systems and current programming (*vide infra*) is in all respects analogous to that given above for linear diffusion, except that, for multi-component systems, the D -containing term of the current impulse response function is placed as a denominator in the individual surface concentration response functions prior to summation.

The formulation of a number of specific chronopotentiometric cases by means of the response function additivity approach will now be presented. In this section and in the one following on current programming, known cases are reviewed to illustrate the method and a variety of new situations are considered to show the scope of the additivity approach.

Power of time current impulses, linear diffusion

Step current impulses. The response function for a step current impulse, $i(t) = t^0 = \tau$, is given in Table I as $2\beta t^{\frac{1}{2}}/\pi^{\frac{1}{2}}$, where β is the magnitude of the step current impulse in amperes cm^{-2} . For a simple two-component system, A_1 and A_2 , the value of the first transition time (that of the most electroactive species A_1) is not influenced by the presence of A_2 and is given by eqn. (6), where $Z(\tau_1)$ is the above response term:

$$n_1 FD_1^{\frac{1}{2}} A_1^* = \frac{2\beta\tau_1^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \quad (14)$$

The total transition time for the complete surface depletion of both species is obtained

from addition of the surface concentration response functions and is

$$n_1 FD_1^{\frac{1}{2}} A_1^* + n_2 FD_2^{\frac{1}{2}} A_2^* = \frac{2\beta(\tau_1 + \tau_2)^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \quad (15)$$

By noting the identity of the left-hand term with eqn. (14), substitution and rearrangement yields

$$(\tau_1 + \tau_2)^{\frac{1}{2}} - (\tau_1)^{\frac{1}{2}} = \frac{n_2 FD_2^{\frac{1}{2}} \pi^{\frac{1}{2}} A_2^*}{2\beta} \quad (16)$$

which is identical to the relation derived by BERZINS AND DELAHAY² for this case using the step-wise application of initial conditions approach.

If j components are present, extension of the above procedure using eqn. (13) written for a step current impulse yields a relation from which the concentration of the j -th species may be obtained:

$$\left[\sum_{m=1,2}^j \tau_m \right]^{\frac{1}{2}} - \left[\sum_{m=1,2}^{j-1} \tau_m \right]^{\frac{1}{2}} = \frac{n_j FD_j^{\frac{1}{2}} \pi^{\frac{1}{2}} A_j^*}{2\beta} \quad (17)$$

This general relation for multi-component systems was originally derived using the surface concentration response function additivity approach¹⁹ and was later verified by a mathematical treatment¹⁶.

Ramp current impulses. From Table I, the response function for a ramp current impulse, $i = \beta t$, is $4\beta t^{\frac{3}{2}}/3\pi^{\frac{1}{2}}$. For a j -component system, eqn. (13) written for this response function yields

$$\left[\sum_{m=1,2}^j \tau_m \right]^{\frac{3}{2}} - \left[\sum_{m=1,2}^{j-1} \tau_m \right]^{\frac{3}{2}} = \frac{3n_j FD_j^{\frac{1}{2}} \pi^{\frac{1}{2}} A_j^*}{4\beta} \quad (18)$$

This equation was originally derived by a mathematical approach for two components⁷ and was later given in the general form⁹ using the diffusion gradient additivity of eqn. (8).

General power of time current impulses. For current impulses which may vary with any power of time, $i = \beta t^r$, a general response function is available and is given in Table I as $\beta \Gamma(r+1) t^{r+\frac{1}{2}} / \Gamma(r+3/2)$, where Γ denotes the Gamma Function. Equation (13) yields for this case, after substitution and rearrangement,

$$\left[\sum_{m=1,2}^j \tau_m \right]^{r+\frac{1}{2}} - \left[\sum_{m=1,2}^{j-1} \tau_m \right]^{r+\frac{1}{2}} = \frac{n_j FD_j^{\frac{1}{2}} A_j^* \Gamma(r+3/2)}{\beta \Gamma(r+1)} \quad (19)$$

This general relation, of which eqns. (17) and (18) are special cases, was originally derived using the diffusion gradient additivity approach⁹.

Step-wise reaction of a single component. The successive reaction of a single component to yield several transition times corresponding to the formation of various stable oxidation states may be considered as a special case of a multi-component system. The electrode reaction for a simple two-step case may be denoted as



Before the first transition time, n_1 electrons are consumed per A_1 and the expression for τ_1 is given by eqn. (14). After τ_1 , n_2 electrons are used in the reaction of the intermediate product A_2 , and $n_1 + n_2$ electrons are required for the reaction of A_1 (either directly or through A_2) as it continues to diffuse to the electrode. To obtain the value

of τ_2 , the response functions of A_1 and A_2 are added to yield a total response function of reacting species. This yields, in the case of a step current impulse, the surface concentrations

$$(n_1 + n_2)FD_1^{\ddagger}[A_1^* - A_{1(0,t)}] + n_2FD_2^{\ddagger}[-A_{2(0,t)}] = \frac{2\beta t^{\ddagger}}{\tau^{\ddagger}} \tag{21}$$

Noting that at $t = \tau_1 + \tau_2$ the values of $A_{1(0,t)}$ and $A_{2(0,t)}$ are both zero, an appropriate substitution of eqn. (14) yields after cancellation of $2\beta/\tau^{\ddagger}$:

$$\tau_1 \left(\frac{n_1 + n_2}{n_1} \right)^2 - \tau_1 = \tau_2 \tag{22}$$

This relation, although arranged in a different form, is identical to that derived by BERZINS AND DELAHAY² by a step-wise application of initial conditions method. Values of $\tau_2/\tau_1 = 3.0, 8.0,$ and $5/4$ are obtained for the cases $n_1 = n_2, n_1 = \frac{1}{2}n_2, n_1 = 2n_2,$ respectively.

For a ramp current impulse, eqn. (21) is rewritten for the ramp response function (see Table I) and yields for $t > \tau_1$:

$$(n_1 + n_2)FD_1^{\ddagger}[A_1^* - A_{1(0,t)}] + n_2FD_2^{\ddagger}[-A_{2(0,t)}] = \frac{4\beta t^{\ddagger}}{3\tau^{\ddagger}} \tag{23}$$

At $t = \tau_1 + \tau_2$, after appropriate substitution of the transition time relation for τ_1 one obtains

$$\tau_1 \left(\frac{n_1 + n_2}{n_1} \right)^{\ddagger} - \tau_1 = \tau_2 \tag{24}$$

Values of $\tau_2/\tau_1 = 0.587, 1.080,$ and 0.310 for $n_1 = n_2, n_1 = \frac{1}{2}n_2,$ and $n_1 = 2n_2,$ respectively, may be calculated from eqn. (24); the shortening of the second transition time is typical of the higher power of time impulses such as the ramp impulse.

A general expression for power of time current impulses ($i = \beta t^r$) may be formulated in a manner analogous to that shown above to yield a general relation between τ_1 and τ_2 :

$$\tau_1 \left(\frac{n_1 + n_2}{n_1} \right)^{\frac{2}{2r+1}} - \tau_1 = \tau_2 \tag{25}$$

Equations (22) and (24) are special cases of $r = 0$ and $r = 1$ in this relation. Equation (25) written for a current impulse varying with the square root of time ($i = \beta t^{\ddagger}$) yields the result $\tau_2/\tau_1 = n_2/n_1$, which is in agreement with a previous mathematical treatment of this case²⁰. It is interesting that in no case of a power of time current impulse is the ratio of transition times dependent on the magnitude of the current impulse or the diffusion coefficients.

Step and square root of time current impulses, cylindrical diffusion

As was pointed out above, the surface concentration response function additivity principle may be applied to cylindrical and spherical diffusion as well as linear diffusion. Using the appropriate cylindrical response function, $Z(r_0,t)$, from Table I, summation of true response functions to yield a total transition time relation gives for the step current impulse case

$$\left[\sum_{m=1,2}^j \tau_m \right]^{\ddagger} = \sum_{m=1,2}^j \frac{n_m FD_m^{\ddagger} \pi^{\ddagger} A_m^*}{2\beta} \left[1 - \frac{D_m^{\ddagger} \pi^{\ddagger}}{4r_0} \left(\sum \tau_m \right)^{\ddagger} + \frac{D_m}{4r_0^2} \left(\sum \tau_m \right) - \dots \right]^{-1} \tag{26}$$

and for the square root of time current impulse case

$$\sum_{m=1,2}^j \tau_m = \sum_{m=1,2}^j \frac{2n_m F D_m^{\frac{1}{2}} A_m^*}{\beta \pi^{\frac{1}{2}}} \left[1 - \frac{2D_m^{\frac{1}{2}}}{3\pi^{\frac{1}{2}} r_0} \left(\sum \tau_m \right)^{\frac{1}{2}} + \frac{3D_m}{16r_0^2} \left(\sum \tau_m \right) - \dots \right]^{-1} \quad (27)$$

where the $\sum \tau_m$ terms in the series are always the complete (through j) transition time summations and for simplicity only three terms of the series are given. It is not possible to obtain an explicit solution for the transition time summation as was the case for linear diffusion and a convenient expression for A_j^* (such as eqn. (17)) cannot be written. Equation (26) agrees with a reported relation for step current impulses²¹; eqn. (27) has not previously appeared. At small $\sum \tau_m$ and large r_0 , the effects of cylindricality become negligible and eqns. (26) and (27) reduce to their linear diffusion counterparts.

Step and square root of time current impulses, spherical diffusion

The response functions for step and square root of time current impulses are given in Table I for spherical diffusion. Addition of the true response functions to yield a total transition time for a j -component system gives for a step current impulse

$$i = \sum_{m=1,2}^j \frac{n_m F D_m A_m^*}{\beta r_0} \left\{ 1 - \exp \left[\frac{D_m}{r_0^2} \left(\sum \tau_m \right) \right] \operatorname{erfc} \left[\frac{D_m^{\frac{1}{2}}}{r_0} \left(\sum \tau_m \right)^{\frac{1}{2}} \right] \right\}^{-1} \quad (28)$$

and for a square root of time current impulse

$$i = \sum_{m=1,2}^j \frac{2n_m F D_m^{\frac{1}{2}} A_m^*}{\beta r_0 \pi^{\frac{1}{2}}} \left\{ \frac{2D_m^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \left(\sum \tau_m \right)^{\frac{1}{2}} - r_0 + r_0 \exp \left[\frac{D_m}{r_0^2} \left(\sum \tau_m \right) \right] \operatorname{erfc} \left[\frac{D_m^{\frac{1}{2}}}{r_0} \left(\sum \tau_m \right)^{\frac{1}{2}} \right] \right\}^{-1} \quad (29)$$

where the $\sum \tau_m$ terms are always the complete (through j) transition time summations. It is not possible to secure an explicit solution for the transition time summation and a convenient expression for A_j^* cannot be given. At large values of r_0 and small $\sum \tau_m$, the exponential-erfc term of eqns. (28) and (29) reduces to $1 - 2D_m^{\frac{1}{2}}(\sum \tau_m)^{\frac{1}{2}}/\pi^{\frac{1}{2}}r_0$ and these equations then yield their respective linear diffusion counterparts. It is of note in the square root of time eqns. (27) and (29) that the individual transition times are not directly proportional to bulk concentration as is the case in linear diffusion multi-component systems²⁰.

CURRENT PROGRAMMING, SINGLE COMPONENT SYSTEMS

In programmed current chronopotentiometry, discontinuities occur in the electrode reaction process through the addition of new current impulses to the original one at some time(s) during the chronopotentiometric experiment. The new impulse(s) may or may not differ in type from the original one; the resulting impulse after the discontinuity may thus be a composite impulse or an impulse of the same type but changed in magnitude. The collection of impulses used in a given case is termed the *current program*. For a series of impulses applied to a single component system, A , the current program defines the surface gradient of species A by the relations

$$\begin{aligned} \left(\frac{\partial A}{\partial x} \right)_{x=0} &= \frac{\beta_0 i(t)_0}{nFD} & 0 < t < t_1 \\ \left(\frac{\partial A}{\partial x} \right)_{x=0} &= \frac{\beta_0 i(t)_0}{nFD} + \frac{i}{nFD} \sum_{p=1,2}^{q-1} \beta_p i(t)_p & t_p < t < t_{p+1} \end{aligned} \quad (30)$$

where $\beta_0 i(t)_0$ is the original current impulse and the times t_p are greater than zero and (if more than one impulse is applied at one time) are permitted to be equal. Assume for the present that the sum of all the current impulses is of the same sign as the original impulse, *i.e.* the total current produces at all times the forward electrode reaction of eqn. (1). It is implied in the statement of the above current program that the transition time for A occurs at some time after the last impulse included in the program, $\beta_{q-1} i(t)_{q-1}$.

Consider now the current program consisting of the impulses $\beta_0 i(t)_0$, $\beta_1 i(t)_1$, and $\beta_2 i(t)_2$ applied at $t = 0$, t_1 , and t_2 with current impulse response functions $Z_0(0, t)$, $Z_1(0, t)$, and $Z_2(0, t)$, respectively. A change in the equations describing the concentration gradient and surface depletion of reactant will occur at times t_1 and t_2 . The new relations may be readily obtained by utilizing the response function additivity principle, according to which the time terms in the individual response functions are written so as to correspond to the time of usage of the respective impulses and are then summed to yield an overall response function. This conclusion may be arrived at by several lines of reasoning; the following is one: Divide the bulk concentration of reactant, A^* , into three concentration levels, $(A^*)_0$, $(A^*)_1$, and $(A^*)_2$, as shown in Fig. 1. Apply the *separate* impulses $\beta_0 i(t)_0$, $\beta_1 i(t)_1$, and $\beta_2 i(t)_2$ to the correspondingly numbered concentration levels for times t , $t - t_1$ and $t - t_2$, respectively. The diffu-

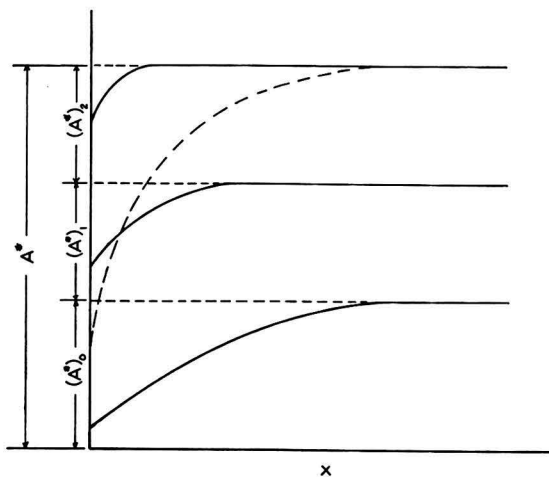


Fig. 1.

sion gradients drawn in Fig. 1 typify the results of these experiments at time t . Note that the times of usage of each of these impulses are the same as in the above current program. In the arbitrary division of the total concentration into the three levels, the relative values of these levels are selected so that the operation of the three separate impulses for times t , $t - t_1$, and $t - t_2$, respectively, brings about a complete surface depletion of species A in all three solutions simultaneously at time τ . If now the diffusion gradients of all three solutions are added together at any time prior to the

common transition time, a total gradient is obtained which is the gradient corresponding to the application of the entire current program to a single solution of concentration A^* . This gradient is shown in Fig. 1 by the dotted line. One may therefore immediately write the following relation:

$$nFD^{\dagger}[(A^*)_0 - (A_{(0,t)})_0] + nFD^{\dagger}[(A^*)_1 - (A_{(0,t-t_1)})_1] + nFD^{\dagger}[(A^*)_2 - (A_{(0,t-t_2)})_2] = \\ nFD^{\dagger}[A^* - A_{(0,t)}] = \sum_{p=0,1}^{q-1} Z_p(0,t-t_p) \quad (31)$$

where $t_0 = 0$ and the summation for this example is over $q - 1 = 2$. This shows that the surface concentration response function may be set equal to the summation of the response functions of the individual current impulses written for the time of usage in each case. At the transition time the above program yields

$$nFD^{\dagger}A^* = Z_0(\tau) + Z_1(\tau - t_1) + Z_2(\tau - t_2) \quad (32)$$

If any larger number of impulses are used in the current program, the general expression for the transition time may be written in an analogous fashion as

$$nFD^{\dagger}A^* = \sum_{p=0,1}^{q-1} Z_p(\tau - t_p) \quad (33)$$

where t_0 is presumed to be zero time and the current impulse $\beta_{q-1}i(t)_{q-1}$ corresponds to the last impulse applied before the transition time. Use of eqn. (33) allows immediate evaluation of the transition time relation for any current program provided the response functions for the current impulses employed in the program are known.

A frequent occurrence in programmed current chronopotentiometry is a change in the sign of the total current impulse at some time during the experiment. A reverse transition time is observed in such a case provided the electrode reaction is reversible and the current impulse proceeds in the backward direction for a time sufficient to bring about complete depletion of the surface concentration of the product, B . Response function additivity may be utilized to evaluate this reverse transition time. The current impulse response function describing the surface concentration response of product B when the forward reaction is proceeding is identical to that for the reactant A , but is of opposite sign. The basic relation for linear diffusion for a single current impulse is then

$$nF(D')^{\dagger}[B^* - B_{(0,t)}] = -Z(0,t) \quad (34)$$

where B^* is the initial concentration of product, n is the number of electrons, D' is the diffusion coefficient, and the response function $Z(0,t)$ is the same as that of eqn. (5). For a current impulse program, diffusion gradients of B resulting from both forward and backward impulses may be added in a manner analogous to that above to yield a total diffusion gradient of B . This results in the general relation for product B , analogous to eqn. (31),

$$nF(D')^{\dagger}[B^* - B_{(0,t)}] = - \sum_{p=0,1}^{q-1} Z_p(0,t-t_p) \quad (35)$$

If the sum of the forward and backward (negative) current impulses becomes negative, the net electrode reaction is reversed. The current impulse response function summation of eqn. (35) is then positive and the value of $B_{(0,t)}$ commences to decrease, resulting in a transition time for B if the summation becomes sufficiently positive. The

relations describing the reverse transition time may then be immediately evaluated from eqn. (35), provided n does not change upon current reversal.

Thus, by using current impulse response function additivity principles, it is possible to provide forward and backward transition time relations for programmed current chronopotentiometry without the necessity for a mathematical derivation from Fick's law if the response functions corresponding to the current impulses used are known. The response functions are simply added together, using a time term appropriate to the time of use of the corresponding current impulse, to give the desired relations.

Step current impulses without reversal

If a step current impulse of magnitude β_0 is applied to a planar electrode in a single component system, A , at time zero and another step impulse, β_1 , is added to this at time t_1 , the surface depletion of A at time greater than t_1 is given by the sum of the step current response functions written for the two times of application, or

$$nFD^{\frac{1}{2}}[A^* - A_{(0,t)}] = \frac{2\beta_0 t^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} + \frac{2\beta_1(t-t_1)^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \quad (36)$$

At the transition time, this relation yields

$$\frac{nFD^{\frac{1}{2}}\pi^{\frac{1}{2}}A^*}{2\beta_0} = \tau^{\frac{1}{2}} + \frac{\beta_1}{\beta_0}(\tau-t_1)^{\frac{1}{2}} = \tau_u^{\frac{1}{2}} \quad (37)$$

The left-hand expression is seen to be equal to the transition time, τ_u , which would have been obtained had the impulse β_1 not been added. Equation (37) is applicable to any pair of step current impulses which do not result in a reversal of the electrode reaction and a reverse transition time.

If a series of $q-1$ step current impulses are used in the current program, a more general form of eqn. (36) results from summing the response functions:

$$\frac{nFD^{\frac{1}{2}}\pi^{\frac{1}{2}}}{2}[A^* - A_{(0,t)}] = \sum_{p=0,1}^{q-1} \beta_p(t-t_p)^{\frac{1}{2}} \quad (38)$$

where $t_0 = 0$. Equations (36), (37), and (38) have been previously derived and experimentally verified³.

If the diffusion geometry is cylindrical, a relation for a multi-step current impulse program may be given using the response function of Table I:

$$\frac{nFD^{\frac{1}{2}}\pi^{\frac{1}{2}}}{2}[A^* - A_{(r_0,t)}] = \sum_{p=0,1}^{q-1} \beta_p(t-t_p)^{\frac{1}{2}} \left[1 - \frac{D^{\frac{1}{2}}\pi^{\frac{1}{2}}(t-t_p)^{\frac{1}{2}}}{4r_0} + \frac{D(t-t_p)}{4r_0^2} - \dots \right] \quad (39)$$

where $t_0 = 0$. Similarly, the spherical diffusion response function of Table I yields for a multi-step current impulse program:

$$\frac{nFD}{r_0}[A^* - A_{(r_0,t)}] = \sum_{p=0,1}^{q-1} \beta_p \left\{ 1 - \exp \left[\frac{D(t-t_p)}{r_0^2} \right] \operatorname{erfc} \left[\frac{D^{\frac{1}{2}}(t-t_p)^{\frac{1}{2}}}{r_0} \right] \right\} \quad (40)$$

where $t_0 = 0$. Equations (39) and (40) are in agreement with a derivation using the zero shift method⁸.

Step current impulses with reversal

Current programs producing a current reversal necessitate the use of eqn. (35) to

secure the reverse transition time relations. If a step current, β_0 , is reversed by the addition of the negative impulse, β_1 , where $\beta_1 > \beta_0$, an equation analogous to eqn. (36) is obtained by insertion of the step current response function from Table I into eqn. (35):

$$\frac{n F(D')^{\frac{1}{2}} \pi^{\frac{1}{2}}}{2} [B^* - B_{(0,t)}] = -\beta_0 t^{\frac{1}{2}} - \beta_1 (t - t_1)^{\frac{1}{2}} \quad (41)$$

As β_1 is negative and greater than β_0 , the right hand side of eqn. (41) is positive and increasing with time after t_1 . A transition time results when $B_{(0,t)} = 0$ at $t = \tau_r + t_1$. When $B^* = 0$, *i.e.* no product is present initially, the case $\beta_1 = -2\beta_0$ yields a diffusion-coefficient independent ratio $t_1/\tau_r = 3$, which is a well-known result². Selection of $\beta_1 = -1.414\beta_0$ yields a ratio $t_1/\tau_r = 1$.

If product B is initially present, the ratio t_1/τ_r becomes dependent on the value of B^* . For $\beta_1 = -2\beta_0$, eqn. (41) yields at τ_r

$$\frac{n F(D')^{\frac{1}{2}} \pi^{\frac{1}{2}} B^*}{2\beta_0} = 2\tau_r^{\frac{1}{2}} - (\tau_r + t_1)^{\frac{1}{2}} \quad (42)$$

and the ratio t_1/τ_r decreases with increasing B^* . The left-hand side of eqn. (42) is the same relation as that obtained for the application of the single current impulse β_0 in the reverse direction at $t = 0$.

For the spherical and cylindrical diffusion cases, current reversal relations may be readily formulated from the appropriate response functions of Table I. The transition time relations thus derived for $\beta_1 = -2\beta_0$ and $B^* = 0$ are for the cylindrical case when B is soluble in the solution

$$\frac{\tau_r + t_1}{4\tau_r} = \frac{\left[1 - \frac{(D')^{\frac{1}{2}} \pi^{\frac{1}{2}} \tau_r^{\frac{1}{2}}}{4r_0} + \frac{(D')^{\frac{1}{2}} \tau_r}{4r_0^2} - \dots \right]^2}{\left[1 - \frac{(D')^{\frac{1}{2}} \pi^{\frac{1}{2}} (\tau_r + t_1)^{\frac{1}{2}}}{4r_0} + \frac{(D')^{\frac{1}{2}} (\tau_r + t_1)}{4r_0^2} - \dots \right]^2} \quad (43)$$

and for the spherical diffusion case

$$1 + \exp \left[\frac{(D')(\tau_r + t_1)}{r_0^2} \right] \operatorname{erfc} \left[\frac{(D')^{\frac{1}{2}} (\tau_r + t_1)^{\frac{1}{2}}}{r_0} \right] = 2 \exp \left[\frac{(D')\tau_r}{r_0^2} \right] \operatorname{erfc} \left[\frac{(D')^{\frac{1}{2}} \tau_r^{\frac{1}{2}}}{r_0} \right] \quad (44)$$

The ratio t_1/τ_r obtained from both these relations is greater than the value of three predicted for linear diffusion conditions in this case, and is also dependent on the values of D' and r_0 . These relations have also been derived by the zero time shift approach⁸.

Square root of time current impulse programs

The square root of time current impulse has the useful property that the transition time is directly proportional to bulk concentration in single and multi-component systems²⁰. The simplicity of this concentration-transition time relationship carries over into forward current programs utilizing square root of time current impulses. For a current program consisting of an impulse, $\beta t^{\frac{1}{2}}$, applied at $t = 0$ and followed at time t_1 by an identical impulse, the relation for the transition time is:

$$\frac{2nFD^{\frac{1}{2}}A^*}{\beta\pi^{\frac{1}{2}}} = 2\tau + t_1 = \tau_u \quad (45)$$

The left-hand side of this equation is the equation corresponding to the application of

the single impulse βt^{\ddagger} ; a simple relationship between the transition time of that case (τ_u) and the transition time of eqn. (45) is seen to exist.

Composite current reversal programs

Step-reverse-ramp impulse program. This program is produced by a step impulse, β_0 , at $t = 0$, to which a step impulse, $-\beta_0$, and a negative ramp impulse, $\beta_1 t$, are added at time t_1 . Taking the step and ramp response functions from Table I, the surface concentration of B may be written from eqn. (35) as

$$nF(D')^{\ddagger}[-B_{(0,t)}] = -\frac{2\beta_0 t^{\ddagger}}{\pi^{\ddagger}} + \frac{2\beta_0(t-t_1)^{\ddagger}}{\pi^{\ddagger}} - \frac{4\beta_1(t-t_1)^{\ddagger}}{3\pi^{\ddagger}} \tag{46}$$

where $B^* = 0$. The reverse transition time, τ_r , is given at $t = \tau_r + t_1$ as

$$(\tau_r + t_1)^{\ddagger} = \tau_r^{\ddagger} \left(1 - \frac{2\beta_1 \tau_r}{3\beta_0} \right) \tag{47}$$

When $\beta_1 = -\beta_0$, the ratio $t_1/\tau_r = 1.779$.

Step-reverse-square root of time impulse program. This program may be generated by a step impulse, β_0 , at $t = 0$, followed at time t_1 by a step impulse, $-\beta_0$, and a negative square root of time impulse, $\beta_1 t^{\ddagger}$. Summation of the appropriate response functions yields

$$nF(D')^{\ddagger}[-B_{(0,t)}] = -\frac{2\beta_0 t^{\ddagger}}{\pi^{\ddagger}} + \frac{2\beta_0(t-t_1)^{\ddagger}}{\pi^{\ddagger}} - \frac{\beta_1 \pi^{\ddagger}(t-t_1)}{2} \tag{48}$$

and at the transition time

$$(\tau_r + t_1)^{\ddagger} = \tau_r^{\ddagger} \left(1 - \frac{\beta_1 \pi \tau_r^{\ddagger}}{4\beta_0} \right) \tag{49}$$

When $\beta_1 = -\beta_0$, the ratio $t_1/\tau_r = 2.19$.

Step plus negative ramp program. This program is defined as a current obeying the relation, $i = \beta_0 - \beta'_0 t$, and may be produced by a step impulse, β_0 , to which a negative ramp impulse, $\beta'_0 t$, is simultaneously added at time $t = 0$. From the step and ramp response functions from Table I, the surface concentration of B may be written as

$$nF(D')^{\ddagger}[+B_{(0,t)}] = \frac{2\beta_0 t^{\ddagger}}{\pi^{\ddagger}} - \frac{4\beta'_0 t^{\ddagger}}{3\pi^{\ddagger}}$$

where $B^* = 0$. The reverse transition time, τ_r , then occurs when $t = 3\beta_0/2\beta'_0$. The current at this time is $-\frac{1}{2}\beta_0$, i.e. the reverse transition occurs when the current has progressed to a negative value whose magnitude is exactly one half the initial positive current.

Ramp-reverse-ramp impulse program. This program is generated by a ramp impulse, $\beta_0 t$, at $t = 0$, followed at time t_1 by a ramp impulse, $-\beta_0 t$, a step impulse, $-\beta_0 t_1$, and a negative ramp impulse, $\beta_1 t$. The surface concentration of B for this program is

$$nF(D')^{\ddagger}[-B_{(0,t)}] = -\frac{4\beta_0 t^{\ddagger}}{3\pi^{\ddagger}} + \frac{4\beta_0(t-t_1)^{\ddagger}}{3\pi^{\ddagger}} + \frac{2\beta_0 t_1(t-t_1)^{\ddagger}}{\pi^{\ddagger}} - \frac{4\beta_1(t-t_1)^{\ddagger}}{3\pi^{\ddagger}} \tag{50}$$

and the transition time relation is

$$2(\tau_r + t_1)^{\ddagger} = 3t_1 \tau_r^{\ddagger} + 2\tau_r^{\ddagger} - \frac{2\beta_1 \tau_r^{\ddagger}}{\beta_0} \tag{51}$$

When the reverse ramp is the same as the forward ramp, *i.e.* $\beta_1 = -\beta_0$, the ratio $t_1/\tau_r = 1.82$. The above relation for this current program is in agreement with a result derived using the zero shift method⁸.

General relations

A general equation for programmed current chronopotentiometry using any power of time current impulse, $\beta_p t^r$, may be formulated using the general response function of Table I for linear diffusion. For a single species, the summation of general response functions yields the relation

$$nFD^{1/2} [A^* - A_{(0,t)}] = \sum_{p=0,1}^{q-1} \frac{\beta_p (t - t_p)^{r+1} \Gamma(r+1)}{\Gamma(r+3/2)} \quad (52)$$

where $t_0 = 0$. The simplicity of the relation between the power of time, r , in the current impulse and the power to which time appears in the corresponding response function, $r + \frac{1}{2}$, is worthy of mention⁹. Equation (52) may be used for any current program containing power of time impulses which does not result in a reverse transition time. If the current impulse changes sign, a similar equation for B must be used to evaluate the reverse transition time:

$$nF(D')^{1/2} [B^* - B_{(0,t)}] = - \sum_{p=0,1}^{q-1} \frac{\beta_p (t - t_p)^{r+1} \Gamma(r+1)}{\Gamma(r+3/2)} \quad (53)$$

Equations (52) and (53) yield as special cases all previous examples of programmed current chronopotentiometry with single component systems.

Polynomial fitting of continuous current programs

If the current program commencing at zero time is a continuous function (*i.e.* no discontinuities), the current program may usually be quite closely fitted to a polynomial series of the type,

$$i = \beta_0 \pm \beta_1 t \pm \beta_2 t^2 \pm \beta_3 t^3 \pm \dots$$

Hence the response functions for the required powers-of-time, as given in Table I for linear diffusion, may be employed to evaluate the surface concentration changes which result from the applied current program. If the current program happens to represent a simple mathematical function, the function itself may be amenable to expansion as a reasonable power series and this series could then be employed to formulate the response function. For example, if an exponential current program ($i = \beta_0 e^t$) is used, the expansion,

$$i = \beta_0 (1 + t + t^2/2! + t^3/3! + \dots),$$

may be used to permit immediate evaluation of the current impulse response function, which for linear diffusion, would be given by

$$\beta_0 (2t^{1/2}/\pi^{1/2} + 4t^{3/2}/3\pi^{1/2} + 8t^{5/2}/15\pi^{1/2} + \dots)$$

which is

$$\frac{2\beta_0 t^{1/2}}{\pi^{1/2}} + \beta_0 t^{1/2} \sum_{r=1}^{r=\infty} \frac{t^r}{r!} \left(\frac{\Gamma(r+1)}{\Gamma(r+3/2)} \right)$$

Periodic current impulses

A particularly interesting application of the response function additivity principle to the derivation of chronopotentiometric relations is in the area of periodic current impulses. Very little theoretical work has been done in this area, and that has been concerned with sine wave impulses superimposed on step impulses¹⁴ (a.c. chronopotentiometry). The theoretical relations for a variety of periodic current programs may be readily formulated by the additivity method. In doing so, it is advantageous to reduce the periodic impulse to periodic combinations of simple impulses for which the response functions are known. Then the overall periodic response function is expressed as the summation of two or more simple periodic impulse response functions. The periodic current programs treated below are typical examples of interest; it is felt that the ability of the response function additivity approach to handle periodic current programs such as these, poses one of the more promising areas of application of this derivation method.

Staircase current program. This periodic program, consisting of a succession of step impulses of equal magnitude and sign and spaced equally in time, is an extension of the general multi-step impulse eqn. (38). That relation, rewritten for a staircase program, yields the following:

$$nFD^{\frac{1}{2}}[A^* - A_{(0,t)}] = \frac{2\beta}{\pi^{\frac{1}{2}}} \sum_{p=0,1}^N (t - pt_1)^{\frac{1}{2}} \quad t \geq Nt_1 \quad (54)$$

where the height of the steps is β , the duration of each step is t_1 sec, and the staircase starts at $t = 0$ (see Fig. 2). Other staircase programs in which the steps are not all of the same size or are not equally spaced may be treated in an analogous manner.

An intriguing aspect of a periodic program of this type is that a staircase program of the proper dimensions may be used to approximate a ramp current impulse. The

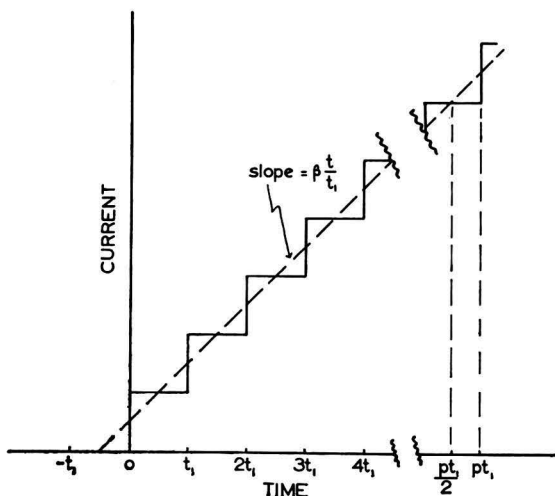


Fig. 2.

staircase eqn. (54) represents an approximation to a ramp impulse which started at time $-\frac{1}{2}t_1$ and which had a current-time proportionality constant of β/t_1 , as shown by the dotted line in Fig. 2. Calculations performed for various times to compare the numerical value of the response function of the ramp impulse (which is in this case $2\beta(t + \frac{1}{2}t_1)^{1/2}/t_1\pi^{1/2}$) with that of the response function of eqn. (54) show that these response functions have very nearly the same values at times $\frac{1}{2}pt_1$; the agreement being better than 1% after a very few steps in the staircase. The values oscillate around one another at times between these values; the size of the oscillations becoming rapidly smaller at larger values of p , as expected. The conclusion may be reached that a staircase of sufficiently short period, *i.e.* short t_1 , yields a reasonably good approximation of a ramp impulse, calculations being readily performed to evaluate the exactness of the approximation.

Square wave current program. This type of periodic program may assume a variety of forms depending on the spacing of the square steps and their relative magnitudes and signs. Square wave programs may be constructed from appropriate combinations of staircase programs, and the form of the square wave response functions will thus

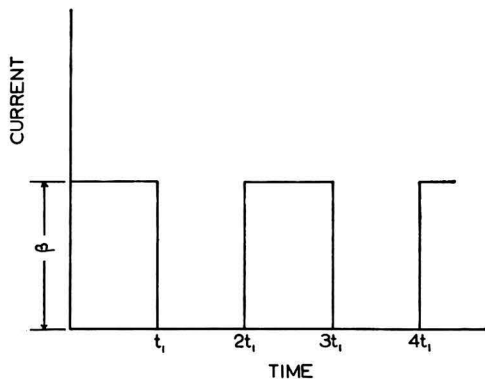


Fig. 3.

resemble that of eqn. (54). A square wave such as that shown in Fig. 3 may be derived from two staircase programs of opposite sign and equal period, $2t_1$, and magnitude, β , one starting at $t = 0$ and the other (negative) starting at $t = t_1$. Combining these periodic impulses in accordance with the response function additivity principle yields the following relation:

$$nFD^{\frac{1}{2}}[A^* - A_{(0,t)}] = \frac{2\beta}{\pi^{\frac{1}{2}}} \left[\sum_{p=0,2,4}^N (t - pt_1)^{\frac{1}{2}} - \sum_{p=1,3,5}^N (t - pt_1)^{\frac{1}{2}} \right] \quad t \geq Nt_1 \quad (55)$$

which is the chronopotentiometric relation for the square wave of Fig. 3. It is noted that at $p = 0$, eqns. (54) and (55) reduce to the familiar Sand eqn. (14). As in the staircase program, square wave programs may be looked upon as approximations to a simpler impulse; in this case a square wave impulse is an approximation to a simple ramp starting at $-t_1/2$ and levelling off at $\beta/2$ at $t = 0$.

It is possible to formulate relations for square wave programs which result in a periodic current reversal. In such cases, if product *B* is initially absent, the negative portions of the square wave must be appropriately adjusted as to spacing and/or magnitude if the occurrence of reverse transition times is undesired.

Sawtooth current program. A regular sawtooth wave of period t_1 may be constructed from a combination of a single ramp impulse starting at $t = 0$ and a negative stair-

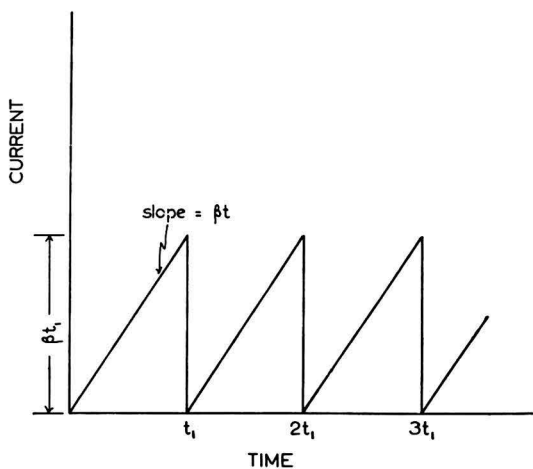


Fig. 4.

case program of appropriate magnitude and of period t_1 starting at $t = t_1$. If the ramp impulse is βt_1 , the negative staircase has a magnitude of βt_1 , resulting in a periodic cancellation of the ramp impulse at times equal to $p t_1$ to yield the sawtooth program. The equation describing this current program, shown in Fig. 4, may be secured from a combination of the ramp and staircase response functions, which yields

$$nFD^{\frac{1}{2}}[A^* - A_{(0,t)}] = \frac{4\beta t_1^{\frac{1}{2}}}{3\pi^{\frac{1}{2}}} - \frac{2\beta t_1}{\pi^{\frac{1}{2}}} \sum_{p=1,2}^N (t - p t_1)^{\frac{1}{2}} \quad t \geq N t_1 \quad (56)$$

Sawtooth waves which have a net change in the magnitude of the “teeth” as a function of time may be obtained by combination of the negative staircase with an appropriate non-linear positive current impulse.

Further analysis and experimental investigation of the nature of periodic current programs such as the above is in progress. Equations (54) (55), and (56) may be obtained by a mathematical derivation using the zero shift method⁸.

PROGRAMMED CURRENT, MULTI-COMPONENT SYSTEMS

The same principles as used above for the cases of multi-component systems with single current impulses and single component systems with programmed current impulses may be applied to a combination of the two situations. The general relations given by eqns. (12) and (52) may thus be combined to yield a general relation applicable to power-of-time impulse programmed current chronopotentiometry with multi-com-

ponent systems. For the forward reaction, the resulting general linear diffusion equation is

$$\sum_{m=1,2}^j n_m F D_m^{\ddagger} [A_m^* - A_{m(0,t)}] = \sum_{p=0,1}^{q-1} \frac{\beta_p (t - t_p)^{r+\ddagger} \Gamma(r+1)}{\Gamma(r+\ddagger/2)} \quad (57)$$

For the backward process, corresponding to a reversal of the current, a general relation may likewise be given for B :

$$\sum_{m=1,2}^j n_m F (D'_m)^{\ddagger} [B_m^* - B_{m(0,t)}] = \sum_{p=0,1}^{q-1} \frac{\beta_p (t - t_p)^{r+\ddagger} \Gamma(r+1)}{\Gamma(r+\ddagger/2)} \quad (58)$$

where $t_0 = 0$. When written for a current program composed of step current impulses only, these equations are in agreement with a previously reported result for step current programmed chronopotentiometry with multi-component systems³.

Eqns. (57) and (58) are very useful in that their generality exceeds that of any previously reported general equation; they include as special cases all chronopotentiometric situations in which linear diffusion is the sole mode of mass transport; this wide scope exists because all types of current programs can be simulated by a suitable combination of power-of-time impulses. The periodic response functions of the cases treated above may be directly substituted for the general response function of eqn. (57) to yield the multi-component relations for these periodic forms of chronopotentiometry. It should be noted that a mathematical derivation by the zero shift method can provide the general response terms of eqns. (57) and (58), but that mode of derivation, unlike the response function additivity method, is not applicable to multi-component systems.

An interesting case of current reversal is that in which a step-reverse-step current program is used and the product of the forward electrode reaction undergoes an immediate decomposition to two electroactive species, B_1 and B_2 . Two transition times are thus observed upon reversing the current. This is in essence a multi-component case and may be treated using the above general eqn. (58). If the current is reversed at time t_1 , the surface concentration of the more electroactive species B_1 is given before the first reverse transition time, τ_{1r} , by the relation

$$n_1 F D_1^{\ddagger} [-B_{1(0,t)}] = -\frac{2\beta_0 t^{\ddagger}}{\pi^{\ddagger}} + \frac{2\beta_0 (t - t_1)^{\ddagger}}{\pi^{\ddagger}} - \frac{2n\beta_1 (t - t_1)^{\ddagger}}{n_1 \pi^{\ddagger}} \quad (59)$$

where n is the number of electrons for the electrode reaction of A , β_0 is the forward step impulse, β_1 is the net backward step impulse, n_1 is the number of electrons for the reaction of B_1 , and $B^* = 0$. The factor n/n_1 arises in the last response function because of the fact that the effectiveness of the current impulse changes by this factor upon reversal of the current; *i.e.* a given quantity of current resulting in the reaction of W units of A during the forward reaction would consume a greater number, nW/n_1 of units of B_1 during the reverse reaction before τ_{1r} . The middle response function arises from the part of the applied backward step impulse (which is $-\beta_0 + \beta_1$) used to cancel out the original impulse, β_0 ; this portion is not used for the net backward process and thus the n/n_1 ratio does not appear in its response function. At the first reverse transition time, τ_{1r} , eqn. (59) gives

$$\frac{t_1}{\tau_{1r}} = \left(1 - \frac{n\beta_1}{n_1\beta_0} \right)^2 - 1 \quad (60)$$

where it should be remembered that β_1 is a negative impulse.

The total reverse transition time, $\tau_{1r} + \tau_{2r}$, may be obtained by summing the response functions of the species B_1 and B_2 ; this gives

$$(n_1 + n_2)FD_1^{\ddagger}[-B_{1(0,t)}] + n_2FD_2^{\ddagger}[-B_{2(0,t)}] = -\frac{2\beta_0 t^{\ddagger}}{\pi^{\ddagger}} + \frac{2\beta_0(t-t_1)^{\ddagger}}{\pi^{\ddagger}} - \frac{2\beta_1 n(t-t_1)^{\ddagger}}{(n_1 + n_2)\pi^{\ddagger}} \quad (61)$$

where again the factor $n/(n_1 + n_2)$ is one which accounts for the changes in the current efficiency during the backward reaction. At the second reverse transition time, $t = \tau_{1r} + \tau_{2r} + t_1$, eqn. (61) yields

$$\frac{t_1}{\tau_{1r} + \tau_{2r}} = \left[1 - \frac{n\beta_1}{(n_1 + n_2)\beta_0} \right]^2 - 1 \quad (62)$$

Eqs. (60) and (62) are the same as has been obtained for this case by a mathematical derivation using the zero shift method¹⁷. If the net reverse step impulse is of the same magnitude as the forward impulse, *i.e.* $\beta_1 = -\beta_0$, the case of $n = 2$, $n_1 = 1$, and $n_2 = 1$ yields the ratios $t_1/\tau_{1r} = 8$, $t_1/(\tau_{1r} + \tau_{2r}) = 3$, and $t_1/\tau_{2r} = 1.667$. It is worthy of note that in any linear diffusion multi-component system in which all products are soluble, for diffusible species a ratio of three is always obtained between the time of reversal and the sum of the forward and backward transition times in a step-reverse-step current program when the sum of the n -values for the forward and backward steps are equal. This is seen to be so in the above relatively complex example and can be shown in a general manner using eqn. (58).

