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REVIEW

ELECTRODES FOR pH MEASUREMENTS

ROGER G. BATES

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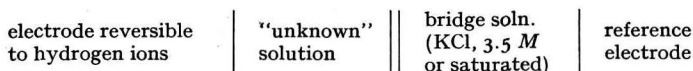
(Received November 26th, 1960)

INTRODUCTION

According to recommendations that are receiving almost universal acceptance¹⁻⁵, the "practical" or experimental pH value is defined in an operational manner, as follows:

$$\text{pH} = \text{pH}(S) + \frac{E - E_s}{(RT \ln 10)/F} \quad (1)$$

In this definition, E and E_s are, respectively, the electromotive force (e.m.f.) of a pH cell of the usual design containing first the "unknown" solution and secondly a standard solution of known pH, namely pH(S). This pH cell is an assembly of the following type,



where the double vertical line marks a liquid junction.

The working reference electrode is usually a calomel or silver-silver chloride electrode of fixed potential or tension relative to the standard hydrogen electrode. For a discussion of reference electrodes the reader is referred to the recent review of MILAZZO AND BOMBARA⁶.

In the present paper, the values of E and E_s are consistent with the Stockholm sign convention of the I.U.P.A.C.⁷ The difference ($E - E_s$) is, however, identical with ($U_s - U$), the difference in the tensions of the cell according to the C.I.T.C.E. nomenclature and definitions⁸.

It is evident from a consideration of eqn. 1 that the cell is utilized only to furnish a *difference* of pH. The definition reflects, therefore, the finding that the pH of a specified standard solution is more reproducible than the standard electrode potential

* It is perhaps advisable to recall to mind that, referring to the scheme of the given cell, the E values (e.m.f.) are given by the difference "electrical potential of the right electrode — electrical potential of the left electrode" whilst for the U values (tension) the reverse difference has to be considered. On the other hand, "electrode potential" (Stockholm convention) and "reversible electrical tension" (of a single electrode, C.I.T.C.E. convention) have the same value and sign.

of individual (supposedly identical) reference electrodes, or of the same reference electrode at widely separated times. The operational definition demands only that the electrode potential of the reference electrode remains constant while the two measurements (of E and E_s) are being made. Most reference electrodes meet this requirement quite satisfactorily.

Furthermore, the operational definition makes no allowance for a change in the liquid-junction potential when the standard solution is replaced by the unknown. Unfortunately, this correction is too unpredictable and complicated to incorporate in a practical definition of the experimental pH value. One must not forget, however, that when the unknown solution has a pH less than 2 or greater than 12 the liquid-junction potential may differ appreciably from the reasonably constant value established with solutions of intermediate pH⁹. If the experimental pH is to be regarded as a quantitative measure of hydrogen ion concentration or activity, we must regard the practical scale as distorted or diffuse near its ends. In these regions, the interpretation of measured pH values should be attempted only with caution. The selection of standard buffer solutions and the assignment of pH(S) values on a useful conventional scale of hydrogen ion activity have already been discussed^{5,10-12}.

The remarkable versatility and convenience of the glass electrode make this electrode the undisputed leader among electrodes reversible to hydrogen ions. There is, perhaps, reason to fear that this popularity will serve to divert attention from other electrodes which have their own advantages in certain special measurement situations. It is therefore the purpose of this paper (1) to examine critically the characteristic properties of the four most useful pH-responsive electrodes, and (2) to assemble this information as an aid in the selection of the most suitable electrode for each specific analytical application.

THE HYDROGEN ELECTRODE

In view of the wide availability of commercial pH-meters of the glass-electrode type, it is easy to overlook the fact that the hydrogen electrode is the primary standard for all pH measurements. Defects in the hydrogen ion response of other electrodes are identified by comparing the performance of these electrodes with that of the hydrogen electrode. In addition, the pH values of the standard buffer solutions are based on the electromotive force of cells containing hydrogen electrodes.

Description

The hydrogen electrode consists essentially of a piece of clean platinum foil coated with a deposit of finely divided platinum or palladium ("platinum black" or "palladium black"), which is capable of making the electrode reaction



proceed reversibly. The metal electrode is immersed in the solution under investigation, and pure hydrogen gas is bubbled through the solution and over the electrode in such a way that the electrode surface and the adjacent solution will be saturated with the gas at all times.

The character of the active catalytic surface appears not to be critical; in most instances substantially the same result is obtained with hardly visible gray deposits

as with spongy, intensely black surfaces. Too heavy deposits of platinum black should probably be avoided, as they appear to make the electrode slow to attain its equilibrium potential. It is also likely that the adsorption of solutes as well as catalytic reduction of solute species (when it can occur) are favored by heavy coatings. A light coating is probably to be preferred in titrations where a rapid response is essential. Although there is less danger of reduction when coatings of palladium are used, palladium electrodes are inferior to platinum electrodes in most other respects and should be avoided when possible.

For most purposes, the following method of applying the platinum black coating is satisfactory. The electrode is electrolyzed as a cathode for 1–2 min in a solution of 3% chloroplatinic acid containing 80 mg of lead acetate trihydrate per 100 ml of solution. A platinum anode is used, and the current density is about 100 mA/cm². Instructions for the preparation of palladium solutions will be found in monographs on pH measurement^{10,13}.

Active hydrogen electrodes should not be allowed to become dry. Nevertheless, they usually lose their activity in 7–20 days, depending on how they are used and stored. The black coating must then be removed and the electrode reactivated. To remove the deposit, the electrode is immersed for a few minutes in a warm mixture of 3 volumes of 12 *M* hydrochloric acid, 1 volume of 16 *M* nitric acid, and 4 volumes of water.

Response

The hydrogen electrode is the ultimate standard of reference for all pH measurements. In the absence of irreversible side reactions, its hydrogen ion response is considered to be exact, by definition.

The primary reference potential or tension is, of course, always that of the standard hydrogen electrode. Furthermore, the electrode potential (E_e) of the Stockholm convention⁷ and the reversible electrode tension ($U_{rev.}$) of the C.I.T.C.E. recommendations⁸ are identical. Formally, this is because the electrode process is written as a reduction in deriving the electrode potential and as an oxidation in expressing the electrode tension. Applying the NERNST equation to (2), one finds

$$E_e = U_{rev.} = -\frac{2.3026 RT}{F} \text{pH} \quad (3)$$

where R , T and F are the gas constant, the temperature in °K and the faraday, respectively.

The "pH response" of the hydrogen electrode is, therefore, given by

$$\text{pH response} = \frac{dE_e}{d\text{pH}} = -\frac{2.3026 RT}{F} = -0.0592 \text{ V/pH at } 25^\circ \quad (4)$$

The hydrogen electrode and the other pH-responsive electrodes to be discussed here become more negative in polarity as the pH increases. The pH response of the hydrogen electrode, namely $-0.0592 \text{ V/pH at } 25^\circ$, is called the "theoretical response".

Interferences

Unfortunately, there are many substances which react irreversibly with the

platinum-hydrogen electrode and cause a disturbance or distortion of the pH response. In general, oxidizing agents such as ferric ion, permanganates, chlorates, and (in acidic solutions) chromates and nitrates must be absent from the solutions. Hydrogen gas in contact with finely divided active platinum is a powerful reducing agent. Consequently, many dissolved aromatic compounds, unsaturated compounds, sulfides, sulfur dioxide, and the like undergo chemical reactions in contact with the hydrogen electrode. Likewise, the electrode is "poisoned" by cyanides, by lead, cadmium and thallos salts, and by the cations of metals of lower electromotive activity than hydrogen (for example, copper, silver and mercury). The latter suffer reduction and are deposited on the platinum surface where they slowly destroy the activity of the electrode. For a detailed description of the limitations of the hydrogen electrode, the reader is referred to BRITTON'S monograph¹³.

The presence of an interfering substance in the solution is often made known by the erratic behavior of the measured e.m.f., which fails to achieve a constant reversible value and which changes with the rate of flow of the hydrogen gas or upon agitation of the solution. The disturbance caused by "poisons" can sometimes be minimized by the use of very thin layers of platinum black. Palladium black is a less active catalyst for hydrogenations than is platinum black; hence, electrodes consisting of palladium deposited upon platinum foil form a stable hydrogen electrode in certain solutions (for example, phthalate buffers) which are reduced by platinized electrodes, as shown by HAMER AND ACREE¹⁴.

Corrections

Hydrogen electrodes become increasingly negative in polarity as the pressure of hydrogen gas is increased. In order that differences of pH be correctly given by eqn. 1, both E and E_s must refer to the same partial pressure of hydrogen.

The potential of the gaseous hydrogen electrode is therefore customarily referred to a standard partial pressure of 1 atm. The corrections to be applied to the measured e.m.f. (in aqueous solutions) are tabulated in Table I for barometric pressures from 720 to 770 mm Hg and for temperatures from 0° to 60°. These corrections are valid for all solutions sufficiently dilute that the vapor pressure of water does not differ

TABLE I

BAROMETRIC PRESSURE CORRECTIONS FOR THE HYDROGEN ELECTRODE FROM 0° TO 60° (in mV)

Barometric pressure (mm Hg)	0°	10°	20°	25°	30°	35°	40°	50°	60°
720	0.71	0.82	0.99	1.13	1.30	1.52	1.81	2.67	4.12
725	0.63	0.73	0.91	1.03	1.20	1.42	1.71	2.56	3.99
730	0.55	0.65	0.82	0.94	1.11	1.32	1.61	2.45	3.87
735	0.47	0.56	0.73	0.85	1.02	1.23	1.51	2.34	3.74
740	0.39	0.48	0.64	0.76	0.92	1.13	1.41	2.23	3.62
745	0.31	0.39	0.55	0.67	0.83	1.04	1.31	2.12	3.50
750	0.23	0.31	0.47	0.58	0.74	0.94	1.21	2.02	3.38
755	0.15	0.23	0.38	0.49	0.64	0.85	1.12	1.91	3.25
760	0.07	0.15	0.30	0.41	0.56	0.76	1.02	1.81	3.14
765	-0.01	0.07	0.21	0.32	0.47	0.67	0.92	1.70	3.02
770	-0.08	-0.01	0.13	0.24	0.38	0.57	0.83	1.60	2.91

greatly from that of the pure solvent. For the most refined measurements, the hydrostatic pressure at the point where the hydrogen gas enters the solution must be considered, for a persistent supersaturation with gas can occur. This is the so-called "depth effect" identified first by HILLS AND IVES.¹⁵

When the hydrogen electrode is combined with a calomel reference electrode, it is the negative electrode of the cell at all normal pH values. The e.m.f. therefore increases with an increase of pressure, and the correction terms given in Table I must be added to the measured e.m.f.