In conclusion, the equations may be presented in a summarized form as

$$\sum_{m,p} \frac{n_m FD_m^{\ddagger} [A_m^* - A_{m(0,t-t_p)}]}{Z_{(0,t-t_p)}} = \sum_{m,p} \frac{n_m FD_m^{\ddagger} [B_{m(0,t-t_p)} - B_m^*]}{Z_{(0,t-t_p)}} = 1 \quad (63)$$

from which all previous relationships may be reached.

ACKNOWLEDGEMENT

This research was supported in part by Advanced Research Projects Agency, Contract No. SD-100.

SUMMARY

The principle of additivity of response functions forms the basis of a new method for derivation of theoretical chronopotentiometric transition time relations for programmed currents and multicomponent systems with diffusion-controlled transport. To use the method it is necessary to have available, for all types of single current impulses used, the characteristic current impulse response functions describing the diffusion gradients and surface depletions for single component systems. These are obtained through solution of Fick's law. Response function additivity is utilized in *multi-component systems* by summing the n - and D -weighted surface depletions of all reactants; the resulting surface concentration response function is then at all times equal to the impulse current response function characteristic of the current impulse used for linear diffusion. In *current programming*, the n and D^{\ddagger} -weighted surface depletion of the electroactive species is, by the response additivity principle for linear diffusion, equal to the summation of the response functions of all current impulses

employed, each current impulse response function being written for the time of usage of the respective current impulse. Solution of Fick's law to obtain the chronopotentiometric transition time relations for such cases is therefore unnecessary. Generalized relations are given for multi-component systems and current programming and for combinations of the two cases. The method of derivation is illustrated using a number of known cases. New equations are derived for the specific cases of (1) single component systems: step-reverse-ramp, step-reverse-square root of time, step-plus-negative ramp and ramp-reverse-ramp current reversal programs, step-wise reactions with any power of time current impulse, square root of time impulse program, staircase, square wave, and sawtooth periodic current programs (linear diffusion), and multi-step and step-reverse-step current programs (spherical and cylindrical diffusion), (2) multi-component systems: step and square root of time current impulses (spherical and cylindrical diffusion).

REFERENCES

- ¹ H. J. S. SAND, *Phil. Mag.*, **1** (1901) 45.
- ² T. BERZINS AND P. DELAHAY, *J. Am. Chem. Soc.*, **75** (1953) 4205.
- ³ A. C. TESTA AND W. H. REINMUTH, *Anal. Chem.*, **33** (1961) 1324.
- ⁴ M. SENDA, *Rev. Polarog. (Japan)*, **4** (1956) 89.
- ⁵ W. H. REINMUTH, *Anal. Chem.*, **32** (1960) 1509.
- ⁶ H. HURWITZ AND L. GIERST, *J. Electroanal. Chem.*, **2** (1961) 128.
- ⁷ R. C. BOWERS, G. WARD, C. M. WILSON AND D. D. DEFORD, *J. Phys. Chem.*, **65** (1961) 672.
- ⁸ R. W. MURRAY, S.E.-S.W. Regional Am. Chem. Soc. Meeting, New Orleans, Dec., 1961.
- ⁹ R. W. MURRAY AND C. N. REILLEY, *J. Electroanal. Chem.*, in press.
- ¹⁰ G. MAMANTOV AND P. DELAHAY, *J. Am. Chem. Soc.*, **76** (1954) 5323.
- ¹¹ A. RIUS, S. POLO, AND J. LLOPIS, *Anales fis. y quim. (Madrid)*, **45** (1949) 1029.
- ¹² D. G. PETERS AND J. J. LINGANE, *J. Electroanal. Chem.*, **2** (1961) 1.
- ¹³ H. HURWITZ, *J. Electroanal. Chem.*, **2** (1961) 142.
- ¹⁴ Y. TAKEMORI, T. KAMBARA, M. SENDA, AND I. TACHI, *J. Phys. Chem.*, **61** (1957) 968.
- ¹⁵ J. C. JAEGER, *Laplace Transformation*, John Wiley and Sons, Inc., New York, 1949, p. 82.
- ¹⁶ T. KAMBARA AND I. TACHI, *J. Phys. Chem.*, **61** (1957) 1405.
- ¹⁷ R. M. KING AND C. N. REILLEY, *J. Electroanal. Chem.*, **1** (1960) 434.
- ¹⁸ R. W. MURRAY, unpublished results.
- ¹⁹ C. N. REILLEY, G. W. EVERETT AND R. H. JOHNS, *Anal. Chem.*, **27** (1955) 483.
- ²⁰ H. HURWITZ, *J. Electroanal. Chem.*, **2** (1961) 328.
- ²¹ D. G. PETERS AND J. J. LINGANE, *J. Electroanal. Chem.*, **2** (1961) 249.

ELECTROPHORESIS OF CASEIN IN A COLUMN STABILISED BY A DENSITY GRADIENT

WILLIAM MANSON

The Hannah Dairy Research Institute, Ayr (Scotland)

(Received July 12th, 1961)

INTRODUCTION

Although electrophoretic examination does not, by itself, yield unequivocal evidence of the homogeneity of a protein, nor consequently of the number of components of a mixture of proteins, it nevertheless has provided means whereby at least a partial fractionation of the casein complex has been achieved. Thus three fractions, designated α -, β -, and γ -casein in order of decreasing mobility, were identified when casein, prepared from cows' milk by precipitation at pH 4.6, was subjected to electrophoresis in phosphate buffer in a Tiselius cell¹. Similar results were later reported by WARNER² with the exception that, in this instance, the evidence for the presence of the γ -fraction was considered to be doubtful, and attributable, in part at least, to an artifact. A fraction having similar electrophoretic properties to γ -casein was however isolated along with the α - and β -components by treatment of crude acid-precipitated casein with urea and ammonium sulphate³. The separation of the casein complex into these three components identifiable by moving boundary electrophoresis, has usually been accomplished on a preparative scale by this urea precipitation method³, and can be considered as preliminary to a complete fractionation. Thus further electrophoretic examination in acid media of the α -component suggested that it was heterogeneous², a finding later confirmed by application of different purification procedures⁴⁻⁷.

While fractionation procedures such as that involving urea, are undoubtedly suitable for large scale preparations, it is possible that preparations on a smaller scale could better be achieved by less time-consuming methods in which the risk of protein denaturation is reduced to a minimum. Such a possibility would appear to be offered by zone electrophoresis in a column stabilised by a density gradient, with the added advantage that the conditions of the original moving boundary electrophoresis upon which the fractionation is based could be matched almost completely. The present report deals with results obtained on applying zonal density gradient electrophoresis to the preliminary fractionation of the casein complex.

EXPERIMENTAL

Preparation of casein solution

The casein used was prepared by acid precipitation following the method of WARNER², from the milk of individual cows. Care was taken to ensure that the cows

selected were free from infection in order to minimise the effect of contamination of the milk by proteolytic enzymes of bacterial origin. The acid-precipitated casein was dissolved by dropwise addition at 4° of 0.1 *N* NaOH, in such a manner that the pH remained between 6.6 and 7.0 throughout. After dilution to a protein concentration of approximately 1% with phosphate buffer of pH 7.05 and ionic strength 0.06, and which had the following composition, 1.20 g $\text{NaH}_2\text{PO}_4 \cdot 2 \text{H}_2\text{O}$, 2.02 g Na_2HPO_4 , and 0.58 g NaCl, per litre, the solution was dialysed exhaustively against the buffer, at 4°. The resulting solution was that employed in the zonal electrophoreses. For moving boundary electrophoreses, a similar phosphate buffer containing 2.92 g NaCl per litre, was used. This had pH 7.05 and ionic strength 0.10.

Zonal electrophoresis

Electrophoresis in a sucrose density gradient was performed using an apparatus constructed to the specification of that described by PARTRIDGE AND ELSDEN⁸, and is illustrated in Fig. 1. The procedure adopted for the preparation of the density gradient, however, differed from that described by them, inasmuch as it was confined to only one limb of the U-tube. This was achieved in the following way.

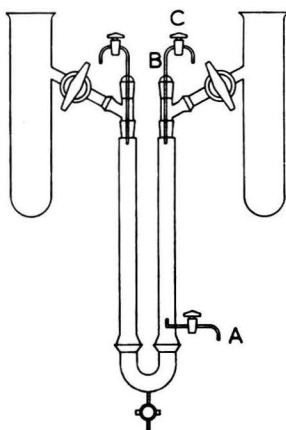


Fig. 1. Apparatus for zonal electrophoresis in a density gradient.

The apparatus was first assembled with its taps, except the two between the electrode vessels and the limbs of the U-tube, closed. The U-tube and electrode vessels were then filled with the buffer described above, so that the liquid level was above the junctions of the U-tube with the electrode vessels. A solution of pure sucrose in phosphate buffer (50 g sucrose/100 ml solution) was run, under a suitable head of liquid, through the tap at the foot of the U-tube thus displacing the lighter buffer solution into the electrode vessels. When the sucrose solution filled the bend of the U-tube and had risen about 1 cm in each of the limbs, the tap connecting the U-tube with the electrode vessel on the left was closed. Thereafter the sucrose solution continued to rise in the right limb only. When it reached the level of the side-arm A, further addition was prevented by closing the inlet tap at the base of the U-tube. At this stage therefore, the dense sucrose solution filled the bend of the U-tube, and

continued up the left limb for approximately 1 cm while in the right limb it reached as far as the side-arm A, approximately 10.5 cm.

The density gradient was now produced in the right limb over the dense sucrose solution, by pumping, through the side-arm A, phosphate buffer containing increasing amounts of sucrose. The increasing concentration of sucrose was obtained by pumping 58% sucrose in phosphate buffer through a closed mixing chamber of 200 ml capacity fitted with a magnetic stirrer, and which initially held 200 ml phosphate buffer containing 7.2 g sucrose. The usual rate of pumping was 100 ml/h, but rates of up to double this were also found to be satisfactory. The metering pump employed was supplied by The Distillers Co., Great Burgh, Epsom, Surrey.

After about 3 h, when the advancing sugar front had reached the lower end of the tube B, mounted concentrically at the top of the right limb of the U-tube, the tap C, attached to it was opened, and that connecting the U-tube with the right electrode vessel was simultaneously closed. As the pumping continued, liquid was displaced from the limb of the U-tube through the tube B, forming a sharp density shelf at the head of the density gradient column. When about 25 ml had been displaced the pumping was stopped, and the tap C closed. In this way a smooth gradient extending over approximately 40 cm was obtained with a change in density per cm of height of approximately 0.005 g/ml, which is almost identical with that used by SVENSSON, HAGDAHL AND LERNER⁹ for electrophoresis of serum proteins. Alternative methods of preparing similar density gradients have been fully discussed by SVENSSON¹⁰.

The protein solution, prepared as already described, was introduced into the column through tube B, by allowing liquid to drip slowly through the tap at the base of the U-tube with the tap C, open. The tip of tube B extended to beneath the surface of the protein sample, and as a result, the protein sample was sucked into the right limb of the U-tube, and deposited on the density shelf. After addition, in a similar manner, of a suitable amount of buffer to rinse tube B, both taps were again closed. Silver-silver chloride electrodes were placed in position, and covered with saturated NaCl solution as described by PARTRIDGE AND ELSDEN⁸, care being taken to place the +ve in the left vessel. Finally the liquid levels in each of the electrode vessels were adjusted to compensate for the differing densities in the U-tube limbs, and the taps connecting the electrode vessels with the U-tube opened cautiously. Only slight movement of the protein layer should take place although gentle movement is not undesirable since it appears to aid diffusion at the boundaries of the layer.

The system was allowed to equilibrate for one hour before electrophoresis was begun. With the buffer previously described the current employed was approximately 20 mA (500 V). This caused no appreciable heating within the tube, even over prolonged periods, but the strong sucrose solution in the bend of the U-tube did become warm. Any effect that this may have had on the electrophoretic separation was however eliminated when water was circulated through plastic tubing wrapped around the right limb from the top to the middle of the U-tube bend, gaps being left opposite the side-arm, and the foot of the outlet tube at the top of the limb.

At the conclusion of the electrophoresis, 3 ml fractions were collected from the side-arm of the right limb, the solution in the column being replaced by buffer from the right electrode vessel. The amount of protein present in each fraction was determined in two ways. Firstly the optical density at 278 m μ was measured. Unfortunately, however, the analytical reagent grade of sucrose used, contained traces of material having

an appreciable light absorption at this wavelength, and consequently increasing background absorption was encountered as the sucrose concentration increased in the column.

A more satisfactory result was obtained when the protein was determined using a variation of the dye-binding method of PLUM, HERMANSEN AND PETERSON¹¹. In this 0.5 ml portions from each fraction were treated with 9 ml of a mixture containing per litre, 37.65 g citric acid monohydrate, 1.14 g Na₂HPO₄, and 0.042 g Naphthalene Black 12B. After mixing, and standing at room temperature for 15 min, the precipitated protein-dye aggregate was removed by centrifugation, and the optical density of the supernatant liquid determined directly in a colorimeter. Using this method no background effect attributable to sucrose was obtained.

Moving boundary electrophoresis

Moving boundary electrophoresis was performed in a Tiselius apparatus equipped with a schlieren optical system, and produced by Hilger and Watts Ltd., London.

RESULTS AND DISCUSSION

When subjected to electrophoresis at pH 7 in a column stabilised by a sucrose density gradient, acid-precipitated casein was split into two main fractions, as illustrated in Fig. 2. The faster moving corresponds to the α : κ -component and the slower to the β -component obtained from the same material on moving boundary electrophoresis, as is also shown in Fig. 2. The results of moving boundary and density gradient elec-

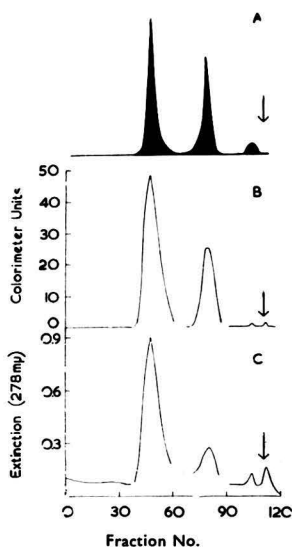


Fig. 2. Electrophoretic patterns of the same sample of acid-precipitated casein, obtained by the density gradient procedure (B,C) and by the moving boundary method (A). In the density gradient separation the protein concentration was determined by optical density (C), and dye-binding capacity (B). Gradient separation: phosphate buffer; pH 7.05 and ionic strength 0.06; 20 mA (500 V) for 65 h. Moving boundary determination: phosphate buffer; pH 7.05 and ionic strength 0.10; 19 mA (250 V) for 2 h. In each case the starting line is indicated by an arrow.

trophoresis were therefore qualitatively similar. The amount of the α : κ -fraction in the moving boundary electropherogram was approximately 1.5 times that of the β -fraction as judged by measurement of the area under each of the curves, a proportion which was apparently much increased when the same technique was applied to the diagram obtained by the optical density measurement of the fractions from zonal electrophoresis. However the analytical data reported for the α - and β -caseins prepared by urea fractionation of acid-precipitated casein¹² indicate that β -casein is relatively deficient in those amino acids showing selective light absorption around 280 m μ . More recently, PAYENS¹³ reported that α -casein free from κ -casein has an extinction coefficient at this wavelength of 1.67 times that of β -casein when measured on an equal weight basis. In these circumstances therefore the amount of the β -fraction obtained on zonal electrophoresis relative to that of the α : κ -fraction will appear small when measured by light absorption at 278 m μ . When however the protein from the same fractionation was determined by its dye-binding capacity, as is also illustrated in Fig. 2, the relative proportion of the two components approached more closely that obtained by moving boundary electrophoresis, on the assumption that the dye-binding capacities of each are approximately equal. On this basis, the faster moving fraction accounted for 67% of the mobile material, and the slower, 33%, compared with 61% and 39% respectively obtained by moving boundary electrophoresis. Before a more accurate estimate of their relative amounts can be made however, a further correction for the dye-binding capacities of the two fractions is probably necessary since SEALS¹⁴ using Orange G and MACRAE AND BAKER¹⁵ applying results obtained from Azocarmine B to Naphthalene Black have reported that β -casein binds less of these acid dyes per mg than does the α : κ -complex.

In addition to the peaks corresponding to the two mobile fractions, the moving boundary electropherogram contained a third peak on, or close to, the origin, amounting to about 5% of the total protein, as judged by measurement of its area. This is in agreement with the original finding of MELLANDER¹ who attributed it to the presence of γ -casein. Density gradient electrophoresis of the same sample of casein however yielded two small fractions situated in the neighbourhood of the origin. These were not artifacts of the system since they were characteristic of samples of acid-precipitated casein being absent when α_s -casein, prepared from skimmed milk by fractionation with CaCl₂, was subjected to identical treatment. In these circumstances no light-absorbing material was detectable near the origin.

The two fractions when determined by area measurement amount to less than 1% of the total protein, substantially less than expected for γ -casein from a comparison of the results from moving boundary electrophoresis. However in having poor dye-binding capacities they behaved similarly to γ -casein which has been reported to bind acid dyes to a considerably lesser extent than either α - or β -casein. Nevertheless after making full allowance for this, the amount of material on or near the origin was very much less than was suggested by the results of moving boundary electrophoresis. Consequently it would appear that only part, at the most, of the origin fraction obtained by moving boundary electrophoresis was attributable to γ -casein, a conclusion fully in agreement with the findings of WARNER². It is of interest that in a recent report on the electrophoresis of acid-precipitated casein in concentrated urea solution on cellulose columns¹³, no evidence of the presence of a γ -casein fraction was obtained, although the presence of α -, β -, and κ -caseins was clearly demonstrated.

From the foregoing it is clear that zone electrophoresis at pH 7 in a density gradient provides results similar to those obtained by moving boundary electrophoresis, at the same pH except in a small area around the origin, likely to be affected in the latter procedure by interference from boundary effects. A preliminary fractionation of the casein complex of the type produced by fractional precipitation with urea, has therefore been achieved on a small scale and under conditions likely to cause a minimum of denaturation. Further fractionation has been found to be possible by application of zonal electrophoresis to certain of the components obtained by CaCl_2 treatment of skimmed milk. In this way, small quantities of α_s - and β -casein each free from κ -casein have been produced.

The amounts of material used in the examples quoted here have been of the order of only 50 mg total protein. However, satisfactory separations have been achieved with between three and four times this amount, providing always that the protein concentration of the solution applied to the column was not substantially greater than 1%. In addition preliminary experiments have indicated that satisfactory separations may be obtained with much larger amounts, added in concentrations of up to 4%, by incorporation of a two-chamber mixing system of the type described by SVENSSON AND VALMET¹⁶, in which the protein is added to the column while the density gradient is being built up.

ACKNOWLEDGEMENTS

The author thanks Dr. S. M. PARTRIDGE and Mr. D. F. ELSDEN of the Low Temperature Research Station, Cambridge, for supplying details of the design and application of their apparatus prior to their publication. The author is indebted also to Dr. G. LEAF, Biochemistry Department, University of Glasgow for his help with the moving boundary electrophoreses, and to Miss H. REID for her technical assistance.

SUMMARY

The application of zonal electrophoresis in a column stabilised by a density gradient to casein is described. In general, the procedure yielded results similar to those obtained by moving boundary electrophoresis, and separated certain of the components of the casein complex in quantities sufficient for further study.

REFERENCES

- 1 O. MELLANDER, *Biochem. Z.*, 300 (1939) 240.
- 2 R. C. WARNER, *J. Am. Chem. Soc.*, 66 (1944) 1725.
- 3 N. J. HIPPEL, M. L. GROVES, J. H. CUSTER AND T. L. McMEEKIN, *J. Dairy Sci.*, 35 (1952) 272.
- 4 D. F. WAUGH AND P. H. VON HIPPEL, *J. Am. Chem. Soc.*, 78 (1956) 4576.
- 5 D. F. WAUGH, *Discussions Faraday Soc.*, 25 (1958) 186.
- 6 J. LONG, Q. VAN WINKLE AND I. A. GOULD, *J. Dairy Sci.*, 41 (1958) 317.
- 7 T. L. McMEEKIN, N. J. HIPPEL AND M. L. GROVES, *Arch. Biochem. Biophys.*, 83 (1959) 35.
- 8 S. M. PARTRIDGE AND D. F. ELSDEN, *Biochem. J.*, 79 (1961) 26.
- 9 H. SVENSSON, L. HAGDAHL AND K-D. LERNER, *Science Tools*, 4 (1957) 1.
- 10 H. SVENSSON, in P. ALEXANDER AND R. J. BLOCK, *A Laboratory Manual of Analytical Methods of Protein Chemistry Including Polypeptides*, Vol. 1, Pergamon Press, London, 1960, p. 193.
- 11 C. L. PLUM, L. HERMANSEN AND I. PETERSEN, *Scand. J. Clin. Lab. Invest.*, 7, suppl. 18 (1954).
- 12 W. G. GORDON, W. F. SEMMETT, R. S. CABLE AND M. MORRIS, *J. Am. Chem. Soc.*, 71 (1949) 3293.
- 13 T. A. J. PAYENS, *Biochim. Biophys. Acta*, 46 (1961) 441.
- 14 R. G. SEALS, *Diss. Abs.*, 20 (1960) 4230.
- 15 H. F. MACRAE AND B. E. BAKER, *J. Dairy Sci.*, 41 (1958) 233.
- 16 H. SVENSSON AND E. VALMET, *Science Tools*, 6 (1959) 13.

THE EFFECT OF CELL RESISTANCE ON
ACUTE POLAROGRAPHIC MAXIMA

I. M. KOLTHOFF, J. C. MARSHALL AND S.L. GUPTA

School of Chemistry, University of Minnesota, Minneapolis 14, Minn. (U.S.A.)

(Received May 2nd, 1961)

INTRODUCTION

In systematic studies of the effect of various factors upon the height of acute polarographic maxima in solutions of high specific resistance, it was noted that the height of such maxima varied with the dimensions of the electrolysis cell and especially with changes in the separation between the dropping mercury electrode (D.M.E.) and the mercury pool reference electrode. It was observed that the effect of increasing the separation between the D.M.E. and the mercury pool electrode was qualitatively equivalent to the introduction of an external resistance into the circuit.

In a private communication Prof. H. A. LAITINEN suggested that the resistance of a polarographic cell consisting of a D.M.E. and a mercury pool reference electrode be considered to be composed of an internal resistance located in the immediate vicinity of the growing drop, designated as R_i , and a constant external resistance residing in the liquid separating the electrodes, designated as R_e . The internal resistance varies during the life of each mercury drop reaching a minimum as the drop falls. The variation of internal resistance with the growth of a mercury drop has been calculated by ILKOVIČ¹. This author idealized the system by considering the electrodes to be concentric spheres of radii r and r' separated from one another by a space filled with an electrolyte of specific resistance ρ . The resistance, R_i , is given by the following expression:

$$R_i = \frac{\rho}{4\pi} \left(\frac{1}{r} - \frac{1}{r'} \right) \quad (1)$$

BRDICKA², who made an extensive study of the effect of external resistance on the height of acute maxima exhibited by weakly acidic mercurous nitrate solutions, pointed out that the effect of r' in eqn. 1 may be neglected when it is greater than 10 r .

Neither ILKOVIČ¹ nor BRDICKA² in their treatments take into account that a fraction of the cell resistance, R_{cell} , acts as an external resistance, R_e . Therefore, eqn. 2 should describe both components of the cell resistance:

$$R_{\text{cell}} = R_i + R_e = \frac{\rho}{4\pi r} + R_e \quad (2)$$

where R_i is the "true" internal resistance and equal to $\rho/4\pi r$. Eqn. 2 predicts that the component which acts as internal resistance in a polarographic circuit depends only on the specific resistance of the solution and the characteristics of the capillary,

and not on conditions of cell geometry. Therefore, any change in total cell resistance arising from changes in cell diameter or electrode separation must be due to changes in the external component, R_e , of the total cell resistance.

According to BRDICKA², the variation of R_t with time (t) during the growth of a drop is given by expression (3):

$$R_t = \frac{qt^{-1/3}}{4\pi\left(\frac{3m/d}{4\pi}\right)^{1/3}} = kt^{-1/3} \quad (3)$$

where m is the mass, in mg/sec, of mercury flowing and d the density of mercury in mg/cm³. This relation is only valid if no polarization occurs. Combination of eqns. 2 and 3 yields the simplified expression:

$$R_{\text{cell}} = R_t + R_e = kt^{-1/3} + R_e \quad (4)$$

According to eqn. 4 a plot of R_{cell} vs. $t^{-1/3}$ during the life of a mercury drop should yield a straight line with a slope of k and intercept R_e . Introducing into eqn. 4 the values of R_e and $kt^{-1/3}$, with t equal to the drop time, yields the minimum cell resistance.

The work presented in this paper is concerned with an experimental determination of the value of k in eqn. 3 and with the validity of the form of eqn. 4.

EXPERIMENTAL

Mercurous nitrate was prepared according to the directions of BLANCHARD³. The final product, a pure white crystalline compound, was stored over anhydrous. Potassium chloride, analytical reagent grade, was twice recrystallized from conductivity water and fused at 800°. Mercury was triply distilled. Nickel perchlorate, copper perchlorate, sodium perchlorate, and potassium nitrate were of C.P. quality and used without further purification.

Air used to saturate solutions for the study of oxygen maxima was pre-treated by passing it through an acidified solution of potassium permanganate and then through water. The water used for the preparation of all solutions was of conductivity grade. All measurements were made at room temperature, $25 \pm 1^\circ$. The measurement of electrode separation was carried out with a cathetometer. The reported values for the rate of flow of mercury, m , were determined under conditions as identical as possible to those used in the determination of $R-t$ curves.

The polarographic cell used in most of the work consisted of a glass tube 2 cm in diameter sealed at the bottom and provided with a "cap" drilled to accommodate the D.M.E. A mercury pool on the bottom of the cell served as a reference electrode in most cases. Electrical contact with the pool electrode was brought about through a platinum wire sealed in the bottom of the cell. Except in experiments with oxygen maxima, solutions were made oxygen-free by purging with Linde nitrogen which had been treated according to the directions of MEITES⁴. A slow stream of nitrogen was directed over the surface of the solution while an experiment was in progress. Cell geometry was changed by surrounding the D.M.E. by a narrow tube of the desired inside diameter which extended into the mercury pool at the bottom of the cell. Occasionally, wider cells of a conventional type were used.

Resistance measurements were made with a Leeds and Northrup Wheatstone Bridge, Model No. 88120, in conjunction with a signal generator operated at 0.5 V and 1000 cycles. An oscilloscope (Tektronic, type 502) with a maximum sensitivity of 200 $\mu\text{V}/\text{cm}$ served as a detector. The variation of resistance of the polarographic cell with time was examined by setting the bridge resistance in the range of cell resistances displayed by the cell during the life of a mercury drop. The elapsed time between the moment the drop fell and the moment bridge balance occurred was timed with a stopwatch. This was repeated at regular increments of bridge resistance throughout the range of resistance exhibited by the cell during the growth of the mercury drop.

Resistance-time measurements were usually made using capillaries of normal diameter (obtained from E. H. Sargent and Co., external diameter about 6 mm); these are denoted as blunt capillaries. In order to study the effect of the size of the diameter of the capillary, capillaries were prepared by drawing out wide bore (original inside diameter of 1 mm) capillary tubing to a very sharp point. Dropping electrodes so prepared had an external diameter at the tip of 0.5 mm or less, and are denoted as sharp capillaries.

All polarograms were run with a Leeds and Northrup Electrochemograph, type E, without damping. The currents plotted in current-potential lines refer to maximum current at the moment the drop falls. The inverse of the slope of lines so plotted was taken to be the minimum cell resistance.

The specific resistances of $1 \cdot 10^{-1}$ and $1 \cdot 10^{-2}$ M potassium chloride solutions were taken from the data of JONES AND BRADSHAW⁵. All other values were measured with a cell of the Washburn type and the above described resistance-measuring apparatus.

RESULTS AND DISCUSSION

The effect of electrode separation on current-potential lines in the electrolysis of $1 \cdot 10^{-3}$ M mercurous nitrate in nitric acid is illustrated in Fig. 1.

In order to obtain large changes in cell resistance with changes in electrode separation a 9 mm tube, extending into the mercury pool, was placed around the D.M.E. The experiments shown in Fig. 1 were repeated by keeping the electrode separation at about 4 cm (corresponding to line 1 in Fig. 1) and inserting ohmic resistance into the external circuit so as to obtain current-potential lines identical with lines 2-7 in Fig. 1.

Current-potential lines in air-saturated solutions that were $1 \cdot 10^{-3}$ to $5 \cdot 10^{-3}$ M in potassium chloride, in oxygen-free copper solutions that were $5 \cdot 10^{-4}$ M in copper perchlorate and $1 \cdot 10^{-3}$ M in potassium nitrate and in oxygen-free nickel solutions that were $1 \cdot 10^{-3}$ M in nickel perchlorate and $1 \cdot 10^{-3}$ M in sodium perchlorate were found to be affected in the same way by changes in electrode separation and external resistance as the current-potential lines shown in Fig. 1. In all instances acute maxima were observed, but the current-potential lines were usually not as straight as those in Fig. 1, indicating partial polarization before the maximum.

As an example of the validity of eqn. 4 the straight line plot of R_{cell} vs. $t^{-1/3}$ determined in 0.1 M potassium chloride is presented in Fig. 2. In order to obtain a relatively large cell resistance, a glass tube 12 mm in diameter and extending into the mercury pool was placed in the polarographic cell.

Similar experiments were carried out in $1 \cdot 10^{-2}$ M potassium chloride, $5 \cdot 10^{-3}$ M

mercurous nitrate that was $1 \cdot 10^{-2} M$ in nitric acid and $1 \cdot 10^{-3} M$ mercurous nitrate that was $2 \cdot 10^{-3} M$ in nitric acid. In all solutions the straight line relation between $t^{-1/3}$ and R_{cell} was found to be obeyed.

According to eqn. 4 the internal resistance, R_t , should depend only on the characteristics of the capillary and the specific resistance of the solution in the cell, but

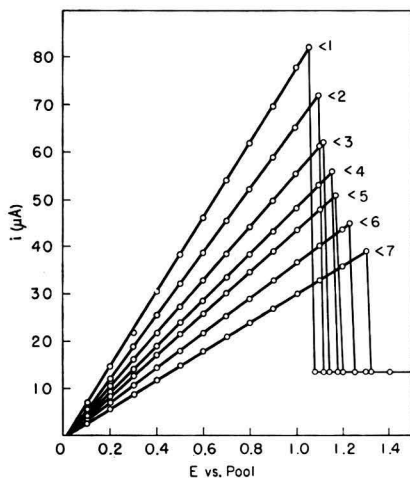


Fig. 1. Current-potential lines in solution $1 \cdot 10^{-3} M$ in $\text{Hg}_2(\text{NO}_3)_2$ and $2 \cdot 0 \cdot 10^{-3} M$ in HNO_3 .
 Electrode separation in cm: 4.0 4.8 5.7 6.5 7.3 8.6 10.5 ;
 R (slope) in ohms: 12,700 15,100 17,800 20,500 22,700 27,100 32,700.

TABLE I

EXPERIMENTS IN 0.1 M POTASSIUM CHLORIDE

Drop time = 9.3 sec; $m = 0.812$ mg/sec; $q = 77.8$ ohm cm; cell diameter 12 mm.

Electrode separation (cm)	Slope R_{cell} vs. $t^{-1/3}$ (ohms sec $^{1/3}$)	$(R_{\text{cell}})_{\text{min}}$ (ohms)	(R_t) (ohms)	$\Delta (R_{\text{cell}})_{\text{min}}$ (ohms)	$\Delta (R_t)$ (ohms)	$(R_t)_{\text{min}}$ (ohms)
0.75	386	241	59	105	102	182
1.91	392	346	161	179	177	185
3.90	392	525	338	152	154	187
6.53	391	677	492	491	500	185
10.19	380	1168	992	403	398	176
14.44	380	1571	1390			181

should be independent of the cell geometry and the distance between the electrodes. Results in Table I show that in a given solution the slope of the R vs. $t^{-1/3}$ plots, and therefore the internal resistance at a given time t remained constant, within experi-

mental error, although the electrode separation was varied from 0.75 to 14.44 cm. Also reported in Table I are values of the minimum cell resistance, $(R_{\text{cell}})_{\text{min}}$, when the drop falls and of the portion of cell resistance which acts as external resistance $(R_e)_{\text{cell}}$. The last column in Table I gives the minimum internal resistance, $(R_i)_{\text{min}}$, being equal to $(R_{\text{cell}})_{\text{min}} - (R_e)_{\text{cell}}$ which is independent of electrode separation. The experiments reported in Table I were repeated in four different solutions with specific resistance varying from 77.8 to 1190 ohm cm. In all instances $(R_i)_{\text{min}}$ was found to vary in proportion to the specific resistance of the solution and to be independent of the geometry of the cell and the separation of the electrodes. Furthermore, according to eqns. 3 and 4 the minimum internal resistance, using the same capillary, in solutions with different specific resistances should be in the same proportion as the specific resistances and independent of the height of the mercury column. This was verified by data obtained in $1 \cdot 10^{-3} M$ mercurous nitrate that was $2 \cdot 10^{-3} M$ in nitric acid where the drop time was 4.0 sec, m , 1.65 mg/sec and $\rho = 1190$ ohm cm; and $5 \cdot 10^{-3} M$ mercurous nitrate which was $1 \cdot 10^{-2} M$ in nitric acid where the drop time was

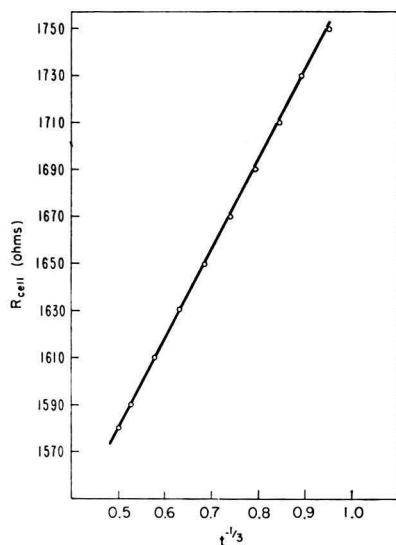


Fig. 2. R_{cell} vs. $t^{-1/3}$ plot in $0.1 M$ KCl. Slope = 380 ohms sec $^{1/3}$; intercept = 1390 ohms.

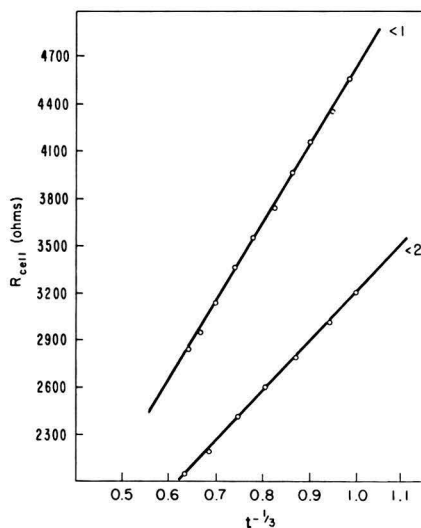


Fig. 3. Effect of diameter of capillary on slope $R_{\text{cell}}-t^{-1/3}$ plots in solution $1 \cdot 10^{-3} M$ in $\text{Hg}_2(\text{NO}_3)$ and $2 \cdot 0 \cdot 10^{-3} M$ in NHO_3 . 1, blunt capillary, drop time = 4.00 sec, $m = 1.65$ mg/sec; 2, sharp capillary, drop time = 4.10 sec; $m = 1.70$ mg/sec.

9.3 sec, m , 0.713 mg/sec and $\rho = 242$ ohm cm. The ratio of the specific resistances of the two solutions, 1190/242, is 4.9 which is in good agreement with the ratio of the respective minimum internal resistances, which was found to be 2820/591 = 4.8.

Eqn. 3 does not consider the effect of the shape and diameter of the glass wall of the dropping electrode. That the diameter of the face of the capillary has an effect

TABLE II
RESULTS OF $R-t$ MEASUREMENTS IN VARIOUS SOLUTIONS
 R determined at 0.5 V, 1000 cycles. Values of m refer to same conditions.

Solution	Cell diameter (mm)	ρ (ohm cm)	Capillary	m (mg/sec)	Drop time (sec)	Slope $R_{\text{cell}} \text{ vs. } t^{-1/2}$ (ohm sec ^{1/2})	Slope calculated (eqn. 3)	Slope calculated (eqn. 5)	$(R_t)_{\text{min}}$
0.1 M KCl	20	77.8	Blunt No. 1	0.812	9.3	382	255	382	183
0.01 M KCl	20	708.9	Blunt No. 1	0.792	9.3	3375	2320	3490	1607
0.005 M Hg ₂ (NO ₃) ₂ 0.01 M HNO ₃	20	242	Blunt No. 2	0.713	9.3	1237	829	1242	589
0.1 M KCl	12	77.8	Blunt No. 1	0.812	9.3	391	255	382	186
0.01 M KCl	12	708.9	Blunt No. 1	0.792	9.3	3378	2320	3490	1580
0.005 M Hg ₂ (NO ₃) ₂ 0.01 M HNO ₃	9	242	Blunt No. 2	0.713	9.3	1247	829	1242	592
0.005 M Hg ₂ (NO ₃) ₂ 0.01 M HNO ₃	20	248	Blunt No. 3	0.557	9.7	1382	921	1380	649
0.005 M Hg ₂ (NO ₃) ₂ 0.01 M HNO ₃	70	248	Blunt No. 3	0.557	9.7	1383	921	1380	650
0.002 M Hg ₂ (NO ₃) ₂ 0.001 M HNO ₃	50	1190	Blunt No. 2	1.65	4.0	4480	3080	4630	2820
0.002 M Hg ₂ (NO ₃) ₂ 0.001 M HNO ₃	50	1190	Sharp	1.70	4.1	3150	3080	—	1970

is illustrated in Fig. 3. With capillaries of about the same characteristics and in the same solution the slope of the $R-t^{-1/3}$ line was found to be considerably less using a sharp capillary with an external diameter of 0.5 mm than with blunt capillaries with diameters of 6 mm. Evidently the value of k is affected by the external diameter of the tip of the capillary.

Slopes of R_{cell} vs. $t^{-1/3}$ lines are reported in Table II in solutions with specific resistance varying from 80 to 1200 ohm cm using both blunt and sharp capillaries. The characteristics of the capillaries measured under experimental conditions are also given in this Table. Because of the shielding effect, the calculated slopes of the lines (eqn. 3) given in column 8 are considerably less than those found with blunt capillaries (column 7). Making an empirical correction by multiplying the k in eqn. 3 by $3/2$ the internal resistance at time t becomes:

$$R_t = 3/2 kt^{-1/3} = \frac{3\varrho}{8\pi \left(\frac{3m/d}{4\pi}\right)^{1/3}} t^{-1/3} = k't^{-1/3} \quad (5)$$

The slopes of resistance-time curves calculated from eqn. 5 were found to be in satisfactory agreement with the experimental slopes, as is evident from comparison of columns 7 and 9 of Table II. The shielding effect of the sharp capillary (last experiment in Table II) is evidently so small that the experimental slope is in satisfactory agreement with that calculated from ILKOVIČ's original equation (eqn. 3).

The variation of the minimum cell resistance with changes in electrode separation was examined for all solutions studied. Plots of the minimum cell resistance vs. electrode separation gave, in all cases, straight lines. The slopes of the plots, when normalized for differences in the specific resistance of the various solutions (*i.e.* $\Delta(R_{\text{cell}})_{\text{min}}/\Delta$ electrode separation ϱ), were found to be constant for a particular cell regardless of the specific resistance of the solution in the cell. This result indicates that $(R_e)_{\text{cell}}$ varies in a linear way with distance in electrode separation. This was verified in plots of $(R_e)_{\text{cell}}$ vs. separation.

After the completion of this work a recent paper in Hungarian by DEVAY⁶ came to our attention. This author considered only $(R_t)_{\text{cell}}$ and not $(R_e)_{\text{cell}}$ and calculated from the dimensions of the capillary the correction to be applied to the k value in the ILKOVIC expression (eqn. 3) to account for the shielding effect of the glass walls of the capillary. Even though he did not consider $(R_e)_{\text{cell}}$ his calculated values of $(R_{\text{cell}})_{\text{min}}$ agreed fairly well with the experimental data. This agreement is accounted for by the small electrode separation throughout his work which minimized the effect of $(R_e)_{\text{cell}}$.

ACKNOWLEDGEMENT

This investigation was supported by a research grant from the National Science Foundation. We are indebted to Prof. LAITINEN for his comments when this work was started.

SUMMARY

In the absence of external resistance in the circuit the resistance of a polarographic cell, $R_{\text{cell}} = R_t + R_e$, in which R_t acts as a true internal resistance in the immediate vicinity of the growing mercury drop and varies with time (t) according to the expression $R_t = kt^{-1/3}$. The component R_e acts as external resistance, is independent of t

and increases with increasing separation between the dropping electrode and the reference electrode. The value of k is smaller than that calculated by ILKOVIC and depends on the diameter of the tip of the capillary. With a capillary with an external diameter of the orifice of 0.5 mm the value of k was in satisfactory agreement with that calculated by ILKOVIC.

REFERENCES

- ¹ D. ILKOVIČ, *Collect. Czechoslov. Chem. Commun.*, 8 (1936) 13.
- ² R. BRDICKA, *Collect. Czechoslov. Chem. Commun.*, 8 (1936) 419.
- ³ A. A. BLANCHARD, J. W. PHELAN AND A. R. DAVIS, *Synthetic Inorganic Chemistry*, John Wiley and Sons, Inc., New York, 1936, p. 232.
- ⁴ L. MEITES, *Polarographic Techniques*, Interscience Publishers, Inc., New York, 1955, p. 34.
- ⁵ G. JONES AND B. C. BRADSHAW, *J. Am. Chem. Soc.*, 55 (1933) 1780.
- ⁶ J. DEVAY, *Magyar Kem. Folyoirat*, 66 (1960) 207.

J. Electroanal. Chem., 3 (1962) 209-216

Short Communications

A.c. polarographic wave — modified equations

Notation

- C_{O^0} — bulk concentration of the oxidant;
 D_O — diffusion coefficient of the oxidant;
 C_{R^0} — bulk concentration of the reductant;
 D_R — diffusion coefficient of the reductant;
 α — transfer coefficient;
 K_s — standard rate constant defined at the standard potential E_0 of the redox system;
 E — steady d.c. potential of the electrolyte referred relative to the standard potential E_0 ;
 E_s — summit potential;
 ΔV — amplitude of the superimposed a.c. ripple;
 Δi — amplitude of the alternating component of the faradaic current;
 $E_{\frac{1}{2}}$ — half-wave potential of the system;
 ψ — nFE/RT ;
 Z — $K_s \sqrt{2/\omega D_R} \left\{ \sqrt{\frac{D_R}{D_O}} + \exp \psi \right\} \exp(-\alpha\psi)$.

The role of a.c. polarography as a powerful technique in the elucidation of the electrode phenomena is well-known¹. It is of interest to evaluate the magnitude of the alternating current and its phase difference (with the superimposed a.c. potential) as functions of the kinetic parameters of the reaction and some other parameters under control (such as the frequency of the a.c. ripple and the base d.c. potential). Several equations have been derived and detailed studies have been made²⁻⁴. Of particular interest is the variation of the summit potential (the d.c. potential at which Δi is maximum for a given ΔV) with the frequency. As some of the equations derived already⁴ (and consequently many conclusions drawn therefrom) are to be modified, a detailed analysis of the expression for the a.c. polarographic wave has been made and only the results are stated below. The details will be published elsewhere.

$$\Delta i = \frac{n^2 F^2}{RT} A K_s \Delta V \sqrt{2} \frac{\left(C_{O^0} + C_{R^0} \sqrt{\frac{D_R}{D_O}} \right) \sqrt{\frac{D_O}{D_R}}}{\left(1 + \sqrt{\frac{D_O}{D_R}} \exp \psi \right)} \times \frac{\exp [(1-\alpha)\psi]}{\sqrt{Z^2 + 2Z + 2}} \quad (nF\Delta V/RT \ll 1)$$

The characteristics of the summit potential are studied and the following observations are made:

- (i) At low frequencies ($K_s \gg \sqrt{2\omega D_i}$), the summit potential *does* coincide with the half-wave potential.
- (ii) At large frequencies ($K_s \ll \sqrt{2\omega D_i}$), the summit potential depends on α and is expressed by

$$E_s - E_i = \frac{RT}{nF} \ln \frac{1 - \alpha}{\alpha}$$

so that $(E_s - E_i)$ is independent of (D_O/D_R) . Thus, formally, $(E_s - E_i)$ determines α .

(iii) If $\alpha = 0.5$, the summit potential coincides with the half-wave potential whatever the frequency.

(iv) The peak height of the a.c. wave for low frequencies is given by

$$\Delta i_s = \frac{n^2 F^2}{4RT} \Delta V A \sqrt{\omega} (C_{O^0} \sqrt{D_O} + C_{R^0} \sqrt{D_R})$$

which reduces to the well-known expression

$$\Delta i_s = \frac{n^2 F^2}{4RT} \Delta V A \sqrt{\omega D} (C_{O^0} + C_{R^0}) \text{ for } D_O = D_R = D$$

(v) At high frequencies ($K_s \ll \sqrt{2\omega D_i}$)

$$\Delta i_s = \frac{n^2 F^2}{RT} \Delta V A k_s \left(C_{O^0} + C_{R^0} \sqrt{\frac{D_R}{D_O}} \right) \times (1 - \alpha)^{1 - \alpha} \alpha^\alpha \left(\sqrt{\frac{D_O}{D_R}} \right)^\alpha$$

which, when $D_O \equiv D_R$, becomes

$$\frac{n^2 F^2}{RT} \Delta V A k_s (C_{O^0} + C_{R^0}) (1 - \alpha)^{1 - \alpha} \alpha^\alpha$$

and

$$= \frac{n^2 F^2}{2RT} \Delta V A K_s (C_{O^0} + C_{R^0}) \text{ if } \alpha = 0.5$$

(vi) The wave is symmetrical about the summit potential at low frequencies and if $\alpha = 0.5$, at all frequencies.

Modified expressions for the width at half-heights of the waves are obtained for the special cases (a) $K_s \gg \sqrt{2\omega D_i}$, (b) $K_s \ll \sqrt{2\omega D_i}$ and $\alpha = 0.5$.

(vii) Case (a). If $E'_{s/2(1,2)}$ are the potentials at which the Faradaic alternating current is one half of its maximum value as measured from the half-wave potential (in this case, the summit potential also)

$$\exp \frac{nF}{RT} E'_{s/2(1,2)} = 3 \pm \sqrt{8} \text{ for case (a)}$$

which is different from the expressions given already⁴.

(viii) Case (b). Under this assumption,

$$\exp \frac{nF}{RT} E'_{s/2(1,2)} = 7 \pm 4\sqrt{3}.$$

Central Electrochemical Research Institute,
Karaikudi (India)

S. K. RANGARAJAN
K. S. G. DOSS

¹ H. H. BAUER, *J. Electroanal. Chem.*, 1 (1960) 363; B. BREYER AND H. H. BAUER, *Rev. Polarog.*, 8 (1960) 157.

² B. BREYER AND S. HACOBIAN, *Australian J. Chem.*, 7 (1954) 225.

³ B. BREYER, H. H. BAUER AND S. HACOBIAN, *Australian J. Chem.*, 8 (1955) 322.

⁴ H. H. BAUER, *J. Electroanal. Chem.*, 1 (1959/60) 2; 2 (1961) 66.

Received July 19th, 1961

A particular influence of the supporting electrolyte on the limiting current of the first polarographic wave of oxygen

When maxima of the first and second kind are absent or suppressed, the amplitudes of the two polarographic waves of oxygen are generally equal, as can be inferred from any diffusion theory. However, for certain compositions, it is not unusual to notice (as first observed by LONGMUIR^{1*}) that the first limiting current is definitely larger than half of the second. This is in particular the case with the following electrolytes:

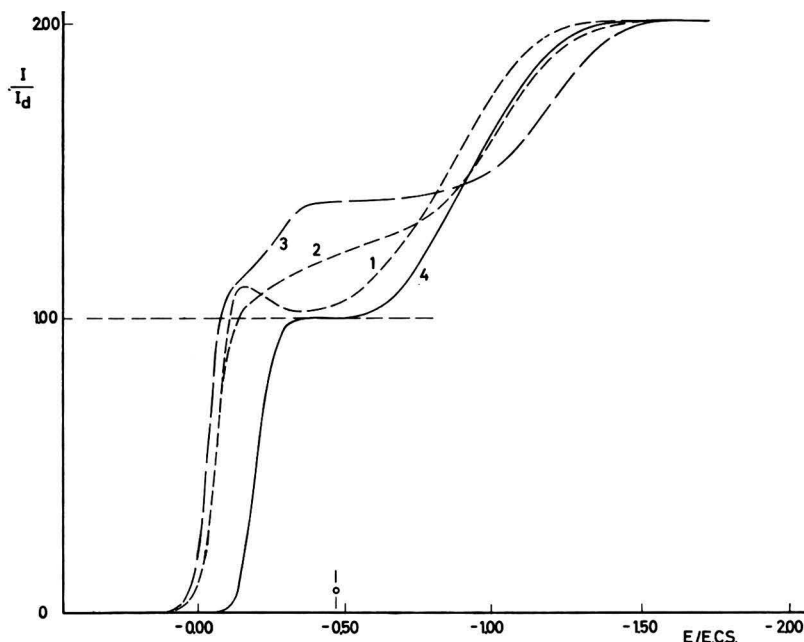


Fig. 1. The influence of composition on the oxygen polarographic wave for: (1) 0.05 *N* NaF; (2) 0.1 *N* (C₂H₅)₄NCl; (3) 0.01 *N* (C₃H₇)₄NCl; (4) 0.1 *N* NaSCN.

0.05 *M* NaF, 0.1 *M* N(C₂H₅)₄Cl, 0.01 *M* N(C₃H₇)₄Cl, selected as typical examples (Fig. 1, curves 1, 2, 3). A common characteristic of these media is that the values of the ψ_δ potentials (at the outer Helmholtz plane) are relatively positive, in the range of electrode tensions where the limiting current is exalted. In the case of sodium fluoride, the "peak" morphology can be correlated with the fact that ψ_δ is the more positive as the electrode tension is made less negative than the tension corresponding

* We are indebted to Prof. J. JORDAN for drawing our attention to this paper.

to the electrocapillarity maximum (-0.47 V/E.C.S.). In tetraalkylammonium solutions, the shape of the limiting current follows the general trend of the adsorption curve of the cations, which are known to be specifically adsorbed, particularly towards negative tensions. Conversely, the addition of tensioactive anions (such as SCN^- or Br^-) restores the normal diffusion current.

This particular influence of the composition may be explained on the basis of the KOLTHOFF-JORDAN catalytic mechanism^{2,3} if the influence of the double-layer is taken into account. The first step in the electro-reduction of oxygen is the irreversible monoelectronic transfer



The particle O_2^- , highly unstable, can undergo further reduction through BAGOTSKII'S⁴ sequence



Alternatively, if a sufficient excess of hydrogen peroxide is present, the following catalytic mechanism^{2,3} may occur



with regeneration of O_2 , the net reaction being the electroreduction of hydrogen peroxide. Although this reaction is generally only detectable when a sufficient excess of H_2O_2 is present, the situation may be modified when the influence of the double-layer is cooperative: if ψ_δ is made increasingly positive, the rate of step (2a) remains substantially unaffected, as the surface impoverishment of protons by electrostatic repulsion is counterbalanced by a reciprocal increase of the O_2^- concentration; on the other hand, the forward rate of reaction (3) increases exponentially with ψ_δ . Consequently, the catalytic reduction of the hydrogen peroxide produced by the electroreduction of O_2 (steps (2a) to (2c)) may become detectable, even without any excess present.

In the presence of an excess of H_2O_2 , not only the exaltation effect, but also the inhibition resulting from specific anionic adsorption can be observed, *e.g.* the addition of small amounts of thiocyanate ions exerts a marked deleterious influence on the catalytic wave.

It can be inferred from the proposed mechanism that the exaltation effect must disappear in solutions containing tensioactive anions (Fig. 1, curve 4), in acid solutions (by increase of the rate of the competitive reaction (2a)) and in strongly basic media (where HO_2^- replaces H_2O_2 as stable species); the importance of the exaltation effect must also increase with the concentration of oxygen (as the rate of reaction (3) is two-fold dependent on this concentration). All these conclusions have been verified experimentally. A rigorous mathematical treatment of the mass transfer problem would of course be extremely arduous (especially in the case when there is no excess of hydrogen peroxide), and has not been attempted.

Whenever oxygen is determined by polarography (or related methods), it should be kept in mind that significant errors may result from indiscriminate applications of the diffusion equation, for either dilute solutions or those containing adsorbable

cations. In those cases where the addition of adsorbable anions or inhibitors is objectionable or impossible, the safest method is to rely on measurements of the total amplitude of the two waves.

Laboratory of Analytical Chemistry,
Free University of Brussels (Belgium)

R. CORNELISSEN*
L. GIERST**

¹ I. S. LONGMUIR, *J. Polarog. Soc.*, 1 (1957) 11.

² I. M. KOLTHOFF AND J. JORDAN, *J. Am. Chem. Soc.*, 74 (1952) 570.

³ I. M. KOLTHOFF AND J. JORDAN, *Anal. Chem.*, 24 (1952) 1071.

⁴ V. S. BAGOTSKII AND I. E. YABLOKOVA, *J. Phys. Chem. U.S.S.R.*, 27 (1953) 1663.

Received July 31st, 1961

* I.R.S.I.A. Doctorate Fellowship.

** Associate of the Belgian National Foundation for Scientific Research.

J. Electroanal. Chem., 3 (1962) 219-221

Book Reviews

Treatise on Analytical Chemistry, Part II, Vol. 3, by I. M. KOLTHOFF, P. J. ELVING AND E. B. SANDELL, Interscience Publishers, New York and London, 1961, \$ 13.25.

This recently published Vol. III of Part II of the *Treatise on Analytical Chemistry* edited by KOLTHOFF, ELVING AND SANDELL contains a series of monographs, each one dealing with the analytical chemistry of a metal, written by the following authors: A. M. CARLSON (Mg); J. F. COETZEE (Hg); W. C. COOPER (Cu); M. FARNSWORTH (Sn); Q. FERNANDO (Cd); H. FREISER (Cd); J. H. KANZELMEYER (Zn); J. PEKOLA (Sn); P. F. REIGLER (Mg); G. B. WENGERT (Mg).

A general scheme has been adopted for the presentation of the material in each section: after a short introduction, the properties, sampling, determination by classical gravimetric and titrimetric methods and determination by physico-chemical methods are dealt with.

A very useful feature of this book is that it gives not only a number of different methods from which each analyst can choose the most suitable procedure for his own problem, but also that at the end of each chapter some specially recommended procedures are given, thus greatly simplifying the task of the analyst. For instance among the many methods for the spectrophotometric determination of copper, diethyldithiocarbamate and 2-2'-biquinoline are selected and given with a detailed procedure, and this is repeated for other methods and other elements. The general treatment is so organized that a good survey of the different analytical procedures on both the macro and micro scales is given and consequently the choice of a particular method for a particular problem is rendered very easy. Electrochemical methods are always given among the recommended procedures for each one of the metals considered.

G. MILAZZO, Istituto Superiore di Sanità, Rome

J. Electroanal. Chem., 3 (1962) 221

Potentiometrie, by J. ČIHALÍK, Publishing House of the Czechoslovak Academy of Sciences, Prague, 1961, 770 pages, Kčs 86.50.

Potentiometric analysis is today one of the most important methods of instrumental analysis. The author, pupil of Prof. TOMÍČEK — one of the founders of potentiometric titration methods — has succeeded in writing probably the largest and most concise book on this subject in world literature.

J. Electroanal. Chem., 3 (1962) 221-222

The theoretical part of the book describes electrodes, electrode tensions and the theory of titrations. Of special interest are the sections on the determination of the end-point and on errors of potentiometric titrations. This part of the book is exceptionally well-written, and reflects the author's wide experience gained in teaching at Charles University.

The part on instruments describes potentiometers, electronic voltmeters, electrodes and auxiliary instruments, and includes important sections on microtitrations and on automation of potentiometric titrations. The next part deals with the measurement of pH, describing indicator electrodes, metallic electrodes, the quinhydrone and the glass electrode. Directions are given for their preparation, as well as descriptions and drawings of factory-made electrodes.

The rest of the book, comprising about two thirds of its scope, is devoted to practical potentiometric titrations. It is divided into sections dealing with neutralisation titrations, titrations based on the formation of insoluble, little dissociated or complex compounds, oxidimetric and reductometric titrations. Oxidative and reductive agents have been kept rigorously apart, so that some redox systems are dealt with in more than one place, depending on whether they are being reduced or oxidised in that particular titration. Difficulties, connected for instance with the correct placing of iodimetry have thus been avoided.

For every group of titrations the indicator and comparison electrodes are described as well as the preparation of volumetric solutions and their standardisation. After this the individual titrations are described, according to the volumetric agent used and the group of elements determined. The part on oxidimetric titrations includes an especially interesting section dealing with reductions by metals, amalgams and the use of metallic reductors. This subject has so far not been dealt with in book form.

A special feature of this book is the inclusion of many less known volumetric agents, for instance sulphides, cyanides, lead and barium salts, fluorides, molybdates in the group of precipitation and complexing titrations, vanadate, iodate, chloramine, hypobromite, ferricyanide, hydrogen peroxide, solutions of Cu(III), Mn(III), gold(III)-chloride, N-bromsuccinimide in the group of oxidimetric reagents and tin(II)-chloride, the lower valency states of molybdenum and tungsten, hydrazine, hydroquinone, ascorbic acid and copper(I)-chloride in the group of reductometric reagents.

The author states that there now exist about 5000-6000 literature references on potentiometry, of which more than 2000 are given in the book. The book thus also forms an exhaustive bibliography of potentiometric literature.

The appendix contains 19 tables, where the author has attempted to gather all the information necessary for the practical application of potentiometric titrations.

Dr. ČIHALÍK's book will be most useful to all chemists engaged in research as well as quality control. Its only drawback is the fact that it is in Czech: the speedy publication of a translation into a more widely known language is to be warmly recommended.

OTA SOFR, Charles University, Prague

J. Electroanal. Chem., 3 (1962) 221-222

X-ray Absorption and Emission in Analytical Chemistry; Spectrochemical Analysis with X-rays, by H. A. LIEBHAFSKY, H. B. PFEIFFER, E. H. WINSLOW AND P. D. ZEMANY, John Wiley & Co., New York, 1961, x + 357 pages, \$ 3.50, £5 8s.

X-ray spectrochemical analysis first attained popularity in research laboratories, and only later became used in analysis and control laboratories. This was after 1940, when high-powered, stable, sealed-off, X-ray tubes became available together with large synthetic crystals, both inorganic and organic, thus offering a wide variety of grating spacing. Technological progress in the construction of sensitive and proportional Geiger counters then made possible rapid and reproducible measurements of X-ray spectra excited by fluorescence.

Almost the same happened with respect to the literature of the field: after the first book by HEVESEY "*Chemical Analysis by X-rays and its Applications*", one had to wait until 1958 to see the publication of other works on spectrochemical analysis. All these books clearly show the concern of their authors with the interests of analytical chemists: theory is contained within the historical introduction; information regarding the electronics is given briefly; many diagrams are given of the apparatus available; both qualitative and quantitative techniques are widely discussed; the limits of sensitivity for different elements are tabulated and compared with ordinary chemical analysis.

The book under review has been written for the chemist and for chemical analysis. This is repeatedly stated in the preface. The matter is split up into eleven chapters, each of which should

J. Electroanal. Chem., 3 (1962) 222-223

be, in principle, self-sufficient. Actually the volume can be divided into five parts: origin and properties of X-rays; equipment; X-ray absorption spectrography; determination of film thickness; and in the appendix, wavelengths of characteristic X-ray lines, approximate intensities of X-ray lines, critical absorption edges and energies.

There are four authors of the book, all from the General Electric Research Laboratories, and twelve collaborators quoted in the preface. Such a qualified and numerous team has certainly enriched the book with much specific data. However it is difficult to avoid the feeling that the book is not homogeneous enough to allow one to become easily familiar with it.

A short comparison with optical spectrography, in the form of a table, is made at the end of the volume. It seems however that some of the present accomplishments of this latter technique have been overlooked when choosing the comparative data on direct reading and on photographic emulsion spectrography, both in vacuum and in air.

R. INTONTI, Istituto Superiore di Sanità, Rome

J. Electroanal. Chem., 3 (1962) 222-223

Physical Methods of Organic Chemistry, 3rd edn. Part 4, by A. WEISSBERGER, Interscience Publishers, New York and London, 1960, xii + 2635-3539 pages, 65 pages of index for Vol. I, \$ 26.

The best judgement and criticism of a book is that given by its readers: therefore the fact that this work (surely not cheap, when the total purchase price is considered) has reached its 3rd edition in a relatively short time, is in itself the best that can be said as a review.

A. WEISSBERGER wisely understands that this monumental work must always be kept up-to-date and in fact its 1st volume, dedicated to physical methods, was published in one Part in the 1st edition, in three Parts in the 2nd edition and has grown to four Parts in this 3rd edition with 1000 pages more than in the 2nd.

About half of this Part 4 deals with electrochemical methods: potentiometry (96 pp. by C. TANFORD AND S. WAWZONEK); conductometry (38 pp. by T. SHEDLOVSKY); transference numbers (*new topic*, 64 pp. by M. SPIRO); electrophoresis (42 pp. by D. H. MOORE); polarography (127 pp. by O. H. MÜLLER); controlled potential electrolysis (*new topic*, 54 pp. by L. MEITES). Other chapters deal with microwave spectroscopy (28 pp. by B. P. DAILEY); nuclear magnetic resonance (*new topic*, 138 pp. by H. S. GUTOWSKY); paramagnetic resonance absorption (*new topic*, 72 pp. by G. F. FRAENKEL); magnetic susceptibility (42 pp. by P. W. SELWOOD); radioactivity (114 pp. by B. M. TOLBERT AND W. E. SRRI); mass spectrometry (91 pp. by D. W. STEWART).

Each section has been written by a specialist very clearly. The book can therefore be recommended not only to organic chemists, perhaps usually less accustomed to physical methods, but also to any one wishing to obtain rapidly, but yet rigorously, some information on theoretical background. It is also a good guide to experimental work.

J. Electroanal. Chem., 3 (1962) 223

Small Scale Experimental Chemistry, by T. A. H. PEACOCKE, Longmans, Green & Co. Ltd., London, 1960, xii + 164 pages, 8s. 6d.

In introducing this short guide, especially meant for those who want to obtain further knowledge of the chemical relationships of the main elements, the author says that the reactions connected with the study of inorganic chemistry should be drawn from laboratory practice rather than from theoretical study. In fact, laboratory practice is the only source that can actually encourage the learner to deduce theory from experimental practice.

On such a basis the author divides the contents of his book into three parts. In the first, which consists of seven chapters, the simple concepts which help to clarify the theoretical principles on which qualitative analysis is based are discussed (chap. 1), with the explanation of some essential rules for drawing up and solving oxido-reduction equations (chap. 2), and a description of the equipment and techniques necessary for semi-micro analysis (chap. 3). In the following chapters, 4 and 6, the author proposes some tests for the learner for typical reactions of most common cations and anions. These tests must be done in order to allow observation of the following

J. Electroanal. Chem., 3 (1962) 223-224

reaction, from which relative equations can be deduced; these are subsequently checked by comparing them with the correct ones collected separately in chapters 5 and 7.

The second part is devoted to qualitative semi-micro analysis: tabulated summaries permit the identification of simple salt components as well as of more complicated mixtures.

Among the methods employed the following deserve mention: the adoption of NaOH for the arsenic sub-group separation from copper, the treatment of this latter sub-group with concentrated HCl for the separate determination of Cu and Hg in respect of Pb, Bi and Cd; orthophosphate ion elimination from the solution by means of zirconyl nitrate. In the third part the author describes twenty inorganic compound preparations, possible on a small scale; among these the following cases are very interesting for the simple method used: cuprous chloride, chromous acetate, chloro-pentamino-chromic chloride. In some cases the analytical method for checking the product obtained is also given.

Two appendices complete the volume: a list of the reagents quoted in the work — with their preparation — and some indication of the equipment needed in the course of the analysis, to encourage the reader's observation and critical understanding. Consequently the work is extremely useful for all those who want to begin the study of chemistry.

The publishers, Longmans, receive credit for the high standard of printing and presentation of the work.

G. RASPI, University of Pisa

J. Electroanal. Chem., 3 (1962) 223-224

Einführung in die qualitative anorganische Halbmikroanalyse, 2. Verb., von G. ACKERMANN, Deutscher Verlag für Grundstoffindustrie, 1961, 161 Seiten, D.M. 14.

It is continually felt that a need exists for giving instruction to chemistry students in semi-micro and micro procedures. In fact such procedures are very useful not only in saving time and materials, but also from the teacher's standpoint, since very clean and exact working is essential for such procedures.

As a result of this need, many, more or less short and complete, manuals and introductory books that may be used as a practical guide for students have been published. This book, written by Prof. ACKERMANN fulfils its requirements very well, with regard to its clarity and conciseness. The first two chapters are concerned with apparatus and procedures on the semi-micro scale.

The next chapters deal with classical qualitative separations (HCl, H₂S, NH₄OH, (NH₄)₂S, (NH₄)₂CO₃, alkali group, anions) on the semi-micro scale, together with the classical reagents for their detection. By following progress in new ways of detecting elements and groups by means of special and, as far as possible, selective reagents, some of which are discussed, students are introduced to this form of thinking and working.

The apparatus needed for this technique, when different from macro scale apparatus is illustrated by means of well-drawn figures. A small selection of photomicrographs of typical crystal precipitates is given at the end.

J. Electroanal. Chem., 3 (1962) 224

1. Fundamental electrochemistry

682 – Is there an alternative to pH? (in English). Francis E. Crane, Jr. (Douglass College, Rutgers, The State University, New Brunswick, N.J., U.S.A.). *J. Chem. Educ.*, 38 (1961) 365–366.

A review of many unsuccessful attempts to replace the pH concept is discussed. A further alternative, " cH " is suggested where $cH = \log [H^+] + 16$ by definition. The cH becomes directly related to $[H^+]$ and is always positive unless the solution is very alkaline. [D.S.Ru.]

683 – Influence of complex-forming substances on the electric tension of oxidation–reduction systems Me_{ox}/Me_{red} and its use in analytical chemistry (in Czech). F. Vydra and R. Přebil (Geochemical Institute, Czechoslovak Academy of Sciences, Czechoslovakia). *Chem. listy*, 55 (1961) 908–918. A review dealing with the influence of complex-forming agents on the redox electric tension of systems consisting of two different oxidation states of one metal. The redox tension of such systems is important in estimating the suitability of such systems for use as titrating agents. After a theoretical discussion of the problem the authors give their own results on the oxidation of cobalt(II) salts by iron(III) salts in the presence of 1,10-phenanthroline and 2,2'-dipyridyl. [Ot.So.]

684 – Sur la conductibilité du proton en solution aqueuse (in French). G. Perrault (Laboratoire de chimie physique du corps solide et électrochimie, Faculté des Sciences, Strasbourg, France). *Compt. Rend.*, 252 (1961) 3779–3781.

L'auteur attribue une énergie d'activation propre à chaque ion. Cette énergie permet d'amener la particule considérée dans un état énergétique tel qu'elle puisse participer à la conduction. L'auteur peut ainsi établir une relation entre la conductibilité d'une assemblée de particules et la température. Dans le cas de l'eau pure, où l'on considère l'existence des seules espèces OH^- et H^+ , l'équation établie par l'auteur permet de déterminer l'énergie d'activation et le rayon du proton ($E_{H^+} = 0.260$ eV et $r_{H^+} = 1.55 \cdot 10^{-5}$ Å) en tenant compte des propriétés physiques connues de l'eau (viscosité, produit ionique, conductibilité équivalente limite). La valeur de r_{H^+} se rapproche de celle du rayon du noyau de l'atome d'hydrogène: l'auteur suppose que le proton participe à la conductibilité sous forme nucléaire, l'énergie d'activation correspondant à l'énergie de désolvation du proton. [Bad.Lam.]

685 – Sur la conductibilité protonique dans l'eau pure. G. Perrault (Laboratoire de chimie physique du corps solide et électrochimie, Faculté des Sciences, Strasbourg, France). *Compt. Rend.*, 252 (1961) 4145–4157.

Dans une étude précédente (G. Perrault *Compt. Rend.*, 252 (1961) 3779) l'auteur a montré que connaissant les propriétés physiques de l'eau il était possible de déterminer par des mesures de conductibilité l'énergie d'activation E_{H^+} et le rayon r_{H^+} . Aux basses températures $r_{H^+} \approx 1.55 \cdot 10^{-5}$ Å (r rayon du noyau de l'atome d'hydrogène): dans ce domaine de température 0–25°, le produit $E_{H^+} \cdot \epsilon$ est constant (ϵ constante diélectrique). Aux plus hautes températures cette relation n'est plus valable: à la conductibilité sous forme nucléaire se superpose une conductibilité sous forme solvatée $H^+(H_2O)_4$. La vérification expérimentale de la relation $E_{H^+} \cdot \epsilon = C$ entre 0 et 25° et son extrapolation valable aux températures supérieures conduit l'auteur à admettre une cohésion d'origine électrostatique pour l'édifice $H^+(H_2O)_4$ dont le rayon serait de 2.06 Å. [Bad.Lam.]

686 – Messungen von bilonischen Potentialen und elektrischen Leitfähigkeiten an Kationenaustauschern. D. Oppen und H. Staudé (Institut für Physikalische Chemie der Universität Frankfurt a.M., Deutschland). *Z. Elektrochem.*, 64 (1960) 834–840.

Es wird ein Herstellungsverfahren für Ionenaustauscher-Membranen mit definierter geometrischer Gestalt beschrieben. An diesen Ionenaustauschern können bilonische Potentiale und elektrische Leitfähigkeiten mit grosserer Genauigkeit und besserer Reproduzierbarkeit als bisher gemessen werden. Die Konzentration der Elektrolytlösungen wurde klein im Verhältnis zur Festionenkonzentration der Austauschermembran gehalten und die äusseren Partien der Membran vollständig mit den Kationen der jeweils benachbarten Elektrolytlösung beladen. Quellungsseffekte wurden vernachlässigt, ebenso Grenzschichteffekte, da bei der gewählten Versuchsanordnung die Oberfläche einen weit geringeren Einfluss hat als bei gekörnten Ionenaustauschern. Dadurch war die Anwendung der Henderson-Formel und somit die Bestimmung der Ionenbeweglichkeiten aus den Membranpotentialen möglich. Die Fehlergrenze der Widerstandsmessungen lag bei $\pm 1.5\%$,

woraus folgt, dass kein durch Polarisation bedingter Anteil vorhanden war. Bei hohen Konzentrationen wird die Leitfähigkeitsmessung gestört durch Konvektionsleitfähigkeit infolge der durch das angelegte Feld entstandenen hydrostatischen Druckdifferenz, die Messung der biionischen Potentiale durch den hetero-ionischen Effekt, beide Messverfahren durch die Netzstruktur des Austauschharzes und durch Coulombsche Kräfte. Die Übereinstimmung, der auf verschiedene Weise ermittelten Ionenbeweglichkeiten wird um so besser, je verdünnter die Lösung ist.

[He.Wen.]

687 - The basis for a new conception of an electrode potential (in English). J. B. Ramsey (University of California, Los Angeles, Calif., U.S.A.). *J. Chem. Educ.*, 38 (1961) 353-356.

A new concept of "electrode potential" is suggested which differs somewhat from the existing European and American concepts. The electric tension of the cell is expressed directly in terms of the escaping tendency of electrons in the two electrode systems. It is suggested that the cell tension is a property of the cell, having a magnitude with no sign.

[D.S.Ru.]

688 - Interpretation of the electrochemical potential (in English). B. Jakuszewski (Department of Physical Chemistry, University of Łódź, Poland). *Bull. acad. polon. sci., série des sciences chimiques*, 9 (1961) 11-15.

Based on Ramsey's expression for the EMF of a cell, (*J. Electrochem. Soc.*, 104 (1957) 265), it was shown that the absolute value of the electrochemical potential of the electron in a metallic electrode can be calculated from experimental data. A relationship was derived, according to which the difference of zero charge potential of two metals is equal to the difference of the work function of the electrons

[Ad.Hu.]

689 - On problems of equivalent-point determinations (in German). C. Litenau and D. Cörmös (Chemische Fakultät der Babes-Bolyai Universität, Cluj, Rumänien). *Acta Chim. Acad. Sci. Hung.*, 27 (1961) 9-20.

Aus der Arbeit ersieht man die Bedeutung, die bei der Berechnung der beiden Geraden einer ursprünglich linearen oder nachträglich linear gemachten Titration - der Eliminierung von übertriebenen fehlerhaften Punkten zukommt.

Die Anwendungsweise zweier statistischer Verfahren für die Eliminierung der fraglichen Wertepaare wird dargelegt. Beide Verfahren stützen sich auf die Bearbeitung der univariaten Reihe, die man mit Hilfe der Differenzen $|(A_0 + A_1x) - y_k|$ erhält.

Anschließend wird die gegenseitige Beeinflussung von v_i und V_i mathematisch behandelt und gezeigt, dass zwischen diesen Werten eine umgekehrte Abhängigkeit besteht und dass, infolge der Amortisation der Differenz $|V_i - v_i|$, der Schnittpunktwert einem Grenzwert zustrebt.

[E. Juh.]

690 - Effect of alternating current on the depolarisation of mercury electrodes. I (in German). T. Erdey-Gruz and J. Dévay (Department of Physical Chemistry and Radiology, L. Eötvös University, Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 25 (1960) 401-424.

Depolarisation occurring on a mercury electrode polarized by direct current is increased by a sine-shaped alternating current. This effect of alternating current increasing the depolarisation reaches a minimum value at the electrical tension of the electrocapillary maximum of mercury. The increase of depolarisation can be explained by the liquid flow due to the inhomogeneous distribution of alternating current on the electrode surface, which takes place under the effect of electrical tension differences in a direction tangential to the electrode surface. The existence of tangential tension differences was demonstrated by experiments. It appears probable that both the electrolyte solution and the electrode mercury begin to flow under the effect of tangential tension differences.

[E. Juh.]

691 - Study of the kinetics of electrode processes with the use of constant current electrolysis. III. Reversible monomerisation and reversible disproportionation (in German). O. Fischer, O. Dračka and E. Fischerová (Masaryk University, Brno, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 25 (1961) 323-337.

Relations were derived, which are valid for constant current electrolysis for the case of the depolariser being formed by a preceding reversible disproportionation. For the evaluation of the rate constants of this reaction the dependence of $i\tau^1$ on $i^1\tau^1$ has been proposed (i being the current density used and τ the time of transformation). In the case of a preceding reversible monomerisation, the dependence of $i\tau^1$ on $i^{4/3}\tau^1$ is used.

The theoretical relations have been proved by the use of experimental data on the anodic oxidation and cathodic reduction of dithionite. Results have been proved in this way which other authors have obtained by polarographic means.

[Ot.So.]

692 – Calculation of the dependence of current density on the overvoltage on a rough electrode with forced electrolyte convection (in German). I. Roušar (Institute of Chemical Technology, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 25 (1961) 1867–1873.

Fundamental equations have been derived for the dependence of the current density on a rough electrode on the overvoltage, (determined by diffusion polarisation), for the case of redox systems. The derived equation has been simplified for the condition of equivalent sand-roughness, and calculated for the case of an η - i curve on a smooth and rough electrode. [Ot.So.]

693 – Limiting diffusion current on the rotating disc electrode in cathodic hydrogen evolution (in Russian). G. P. Desideriyev and S. I. Berezina (M. V. Lomonosov State University, Moscow, U.S.S.R.). *Doklady Akad. Nauk. S.S.S.R.*, 130 (1961) 1270–1276.

The electric tension of a platinum disc cathode of 6 mm diameter, rotating at 1000–20000 rev/min has been determined. H_2SO_4 solutions, 0.0005 N –0.05 N were used: cathodic and anodic spaces were separated, hydrogen being introduced into the cathodic space. The dependence of the limiting current on the square root of the rate of rotation is linear. Increase of the acid concentration and of the rate of rotation leads to a sharp increase of the limiting current. [Ot.So.]

694 – The velocity of rate controlling surface diffusion reactions in the electrodeposition of metals as a function of dislocation density (in English). H. Kita, M. Enyo and J. O'M Bockris (John Harrison Laboratory of Chemistry, University of Pennsylvania, Philadelphia 4, Pa., U.S.A.). *Can. J. Chem.*, 39 (1961) 1670–1676.

The surface diffusion velocity of Cu anions appears to depend on the current density used during measurements of the deposition of copper. It is suggested that the number of growth sites during the deposition under monolayer conditions depends upon the electric tension, and the dependence of the critical radius of growth on supersaturation. [D.S.Ru.]

695 – Effect of periodic reversal of current on concentration polarisation (in Russian). N. T. Kudryavtsev, R. Yu. Bek and M. R. Tarasevitch (Institute of Chemical Technology, Moscow, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 1507–1511.

The effect of periodic reversal of current on concentration polarisation in solutions of silver nitrate and of an equimolar mixture of potassium ferrocyanide and ferricyanide has been investigated for alterations of from 2000–3000 c/min and temperatures between 30–50°. It has been found that for equal rates of deposition of metals with reversing current, reversals of less than 60 c/min are accompanied by higher concentration polarisation than in the case of direct current. Concentration polarisation on reversing the current greatly depends upon the reversing frequency, decreasing with increase in the latter and approaching the value for direct current electrolysis. The relations may be explained in terms of the retarding effect of deposit dissolution in the anodic time interval on the rate of diffusion of the metallic ions from the bulk of the solution to the electrode surface. [Ot.So.]

696 – Autovibration processes in some electrochemical processes (in Russian). Yu. A. Tshizmadev (Institute of Electrochemistry, Academy of Sciences, U.S.S.R.). *Doklady Akad. Nauk, S.S.S.R.*, 133 (1960) 1136–1139.

The author deals with cases where the curve of the interdependence of variables describing an electrochemical system is S-shaped, and explains these using the theory of vibrations. The calculation is illustrated by the example of the Law of Conservation of the Electrode Charge (representative of establishing equilibrium in a system with one degree of freedom) and of the ionisation of hydrogen on a passivated Pt-electrode. [Ot.So.]

697 – Comparative radioactive tracer study of the electrode and exchange properties of the glass electrode. II. Behaviour of the potassium glass electrode in solutions of alkaline metal salts (in Russian). E. A. Materova, V. V. Moiseev and A. A. Belyustin (Leningrad State University, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 1258–1264.

The electrode properties of potassium glass in solutions of pure alkali-metal chlorides and of potassium chloride together with Li, Rb and Cs chlorides have been investigated. Exchange electrodes have been obtained with electrode functions of other alkali metals. These results, and the calculated exchange constants, lead to the following order of alkali metal ions, with respect to their effect on the potassium function: Na^+ , Rb^+ , Li^+ , Cs^+ . The sorption of K^+ , Rb^+ and Cs^+ ions on potassium glass electrodes has been investigated with the aid of isotopes. The ions were found to be sorbed in amounts corresponding to the above mentioned order. Data obtained on the rate of penetration of various cations in glass, lead to the assumption that the interaction of alkali metal ions with the potassium electrode glass proceeds according to a diffusion mechanism. [Ot.So.]

698 – Electrochemical behaviour of copper in sulphuric acid solutions (in Russian). N. N. Milyutin (Railway Transport Research Institute, Leningrad, U.S.S.R.). *Zhur. Priklad. Khim.*, 34 (1961) 848–856.

In investigating the anodic behaviour of copper in 1.83, 5.0 and 8.7 *N* sulphuric acid solutions at 25° it has been shown that copper is oxidised in the range of electric tension 0.20–0.35 V according to the equation

$$\lg i = -8 + 20\varphi,$$

Cu⁺ and Cu²⁺ being liberated simultaneously. The saturation of the layer nearest to the electrode by salts stabilises the divalent ion concentration by the reaction



by which copper slime is formed.

[Ot.So.]

699 – Determination of the silver zero-discharge electric tension (in Russian). D. I. Leykis (Institute of Electrochemistry, Academy of Sciences, U.S.S.R.). *Doklady Akad. Nauk, S.S.S.R.*, 135 (1960) 1429–1431.

Measurements were carried out on silver wire fused into molybdenum glass. The electrode was polarised at -0.5 V. In dilute Na₂SO₄ solutions at $\varphi = -0.7$ V a clearly defined minimum is observed, which deepens with dilution of the electrolyte. This is not observed in more concentrated, 1 *N*, solutions. It is deduced that silver zero-discharge electric tension is -0.7 ± 0.05 V. (All tension values are in terms of the S.C.E.). This is proved by comparison of data obtained with K₂SO₄, KCl and KBr solutions. The value obtained also agrees with results of electrocapillary measurements on fused salts.

[Ot.So.]

700 – Influence of anions on anodic dissolution of indium amalgam (in Russian). V. V. Losev and A. I. Molodov (Oil Research Institute, Grozno, U.S.S.R.). *Doklady Akad. Nauk, S.S.S.R.*, 130 (1960) 111–116.

By correlation of polarisation and radiochemical measurements, it has been found possible to separate and investigate one of the electrode processes, in this case the anodic process. Thus the influence of the concentration of halogens and sodium sulphate on the rate of dissolution of a 0.1 *M* indium amalgam has been studied in a medium of 0.01 *M* In(ClO₄)₃ + 0.01 *M* HClO₄ at 20° and a constant ionic strength of 3 *M*, regulated by addition of NaClO₄. The dependence of the equilibrium electric tension on concentration of the anions mentioned has also been investigated. A linear dependence of φ and $\lg i_a$ has been found. With increasing concentration of Cl⁻ and SO₄²⁻ the anodic curves rise to the negative side, *i.e.* the rate of the anodic process increases. Results are given in a number of graphs.

[Ot.So.]

701 – On some electrochemical properties of titanium in fluoroboric acid solutions (in Russian). F. K. Andryushenko and I. E. Vlasenko (Polytechnic Institute, Kharkov, U.S.S.R.). *Zhur Priklad. Khim.*, 34 (1961) 1266–1270.

Empirical equations are set up for the dependence of the rate of solution of titanium on the concentrations of its ions in aqueous, alcoholic and ethylene glycol solutions of fluoroboric acid at 30°. Similarly, equations for the "critical" cathodic current densities are given. Under these conditions titanium forms tetravalent ions. The electric tension of titanium on solution is -0.6 to -0.7 V. Redox tensions of the solutions formed and their changes during the process are given. These lie in the range -0.03 to -0.13 V.

[Ot.So.]

702 – The first ionization constant of hydrogen sulphide in water (in English). H. L. Loy and D. M. Himmelblau (Department of Chemical Engineering, The University of Texas, Austin 12, Texas, U.S.A.). *J. Phys. Chem.*, 65 (1961) 264–267.

The values for the first ionization constant were $0.271 \cdot 10^{-7} \pm 4\%$, $0.87 \cdot 10^{-7} \pm 4\%$, and $1.52 \cdot 10^{-7} \pm 7\%$ at 0, 25 and 50° respectively. Radioactive tracer techniques were employed to determine the low concentrations of sulphide. The values agree with those of previous investigators.

[D.S.Ru.]

703 – Acidität und Wasserstoffbrücken bei Hydroxy-Biphenylen und Hydroxy-Biphenylchinonen. Hans Musso und Hans-Georg Matthies (Organisch-chemisches Institut der Universität Göttingen, Deutschland). *Chem. Ber.*, 94 Jahrg., 2 (1961) 356–368.

Spectroscopic and potentiometric methods make it possible to measure the p*K* values of molecules with two adjacent acid functions. The difference p*K*₁ – p*K*₂ = Δ p*K*_{1,2} is especially large in the case of a hydrogen bond, stabilizing the mono-anion after the release of the first proton. The 2,2' dihydroxy-biphenyls non-substituted in the 6,6' positions show a Δ p*K*_{1,2} of about five p*K* units corresponding to an energy increase after the first ionization of about four Kcal/mol. Substitution in 6,6' positions leads to steric hindrance, which maintains the phenyl rings perpendicular to one another. The hydroxy groups are too far apart for any association to occur. Such independence

results in about the same value for both pK 's as for isolated half-molecules. Hydroxybiphenyl quinones have two pK values resulting from the existence, after the first ionization step, of three negatively charged oxygen atoms which make the departure of the last proton difficult. Spatial configurations of biphenyl derivatives may also be inferred from the pK values. [H.Hur.]

See also abstracts nos. 724, 727, 814, 815, 884, 885, 890.

2. Apparatus and accessories

704 – Design and use of a refined microelectrophoresis unit (in English). B. W. Grünbaum (Department of Pathology, University of California, School of Medicine, San Francisco, Calif., U.S.A.). *Anal. Chem.*, 32 (1960) 564.

The microelectrophoresis apparatus described in this paper is constructed of Plexiglas except for the electrical fittings and paper holder. These are made of aluminium and stainless steel. Eight 0.01–0.1 μ l samples can be subjected to electrophoresis simultaneously. The quality of the separations is tested with an ink dye, proteins from blood serum and ferritin solution. Some photographs of the apparatus and its details are given. [Kl.Gr.]

705 – A new type of tank for paper microelectrophoresis of proteins from biological fluids (in English). A. Seniów (Department of Parasitology and Parasitic Diseases, High School of Agriculture, Wrocław, and Department of Animal Physiology, Zoological Institute, University of Wrocław, Poland). *J. Chromatog.*, 3 (1960) 586–588.

A cheap and easily assembled apparatus described holds up to ten paper strips. The strips are securely fixed on to rotating electrode vessels, no supporting frame being needed; even when soaked with buffer, the paper can be stretched without tearing. Details are given for construction and operation of the apparatus. [J.E.Le.]

706 – A simple device for accurate time-measurement in coulometric analysis (in English). F. Vorstenburg and A. W. Löffler (Laboratory for Analytical Chemistry, Technical University, Delft, The Netherlands). *J. Electroanal. Chem.*, 1 (1959–1960) 422–423.

A device is described for measuring time in coulometric analysis, based on the use of an electronic counter which counts the number of pulses of a constant frequency oscillator. By using a diode, it is possible to switch on and off practically without inertia. The error per measuring period is considerably reduced as compared with the stop clock method. [Su.Mo.Co.]

707 – An inexpensive coulometer for titrations with externally generated reagents (in English). William F. Head and Max M. Marsh (Eli Lilly and Company, Indianapolis, Ind., U.S.A.). *J. Chem. Educ.*, 38 (1961) 361–362.

The circuit and details of construction are given for a coulometer. The unit measures a varying current through the use of a current integrating, low inertia motor and gear driven register. The coulometer may be used with the burette described by DeFord, Pitts and Johns for externally generated titrants. The end points may be determined by the usual standard systems and the coulometer may be coupled with an automatic titrator. [D.S.Ru.]

708 – Apparatus for electroconductivity measurements of non-aqueous solutions (in Russian). N. Ya. Turova (M. V. Lomonosov State University, Moscow, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 1634–1635.

An electroconductivity apparatus is described, designed to ensure complete isolation from air humidity. Preparation and dilution of the solutions are carried out in the cell itself. Electroconductivity measurements over a broad range of concentrations may be carried out with a single charge. [Ot.So.]

709 – Improvements in the design of conductivity cells (in English). Karol J. Mysels (Chemistry Department, University of Southern California, Los Angeles 7, Calif., U.S.A.). *J. Phys. Chem.*, 65 (1961) 1081–1082.

Some desirable features of cells are discussed. A detailed description of a low volume, low cell constant cell and doughnut-type dilution cell are given. [D.S.Ru.]

710 – Researches on metal alloys and salt mixtures by high-frequency methods (in German). Th. Weber and K. Cruse (Physikalisch-chemisch Institut der Bergakademie, Clausthal, Germany). *Z. anal. Chem.*, 166 (1959) 333–355.