THE QUINHYDRONE ELECTRODE

Description

The quinhydrone electrode is an oxidation-reduction electrode. For the measurement of pH with this electrode, it is only necessary to saturate the solution of the electrode compartment with quinhydrone and to immerse an inert electrode of bright platinum or gold into it. For best results, the metal electrode should be cleaned with hot chromic acid-sulfuric acid mixture and then washed with water and alcohol¹⁶. It is desirable that it be in contact with some of the solid quinhydrone in the cell.

Quinhydrone is a molecular compound composed of one mole of benzoquinone ($\text{OC}_6\text{H}_4\text{O}$) and one mole of hydroquinone ($\text{HOC}_6\text{H}_4\text{OH}$). It is soluble in water to the extent of about 0.02 mole/l at room temperature, and about 93% of the dissolved compound is dissociated into its two components, as the equilibrium measurements of BERTHOUD AND KUNZ¹⁷ show.

Quinhydrone is obtainable commercially. Some of the quinone constituent, however, may in time be lost through volatilization. In order to assure that the quinone and hydroquinone are present in equimolar amounts, therefore, it is recommended that the quinhydrone be recrystallized from warm water before use.

The electrode half-reaction is



and, consequently, the electrode potential is a function of the pH and of the ratio of the activities ($a = mf$) of the quinone (Q) and hydroquinone (H_2Q):

$$E_e = E_e^0 - \frac{2.3026 RT}{F} \text{pH} - \frac{2.3026 RT}{2 F} \log \frac{m_{\text{H}_2\text{Q}} f_{\text{H}_2\text{Q}}}{m_{\text{Q}} f_{\text{Q}}} \quad (6)$$

If the dissolved quinhydrone is equimolar and the ionic strength of the solution is not too high, the last term of eqn. 6 is zero. It is not necessary to know the standard potential (E_e^0) in order to determine pH by the operational definition, eqn. 1.

The quinhydrone electrode is often described as a hydrogen electrode in equilibrium with the very low hydrogen pressure provided by the quinone-hydroquinone system. As far as the mechanism of the electrode process is concerned, this view probably has little to recommend it. It may, however, serve to remind the user that the quinhydrone electrode is much less negative (*i.e.*, a much less powerful reducing agent) than the standard hydrogen electrode. As eqn. 6 shows, the electrode potential becomes more positive as the pH decreases. At pH values below 7.7, the quinhydrone electrode is actually positive with respect to the saturated calomel reference

electrode. The values of E and E_s in eqn. 1 will then be positive, in accordance with the Stockholm sign convention⁷.

Response

The pH response of the quinhydrone electrode is close to the theoretical value at pH values less than 8. The impairment of response, when it occurs, can usually be explained by a departure of the last term of eqn. 6 from its "normal" value of zero. At pH values greater than 8, the acidic dissociation of hydroquinone becomes appreciable, and the ratio m_{H_2Q}/m_Q is no longer unity. The "apparent" pH, found by neglecting the last term, is too small at pH 8.5 by about 0.01 unit and at pH 9.0 by about 0.04 unit, as LAMER AND PARSONS¹⁸ have shown.

The response is likewise impaired by the presence of high concentrations of electrolytes. This "salt error" results from the unequal effect of the electrostatic fields of the ions upon the activities of the two species Q and H₂Q in the solution. Inasmuch as both of these species are uncharged, the salt error is not large, but it may be either positive or negative, depending on the nature of the electrolyte present. Among the largest errors of this type are those caused by nitric and hydrochloric acids. Even here, however, the error is only about 0.04 unit at an ionic strength of 0.5.

Advantages

In acidic solutions, the quinhydrone electrode is capable of yielding potentials of the same order of reproducibility as those of the hydrogen electrode. Equilibrium is established with extreme rapidity (a few minutes or less, as compared with 30 min to 1 h for the hydrogen electrode under usual conditions), and no corrections for barometric pressure are needed. The electrical resistance of the electrode is low, so that electronic amplifiers need not be used to measure the potentials developed. The quinhydrone electrode is readily adapted to micro-scale measurements, and exclusion of air is unnecessary.

Inasmuch as quinhydrone is a considerably weaker reducing agent than hydrogen on platinum, the electrode can be used in the presence of unsaturated and aromatic compounds, in many oxidizing media, and in some biological media reduced by hydrogen. It functions satisfactorily in the presence of the ions of copper and some of the other metals more noble than hydrogen and can be used in many alcoholic solvents and in acetone.

Disadvantages

The major limitations of the quinhydrone electrode are attributable to the acid-base properties of hydroquinone. As already mentioned, precise applications of the electrode are restricted to solutions of pH less than 8. A saturated solution of quinhydrone, however, has a pH somewhat less than 6. Consequently, there is a slight buffering action at pH values between 6 and 8, and a disturbance of the pH of dilute test solutions may occur. The quinhydrone electrode is, therefore, usually considered unsuitable for use in solutions more dilute than 0.001 *M*. In strongly acidic solutions, the basic properties of quinone may cause departures from ideal behavior¹⁹.

Hydroquinone is subject to oxidation by air at pH values above 8, but in acidic

solutions this reaction is usually so slow as to cause no difficulty. The high chemical reactivity of quinone gives rise to an appreciable error in protein solutions and in the presence of certain amino compounds.

Corrections

The response of a pH electrode is assessed by comparing it with the response of a hydrogen electrode, which is, of course, $-2.3026 RT/F V$ ($-0.0592 V$ at 25°) for a unit change of pH. As eqn. 6 shows, a quinhydrone electrode displays the "theoretical response" only when the last term of this equation is zero. Errors can be caused either by the inequality of m_Q and m_{H_2Q} (which occurs, for example, at pH values greater than 8) or by the inequality of the activity coefficients, f_Q and f_{H_2Q} (which may occur at high ionic strengths and which is termed the "salt error").

Although one can probably apply corrections for the voltage departure of the quinhydrone electrode with safety to pH 9, it is strongly recommended that the electrode should not be used at pH values greater than 8, and that no corrections should be attempted. The salt error in pH units has been found to be a linear function of the normality (c_s) of salt present:

$$\Delta pH = kc_s \quad (7)$$

Values of k for 15 electrolytes, taken from the work of HOVORKA AND DEARING²⁰ and STONEHILL²¹ are given in Table II. A negative value of k means that the pH indicated by the quinhydrone electrode potential is too high; a positive value means that it is too low.

TABLE II
SALT ERRORS OF THE QUINHYDRONE ELECTRODE: VALUE OF k IN EQN. 7

Electrolyte	k
HCl	-0.0616
HNO ₃	-0.0895
LiCl	-0.0353
NaCl	-0.0413
KCl	-0.0372
KNO ₃	-0.0645
MgCl ₂	-0.0346
CaCl ₂	-0.0367
SrCl ₂	-0.0379
BaCl ₂	-0.0438
H ₂ SO ₄	-0.0314
Li ₂ SO ₄	0.0269
Na ₂ SO ₄	0.0227
K ₂ SO ₄	0.0238
MgSO ₄	0.0206

THE ANTIMONY ELECTRODE

Description

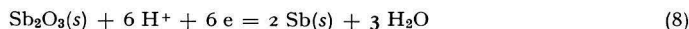
The antimony electrode—or, more correctly, the antimony-antimonous oxide electrode—is the most useful metal-metal oxide electrode for pH measurements. It consists of metallic antimony in any one of a number of convenient forms. An invisible surface coating of oxide seems always to be present, and no special precau-

tions to form the antimonous oxide are necessary. "Tarnished" electrodes display superior accuracy and reproducibility. The surface of the metal must, however, be very clean. It is believed that the many pre-treatments that have been recommended, namely polishing, scraping, brushing, etching with acid, or treatment with sodium carbonate and strong alkalis, have little advantage beyond the assurance of a clean, oxidized surface.

Antimony powder and electrodeposited antimony have been used with reasonable success. The simplest electrodes, however, are formed from antimony cast in sticks. Sometimes antimony trioxide is added to the molten antimony in the manner described by KOLTHOFF AND HARTONG²², but the procedure appears to offer no particular advantages. A short stick of the metal is commonly cemented into a glass tube, projecting from the end. The electrode described by PERLEY²³ consists of cast antimony mounted in a hard rubber sleeve.

It appears that the purity of the metal is of considerable importance. According to ROBERTS AND FENWICK²⁴, who made a careful study of the properties of antimony electrodes, crystalline antimony of high purity can be obtained by rapid electrolysis on a platinum sheet from a solution of antimony trioxide in aqueous hydrofluoric acid. The solutions in which the antimony electrode is used should preferably contain dissolved air, although the presence of air has not been proved essential.