The sample to be analysed is placed in a high frequency oscillator circuit. By frequency measurements, it is possible to follow phase changes. This allows the method to be used in constructing phase diagrams. In the paper, the wiring diagrams, the special cells with coils for high temperature measurements (up to 650°C), the oscillating characteristics of the circuit and measuring techniques are fully described. The method is applied particularly to the thermal behaviour of Sn–Zn, Pb–Sn and Bi–Sb alloys, following the variations of the frequency (ΔF) on varying the sample temperature (“ ΔF -polytherms”); the frequency variations caused by varying the sample composition at a fixed temperature (“ ΔF -isotherms”) are also reported. A physico-mathematical discussion of the ΔF -polytherms, applied to para- and diamagnetic metals, is made before the explanation of the experimental results, which agree with calculated ΔF -polytherms. [G.deAn.]

711 – The “Oscillographic step polarizer” (in Japanese). Takeshiro Mine (Department of Applied Chemistry, Faculty of Engineering, Kyūshū University, Fukuoka, Kyūshū, Japan). *J. Electrochem. Soc. Japan*, 28 (1960) 106–110. (English translation in *J. Electrochem. Soc. Japan*, (Overseas Suppl. Edn.) 28 (1960) E 51).

In measurements of decomposition voltages, it is desirable to observe the current-electric tension curve, the polarizing characteristics or the decomposition voltage, directly and instantly, on the oscillograph, suppressing the transitions of electrodes and bath conditions due to polarization. Measurements should be carried out during the shortest possible time. In this respect, a new measuring apparatus called “oscillographic step polarizer” (O.S.P.) has been devised and examined. This is an apparatus to repeat polarizing and depolarizing periods (both 1/10 sec) alternately, and to observe the changes of electrode tension which occur as the intermittent polarizing current increases rapidly, and are immediately visible as current electric tension curves on a cathode-ray oscillograph. The following further advantages were expected by the O.S.P. method:

(1) Electric tensions free from errors due to IR drops can be obtained by the measurement of electric tensions after interruptions of polarizing current. (2) As the polarization can be initiated from an optional electric tension previously settled, and scanned within an optional range of current, the electrode behavior under various conditions can be observed. [Ta.Fu.]

712 – Synthetic resin membranes for acid–base titration observations (in German). R. Geyer and P. Niklas (Institut für analytische Chemie, Technische Hochschule für Chemie, Leyna-Merseburg, Deutschland). *Z. anal. Chem.*, 177 (1960) 166–175.

Five different synthetic resin membranes have been examined. By sticking thin plates of the membranes at the ends of glass tubes, simple measuring electrodes may easily be obtained. The membranes containing anthranilic acid favour the identification of the acid–base titration end point. [Di.Ciò.]

713 – Alternating current voltammetry with controlled alternating potential. D. E. Walker and J. R. Alden (Department of Chemistry, University of Kansas, Lawrence, Kan., U.S.A.). *Anal. Chem.*, 33 (1961) 308.

An instrument built according to the circuit of Booman is described. Its use is extended to alternating current voltammetry by applying an alternating voltage of the desired wave form, frequency and magnitude across a 5 ohm resistor in series with the ground connection of the Philbrick stabilizing plug in the unit of the amplifier. A better separation of capacitative and faradic currents is made by this instrument. Higher ohmic resistance systems can be studied effectively. [Kl.Gr.]

714 – An i -R compensator for nonaqueous polarography and amperometric titrations. P. Arthur and R. H. Vanderkam (Department of Chemistry, Oklahoma State University, Stillwater, Okla., U.S.A.). *Anal. Chem.*, 33 (1961) 765.

The construction of an i -R compensator is described which allows polarography in nonaqueous solutions, in connection with a conventional polarograph. A special polarographic cell is used with three electrodes; the dropping mercury electrode, a calomel electrode and a platinum wire electrode. The electric tension between the comparison electrode and the extra reference electrode is fed into an amplifier which is in series with the polarograph and the reference electrode. This amplifier adds in a correcting voltage. A schematic circuit diagram and a construction diagram for the compensator are given. [Kl.Gr.]

715 – Purification of certain quarternary ammonium compounds used in polarography (in Russian). G. S. Supin (Research Institute of the Tyre Industry, Moscow, U.S.S.R.). *Zhur. Anal. Khim.*, 16 (1961) 359–361.

New methods have been developed for the purification of tetramethylammonium chloride and iod-

ide, and tetraethylammonium bromide and iodide. The purified products can be used in the extreme negative region.

The purification method consists of dissolving the reagent in one solvent, filtering, precipitating the reagent by another solvent and drying. Solvents used, differing for each of the four reagents are methyl alcohol, ethyl alcohol, chloroform, ether and benzene. [Ot.So.]

716 – Vector-polarograph (in Russian). S. B. Tsfasman. *Zavodskaya Lab.*, 26 (1960) 888–889.

The instrument has been developed for continuous control of cadmium in zinc electrolytes. The source of the polarising voltage provides a linear variation of the voltage applied to the polarographic vessel, from 0.5–10 mV/sec, with cathodic or anodic polarisation. A source of sinusoidal voltage provides fixed amplitude values of 4–40 mV. A compensator serves to keep polarising and alternating voltages applied to the vessel constant, irrespective of the current. A filter separates the active current component from low-frequency components of the vessel, whose period is equal to the life of the mercury drop. Sensitivity of the polarograph was found to be 10^{-7} M cadmium. [Ot.So.]

717 – Differential electronic polarograph (in Russian). Yu. V. Gorelkinskii, I. G. Grinman and G. S. Kozlov (Institute of Nuclear Physics, Kazachian Academy of Sciences, U.S.S.R.) *Zavodskaya Lab.*, 26 (1960) 1141–1145.

An instrument is described, differing from conventional ones, by the use of a phase-sensitive bridge to separate the Faraday current from the capacity current. This arrangement has helped to simplify the instrument. A detailed description of a wiring diagram is included. [Ot.So.]

718 – Convenient pH — stat assembly (in English). K. I. Wood (Division of Protein Chemistry, CSIRO Wool Research Laboratory, Parkville, N. 2, Melbourne, Victoria, Australia). *Anal. Chem.*, 32 (1960) 537.

A highly accurate and stable pH-stat, which has a shift of no more than 0.03 pH units over 3 hours is described. The thermostatically controlled titration vessel, the pH meter and the pH controller are described in detail. A wiring diagram is given. A 0–10 mV recorder is used in connection with the apparatus. [Kl.Gr.]

719 – Two electronically-operated titrant valves (in English). J. T. Stock and M. A. Fill (Department of Chemistry, University of Connecticut, Storrs, Conn., U.S.A.). *Lab. Practice*, 10 (1961) 302–304. Two electrically-operated titrant valves are described; both are designed to operate on a 4–6 V d.c. supply and have built-in controls for wide adjustment of the rate of titrant delivery. In addition, the response of the second of the valves is designed to be quite sensitive to the operating voltage, so that remote control of the flow rate is possible. Such remote and continuously variable control of titrant flow may be of value in automatic potentiometric and other titrimetry. By continuous electronic differentiation of the titrant curve during the process, an initially high rate of titration can be smoothly and progressively reduced as the end point is approached. [Di.Ciò.]

See also abstracts nos. 904, 906, 939.

3. Polarography

720 – The reproducibility of polarographic measurements (in German). F. V. Sturm (Forschung Laboratorium der Siemens-Schuckertwerke AG, Erlangen, Germany). *Z. anal. Chem.*, 166 (1959) 100–114.

By controlling all the terms which are included in the Ilkovič equation (*Collection Czechoslov. Chem. Commun.*, 6 (1934) 498) and in its modification (Strehlow and Stackelberg, *Z. Elektrochem.*, 54 (1950) 51) and by selecting the best experimental conditions (including resistances, capillary length and radius, solution volume, concentration, etc.) it is possible to determine the reproducibility of the half-wave tension ($E_{1/2}$) and of the diffusion current (i_d) in direct-current polarographic analysis with the dropping mercury cathode. The same can be done for the peak tension (E_p) and the peak height (or current, Ei_p) in alternating-current polarography.

All the apparatus and measurement details are described, and data on the reproducibility of measurements in solutions of different ions at various concentration are given. [G.deAn.]

721 – Investigations in the field of polarographic catalytic hydrogen waves. I (in German). E. Pungor and Gy. Farsang (Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 25 (1960) 293–303.

The dependence of the catalytic hydrogen wave on the buffer concentration and on the pH value was studied by the authors with several model substances. According to the working assumption evolved on the basis of experimental results, the conditions of concentration in the vicinity of the electrode surface are supposed to affect the formation of the catalytic wave proper. [E. Juh.]

722 – The role of a polarographic method in activation analysis (in French). Z. Ferenczy (Institut de Recherches Chimiques des Industries Lourdes, Veszprém, Hungary). *Acta Chim. Acad. Sci. Hung.*, 26 (1961) 229–234.

Pour examiner les vestiges radioactifs des matières d'activation, les mesures s'effectuaient par polarographie. Au cours de nos expériences on constatait que cette méthode est bien utilisable dans le cas, où le but de l'examination est la preuve de la présence des métaux lourds, qui produisent des amalgames stables. L'emploi de la méthode se montre encore plus avantageux, si la durée de décomposition de la matière constitutive est courte, mais la trace à examiner reste longtemps active. [E. Juh.]

723 – Investigation of polarographic catalytic waves, in connection with the effect of tetraethylammonium salts (in German). E. Pungor and Gy. Farsang (Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 27 (1961) 175–182.

Die Rolle der Zusammensetzung der Lösung, als einer der den polarographischen Strom bestimmenden Faktoren wurde einer Prüfung unterzogen. Es werden jene Untersuchungen beschrieben, die Ermittlung der Wirkung fremder Elektrolyte auf die katalytische Stufe bezweckten. Die bei Anwendung von Kaliumbromid und Tetraethylammoniumbromid als Versuchsmodelle erhaltenen Angaben bewiesen eindeutig, dass die Erhöhung der Salzkonzentration zu eine Verminderung der katalytischen Stufe führt. Bei den Tetraäthylammoniumsalzen wurden die Annahme, nach der man bei der Deutung dieser Vorgänge ausser der Salzwirkung noch den Verschiebung des pH-Wertes auf der Elektrodenoberfläche nach dem sauren Gebiet in Rücksicht nehmen muss, mittels einer quantitativen Formulierung bewiesen. [E. Juh.]

724 – Theory of polarographic currents in electrostatic repulsion of the depolarisator in the double layer (in German). O. Dražka (Institute of Hydrodynamics, Czechoslovak Academy of Sciences, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 26 (1961) 1999–2014.

Relations have been derived for the polarographic current for the case when the depolariser is transported to the electrode surface by diffusion and is repulsed in the electrode space electrostatically as a result of potential distribution in the double layer. The theory also includes possible slow discharge and repulsion of the product of depolarisation. It has been found that the thickness of the diffusion layer is sufficiently larger than the thickness of the double layer, and the dependence of the ratio i/i_d on the drop-time and therefore also the dependence of i on the reservoir height is given formally by the same equation, as in the case of a kinetic current with a preceding rapid I order reaction. With increasing concentration of the supporting electrolyte the ratio i/i_d decreases and nears its limiting value. [Ot. So.]

725 – Selection of supporting electrolytes for inorganic square wave polarography (in English). Jutaroh Seto and Susumu Yamazaki (Ajinomoto Co., Inc., Kawasaki Factory, Kawasaki City, Japan). *Review of Polarography*, 8 (1960) 153–156

As is well known, the choice of supporting electrolyte in square wave a.c. polarography is much more important than that in d.c. polarography, since the peak height due to the electrode reaction of the depolarizer depends very prominently on the reversibility of the reaction concerned. The applicability of sixteen kinds of common supporting electrolytes to square wave a.c. polarographic analysis are studied in this paper. [Ta. Fu.]

726 – Elucidation of electrode processes by the use of a.c. polarography (in English). B. Breyer and H. H. Bauer (Section of Agricultural Chemistry, Faculty of Agriculture, University of Sydney, Australia). *Review of Polarography*, 8 (1960) 157–168.

The object of this article is to show how a.c. polarography can be used with advantage for the elucidation of electrode reactions. More specifically, the aim of the present communication is to discuss the types of observations made in a.c. polarography, and their interpretation, in terms of the underlying electrode reactions.

The three main variables studied in a.c. polarography are the magnitudes of the a.c. polarographic current and of the a.c. base current and the value of the summit value of the a.c. polarographic wave. In order to apply a.c. polarography to the elucidation of electrode reactions, the dependence

of these three variables on various factors—such as the frequency and amplitude of the alternating voltage and the nature and concentration of the supporting electrolyte, is studied. [Ta.Fu.]

727 – Insoluble depolarisers (in Czech). K. Micka (Polarographic Institute, Czechoslovak Academy of Sciences, Prague, Czechoslovakia). *Chem. listy*, 55 (1961) 852–890.

A review, dealing with the electrochemical, especially polarographic, behaviour of insoluble depolarisers. These can be in the form of suspensions, emulsions, surface films, crystals, solidified melts and porous pressed bodies. All are characterised by electron transport between a solid phase of semiconducting character and a fluid electrolyte, or a metallic phase and a solid semiconductive phase. Elements, oxides, sulphides, selenides, tellurides, insoluble organic depolarisers and some minerals are dealt with. [Ot.So.]

728 – Discussion of Gerischer's paper: Rapid chemical reactions (*Z. Elektrochem.*, 64 (1960) 29). P. Delahay and S. Oka (Cates Chemical Laboratory, Louisiana State University, Baton Rouge, La., U.S.A.). *Z. Elektrochem.*, 64 (1960) 35.

Die Verfasser haben auf dem gleichen Gebiet wie Gerischer (Max-Planck-Institut für Metallforschung, Stuttgart) gearbeitet. Sie untersuchten neuerlich potentiostatisch Elektrodenreaktionen, insbesondere die Kinetik der Dissoziation von Merochloroessigsäure in einer Äthanol Wasser Mischung (je 50% Volumen) bei einer Ionenstärke von 1. Sie beobachteten einen Grenzstrom bei Addition von Azobenzol, deren Halbstufenspannung vom pH-Wert abhängig ist und ermittelten $(1.8 \pm 0.5)10^6 \text{ sec}^{-1}$ für die Dissoziation. Sie weisen auf zwei Fehlerquellen hin, den sekundären Wien-Effekt und die Näherung bei der Anwendung einer modifizierten Fick-Gleichung auf Prozesse mit Reaktionsschichten von molekularer Grössenordnung. Sie geben weitere Literatur an. [He.We.]

729 – Double layer corrections in the evaluation of rate and equilibrium constants of fast homogeneous reactions, coupled with electrode reactions. Some potentialities of the galvanostatic method. L. Gierst and H. Hurwitz (Universität Brüssel, Belgien). *Z. Elektrochem.*, 64 (1960) 36–41.

Die Autoren erörtern das Verhältnis zwischen äquivalenten Dicken einer Reaktionsschicht und des diffusen Teiles der Doppelschicht und diskutieren den Einfluss der Doppelschicht auf die Gesamtgeschwindigkeit eines Elektrodenprozesses, der durch eine vorgelagerte chemische Reaktion kontrolliert wird. Sie schlagen eine Theorie vor und erklären mit deren Hilfe den Einfluss der Spannung und der Ionenstärke auf polarographische Wellen. Experimentell untersucht wurden die Ionen Ni^{2+} und $[\text{Cd}(\text{CN})_4]^{2-}$. In einem Anhang sind mathematische Ausdrücke für die verschiedenen elektrochemischen Methoden zusammengestellt; in einem zweiten Anhang werden die Möglichkeiten sowie die Vor- und Nachteile der galvanostatischen Methode erörtert und die gleichzeitige Anwendung der polarographischen und der galvanostatischen Methode für kinetische Untersuchungen empfohlen. [He.We.]

730 – Amperometric titration of aldehydes and ketones with 2,4-dinitrophenylhydrazine (in Russian). E. V. Zbov, Y. S. Lyalikov and O. M. Mukhammednazarova. *Izvest. Akad. Nauk, Turkmen S.S.R.*, (1959) 45–50.

Ultrasonic vibrations improve the amperometric titration of carbonyl compounds with 2,4-dinitrophenylhydrazine (I). Heavy precipitates of the hydrazones are formed which do not interfere with the titration. Details of the technique are given. The solution is treated with ultrasonic vibrations for 30 sec after each addition. The optimal concentration for the titrating solution is 0.005 to 0.05 M of (I) and this solution is stable for 22 days. The range of concentration in which the aldehydes are satisfactorily determined is between 0.00 M and 0.04 M. The error is 1.6%. [Gio.Ser.]

731 – Thionyltrifluoroacetone: polarographic and spectrophotometric behaviour and dissociation equilibria (in English). P. J. Elving and Ph. G. Grodzka (Department of Chemistry, University of Michigan, Ann Arbor, Mich., U.S.A.). *Anal. Chem.*, 33 (1961) 2.

The polarographic behavior of thionyltrifluoroacetone (TTA) is studied in various buffer systems. The influence of pH, buffer component concentration and salt effects are investigated. TTA gives four waves in the usual pH range. An explanation of the complex polarographic behaviour is given in a summary of the postulated polarographic reduction mechanisms, with their dissociation products, tautomeric and hydrolytic equilibria states. The scheme is made with the help of electrolysis at controlled tension at a massive mercury cathode, and spectrophotometric measurements. The buffer systems used are: acetate, borate, phosphate and ammonia. For details see the original paper. [Kl.Gr.]

732 – Polarographic properties of 5-nitrofural and its determination (in Czech). F. Kupčík, M. Liška and M. Konupčík (Pharmacon, National Enterprise, Olomouc, Czechoslovakia). *Českoslov. farm.*, 10 (1961) 295–297.

In a strongly acid medium the reduction of 5-nitrofural takes place in six stages, and in slightly acid, neutral and alkaline media in four stages. The dependence of the height of the double wave of the NO_2 reduction indicates the diffuse character of the depolarisation and is well suited for analytical purposes. The half-wave tension is a function of pH. To determine 5-nitrofural, the sample is dissolved in ethanol to make a $5 \cdot 10^{-4} M$ solution. The final alcohol concentration is brought to 20%. A Britton-Robinson buffer pH 4-5 is used as supporting electrolyte. The solution is bubbled with an inert gas. The half wave value is $-0.17 V$ vs. S.C.E. at pH 4.2. [Ot.So.]

733 - Observation of a discrete oxidation wave for acetate ion in acetonitrile (in English). D. H. Geske (Department of Chemistry, Harvard University, Cambridge 38, Mass., U.S.A.). *J. Electroanal. Chem.*, 1 (1959-1960) 502-503.

An oxidation anodic wave for the acetate ion has been obtained with a rotating platinum electrode for a 0.30 mM solution of tetra-*n*-propylammonium acetate with 0.1 M tetraethylammonium perchlorate in acetonitrile.

The measured limiting current/conc. value ($4.7 \pm 0.3 \mu\text{A}/\text{mM}$) indicates a one electron oxidation; this one-electron process for the acetate ion oxidation has been verified by chronopotentiometry and electrolysis at controlled electric tension. The electrode reaction is irreversible; the half wave tension is slightly dependent on concentration. [Su.Mo.Ce.]

734 - Polarographic determination of methyl methacrylate in polymethylmethacrylate (in Polish). J. Paściak (Research Laboratory, Chemical Works, Oświęcim, Poland). *Chem. anal. (Warsaw)*, 6 (1961) 411-417.

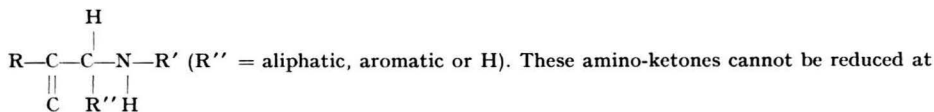
A new procedure for polarographic determination of methyl methacrylate in polymethylmethacrylate has been described. In this method the sample was dissolved in acetone and 0.1 M $(\text{C}_4\text{H}_9)_4\text{NI}$ in dimethylformamide was used as a supporting electrolyte. In these conditions no precipitation of the polymer occurred. For low concentrations of methyl methacrylate one wave at $U_{\frac{1}{2}} = -2.20 V$ was observed. When the concentration increased two waves appeared at $U_{\frac{1}{2}} = -2.17 V$ and $U_{\frac{1}{2}} = -2.35 V$. On the first wave a maximum was observed. The total wave height, and the first wave height are proportional to concentration of methyl methacrylate. This method made possible the determination of 0.05-5% monomer in the polymer. The total time of analysis was about 2.5 hours. [Ad.Hu.]

735 - Der Einfluss der Hydratbildung auf das polarographische Verhalten von α -Oxocarbonsäuren. M. Becker und H. Strehlow (Max-Planck-Institut für physikalische Chemie, Göttingen, Deutschland). *Z. Elektrochem.*, 64 (1960) 129-130.

Bei nichtelektrochemischen Verfahren ist die Rekombinationsgeschwindigkeit von Protonen mit Säureanionen diffusionsbedingt. Nach der polarographischen Methode wurden stark abweichende Werte gefunden. Die partielle Hydratation der Oxogruppe bedingt bei α -Oxocarbonsäuren ein kompliziertes Reaktionsschema für die Nachlieferung der bei positiven Spannungen allein reduzierbaren unhydratisierten und undissoziierten Säure im Reaktionsraum vor der Elektrode. Aus einem allgemeinen Schema werden Massenwirkungsgleichungen abgeleitet. Eine Gleichung für die polarographische Stromstärke wird angegeben. Zwei Specialfälle, Brenztraubensäure und Glyoxylsäure, wurden untersucht. Bei der ersteren wurde aus spektralphotometrischen Messungen geschlossen, dass das Anion praktisch unhydratisiert ist, die Säure dagegen zu 71% in hydratisierter Form vorliegt, während Glyoxylsäure als Anion und als freie Säure völlig hydratisiert ist. Die Rekombinationsgeschwindigkeit der Brenztraubensäure wird angegeben: $k = 1.3 \cdot 10^{10} \text{ l. mol}^{-1} \text{ sec}^{-1}$ (ohne Hydratation $k = 3.8 \cdot 10^9 \text{ l. mol}^{-1} \text{ sec}^{-1}$). Die Genauigkeit dieser Werte ist nicht sehr gross, da die Reaktionsschicht nur 24 Å dick ist. Bei Glyoxylsäure ist der Grenzstrom von 2 polarographischen Stufen bei pH 6.2 um den Faktor 50 kleiner als derjenige von Brenztraubensäure gleicher Konzentration. [He.We.]

736 - Polarographische Untersuchungen an Amadori-Produkten und α -Amino-ketonen. Fritz Micheel und Elmar Heiskel (Organisch-Chemisches Institut der Universität Münster, Westf., Deutschland). *Chem. Ber.*, 94 Jahrg. 1 (1961) 143-150.

Polarographic behaviour of amadori products (derivatives of 1-desoxy-1-amino-D-fructose) may be explained through polarographic study of different α -amino-ketones with the general structure



the mercury electrode when the free electron pair of the N contributes to mesomerism with an adjacent aromatic nucleus ($\text{R}' = \text{aromatic radical}$) or to salt formation at $\text{pH} < 5$. Apart from these

cases, the tautomeric enol form is stabilized by a mesomeric structure and gives a reducible immonium function which is easily detected polarographically. When the ketones are also reducible like acetophenone ($R =$ aromatic radical) two polarographic waves may be observed for $\text{pH} > 5$ and $R' =$ aliphatic function. The first discharge corresponds to the immonium form, the second one to the acetophenone.

The same reasons as for α -amino-ketones make cathodic reduction of amadori products possible with aliphatic amines, and limit here too the pH range to $\text{pH} > 4-5$. The open chain of the amadori products is in equilibrium with the non reducible hemiacetal form. The increasing basicity shifts this equilibrium to the open form so that the diffusion current grows with the pH. On the other hand, boric acid used as a supporting electrolyte may be stabilized in the annular form by complex formation. It is possible to infer the composition of this complex in the case of 1-desoxy-1-*n*-butylamino-D-fructose (one molecule boric acid for two molecules amadori products) and to calculate the equilibrium constant ($K = 3.4 \cdot 10^{-7}$). [H.Hur.]

737 – Polarographic investigation of nitro-aci tautomerism in nitrocyclohexane (in Russian). Ya. I. Turyan, Yu. M. Tyurin and P. M. Zaytsev (Research Institute of the Nitrogen Industry and of Organic Synthesis Products, Lisitshan, U.S.S.R.). *Doklady Akad. Nauk S.S.S.R.*, 134 (1966) 850–852.

Solutions of the substance studied were prepared in water or alkaline solutions, according to the form studied. Supporting electrolytes were citrate-phosphate and borate buffers, with ionic strength kept constant by KCl additions to $\mu = 1.0-1.4$. The nitro-aci transformation was studied in the pH range 8–12, the reverse process at 3–9.5. The nitro-form gives a well defined wave in a broad pH range: the aci-form is not reduced on the mercury drop electrode. [Ot.So.]

738 – Determination of styrene as pseudonitrosite ((in German). V. Šedivec and J. Flek (Institute of Hygiene and Occupational Diseases, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 25 (1961) 1293–1301.

Styrene is transformed to styrene-pseudo-nitrosite by treatment with sodium nitrite in glacial acetic acid. The nitrosite (α -nitroso- β -nitroethylbenzene) is polarographically active, giving a well developed wave of $E_{\frac{1}{2}} = -0.27$ V. Under the given conditions, nitrosation is 100%, 0.01–10.0 mg styrene may be determined with a precision of 3%. The presence of aromatic and aliphatic hydrocarbons, halogenated hydrocarbons, aldehydes, alcohols, ketones, ethers and some unsaturated compounds does not interfere. [Ot.So.]

739 – Polarographic determination of *p*-diphenylaldehyde (in Russian). E. A. Preobrazhenskaya and V. D. Bezuglii (State Research Institute of Chemical Reagents, Kharkov, U.S.S.R.). *Zavodskaya Lab.*, 27 (1961) 814–816..

To determine diphenylaldehyde in polystyrene a 0.5–1.0 g sample is dissolved in 10 ml benzene and made up to 25 ml with 92% methyl alcohol. A 0.5 ml aliquot is taken, 9.5 ml buffer solution of pH 7 is added, and after passing nitrogen through the solution, a polarogram is registered and evaluated using a calibration curve. Waves are observed at -1.1 and -1.4 V. [Ot.So.]

740 – Polarographic determination of 2,2'-bis-pyrazolanthron in the presence of pyrazolanthron (in German). M. Matrka, F. Navrátil, V. Šterba and J. Arient (Institute of Organic Syntheses, Pardubice, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 26 (1961) 1763–1767.

A polarographic method has been worked out for the determination of pyrazolanthron and bis-pyrazolanthron in mixtures in alkaline media. The method is based on the difference of the half-wave tensions of the two compounds. 0.00025 mole (0.1096 g) of the bis-compound was weighed, and was dissolved with heating in 65 ml 2.5 *N* NaOH and 125 ml ethanol. 2.5 ml 0.5% gelatine solution was added and the solution made up to 250 ml with water. An aliquot was polarographed in a vessel according to Kalousek after removal of oxygen. A linear dependence of concentration and wave height was found, and the method of calibration curves was employed. Half-wave values are -1.24 V vs. S.C.E. for pyrazolanthron and -0.91 V vs. S.C.E. for 2,2'-bis-pyrazolanthron. Reversibility of the process was not investigated. [Ot.So.]

741 – Physicochemical measurements on N-oxides (in German). G. Horn (Institut für Mikrobiologie und experimentelle Therapie, Jena, Deutschland). *Acta Chim. Acad. Sci. Hung.*, 27 (1961) 123–161. In Abhängigkeit vom pH-Wert werden verschiedene N-Oxyde in ihrem Verhalten an der Quecksilbertropfelektrode untersucht. Die Strom-Spannungskurven zeigen, dass von Pyridin- und Picolin-N-Oxyden nur die protonisierte Form reduziert wird. Chinolin, Chinaldin und Chinoxalin mit seinen Methylderivaten gibt auch im alkalischen pH-Bereich gut ausgeprägte polarographische Stufen. Die Abhängigkeit der Stufenhöhe von der Konzentration ist über dem gesamten pH-Bereich linear. Die Polarographie kann nach diesen Untersuchungen zur Bestimmung der N-Oxydverbindungen verwendet werden. [E.Juh.]

742 – Investigation of adsorption phenomena occurring at the dropping mercury electrode (in English).

F. Péter, I. Szabados and Gy. Pályi (Department of Applied Chemistry, Technical University, Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 27 (1961) 163-174.

The effect of a sulphuric acid ester derivative of leukoanthraquinone (Indigosolgelb V) on the reduction wave of nitrobenzene-3-sulphonic acid was studied in a Britton Robinson buffer of pH 3.30. It was found that the wave of the nitro group is split by the surface active agent. On raising the concentration of the surface active agent, the participation, in total wave height, of the wave shifted to higher electric tension gradually increases. On applying an adequate concentration the whole wave shifts to more negative electric tension.

The nature of the inhibition processes was examined qualitatively by plotting the correlations of the split wave with mercury level and temperature.

The phenomena investigated can be utilized in the quantitative determination of Indigosolgelb V, and of substances which behave similarly. [E. Juh.]

743 – Hydrirgeschwindigkeit und Redoxpotential bei Chinonen. Hans Musso, Karl Figge und Dieter Joachim Becker (Organisch-Chemisches Institut der Universität Göttingen, Deutschland). *Chem. Ber.*, 94 Jahrg. 4 (1961) 1107-1115.

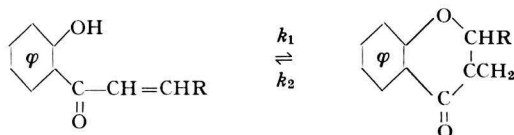
The hydrogenation rate of benzo-, naphtho-, anthra- and diphenyl-quinone on 5% palladium on barium sulphate is measured in terms of the logarithm of the reciprocal half life. The catalyst is poisoned so that it keeps the rates within convenient limits (5-60 minutes). Then a linear relation of the form

$$\log (1/t_{1/2})_1 - \log (1/t_{1/2})_2 = a(E_1 - E_2) \quad (1)$$

exists between the redox tensions E and the hydrogenation rates. The coefficient a depends on experimental conditions. One exception is found for tertiary butyl substituted quinone where the hydrogenation is slowed down by steric hindrance. It may also be proved that the rate determining step is the reduction of the adsorbed molecule. Further, the increasing reaction rate increasing with polarity of the medium seems to confirm the existence of a polar mechanism and an intermediate polar state. The polarographic half-wave tensions of benzo-quinones follow the same sequence as the redox tensions but do not correspond as well as the last to equation (1). The half wave tensions of alkyl substituted diphenyl-quinones decrease with growing alkyl substitution on the α carbon of the side chain. [H.Hur.]

744 – Etude polarographique de la réaction hydroxy-chalcone \rightleftharpoons chromanone. Influences structurales et mécanismes de la réaction (in French). J. Tirouflet et A. Corvaisier (Faculté des Sciences, Dijon, Côte d'Or, France). *Compt. rend.*, 252 (1961) 3818-3820.

Les auteurs suivent l'évolution de la réaction hydroxychalcone \rightleftharpoons chromanone en caractérisant l'hydroxychalcone par sa première vague de réduction électrochimique à l'électrode à goutte de mercure. Soit la réaction:



Les auteurs étudient l'influence du pH d'une part et de la nature du groupement R d'autre part, successivement sur l'équilibre de cette réaction et sur sa cinétique. Entre pH 1-8 ces deux facteurs sont sans influence sur l'équilibre. Lorsque le pH est supérieur à 8 on observe: 1) un déplacement de l'équilibre en faveur de l'hydroxychalcone (1% de chromanone à pH 13); 2) une décomposition rapide de l'hydroxychalcone, selon les réactions hydroxychalcone \rightarrow phénolate \rightarrow aldéhyde + acétophénone.

Selon la nature de R (pyrryl, furyl, thiényl, phényl, pyridinyl, quionléinyl) le pourcentage de l'hydrochalcone à l'équilibre varie respectivement de 85 à 2-3.

La constante de vitesse k_1 est également dépendante de la nature de R. Les auteurs donnent une interprétation de l'ensemble de ces phénomènes et en tirent des conclusions sur les conditions optimales de préparation des composés étudiés. [Bad.Lam.]

745 – Determination of anthraquinone in capacitor dielectrics (in English). P. D. Garn and M. Campbell Bott (Bell Telephone Laboratory Inc., Murray Hill, N.J., U.S.A.). *Anal. Chem.*, 33 (1961) 84.

A polarographic procedure for the determination of anthraquinone in capacitor impregnants, mineral oil, chlorinated naphthalene, and chlorinated diphenyls is described. The impregnant is dissolved in chloroform and aliquots are subsequently diluted with chloroform-methanol solvent.

HCl is added to shift the electric tension to more negative values. $MgCl_2$ is used as supporting electrolyte. The current is measured at -0.4 V vs. a mercury pool anode. The exact analytical procedure is described in the paper. [Kl.Gr.]

746 – Investigation of adsorption waves. I. Investigation of the reduction of anthraquinone-1-sulphonic acid at the dropping mercury electrode (in English). F. Péter, I. Rusznák, Gy. Pályi and I. Szabados (Department for Applied Chemistry, Technical University, Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 24 (1960) 363–370.

The reduction of anthraquinone-1-sulphonic acid at the dropping mercury electrode was investigated. In general, polarograms with two waves were obtained. On examining the effect of variations of mercury level, temperature and concentration of depolarizer, the wave appearing at a more positive (-0.700 V vs. S.C.E.) electrical tension proved to be a diffusion wave, whilst that at a more negative (-0.835 V vs. S.C.E.) electrical tension was identified as an adsorption post wave. [E. Juh.]

747 – Infrared spectra, kinetics of reduction and polarography of aromatic polynuclear nitro compounds (in English). R. Zahradník and K. Boček (Institute of Hygiene and Occupational Diseases, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 26 (1961) 1733–1748.

The effect of the aryl structure on the properties of the nitro-group has been studied. Comparison of the half wave tensions and the velocity constants for the reduction of nitro compounds indicates that the surface of the drop-electrode shows a tendency to bring sterically hindered derivatives of nitro compounds into coplanarity. A parallel exists between IR data, velocity constants and half wave tensions for the reduction of nitro compounds and the quantum chemical indices for reactivity of the position where the nitro group is attached. For polarography 1.10^{-4} M solutions in buffers containing 55% ethanol were used. Glycine buffers (pH lower than 2.4 and higher than 9) and phosphate buffers (pH 2.4–7.7) were used. [Ot. So.]

748 – Polarographic determination of dimercaptopropylphthalamidic acid (in German). A. Contrea, Gh. Ciuhandu and M. Rocsin (Landwirtschaftliche Hochschule, Timisoara, Rumania). *Acta Chim. Acad. Sci. Hung.*, 27 (1961) 99–103.

Es wurde der katalytische Effekt der Dimercaptopropylphthalamidsäure (DMS) sowie deren Disulfidabkömmling (DSS) in $CoCl_2$ - bzw. $(CoNH_3)_6Cl_3$ Pufferlösungen, in Gegenwart eines 0.01% Gelatinezusatzes untersucht.

DMS ergibt einen intensiveren katalytischen Effekt als DSS.

Die katalytische Stufe steigt linear mit der DMS Konzentration in Co(II), sowie in Co(III) Salzlösungen. Die Empfindlichkeit der polarographischen Bestimmung ist im Co(II) Puffer am grössten. [E. Juh.]

749 – Polarographic determination of amino acids (in English). T. Noto, H. Sawasa and M. Matsuoka (Tanabe Seiyaku Co., Ltd., Osaka, Japan). *Review of Polarography*, 8 (1960) 36–37.

The polarographic determination of amino acids as a copper complex, which has been introduced by Jones and others, is based on the fact that a soluble copper-amino acid complex is formed by the addition of a copper phosphate suspension into amino acid solution.

Considerable errors are encountered in this method because of a relatively high solubility of copper phosphate and lack of reproducibility.

In this paper, a solution of copper is used instead of the copper phosphate suspension. The pH of the solution is adjusted to 9.0, the precipitate is filtered off and the concentration of copper ion in the filtrate is determined polarographically. [Ta. Fu.]

750 – Polarographic determination of caprolactam and amino acids—the intermediate products of synthetic fibres (in Russian). Ya. I. Turian, Yu. M. Tyurin and B. P. Zhantalai (State Research Institute of the Nitrogen Industry, Lishiansk, U.S.S.R.). *Zhür. Anal. Khim.*, 16 (1961) 352–358.

Methods have been developed for the polarographic determination of caprolactam as ϵ -aminocaproic acid, and of other amino acids by their rapid conversion (in a 0.2 N NaOH solution) into polarographically active Schiff's bases by reaction with formaldehyde, which give a well defined wave at any pH of the supporting electrolyte. This wave is more positive than that of formaldehyde. In a 0.1 N H_2SO_4 solution a linear relation exists between the limiting current and total amino acid concentration. The limiting current constant increases in the series ϵ -aminocaproic: 7-aminoheptanoic: 9-aminopelargonic: 11-aminoundecanoic acids. The half-wave tensions shift to more positive values in the same series. [Ot. So.]

751 – Polarographic determination of cystine, cystine S^{2-} , SO_3^{2-} , $S_2O_3^{2-}$, SO_4^{2-} in the alkaline destruction of keratin (in English). J. Cernák, A. Blazej, J. Stefanec and B. Siles (Department for Chemistry, Slovakian Technical University, Bratislava, Czechoslovakia). *Acta Chim. Acad. Sci. Hung.*, 27 (1961) 87–98.

The knowledge of the fission mechanism of disulphidic bonds in alkaline media is of great interest from the point of view of organic chemistry, to explain the behaviour of alkyl and aryl disulphides at $\text{pH} > 11$, especially in the case of textile technology for the working up of wool, and in leather technology for dehairing and liming leather. The method evolved permits the determination of cystine, cysteine, sulphides, sulphites and thio-sulphates in the presence of each other directly in the samples, without any rearrangement or radical analytical changes. Further, the determination can be made in an inert medium. The method is sensitive, relatively quick and gives reproducible results. This method will be applied in the study of the alkaline destruction of keratin. [E.Juh.]

752 – Polarographic determination of cystine and cysteine in wool (in German). L. Benisek (Wollforschungsinstitut, Brno, Czechoslovakia). *Z. anal. Chem.*, 175 (1960) 244-255.

The polarographic determination of cystine and cysteine in wool is based on the cathodic wave of the cystine and on the anodic wave of the cysteine. The method is simple and no addition of chemical substances to the sample is necessary. The origin of the sulphur dioxide, recognizable in the polarographic curve of the hydrolyzed wool, is discussed. [Di.Ciò.]

753 – On the polarographic study of retinene in the retina homogenate (in English). A. Dolének, M. Černoch and F. Šantavý (Department of Chemistry and Department of Ophthalmology, Medical Faculty, University of Olomouc, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 25 (1961) 1683-1685.

It has been found that native homogenates of bovine retina give a cathodic polarographic wave. The authors draw the conclusion that this wave corresponds to retinene from the decrease of the height of this wave on illumination, and from the fact that a similar wave is not found with other animal organs. On illumination together with the decreasing retinene wave height, the wave height of the anodic waves of SH- compounds increased. [Ot.So.]

754 – The part played by dehydroascorbic acid in the polarographic determination of uranium(VI) in ascorbic acid as supporting electrolyte (in Russian). E. Pálfi and B. Hadobás. *Acta Chim. Acad. Sci. Hung.*, 27 (1961) 155-162.

Versuche wurden durchgeführt um festzustellen, wie und unter welchen Bedingungen die Reduktionsstufe der Dehydroascorbinsäure bei der Bestimmung von Uran(VI) in einer ascorbinsäuren Grundlösung störend wirkt. Es wurde bestätigt, dass sich hier der Grenzstrom der Uranstufe infolge des Superponierens der Stufe der in Gegenwart von reduzierbaren Kationen gebildeten Dehydroascorbinsäure deformiert, und dadurch bei der Auswertung ein negativer Fehler entsteht. Dieser Fehler ist jedoch in Anwesenheit einer zehnfachen Menge an Eisen(III) praktisch vernachlässigbar, und bei einer entsprechender Auswertung erreicht nicht einmal 5% eben einer fünfzigfachen Eisen(III) Menge. Bei noch grösseren Gehalten an Eisen(III) bzw. an einem damit äquivalenten reduzierbaren Kation wurden besondere Verfahren entwickelt, um die Bestimmung von Uran(VI) bei genügender Genauigkeit durchzuführen. Vorliegende Mitteilung gilt als ein Beitrag zu den grundlegenden Arbeiten von Susic und Györbiro. [E.Juh.]

755 – Polarographic study of anabasine and N-methylanabasine N-oxides (in Russian). S. G. Mairanovskii and N. V. Beresheva (Institute of Organic Chemistry, Academy of Sciences, U.S.S.R.). *Izvest. Akad. Nauk U.S.S.R., Otdel-Khim.*, (1960) 938-945.

A thermostatically controlled vessel was used, with two saturated calomel electrodes (the anode and the comparison electrode) at $25 \pm 0.1^\circ$. Polarographic curves were registered partly point by point, with potentiometric control of the drop-electrode tension, and partly by using a registering polarograph. Supporting electrolytes were citrate-phosphate buffers, and borate and KCl-HCl buffers. Waves of all the N-oxides are of diffuse character, their height being proportional to concentration, and they correspond to two-electron transitions. It has been found that the polarographic character of the reduction of N-oxide groups is different for pyridine and piperidine rings, making it possible to distinguish these by polarographic means. [Ot.So.]

756 – Possibilities of polarographic determinations of noradrenalon, adrenalon and aludron. E. Ramontian, A. Gross and I. Schwartz. *Rev. Chim., Acad. répub. populaire Roumaine*, 10 (1959) 111-115. A polarographic method is described for the determination of noradrenalon, adrenalon and aludron in the following electrolytes and at the following pH values:

$\text{NH}_4\text{Cl} + \text{HCl}$	pH = 1.5
$\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH}$	pH = 3.42
NH_4Cl	pH = 4.5
$\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$	pH = 8
$\text{Ca}(\text{OH})_2$	pH = 8.5
KOH	pH = 9.5
LiOH	pH = 9.5

Two polarographic waves are always obtained with the compounds indicated.

[Di.Ciò.]

757 – Polarographic determination of pregnane 3 α , 17 α , 20 α -triol and other acetaldehydogenic urime steroids (in German). L. Stárka and H. Brabenková (Research Institute for Endocrinology, Prague, Czechoslovakia). *Clin. Chim. Acta*, 5 (1960) 423–430.

A urine extract is treated with glycuronidase as described by Stern (*J. Endocrinol.*, 16 (1957) 180). The acetaldehyde and formaldehyde obtained by the hydrolysis may be determined polarographically after periodate oxidation and removal of the excess periodate with bisulphite. The results of the method are in agreement with those obtained by the Stern method. [Gio.Ser.]

758 – Polarographic behaviour of vincamine, the alkaloid of the evergreen Vinca Minor L. (in English). T. Damokos (Institute for Inorganic Chemistry, Technical University, Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 27 (1961) 105–111.

Vincamine, the polarographically inactive alkaloid of Vinca Minor L., can be converted to a polarographically active product by photolysis. This reaction occurs oxidatively. A procedure is given for the polarographic determination of the alkaloid, based upon recording its catalytic wave at -1.90 V vs. a mercury drop electrode in a solution of pH 6.8–7.4. [E.Juh.]

759 – Polarographic determination of rutin in natural extracts after chromatographic separation on polyamide powder (in German). J. Davidek (Zentralforschungsinstitut für Lebensmittellindustrie, Prague, Czechoslovakia). *Z. Lebensm. Untersuch. u. Forsch.*, 112 (1960) 272–275.

A 2–20 g dried sample is extracted in a Soxhlet for 6 h with methanol. The solution is evaporated to dryness and made up to 100 ml with water. An aliquot is percolated through a column of 2 g of polyamide powder. The column is washed with water and then eluted with 30% methanol under UV light. The brown fluorescent fraction is collected. 0.2–1 ml of the eluate is added to 5 ml of 0.2 N H₂SO₄ and 2 ml of 3 M KNO₃ in a Kalousek polarographic vessel, and nitrogen is bubbled through. After 6 min, 2 ml of 2.5 M sodium acetate are added and nitrogen is bubbled through for an additional 4 min. The polarogram is recorded. The half-wave electric tension is -0.54 V vs. S.C.E. [Gio.Ser.]