Antimony is known to exist in solution in a variety of forms, each stable at a particular range of pH. The electrode reaction is usually written as follows:



If equilibrium between electrode and solution exists, the potential of the electrode is given by

$$E_e = E_e^0 - \frac{2.3026 RT}{F} \text{pH} \quad (9)$$

regardless of the nature of the antimony species in the solution phase. Nevertheless, the standard potential of the antimony electrode is not very reproducible, nor is the slope of the e.m.f.-pH curve constant over a very wide pH range. These characteristics alone make the antimony electrode a rather unreliable tool for accurate pH measurements, although it may be quite useful for titrations and in certain industrial applications. Unfortunately, the electrode needs frequent reconditioning, and the magnitude of its pH response must be determined by calibration in buffer solutions.

Response

It is difficult to characterize the response of the antimony electrode with certainty, for the responses of individual electrodes are often quite divergent. A plot of the electrode potential with respect to pH should, of course, yield a single straight line with the theoretical slope, namely -0.0592 at 25° . For most electrodes, however, no portion of the line so obtained has exactly the theoretical slope, and the slope of the line usually changes from one region of the pH scale to another. Indeed, TOURKY AND EL WAKKAD²⁵, in a study of the electrode under air-free conditions, found that the potential-pH curve consisted of four branches, separated by slight breaks at pH values of about 2, 5 and 8.

The slope usually appears to be somewhat less than the theoretical; the values range from about 0.05 to 0.059 at 25°. The low values of the slope are believed to result from the variation of the standard potential of the electrode with pH. Typical results for the pH response of a hydrogen electrode and an antimony electrode in buffer solutions at 14° are compared in Fig. 1. The points were calculated from data given by BRITTON¹³. A defective response is clearly evident.

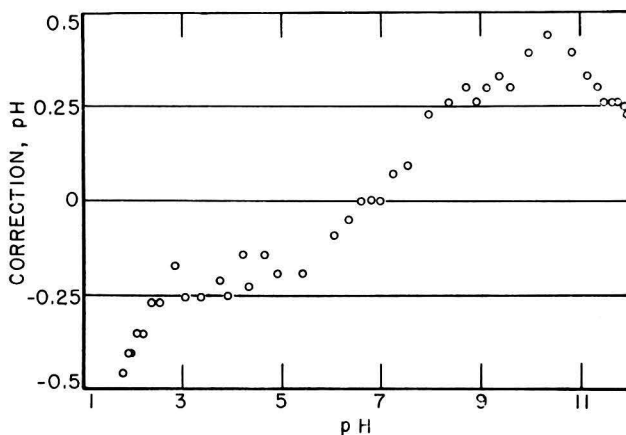


Fig. 1. pH response of an antimony electrode in buffer solutions (correction in pH units to be added to the apparent pH).

As has already been mentioned, the potentials of individual antimony electrodes are not very reproducible. As long as the response of a particular electrode remains constant, however, pH measurements with the electrode are possible, as only differences of potential are required. Furthermore, the slope of the e.m.f. -pH line, if different from the theoretical value, can be established by calibration with several different buffer solutions of known pH. This procedure is essential if accurate results with the antimony electrode are to be obtained. A properly-calibrated antimony electrode, it appears, can be used successfully from pH 1 to about pH 10. According to STOCK, PURDY AND GARCIA²⁶, the temperature coefficient of the e.m.f. of the antimony-saturated calomel cell appears to be rather large, namely about 2-3 mV/degree.

Advantages

The antimony electrode is rugged, simple and inexpensive. It has a very wide field of application, especially in indicating the end-points of acid-base titrations and in industrial pH measurements where high accuracy is not required. The electrode behaves satisfactorily in solutions containing sulfur dioxide, phosphates, agar and gelatin. Although the antimony electrode has a low resistance, it has a marked tendency to polarize. It is therefore recommended that the e.m.f. of cells containing an antimony electrode be measured with an electronic voltmeter rather than with a potentiometer of the low-resistance variety. The antimony electrode has numerous applications in non-aqueous solutions. These have been reviewed by STOCK AND PURDY²⁷.

Disadvantages

The antimony electrode is a far less reliable tool for pH measurements than the hydrogen electrode or the quinhydrone electrode. Inasmuch as its pH response usually departs from the theoretical value, the electrode must be calibrated with buffer solutions, and frequent reconditioning may also be required. Oxygen is permitted in the solutions in which the antimony electrode is used. There is, however, some indication of an oxygen-electrode effect, that is, a changing potential with the partial pressure of oxygen to which the electrode is exposed. The potential of the electrode likewise appears to be altered by stirring the solution.

In view of the considerable number of chemical interferences, it is unsafe to use the antimony electrode in solutions of unknown composition. Oxidizing and reducing agents normally cause difficulty, and there is also a marked sensitivity to complexing agents, notably the anions of hydroxy acids—tartrates, citrates, and to oxalates. It is, of course, not surprising that cations replaceable by antimony cause a disturbance when present in the solution; copper ion, however, has an unusually pronounced effect.

THE GLASS ELECTRODE

Description

The glass electrode, strictly speaking, belongs to the class of membrane electrodes. In contrast with most membrane electrodes, which display very little selectivity, the glass electrode is remarkably specific for hydrogen ions over a very wide range of pH values. The utility of the glass electrode can be attributed to the fact that the magnitude of the potential difference across the boundary between the glass surface and the electrolytic solution is determined almost exclusively by the hydrogen ions present in the solution. The glass electrode, however, has a very high electrical resistance, and it has, as well, a limited durability in solutions of high pH and elevated temperature.

In order to achieve the desired pH response and at the same time to maintain a reasonable electrical resistance and adequate durability, the choice of glass compositions is of the utmost importance. The earliest successful formulation consisted of 72.2 mole % SiO_2 , 6.4 mole % CaO and 21.4 mole % Na_2O . This composition was selected by MACINNES AND DOLE²⁸ in an extensive investigation of many glasses. Glass of this composition has been produced commercially under the name Corning 015 and Schott 4073^{III} for many years. It has a low melting point, a comparatively low resistance, and favorable hygroscopicity. Above pH 9, however, it displays a rather serious error in the presence of the ions of the alkali metals, as DOLE²⁹ and KRATZ³⁰ have indicated in their monographs.

Other glasses with considerably smaller alkaline errors have therefore been developed, largely by the substitution of lithium for the sodium constituent. A rare-earth oxide contributes favorably to the performance of the electrode glass, as PERLEY has shown³¹. Other metals are sometimes added for special reasons. Thus, SCHWABE³² has found that uranium dioxide lowers the electrical resistance of the glass, while SIMON AND WEGMANN³³ report that germanium dioxide improves its workability.

In order to understand the mechanism by which hydrogen ions affect the potential of the glass surface, it is necessary first of all to visualize the structure of the outer layers of the glass. The mechanical framework itself consists of chains of silicon and

oxygen atoms. The cations (largely of the alkali metals and alkaline-earth metals) occupy holes in this network. They are held in these positions only by secondary valence forces and are free to some extent to move under the influence of an electrical field. The ease with which they can move or with which they can be extricated from this network depends, of course, not only upon the strength of the valence forces but upon the relative sizes of the ions and the spaces they occupy.

Water appears to play an important part in the development of the pH response of a glass membrane. Indeed, it has been shown by HUBBARD and his associates^{34,35} that non-hygroscopic glasses rarely can be made to develop a response to hydrogen ions.

In order to acquire a pH response, all new glass electrodes must be conditioned for a time by soaking in water or in a dilute buffer solution. The chemical analysis of the conditioning solution and dimensional studies of the glass itself show clearly that the conditioning process is accompanied by extraction of alkali metal ions from the glass surface, the migration of hydrogen ions or protons into the glass, and a swelling of the glass surface, presumably through the absorption of water. The nature of the conditioning process was clarified considerably by the work of MAC-INNES AND DOLE²⁸, HAUGAARD³⁶ and HUBBARD, HAMILTON AND FINN³⁷.

The pH-response of the electrode after conditioning appears to be due to the readily reversible exchange of hydrogen ions between solutions and the outer hydrous silica layer of the conditioned surface. Glass electrodes should therefore be conditioned in water even though they may be used subsequently in media that are only partly aqueous.

Inasmuch as the function of a glass electrode requires the penetration of water into the lattice and the extraction of soluble components, it is easy to understand that the life of a glass electrode is limited. As the extraction process proceeds, the leached silicon-oxygen skeleton becomes thicker, and the resistance of the electrode increases. Furthermore, a certain amount of attack of this network by the alkali in the inner layers of the glass is unavoidable, and eventually the thin membrane fails through mechanical breakdown. When old glass electrodes become dry, the well-leached outer skeleton of the membrane is subjected to such a considerable stress that mechanical failure may result.

KRATZ³⁰ has recommended that glass electrodes, once they have been conditioned, be kept immersed in water. He has shown that the deterioration due to leaching is less under these conditions than when the electrode is subjected to repeated drying and reconditioning.

Both surfaces of the glass membrane are pH-responsive. The changes in the electric potential of the outer membrane surface are measured by means of an inner electrode dipping into a solution of fixed hydrogen ion concentration. The nature of the inner electrode and the composition of the inner solution are so chosen as to prolong the life of the electrode and to minimize errors caused by fluctuating temperatures.

The most common inner electrodes are the silver-silver chloride electrode and the calomel electrode, although the newly developed thallium amalgam-thallic chloride inner reference, described by FRICKE³⁸ and produced by Jenaer Glaswerk, shows considerable promise. The inner reference solution may be a citrate-buffered chloride solution or even a saturated potassium chloride solution buffered with

acetate. Calomel electrodes are not highly stable above 80°. The silver-silver chloride electrode operates satisfactorily at 100°, however, if precautions to saturate the solution with silver chloride are taken. The thallium electrode is said to be capable of operation at 135°.

Commercial glass electrodes are fabricated in many special forms. Many of these are designed to facilitate special types of measurements. Some require only one or two drops of solution, while others will penetrate soft solids or are designed for measurements on smooth surfaces. Still another is mounted within a hypodermic syringe. The most useful type for general use is, however, the immersion or bulb-type electrode.

Advantages

The glass electrode displays an amazing versatility. It is uninfluenced by oxidizing and reducing agents, it is not poisoned by heavy metals, and it functions well in numerous partly aqueous media. Its response may be very nearly theoretical over quite wide ranges of pH. It does not normally alter the composition of the solution in which it is immersed. The glass electrode has, indeed, many of the characteristics of an ideal indicator electrode for practical pH measurements.

Disadvantages and limitations

The chief disadvantages of the glass electrode are (1) the high electrical resistance, which makes complicated and expensive measuring devices necessary; (2) a limited durability, which not only shortens the life of the electrode but leads to some contamination of the solutions being measured; (3) the tendency of the glass membrane to absorb materials from the solutions in which it is immersed; and (4) its marked response to some cations in alkaline solutions ("alkaline error").

The electrical resistance of most glass electrodes lies between 5 and 500 megohms. Nevertheless, stable electronic voltmeters capable of measuring the electromotive force (tension) of glass-electrode cells with an accuracy of ± 0.2 mV are now available commercially. It is unfortunate that the resistance of the glass membrane is profoundly affected by changes in temperature. It is indeed not unusual for the resistance of a glass electrode to increase tenfold when the temperature is lowered from 50° to 25°. If the resistance is too high, charging effects accompanied by a sluggish response become apparent, and the usefulness of the electrode is impaired.

Furthermore, the durability of the glass membrane changes, in general, in the same manner as the electrical resistance. The design of an electrode with the most desirable properties therefore becomes a matter of some difficulty. Electrodes that are durable at elevated temperatures may normally be expected to have excessive electrical resistances when the temperature is lowered. Conversely, electrodes of suitable resistance for use at room temperatures will normally corrode rapidly in solutions at high temperatures. The most satisfactory solution of this dilemma has been to design electrodes for specific ranges of temperature, in order to avoid large errors and a premature failure of the electrode. It is important to choose the most suitable electrode for the conditions under which the measurement is to be made. Failure of the electrode comes without warning and may often go undetected unless the response of the electrode is regularly confirmed by standardization with at least two standard buffer solutions.

Inasmuch as alkali ions must be present in the glass to assure adequate conductivity and the desired pH response, it is not surprising that the glass electrode will respond to certain alkali metal ions when the concentration of hydrogen ions in the solution becomes exceedingly small. It is indeed remarkable that an electrode containing sodium ions displays such a high selectivity for hydrogen ions as to have a substantially unimpaired pH response when the concentration of sodium ions is 10^9 times the concentration of hydrogen ions. As EISENMAN, RUDIN AND CASBY³⁹ have shown, the addition of aluminum oxide or boric oxide to the glass enhances the sodium ion response to such an extent that the glass electrode becomes a useful tool for the measurement of sodium ion concentration or activity.

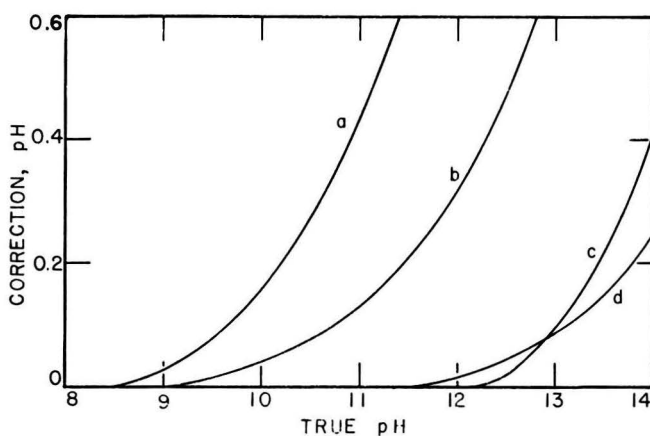


Fig. 2. Sodium ion error of six commercial glass electrodes in 1 M Na^+ as a function of "true" pH (correction in pH units to be added to the apparent pH): a, Corning 015 and Schott 4073 III; b, Beckman General Purpose; c, Leeds and Northrup "Black Dot"; d, Electronic Instruments GHS and Beckman type E-2.

The sodium ion errors of some electrodes of different compositions are plotted as a function of "true" pH in Fig. 2. The magnitude of the correction to be applied is, of course, dependent upon the composition of the glass. The user should obtain tables of alkaline errors from the manufacturer of the electrode and should apply corrections to his measurements when necessary. Some glass electrodes, including those fabricated from Corning 015 glass, also display an error in strongly acidic solutions²⁹.

Glass membranes are likewise characterized by an asymmetry potential, or difference between the potentials generated at the two surfaces under identical conditions. Asymmetry is believed to have many different causes; one of the most important is probably unequal leaching of the two surfaces, giving rise to differences in alkali-metal content, water sorption and thickness of the swollen layer. For practical purposes, however, only *changes* of the asymmetry potential are of concern. Unless the electrode has been subjected to severe dehydration or damage in the recent past, the asymmetry potential can usually be considered to be constant and can be "balanced out" in the standardization of the electrode.

Commercial glass electrodes

The characteristics of some commercial glass electrodes are given in Table III. The data were taken in part from the work of SIMON AND WEGMANN⁴⁰.

TABLE III
CHARACTERISTICS OF SOME COMMERCIAL ELECTRODE GLASSES AT 25°
(data taken in part from SIMON AND WEGMANN⁴⁰)

Electrode	Composition of glass	Resistance (megohms)	Correction* (pH units)	
			in 0.1 M NaOH	1 M NaOH
Beckman E-2	SiO ₂ , BaO, Li ₂ O	375	0.03	0.17
Beckman General Purpose	SiO ₂ , BaO, Li ₂ O	150	0.43	1.4
Beckman Amber	SiO ₂ , BaO, Li ₂ O	550	0.02	0.17
Cambridge Alki	—	400	—	0.15
Corning 015	SiO ₂ , CaO, Na ₂ O	90	1.0	2.5
Doran Alkacid M4999	—	300	0.02	0.10
Electronic Instruments GHS	SiO ₂ , Li ₂ O, Cs ₂ O	200	0.02	0.15
Ingold UN	SiO ₂ , Li ₂ O	30	0.70	1.9
Leeds and Northrup "Black Dot"	SiO ₂ , La ₂ O ₃ , Li ₂ O	70	0.02	0.25
Metrohm H	SiO ₂ , BaO, Li ₂ O	1400	0.08	0.15
Metrohm X	SiO ₂ , CaO, Li ₂ O	100	0.90	2.2
Metrohm U	SiO ₂ , BaO, Li ₂ O	500	0.08	0.26

* To be added to apparent pH value.

For best results and for longest life the glass electrode should be kept moist after initial conditioning. The deterioration of the inner layers of the glass is believed to be retarded by this procedure, whereas frequent drying and reconditioning accelerate the breakdown of the lattice structure. It must always be remembered, however, that a certain amount of chemical attack is always taking place and that the electrode has, therefore, a limited life. In order to detect impairment of the response as soon as possible, the electrode should be standardized frequently with two buffer solutions which differ in pH by several units. The mechanical stresses caused by chemical attack followed by drying may produce cracks in the glass membrane and bring the life of the electrode to an untimely end.

Mechanical damage of the membrane may also result from contact with solution cups, by scratching with abrasive solids, or from the etching effects of corrosive solutions. Likewise, the pH response may be impaired by surface deposits which prevent the attainment of rapid equilibrium between electrode and solution. Among these are greases, certain colloids, and proteins. It goes without saying that the electrode should be kept free of all deposits. Immersion of the bulb in 6 M hydrochloric acid, rinsing with water and wiping with soft tissue is often a satisfactory means of removing surface contaminants. For the removal of organic films, 70 % ethanol is often useful.

SUMMARY, CHOICE OF pH METHODS

The characteristics of the four most common pH electrodes, namely the hydrogen, quinhydrone, antimony and glass electrodes, have been discussed in some detail in the foregoing sections. The most important properties are summarized and com-

pared in Table IV, which may be used as a guide in the choice of the most suitable electrode for a particular measurement problem.

The hydrogen electrode is the primary standard for all pH measurements and is unquestionably the most precise of the pH-responsive electrodes whenever conditions are favorable for its use. The hydrogen electrode is not versatile in any sense of the word, however, nor can hydrogen electrode measurements be made simply and rapidly.

TABLE IV
COMPARISON OF pH-RESPONSIVE ELECTRODES
(+ = low; ++ = medium; +++ = high)

Property	Hydrogen	Quinhydrone	Antimony	Glass
pH range	Unlimited	0-8	0-11	0-13 (with corrections)
pH response	Theoretical	Theoretical	Variable	Theoretical (pH 0-11)
Precision (pH)	± 0.001	± 0.002	± 0.1 (when properly calibrated)	± 0.005
Convenience of measurement	+	++	+++	+++
Time required for measurement (min)	30-60	5	3	<1
Versatility	+	++	++	+++
Cost of equipment	++	+	+	+++
Electrical resistance	+	+	+	+++
Disadvantages	Strong reducing action, air must be excluded	Limited pH range, salt error	Defective response, not completely reversible	Variable asymmetry potential, high resistance, alkaline error
Interferences	Oxidizing agents, reducible organic substances, noble metal ions, SO ₂ , CN, unbuffered solutions	Proteins, some amines	Some oxidizing agents, Cu ion, anions of hydroxy acids	Dehydrating solutions, some colloids, fluorides, surface deposits on the electrode

Both the quinhydrone electrode and the glass electrode are capable of furnishing very precise results within limited ranges of pH. The quinhydrone electrode is unsuitable in solutions of pH greater than 8. Although its response is almost instantaneous, this electrode is neither simple nor convenient to construct. Interfering substances are not numerous.