760 – Potassium microdetermination. N. P. Penceff (University of Sofia, Bulgaria). *Rev. Chim., Acad. répub. populaire Roumaine*, 10 (1959) 231–232.

Two methods are described for the determination of potassium in human serum. About 0.2 cm³ serum (10–100 μ g K) are burned and the ash is dissolved in 0.2 cm³ distilled water. The first of the two methods is based on the precipitation, from the water solution, of a potassium–sodium–cobalt nitrite complex (K_{1.84}Na_{1.16}[Co(NO₂)₆]): the cobalt is then polarographically determined in the precipitate. By the second method, the potassium is precipitated as K₃[Bi(SiO₃)₃]: the bismuth is then determined, with a spectrophotometer, as (BiI)₄⁻. The error, with the two methods, is $\pm 4\%$. [Di.Ciò.]

761 – Amperometric titration of the thio-groups in flour with mercury(II) or silver nitrate. A. H. Bloksma (Instituut voor Graan, Meel en Brood, T.N.O., Wageningen, The Netherlands). *Cereal Chem.*, 36 (1959) 357–368.

The thio-groups in flour may be determined by amperometric titration with mercury(II) or silver nitrate, even at the same pH value of the buffer solutions employed. Comparable results have been obtained with the same sample (2–4 g flour in 100 cm³). The amperometric titration with mercury (II) nitrate occurs with a platinum electrode at -0.15 V. The titration with silver nitrate occurs at -0.10 V in acid or weakly alkaline buffer solutions, at -0.15 V in strongly alkaline [tri(hydroxymethyl)-amino-methane] and at -0.30 V in ammoniacal buffer solutions. [Di.Ciò.]

762 – The polarographic determination of copper, lead, tin and zinc in foodstuffs (in English). W. F. Condliffe and A. J. H. Skrimshire (H. J. Heinz Company, Ltd. Analytical Laboratories, Waxlow Road, Harlesden, London, N.W. 10, England). *J. Polarog. Soc.*, 7 (1961) 10–14.

Methods are described for the determination of copper, lead, tin and zinc in foodstuffs. The procedure involves the wet oxidation of a 5 g sample followed by direct determination in a tartaric acid–nitric acid base electrolyte. Polarography was carried out on a K.1000 linear-sweep cathode ray polarograph in view of the sensitivity and rapidity of this instrument. No extraction procedures are necessary.

Full experimental details are given and recoveries are quoted. An appendix gives details of the methods used to eliminate external vibration which causes difficulties when operating the cathode ray polarograph at high sensitivities. [G.J.Rey.]

763 – Determination of bismuth, copper, lead and antimony in copper anode slime by an a.c. polarograph (in Japanese). Kamihiko Itsuki and Kazuo Nishino (Mitsubishi Metal Mining Co. Ltd., Osaka Refinery, Osaka, Japan). *Japan Analyst*, 9 (1960) 886–889.

A sample is dissolved in nitric and sulfuric acids, and then Bi, Cu, Pb and Sb are precipitated as

sulfides. Antimony sulphide is re-dissolved using sodium sulfide solution. The residual precipitates of Bi, Cu, and Pb are dissolved in nitric acid containing bromine, and the solution is evaporated to dryness.

After the residues have been dissolved in hydrochloric acid, Bi, Cu, and Pb are determined by an a.c. polarographic method.

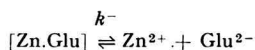
The reserved solution of Sb is treated with sulfuric acid and evaporated to dryness. The residues are dissolved in hydrochloric acid containing hydrazine to reduce antimony, which is determined by an a.c. polarographic method. Results are satisfactory in precision and accuracy for a rapid determination of Bi, Cu, Pb and Sb in copper anode slime. [Ta.Fu.]

764 – Determination of traces of copper, lead and cadmium in water by a hanging mercury drop (in German). Z. Kublik (Laboratorium der Physiko-Chemischen Methoden der Analytischen Chemie des Institutes für Physikalische Chemie, Warszawa, Polen). *Acta. Chim. Acad. Sci. Hung.*, 27 (1961) 79–86.

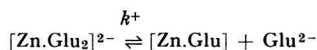
Es wurde eine elektrolytische Methode beschrieben, die Bestimmung von Kupfer-, Blei- und Cadmiumionen im Konzentrationsbereich bis 10⁻⁷% ermöglicht. Die Wasserprobe wird nach Zugabe einer kleinen Menge entsprechender Grundlösung bei konstanter Spannung unter Umrühren elektrolysiert. Nach Beendigung der Anreicherungs elektrolyse wird die Spannung der Kathode kontinuierlich zu positiveren Werten verschoben. Die Oxydationsvorgänge verursachen an den polarographisch registrierten Oxydationskurven die entsprechenden Minima, bei einer für das amalgambildende Metall charakteristischen Spannung. Die Grösse dieses Minimums dient zur Auswertung der Konzentration des zu bestimmenden Stoffes. [E.Juh.]

765 – Polarographic behaviour of aminocompounds in the polarography of inorganic substances. IX. Polarographic behaviour of zinc in a medium of glutamic acid (in German). Tshang-Ye-Sia, J. Doležal and J. Zýka (Institute of Analytical Chemistry, Charles University, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 26 (1961) 1768–1774.

On the basis of experiments carried out, it may be supposed that the determining rate is the dissociation



preceded by the equilibrium



The rate constant of the formation of the complex [Zn.Glu] has been calculated and the value of the stability constant of this complex was found to be $\log K_1 = 5.73$, agreeing well with the value obtained by potentiometric measurement. Experimental data are to be found in the preceding communication (*Collection Czechoslov. Chem. Commun.*, 25 (1960) 3143). [Ot.So.]

766 – Polarographic determination of traces of zinc and acetaldehyde in ethanol (in Czech). L. Miczko. *Ceskoslov. farm.*, 10 (1961) 289–299.

A method for determining substances present in ethanol stored in zinc coated iron barrels has been worked out. Using an ammoniacal ammonium chloride solution the determination of both substances can be carried out without preliminary preparation of the sample, and a rapid evaluation of the quality of pharmaceutical alcohol is made possible. 5 ml of the ethanol sample is mixed with 5 ml of a 0.3 M NH₄Cl and 0.5 M NH₃ solution. The mixture is cooled, and after 5 minutes nitrogen bubbling, a polarogram is traced. The method of standard additions is used. Three waves are observed, the first corresponding to zinc, the second and third to acetaldehyde. [Ot.So.]

767 – High temperature polarography of zinc oxide dissolved in a molten bath of Na₃AlF₆CaF₂ using a platinum micro-cathode (in Japanese). Hidehiko Kido, Masatsugu Ishibashi and Yasumasa Hayakawa (Department of Chemistry, College of Liberal Arts, Saitama University, Urawa, Japan). *J. Electrochem. Soc. Japan*, 28 (1960) 117–119. (English translation in *J. Electrochem. Soc. Japan*, (Overseas Suppl. Edition), 28 (1960) E60).

Numerous polarographic studies on molten salts at low temperatures have been presented, but few at high temperatures, due to technical difficulties. In this paper, the influence of temperature, concentration of ZnO and frequency of vertical vibration of the micro-cathode on the polarographic wave of zinc ion, from zinc oxide dissolved in a molten fluoride bath, (solubility of ZnO in cryolite was 3.2% at 1000°) are discussed. The melt of Na₃AlF₆-CaF₂ (52:48 mole %) was used for the supporting electrolyte, in which ZnO was dissolved.

The following conclusions were made from the results:

- (1) Reproducibility was obtained in the case of a pretreated electrode.
- (2) Concentration of ZnO in the range of 0.3–1.0 wt. %, and temperature of the bath in the range of 960–1020° showed linear relations with the wave height respectively. Depth of the cathode in the bath and frequency of vertical vibration affected the wave height. [Ta.Fu.]

768 – Determination of zinc with ferrocyanide by means of dead stop end-point method (in Japanese). Yoshihiro Ishihara, Moriyuki Koga and Takeo Hirasawa (Mitsubishi Mining and Metallurgical Laboratory, Ōmiya, Saitama Pref., Japan). *Japan Analyst*, 9 (1960) 891–893.

The end-point in the titration of zinc with potassium ferrocyanide is usually decided by a potentiometric method, but measurements of the end-point take a long time and are often difficult when the samples contain trace amounts of zinc. In this paper, the titration of zinc with potassium ferrocyanide in hydrochloric acid solution by means of a dead stop end-point method was studied, and satisfactory results were obtained in the analyses of minerals. [Ta.Fu.]

769 – Determination of zinc in cadmium by a square wave polarographic method (in Japanese). Kamihiko Itsuki and Kazuo Nishino (Mitsubishi Metal Mining Co., Ltd., Osaka Refinery, Osaka, Japan). *Japan Analyst*, 9 (1960) 1062–1065.

The sample is dissolved in nitric and hydrochloric acids. After the solution has been evaporated to dryness, the residue is dissolved in 0.1 M KCl as supporting electrolyte. 0.002% of zinc in cadmium can be determined by the square-wave polarographic method. [Ta.Fu.]

770 – Formation constants of metal acetate complexes. III. Polarographic determination of the formation constants of acetatocadmium(II) and acetatocobalt(II) complexes (in English). N. Tanaka, M. Kamada, H. Osawa and G. Sato (Department of Chemistry, Faculty of Science, Tohoku University, Sendai, Japan). *Bull. Chem. Soc. Japan*, 33 (1960) 1412–1416.

A previously described polarographic method (*Bull. Chem. Soc. Japan*, 32 (1959) 516) was used to determine formation constants of acetatocadmium(II) and acetatocobalt(II) complexes. At ionic strength 0.2 the constants were:– for acetatocadmium(II), 27 at 15°, 16 at 25°, and 20 at 35°; for acetatocobalt(II), 2.1 at 15°, 0.6 at 25° and 35°. [H.H.Fa.]

771 – Determination of Ba and Sr concentrations in NaCl and KCl crystals (in German). J. Trnka (Institute of Technical Physics, Czechoslovak Academy of Sciences, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 25 (1961) 2232–2234.

In connection with the investigation of the influence of additions of barium and strontium in crystals of alkaline halogenides, these elements had to be determined in very small samples, for instance of dimensions 4 × 4 × 0.5 mm in concentrations of the order of magnitude 0.01–0.001%. The differential polarographic arrangement according to Semeramo (*Chemie (Prague)*, 55 (1942) 351) was used. A scheme of the arrangement is included. Capillaries were chosen carefully so as to obtain equal drop rates in both electrode systems. Small differences were eliminated by adjusting the reservoir height. Solutions were prepared in such a way, that one solution contained about 1 g per 5 ml water of the pure sample, the other exactly the same amount of the salt and a small amount of the element to be determined. Into each electrolytic vessel 2 ml of one of the solutions and 5 drops of a 0.5% gelatine solution were placed. The determination was carried out by the method of standard additions. The differential curve was registered first, and then a certain amount of standard solution placed in one vessel, the same amount of water in the other, and a differential curve was again registered. [Ot.So.]

772 – The polarographic determination of boron. Further studies of the mannitol-sulphite system. Application of the cathode ray polarograph (in English). G. F. Reynolds and E. A. Terry (Chemical Inspectorate, Royal Arsenal, Woolwich, London, S.E. 18, England). *J. Polarog. Soc.*, 7 (1961) 2–9.

A study has been made of the polarographic determination of boron by means of the formation of mannitol-boric acid and its subsequent reaction with sodium sulphite. It has been shown that earlier conclusions are valid and that the limit of detection of the original method is about 2 μg/ml of boron. A new step height–concentration relationship has been found, which offers greater simplicity and a linear calibration graph. Modifications in technique and the use of the linear-sweep cathode ray polarograph have enabled the limit of detection to be extended to 0.1 μg/ml of boron. [G.F.Re.]

773 – Determination of boric acid (in Czech). F. Ráb (Department of Chemistry, Agricultural School, Brno, Czechoslovakia). *Chem. listy*, 55 (1961) 919–929.

An exhaustive review of the determination of boric acid, based on 253 literature references. In the paragraph on polarographic methods it is stated that no direct methods are known, but that on using a supporting electrolyte of mannite and sodium sulphite two reduction waves are observed at –0.50 V and –1.01 V vs. S.C.E., both corresponding to the reduction of boric acid by sulphite ions. [Ot.So.]

774 – Polarographic examination of aluminium alloys (in German). G. Farsang and E. Pungor (Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 27 (1961) 113–117.

Es wurde ein Verfahren für die polarographische Bestimmung der Schwermetallkomponenten von Aluminiumlegierungen entwickelt. Das vorgeschlagene Verfahren bietet den Vorteil, dass die Analyse in derselben Lösung mit genügender Genauigkeit durchgeführt werden kann. Wendet man die vorgeschlagene, mit Ammoniak alkalisierte, seignettesalzhaltige Grundlösung an, so ist Kupfer, Nickel, Zink, Mangan und Eisen nebeneinander in Anwesenheit von Aluminium gut messbar. In Gegenwart der erwähnten Komponenten ist es ratsam, die Bestimmung des Nickels nach Zugabe von Kaliumzyanid durchzuführen. [E. Juh.]

775 – Polarographic determination of indium in gallium metal (in Russian). S. I. Sinyakova, N. A. Rudnev, Shen-Yu-Chi and R. Jumaev (Institute of Geochemistry, Academy of Sciences, U.S.S.R.). *Zhur. Anal. Khim.*, 16 (1961) 32–35.

A polarographic and an oscillographic method are suggested for the determination of indium in gallium metal. It is possible to determine as little as 10⁻⁶% indium with $\pm 15\%$ accuracy. The metal is dissolved in aqua regia and indium is coprecipitated with cobalt sulfide after addition of cobalt chloride and sodium sulfide. After extraction of indium by CCl₄, the polarogram is registered in a hydrochloric acid medium. [Ot. So.]

776 – Reduction of indium on the mercury drop electrode in the presence of some inorganic and organic cations (in Russian). Kh. Z. Braygina (A. M. Gorkii Uralian State University, U.S.S.R.). *Doklady Akad. Nauk S.S.S.R.*, 130 (1961) 797–799.

In 0.1–3.0 N KCl solutions the following complexes have been found: InCl²⁺, InCl₂⁺, InCl₃. Indium reduction in chloride solutions begins at an electric tension near to the mercury zero discharge value. The influence of Na, K, Rb, Cs, La, Sr ions and of tetramethyl and tetrabutylammonium chloride has been investigated. The results are discussed in detail. [Ot. So.]

777 – Determination of zirconium in niobium alloys (in Russian). Yu. A. Tshernikov and V. M. Vladimirova (State Research Institute of Rare Elements, U.S.S.R.). *Zavodskaya Lab.*, 26 (1960) 1207–1210.

0.3 g of the alloy are dissolved in HNO₃, and a few drops of HF are added. 15 ml 1:1 H₂SO₄ are added to the solution, which is then evaporated. After adding 2 g KHSO₄ the solid is dissolved in 20% tartaric acid and made up to volume. An excess of 0.01 M EDTA is added to an aliquot of this solution, which is neutralised to Tropaeolin OO (pH 2). The EDTA excess is then titrated with 0.01 M Bi solution, using amperometric titration with a mercury drop electrode and a saturated calomel electrode. 0.3 V are applied to the electrodes. [Ot. So.]

778 – Determination of traces of lead in high-purity metals (in Japanese). Tadasi Yanagihara, Nobuhisa Matano and Akira Kawase. (National Research Institute for Metals, Tokyo, Japan). *Japan Analyst*, 8 (1959) 576–581.

Lead chromate has a low solubility, and thus chromate is useful as a precipitating agent for lead. Barium chromate coprecipitates well with lead chromate and can be used as a coprecipitating agent.

The metal sample is converted, directly or indirectly, into perchlorate. Coprecipitation with barium chromate is effected in alkaline ammonia solution for those samples containing copper, zinc and silver, and in slightly alkaline solution for those containing nickel and magnesium. The chromium is dissolved and oxidized to chromic acid with perchloric acid, and barium salt is added in dilute acetic acid solution for coprecipitation.

The mixture of coprecipitated barium chromate and lead chromate is treated with perchloric acid–hydrochloric acid mixture to remove chromium, and the lead is determined spectrophotometrically with dithizone, or by a polarographic method (square-wave polarograph) using hydrochloric acid as a supporting electrolyte. Several microgram quantities of lead in high-purity metals can be determined by this method. [Ta. Fu.]

779 – Polarographic reduction of tetraethyl lead hydroxide (in Russian). I. A. Korshunov and N. I. Malyugina (Chemical Research Institute of the State University, Gorkovsk, U.S.S.R.). *Zhur. Obshchei Khim.*, 31 (1961) 1062–1067.

An electronic type CLA polarograph was used, with a mercury drop period of 1.1 sec, using a saturated calomel comparison electrode. As supporting electrolytes, neutral salts, alkaline solutions, acetate–phosphate buffers (Britton–Robinson) pH 1.86–11.58 and ammonium oxalate solutions of pH 3.0–11.1 were used. Two waves are observed, the first being removed on addition of gelatine. The second wave in acid solutions is covered by the hydrogen wave of the electrolyte. $E_{\frac{1}{2}}$ values and diffusion current values are tabulated for the different supporting electrolytes used. It is proposed that the reduction process includes the formation of a free radical (C₂H₅)₃Pb⁺. [Ot. So.]

780 – A.c. polarographic analysis by harmonics measurements (in English). H. H. Bauer (Section of Agricultural Chemistry, Faculty of Agriculture, University of Sydney, Australia). *J. Electroanal. Chem.*, 1 (1959–1960) 256–258.

Measurement of the amplitude of the second harmonic provides an analytical method for the estimation of the concentration of unknown samples. As compared with normal a.c. polarographic analysis this method is far more sensitive and allows a better separation of the individual ion peaks in a solution containing lead, thallium and cadmium. Typical curves are reproduced. [Su.Mo.Ce.]

781 – Analytical chemistry of wine. IX. Voltammetric determination of traces of thallium (in German). H. Eschnauer and R. Neeb (Analytische Abt. anorganisch-chemisches Institut, Mainz a. Rhein, West Deutschland). *Z. Lebensm. Untersuch.*, 112 (1960) 275–280.

Minute traces of thallium cannot be determined by polarography at the dropping mercury electrode, since the diffusion current is much smaller than the condenser current. A voltammetric method using a mercury-plated Pt wire electrode has therefore been set up.

The organic matter from 50–100 ml of wine is destroyed by boiling with H_2SO_4 and H_2O_2 ; the Tl is extracted with bromide–ether, and the polarogram is recorded. The curve displays a sharp peak whose height is proportional to the Tl concn. $1.5 \mu\text{g}$ of Tl can be determined with good accuracy. [Gio.Ser.]

782 – Polarographic and acid properties of thorium perchlorate in acetonitrile (in English). I. M. Kolthoff and S. Ikeda (School of Chemistry, University of Minnesota, Minneapolis, Minn., U.S.A.). *J. Phys. Chem.*, 65 (1961) 1020–1026.

In acetonitrile solution, thorium perchlorate behaves like a strong dibasic acid with the first dissociation constant about 10^{-6} and the second relatively large. The insoluble product formed by electrolysis, and the neutralization product formed with diphenylguanidine, contain about 2 ClO_4^- per thorium atom. The polarographic wave height of thorium perchlorate in acetonitrile is proportional to concentration. [D.S.Ru.]

783 – Polarography in liquid ammonia above its critical temperature (in English). W. Hubicki and M. Dabkowska (Department of Inorganic Chemistry, University of Mariae Curie Sklodowska, Lublin, Poland). *Anal. Chem.*, 33 (1961) 90.

The preparation and chemical properties of the anhydrous liquid ammoniate of lithium perchlorate are described. This liquid can be taken as the supporting electrolyte for polarography of several cations, such as Tl^+ , Cu^{2+} , Pb^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , Cr^{3+} , In^{3+} , Zn^{2+} , IO_3^- , IO_4^- , CrO_4^{2-} , and BrO_3^- . The paper gives the results for the polarographic measurements of lead, cadmium and zinc at temperatures from 25–190°. Half wave data and wave heights for concentrations of the ion in question of about $10^{-3} M$ are tabulated. A figure of the polarograms of the three ions is shown. $N \text{ LiClO}_4 \cdot \text{NH}_3$ itself gives well defined waves, beginning at -1.7 V vs. a mercury pool anode.

[Kl.Gr.]

784 – Polarographic determination of niobium, titanium and iron in tantalum metal and oxide (in Russian). D. I. Kurbatov (Institute of Chemistry, Academy of Sciences, U.S.S.R.). *Zhur. Anal. Khim.*, 16 (1961) 36–38.

Small amounts of Fe, Ti and Nb (0.01–1.0%) give distinct polarograms in the presence of large quantities of tantalum (99%) using pyrophosphoric acid as supporting electrolyte. The limiting currents are proportional to concentration. A method has been developed for the determination of the elements named in tantalum metal and oxide on a single polarogram with a relative error of 3–5%. The metal is dissolved in HF and HNO_3 ; for the oxide HNO_3 is unnecessary. Pyrophosphoric acid is added and evaporated to eliminate HF and nitrogen oxides. The resulting solution is used for polarography. [Ot.So.]

785 – Determination of antimony in titanium sulfate solution by alternating-current polarography (in Japanese). Kamiyoko Itsuki and Mitsuyoshi Nagao (Mitsubishi Metal and Mining Co., Shinkawasaki-cho, Kita-ku, Osaka, Japan). *Japan Analyst*, 8 (1959) 824–826.

In the usual determination of antimony in concentrated titanium sulfate solution, tedious procedures for the separation of large amounts of titanium are needed. In this paper, the simple and rapid determination of antimony was investigated by the use of alternating current polarography. The effect of acid concn. upon a.c. polarography of Sb is minimized in 2N HCl containing 6N H_2SO_4 , and the influence of Ti (< 4 g per 100 ml) and Fe^{2+} (< 2 g) is negligible. The working curve is linear for < 2 mg of Sb per 100 ml. The error is 1.3%. [Ta.Fu.]

786 – Polarographic determination of the stability-constant of EDTA–Bi complexes and their analytical importance (in German). I. Miklós and R. Szegedi (Institut für Industrielle Metallforschung, Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 26 (1961) 365–374.

Verfasser bewiesen, dass Wismut mit Äthylendiamintetraessigsäure einen sehr stabilen Komplex bildet. Auf Grund zweier Methoden, namentlich aus der Verschiebung der Halbstufenspannung als Funktion des pH Wertes und aus dem Zustand des Austauschgleichgewichtes Verfasser bestimmen

den Annäherungswert der Stabilitätskonstante obigen Wismutkomplexes. Aus den Mittelwerten der in Betracht genommenen Ergebnisse, die Stabilitätskonstante ergab sich zu $\log K = 27.94$. Verfasser arbeiteten weiterhin ein indirektes analytisches Verfahren zur polarographischen Bestimmung des Wismutgehaltes von metallischem Zink in Anwesenheit von Kupfer und Blei als Begleitelementen unter Anwendung von Komplexon(III) aus. [E. Juh.]

787 – Investigation of the kinetics of chromic acid reduction on a rotating disc electrode (in Russian). E. Budevskii and S. Toshev (State University, Sofia, Bulgaria). *Doklady Akad. Nauk S.S.S.R.*, 130 (1961) 1047–1050.

The mechanism and kinetics of the electrochemical reduction of chromic acid have been investigated using a rotating gold disc electrode at constant electric tension. The solution contained 200 g/l chromic acid (CrO_3) and 0.5–8 g/l H_2SO_4 . Temperatures were held constant at 10, 25 and 45°. The dependence of maximum current i_{max} on $z^{\frac{1}{2}}$ (z being the speed of rotation) is more complicated than would correspond to purely diffusion-limited current (when this dependence would be linear). At high rotation speeds current intensity is less than would correspond to a linear dependence, which is probably caused by some preceding process (e.g. dissolution of a surface layer, formation of electroactive complexes etc.). For the case of this process being of first order with respect to sulphate ion concentration, the equation

$$\frac{\eta}{i} = \frac{1}{i_d} + \frac{1}{i_k}$$

is proposed, i_d being the diffusion-limited current and i_k the current limited by the kinetics of the said process. [Ot. So.]

788 – Contributions to the polarography of selenium. IV (in German). K. Jónás (Institute of General and Inorganic Chemistry, University for the Chemical Industries, Veszprém, Hungary). *Acta Chim. Acad. Sci. Hung.*, 25 (1960) 379–389.

In acidic solutions of selenium(IV) the H_2SeO_3 molecule and the HSeO_3^- ion, respectively, are polarographically reduced to hydrogen selenide. In an alkaline pH range, selenite ions (SeO_3^{2-}) undergo a four electron reduction in the presence of bivalent cations or of NH_4^+ ions. The diffusion-current constant markedly decreases, due to the formation of mercury selenide, when the concentration of selenium(IV) is raised in an acidic medium. An ammoniacal ammonium chloride buffer solution of pH 8–10 is suggested for analytical purposes. [E. Juh.]

789 – Determination of tellurium in crude copper, silver and selenium by square wave polarography (in Japanese). Kamihiko Itsuki, Asatsugu Ide and Akiyoshi Minehira (Mitsubishi Metal and Mining Co., Ltd., Osaka Refinery, Osaka, Japan). *Japan Analyst*, 9 (1960) 840–844.

An analytical method has been devised for the determination of tellurium in crude copper, silver bullion and high purity selenium by square wave polarography.

Tellurium was separated from copper or silver by co-precipitation with ferric hydroxide, and from selenium by volatilization of selenium, and then determined by a square wave polarographic method in 1.5 N phosphoric acid as a supporting electrolyte. The proportionality between height of the wave and concentration of tellurium, and the effects of coexisting elements were investigated; from the results an analytical procedure was established.

Analytical values obtained by the recommended method using relatively small samples agreed with those obtained by the d.c. polarographic method and the time necessary for an analysis was relatively short. [Ta. Fu.]

790 – Polarographic determination of uranium in ascorbic acid as supporting electrolyte (in German). J. Minczewski and A. Sobkowska (Institut für Kernforschung der Polnischen Akademie der Wissenschaften, Warszawa, Polen). *Acta Chim. Acad. Sci. Hung.*, 27 (1961) 143–153.

Die polarographische Wellen von UO_2^{2+} und VO^{2+} in Überchlorsäure und Ascorbinsäure wurden in verschiedenen pH-Bereichen geprüft.

Die UO_2^{2+} -Welle in Überchlorsäure und Ascorbinsäure ist reversibel und gestattet die quantitative Bestimmung des Urans. Die VO^{2+} -Welle ist sowohl in Überchlorsäure als auch in Ascorbinsäure irreversibel.

Die UO_2^{2+} -Reduktionswelle erhöht sich in Gegenwart von VO^{2+} -Ionen in pH-Bereich von 3–5 in Ascorbinsäure, weil unter solchen Umständen die VO^{2+} -Ionen in der Nähe des UO_2^{2+} -Abscheidungs-potentials eine kleine Welle bilden. Bei pH ca. 10 können die UO_2^{2+} -Ionen auch bei einem fünf-fachen Überschuss an VO^{2+} mit einem maximalen Fehler von 4% bestimmt werden. [E. Juh.]

791 – Increase in the sensitivity of the polarographic determination of uranium in the presence of vanadium and phosphate ions (in Russian). V. G. Sochevanov, N.V. Shmakova, L.T. Martynova and G. A. Volkova. *Zhur. Anal. Khim.*, 16 (1961) 362–363.

It has been found that the polarographic uranium wave, catalysed by uranium(IV) ions is better defined in the presence of phosphate ions. The solution for analysis is placed in a 25 ml volumetric flask, 2 ml conc. HCl and a defined amount of sodium vanadate are added. The orange coloured solution is then reduced at 40–50° by ascorbic acid. The reduction is complete when the solution is coloured pure blue. 0.6 ml 10 M NaOH and 10 drops 0.1% thymol solution are added and the solution is made up to volume. From a portion of this solution oxygen is removed by CO₂, and a polarogram is registered from 0.0–0.4 V vs. S.C.E. [Ot.So.]

792 – Polarographic determination of uranium(VI) in uranium dioxide (in Japanese). Fumito Nakashima (Hitachi Research Laboratory, Hitachi Ltd., Hitachi, Ibaragi Pref., Japan). *Japan Analyst*, 9 (1960) 961–962.

Uranium(VI) is determined polarographically after the sample (ca. 100 mg) has been dissolved by boiling for 5 minutes with 4 ml of concentrated phosphoric acid and diluted with 10 ml of distilled water.

It takes only about 15–20 minutes for the whole procedure. This method can be applied to the determination of U(VI) in uranium dioxide of which the oxygen:uranium ratio is 2:3 and in various uranium compounds. U(VI) can be determined satisfactorily at the low concentration of 0.05% as UO₂²⁺. [Ta.Fu.]

793 – Polarography in water and water-ethanol. I. Uranium(IV) in chloride and perchlorate media in one molar acid (in English). William Ves Childs and Edward S. Amis (Chemistry Department, University of Arkansas, Fayetteville, Ark., U.S.A.). *J. Phys. Chem.*, 65 (1961) 1080–1081.

The reduction of U(VI) has been studied in 1 M acid solution in water and ethanol concentrations up to 92.2 wt.%. The Ilkovič diffusion current constant (I) has been calculated and is given for a number of solutions. The data have also been examined by the use of Lingane's equation.

Evidence in perchlorate media indicated the reduction to be reversible with one electron transferred. However, as the chloride concentration increased, especially in high ethanol solvents, the reduction appeared to be irreversible and approached a two electron reduction. [D.S.Ru.]

794 – Oscillographic polarography. Kinetics of cathodic and anodic polarisation for UO₂²⁺ in HClO₄ solution (in Russian). Ya. P. Gokhstein and Gao Tsai-shen (V. I. Vernadski Institute of Geochemistry and Analytical Chemistry, Moscow, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 1611–1615.

The cathodic and anodic processes of the first uranium wave in 0.05 N HClO₄ + 0.45 N NaClO₄ are shown to be irreversible. Also the second stage of UO₂²⁺ reduction is irreversible. The second anodic peak corresponds to oxidation of UO⁺ to UO²⁺. Rate constants and free energies of activation have been calculated for both stages of the two-step electrode process. [Ot.So.]

795 – Amperometric titration of uranium(VI) with chromous salts (in Russian). Z. A. Gallai and G. E. Kalentshuk (State University, Moscow, U.S.S.R.). *Zhur. Anal. Khim.*, 16 (1961) 63–67.

A vibrating platinum microelectrode and a saturated calomel electrode were used. Titrating solutions used were 0.04195 N CrCl₂ or 0.04771 N CrSO₄, whose titre was determined by bichromate. The titre was stable 25–30 days. Supporting electrolytes investigated were HCl and H₂SO₄. 2–6 N H₂SO₄ media are most suitable. Lead does not interfere up to a ratio of 1:50, zirconium and thorium up to 1:1000. Iron does not interfere. [Ot.So.]

796 – Polarographic determination of traces of rhenium on the basis of catalytic waves (in German). K. Györbirö (Institute for Inorganic Chemistry, Technical University, Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 27 (1961) 119–122.

Es wurde festgestellt, dass das Perrhenat-ion die polarographische Reduktion der Tellursäure in saurer Lösung katalysiert. Auf Grund der Messung der Höhe der katalytischen Welle lässt sich das Perrhenat-Ion in 1:4 verdünnten schwefelsäuren Grundlösungen in Konzentrationen von 4.10⁻⁷–10⁻⁵ M bestimmen. [E.Juh.]

797 – Polarographic analysis of traces of metals in iron ores (in Italian). G. Odone and G. Picasso (Cornigliano S. p. A., Genoa, Italy). *Chim. e Ind. (Milan)*, 42 (1960) 598–605.

Methods of rapid polarographic determination of Cu, Pb, Zn, Ni and Sn in iron ores are described. Cu, Pb and Zn are determined in 1 M HCl at pH 4; Ni and Zn in 1 M NH₄Cl and 1 M NH₃; Sn in 6 N HCl. Some typical polarograms and results are shown. The whole procedure for the determination in iron ore of the above mentioned metals can be effected in 24 hrs. [Gio.Ser.]

798 – Polarographic determination of nickel, zinc, manganese and iron in ferrites (in German). W. Kemula and S. Rubel (Institute of Inorganic Chemistry, University of Warsaw, Poland). *Acta Chim. Acad. Sci. Hung.*, 27 (1961) 133–136.

Zur Bestimmung von Nickel, Zink, Mangan und eventuell Eisen in Ferriten wird eine schnelle und

genügend genaue und zuverlässige Methode empfohlen, die zur Produktionskontrolle bei der Herstellung der Ferrite gut Anwendung finden kann. Bei Serienanalysen ist die nötige Zeitdauer noch geringer. [E.Juh.]

799 – Determination of iron in sulfuric acid by square-wave polarography (in Japanese). Yoshikazu Yasumori and Tadashi Eguchi (Yanagimoto Co., Ltd., Kyoto, Japan). *Japan Analyst*, 9 (1960) 1049–1052.

In experiments in which a square-wave polarogram of an iron-complex was taken in 0.36 *M* sulfuric acid saturated with oxalic, citric or tartaric acid, respectively, the wave of the iron-complex appeared only in the electrolyte saturated with oxalic acid. The iron-wave became higher as the concentration of sulfuric acid was decreased in the 1 *M* oxalic acid electrolyte and it was overlapped with the mercury-wave when the concentration of sulfuric acid was over 1 *M*. The iron-wave became higher as the concentration of oxalic acid increased in 0.36 *M* sulphuric acid, but the variation of the wave-height was not so large when the sulfuric acid concentration was changed.

The temperature coefficient of the wave-height of the iron-complex in 0.36 *M* sulfuric acid and 1 *M* oxalic acid electrolyte was about 1% per degree. Although copper is often contained in oxalic acid as an impurity, the copper-wave appeared at the potential of -0.4 V more negative than the iron-wave in the above electrolyte. [Ta.Fu.]

800 – Polarographic determination of copper, zinc and chromium in cast-iron turnings. J. Stabryn (Moravské Chem. Závody, Ostrava, Czechoslovakia). *Hutnické listy*, 15 (1960) 302.

A 5 g sample is dissolved in HNO_3 and HCl. Carbon and SiO_2 are removed by the usual methods. Fe is extracted with ether and the remaining solution is diluted to 100 ml. To 20 ml, 5 ml of conc. NH_3 , 10 ml of 5 *M* NH_4Cl and 1 ml of 0.5% gelatin solution are added. The solution is brought to 50 ml and polarographed. Cu is determined between 0–0.7 V and Zn between 1.1–1.5 V.

To 10 ml of the original solution, 2 ml of H_2O_2 (30%) and 10 ml of NaOH (20%) are added. After heating to remove excess H_2O_2 , 1 ml gelatin solution is added, the solution is diluted to 50 ml and polarographed. CrO_4^{2-} is determined between -0.4 and -1.2 V. Results are evaluated by the standard addition method. [Gio.Ser.]

801 – Determination of traces of copper and lead in cast iron and pig iron. (Studies on the technoanalytical method by means of S.W. polarograph. I.) (in Japanese). Nobuo Tajima and Moriji Kurobe (Toyoda Automatic Loom Works, Ltd., Aichi Pref., Japan). *Japan Analyst*, 9 (1960) 801–806.

Quantitative determinations of 0.005–0.02% copper and 0.0002–0.002% lead in pig iron and cast iron were made by means of a square wave polarograph. 1 g of sample is dissolved by heating in a mixture of 15 ml hydrochloric acid, 5 ml nitric acid and 5 ml water, and the solution is evaporated to dryness. The residue is taken up in 6 *N* hydrochloric acid, the precipitate is filtered off, and the filtrate is transferred into a separating funnel. This is shaken with 30 ml methylisobutyl ketone to separate iron. The aqueous layer is transferred into another separating funnel and one more extraction is performed. The aqueous layer is concentrated to about 2 ml, and is heated with nitric acid to decompose organic compounds by oxidation. It is further concentrated, 2.5 ml hydrochloric acid is added, and the polarogram is taken after dilution to 25 ml with water.

By using a 1 g sample containing 1% manganese and chromium, and 0.1% arsenic, estimation of the above content of copper and lead was possible for a sample containing 0.0005% lead and 0.1% copper. The time required for the estimation of copper and lead was about 40 min. [Ta.Fu.]

802 – Determination of calcium in iron and steels by a polarographic method. (Studies on the determination of traces of elements in iron and steels. III.) (in Japanese). Shizuya Maekawa and Yoshio Yoneyama (Muran Plant, The Japan Steel Works, Ltd., Muroran, Hokkaido, Japan). *Japan Analyst*, 9 (1960) 811–815.

The sample is decomposed by aqua regia. Silica is removed after evaporating to dryness. Hydrochloric acid is added to the residue, and iron in the solution is extracted into butyl acetate. The aqueous layer is evaporated with nitric and perchloric acid until it fumes vigorously. After cooling and dilution, the solution is transferred to a mercury cathode electrolysis apparatus to remove the bulk of manganese etc. After the electrolysis is completed, calcium is precipitated as oxalate from the homogeneous solution. The residue is ignited and dissolved in hydrochloric acid and is transferred to a small volumetric flask. Then, Přibil's zinc-EDTA basic solution is added, and calcium is determined indirectly from the wave height of zinc ammin isolated. It shows $E_{\frac{1}{2}} = -1.38$ V vs. S.C.E. The behaviour of a micro amount of calcium was investigated with the aid of ^{45}Ca . When three grams of sample were taken, calcium in the range of 10–300 ppm was determined by the proposed method within a deviation of 12%. [Ta.Fu.]

803 – Methods of analysis of ferrites. I. Polarographic and complexometric determination of nickel and zinc in manganese-zinc, and nickel-zinc ferrites (in Polish). W. Kemula, K. Brajter and S.

Rubel (Department of Inorganic Chemistry, University, Warsaw, Poland). *Chem. anal. (Warsaw)*, 6 (1961) 331-341.

Complexometric and polarographic methods of nickel and zinc determination in Mn-Zn and Ni-Zn ferrites have been developed. For complexometric determination, zinc was separated on the anion-exchanger Lewatit M II, and titrated with EDTA using Eriochromblack T as an indicator. Nickel was precipitated as dimethylglyoxime, dissolved in hydrochloric acid and after addition of an excess of EDTA, back-titrated with standard zinc solution.

In the polarographic method both metals were determined in a supporting electrolyte consisting of 0.1 M KCNS, 0.04 M sodium tartrate (to complex excess of iron) and 0.005% of tylose. If necessary NaOH solution was added dropwise to provide pH 4-5. The solutions were deaerated and the polarograms were recorded in the range from -0.45 to -1.25 V. In this supporting electrolyte the half-wave electric tensions were $U_{\frac{1}{2}} = -0.75$ V, and $U_{\frac{1}{2}} = -1.05$ V vs. S.C.E. for nickel and zinc respectively. Results obtained with both methods were compared and discussed. In the complexometric determination the error is about 1.5% and in polarographic determination about 2.5%. [Ad.Hu.]

804 - Methods of analysis of ferrites. III. Polarographic determination of manganese and iron (in Polish). W. Kemula and S. Rubel (Department of Inorganic Chemistry, University of Warsaw, Poland). *Chem. anal. (Warsaw)*, 6 (1961) 347-352.

A polarographic method for determination of manganese and iron in ferrites has been developed. As a supporting electrolyte the alkaline solution of triethanolamine, containing sodium sulphite was used. The best developed polarographic waves, and therefore most convenient analytical conditions (lack of mutual influences, proportionality of wave height to concentration) were obtained in 0.1 M triethanolamine and 0.2 M KOH (pH \sim 13). In this solution the half-wave electric tensions are $U_{\frac{1}{2}} = -0.50$ V and $U_{\frac{1}{2}} = -1.10$ V vs. S.C.E. for manganese and iron, respectively. The precision of the determination was about 2%. The time necessary for determination of both elements was 50 min, and for manganese alone, 30 min. [Ad.Hu.]

805 - Influence of the adsorption of oxygen on the oxidation of ferrocyanide ions on a gold electrode (in Russian). O. L. Kabanova (V. I. Vernadski Institute of Analytical Chemistry, Academy of Sciences, U.S.S.R.). *Zhur. Anal. Khim.*, 16 (1961) 135-140.

The anodic oxidation of ferrocyanide ions on a rotating gold electrode has been studied polarographically in 1 N and 10^{-3} N HClO₄. The adsorption of oxygen decreases the rate of oxidation of ferrocyanide ions 1-1.5 times. The deceleration of the oxidation reaction is greater in 1 N than in 10^{-3} N HClO₄. The deceleration of the ferrocyanide oxidation increases with increasing potential of the oxygen adsorption up to the value of 1.60 V in 1 N HClO₄ and 1.1-1.3 V in 10^{-3} N HClO₄. After reaching this electric tension the deceleration decreases. [Ot.So.]

806 - Determination of trace amounts of cobalt (in German). W. Haerdi, J. Vogel and D. Monnier (Laboratorium für anorganische, analytische und Mikrochemie, Universität Genf, Schweiz). *Acta Chim. Acad. Sci. Hung.*, 26 (1961) 105-111.

Auf Grund eingehender Versuche werden die absoluten und relativen Bestimmungsgrenzen von drei verschiedenen Methoden, nämlich Polarographie, Spektrophotometrie und Aktivierungsanalyse, zur Bestimmung von Kobaltspuren vorgeführt, und ihre Empfindlichkeit, Einfachheit und Schnelligkeit bei der praktischen Durchführung der Analysen einem kritischen Vergleich unterworfen. [E.Juh.]

807 - Polarographic studies of metallic complexes. VI. Tetracyanocobaltate(III) complex (in English). N. Maki and R. Tsuchida (Department of Chemistry, Osaka University, Kita-Ku, Osaka, Japan). *Bull. Chem. Soc. Japan*, 34 (1961) 891-892.

Disulphono-tetracyanocobaltate(III) (Co(CN)₄(SO₃)₂)⁵⁻ gave a well defined polarographic wave in 0.5 M sodium sulphite. The diffusion current was proportional to concentration in the range $5 \cdot 10^{-4}$ - 10^{-2} M. The process involved transfer of two electrons, and was quasi-reversible. Oscillo-graphic studies on this point are to be published later. Suggestions for the mechanism of the reduction are made in terms of the atomic orbitals involved. [H.H.Ba.]

808 - Polarographic and amperometric determination of ruthenium (in Russian). N. K. Pshenitsin and N. A. Ezerskaya (Institute of General and Inorganic Chemistry, Academy of Sciences, U.S.S.R.). *Zhur. Anal. Khim.*, 16 (1961) 196-200.

A method for the polarographic determination of ruthenium, using the wave of RuCl₆²⁻ reduction on a platinum microelectrode has been worked out. The method permits the determination of 1-200 μ g/ml ruthenium in the presence of Pt, Pa, Rh, Os and some other non-precious metals. The solution of Na₂RuCl₆ is obtained by evaporating with NaCl and after dissolution of the residue, heating in the presence of HCl. The solution is diluted with HCl, made up to volume and a polaro-

gram is registered from +0.9–+0.5 V. $E_{1/2} = 0.72$ V vs. S.C.E. A method for the amperometric titration of ruthenium solutions has also been worked out, which is useful for the same concentrations as above, but simpler. The titrant is hydroquinone volumetric solution. A rotating platinum electrode is used. The cathodic current of tetravalent ruthenium at +0.5 V vs. S.C.E. is used. [Ot.So.]

809 – Contribution to the polarography of rhodium oxalate complexes (in German). D. M. Wagnerová (Institute of Nuclear Research, Czechoslovak Academy of Sciences, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 26 (1961) 2076–2078.

Polarographic behaviour of rhodium oxalate complexes has been investigated in oxalic and perchloric acid media. The red modification of rhodium(III) chloride gives in 0.5 M HClO₄ a cathodic wave of $E_{1/2} = -0.39$ V vs. S.M.E. After heating Rh(III) chloride with excess oxalic acid for a short time the wave shifts 40 mV to the negative. At the same time the colour of the solution changes from red-brown to yellow. The $E_{1/2}$ of this oxalate complex in 0.5 M oxalic acid is -0.43 V vs. S.M.E. Wave height is linearly dependent on concentration and as with Rh(III) chloride corresponds to a two-electron reduction. When heating with oxalate is continued for longer than 3 minutes, another wave appears at -0.83 V. [Ot.So.]

810 – Polarographic determination of Pt on the rotating platinum micro-disc electrode (in Russian). V. S. Temianko, M. B. Bardin and Y. S. Lyalikov. *Izvest. Vysshikh Ucheb. Zavendi. Khim. i. Khim. Technol.*, 2 (1959) 503–508.