The glass electrode, on the other hand, can be used over the pH range 0-11 under most circumstances and, with the application of corrections, at even higher pH values. The response is rapid, and no more convenient electrode than the simple dipping or immersion type could be desired. Unfortunately, frequent standardization is necessary, as neither the standard potential nor the asymmetry potential are stable over long periods of time.

The antimony electrode is somewhat less precise and reliable than the other three. It is remarkably simple and rapid, however, and has proved itself eminently suited for titrations and for industrial pH measurements in the range pH 1-10. For a precision greater than ± 0.2 pH, however, care must be given to frequent reconditioning and recalibration.

It should be noted that the equipment needed to measure accurately the potentials developed by hydrogen, quinhydrone and antimony electrodes is relatively inexpensive, as the internal resistance of cells containing these electrodes is small. The high resistance of glass electrode cells, on the other hand, makes necessary the availability of the relatively costly electronic voltmeters.

The overall precision of an electrometric pH measurement is, however, influenced not only by the precision of the indicator electrode and of the measuring system but also by the reproducibility of the reference electrode and the liquid junction. The design of the liquid junction is of particular importance at very low and very high pH. At pH values less than 2, the reproducibility of the liquid-junction potential is seriously impaired. The errors thereby introduced often exceed those attributable to the pH-responsive electrode.

SUMMARY

The experimental pH value is defined in terms of a difference in the electromotive force or tension of a pH cell containing (1) the "unknown" solution and (2) a standard solution of assigned pH. The pH cell consists of a reference electrode, a liquid junction and an electrode whose potential is a function of pH. The potential or tension of the reference electrode, including that at the liquid junction, is assumed to remain unchanged while measurements (1) and (2) are being made and during the time interval between these measurements.

Although the glass electrode is the most common pH-responsive electrode, the hydrogen electrode, the quinhydrone electrode and the antimony electrode all have their place in pH measurements. This paper describes these four indicator electrodes, discusses the advantages, limitations, and accuracy of each one, and summarizes the information needed for a selection of the best electrode for each special measuring situation.

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APPLICATIONS OF CATHODE-RAY POLAROGRAPHY IN
THE FIELD OF OCEANOGRAPHY

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INTRODUCTION

Present day research on the physical, chemical, and biological phenomena of the deep ocean has placed new requirements on the methods of analysis that are needed in support of this work. Modern electro-chemical methods of analysis appear to have the desired range of precision, reproducibility, and sensitivity that will be required, plus the feature of using the basic principles in direct reading instrumentation with digital recording of data.

One of the more promising electrochemical methods of analysis is that of polarography¹; although very little application of this method to oceanography has been reported². This method is specific, very rapid, precise, and is particularly adapted to the qualitative or quantitative determination of trace amounts of reducible ions in solution. The sea water itself serves as a very good supporting electrolyte. In addition, many organic compounds such as vitamins, hormones, sugars, amino-acids, enzymes, protein, etc. may be determined in trace amounts. For example, the determination of one part of Al in 100 million is now possible by cathode-ray polarography. Other polarographic techniques that should find application are those of "anodic stripping", square-wave polarography, pulse polarography, and radio frequency polarography, where concentrations in the neighborhood of 10^{-8} M have been reported as measurable³⁻⁶. Thus, it can be seen that polarography should be ideally suited for studies on the chemical composition of sea water, bottom samples, cores of sediments, and marine organisms.

In cathode-ray polarography several techniques have been developed, but the principle of RANGLES⁷⁻⁸ at the present time, appears to be the best for analytical purposes. The method developed by RANGLES involves a single voltage sweep, which occurs just before the drop of Hg detaches from the electrode. At this instant, a fall in current occurs which is used to trigger off the time base. The current is shown on the cathode-ray tube against the applied voltage. However, the resulting polarogram generally has a peak current whose height is directly proportional to concentration. This peak is caused by an increase in current when the potential begins to "strip-out" ions at the electrode surface, followed by a decrease in current as a diffusion layer extends further out into the solution and the concentration gradient at the electrode surface decreases.

A single sweep cathode-ray polarograph has recently been manufactured by Southern Instruments Company, England, and is known as the "Polarotrace". With this

instrument the voltage range from $+0.50$ to -2.50 V may be covered in a few seconds. The voltage is applied in increments of 0.50 V so that one sees all the electrode processes occurring in this range as a trace on a cathode-ray screen. The trace is reproduced on the screen every 7 sec and thus conditions are very favorable for continuous recording and studies of fast electrode reactions. By making use of a derivative circuit, waves differing by only 0.04 V may be resolved and measured. This circuit also allows one to measure the concentration of a trace element when a large preceding reduction is taking place. The potential sweep takes 2 sec and the delay time is set at 5 sec. The sweep is thus synchronized with a dropping Hg electrode of 7 sec drop rate.

Because of the increased sensitivity, higher resolution and great speed of recording, the single-sweep cathode-ray polarograph is particularly adapted to rapid, precise, and continuous recording determinations of constituents found in sea water with either the dropping Hg electrode or solid electrodes. It is the purpose of this report to present some data on the use of such an instrument in the field of oceanography.

EXPERIMENTAL

Apparatus and materials

A single-sweep cathode-ray polarograph known as the "Polarotrace K-1000" and manufactured by Southern Instruments Company, England, was used in this work⁸.

The dropping Hg electrode had the following characteristic on open circuit in distilled water: $m = 7.7$ mg/drop.

C.P. redistilled Hg was used in all work. Pure Ag wire (0.02 in. diameter) was purchased from The American Platinum Works, Newark, N. J., and carefully cleaned before use.

Pyrex polarographic cells, furnished with the "Polarotrace", and provided with side arms for the anodic connection and for bubbling with nitrogen, were used in studies with the dropping Hg electrode. About 2 ml of solution was placed in the cell. The solution was flushed with dry nitrogen for 3 min, and then polarographed with nitrogen flowing over the solution. The nitrogen was purified by passing it through "oxsorbent" and then through distilled water before allowing it to bubble through the sample. The "oxsorbent" was obtained from the Burrell Corporation, Pittsburgh, Pa. With solid electrodes a small (30 ml) beaker served as the cell. A rubber stopper, to which were attached the electrodes and a gas flushing tube with a fritted disk, was placed over the top of the beaker.

All polarographic measurements were made in a constant temperature bath at $25^{\circ} \pm 0.25^{\circ}$. pH measurements were made with a Beckman Model G pH-meter.

The solid electrode coatings were produced with the "Electropode", manufactured by Fisher Scientific Company, Pittsburgh, Pa.

Synthetic and natural sea water samples were used in this work. The synthetic sea water was prepared according to the formula of SUBOW⁹. "Copenhagen" sea water was used as the supply of standard natural sea water. The "Copenhagen" water was obtained from Kahl Scientific Instrument Company, El Cajon, Calif., and contained 19.379 parts per thousand chlorinity. Other samples of natural sea water were obtained off the coast of Southern California.

Standard solutions of the ions used in the trace element studies were obtained from Southwestern Analytical Chemicals, Austin, Texas. Dry reagent grade (Baker and Adamson) chemicals were used in preparation of the synthetic sea water. The sodium

nitrate used in preparation of the supporting electrolyte for the chloride studies was also reagent grade (Baker and Adamson).

Measurement of chloride ion

The chlorinity of sea water⁹ usually falls in the concentration range of 15.00 to 21.00 parts per thousand (‰). The Knudsen volumetric method of analysis is generally used to measure this concentration¹¹ and "Copenhagen" sea water is used as a primary standard. With careful technique an accuracy of ± 0.03 ‰ Cl can be realized. However, samples of sea water must be obtained precisely and then analyzed either aboard ship or in the laboratory after a cruise. Using cathode-ray polarography with the "Polarotrace" the chloride ion concentration can be measured continuously, directly, and rapidly in sea water with solid electrodes.

Fig. 1 shows the two-peak trace obtained from a sample of natural sea water with AgCl-Ag wire electrodes (0.02 in. dia.) immersed in 10 ml of the sea water. The system

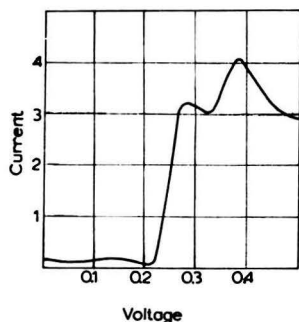


Fig. 1. Trace for Cl^- in natural sea water: electrodes, AgCl-Ag (1/2 in. immersion in sea water); starting potential = +0.20 V; scale factor = 10; derivative.

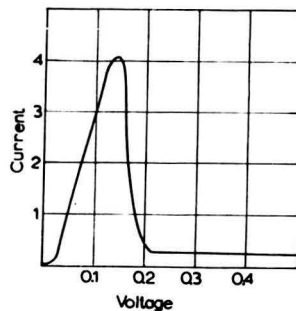
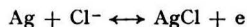


Fig. 2. Trace for Cl^- in natural sea water: electrodes, DME-Hg pool; starting potential = +0.60 V scale factor = 100; direct.

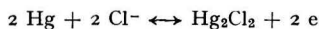
appeared to equilibrate within a few sweeps after immersing the electrodes in the sea water, and the total peak height remained constant within $\pm 1\%$ on the cathode-ray screen of the "Polarotrace" for 72 h of continuous operation.

Peak heights, with sea water in the range of 10–20 ‰ Cl, were proportional with concentration. A difference in chlorinity of ± 0.10 ‰ could be distinguished readily. The solution was stirred rapidly with an automatic stirrer and no change in peak height was observed. Thus, flow does not appear to affect the system. About 25 mg of reagent grade MgSO_4 were added to the 10 ml of sea water. No increase in peak height or change in peak voltage was observed. Thus, a change in total ionic strength of the solution does not appear to affect the system. The two peaks are due apparently to a reaction of chloride ion with Ag ion as follows:



The explanation for two peaks may lie in the formation of an intermediate compound such as Ag_2Cl^+ , AgCl_2^- , AgO, or Ag_2O . The formation of Ag_2O and AgO in alkaline solution has been reported¹⁰ but no evidence of a peak from this source appears in curve 1, Fig. 3.