H₂PtCl₆ gives two waves on a rotating Pt disc electrode (0.78 sq. cm) in a supporting medium containing 0.1 M NaNO₃. The first one, with a half wave value of -0.343 V vs. S.C.E., corresponds to the reduction of Pt(IV), and the second one is due to the reduction of H⁺.

Various conditions are studied and the use of 0.1 N NaNO₃ as supporting electrolyte is recommended. A Pt plate having an area of 400 sq. mm is used as an anode.

The polarograms are recorded in the usual way. The proportionality between concentration and wave height is good in the range $3.6 \cdot 10^{-5}$ – $7.2 \cdot 10^{-4}$ M. The error is 5%. [Gio.Ser.]

811 – Polarographic determination of base-metal impurities in refined iridium (in Russian). N. K. Pshenitsyn, N. A. Ezerskaya and V. D. Ratnikova. *Analiz. Blagorod. Metal. Akad. Nauk S.S.R., Institut Obschei i. Neorg. Khimii im N.S. Kurnakova*, (1959) 70–74.

A sample of 5 g of iridium is dissolved in HCl (1:1) by electrolysis at 5 V and 0.15 A/sq cm. The solution is evaporated to dryness and dissolved in 500 ml of water containing 0.5 g of NaCl and HCl to pH 1. The solution is passed through a column of cationite KUr (2 × 50 cm). The column is washed with water and Cu, Ni and Fe are eluted with 150–200 ml of HCl (1:1). The procedure is repeated on a smaller column and the eluate is concentrated to 2 ml. HNO₃ is added to oxidise Fe²⁺, and after evaporating twice with HCl, the solution is brought to 25 ml.

Fe is determined colorimetrically by adding 5–10 ml of 10% sulphosalicylic acid and aqueous ammonia to 2–5 ml of the solution and measuring the red colour.

Cu and Ni are determined by evaporating part of the solution to a small volume, adding 1 N NH₄Cl and aqueous ammonia to 10 ml, and polarographing after addition of 0.1 g Na₂SO₄ and 2–3 drops of gelatin.

The method gives satisfactory results of Cu from 4–400 g, Ni 2–400 g, and Fe 10–600 g/ton of iridium. [Gio.Ser.]

812 – Mechanism of the electrochemical reduction of halide complexes of platinum at the dropping mercury electrode (in Russian). N. V. Nikolayeva-Fedorovich and O. A. Petrii (State University, Moscow, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 1270–1278.

The effect of various additives on the reduction of platinum halide complexes at the dropping mercury electrode has been investigated. It has been shown that the retardation of the reaction observed at electric tensions more negative than the zero charge potential of mercury may be explained as the result of repulsion of anions from the negatively charged electrode surface, causing them to become ineffective in the double layer. A study of the rate of reduction as a function of concentration of the supporting electrolyte, magnitude of charge and radius of its cation, and the observed difference in effects of surface active organic cations on the reduction of PtCl₆²⁻, PtCl₄²⁻ and PtBr₄²⁻ showed that the varying susceptibility of the anionic reduction reaction to the additions may be associated with the geometric structure of the anions. [Ot.So.]

813 – Square wave polarography of plutonium. K. Koyama (J. J. Hopkins Laboratory for Pure and Applied Science, Box 608, San Diego 12, Calif., U.S.A.). *Anal. Chem.*, 32 (1960) 523.

A square wave polarograph with reduced frequency (85 cycles per sec) is used for the polarography of plutonium with stationary platinum electrodes. The polarograms were obtained by superimposing a square wave on a direct current voltage scan of 50 mV per minute. Two platinum wire elec-

trodes and a calomel comparison electrode are used. A large capacitor (300 μF) is connected between the calomel electrode and a platinum wire. The wave heights are proportional to the concentration as predicted by the square wave theory. 1 M hydrochloric and 2 M nitric acid are used as supporting electrolytes. The half wave values are +0.71 and +0.66 V vs. S.C.E. respectively for the couple Pu(IV) to Pu(III). [Kl.Gr.]

See also abstracts nos. 693, 711, 713, 714, 715, 716, 717, 846, 898.

4. Potentiometry

814 – On the alkali error of the glass electrode. I (in German). B. Lengyel, B. Csákvári and Z. Boksay (Institute of General and Inorganic Chemistry, L. Eötvös University, Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 25 (1960) 225–242.

To interpret the alkali error, the authors presume that the bond strength of the ions H_3O^+ and Na^+ participating in the ion exchange between the solution and the glass depends on the quality and quantity of the cations in the surface layer of the glass, in proximity to these ions, as these cations have a different polarisation capacity. Statistical methods were applied for establishing the distribution of ions. The activation energies of the ions of various bonds leaving the glass, together with the number of ions leaving the glass in unit time were determined. On applying the principle of dynamic equilibrium, the equilibrium constant was determined, and its correlation with the composition of the glass surface and with the electrode tension established. From the point of view of the alkali error, glasses are characterized by three constants, one of which is the coordination number of cations referred to each other. The measured and calculated values of the alkali error showed a fair agreement within the error limits. [E.Juh.]

815 – On the alkali error of the glass electrode. II (in German). B. Lengyel and B. Csákvári (Institute of General and Inorganic Chemistry, L. Eötvös University, Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 25 (1960) 369–377.

Changes in the character of the electrode function (D_1 , D and transitional type) plotted against the composition of glass were studied. Starting from the composition of the MacInnes-Dole glass, a portion of SiO_2 (12 mole%) was replaced by an equivalent amount of glass forming and transitional oxides, GeO_2 , P_2O_5 , V_2O_5 , B_2O_3 , Al_2O_3 , ZrO_2 , TiO_2 , PbO , ZnO , BeO . The ideal sodium ion function is shown by the effect of Al_2O_3 , ZrO_2 and B_2O_3 at the lowest pH values. The behaviour of glasses containing Al_2O_3 and B_2O_3 was interpreted by the presence of particular structural groups. [E.Juh.]

816 – Analytical possibilities of the method of potentiometric surfaces (in German). A. Swinarski and J. Wojtczak (Institut für Anorganische Chemie der Universität N. Copernicus, Torun, Polen). *Acta Chim. Acad. Sci. Hung.*, 26 (1961) 381–391.

Eine durch Lefebvre entwickelte Methode der potentiometrischen Oberfläche ermöglicht die Untersuchung der Verhältnisse eines Mehrkomponenten-Systems einer Lösung mit sehr einfachen Mitteln und verhältnismässig wenigen Messungen. Die Anwendung dieser Methode wird an Hand der Bestimmung der Ammoniakkomplexe des zweiwertigen Kupfers dargelegt. [E.Juh.]

817 – On the use of membrane electrodes for concentration determinations (in German). E. Pungor and E. Hollós-Rokosinyi (Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 27 (1961) 63–68.

Aus einer Masse von Silberjodid und Paraffin wurden von den Verfassern Membranelektroden hergestellt, die zur Verfolgung der Aktivität von Jodid- bzw. Silberionen im Konzentrationsbereich 10^{-1} – 10^{-6} mol/l geeignet waren. Die Umstände der Herstellung von gut arbeitenden Membranen wurden untersucht. Es wurde auf den Zusammenhang zwischen Elektrodenfunktion und Leitfähigkeit hingewiesen, und eine theoretische Formel für die Spannung abgeleitet.

Ferner wurden auch Messungen in Anwesenheit von fremden Elektrolyten (Kaliumchlorid, Natriumsulfat) durchgeführt. [E.Juh.]

818 – A general formula correlating the reactive addition to the electric tension change in analysis (in German). F. L. Hahn (Angel Urraza 718–303, Mexico 12, Mexico). *Z. anal. Chem.*, [2] 177 (1959) 113–121.

It is possible to correlate the electric tension change ΔE to the volume ΔV of the reagents employed, where:

V_i = initial volume of the solution

v = volume of the reagent added up to a given moment

v_i = volume of the reaction product

x = consumption of reagent up to the equivalence point

n = valence change of the compound during the titration

E_0 = chosen comparison tension (generally the instantaneous electric tension change of the titration).

Electric tension after the addition v of the reagent is:

$$E_0 \pm \frac{1}{n} \lg \frac{x-v}{V_i+v}$$

The immediately preceding electric tension is:

$$E_0 \pm 1 \lg \frac{x+v+\Delta v}{i+v+\Delta v}$$

The electric tension difference between these two points is:

$$\pm n\Delta E = \lg \frac{x-v+\Delta v}{x-v} - \lg \frac{i+v-\Delta v}{i+v}$$

[Di.Ciò]

819 – The temperature dependence of the ΔpD correction for the use of the glass electrode in D_2O (in English). Thomas H. Fife and Thomas C. Bruce (Department of Chemistry, Cornell University, Ithaca, New York, U.S.A.). *J. Phys. Chem.*, 65 (1961) 1079–1080.

The expression:

$$pD = \text{pH meter reading} + \frac{4.29 \times 10^2}{\Delta T} - 1.04$$

has been developed to incorporate the temperature factor in the determination of pD from the pH meter reading on a conventional pH meter. The equation holds for low resistance electrodes at ambient temperatures. [D.S.Ru.]

820 – On the formation of H_2O_2 in deaerated aqueous solutions under the influence of ^{60}Co radiation and the influence of hydration energy of cations on the average yield of the investigated process (in English). E. Weźranowski and S. Minc (Institute of Nuclear Research, Polish Academy of Sciences, Warsaw, Poland). *Nucleonika*, 8 (1961) 33–47.

The amount of H_2O_2 was measured polarographically over the concentration range 10^{-4} – 10^{-6} M, using the full sensitivity of the Radiometer Polarograph PO 3 in H_2SO_4 as a supporting electrolyte. The effect of gamma radiation on the behaviour of mercuric ions in solution was observed. The influence of the Hg^{2+} concentration on H_2O_2 yield was studied. The relation between the average yield of H_2O_2 in deaerated aqueous solutions and the hydration energy of cations added to the solutions from the standpoint of Franck-Rabinovitch "cage effect" was investigated. The following relation was obtained:

$$G = 1.2 Q^{-0.29} - 0.062 c$$

where G is the average yield of H_2O_2 (molecules/100 eV), Q is the hydration energy (kcal/mole), c is the concentration of cations (mole/l) over the range 0.2–1.0 M. [Ad.Hu.]

821 – Sulphuric acid determination in organic and inorganic acids by potentiometric titration in methanol (in German). W. Stuck (Analytischen Laboratorium der Farbenfabriken Bayer A.G., Werk Verdingen, Germany). *Z. anal. Chem.*, 177 (1960) 338–344.

The author has found that sulphuric acid may easily be potentiometrically titrated in organic and inorganic acids and methanol, using cyclohexylamine as titrating medium. Saline mixtures containing SO_4^{2-} may be converted into the corresponding acids, in aqueous methanol solutions and by means of cationic ion exchange resins, and titrated potentiometrically with cyclohexylamine. The methanol soluble sulphates of organic and inorganic bases may be directly titrated potentiometrically with strong acids. [Di.Ciò]

822 – Separate potentiometric titration of mixtures of organic bases in methyl ethyl ketone medium with perchloric acid solution (in Russian). A. P. Krshov, L. N. Byokva and N. Sh. Shemet (D. I.

Mendeleev Institute of Chemical Technology, Moscow, U.S.S.R.). *Zhur. Anal. Khim.*, 16 (1961) 331-336.

A new potentiometric method has been developed for the separate determination of bases in mixtures, by titration in a methyl ethyl ketone medium, with perchloric acid solution. Methyl ethyl ketone, used as solvent for the substance determined as well as for the volumetric solution, has distinct advantages in comparison with anhydrous acetic acid. It permits the separate titration of multi-component mixtures of bases, whose strengths in this medium are widely different. A glass and a modified calomel electrode are used. Titrations are carried out in a stream of dry nitrogen using a magnetic stirrer. [Ot.So.]

823 – Titration of pharmaceutical products in non aqueous media (in French). Ph. Kemy, J. P. Billon and F. Bigeard (Laboratoire Rech. analytiques, Vitry-sur-Seine, France). *Ann. pharm. franç.*, 17 (1959) 284-294.

A potentiometric method is described to titrate in the presence of indicators the following pharmaceutical products with 0.1 N perchloric acid: acetylcholine hydrochloride, chlorinpromazine hydrochloride, choline hydrochloride, ephedrine hydrochloride, procaine hydrochloride, promethazine hydrochloride, tetracaine hydrochloride, adrenaline, amidopyrine, tioamine, pyridoxine. With 0.1 N potassium methylate, the potentiometric titration of sulfur drugs and purine bases is possible. [Di.Ciò]

824 – Hydrazine sulphate as a volumetric agent. (Hydrazinometry). VI (in Russian). J. Vulterin and J. Zýka (Department of Analytical Chemistry, Charles University, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 25 (1961) 206-209.

Conditions have been found for the direct potentiometric determination of silver salts using hydrazine sulphate volumetric solutions. A silver and a calomel electrode were used. 40 to 200 mg Ag are complexed with ammonia, 20 ml 30% NaOH are added, the solution is diluted to 50 ml and titrated with a 0.05 M volumetric solution of hydrazine sulphate. The inflexion point is in the vicinity of -250 mV. Silver may be thus determined in the presence of Al, Cd, Pb, Ni, Cu and Zn. [Ot.So.]

825 – Rate of hydrolysis of monohalogenalkane acids in aqueous solutions. II. Kinetics of the hydrolysis of bromoacetic acid in water (in German). (Institute of Organic Chemistry and Biochemistry, University of Bratislava, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 25 (1960) 2590-2598.

The rate of hydrolysis of bromoacetic acid was investigated in acid media, and in solutions of the free acid and of its sodium salt at 70°. The hydrogen ion concentration was measured by potentiometric measurement of the pH value using a high temperature glass electrode. The bromide ion concentration was followed potentiometrically using a silver bromide electrode. An arrangement was used including a glass, a silver bromide and a saturated calomel electrode. The calomel electrode was connected by a modified, potassium nitrate filled, agar bridge. [Ot.So.]

826 – Potentiometric titrations in trimethylamine acetate (in German). W. Hubicki and K. Wiacek. (Institut für anorganische Chemie der Curie Sklodowska Universität, Lublin, Polen). *Z. anal. Chem.*, 175 (1970) 97-103.

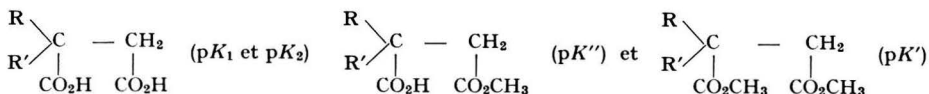
The chemical and physical properties of trimethylamine acetate, with three solvated molecules of acetic acid $[(\text{CH}_3)_3\text{N} \cdot 4\text{CH}_3\text{COOH}]$, are described. This complex (TAT) acts like a good non-aqueous solvent for many organic and inorganic compounds. The potentiometric and redox titration (in TAT) curves show regular development and are reproducible. [Di.Ciò.]

827 – Semimicrodetermination of nitrogen glycosides by potentiometric titration (in Polish). J. Sokolowski and S. Kolka (Department of Organic Chemistry, School of Pedagogy, Gdańsk, Poland). *Chem. anal. (Warsaw)*, 6 (1961) 331-341.

A semimicro method of potentiometric titration of nitrogen glycosides has been developed. Determination was performed with glass and silver chloride electrodes in the following solvents: glacial acetic acid, ethyl acetate, nitromethane and acetonitrile. Pure substances: amines, N-glycosides, Amadori product formed from N-D-glycosyl-p-anisidine, as well as most of their mixtures, were titrated successfully with an error of about +1%. Using this method, quantitative determination of amines in the presence of N-glycosides was possible, and in some cases both components could be determined as well as N-glycoside and Amadori product. This method can be used in studying formation of nitrogen glycosides and in the analysis of natural products. [Ad.Hu.]

828 – Constantes d'ionisation de quelques diacides et acides-esters succiniques dissymétriquement substitués (in French). A. Foucaud et Mlle P. le Guellec (Laboratoire de chimie générale et M.P.C., Faculté des Sciences, Rennes, France). *Compt. rend.*, 252 (1961) 3063-3065.

Les auteurs déterminent par potentiométrie en solution aqueuse et hydroalcoolique (20% éthanol) les pK des acides suivants:



R' représente les groupements suivants: H, CH₃, C₂H₅ et R, les groupements C₆H₅CH₂, NO₂C₆H₄CH₂, C₆H₅, NO₂C₆H₄, soit 28 valeurs numériques pour chacun de deux solvants. Dans l'eau, toutes les valeurs de pK' et pK'' sont comprises entre 4.65-3.69; en milieu hydroalcoolique entre 5.11-3.95. L'incertitude sur les valeurs de pK', pK'' et pK₁ est de ±0.04 et sur les valeurs de pK₂ de ±0.08. Les auteurs constatent que l'ordre d'acidité pour les acides-esters est le même que celui des acides amides précédemment établi. L'introduction d'un groupement NO₂ dans le substituant phényle provoque une diminution importante de la valeur du rapport K₁/K₂ (1120 → 425). [Bad.Lam.]

829 - Perbenzoic acid as volumetric reagent, in determining inorganic reducing agents (in English).

B. Singh, S.S. Sahota and A. Singh (Department of Chemistry, Panjab University, Hoshiarpur, India). *Z. anal. Chem.*, 169 (1959) 106-109.

In the paper the analytical oxidation of inorganic compounds by perbenzoic acid is described for the first time. Perbenzoic acid solution in chloroform is a suitable reagent for the titration of ferrocyanide, arsenious oxide, tartar emetic, sodium sulphite, stannous chloride, hydrazine sulphate and sodium thiosulphate. These substances are dissolved in 40-50 ml of water; 5-20 g of sodium acetate and 10-15 ml of acetic acid are added in order to obtain pH 4-4.5. Then 5 ml of chloroform and one drop of 0.04 N iodine (as catalyst and preoxidiser) are added. The solution is titrated with 0.05 M perbenzoic acid-chloroform solution with vigorous stirring. The end point can be observed visually (chloroform layer becomes faintly violet), or better, potentiometrically, with the aid of a bright platinum indicator electrode and a S.C.E. At the equivalence point there is a very sharp electrical tension change. The results are almost exact. [G.deAn.]

830 - Potentiometric determination of arylsulfonic acids (in English). L. Gringras and G. Sjöstedt (The Laboratory of AB Ceaverken, Strängnäs, Sweden). *Acta Chem. Scand.*, 15 (1961) 433-434.

The titration was carried out potentiometrically with a Metrohm Potentiograph. The end point was also very distinct at high dilution. The very steep tension break indicated that the reaction was practically irreversible and was marked by a tension jump amounting to about 200 mV after the addition of only one drop.

A series of runs was made with p-toluene sulfonic acid ranging from 10⁻⁴-10⁻¹ M. Plotting the mole ratio, Ce⁴⁺/RSO₂⁻ on the ordinate vs. the logarithm of the concentration of the titrated solution on the abscissa, gave the ratio 1.5, if the concentration was above 5 · 10⁻³ M. If it was lower, the mol ratio gradually decreased. The overall reaction in the range from 5 · 10⁻³ M to 1 · 10⁻¹ M is summed up by the reaction:



For salts with divalent or tetravalent cations the factor 1.5 has to be replaced by 3.0 or 4.5.

[Sv.Li.]

831 - Potentiometric methods for the titration of multicomponent acid mixtures in non-aqueous media (in Russian). A. P. Kreshkov, L. N. Bikova and H. A. Kazaryan. (D. I. Mendeleev Institute of Chemical Technology, Moscow, U.S.S.R.). *Zhur. Anal. Khim.*, 16 (1961) 129-134.

The titration of phenol derivatives, acetic and benzoic acids and their mixtures with organic and inorganic acids and (C₂H₅)₄NOH in organic solvents has been studied. It is possible to titrate mixtures composed of 3-5 acids in methyl ethyl ketone medium, accuracy being within 0.1%. In this communication, results of the titration of many compounds in various mixtures and using various media are discussed, the procedure having been described in a previous paper (*Zhur. Anal. Khim.*, 14 (1959) 529). [Ot.So.]

832 - Gravimetric, spectrophotometric and potentiometric determination methods of "Flaxedil".

P. Spacu and E. Antonescu (Akad., R.P.R. Bucarest, Rumania). *Studii Cercetari Chim. (Bucarest)*, 7 (1959) 389-397.

The potentiometric method is the following: 0.03-0.05 g "Flaxedil" [tri (diethylamine-2-ethoxy)-1, 2, 3 benzene] are dissolved in 100 cm³ water, acidified with 5 cm³ HCl (D = 1.19) and titrated, as far as the potential jump, with a 0.1 N bromate-bromite solution. Platinum and standard calomel electrodes are used. [Di.Ciò]

833 - Determination of resazurine, resorufine and their derivatives by means of ascorbic acid (in German).

E. Ružička (Chemisch Institut der Naturwissenschaftlichen Fakultät, Palacky Universität, Olomouc, Czechoslovakia). *Z. anal. Chem.*, 168 (1959) 414-417.

Ascorbic acid reduces red solutions of resazurine (7-hydroxyphenoxazon-(2)-10-oxide), resorufine (7-hydroxyphenoxazon-(2)) and their derivatives to colourless or blue-green compounds in the presence of hydrochloric acid. The reaction can be useful for a qualitative test; the sensitivity has $pD = 5.8-6.0$. Amino-oxazone, gallocyanine, some oxazine, thionine, thionol and azo-dyes must not be present. The potentiometric quantitative titration of resazurine, resazurinethyl ether, *o*-acetyl-resazurine, resorufine, resorufinethyl ether and *o*-acetylresorufine is also possible with an average relative error less than $\pm 1\%$ using bright platinum and S.C.E. electrodes and operating in a CO_2 atmosphere. The ethanolic sample solution is diluted with an equal volume of $4 N$ HCl, heated up to 65° and titrated with $10^{-3} M$ ascorbic acid standard solution. The equivalence point at 250, 293, 277, 248, 245 and 266 mV vs. S.C.E. and 1 ml of titrant corresponds, respectively, to 0.251, 0.257, 0.259, 0.213, 0.241 and 0.255 mg of the titrated compounds. Gallocyanine and azo-dyes can be present, while aminooxanone, oxazine and thionine interfere. [G.deAn.]

834 – pH-static method for the assay of arginase. M. Rigby (Hebrew University, Jerusalem, Israel). *Bull. Res. Council Israel, A*, 9 (1960) 149-156.

Arginase activity is accompanied by H^+ production because the $\delta-NH_2$ group of ornithin is less basic than the guanido group of arginine and urea is a very weak base. By measuring the rate of addition of alkali necessary to maintain constant the pH of a poorly buffered arginase system, the arginase can be determined. The method can also be used for the determination of L-arginine, measuring the amount of alkali added after the end of the hydrolysis. The optimal pH for the determination is near 10.

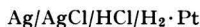
A "pH 10.2 arginase unit" is defined as that quantity of enzyme decomposing $1 \mu M$ of arginine in 1 min at pH 10.2 and 25° , when the substrate is at a concn. of 0.285 M . In this conditions $1 \mu M$ of L-arginine corresponds to 0.4 μM of alkali. [Gio.Ser.]

835 – Activity coefficients of bipolar electrolytes. Silver succinate and sebacate in aqueous sodium nitrate (in English). F. R. Meeks and R. A. Marcus (Department of Chemistry, Polytechnic Institute of Brooklyn 1, New York, U.S.A.). *J. Phys. Chem.*, 65 (1961) 306-309.

The solubility method was used to determine the activity coefficients of silver succinate and sebacate. The silver ion was measured potentiometrically using an empirical calibration equation. A simple theoretical model for "bipolar" ions is in good agreement with the results indicated by the electrostatic contribution to the activity coefficients. [D.S.Ru.]

836 – La tension standard de l'électrode Ag/AgCl dans le *n*-propanol (in French). A. Tézé et R. Schaal (Laboratoire de Chimie IV, P.C.B., 11 rue Pierre-Curie, Paris 5e, France). *Compt. rend.*, 252 (1961) 3995-3997.

Les auteurs ont déterminé par potentiométrie la tension standard dans trois solvants (propanol, éthanol, isopropanol) de l'électrode Ag/AgCl. La détermination expérimentale de la tension de la suivante:



permet d'atteindre la tension standard π°_{AgCl} par la formule:

$$E = \pi^\circ_{AgCl} - \frac{2RT}{F} \log m_{HCl} - \frac{2RT}{F} \log \gamma_{HCl}^\pm$$

(m_{HCl} molalité de l'acide chlorhydrique, γ^\pm coefficient d'activité moyen). La valeur de E extrapolée à force ionique nulle permet d'obtenir les valeurs suivantes de π°_{AgCl} : -0.092 et -0.102 V respectivement à 20° et 25° dans le propanol; -0.065 et -0.0723 V dans l'éthanol et -0.0995 et -0.122 V dans l'isopropanol. [Bad.Lam.]

837 – Use of a silver chloride comparison electrode for the continuous regulation of the pH value of ammonium nitrate solutions at high temperatures (in Russian). Ya. I. Turyan and N.S. Anikina (Institute of Automation and Institute of the Nitrogen Industry, Lisitshan, U.S.S.R.). *Zhur. Priklad. Khim.*, 34 (1961) 1077-1081.

The behaviour of the silver chloride electrode in NH_4NO_3 solutions (600-800 g/l) in the pH range 0.5-7.0 at 100° has been investigated. It has been shown that in the pH range 1-6.5 the electrode tension is little dependent on pH (it changes only by 10 mV). It also is little influenced by concentration variations in the range 600-800 NH_4NO_3 g/l. The reproducibility and stability of the electric tension is exceptionally good. This electrode has been found to be suitable for use as a comparison electrode for automatic pH regulation in the process of neutralisation in the manufacture of ammonium nitrate. The comparison and indication electrode may be placed in the same solution. [Ot.So.]

838 – Determination of mercaptans by titration with mercury(II) (in English). J. S. Fritz and Th. A. Palmer (Institute for Atomic Research and Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa, U.S.A.). *Anal. Chem.*, 33 (1961) 98.

A rapid and accurate method for the determination of mercaptans by visual and potentiometric titration with mercury(II) perchlorate in neutral, aqueous or acetone medium is described. The endpoint is detected visually by using thio-Michlers ketone, or potentiometrically with a mercury indicator electrode. For potentiometric determination the sample containing 0.3 to 1 mmole of mercaptan is weighed into a 250 ml beaker with 125 ml of solvent. 1 ml pyridine is added and titrated with 0.05 M mercury(II) perchlorate solution. The average error for all titrations reported is $\pm 0.5\%$. [Kl.Gr.]

839 – Behavior of cuprocyanide complexes in the course of titration of CuCN–NaCN aqueous solution with silver nitrate (in Japanese). Yoshihiko Kuwa (College of Engineering, University of Osaka Prefecture, Sakai City, Osaka, Japan). *J. Electrochem. Soc. Japan*, 28 (1960) 145–148. (English translation in *J. Electrochem. Soc. Japan*, (Overseas Suppl. Edition), 28 (1960) E63).

Muraca investigated the $Zn(CN)_2$ –NaCN system in aqueous solution, (an essential constituent of a zinc cyanide plating bath), by the potentiometric titration method. An appropriate amount of argentocyanide complex was introduced in the solution and the mixture was titrated with $AgNO_3$ solution using a silver comparison electrode.

It has been found that cyanide in excess of $Na_2Zn(CN)_4$, cyanide in excess of $Zn(CN)_2$ and total cyanide can be determined from the points of inflection observed on the potentiometric titration curve.

In this paper, the author investigated the CuCN–NaCN system in aqueous solution, (an essential constituent of a cuprocyanide plating bath), using a method similar to the one mentioned above. Each step of the titration curve was investigated in relation to the species of the complex ions in solution. [Ta.Fu.]

840 – Formation and stabilities of mixed copper chelates of 1,2-diamino-propane and 5-sulphosalicylic acid in aqueous solutions (in English). Reino Näsänen and Paavo Meriläinen (Department of Chemistry, University of Helsinki, Helsinki, Finland). *Suomen Kemistilehti*, 34, 7–8 (1961) B75–78. Potentiometric titrations of mixed solutions of copper ion, 5-sulphosalicylic acid (H_3X) and 1,2-diaminopropane (Y) have been carried out. The potentiometric data can be explained satisfactorily only by assuming the formation of a mixed complex ($CuXY$). The value 20.3 ($T = 0.25^\circ$) was calculated for the logarithmic stability constant of this species from the experimental data. [Sv.Li.]

841 – Potentiometric titration of metals by means of sodium diethylthiocarbamate (in English). A. Hulanicki (Department of Inorganic Chemistry, University, Warsaw, Poland). *Acta Chim. Acad. Sci. Hung.*, 27 (1961) 41–47.

Solubility products of silver, copper, lead, zinc, nickel and cadmium diethylthiocarbamates were determined by means of electric tension measurements with a silver electrode. The possibility of determining milligram amounts of these metals was investigated in various buffering and complexing solutions. The end-point of the titration was detected potentiometrically using the silver electrode as pM electrode. On this basis a procedure for lead determination in the presence of excess nickel, zinc, iron and manganese was developed. The error of the determination was about $\pm 0.5\%$. [E.Juh.]

842 – The electric tension of the powder barite electrodes in the presence of flotation reagents (in Polish). A. Waksmundzki, J. Szczypa and M. Rokicka (Department of Physical Chemistry of Surface Phenomena, Polish Academy of Sciences, Lublin, Poland). *Przemysl chem.*, 40 (1961) 146–148.

The electric tension of the powder barite electrode was measured in the presence of flotation agents: oleic acid as a collector and sodium silicate as a depressor. Most reproducible electric tensions were obtained when the difference of electric tensions between the platinum electrode in the collector solution and the same electrode in the presence of barite powder was considered. The changes of electric tension were examined in the pH range from 6–11. The electric tension of the electrode depends distinctly on the addition of the flotation agent, and therefore the flotation process may be characterized by changes of the electric tension of the powder electrodes. [Ad.Hu.]

843 – Investigation of the state of boron by potentiometric and ion-exchange techniques in fluoroborate solutions (in Russian). E. A. Materova and T. I. Rozhanskii (State University, Leningrad, U.S.S.R.). *Zhur. Neorg. Khim.*, 6 (1961) 177–181.

In the potentiometric investigation, tetrafluoroboric acid solutions were titrated against NaOH solutions using a hydrogen electrode. HBF_4 solutions were 0.11 and 0.13 M and, the NaOH titrant

was 0.15 *M*. The titration curves included three changes of electric tension. The first and second changes were diffuse, the third one was sharp. The first change of electric tension (pH 2–5) was interpreted as neutralisation of HBF_4 , HBF_3OH and $\text{HBF}_2(\text{OH})_2$. The second change (pH 6–8 for 0.11–0.13 *M* HBF_4 , and pH 5–8 for 0.16 *M* HBF_4) was interpreted as the neutralisation of NaBF_3OH and $\text{NaBF}_2(\text{OH})_2$ formed in the first neutralisation, liberating boric acid, which was neutralised in the third change. [Ot.So.]

844 – Superficial acidity and activity of exchange cations on kaolinite (in Spanish). J. R. Masaguer and F. Guitian Ojea (Centro de Edafología y Biología Vegetal de Santiago de Compostela, Spain). *Anales real soc. españ. fis. y quim.*, (Madrid), 55B (1959) 215–230.

The surface acidity of kaolinite saturated with protons and with various exchange cations has been evaluated (for protons: by titration with donors of electron pairs, using a Hammett indicator; for exchange cations: by titration with piperidine and diphenylguanidine in an aprotic solvent). The extremely acidic character which is observed is explained assuming that the electrostatic forces exerted on the exchange cations are lower than the capacity of bending, and that steric factors are involved. [L.Gi.]

845 – Cerimetric determination of thallium. I (in English). K. Bhaskara Rao and G. Jagga Rao (Department of Chemistry, Andhra University, Waltair, India). *Z. anal. Chem.*, 168 (1959) 83–86.

The cerimetric determination of thallium (I) is reinvestigated. Titration to the *visual end point* using ferroin as indicator and iodine monochloride as catalyst is possible at 50° if the hydrochloric acid concentration is kept at 2 *N* and 1 ml of 0.005 *M* iodine monochloride is used for 50 ml of final solution. Titration to the *potentiometric end point* is possible at room temperature in 1 *N* HCl and with 5 ml of 0.005 *M* ICl catalyst in 50 ml. The relative error is less than $\pm 1\%$. Titrating with 0.05 *N* ceric sulphate solution, the electrical tension break at the end point is 264 mV in 1 *N* HCl for 0.03 ml of titrant, 204 mV in 2 *N* HCl and 110 mV in 3 *N* HCl. [G.deAn.]

846 – Analytical chemistry of thallium (in Russian). P. I. Buseva and V. G. Tiptsova (State University, Moscow, U.S.S.R.). *Uspekhi Khim.*, 29 (1960) 1011–1028.

It is stated that titrimetric methods are very important for the determination of Tl(I), titrants used being KMnO_4 , KBrO_3 , KIO_3 and KIO_4 . Tl(III) may be determined by backtitration of iodine liberated from KI with thiosulphate. Indication is mostly potentiometric, using as an indicator electrode platinum spiral or foil. Other methods of indicating end points, amperometry and conductimetry, have not found many applications. Some coulometric methods exist, based on the oxidation of Tl(I) by electrolytically generated oxidants, e.g. free halogens, ferricyanide etc. Polarography is used for determining thallium in industrial materials, after separation from the sample solution e.g. by extraction. The paper describes in great detail the individual reactions of Tl(I) as well as Tl(III) and includes 280 literature references. [Ot.So.]

847 – Oxalate interference in cerimetry (in English). L. J. Csanyi and F. Szoke (Institute for Inorganic and Analytical Chemistry, University of Szeged, Hungary). *Z. anal. Chem.* 175, 3 (1960) 187–195.

The fundamental question is the rate of reaction between oxalic acid and cerium(IV) ions; this reaction has scarcely been investigated until recently. The Authors prove that the positive errors occurring during cerimetric determination of iron(II) ions, hydroquinone, indigo carmine, etc., in the presence of oxalic acid is not of an induced character but may be ascribed to a rather rapid competing reaction between oxalate and cerium(IV) ions. Therefore any factor which decreases the rate of this latter reaction diminishes the positive error. [Di.Ciò.]

848 – Determination of basicity of substituted phosphines by nonaqueous titrimetry (in English). C. A. Streuli (Central Research Division, American Cyanamid Co., Stamford, Conn., U.S.A.). *Anal. Chem.*, 32 (1960) 985.

A precision-Dow titrator and a glass-calomel electrode system are used for the determination of the basicity of 36 substituted phosphines. The samples are titrated in nitromethane and calculated for water. 0.1 *N* hydrochloric acid is used as the titrant. Diphenylguanidine is used as the reference standard base for all nonaqueous titration work. For the titration about 1 mmole is dissolved in 100 ml of solvent. [Kl.Gr.]

849 – The iodimetric determination of antimony(III) and arsenic(III) by potentiometric titration (in Japanese). Kozo Ueno and Tetsuhei Tachikawa (Chemical Section, Muroran University of Engineering, Hokkaido, Japan). *Japan Analyst*, 8 (1959) 572–576.

The iodimetric determination of Sb(III) and As(III) by potentiometric titration has been carried out in the concentration range of 0.1 *N* to 0.001 *N* by using four kinds of bimetallic electrodes;

Pt-Ni, Pt-Ag, Pt-W, and Pt-Sb. The titration curves and the changes of the electric tension at the end point ($\Delta E/\Delta V$) have been obtained at the same time.

As a result of this experiment, Pt-Ni, Pt-Ag and Pt-W were found to be applicable with good results: they give a sharp indication at the end point and their electric tensions increase rapidly. For Pt-Ag, a S-shaped titration curve is obtained; on the other hand, each of the three others forms a titration curve having a peak, in both determinations.

Pt-Sb shows a sharp change of electric tension at the end point in 0.1 N solution, but the deviation of the end point in the case of determining Sb(III) and As(III) is 0.1 and 0.5% respectively. The titration cannot be carried out in 0.1 N and 0.001 N solutions. Accordingly, this couple is not suitable for the titration.

The values of $\Delta E/\Delta V$ at the end point for Pt-Ni, Pt-Ag and Pt-W in 0.01 N solution are greater than those in 0.1 N solution. The reason cannot be clarified at the present time, but it will be elucidated later on.

Samples containing Sb(III) in the range of 3-300 mg and As(III) in the range of 1.2-120 mg can be directly titrated by this method satisfactorily. [Ta.Fu.]

850 - Trivalent molybdenum as a volumetric reducing agent (in English). M. Y. Farah and S. Z. Mikhail (Atomic Energy Establishment, Sh. Tahrir, Dokki, Cairo, Egypt). *Z. anal. Chem.*, 166 (1959) 24-31.

Trivalent molybdenum solutions are obtained by reducing pure molybdic acid on a platinised wire-gauze cathode in a 300 ml cell containing 8 N HCl and a platinum-spiral anode; the anodic and cathodic compartments are separated by a sintered-glass diaphragm. The same solution can be obtained by reduction through metallic mercury in 9 N HCl (Furman and Murray, *J. Am. Chem. Soc.*, 58 (1936) 1689), filtered, and washed with 1 : 1 HCl. Stock solutions in 8 N HCl are stable; only after two months is the titre reduced to half its original value. The titration cell is a pyrex glass beaker with a ground joint stopper provided with holes for the indicator Pt-electrode, the salt bridge, the tip of a 10 ml burette, the mercury-seal stirrer and the inlet and the outlet for the inert gas (CO₂). Approximately 0.1 N solutions are employed.

a) Reduction of ceric, dichromate, ferric and vanadate ions.

Titration of ceric sulphate in 2 N H₂SO₄ at 80° is exact and the equivalence inflection is about 475 mV for 0.1 ml of the molybdenum solution. Dichromate titrations in 0.5-4 N HCl are performed in the cold as the reduction is instantaneous with a percentage error of less than $\pm 1\%$ with an equivalence inflection of 272-436 mV. In 0.1-4 N H₂SO₄ it is necessary to heat at 80° for a rapid equilibrium. The error is as above and the equivalence inflection is about 290 mV. In 0.1 N acid the equivalence point is also visually observed by the appearance of a pale blue colour. In the case of ferric chloride in 0.1-4 N HCl the equivalence inflection varies from 39-1 mV; the error is less than $\pm 1\%$ and the most accurate results are obtained in heated solutions. Vanadate gives better results in 2-4 N HCl than in 6 N HCl, the electrical tension jump at the equivalence varying from 100 to 442 mV.

b) Titration of Mo(III) with iodate, bromate and ceric solutions.

With iodate and bromate the best results (error less than 1%; inflection: 168 and 47 mV) are obtained in 6 N HCl solutions; more or less concentrated HCl solutions need more time for the equilibrium, give more or less pronounced deviations and need a very accurate control of the inert atmosphere. Cerium(IV) in 4 N HCl gives an error of about + 1% with an inflection of 362 mV. [G.deAn.]

851 - Potentiometric titration of molybdenum(V) with ferric alum (in English). G. Gopala Rao, Seetharamaraju Sagi and M. Suryanarayana (Department of Chemistry, Andhra University, Waltair, India). *Z. anal. Chem.*, 169 (1959) 248-253.

The reaction between molybdenum(V) and ferric alum in acid solution is slow (about 4 hrs) at room temperature as can be shown from a spectrophotometric investigation. Thus it is necessary to heat the solution at 98-100°. At this temperature the molybdenum solution is not stable owing to oxidation by air, and therefore the titration must be performed under CO₂. Also the acidity of the solution affects the tension jump at the equivalence point. Using a bright platinum indicator electrode and a S.C.E., with 0.05 M solution of Mo(V) and Fe(III) the electrical tension jump is about 50, 30, 0 mV for 0.1 ml of Fe(III) solution when the normality of the hydrochloric acid is respectively 0.5, 1, 4 N. Using 0.1 M solutions of Mo(V) and Fe(III) the tension jump in 0.5 N HCl is about 90 mV. The reaction is slow at the beginning and it is necessary to add a little Mohr's salt. Therefore the best conditions are: temperature 98-100°; presence of Fe(III); normality of HCl about 0.5; concentration of Mo(V) and Fe(III) about 0.1 M; carbon dioxide atmosphere. The relative error is about $\pm 3\%$. [G.deAn.]

852 - Potentiometric determination of chlorine in haemolized erythrocytes. M. v. Bubnoff and G. Riecker (Klinik, Medizinische Universität, München, Deutschland). *Biochem. Z.*, 331 (1959) 577-579.

A method is described which gives values that always indicate the real chlorine content with an error ranging from $+34 - +43\%$, according to the haemoglobin concentration. [Di.Ciò.]

853 – Determination of hypochlorites, chlorites and chlorates from a single sample by means of arsenite using OsO_4 as a catalyst (in Russian). P. K. Norkus and Yu. Prokoptshik (Institute of Chemistry, Academy of Sciences, Lithuanian S.S.S.R., Vilnius, U.S.S.R.). *Zhur. Anal. Khim.*, 16 (1961) 323–326.

The analysed solution is made alkaline by addition of 2–5 ml 1 N NaOH, platinum and saturated calomel electrodes are inserted, and the solution is titrated against standard sodium arsenite solution to determine hypochlorite. After the titration an amount of 1 N NaHCO_3 , 1.5–2 times larger than the volume of hydroxide added previously is added to convert the hydroxide to carbonate. 4–5 drops (0.2 ml) of a 0.1% solution of OsO_4 are added, and the chlorite content is titrated against the standard arsenite. Finally, the same solution is used for the bromometric determination of chlorate. Excess arsenite is added, the solution neutralised to methyl orange, acidified by 1–2 ml conc. hydrochloric acid, 0.1 g KBr is added, and the solution is boiled. In the hot solution excess arsenite is titrated by bromate, using methyl orange as a visual indicator. [Ot.Sø.]

854 – Oxidation with manganate solutions. III. Reduction of manganate with hydrogen peroxide and bivalent manganese (in English). I. M. Issa and M. G. E. Allam (Chemical Department, Faculty of Science, Cairo and Assiut University, U.A.R.). *Z. anal. Chem.*, 175, 2 (1960) 103–110.

The reduction of manganate with hydrogen peroxide and Mn^{2+} is described: the potentiometric titration curves are given.

Quantitative results may be obtained with H_2O_2 only when neutral or weakly acidified solutions are used, provided that telluric acid is present and the alkalinity is 1–2 N. Less accurate results are obtained with strongly acidified H_2O_2 solutions and in 0.5 M NaOH. In the absence of telluric acid large errors may be made, owing to the potential formation of Mn_2O_3 , both in H_2O_2 and Mn^{2+} solutions. Good results are obtained in the case of Mn^{2+} : the ratio of $\text{MnO}_4^{2-} : \text{Te}^{6+}$ should then not be less than 1 : 15. [Di.Ciò.]

855 – Reductometric determination of manganese in alloys and minerals (in German). I. Klüh, J. Dolezal and J. Zyká (Institut für analytische Chemie der Karlsuniversität, Prague, Czechoslovakia). *Z. anal. Chem.*, 177 (1960) 14–20.

The volumetric determination of manganese by oxidation with perchloric acid, gives inaccurate values. The Authors have developed a new volumetric method based on oxidation of manganese with potassium bromate in the presence of phosphoric acid, and on successive reductometric titration of Mn(III) with Fe(II) or hydroquinone solution.

The titration may be potentiometric or visual, using diphenylamine as indicator. The proposed method is suitable for mineral, manganese, cast iron, or bronze analysis. [Di.Ciò.]

856 – Analytical applications of the “chelones”. XI. Study of the action of oxidising agents on AEDT, and the possibility of its potentiometric titration (in Spanish). F. Bermejo Martínez and R. Rey Mendoza (Laboratorio de Química analítica de la Facultad de Ciencias, Santiago de Compostela, Spain). *Anales real soc. españ. fis. y quim.*, (Madrid), 55B (1959) 309–314.

The potentialities of KMnO_4 , $\text{Ce}(\text{SO}_4)_2$, $\text{K}_2\text{Cr}_2\text{O}_7$ (in acid medium) and KMnO_4 (in alkaline medium) as oxidising agents have been investigated.

The fact that the amount of titrant depends on its nature (and also on the pH for KMnO_4) is qualitatively discussed. Compared with KMnO_4 , $\text{Ce}(\text{SO}_4)_2$ presents the advantages of needing no catalyst, and of a lower working temperature. [L.Gi.]