Fig. 2 shows the trace obtained from natural sea water with a dropping Hg electrode *vs.* a Hg pool. Only one peak is now obtained. The peak height is not proportional to the concentration of chloride ion. The chloride ion apparently reacts with Hg to form slightly soluble Hg_2Cl_2 as follows¹:



However, at the dropping Hg electrode such large amounts of chloride ion as found in sea water will not produce anodic waves that are proportional to the chloride ion concentration.

Studies with the AgCl-Ag solid electrodes were made in 0.1 M NaNO_3 solution. The series of traces in Fig. 3 shows the effect of chloride ion concentration on the trace. With only 1.0 mg of Cl^- as NaCl in 10 ml of 0.1 M NaNO_3 solution, two distinct peaks are barely discernible, Fig. 3 (2). However, with 10, 20, and 25 mg respectively of Cl^- in 10 ml of 0.1 M NaNO_3 (Fig. 3 (3), (4), (5), respectively) the trace appears like that found with the electrodes immersed in real sea water (Fig. 1).

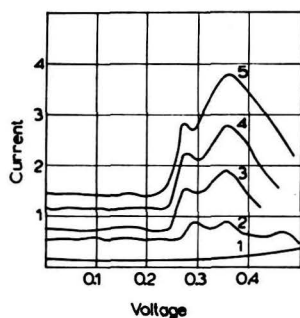


Fig. 3. Effect of Cl^- concentration on trace: supporting electrolyte, 10 ml of 0.1 M NaNO_3 ; electrodes, AgCl-Ag; starting potential = +0.20 V; scale factor = 4.0; derivative. Curve 1, no Cl^- ; curve 2, 1 mg Cl^- ; curve 3, 5 mg Cl^- ; curve 4, 10 mg Cl^- ; curve 5, 25 mg Cl^- .

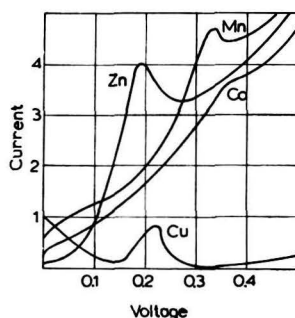


Fig. 4. Traces for $1 \cdot 10^{-7}$ g/ml solutions of Cu^{2+} , Zn^{2+} , Co^{2+} , and Mn^{2+} ; supporting electrolyte, 0.05 M KCl; electrodes, DME-Hg pool; starting potential = +0.35 V, Cu^{2+} ; -0.80 V, Zn^{2+} ; -1.00 V, Co^{2+} ; and -1.30 V, Mn^{2+} ; scale factor = 0.04 for Zn^{2+} , Co^{2+} and Mn^{2+} ; 0.25 for Cu^{2+} ; direct.

Measurement of trace elements

Trace elements such as Cu, Pb, Zn, and Mn may be determined in sea water. Fig. 4 shows traces for a KCl solution containing $1 \cdot 10^{-7}$ g/ml of Cu^{2+} , Co^{2+} , Zn^{2+} , and Mn^{2+} respectively. By quickly adjusting the start potential of the "Polarotrace" these 4 cations may be determined on the same sample in a matter of minutes. If the concentration of the ion is less than $5 \cdot 10^{-8}$ g/ml in the final solution for analysis, then the ions must be concentrated before submitting the sample to cathode-ray polarography. In some cases it may be possible to measure the concentration, and obtain the ratios of some trace ions directly in the sea water without treating the sample before analysis. Peak potentials of several ions in sea water are given in Table I along with the start potentials of the "Polarotrace". It can be seen that all 7 cations may be determined in the same solution by merely changing the start potential of the polarograph. Thus, one could in a few minutes analyze for all 7 cations in a single sample of sea water in concentrations as low as $5 \cdot 10^{-8}$ g/ml.

Measurement of dissolved oxygen

Dissolved oxygen occurs in sea water in the range of 2–6 ml/l. It can be measured with either solid electrodes or the dropping Hg electrode. Fig. 5a shows a trace of dissolved oxygen in a sample of sea water using a Pt *vs.* Hg solid electrode system. Fig. 5b shows a trace for the same sample using a dropping Hg electrode *vs.* Hg pool. One can thus obtain either a direct continuous record of dissolved oxygen on samples of sea water, or rapidly analyze different samples aboard ship for their dissolved oxygen content. Solid electrode systems such as Ag–Pt, Ag–AgCl, and Au + Hg–Ag should be useful for continuous *in situ* studies of the dissolved oxygen content of sea water.

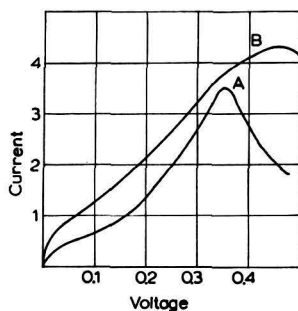


Fig. 5. Dissolved oxygen in sea water: electrodes, curve A: Pt *vs.* Hg on Au; curve B: DME *vs.* Hg pool; starting potential, curve A = 0.0 V; curve B = -0.50 V; scale factor, curve A = 25; curve B = 1.0; direct.

TABLE I
PEAK POTENTIALS OF SOME IONS IN SEA WATER (POLAROTRACE K-1000 AND DME)

Ion*	Start potential (V)	Peak potential (V) (<i>vs.</i> Hg pool)**
Cl	+0.60	+0.52
Cu	+0.35	+0.23
Pb	+0.35	-0.08
Cd	0.00	-0.29
Zn	-0.60	-0.95
Ni	-0.60	-1.00
Co	-1.00	-1.38
Mn	-1.20	-1.50

* $1 \cdot 10^{-6}$ g/ml concentration added to Copenhagen Sea Water.

** Saturated calomel electrode *vs.* Hg pool = -0.058 V in Copenhagen Sea Water.

SUMMARY

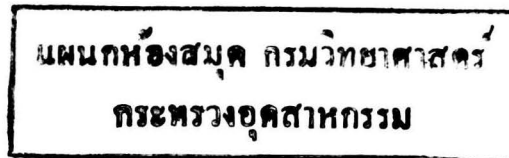
Some applications of cathode-ray polarography in the field of oceanography have been discussed. Emphasis in this report has been placed on results of a preliminary study of the behavior of chloride ion, some trace elements, and dissolved oxygen in sea water. The advantages of rapidity, specificity, sensitivity, and adaptability to solid electrode systems and direct reading instrumentation for continuously recording these constituents found in sea water have been pointed out. It would seem that further research should extend the potentialities of cathode-ray polarography and

other polarographic techniques in the field of chemical oceanography. Especially, the great advantage of *in situ* measurement may at last be realized.

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LE COMPORTEMENT POLAROGRAPHIQUE DE L'ION NICKEL EN MILIEU
NON-COMPLEXANT

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INTRODUCTION

En milieu non-complexant, les ondes polarographiques de réduction de l'ion Ni sont typiquement irréversibles, et présentent un palier bien défini dont l'amplitude obéit à la relation d'ILKOVIC. Cependant, à mesure que l'on augmente la concentration de l'électrolyte-support (au-delà d'une valeur de l'ordre de $10^{-1} N$), on observe un abaissement graduel du courant-limite, qui croît par ailleurs de manière continue avec la tension imposée. C'est ainsi qu'en milieu NaClO_4 4 M, le palier est considérablement étiré, et son amplitude mesurée au sommet du front de l'onde est approximativement réduite de moitié.

Ainsi que l'ont montré les expériences comparatives de FORSS¹, il est difficile d'attribuer l'entière de cet abaissement à une diminution du coefficient de diffusion de l'ion Ni. Cette conclusion a été corroborée par REYNOLDS, SHALGOSKY ET WEBBER², puis par SANBORN ET ORLEMAN³; ces derniers suggèrent que la réduction électrochimique amènerait la formation d'ions Ni monovalents, susceptibles de se dismuter en Ni métallique et en Ni bivalent, à une vitesse d'autant plus faible que la force ionique est élevée. Cette hypothèse, qui permet d'expliquer pourquoi l'amplitude du courant-limite paraît tendre vers la moitié du courant de diffusion pure, peut également rendre compte du fait que le rendement coulométrique en Ni métallique est faible en milieu concentré, et plus particulièrement en présence d'ions bromate, qui seraient par conséquent réduits catalytiquement à l'intervention des ions Ni monovalents. Cependant, les auteurs signalent qu'il est impossible d'isoler ces ions et de les caractériser chimiquement, même en milieu très concentré, où leur stabilité devrait être suffisante pour permettre leur détection. Par ailleurs, la raison exacte de l'influence du milieu sur la constante de vitesse de la réaction de dismutation proposée reste indéterminée.

VLCEK⁴, dans une courte communication, interprète l'abaissement de l'onde en termes d'un courant cinétique de décomplexion, et signale l'existence d'un comportement analogue pour l'ion Co^{2+} .

Quoique très apparente, l'inclinaison du courant-limite n'a reçu jusqu'ici aucune explication. L'objet de cette communication est de reconsidérer le problème, en tenant compte de l'action cinétique indirecte qu'est susceptible d'exercer la double couche électrochimique. On dispose à l'heure actuelle de traitements théoriques satisfaisants permettant d'interpréter l'influence de ce facteur sur la morphologie des courbes de

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polarisation pour divers schémas réactionnels (décharge directe totalement ou partiellement irréversible, décharge précédée d'une étape chimique déterminante). En fait, les déplacements en tension des ondes de réduction de l'ion Ni en fonction de la concentration de l'électrolyte-support ont déjà été expliquées par TURKAN⁵ sur la base de la théorie de FRUMKIN⁶; on remarquera toutefois que la validité de cette interprétation est subordonnée à l'élucidation de la nature du phénomène responsable de l'abaissement du courant-limite.

Le fait que l'abaissement observé en milieu concentré est lié pour une certaine part à la diminution du coefficient de diffusion de l'ion Ni limite considérablement l'utilité de la méthode polarographique: en effet, les constantes de vitesse réactionnelles ne peuvent se calculer qu'à partir des valeurs de l'amplitude relative I/I_d du courant, dont l'évaluation exacte est pratiquement impossible. Cette difficulté peut être évitée si l'on opère simultanément en régime galvanostatique: en portant en fonction de la densité de courant imposée i_0 les valeurs du produit $S = i_0 \sqrt{t_E}$ (où t_E est le temps requis pour que l'électrode atteigne la tension arbitraire E), on obtient, dans le cas d'un processus totalement irréversible, une droite plus ou moins inclinée, dont la pente est une fonction simple de la constante de vitesse, et dont l'extrapolation pour $i_0 = 0$ donne la quantité S_0 , indépendante de la vitesse réactionnelle et proportionnelle à la racine carrée du coefficient de diffusion, selon la relation de SAND⁸

$$2 S_0 = nFC \sqrt{\pi D}$$

Dans cette relation: n est le nombre d'électrons échangés par particule;

C est la concentration du dépolarisant, en mol cm^{-3} ;

et D est le coefficient de diffusion en $\text{cm}^2 \text{sec}^{-1}$;

S_0 étant exprimé en $\text{A cm}^{-2} \text{sec}^{1/2}$.

RÉACTIFS ET APPAREILLAGE

Les produits utilisés étaient de la qualité pro analysi. Etant donné la nécessité d'opérer en milieu très concentré, les divers électrolytes-supports ont été soumis à une purification poussée, de manière à en éliminer les matières organiques adsorbables et les traces déchargeables. A cet effet, on a généralement procédé à une calcination prolongée, opérée à une température comprise entre 300° et 500° (selon le degré de stabilité thermique), suivie d'une préélectrolyse à tension contrôlée sur cathode de mercure.

Toutes les mesures ont été effectuées à $25.0^\circ \pm 0.1$. Les diverses solutions, réalisées à l'aide d'eau distillée, ont été désaérées à l'aide d'azote pur dont la teneur en oxygène était inférieure à 0.0005%. Le Hg utilisé était soumis à une double distillation sous vide, précédée d'une oxydation par barbotage d'air sous acide nitrique dilué.

Mesures polarographiques

La période de l'électrode à gouttes a été fixée à 4.00 sec à l'aide d'un dispositif électromécanique, de manière à éliminer la distorsion des courbes polarographiques due à la variation de la tension interfaciale avec la tension imposée. L'électrode auxiliaire était constituée par une nappe de Hg. Le polarographe, du type conventionnel, comprend comme instrument de mesure un millivoltmètre Brown Elektronik type 153X17 monté en microampèremètre à sensibilité variable; cet instrument fonctionne sans circuit d'amortissement extérieur, et il a été tenu compte uniquement

des courants instantanés maxima. Les polarogrammes ont été enregistrés à une vitesse de déroulement en temps de l'ordre de 20 mV par minute, de manière à obtenir des courbes très étalées. Les tensions imposées à l'électrode à gouttes étaient mesurées par rapport à une électrode de comparaison au calomel saturé, en utilisant un millivoltmètre à haute impédance d'entrée.

Mesures galvanostatiques

La description détaillée de l'appareillage utilisé a fait l'objet d'une communication antérieure⁹. Le circuit de polarisation à courant constant est constitué d'une source de haute tension stabilisée, qui débite dans une résistance de charge variable. Le principe de fonctionnement de l'appareil peut être sommairement décrit comme suit : on provoque simultanément la chute de la goutte de Hg et la mise en marche d'un circuit retardateur. Ce dernier, après un temps qui peut être ajusté dans de larges limites et qui est connu avec une grande précision, commande l'imposition du courant constant, et l'enclenchement simultané d'un chronomètre électronique. Celui-ci s'arrête lorsque la tension de l'électrode par rapport à l'électrode de comparaison atteint une valeur arbitrairement choisie. L'instrument est muni d'un circuit de contrôle, comprenant un élément Weston, un diviseur de tension et un galvanomètre, permettant de vérifier à tout moment la valeur absolue de l'intensité du courant imposé, de telle sorte que celle-ci est connue à environ 0.1% près. La durée de la mesure étant très brève par rapport à l'âge de la goutte au moment où elle est polarisée, l'expansion de surface a été tenue pour négligeable. L'électrode à gouttes est constituée par un capillaire polarographique étiré dans sa partie médiane, de manière à assurer une période de chute libre comprise entre 40 et 60 sec. L'aire de l'électrode au moment de la mesure est calculée, à partir du temps de retard et du débit du capillaire, avec

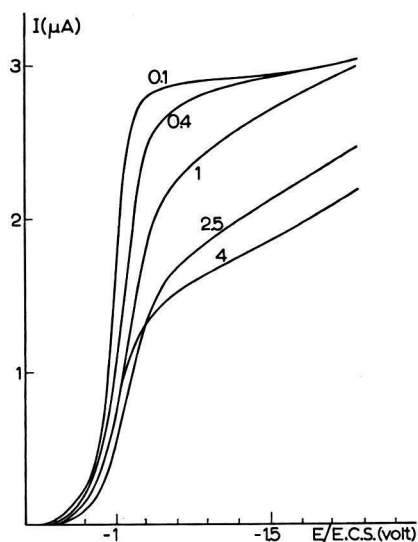


Fig. 1. Courbes polarographiques de l'ion Ni en milieu perchlorate de sodium : $[\text{Ni}^{2+}] = 10^{-2} M$; les chiffres expriment les concentrations de NaClO_4 , en M.

une précision de l'ordre de 0.1%. Les mesures de temps s'effectuent avec une précision de $\pm 2 \cdot 10^{-4}$ sec, et les tensions d'électrode qui y correspondent sont connues à environ ± 1 mV.

COMPORTEMENT DE L'ION Ni EN MILIEU PERCHLORATE DE SODIUM

Ce milieu a été choisi en raison de l'inactivité quasi totale de l'ion perchlorate sous le double rapport du pouvoir complexant et de la tendance à l'adsorption spécifique dans le domaine des tensions considérées. Les conditions expérimentales se trouvent ainsi considérablement simplifiées, ce qui facilite d'autant l'élucidation du mécanisme réactionnel.

Données expérimentales

On a polarographié diverses solutions 10^{-3} M en Ni à teneur variable en perchlorate de sodium. Les ondes sont d'autant plus abaissées que la force ionique est élevée (Fig. 1), les paliers étant particulièrement mal définis pour des concentrations de l'ordre de 1 à 2 M. Aux concentrations très élevées, les ondes tendent à se déplacer vers des tensions moins négatives: cet effet est vraisemblablement lié à la très grande variation des coefficients d'activité, et à l'apparition de tensions de jonction non-négligeables.

De manière à apprécier la part de l'abaissement due à l'accroissement de la viscosité du milieu, des expériences parallèles ont été effectuées en régime galvanostatique; la concentration en Ni a été ici portée à 10^{-2} M, afin de rendre négligeable l'allongement des temps d'électrolyse causé par l'interférence du courant de charge capacitive¹⁰. L'établissement de graphiques de coordonnées S et i_0 permet l'évaluation par extrapolation de la quantité S_0 , avec une précision de l'ordre du pourcent (cf. Fig. 2, présentée à titre d'exemple). L'amplitude I_a du courant polarographique maximum que l'on observerait si la diffusion était seule déterminante est ensuite calculée à partir de la relation

$$I_a = 799 S_0 m^{2/3} t_g^{1/6} \quad (1)$$

(où m est le débit de l'électrode à gouttes polarographique, en mg. sec⁻¹, et t_g sa période de chute en sec). Cette relation (écrite ici pour des concentrations égales)

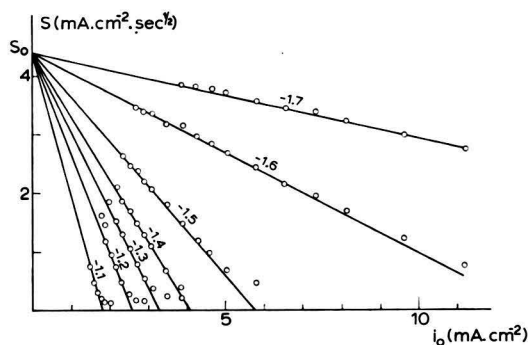


Fig. 2. Diagramme galvanostatique $S = f(i_0)$, pour la composition $[\text{Ni}^{2+}] = 10^{-2}$ M et $[\text{NaClO}_4] = 4$ M; les chiffres expriment les tensions mesurées par rapport à l'électrode au calomel saturé.

s'obtient aisément en couplant les relations de SAND et ILKOVIC. Il est ainsi possible de ramener les divers polarogrammes à la même échelle relative I/I_a (Fig. 3).

La comparaison entre les Figs. 1 et 3 montre, en accord avec diverses conclusions antérieures, que l'abaissement du courant-limite n'est que partiellement causé par la diminution du coefficient de diffusion, et qu'il est par conséquent *simultanément déterminé par un processus distinct de la diffusion proprement dite*.