857 – Analytical applications of the “chelones”. X. Iodometric determination of Fe(II) in the presence of 1, 2 diaminocyclohexanetetraacetic acid (ADCT) (in Spanish). F. Bermejo Martínez and R. Rey Mendoza. (Laboratorio de Química analítica de la Facultad de Ciencias, Santiago de Compostela, Spain). *Anales real soc. españ. fis. y quim.*, (Madrid), 55B (1959) 305–308.

The influence of pH on the electrode equilibrium electric tensions of the Fe(II)–Fe(III) system in A.D.C.T. has been studied. A procedure which is claimed to be as precise as the classical method is proposed for the iodometric titration of Fe(II). The method is essentially based on the fact that the reducing power of Fe(II) can be sufficiently increased, by proper control of pH, to render possible quantitative reduction of iodine; the excess of iodine is titrated by thiosulphate. [L.Gi.]

858 – Electrometric titration of alkaline ferricyanide with hydrazine sulphate and arsenic. (III) (in English). Suseela B. Sant (Department of Chemistry, Mount Holyoke College, South Hadley Mass. U.S.A.). *Z. anal. Chem.*, 168 (1959) 112–115.

A method is described for the determination of ferricyanide or of hydrazine or arsenic(III) at room

temperature (25–30°) and at low alkali concentration (2–3 N). The couple Pt–S.C.E. is used for the potentiometric titration. The solution of a known quantity of 0.1 N $K_3Fe(CN)_6$ is made 2–3 N in alkali hydroxide, and 2–3 drops of osmic acid (0.25 g OsO_4 in 100 ml 0.1 N H_2SO_4) are added as catalyst. A 0.1 N hydrazine sulphate solution is added measuring the electrical tension of the system. The titration can be performed also with a 0.1 N solution of As_2O_3 instead of hydrazine; in this case the solution is made 1–2 N in alkali and 0.1–0.2 ml of osmic acid are added. At the equivalence point there is a tension jump of about 150 mV. The relative errors are always less than $\pm 1\%$. [G.deAn.]

859 – Potentiometric determination of cobalt with ferricyanide in a glutamic acid medium (in Russian). Chang-E-Siya, J. Doležal and J. Zýka (Charles University, Prague, Czechoslovakia). *Zhur. Anal. Khim.*, 16 (1961) 308–312.

The quantitative oxidation of cobalt(II), as the cobalt(II)–glutamic acid complex with potassium ferrocyanide has been studied potentiometrically, varying pH, glutamine and cobalt concentrations. It has been found that the cobalt(II)–glutamic acid compound is stable in the air at pH 9.8–11.4, and it is possible to oxidize it quantitatively with potassium ferricyanide. A method has been developed, as a result of the investigation, for the determination of cobalt in various materials e.g. steel and ores. The method permits the determination of 1% cobalt in zinc, bismuth cadmium, copper and molybdenum. Manganese in 5-fold quantities does not interfere. [Ot.So.]

860 – The behaviour of a platinum electrode in silicate melts (in Russian). V. I. Minenko, S. M. Petrov and N. S. Ivanova (Institute of Economic Engineering, Kharkov, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 1534–1537.

The dependence of the electric tension of a platinum electrode upon the activity of oxygen ions in the melt, partial pressure of oxygen in the gaseous phase and the temperature has been investigated. It has been shown that in melts the platinum electrode is reversible with respect to oxygen ions. A mechanism of the electrode process has been proposed. [Ot.So.]

861 – Electric tension of the platinum electrode in an irradiated solution of sulphuric acid (in Russian). G. Z. Gotshaliev, C. I. Zalkind and V. I. Veselovskii (L. Ya. Karpov Institute of Physical Chemistry, U.S.S.R.). *Doklady Akad. Nauk, S.S.S.R.*, 132 (1960) 872–875.

Results are given of the investigation of the effect of high radiation doses on the system platinum–sulphuric acid solution. A ^{60}Co source was used, giving doses of $6.1 \cdot 10^{16}$ eV/cm²/sec. During the first five minutes the electric tension of the platinum electrode fell rapidly, remained constant and near to zero, and then after about 60 minutes irradiation regained the original value. The polarisation current rose to a maximum after about 20 minutes irradiation, and then decreased steadily. The observed effects are explained by the radiolysis of water, the hydrogen evolved interfering in the equilibrium of the oxidised and reduced systems. [Ot.So.]

See also abstracts nos. 683, 686, 687, 688, 703, 712, 900, 930.

5. Conductometry

862 – Direct current conductometry with non-polarizable external electrodes. I (in English). Ch. Muzsnay and L. Kéhedy (Chair of Inorganic and Analytical Chemistry, Babes-Bolyai University, Cluj, Roumania). *Acta Chim. Acad. Sci. Hung.*, 27 (1961) 21–30.

A method has been devised whereby conductometric titration of electrolyte solutions can be performed with direct current technique. Contrary to previous d.c. methods two nonpolarizable redox electrodes were used (ferro–ferricyanide/graphite) which made possible the use of quite low electrical tension (a few volts instead of some hundreds). For this reason, and because the electrodes are non-polarizable, Ohms law is valid and the variation of conductivity during the titration can be followed by the measurement of any parameter of the circuit. In the present investigation the current intensity was measured, which is, from an experimental point of view, the simplest technique. A new titration cell was designed and some titrations were made. The theoretical shape of the titration curves is discussed and compared with the experimental results. Some aspects of further investigations are also reported. [E.Juh.]

863 – The Soret effect as a source of error in conductance measurements (in English). R. H. Stokes (Department of Physical and Inorganic Chemistry, University of New England, Armidale, N.S.W. Australia). *J. Phys. Chem.*, 65 (1961) 1277–1278.

A study carried out using specially designed conductivity cells has shown that error in measurements may occur if the contents of the cell are not mixed well after the system has reached thermal equilibrium. A change in temperature causes diffusion due to uneven temperatures, giving rise to erratic results. [D.S.Ru.]

864 – Contribution to the investigation of the formation of some metal complexes by high-frequency titrimetry (in German). E. Pungor and E.É. Zapp (Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 25 (1960) 133–143. The complex titration method suggested by Hara was critically investigated by the authors. The results are discussed. It was found that by way of the complexes mentioned by Hara, and by using high-frequency titrimeters, it is impossible to carry out analysis of the given components or to solve the physico-chemical problems of the complexes. Also, it was found by the authors that titrations with ethylenediamine tetraacetic acid can well be followed *e.g.* in the case of thorium, by high-frequency titration. [E.Juh.]

865 – Conductometric investigation of the interaction of some nitriles with hydrogen chloride (in Russian). E. N. Zilberman, T. S. Ivtsher and E. M. Perepletshikova. *Zhur. Obshchei Khim.*, 31 (1961) 2037–2039.

The electroconductivity of HCl in adiponitrile, benzonitrile, β -chloropropionitrile etc. has been investigated. A conventional bridge circuit was used with an oscillographic zero indicator. Measurements were carried out at $25 \pm 0.1^\circ$ with 0.5% precision. Vertical, parallel platinum electrodes were used. Solutions were prepared directly in the measuring cells by introducing dry HCl gas. HCl contents in the nitrile solution were determined by titration according to Volhard before and after the electroconductivity measurement, both results being identical. Isotherms of equivalent conductivity are given. [Ot.So.]

866 – The conductance of tetra-*n*-butylammonium picrate in 50 mole % benzene-*o*-dichlorobenzene and bromobenzene as a function of temperature (in English). W. R. Gilkerson and R. E. Stamm (Department of Chemistry, University of South Carolina, Columbia, S.C., U.S.A.). *J. Phys. Chem.*, 65 (1961) 1466–1467.

The electrical conductances of tetra-*n*-butylammonium picrate in 50 mole % benzene-*o*-dichlorobenzene at 44.26° and 64.74° and in bromobenzene at 25, 35, 44.58, 55 and 65° are given. [D.S.Ru.]

867 – The conductance of solutions in which the solvent molecule is “Large”. VI. Solutions in heptane-phosphonate ester mixtures (in English). C. M. French and P. B. Hart (Department of Chemistry, Queen Mary College, Mile End Road, London, E.1., Great Britain). *J. Chem. Soc.*, (1960) 1679–1682.

An investigation of the behaviour of tetrabutylammonium picrate in three mixtures of heptane with diethyl ethyl- and dibutyl butyl-phosphonates (conc. range from $9 \cdot 10^{-3}$ – $5.5 \cdot 10^{-6} N$; temp.: 15°, 25°, 45° and 65°). The comparison indicates that the size of the solvent molecule exerts little effect. It is therefore concluded that the determining factor is the formation of a dipolar atmosphere around the ion, the characteristics of which are influenced both by the moment of the polar group of the solvent, and by the dielectric constant of the medium. These factors, however, are insufficient to explain some specific effects. [L.Gi.]

868 – The conductance of solutions in which the solvent molecule is “Large”. V. Solutions in dialkyl alkylphosphonates (in English). C. M. French and P. B. Hart (Department of Chemistry, Queen Mary College, London, E.1., Great Britain). *J. Chem. Soc.*, (1960) 1671–1679.

The behaviour of various tetraalkylammonium picrates (alkyl = ethyl, propyl, butyl and pentyl) in three dialkyl alkylphosphonates (diethyl ethyl-, dibutyl butyl-, and di(2-ethylhexyl) at 15°, 25°, 45° and 65°, over the concentration range 10^{-2} – $10^{-6} N$ is described. Limiting equivalent conductances and ion-pair association constants have been determined from Shedlovsky plots for all systems (except tetraethyl and tetrapropyl-ammonium picrate in the 2-ethylhexyl compounds). It is suggested that some characteristics of the observed behaviour could be qualitatively explained in terms of interaction of solvent dipoles with the electrical field surrounding the ions. [L.Gi.]

869 – Titration of pyridine, quinoline, nicotine and strychnine with picric acid (in German). E. Nebe (Institut für Entwicklung chem.-phys. Analysen-methoden, Weilheim/Obb., Germany). *Pharmazie*, 14 (1959) 510–511.

The author has found two breaks in the titration curve using high frequency titration methods for

pyridine, quinoline, nicotine and strychnine against picric acid. The first corresponds to formation of a salt, but a more marked break, corresponding to the formation of an addition compound with the picric acid, is also formed. [Di.Ciò.]

870 – Method for the analysis of extracted inorganic compounds. Application of Job's continuou variation method and conductometric titrations (in German). H. Specker and E. Jackwerth (Institut für Spektrochemie und angewandte Spektroskopie, Dortmund-Aplerbeck, Germany). *Z. anal. Chem.*, 167 (1959) 416–423.

With the aim of studying the mechanism of the extraction of inorganic compounds from dilute aqueous solutions two methods are applied: the first is a modification of Job's method of continuous variation (Job, *Ann. Chim.*, 9 [10] (1928) 113; 6 [11] (1936) 97); the second is a new method called "conductometric extraction titration". The first involves the extraction of *A* and *B* from an aqueous solution containing different quantities of *A* and *B*, always being $\text{mmol}_A + \text{mmol}_B = \text{const}$. After extraction, the organic phase is analysed with respect to *A* and to *B*. Plotting the quantity of *A* and *B* in the organic phase separately against the mmol_A (or mmol_B) originally present in the aqueous phase, a maximum is obtained corresponding to the stoichiometric ratio of *A* and *B* in the compound extracted. The second method is as follows: let us suppose that *A* is in the aqueous phase; an organic solvent is added and the conductivity of the organic phase is measured. From a burette a solution of *B* is added in small portions; after each addition the solution is shaken and the conductivity of the organic layer measured. The conductivity is plotted against the quantity of *B*: if there is an inflection point, this leads to the stoichiometric ratio of the extracted compound. In the paper three examples are reported: $\text{Fe}^{3+}-\text{CNS}^-$ (1:3), $\text{In}^{3+}-\text{I}^-$ (1:4) and $\text{Hg}^{2+}-\text{I}^-$ (1:2 and 1:3), all extracted with cyclohexanone. The two methods agree. The formula of other compounds formed from Hg^{2+} , Cd^{2+} , In^{3+} , Sb^{3+} , Bi^{3+} and I^- , Br^- , CNS^- and extracted as above are given; for Bi^{3+} and I^- the effect of a different solvent on the extracted compound is also indicated. [G.deAn.]

871 – Electrical conductivity of ice containing different electrolytes (in French). J. V. Iribane, L. Levi, R. G. de Pena and R. Norscini (Facultad de Ciencias Exactas y Naturales, avenida de Mayo 760, Piso 6°, Buenos-Aires). *J. chim. phys.*, 58 (1961) 208–215.

Electrical conductivity and polarization phenomena, produced by the formation of spatial charges in ice containing the following electrolytic impurities have been studied: acids; HF, HCl; hydroxides; NaOH, LiOH, NH_4OH ; halides; LiF, NaF, NH_4F , LiCl, NaCl, KCl, RbCl, CsCl, NH_4Cl . Oscillographic observations of the transitory effect produced in the current at the time of application of the field and the distribution of the potential studied by an electrometer, have shown that with hydracids the polarization phenomenon is negligible while with halides it is very pronounced. The phenomenon is found to depend on the concentration of the impurity.

Equilibrium constant values of the acids and hydroxides in ice have been determined. From these values the dissociation state of the halides in ice has been studied.

Some possible relations between the state of dissociation of the electrolytes and the characteristics of the phenomenon of spatial charges have been indicated. [S.K.Shu.]

872 – Electrical conductivity of solutions of metals in their molten halides. II. Sodium–sodium iodide–potassium–potassium iodide and potassium–potassium fluoride (in English). H. R. Bronstein and M. A. Bredig (Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.). *J. Phys. Chem.*, 65 (1961) 1220–1224.

The equivalent conductance of the dissolved potassium rises monotonically toward that of pure potassium, while the conductance of sodium goes through a deep minimum. It is suggested that electrons are trapped by the covalent bonds of sodium molecules.

At 900° , Λ_{∞} in $\text{KF}-\text{K}$ is 800 and in $\text{KI}-\text{K}$ is 8100 $\text{ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}$ demonstrating the enhancing effect of the polarizability of the anion. The difference in Λ_{∞} , 16000 $\text{ohm}^{-1} \text{cm}^2$ for $\text{NaI}-\text{Na}$ and 8100 for $\text{KI}-\text{K}$ indicates the relative abilities of Na^+ and K^+ to polarize the iodide ion. [D.S.Ru.]

873 – Conductance of the alkali halides. I. Potassium chloride in dioxane–water mixtures (in English). John E. Lind and Raymond M. Fuoss (Sterling Chemical Laboratory of Yale University, New Haven, Conn., U.S.A.). *J. Phys. Chem.*, 65 (1961) 999–1004.

The conductance of potassium chloride in dioxane–water solutions was determined at 25° and was found to conform with the expression $\Lambda = \Lambda_0 - S(c\gamma)^{\frac{1}{2}} + E\gamma + J\gamma + J_2(c\gamma)^{\frac{3}{2}} - K_A c\gamma^2 \Lambda$ within the precision 0.01–0.05%. Below $D \approx 40$ the association to ion pairs became increasingly significant. At $D = 12.74$ the association constant was 1700. [D.S.Ru.]

874 – Conductance of the alkali halides. II. Caesium iodide in dioxane–water mixtures (in English). John E. Lind Jr. and Raymond M. Fuoss (Sterling Chemistry Laboratory of Yale University, New Haven, Conn., U.S.A.). *J. Phys. Chem.*, 65 (1961) 1414–1417.

Conductance data were obtained in dioxane-water solutions covering the range of dielectric constant $12.81 \leq D \leq 78.54$. The requirements of the Fuoss conductance equation were met in the range where Ka is less than 0.2. The contact distance \bar{a}_j was found to vary between 5.04 and 3.04 Å and the limiting conductances gave a hydrodynamic contact distance of 2.93 Å.

875 – Conductibilité du nitrate d'argent dans la diméthyl-formamide (in French). H. Chateau et M. C. Moncet (Laboratoire de Recherches, 30 rue des Vignerons, Vincennes, Seine, France). *Compt. rend.*, 252 (1961) 2875–2877.

Les auteurs ont déterminé par conductimétrie la constante de dissociation du nitrate d'argent dans la diméthylformamide ($K = 3.94 \cdot 10^{-3}$). Les solutions de nitrate d'argent ne se conservent pas, en raison d'une réduction lente en argent métallique, toutes les mesures sont effectuées dans la demi-heure qui suit leur préparation. Pour des concentrations de nitrate d'argent inférieures à $5 \cdot 10^{-3} M$ on obtient une relation linéaire entre la conductibilité équivalente molaire (Λ) et la quantité \sqrt{C} (C concentration). La pente expérimentale est de 591, dans le cas d'une dissociation complète celle-ci serait de 162.8. Les auteurs ont utilisé la technique de Shedlovsky pour calculer la constante de dissociation K à partir des résultants expérimentaux précédents. Par ailleurs, en s'appuyant sur la théorie de Fuoss, les auteurs calculent la plus petite distance d'approche " a " des ions, $a = 1.5 \text{ Å}$. Les auteurs en concluent que les ions Ag^+ et NO_3^- ne sont pas solvatés dans la diméthylformamide. [Bad.Lam.]

876 – Sodium triphenylcyanoborate as reagent for the detection and determination of caesium (in German). J. Havří (Military Technical Academy, Brno, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 26 (1961) 1775–1783.

Weighed amounts of the sodium-triphenylcyanoborate solution were titrated with a 0.05 M solution of thallium(I) nitrate. Near the point of equivalence large amounts of precipitate were formed. Conductometric titration curves show that conductivity of the solution rises nearly linearly with addition of the reagent. Near the point of equivalence the curve is rounded, and rises more rapidly and again linearly after the point of equivalence.

For the indirect potentiometric determination of caesium a caesium-triphenylcyanoborate salt was precipitated, washed with distilled water, dried in the air and kept in a desiccator over calcium chloride. Weighed amounts of this salt were dissolved in 10 ml acetone, and diluted with 90 ml water. The resulting solution was titrated with a 0.05 N silver nitrate solution with potentiometric indication using a silver wire indicating electrode and a saturated calomel comparison electrode (dipped in 10% potassium nitrate solution). [Ot.So.]

877 – Conductometric titration of caesium by antimony(III) chloride (in German). J. Havří (A. Zápotocký Technical Academy, Brno, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 25 (1960) 695–700.

A dilute solution of caesium chloride in glacial acetic acid was titrated against 0.3 to 0.5 M SbCl_3 volumetric solution, standardised by gravimetric methods. Conductivities were measured on the "Konduktoskop" (Laboratorní přístroje, Praha) using a platinum cell at 50 c/min and $25 \pm 0.1^\circ$. Corrections were made for the conductivity of acetic acid. As long as conductivity decreases, caesium-antimony(III) chloride is precipitated. After reaching the point of equivalence conductivity remains constant. When titrating solutions containing 1 mg Cs or less in 1 ml, precipitation is slow and titration errors are large. Presence of FeCl_3 interferes. [Ot.So.]

878 – Kinetic investigations of aluminium complexes by high frequency titrations (in German). E. Pungor and E. É. Zapp (Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 27 (1961) 69–75.

Die sich zwischen Aluminium und Komplexon(III) bzw. Komplexon(IV) abspielenden Reaktion wurde durch Verfasser einem kinetischen Studium unterworfen. Es wurde festgestellt, dass der Austausch gewisser Ligandgruppen des Komplexons und der sich zum Aluminium vor Reaktionsbeginn anknüpfenden Wassermoleküle ein Zeitvorgang ist, dessen Geschwindigkeit vom Protongehalt des als Komplex anwesenden Komplexonats abhängt. Nachdem dieser Gehalt durch den Gesamtprotongehalt der Lösung bestimmt wird, beeinflusst der pH-Wert der Lösung die Geschwindigkeit in entscheidender Weise. [E.Juh.]

879 – Solubility and conductivity of substituted ammonium iodides in pentaborane (in English). Henry E. Wirth and Paul I. Slick (Department of Chemistry, Syracuse University, Syracuse, New York, U.S.A.). *J. Phys. Chem.*, 65 (1961) 1447–1449.

The equivalent conductance and solubilities of tetra-*n*-butylammonium iodide and tetra-*n*-propylammonium iodide were determined in the temperature range $0-25^\circ$. [D.S.Ru.]

880 – Etude de la conductibilité des iso-polyacides en milieu sel de fond. Applications aux iso-polyvanadates en milieu acide (in French). B. Varoqui et J. Brenet (Laboratoire de chimie physique du corps solide, Faculté des Sciences, Strasbourg France). *Compt. rend.*, 252 (1961) 3033-3035.

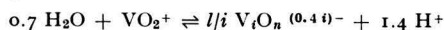
Par une méthode conductimétrique en milieu de sel de fond, les auteurs ont mis en évidence la possibilité de déterminer le degré de condensation de l'ion isopolydique. Cette méthode est supérieure à la méthode potentiométrique dès que la concentration en proton devient importante dans la solution.

Les auteurs étudient la variation de la concentration des ions H^+ au cours de l'introduction d'acide chlorhydrique dans une solution de vanadium. Ces études sont traduites par deux graphiques:

1) H^+ (mesuré à l'électrode de verre) = f (HCl/vanadium)

2) conductibilité de la solution = f (HCl/vanadium)

En l'absence d'hydrolyse on obtient une droite ($HCl/V > 3.5$). Lorsque l'acidité diminue la courbe expérimentale s'écarte de la droite. Si l'on admet que l'anion le moins chargé possède 0.4 charge négative par atome de vanadium, cet écart permet de calculer le degré de condensation et la constante K relative à l'équilibre:



soit $i = 10$ et $\log K = 0.624$.

[Bad.Lam.]

881 – The conductance of hydrochloric acid at 25° (in English). R. H. Stokes (Department of Physical and Inorganic Chemistry, University of New England, Armidale, N.S.W. Australia). *J. Phys. Chem.*, 65 (1961) 1242-1247.

The determination of the conductivity of sodium chloride provides a new method for the analysis of hydrochloric acid which is highly accurate. The elimination of errors and Soret effect permitted the determination of the conductance of hydrochloric acid to $\pm 0.005\%$.

The Fuoss-Onsager theory was used to examine the results, $A^\circ = 426.50 \text{ cm}^2 \text{ ohm}^{-1} \text{ equiv}^{-1}$ at 25°. The Fuoss-Onsager equation holds up to 0.004 N , the Pitts equation up to 0.02 N .

[D.S.Ru.]

See also abstracts nos. 684, 685, 686, 694, 708, 709, 710, 905, 947, 952.

6. Electrolysis

882 – Internal electrolysis with the aid of vibrating electrodes (in German). G. Facsko and I. Radoi (Polytechnisches Institut, Timisoara, Rumänien). *Acta Chim. Acad. Sci. Hung.*, 27 (1961) 31-40. Wenn die innere Elektrolyse als eine Frage der Lokalelemente betrachtet wird, ergibt sich ein äusserst fruchtbarer Weg zur Behandlung des Mechanismus der Inneren Elektrolyse und es ist möglich, den Einfluss verschiedener Faktoren auf die Dauer und die Genauigkeit der Bestimmung abzuschätzen.

Einen besonders günstigen Einfluss auf diesen beiden Grössen hat die Depolarisierung des kathodischen Vorganges, was wir durch vibrieren der Kathode bei entsprechender Frequenz und Amplitude erreichten. Die bei der inneren Elektrolyse mit vibrierender Kathode erhaltenen experimentellen Ergebnisse beweisen die Richtigkeit der angestellten theoretischen Betrachtungen und bilden die Grundlage einer neuen Bestimmungsmethode mittels innerer Elektrolyse. [E.Juh.]

883 – Rotating amalgamated cathode for the preparation of salicylaldehyde (in English). H. V. K. Udupa (Central Electrochemical Research Institute, Karaikudi 3, India). *Bull. acad. polon. sci., Série des Sciences Chimiques*, 9 (1961) 51-56.

Experiments were performed to study the possibility of using lead and copper amalgamated electrodes in the electrochemical reduction of salicylic acid to salicylaldehyde. Current efficiency obtained is compared with that reported with a mercury cathode. A large laboratory cell for production of 200-240 g salicylaldehyde has been described, as well as the recovery of unreduced salicylic acid. Material yield of 66% was obtained, whereas the current efficiency of the electrolytic process was not more than 50-60%. [Ad.Hu.]

884 – Theory of electrolysis on a rotating disc electrode (in Russian). L. P. Kholpanov (Mendeleev Institute of Chemical Technology, Moscow, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 1538-1542. With the aid of the boundary condition accounting for ion transport by migration and by ionic

diffusion, an equation has been derived relating the current density at the surface of a rotating disc electrode and its angular velocity. According to this correlation the current density does not assume zero value in the absence of rotation of the electrode. [Ot.So.]

885 – Theory of electrolysis on the rotating disc electrode under conditions of combined concentration and chemical polarisation (in Russian). L. P. Kholpanov (Mendeleev Institute of Chemical Technology, Moscow, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 1567–1570.

A method for the theoretical calculation of the rate of electrochemical reactions under conditions of combined chemical and concentration polarisation has been proposed. An expression for the relation between the current strength and angular velocity of rotation of a disc electrode has been derived for such conditions. Based on this a formula is proposed for determining the effective activation energy of the electrode process on a rotating disc electrode. [Ot.So.]

886 – A rapid method of porosity determination of organic protective coatings (in Polish). Z. Hippe and Z. Jedliński. *Przemysł chem.*, 40 (1961) 40–41.

A new method of porosity determination of organic protective coatings was developed. This method can be used in the case of steel or other metallic surfaces, for instance aluminium. The method consists of short (1–2 sec) electrolysis of a sodium chloride solution (3%) containing phenolphthalein and bromothymol blue, with a total voltage 20 V. One electrode consists of a platinum wire, the second being the examined metal plate covered with a coating. The number of coloured points appearing in the places where electrolysis proceeded is taken as a measure of porosity. Results were compared with other methods and a good agreement was found. [Ad.Hu.]

887 – Studies on the electrolytic oxidation of benzene to quinone (in English). K. S. Udupa, G. S. Subramanian and H. V. K. Udupa (Central Electrochemical Research Institute, Karaikudi 3, India). *Bull. acad. polon., Série des Sciences Chimiques*, 9 (1961) 45–50.

Conditions for electrochemical oxidation of benzene to quinone have been studied using a lead dioxide anode formed on lead or deposited on graphite or carbon substrate. High efficiency was favoured by low current densities. Electrolysis was performed at various temperatures and the best yield was obtained with a PbO_2 -graphite anode at 15–25°, and with a PbO_2 -lead anode at 40–45°. The electrolyte was composed of 5% H_2SO_4 . When the duration of electrolysis was short the conditions for oxidation were favourable but the efficiency decreased as the time of electrolysis was prolonged. The influence of addition CoSO_4 , $\text{Ce}_2(\text{SO}_4)_3$, V_2O_5 and $\text{K}_3\text{Fe}(\text{CN})_6$ was studied. The maximum, i.e. 60% efficiency, was obtained on a PbO_2 -graphite anode. [Ad.Hu.]

888 – Electrolytic reduction of benzaldehyde at a mercury cathode—preparation of dibenzyl mercury (in English). T. Arai and T. Oguri (Department of Chemistry, Shinshu University, Matsumoto, Japan). *Bull. Chem. Soc. Japan*, 33 (1960) 1018.

Dibenzyl mercury could be obtained by electrolysis of benzaldehyde in aqueous sulphuric acid at a mercury cathode. Current density had no effect in the range 20–40 A/cm^2 . Yield of dibenzyl mercury was optimum (8.5%) in 50% sulphuric acid and temperatures below 25°; at higher temperatures yield decreased and at 50° only hydrobenzoin and an oily material were produced. Electrolysis of vanillin, piperonal, anisaldehyde, furfural and salicylaldehyde, under similar conditions, yielded only resinous materials. [E.H.Ba.]

889 – Electroreduction as a method for the investigation of protein (in Russian). A. A. Akimova and N. I. Gavrillov (State University, Moscow, U.S.S.R.). *Zhur. Obshchei Khim.*, 31 (1961) 38–42.

The instrument used is described in a previous publication. (*Zhur. Obshchei Khim.*, 25 (1955) 1802). A rotating mercury electrode with 40–50 ml Hg is used, cathodic current density 0.056 A/cm^2 , cathodic solution volume 100 ml, temperature of catholyte 15 to 20°, medium of 5% HCl, direct current of 120 V, 5 A, time 5–7 hours. The electroreduction of serine, glycylserine, alanylserine, glycytyrosine and tyrosine diketopiperazines has been investigated. Only piperazines are formed, and their chromatographic R_F values and electrophoretic v values have been determined. [Ot.So.]

890 – The simultaneous electrochemical discharge of the base metal and impurities, with regard to the depolarisation effect (in Russian). B. L. Kheifets, A. L. Romiyana, O. P. Kalganova and P. G. Lebenshits. *Zhur. Priklad. Khim.*, 34 (1961) 1519–1528.

A method for estimation of the depolarisation effect is described for the case where large amounts of one metal and small amounts of other metals are discharged simultaneously. An equation is derived showing how the purity of the main precipitated metal depends on various factors, when both metals are discharged by chemical polarisation. [Ot.So.]

891 – Separation of trace amounts of silver using mercury as a collector (in Japanese). Shizo Hirano and Atushi Mizuike (Faculty of Engineering, University of Tokyo, Tokyo, Japan). *Japan Analyst*, 8 (1959) 746–749.

Methods are described for the separation of microgram quantities of silver using mercury as a collecting agent. Electrolysis with a mercury cathode can be applied to the separation of silver from a dilute sulfuric acid solution. This method fails, however, in the presence of large amounts of copper or iron, because these metals deposit on the mercury cathode together with silver.

The present authors have found that silver is rapidly collected into mercury globules as dilute amalgam from a sulfuric acid or ammoniacal solution when the solution is stirred vigorously in a conical beaker by a magnetic stirrer. In this procedure, copper or iron in the solution do not deposit on the mercury. The dilute amalgam thus obtained is heated in a silica boat at 350°C in a stream of nitrogen to remove mercury, and silver in the residue is determined by the photometric *p*-dimethylaminobenzylidene-rhodanine method. Tracer experiments indicated that recoveries of silver are usually over 95%. [Ta.Fu.]

892 – Possibilities of electrolytic isolation of copper and zinc with a lowered voltage (in Polish). W. Tomassi and J. Komorowska (Department of Physical Chemistry, Politechnika, Warsaw, Poland). *Przemysł chem.*, 40 (1961) 88.

Using graphite powder electrodes it was possible to decrease significantly the electric tension of the anode, causing an appreciable decrease in the total voltage for electrolytic isolation of copper or zinc. Isolation of copper (30 g/l) from H₂SO₄ solution with current density 100 A/m² needs only 0.45–0.6 V. From a solution of zinc (75 g/l) and current density 200 A/m² the metal isolation proceeds at 1.6–1.9 V. The energy gain in these processes is about 65% and 45% respectively. The graphite powder electrode can be continuously regenerated. [Ad.Hu.]

893 – Electrolytic and electrochemical separation of radium D, radium E and polonium from ethylenediaminetetraacetic acid (EDTA) solutions (in German). V. Vebersik (Fachschule für Kerntechnik, Prague, Czechoslovakia). *Z. anal. Chem.*, 175 (1960) 405–415.

A method is described for the electrolytic separation of radium D and E from EDTA solutions. The electrode employed is formed from a platinum plate, 0.2 mm thick and 10 × 10 mm square; the applied voltage is 3.5 V. For the electrochemical separation of polonium from EDTA solutions, a silver electrode, 0.2 mm thick and 10 × 10 mm square, has been employed. This method has been used for rapid separations of the two metals. [Di.Ciò.]

894 – Redox tension of tungsten in hydrochloric acid (in German). R. Geyer, G. Menze (Institut für analytische Chemie, technische Hochschule für Chemie, Leuna-Merseburg, Deutschland). *Z. anal. Chem.*, 177 (1960) 185–190.

The cathodic reduction of tungsten (VI) solutions in HCl, with lead or mercury electrodes, goes as far as tungsten (III). Tungsten (IV) does not appear. Pure solutions of W (III) always have a green colour; at low tungsten concentrations a yellow–green colour may appear. Further reduction of W (III) has not been confirmed. [Di.Ciò.]

895 – Electrolysis of hydrochloric acid on powder electrodes (in Polish). W. Tomassi, H. Jankowska and B. Batijewski (Department of Physical Chemistry, Politechnika, Warsaw, Poland). *Przemysł chem.*, 40 (1961) 86–87.

The process of electrolysis of hydrochloric acid was examined with powder electrodes of platinum black and silica gel. The electrolysis voltage can be significantly decreased if powdered material capable of electron exchange is used in the electrode process. For instance 0.5 N HCl was electrolyzed at 0.20 V and current density 33 A/mm² with platinum black on both electrodes. The type of lead-out electrode does not influence the results. The silica gel electrode has an unfavourable effect on the electrolysis voltage. [Ad.Hu.]

896 – Dissolution of a platinum anode during electrolysis with a mercury cathode (in Japanese). Shizo Hirano, Atsushi Mizuike and Masao Saeki (Tech.-anal. Chem., Faculty of Engineering, Tokyo University, Hongo, Tokyo, Japan). *Japan Analyst*, 8 (1959) 827–828.

In the colorimetric determination of trace amounts of cobalt in metals using mercury-cathode electrolysis, fairly high blank values (about 0.1–0.4 μg) were observed.

A sulfuric acid solution containing 1 g of the metals is electrolyzed with 2 ml of mercury as a cathode and a platinum spiral (1 mm ø × 16 cm) as an anode.

The amount of Pt which dissolves in the mercury cathode is ≈ 10 μg in 3 h at 7° (2 V, 6 A) in N H₂SO₄ electrolyte and 50–80 μg in 6 h at 16° (2 V, 7 A). The Pt appears to be the source of the blank value in colorimetric determination of Co with nitroso-R salt.. [Ta.Fu.]

See also abstracts nos. 698, 700, 701, 731.

7. Coulometry

897 – Continuous coulometric determination of alkalinity in water. (Studies on automatic continuous coulometric titration. VII.) (in Japanese). Akira Takahashi (Denkishiki Kagaku Keiki Kenkyujo, Musashino-shi, Tokyo, Japan). *Japan Analyst*, 9 (1960) 921–925.

The alkalinity of water, which is one of the important factors to be measured in water cleaning treatment, was continuously determined by an automatic continuous coulometric titration method. The sample of water and the electrolyte solution (*ca.* 0.15 *M* sodium sulfate), both of which were poured into the titration cell with a constant flow rate, were mixed with each other, and the alkaline constituent contained in the sample water was titrated with the hydrogen ion generated by electrolytic oxidation of the Na₂SO₄ solution. A glass electrode (pH of the inner solution = 2) and a saturated calomel electrode were used as detecting electrodes, and the operating voltage was not selected at –300 mV (corresponding to pH 7) but at –215 mV *vs.* S.C.E., based on the data obtained experimentally for determining total alkali.

The alkalinities of several sample solutions prepared with NaOH and Na₂CO₃ were measured, and successful results were obtained for the relationship between the electrolysis current and the alkalinity, with good reproducibility of measurement and very stable recordings. [Ta.Fu.]

898 – Propriétés électrochimiques des oxydes de plomb (in French). Mme Machtinger-Convers (Laboratoire de Chimie Analytique, E.P.C.I. 10 rue Vauquelin Paris 5, France). *Ann. chim. (Paris)*, 6 (1961) 395–448.

Une étude voltammétrique permet à l'auteur de préciser les caractéristiques électrochimiques du système oxydo-réducteur Pb(II)/Pb(IV). Selon le pH de la solution l'auteur étudie la réduction de PbO₂ en sesions (pH < 7 ou pH > 12) ou en oxydes inférieurs PbO, Pb₂O₃, Pb₃O₄ (7 < pH < 12). L'auteur étudie de la même façon l'oxydation du plomb métallique et du plomb(II) à différents pH. Le système Pb(II)/Pb(IV) est intermédiaire entre un système lent et un système rapide. La réduction de PbO₂ en oxydes inférieurs et l'oxydation du plomb métallique ont fait l'objet d'études coulométriques à intensité constante et à tension électrique contrôlé qui ont permis de préciser les formules des divers oxydes intermédiaires et les différents tensions électriques de transformation d'un oxyde en l'autre.

Les propriétés électrochimiques déterminées par l'auteur ont été appliquées à la précision de diverses réactions chimiques: attaque du plomb, réduction par le plomb métallique, oxydation par PbO₂ (cas de la méthionine). La dernière partie de l'article est consacrée à la détermination par voltammétrie du domaine d'électroactivité de l'eau à différentes électrodes (Pt, PbO₂, Tl₂O₃) et à différents pH. Deux réactions d'oxydation sont possibles: 2 H₂O → O₂ + 4 H⁺ + 4 e, en milieu acide et neutre et 4 HO⁻ → O₂ + 2 H₂O + 4 e, en milieu alcalin. [Bad.Lam.]

899 – Coulometric titrations with electrolytically generated sulfhydryl compounds. Application of thioglycolic acid (in English). B. Miller and D. N. Hume (Department of Chemistry and Laboratory for Nuclear Science, Massachusetts Institute of Technology Cambridge 39, Mass., U.S.A.). *Anal. Chem.*, 32 (1960) 524.

Thioglycolic acid is used as complexing reagent for the determination of Hg, Au, Cu, and ferri-cyanide. The method seems to be useful for metals, which are less suitable for determination with EDTA and other complex forming reagents of the same type. The reagent is generated from the very stable mercuric complex, which is soluble at pH values above the pK₁ of the acid, *i.e.* 3.6. The end point can be detected potentiometrically with a mercury pM electrode, or amperometrically with two mercury electrodes. The determination and generation of the reagent must be carried out under an inert gas atmosphere to avoid air oxidation of the free thioglycolic acid. Apparatus and procedure is described. Some typical titration curves are shown. Accuracy is about ±0.5% at the mg level. [Kl.Gr.]

900 – Coulometric–acidimetric titration of fluoride in acetic anhydride W. B. Mather, Jr. and F. C. Anson (California Institute of Technology, Pasadena, Calif., U.S.A.). *Anal. Chem.*, 33 (1961) 132.

Fluoride is titrated as a base in an electrolyte containing sodium perchlorate, acetic anhydride and a small amount of acetic acid. The acid used to neutralize the base is perchloric acid, which is generated coulometrically with 100% current efficiency at a mercury anode. The end-point is detected potentiometrically. Most anions other than perchlorate are titrated together with the fluoride. In some cases two end-points can be observed with binary mixtures as chloride–fluoride. The end-point of the titration is indicated by a mercury or glass electrode. A mercury–mercurous acetate comparison electrode is used. The inflection of the potentiometric curve is sharp and taken as the end-point. A 5 sq. cm gold foil amalgamated with mercury is used for generation of the perchloric acid. The accuracy in the case where only fluoride is present is below 0.17%. [Kl.Gr.]

901 – Coulometric titration method for ferrous ion by electrolytically generated bromine (in Japanese). Takeo Takahashi and Hiroshi Sakurai (Institute of Industrial Science, University of Tokyo, Tokyo, Japan). *Japan Analyst*, 9 (1960) 1027–1031.

It was found that ferrous ion reacted with bromine more smoothly in acetic acid–sodium acetate medium than in sulfuric acid medium, and that a marked change of electric tension occurred at the end-point. The titration curves and the reaction velocities of the above reaction were studied with regard to the various compositions of the electrolytic solution. The end-points were detected by potentiometric or dead-stop method; the potentiometric curve was a typical logarithmic one having a jump of electric tension of about 0.5 V; the dead-stop curve was V shaped, the minimum point being near the end-point.

As a result, ferrous ion in the concentration range of 0.01 to 0.1 mequiv. was titrated coulometrically within about 1% error if the electrolytic solution contained 0.1 M potassium bromate, 1 N acetic acid and 0.2 N sodium hydroxide. [Ta.Fu.]

902 – Coulometric estimation of ferricyanide (in English). K. S. V. Santhanam and A. P. Mandhavan Nair (Alagappa Chettiar College of Technology, University of Madras, India). *Z. anal. Chem.*, 169 (1959) 102–105.

Coulometric determination of ferricyanide can be performed at + 0.220 V vs. C.S.E., using a silver anode and an inner platinum gauze cathode. A hydrogen–oxygen coulometer in series with the cell and filled with 0.5 M K_2SO_4 gives the quantity of electricity passed through the solution until the current reduces itself to less than 1 mA. The determination is performed both with and without a supporting electrolyte; the best supporting electrolyte is found to be an acetate buffer at pH 5 (obtained from 50 ml of 0.1 M $CH_3COOH + CH_3COONa + H_2O$ up to 200 ml). The solution is deaerated with hydrogen before the determination, with stirring. When ferricyanide is the only solute, the presence of the supporting electrolyte does not affect the accuracy (which is about $\pm 1\%$), but it shortens the duration of the electrolysis to about half the time. When chloride ions are present the accuracy is not good; the presence of the selected electrolyte reduces the error, but not entirely; *i.e.* chloride ions interfere.

Compared with the standard volumetric or gravimetric procedures, a coulometric technique gives the best accuracy. [G.deAn.]

903 – Coulometric generation and back-titration of intermediate reagents at controlled potential. W. D. Shults (Analytical Chemistry Division, Oak Ridge National Lab., Oak Ridge, Tenn., U.S.A.). *Anal. Chem.*, 33 (1961) 15.

The technique of coulometric generation and back-titration of intermediate reagents at controlled tension is applied to the indirect determination of plutonium(VI) with iron(II). A sample containing 10 to 50 mg plutonium is oxidized with 1 ml $HClO_4$ and 2 drops HNO_3 , under carefully controlled conditions. After oxidation the sample is transferred into a 10 ml volumetric flask. The electrolyte, containing 13 to 14 ml 1 M H_2SO_4 and about 0.5 ml of a standard iron solution containing 5 mg Fe/ml is placed into the electrolysis vessel. CO_2 is led into the cell and the iron is oxidized at + 0.660 V. 1.00 ml of the plutonium sample is pipetted into the cell and an excess of about 10–20 μeq . Fe(II) is generated at + 0.270 V vs. S.C.E. The read-out voltage of the integrator is recorded and the integrator is set to zero. After this the solution is oxidized at + 0.660 V until the current again falls to 50 μA . The read-out voltage is recorded and the weight of the plutonium is obtained from the relationship 10.14 ($Q_r - Q_0$). [Kl.Gr.]

See also abstracts nos. 706, 707, 846.

8. Electrophoresis

904 – A new technique of agar electrophoresis. R. J. Wieme (Laboratory of the Medical Clinic, University of Ghent, Belgium). *Clin. Chim. Acta*, 4 (1959) 317–321.

Preparation of the agar plates for electrophoresis is accurately described. The space between the plates is filled with petroleum ether (25–70°). Good separations are obtained in 25 min at 25–35 mA and 130–150 V. The plates may be recovered by washing with suitable solutions. For quantitative determinations, the plates are examined with an Eppendorf photometer. This method is suitable for examinations of pathologic human serum and albumin. [Di.Ciò.]

905 – Counter-current paper electrophoresis. IV. Determination of porosity and the tortuosity coefficient of chromatographic papers (in German). J. Vacík and J. Cabicar (Institute of Physical Chemistry, Charles University, Prague, and Institute of Physical Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 25 (1961) 404–409. A new method for the determination of porosity of wet chromatographic paper has been determined, based on the investigation of the kinetics of water evaporation from the paper. Further, the method of measuring electrical conductivity of a porous medium filled with electrolyte solution has been applied to the measurement of the conductivity of chromatographic paper. A combination of both methods allows calculation of the tortuosity coefficient. [Ot.So.]

906 – An investigation of conditions of separating substances by high-voltage electrophoresis on paper (in English). Z. Prusík and B. Keil (Department of Biochemistry, Institute of Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 25 (1961) 2049–2058.

The construction of a cooled high-voltage paper electrophoresis apparatus, operated at potential gradients up to 120 V/cm is described. This arrangement makes it possible to achieve a reproducible degree of moisture in the paper, to maintain a constant temperature and to measure the potential gradient in the paper itself. Thus the direct determination of the mobilities of some compounds is possible. Electrophoretic mobilities of different dinitrophenyl derivatives of amino acids were studied as a function of pH and ionic strength of the medium. Relative mobilities of certain amino-acids and peptides were determined. The procedure outlined is suitable for separations on a preparative scale. [Ot.So.]

907 – Physico-chemical measurements in finding the best conditions for paper electrophoresis (in German). W. Croon and H. Croon (Chemischen Abteilung des Staatlichen Institutes für Hygiene und Infektions-Krankheiten, Saarbrücken, Germany). *Z. anal. Chem.*, 168 (1959) 115–119.

The best conditions for paper electrophoretic separation of proteins are obtained by controlling the energy equilibria involved and the pH and conductivity of the solutions. Maintaining an exactly constant current (0.5 mA/cm for 30 cm S. & S. 2043b paper strips) with an initial applied electrical tension of 650 V in a Veronal buffer solution at pH 8.6, the tension falls to 250 V after 4 hr, and the temperature remains constant without cooling and the best separations are obtained. The pH is important and the best results are obtained at pH 8.6–8.8, but the less the conductivity of the buffer solution the more pronounced the mobility of proteins; when the conductance is less than 1/180 S the mobility is practically constant: at 1/180 S a pherogram of 9–10 cm can be obtained in 2–2.5 hrs. The method is promising for the analysis of the proteins in the *Liquor cerebrosppinalis*. [G.deAn.]

908 – Separation of salicylate metabolites by paper electrophoresis (in English). J. Franz, D. Schottelius, E. Arredando, W. D. Paul and J. I. Routh (State University of Iowa, Iowa City, U.S.A.). *Proc. Iowa Acad. Sci.*, 66 (1959) 205–209.

The end products of salicylate metabolism are separated by paper electrophoresis. The best separation is obtained in phthalate buffer, pH 3.2 and ionic strength 0.0125–0.05.

The spots of salicylic, acetylsalicylic, salicyluric and gentisic acids are detected by their fluorescence under UV light.

1 μ g of each product can easily be detected on the strip. [Gio.Ser.]

909 – Electromigration methods. II. Relation between the structure of anthraquinone derivatives and their mobility in paper electrophoresis (in German). J. Franc and M. Wurst (Research Institute of Organic Syntheses, Pardubice, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 25 (1960) 657–661.

The influence of the steric structure of anthraquinone derivatives on magnitude and direction of their paper-electrophoretic migration has been investigated. For identification of the derivatives the method has been combined with paper chromatography. R_F values have been used to calculate the equivalent of chromatographic binding of hydrogen, R_E . Results are tabulated for some 80 compounds. [Ot.So.]

910 – Electromigration methods. III. Mobility of some azo-dyes of I- and γ -acids (in German). J. Franc and M. Wurst (Research Institute of Organic Syntheses, Pardubice, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 25 (1960) 663.

The influence of functional groups and of intermolecular hydrogen bridges on mobility of azo-dyes has been investigated. Results are tabulated, showing R_F values for petroleum–alcohol and petroleum–alcohol–ammonia systems, and mobilities are tabulated for 3 N NH_4OH and 1 N CH_3COOH . [Ot.So.]

911 – Starch electrophoresis. II. Starch column electrophoresis (in English). H. Bloemendal (Department of Biochemistry, A. van Leeuwenhoek-Huis, The Netherlands Cancer Institute, Amsterdam, The Netherlands). *J. Chromatog.*, 3 (1960) 1–10.

Second part of a review paper, with 25 additional references (first part: *J. Chromatog.*, 2 (1959) 121). Column electrophoresis, as discussed here, differs from block electrophoresis in that it involves a continuous, rather than discontinuous, elution of individual zones. Current methods are described shortly, and compared; the theoretical basis for estimating temperature effects is discussed; a set-up for elution and automatic recording is presented; electro-osmotic effects are briefly reviewed. A brief discussion quotes some selected problems where the method was found useful. It appears that column fractionation is not widely favoured since, while technically more involved than starch block techniques, it affords no better or even poorer separation. [J.E.Le.]

912 – Starch electrophoresis. III. Starch gel electrophoresis (in English). H. Bloemendal (Department of Biochemistry, A. van Leeuwenhoek-Huis, The Netherlands Cancer Institute, Amsterdam, The Netherlands). *J. Chromatog.*, 3 (1960) 509–519.

Third part of a review paper, with a further 62 references (first and second part: *J. Chromatog.*, 2 (1959) and *ibid.*, 3 (1960) 1). Starch gel electrophoresis is a rather recent procedure, characterized by its uncommonly high resolving power. Technical details are described: apparatus, preparation of the gel, insertion of the sample, recommended buffers. There is also a discussion of problems specific to starch gels: temperature effects, location of zones, quantitative estimations, elution. So far, applications are found in the field of protein chemistry, mostly for serum proteins. The method has definite advantages as an analytical tool, but it does not appear particularly promising for preparative work. [J.E.Le.]

913 – Paper ionophoresis of polyhydroxy compounds in tellurate and germanate solution (in English). W. J. Popiel (Chemistry Department, Brighton Technical College, Sussex, Great Britain). *Chem. & Ind.*, 14 (1961) 434–435.

The separation of polyhydroxy compounds was investigated by ionophoresis using an electrolyte 0.05 M in telluric acid. Although the results are of interest, better separations were effected by borate and germanate buffers.

The values of Mg for a number of carbohydrates was determined using a 0.04 M germanium hydroxide buffer adjusted to pH 10.0 with sodium hydroxide. Some values were 10–30% higher than those previously reported under slightly different conditions. [D.S.Ru.]

914 – An electrophoretic study of polymer interaction (in English). David Platt (Biochemistry Department, University of Pittsburgh School of Medicine, Pittsburgh, Pa., U.S.A.). *J. Electroanal. Chem.*, 1 (1959–60) 258–259.

Electrophoretic analysis of mixtures of sodium carboxymethylcellulose (SCMC) and methylcellulose (MC), or SCMC and polyacrylamide (PAM) has demonstrated an interaction of the strongly acidic polysaccharide (SCMC) with the slightly charged polymers (MC and PAM). This interaction is reflected in changes in the electrophoretic mobilities; the author suggests that hydrogen bonding seems to be the force involved in the binding between the polymers. [Su.Mo.Ce.]

915 – Separation of fungal carbohydrases by starch block zone electrophoresis (in English). Mary Mandels, G. L. Miller and R. W. Slater Jr. (Pioneering Research Division, Quartermaster Research and Engineering Center, Natick, Mass., U.S.A.). *Arch. Biochem. Biophys.*, 93 (1961) 115–121.

A method is described for the separation and identification of different carbohydrases found in the culture filtrates of various fungi. Each fungus produces different carbohydrases with different electrophoretic mobilities and different activities on various substrates. The patterns obtained electrophoretically by different fungi vary greatly. The results are discussed. [Gio.Ser.]

916 – The fractionation and estimation of free amino acids in serum (in English). E. R. Cook and Mollie Luscombe (Rheumatism Research Unit, Royal National Hospital for Rheumatic Diseases, Bath, Great Britain). *J. Chromatog.*, 3 (1960) 75–84.

Amino acids are first isolated from other serum components, by adsorbing them on a small column of Zeocarb 225(H). After being eluted with ammonia, they are separated into six groups by means of high voltage electrophoresis (1350 V; 1 N acetic acid buffer; 2½–3 h). Fluorescence is used to locate the bands, which are cut out, eluted and separately submitted to paper chromatography (descending; *n* butanol-ethanol-ethyl acetate–acetic acid–water systems). Final estimation is made, photometrically, after treating the spots with ninhydrin followed by cadmium sulphate. Microgram quantities are estimated (1–50 µg); as quoted, recoveries range from 41% (methionine) to 124% (glycine), most cases falling in the range 75–110% (average 86%). [J.E.Le.]

917 – Analysis of biological amines by means of chromato-ionophoresis, electrophoresis and paper chromatography (in French). J. Blass and A. Sarraff (Institut Pasteur, Annexe de Garches, Serv. de Chimie Bactérienne, Garches, France). *J. Chromatog.*, 3 (1960) 168–177.

Techniques are described which are suitable for the identification of non-volatile amines in broth cultures. Bacterial bodies and volatile amines are first removed; samples of hydrolyzed and samples of unhydrolyzed broth are next submitted to paper electrophoresis and compared; for better resolution, descending paper chromatography followed by paper electrophoresis is to be preferred. Microgram amounts of non-volatile amines can be identified, even in the presence of up to 500 μg total nitrogen from the broth. In addition, volatile amines can be separately analyzed; the sensitivity and specificity of such techniques as paper electrophoresis or chromatography on buffered paper are discussed. [J.E.Le.]

918 – Paper electrophoresis (in Polish). W. Swiecicki. *Farm. Polska*, 16 (1960) 27–32.

Theory, apparatus and applications of paper electrophoresis to the analysis of proteins, amino-acids, alkaloids, sugars and fats are discussed.

919 – Globuline. K. H. Hofle (Medizinische Klinik, Darmstadt, Germany). *Ärztzl. Lab.*, 5 (1959) 185–199.

The dependence of the α , β , and γ globuline path amplitude on the health condition of the serum furnishers is described. The path amplitude values, obtained by electrophoresis measurements, are employed for clinical diagnosis. [Di.Ciò.]

920 – Paper-electrophoresis of hog's milk proteins. R. Ferrando, C. J. van Oss and J. Froget (Ecole nationale Vétérinaire, Alfort/Seine, France). *Bull. Soc. Chim. Biol.*, 41 (1959) 1297–1301.

The paper-electrophoresis of hog's milk proteins is described. The milk is drawn at the beginning of lacteous secretion. The γ -globulines of the slow type are predominant up to the second day of secretion. After and up to the fifth day, the γ -globulines of the swift type appear. At that time the α -globulines are recognizable from the β . [Di.Ciò.]

921 – Paper electrophoresis of proteins in acid buffer (in English). J. H. Geller, J. H. Custer and C. A. Zittle (Eastern Regional Research Laboratory, Philadelphia, Pa., U.S.A.). *J. Chromatog.*, 3 (1960) 369–371.

A new buffer is proposed, which permits paper electrophoresis of proteins at a pH acid to their isoelectric point; adsorption to the paper is reduced and sharp bands can be obtained. Screening tests have led to a lactic acid-citric acid buffer of pH 2.6. α -Casein can be split into two well separated components, with a run at 250 V for 5–10 hours. [J.E.Le.]

922 – Paper electrophoresis method for the identification of raw material used for the manufacture of cottage-cheese (in German). G. Zimmermann (Technion-Israel Institute of Technology, Haifa, Israel). *Mitt. Lebensm. u Hyg.*, 51 (1960) 151–157.

The whey is expressed from cheese and filtered. 10 ml of whey are treated with 6.25 g $(\text{NH}_4)_2\text{SO}_4$, the precipitate is dissolved in 1 ml of water, and 6–10 μl are applied to paper electrophoretic strips. Electrophoresis is carried out at 0.3 mA/cm of paper in barbitone buffer at pH 8.6. The paper is dried and stained according to the method of Durrum (*J. Am. Chem. Soc.*, 72 (1950) 2943). The spots are rendered more sharply visible by subjecting them to NH_3 fumes.

For the quantitative determination of the proteins, strips 2 mm \times 1 cm are cut from the coloured zones and eluted with methanol containing 4% NaHCO_3 . The extinction is measured at 6000 Å. By this method it is possible to distinguish between cottage cheese made from fresh skim or full-cream milk or from high temperature skim milk powder. [Gio.Ser.]

923 – Rapid staining of serum lipoprotein electropherograms (in English). R. L. Searcy, L. M. Berquist and R. C. Joung (Los Angeles County Osteopathic Hosp., Calif., U.S.A.). *Clin. Chim. Acta*, 5 (1960) 449–450.

Strips are dried in air and then sprayed with a 10% solution of phosphomolybdic acid in ethanol. After 30 sec at 130°–140° the α - and β -lipoprotein areas appear stained in a sharp blue green. The colour is stable. [Gio.Ser.]

924 – Starch-gel electrophoresis of "purified" albumins (in English). A. Saifer, M. Robin and Marguerita Ventrice (Biochemical Department, Isaac Albert Research Institute, Jewish Chronic Disease Hospital, Brooklyn, N.Y., U.S.A.). *Arch. Biochem. Biophys.*, 92 (1961) 409–419.

The separation of purified serum albumins into four or five sub-fractions was obtained by means of urea-starch gel electrophoresis in a (tris-citrate)-borate buffer pH 8.6. The three fastest moving components of ^{131}I labelled human serum albumin were isolated and run again in the same condi-

tions giving single bands of the same mobility. Chemically modified or ether treated albumins display fewer higher molecular weight components of decreasing mobility.

These components could not be detected in normal or abnormal serum so that they are probably a series of stable high molecular weight polymers of the albumin monomer resulting from the fractionation and purification procedure. Evidence to support this hypothesis is presented. [Gio.Ser.]

925 – Application of paper ionophoresis for separation of potassium, rubidium and caesium ions (in Polish). T. Pompowski, J. Kowalczyk and I. Siemianowska (Department of Technical Analysis, Politechnika, Gdańsk, Poland). *Chem. anal. (Warsaw)*, 6 (1961) 393–398.

Separation of K^+ , Rb^+ and Cs^+ was studied by means of paper ionophoresis on 200×30 mm Whatman No 4 paper strips. Hydrochloric acid, hydrochloric acid + phenol, lactic or formic acid were investigated as electrolyte solutions. Best separation was obtained in $0.1 N$ HCl + 1.2% phenol when the potential gradient was 12.5 V/cm. It was observed that in more dilute solutions than $0.08 N$, potassium behaved as an anion and moved towards the anode. [Ad.Hu.]

926 – Electrochromatographic separation of silver and thallium ions from each other and from mixtures of various polyvalent cations (in English). H. J. Strain, J. F. Binder, G. H. Evans, H. D. Frame and J. J. Hines (Argonne National Laboratory, Argonne, Ill., U.S.A.). *Anal. Chem.*, 33 (1961) 527.

The complete separation of Tl from Ag and polyvalent cations by differential electrical migration is described. An ammoniacal solution of oxalate plus cyanide, ammonia plus triacetic acid solution, and ammoniacal oxalate solution are taken as supporting electrolytes. The separations are complete and rapid. The apparatus for the electrochromatography and details of the separation procedures are described. Some photographs of the chromatograms illustrate the method. [Kl.Gr.]

927 – Filter paper ionophoresis of cupric complexes of neutral amino acids and oligopeptides (in English). P. R. Carnegie and R. L. M. Syngé (Rowett Research Institute, Bucksburn, Aberdeen, Scotland). *Biochem. J.* 48 (1961) 692–696.

An electrophoretic study has been made of the behaviour of glycine, glycyglycine, diglycyglycine and triglycyglycine at pH 9.2 in the presence of free cupric ion. The behaviour of the cupric complexes is compared with the behaviour of the free amino-acid and of the three peptides. This behaviour is discussed in connection with the results obtained by other workers, and the results show that the method can be used to obtain a separation of neutral di- and tri-peptides and perhaps of higher peptides. The separation of oligopeptides from free amino acids is scarcely favoured by the use of cupric complexes. [Gio.Ser.]

928 – Paper-chromatography and paper-ion-electrophoretic separation of the platinum and gold elements (in German). E. Blasius and M. Fischer (Anorg.-Chemischen Institut der technischen Universität, Berlin, Germany). *Z. anal. Chem.*, 177 [6] (1960) 412–420.

The separation of the six elements of the platinum and gold group is possible by paper-chromatography and paper-ion-electrophoretic methods. A theoretical explanation is given. [Di.Ciò.]

929 – Application of paper ionophoresis for separation of ferric, aluminium and titanium ions (in Polish). T. Pompowski, J. Kowalczyk and A. Krasowska-Grudowska (Department of Technical Analysis, Politechnika, Gdańsk, Poland). *Chem. anal. (Warsaw)*, 6 (1961) 387–362.

Separation of Fe^{3+} , Al^{3+} , Ti^{3+} was studied by means of paper ionophoresis. In $0.1 N$ HCl best results were obtained for the potential gradient 8.5 V/cm. Better results were obtained in mixed media of the type used in chromatographic separation of these ions. Among mixtures studied the best results were obtained in the following cases: pentanol + isopropanol + $0.1 N$ HCl (1 : 3 : 4) with the potential gradient 4.5 V/cm, pentanol + isopropanol + $1.0 N$ HCl (1 : 2 : 2) with the potential gradient — 5.5 V/cm, pentanol + $1.0 N$ HCl (2 : 1) with the potential gradient 4.4 V/cm. [Ad.Hu.]

See also abstracts nos. 704, 705, 888.

9. Other methods

930 – Electrode properties of ion-exchange membranes (in Russian). E. A. Materova and F. A. Belinskaya (State University, Leningrad, U.S.S.R.). *Uspekhi Khim.*, 30 (1961) 914–931.

An exhaustive review of the literature dealing with ion-exchange membranes, which may become

very useful in potentiometric analysis as indicating electrodes, and in various aspects of electro-dialysis. The membranes are grouped under the headings: mineral membranes, membranes based on various organic substances, and membranes made of ion-exchange resins. 169 literature references are included. [Ot.So.]

931 – Über die kontinuierliche Trennung von Ionengemischen in wässriger Lösung durch elektrolytische Wanderung im Gegenstrom, Teil I. Trennung isotoper und molekularer Ionen (in German). K. Wagener (Physikalisch-Chemisches Institut der Universität Zürich, Schweiz). *Z. Elektrochem.*, 64 (1960) 922–929.

Ein von Brewer und Mitarbeitern zur Entmischung von Kalium-Isotopen angewandtes und von Clusius und Mitarbeitern verbessertes Prinzip einer elektrolytischen Trennung wird vom Autor dargestellt und berichtet, dass es in erweitertem Umfang verwendet werden kann. Man kann den Vorgang ohne Steuerung führen, wenn man annimmt, dass die Ionen sich nur im Betrag des Diffusionskoeffizienten unterscheiden. Temperatur, Elektrolytenspannung und Strömungsgeschwindigkeit müssen stabilisiert werden. Die Anwendungsmöglichkeiten des Verfahrens werden nochmals erweitert, indem mit Hilfe eines potentialbestimmenden Fremdions auch solche Ionengemische getrennt werden können, bei denen ein Elektrodenkontakt vermieden werden muss. Berechnungen des Vorganges sowohl bei „geschlossener Betriebsweise“, bei der während des Prozesses vom Trennprodukt nichts entnommen wird als auch bei „offener Betriebsweise“, bei der kontinuierlich Trennprodukt entnommen und Ausgangsprodukt nachgegeben wird, werden durchgeführt. Der Konzentrationsverlauf längs des Troges wird untersucht und der Einfluss von Temperaturschwankungen durch örtlich erzeugte Joulesche Wärme betrachtet, der jedoch bei rein kinetischer Betrachtung ein geringes Ausmass hat. [He.We.]

932 – Über die kontinuierliche Trennung von Ionengemischen in wässriger Lösung durch elektrolytische Wanderung im Gegenstrom. Teil II. Die Auswirkung von Dissoziations- und Komplexbildungsgleichgewichten auf den Trennfaktor (in German). K. Wagener (Physikalisch-Chemisches Institut der Universität Zürich, Schweiz). *Z. Elektrochem.*, 64 (1960) 1163–1165.

In Teil I wurde über ein elektrolytisches Gegenstromverfahren zur kontinuierlichen Trennung gleichgeladener Ionengemische berichtet, wobei vereinfachend unterstellt worden war, dass sich die Ionen nur im Betrag ihres Diffusionskoeffizienten unterscheiden sollten, während alle übrigen Eigenschaften, wie Solvation und Ladungszustand als konstant betrachtet wurden. Im vorliegenden Teil II wird diese Voraussetzung fallengelassen und der Trennfaktor auch für diesen allgemeineren Fall berechnet. Er setzt sich aus zwei Teilfaktoren zusammen, von denen der eine exponentiell mit der Strömungsgeschwindigkeit und der Troglänge, der andere exponentiell mit der angelegten Elektrolytenspannung wächst. Der erstere Teilfaktor rührt vom Unterschied des mittleren Reibungskoeffizienten, der letztere vom Unterschied des zeitlichen Mittels der Ladungszahlen her. Eine Gleichung für den Trennfaktor wird angegeben. [He.We.]

933 – Effect of electrode configuration and transition time in solid electrode chronopotentiometry (in English). A. B. Bard (Department of Chemistry, University of Texas, Austin, Tex., U.S.A.). *Anal. Chem.*, 33 (1961) 11–15.

To ascertain the cause of the variations in chronopotentiometric measurements and to define the conditions under which the transition time-constant is really constant, $i_0 t^{1/2}/C^\circ$ is measured with plane electrodes of different construction and orientation in the solution over a very wide range of current densities and transition times. The reduction of Ag and Pb and the oxidation of iodide and hydroquinone are measured over a transition time of 0.001–300 sec. The results of the measurements with an unshielded electrode and a shielded electrode with horizontal diffusion upwards and downwards, and vertical diffusion are tabulated. The results of the investigations show that the most applicable electrode for chronopotentiometry is a disk sealed in glass tubing, and mounted horizontally, with upward or downward diffusion. The optimal range of transition time for analytical application is 10–60 sec. [Kl.Gr.]

934 – Dielectric analysis of multicomponent systems (in English). S. B. Nagy (Research Institute for the Organic Chemical Industry, Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 27 (1961) 49–62.

A new, universal instrument with an auxiliary oscillating circuit and with several new measuring condensers, has been evolved. This new instrument is equally suitable for measuring a dielectric constant or a loss angle, and for high-frequency titrations both in aqueous and non-aqueous media. With the help of a dielectric constant curve, measured either by the compensation or the deflection method, and with the help of a new dielectric titration apparatus, a number of binary mixtures could be investigated which are difficult to analyse in any other way. For ternary mixtures the triangular dielectric constant diagrams furnish rapid analytical methods for industrial applica-

tion. With the help of the instrument, and using dielectrometric methods, distillations, extractions and chemical processes have been followed. [E.Juh.]

935 – Electric dipole moments of some disubstituted cyclohexane derivatives in the vapor state (in English). Max T. Rogers and James M. Canon (Department of Chemistry, Michigan State University, East Lansing, Mich., U.S.A.). *J. Phys. Chem.*, 65 (1961) 1417–1419.

The moments of trans-1,2-dibromocyclohexane, trans-1,2-dichlorocyclohexane, trans-1-chloro-2-bromocyclohexane and 1,4-cyclohexane were determined in the vapor phase. An anomalous solvent effect was revealed by comparison of the data with that previously obtained from measurements in solution. [D.S.Ru.]

936 – Electric moments of some addition compounds of zinc chloride with organic bases (in English). M. Judith Schmelz, M. Ann Gertrude Hill and Columba Curran (Department of Chemistry, University of Notre Dame, Notre Dame, Ind., U.S.A.). *J. Phys. Chem.*, 65 (1961) 1273–1274.

The dipole moments of the addition compounds of zinc chloride with α , β and γ picoline, pyridine and triethylphosphine were determined in dioxane and benzene.

	μ , Debyes
In dioxane: $\text{ZnCl}_2 (\text{C}_5\text{H}_5\text{N})_2$	9.20 \pm 0.04
$\text{ZnCl}_2 (\alpha\text{CH}_3\text{C}_5\text{H}_4\text{N})_2$	8.86 \pm 0.04
$\text{ZnCl}_2 (\beta\text{CH}_3\text{C}_5\text{H}_4\text{N})_2$	9.54 \pm 0.04
$\text{ZnCl}_2 (\gamma\text{CH}_3\text{C}_5\text{H}_4\text{N})_2$	9.75 \pm 0.1
In benzene: $\text{ZnCl}_2 (\beta\text{CH}_3\text{C}_5\text{H}_4\text{N})_2$	9.53 \pm 0.04
$\text{ZnCl}_2 (\text{Et}_3\text{P})_2$	7.57 \pm 0.1
$\text{BCl}_3 (\text{C}_5\text{H}_5\text{N})$	7.50 \pm 0.04

[D.S.Ru.]

937 – Electrometric titration of hydrazine with cerium (IV) sulphate (in English). P. V. Krishna Rao, I. Subramanyam and G. Gopala Rao. (Department of Chemistry, Andhra University, Waltair, India). *Z. anal. Chem.*, [9] 177 (1960) 36–41.

A method is described for the determination of hydrazine in sulphuric acid solution by direct electrometric titration with cerium(IV) sulphate, in the presence of manganese(II) or chromium (III) sulphate as catalyst. A correction factor is given. Using this factor, the error is $\pm 0.2\%$. The proposed method has the advantage that it does not involve the intermediate use of ferricyanide. Other catalysts have been tried without success. [Di.Ciò.]

938 – Triphenylmethane dyes as oxidation–reduction indicators in titrations with cerium (IV) perchlorate (in English). V. Pandu Ranga Rao and G. Gopala Rao (Department of Chemistry, Andhra University, Waltair, India). *Z. anal. Chem.*, 168 (1959) 172–177.

In nitric or perchloric acid solution only nitroferroin and ruthenium-dipyridyl are useful as internal indicators in cerimetry; these indicators are costly and so three new indicators (eriolglauine A, eriogreen B and xylene cyanol FF) have been investigated for the titration of iron(III), uranium (IV), molybdenum(V), vanadium(IV), arsenic(III), oxalic acid and hydroquinone with ceric ammonium nitrate in nitric acid and perchloric acid media. In nitric acid media the indicators are not suitable and show anomalous behaviour. The triphenylmethane dyes are dissolved in water (0.1%); the solution is stable for several months and 0.5 ml are sufficient for 50–100 ml of the solution to be titrated. The indicator correction is negligible for 0.1 and 0.05 N cerium(IV)–ammonium nitrate (in 1 N perchloric acid) solutions; for 0.01 N ceric solution the correction amounts to 0.1 ml. The three indicators show a yellow colour in 0.5–4 N HClO_4 turning to orange red when there is a slight excess of the ceric solution. The titrations of iron, uranium, molybdenum, vanadium, arsenic, oxalic acid and hydroquinone in 0.5–4 N HClO_4 are fully discussed; the details and application limits are given. From all the experiments, it can be deduced that the indicators are not suitable for the titration of vanadium and molybdenum. [G.deAn.]

939 – The use of the “Hersch Cell” for the measurement of oxygen in biological material (in English). D. L. Dewey and L. H. Gray (British Empire Cancer Campaign Research Unit in Radiobiology, Mount Vernon Hospital, Northwood, Middlesex, England). *J. Polarog. Soc.*, 7 (1961) 15–25.

The principles of the Hersch galvanic cell for the determination of oxygen are given and the constructional layout is described in great detail. The manner of operation is fully described with emphasis on the sequence of operation, and necessary practical details and precautions to be taken. Several models of the cell, (D, G and H) are discussed. The performance characteristics and accuracy obtainable with model H at ambient room temperature are presented.

Applications of the Hersch cell discussed are as follows:-

1. The continuous monitoring of the oxygen content of a flowing gas, to measure the exact concentration of oxygen available to biological material at the time of irradiation with X rays.

2. The measurement of higher concentrations of oxygen in flowing gas.
 3. The measurement of the amount of oxygen in a liquid sample in connection with the determination of respiration rates of biological material where the quantities available and the respiration rates are too small for accurate determination to be made by the standard Warburg apparatus. Oxygen consumptions of the order of $1 \mu\text{l}$ per hour have been conveniently measured.
 4. The direct evaluation of oxygen tension in a fluid by the measurement of partial pressure of oxygen in a small bubble, which has been brought into equilibrium with the fluid. Two different procedures are given in the cases where the oxygen consumption by the fluid is negligible and where the fluid contains respiring cells and is held at a constant oxygen tension by equilibration with a gas phase.
 5. Measurement of the total oxygen content of a cell suspension, used to measure directly the total oxygen content of bacterial cells.
- Finally the effect of interfering substances, such as cyanide is discussed. [G.F.Rey.]

940 – Redoxykinetic titration of potassium ferricyanide against cobaltous sulphate (in English). K. Sundararajan (Central Electrochemical Research Institute, Karaikudi, India). *J. Electroanal. Chem.*, 1 (1959–1960) 339–340.

The redoxykinetic method for the determination of end-points has been used in the titration of potassium ferricyanide against $0.05 M$ cobaltous sulphate. Precision attained, as compared with potentiometric titration, is better than $\pm 0.1\%$ with $0.05 M$ solutions; with $0.01 M$ solutions the change in the redoxykinetic potential at the end-point was not sharp and the precision was $\pm 1\%$. Details of the technique are given. [Su.Mo.Ce.]

10. Related topics

941 – Faradaic rectification and electrode processes. II. (in English). Mitsuga Senda, Hideo Imai and Paul Delahay (Coates Chemical Laboratory, Louisiana State University, Baton Rouge, La., U.S.A.). *J. Phys. Chem.*, 65 (1961) 1253–1256.

The quantitative relation between the mean rectification voltage (ΔE_{∞}) and mean rectification current and the effect of circuit resistance is discussed. The variations in rectification current with time are examined and methods of determining ΔE_{∞} are suggested. Equipment is described which was used up to 51 mc and which is probably suitable for higher frequencies. Experimental data are given. [D.S.Ru.]

942 – Study of the kinetics of electrode processes with the use of constant current electrolysis. IV. Theory of the measurement of a first order reaction by reversing the current direction (in German). O. Dračka (Masaryk University, Brno, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 25 (1961) 338–347.

A method especially suitable for rapid reactions is proposed, for measuring kinetic constants of reactions which occur after reversal of the direction of the current. The concentration at the electrode surface is calculated for the depolarisation product of the original electrolysis, formed during a first order reaction. From the results it follows that the measurement of the dependence of the time of transformation τ' of the electrode reaction (calculated from t_1 as start) at the moment t_1 at which the current reversion takes place is most suitable for calculating the subsequent reaction. [Ot.So.]

943 – Zur Struktur der elektrochemischen Doppelschicht. II. H. Brodowsky und H. Strehlow (Max-Planck-Institut für Physikalische Chemie, Göttingen, Deutschland). *Z. Elektrochem.*, 64 (1960) 891–897.

In einer vorangegangenen Arbeit hatten die Autoren eine Erweiterung der Gouy-Chapman-Theorie der diffusen Doppelschicht beschrieben. Dabei war dem Einfluss des endlichen Ionenvolumens und der dielektrischen Sättigung Rechnung getragen worden. Die neuerlichen Messungen von Potentialdifferenzen an adsorbierten Seifenfilmen mit verschiedenen Gegenionen mittels eines Schwingkondensators bei vorgegebener Ladungsdichte zeigen, dass der Einfluss des Ionenvolumens die erwartete Richtung hat. Ausserdem wurden Kapazitätsmessungen an Quecksilbertropfen erörtert. Die Doppelschicht wirkt auch als Ionenaustauscher für gleichgeladene Ionen von verschiedenem Volumen. Es werden weitere Anwendungsmöglichkeiten der Theorie gezeigt. [He.We.]

944 – Courant d'écoulement et épaisseur de la double couche en milieu hydrocarbure (in French). J. Briant (Institut Français du Pétrole, Rueil-Malmaison (S & O), France). *Compt. rend.*, 252 (1961) 2699–2701.

L'auteur établit une équation reliant le "courant d'écoulement" à l'épaisseur de la double couche. Le courant électrique dû à la différence de niveau que l'on peut réaliser dans une cellule en U à diaphragmes de verre fritté, a été déterminé dans différentes conditions expérimentales. Le liquide remplissant la cellule est constitué par diverses solutions de dioctylsulfosuccinate d'aluminium dans du pétrole lampant. Lorsque la quantité de sel d'aluminium varie de 0.004% (en poids) à 10%, l'épaisseur "e" de la double couche varie de 2.25 μ –0.6 μ . Ces valeurs sont du même ordre de grandeur que celles qui ont été déterminées par électroosmose (J. Briant, *Compt. rend.*, 251(1960) 2924). [Bad.Lam.]

945 – Potentiel d'écoulement et électroosmose en milieu hydrocarbure (in French). J. Briant (Institut Français du Pétrole, Rueil-Malmaison (S & O), France). *Compt. rend.*, 252 (1961) 2878–2880. L'écoulement d'un liquide à travers un diaphragme de verre fritté ou un capillaire provoque l'apparition d'une tension électrique entre les deux faces du diaphragme ou les deux extrémités du capillaire. Utilisant une solution de dioctyl-sulfosuccinate d'aluminium dans du pétrole lampant, l'auteur met en évidence un phénomène d'électroosmose en sens inverse de l'écoulement. La diminution de débit qui en résulte varie de 1.17%–0.15% lorsque la concentration du sel d'aluminium varie de 0.019%–4% en poids. Cette diminution de débit peut être reliée d'une façon approximative à l'épaisseur "e" de la couche double: $e = 0.025 \mu$ lorsque le débit diminue de 2%. Cette valeur est inférieure à réalité. [Bad.Lam.]

946 – The effect of the amount of added solvent in the electrolytic reduction of azobenzene (in Japanese). Taro Sekine (Laboratory of Organic Electrochemistry, Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Tokyo, Japan). *J. Electrochem. Soc. Japan*, 28 (1960) 390–392. (English translation in *J. Electrochem. Soc. Japan*, (Overseas suppl. Edition), 28 (1960) E 141).

Fundamental conditions for the electrolytic formation of hydrazobenzene from nitrobenzene in alkaline emulsion, such as cathode material, current density, concentration of sodium hydroxide, and the effect of agitation have been described in the previous papers.

During these studies, adherence of reaction products to the cathode surface frequently occurred, at the stage of reducing azobenzene to hydrazobenzene, and then electrolysis could not proceed further, because of the rapid increase of the cell voltage. As is well known, this trouble has been settled effectively by adding solvent. These studies were carried out to verify the relation between the amount of solvent, degree of agitation and current efficiency of reduction of azobenzene to hydrazobenzene. The optimum amount of solvent added to the catholyte was 10–15 cc per 90 cc of alkaline emulsion (7.00 g of azobenzene included in 90 cc of 10% sodium hydroxide soln.). The solution was agitated by shaking the cathode 140–180 times per min. [Ta.Fu.]

947 – Electrical properties of ice (in French). M. Dupuis. *J. chim. phys.*, 58 (1961) 377.

A brief description of the structure and electrical properties of ice is given. At about -10° the mobility of hydrogen ion is at least fifty times higher than in water. The reason for this great difference is that in water the mechanism determining the speed of transfer is the structural rearrangement of neighbouring molecules, while in ice it is only the transfer mechanism which determines the rapidity. [S.K.Shu.]

948 – Effect of chloride on the kinetics of electro-oxidation of chromium(II) in acidic perchlorate medium (in English). David A. Aikens and James W. Ross, Jr. (Department of Chemistry and Laboratory of Nuclear Science, Massachusetts Institute of Technology, Cambridge, Mass., U.S.A.). *J. Phys. Chem.*, 65 (1961) 1213–1216.

A study was carried out using the potentiostatic technique at the hanging mercury drop electrode, and the chromium(II) was generated in situ. The oxidation of the chromium(II) at constant electric tension is enhanced by chloride with the reaction taking two paths. The first, to produce $\text{Cr. 6H}_2\text{O}^{3+}$ is independent of chloride, while the second produces $\text{Cr. 5H}_2\text{O. Cl}^{3+}$ by a reaction of the first order in chloride, in concentrations up to 50 mM. The tendency toward specific adsorption at the electrode surface determines their relative efficiencies in enhancing the reactions, since the enhancement increases from fluoride, chloride to iodide. [D.S.Ru.]

949 – Polarization during electrodeposition of iron group metals. I. The steady state electric tension and overvoltage of iron deposition (in Russian). V. N. Kuznetsova, A. P. Popkov, L. A. Uvarov, and A. T. Vagramyan. *Zhur. Fiz. Khim.*, 35 (1961) 1406–1410.

The steady state electric tension and the rate of self-dissolution of an iron electrode in sulphuric acid solution have been investigated in relation to hydrogen ion concentration, aluminium sulphate

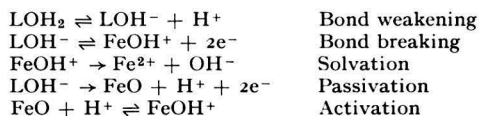
additions and temperature. It has been shown that owing to intensive self-dissolution of iron and to a number of other reactions, the equilibrium electric tension of an iron electrode and hence the exact value of iron deposition cannot be determined. [Ot.So.]

950 – Polarisation during electrodeposition of iron group metals. II. Electrodeposition of iron (in Russian). A. T. Vagramyan, V. N. Kuznetsova, A. P. Popkov and others (Institute of Physical Chemistry, Academy of Sciences, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 1411–1415.

Polarisation during the electrodeposition of iron has been investigated galvanostatically as a function of electrolyte pH. The polarisation curve has been shown to pass through a maximum. The low values of the deposition electric tension at the descending and ascending branches of the curve correspond to predominant reduction of one or other ionic species. Maximum values of the reduction electric tension correspond to concurrent discharge of both types of ions, which thus gives evidence of the mutual retardation of these processes. Hydrogen evolution at a hydrogen occluded iron electrode has been shown to take place more easily than at a non-occluded one. Discharge of iron is retarded on concurrent evolution of hydrogen occluded in the iron, and is facilitated in the absence of such hydrogen. [Ot.So.]

951 – Anodic dissolution of iron. I. General mechanism (in English). K. A. Christiansen, H. Hoeg, Kirsten Michelsen, G. Bech Nielsen and H. Nord (Chemistry Department A, Technical University of Denmark, Copenhagen, Denmark). *Acta Chem. Scand.*, 15 (1961) 300–320.

It is suggested that the kinetics of the anodic dissolution of iron is essentially governed by a mechanism in which the pH dependent and the electric tension dependent dissociation of chemisorbed water plays a dominant role. The steps in this mechanism are



LOH_2 is a surface iron atom, still belonging to the metal lattice, with a chemisorbed water molecule. LOH^- is a surface iron atom with a chemisorbed hydroxyl ion. FeOH^+ and FeO are adsorbed oxidized forms and Fe^{2+} the solvated ferrous ion.

The system of differential equations for this mechanism is derived and solved for steady state conditions. The resulting kinetic expression is

$$s = \frac{N}{A + B \cdot h + C/h}$$

where s is the rate of dissolution and N the number of sites on the surface, able to accommodate water molecules and hence to go through the series of steps described above. A , B and C are functions of the electric tension dependent rate constants and h is the concentration of proton donor in the solution. Experiments illustrating the qualitative validity of this expression are described.

A more thorough analysis of the mechanism, both for steady state and for non-steady state experimental conditions, is given, and compared with experimental results, quantitative as well as qualitative. It is shown that the general mechanism given above is in good agreement, both with new experimental findings of the present paper and with results from other laboratories.

An interesting consequence of the above is that the mechanism of passivity is the electrostatic repulsion of hydrogen ions, necessary for the dissolution of surface oxide layers. The striking influence of oxygen, dissolved in the aqueous phase, and of hydrogen, dissolved in the metal phase, is discussed on the basis of new experiments. [Sv.Li.]

952 – Cathodic liberation of hydrogen on electrolytically deposited nickel. I. Influence of the method of the preparation of cathodes (in French). A. M. Peers (Laboratoire Curie, 11 rue Pierre Curie, Paris V^e). *J. chim. phys.*, 58 (1961) 338–346.

Cathodic activity, in 0.1 N sulphuric acid, of nickel electrodes prepared under different conditions has been studied. The author proposes diverse mechanisms to explain the observed results and points out that the new arguments tend to confirm that the desorption reaction on clean nickel is an electrochemical reaction: namely, ion + atom. [S.K.Shu.]

953 – Cathodic liberation of hydrogen on electrolytically deposited nickel. II. Poisoning by labelled antimony (in French). A. M. Peers (Laboratoire Curie, 11 rue Pierre Curie, Paris V^e). *J. chim. phys.*, 58 (1961) 347–354.

Influence of antimony on the cathodic behaviour of nickel in 0.1 *N* sulphuric acid has been studied with the help of antimony labelled with ^{124}Sb . Assuming that the adsorption of hydrogen on nickel electrodes follows the Temkin's logarithmic isotherm, it is concluded that antimony diminishes the adsorptive capacity of the cathode for hydrogen and also probably the adsorption energy of hydrogen. It has been pointed out that the desorption of hydrogen on the cathode takes place by recombination of hydrogen atoms. A simple quantitative theory is proposed to explain the variation of the overvoltage with the amount of antimony on the cathode. The author concludes that an atom of antimony modifies the electronic properties of only its close neighbouring atoms of nickel. It is shown that the action of an iodide anion adsorbed on silver is 5-10 times greater than that of antimony on nickel. [S.K.Shu.]

CONTENTS

Review

- Application of polarography to organic chemistry
by P. ZUMAN (Prague) 157

Original papers

- Anwendungen von Aminobindungen in der Polarographie anorganischer Stoffen
XI. Das polarographische Verhalten von Mangan und Eisen in Medien von Bis-(2-hydroxypropyl)-2-hydroxyäthylamin, Bis-(2-hydroxybutyl)-2-hydroxyäthylamin und alkalischem Hydroxyd
von J. DOLEŽAL, V. PETRUS UND J. ZÝKA (Prague) 169
- Chronopotentiometry with programmed current
II. Response function additivity principles applied to current programming and multi-component systems
by R. W. MURRAY AND C. N. REILLEY (Chapel Hill) 182
- Electrophoresis of casein in a column stabilised by a density gradient
by W. MANSON (Ayr, Scotland) 203
- The effect of cell resistance on acute polarographic maxima
by I. M. KOLTHOFF, J. C. MARSHALL AND S. L. GUPTA (Minnesota) 209
- Short communications*
- A.c. polarographic wave — modified equations
by S. K. RANGARAJAN AND K. S. G. DOSS (Karaikudi). 217
- A particular influence of the supporting electrolyte on the limiting current of the first polarographic wave of oxygen
by R. CORNELISSEN AND L. GIERST (Brussels) 219
- Book reviews. 221

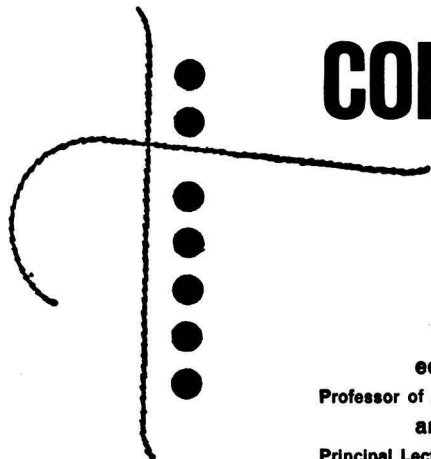
All rights reserved

ELSEVIER PUBLISHING COMPANY, AMSTERDAM

Printed in The Netherlands by

NEDERLANDSE BOEKDRUK INRICHTING N.V., 'S-HERTOGENBOSCH

ANNOUNCING THE PUBLICATION OF VOLUME 1C OF



COMPREHENSIVE ANALYTICAL CHEMISTRY

edited by **CECIL L. WILSON**

Professor of Analytical Chemistry The Queen's University, Belfast
and **DAVID W. WILSON**

Principal Lecturer Sir John Cass College London

6 x 9"

xxx + 728 pages
140 s. Dfl. 70.- 1962

The contents of
Volume 1C are

Chapter IX
Main Group Elements

Chapter X
Transition Elements

The general methods of classical analysis discussed in parts IA and IB are here amplified by the presentation of specific applications of the classical procedures of gravimetric and titrimetric analysis in the inorganic field. The analytical chemistry of the elements is systematically presented (following the Periodic Table) and details are given of the methods which are of greatest use to the analytical chemist. As in the parts already published extensive reference lists have been included so that immediate recourse may be had to the original literature.

Take advantage of the Advance Subscription Price for this great work by ordering the complete set now. Such orders qualify for a reduction of at least 15% on the post-publication price of the individual volumes. The total number of pages is estimated at about 5000. The subscription price is 15 s. per 100 pages. This price will hold until the appearance of each volume, after which it will be increased to 18 s. per 100 pages.

The complete set includes

- Volume 1A Classical Analysis: General Methods of Analysis, 608 pages, 110s, Dfl. 55.-
- Volume 1B Classical Analysis: General Methods of Analysis, 900 pages, 164s, Dfl. 82.-
- Volume 1C Classical Analysis: Gravimetric and Titrimetric Determination of the Elements 758 pages, 140s, Dfl. 70.-
- Volume II Electrical Methods, Physical Separation Methods.
- Volume III Optical Methods
- Volume IV Industrial and other Specialist Applications
- Volume V Miscellaneous Methods; General Index



ELSEVIER PUBLISHING COMPANY

AMSTERDAM