Discussion

Le fait que les courants relatifs I/I_a correspondant à l'étendue du „palier” *augmentent* lorsque la *tension est rendue plus négative* ou lorsque l'on *diminue la concentration de l'électrolyte-support*, suggère que le processus déterminant est d'autant plus *rapide*

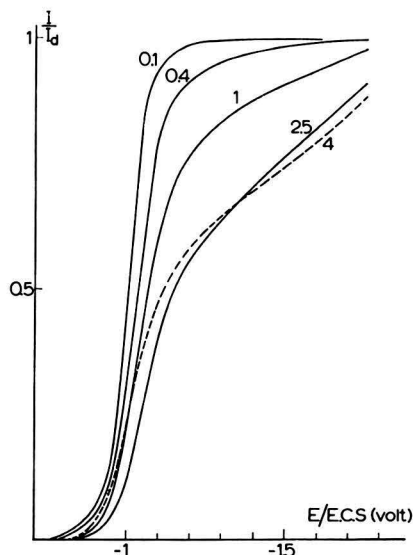


Fig. 3. Courbes polarographiques de l'ion Ni en échelle de courant relative: les compositions sont celles de la Fig. 1.

que la double-couche est polarisée *négativement*. En effet, sur la base du modèle de double-couche diffuse de GOUY-CHAPMAN¹¹, les valeurs du potentiel ψ_0 (au plan externe de HELMHOLTZ¹²) dépendent de la concentration C_t de l'électrolyte-support (supposé symétrique, de charge électrique Z) et de la densité de charge de l'électrode (qui croît à peu près linéairement avec la tension) selon

$$\psi_0 = \frac{2 RT}{ZF} \operatorname{arc} \sin h \frac{q}{\sqrt{C_t}} \sqrt{\frac{\pi}{2 RT \epsilon}} \quad (2)$$

Dans cette relation, ψ_0 est exprimé en V, q en coulomb cm^{-2} et C_t en mol cm^{-3} . ϵ est la constante diélectrique, supposée constante; les autres termes ont leur signification habituelle.

Le graphique de la Fig. 4 a été construit à l'aide de cette relation, en admettant une capacité d'électrode de $18 \mu\text{F cm}^{-2}$, indépendante de la tension imposée. φ est la tension rationnelle de GRAHAME¹² ($\varphi = 0$ correspondant à $E = -0.47$ V par rapport à l'électrode au calomel saturé).

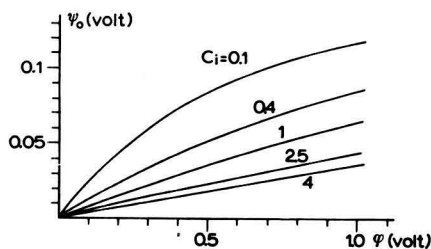


Fig. 4. Diagramme $\psi_0 = f(\varphi)$ établi à partir de la relation (2); pour une capacité d'électrode de $18 \mu\text{F cm}^{-2}$ et un électrolyte symétrique 1-1, de concentration C_i (en mol/dm³).

Pour expliquer l'influence exercée par la double-couche, divers schémas réactionnels peuvent être considérés. Dans le cas présent, la seule interprétation qui rende compte de manière satisfaisante des données expérimentales consiste à admettre que *la réaction de décharge ne peut procéder qu'à l'intervention d'une réaction chimique antécédente, mettant en jeu des particules positivement chargées*. Dans de telles conditions, le courant cinétique doit être d'autant plus élevé que l'attraction électrostatique des particules réagissantes est grande, c.à.d. que les tensions ψ_0 sont négatives. De manière à apprécier la validité d'un tel mécanisme et à en établir le schéma réactionnel, il est plus utile de considérer non pas les courants polarographiques, mais les valeurs correspondantes du paramètre χ de KOUTECKY¹³, que l'on trouve tabulé en fonction du rapport I/I_a .

Pour une réaction chimique antécédente monomoléculaire (ou pseudomonomoléculaire)



procédant à des tensions d'électrode telles qu'elle soit déterminante, on a, en l'absence de double-couche:

$$(\sqrt{K \vec{r}})_{\psi=0} = \chi \left(\frac{7}{1.2 t_g} \right)^{1/2} \quad (4)$$

En présence de double-couche, (4) peut être mis sous la forme

$$(\sqrt{K \vec{r}})_{\psi} = \chi \left(\frac{7}{1.2 t_g} \right)^{1/2} f(\psi_0, \dots) \quad (5)$$

Le facteur correctif $f(\psi_0, \dots)$ dépend de ψ_0 et de divers facteurs parmi lesquels l'épaisseur de la couche de réaction, celle de la partie diffuse de la double-couche, les charges des partenaires réactionnels et le sens de l'interaction électrostatique. Son expression mathématique complète^{14,15} étant assez compliquée, il est préférable de reconnaître expérimentalement l'allure de cette fonction, de manière à pouvoir éventuellement recourir à des expressions simplifiées, représentatives de certaines

conditions particulières du système réactionnel^{16,17}. A cet effet, les valeurs du logarithme décimal du paramètre χ ont été portées en fonction des valeurs correspondantes de ψ_0 , pour les diverses concentrations en électrolyte-support utilisées. Les valeurs de ψ_0 ont été calculées à partir de la relation (2), en postulant une capacité d'électrode de $18 \mu\text{F}$; elles sont par conséquent très approximatives, étant donné les nombreuses causes d'écarts à l'idéalité dont il n'a pas été tenu compte, et le degré d'extrême simplification du modèle de double-couche adopté.

L'examen du graphique de la Fig. 5 (qui correspond au domaine de tension où les paliers inclinés sont observés) montre que les points expérimentaux tendent à se disposer selon des droites parallèles, dont la pente commune vaut environ 33 V^{-1} . Il

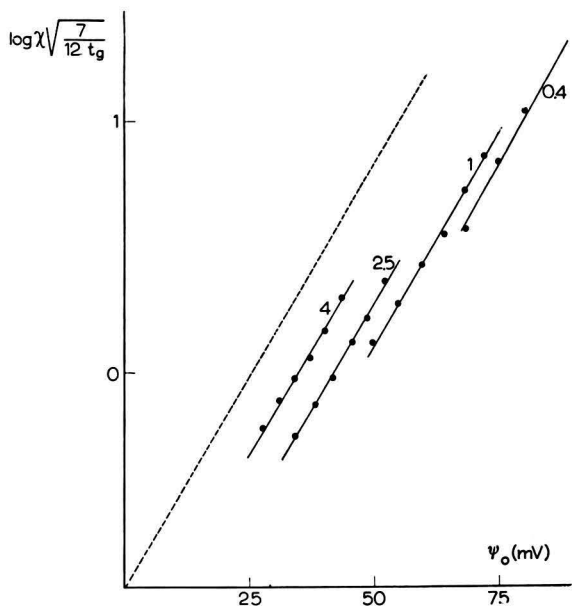


Fig. 5. Relation entre χ et ψ_0 : les compositions sont celles de la Fig. 1.

s'ensuit que la relation (5) peut être explicitée sous la forme empirique particulièrement simple:

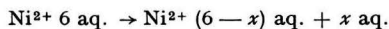
$$(\sqrt{K\vec{r}})_{\psi, c_i} = (\sqrt{K\vec{r}})_{0, c_i} \times \exp\left(-\frac{2F}{RT} \psi_0\right) \quad (6)$$

en accord satisfaisant avec l'ensemble des données expérimentales.

La valeur trouvée pour le coefficient affectant ψ_0 peut être expliquée si l'on admet que (1) l'étape chimique déterminante amène la formation d'une particule réductible de charge $+2$, et que (2) l'épaisseur de la couche de réaction est petite, comparée à celle de la partie diffuse de la double-couche. Ainsi qu'il en a été discuté ailleurs^{16,17}, la réaction chimique est alors consécutive à l'adsorption électrostatique, et tout se passe comme si la réaction se déroulait en l'absence de double-couche dans une solution

où la concentration des partenaires réactionnels était multipliée par le facteur $\exp\{- (2F/RT) \psi_0\}$. Le fait que la partie diffuse de la double-couche est elle-même extrêmement comprimée aux concentrations utilisées, indique que la couche de réaction est d'épaisseur pratiquement monomoléculaire.

Etant donné que les ions Ni ne sont pas complexés par les ions perchlorate, le seul mécanisme réactionnel concevable est une réaction de déshydratation, du type



Ainsi que l'on peut s'y attendre pour des solutions aussi concentrées, la quantité $(K\vec{\tau})_0$ n'est pas constante: elle croît appréciablement avec la force ionique (Tableau I), ce qui explique pourquoi l'amplitude *relative* du courant cinétique tend à *croître* avec la concentration de l'électrolyte-support dès que $C_i > 3 M$, les conditions étant alors telles que l'effet décélérateur dû au terme exponentiel de la relation (6) n'est plus suffisant pour compenser l'accroissement du terme $K\vec{\tau}$.

TABLEAU I

INFLUENCE DE LA CONCENTRATION EN PERCHLORATE SUR LA VALEUR DE LA QUANTITÉ $K\vec{\tau}$

$[\text{NaClO}_4]$ (M)	$\text{Log}(K\vec{\tau})$
0.4	-3.45
1	-3.2
2.5	-2.95
4	-2.35

INFLUENCE DE LA NATURE DE L'ÉLECTROLYTE-SUPPORT

On peut déduire du mécanisme réactionnel proposé que le courant cinétique distordu *doit* s'observer dans tous les milieux où l'ion Ni n'est pas complexé. En outre, tout facteur dont l'action entraîne une modification dans la structure de la double-couche, doit exercer une influence concomitante sur la morphologie des courbes de polarisation.

Etant donné que l'onde de réduction de l'ion Ni ne se développe qu'à partir des tensions assez négatives par rapport au point de charge nulle, on peut prévoir que les anions, difficilement adsorbables à de telles tensions, n'exerceront qu'une influence spécifique assez limitée (les effets de complexion étant mis à part). Par contre, les caractéristiques du courant cinétique doivent dépendre dans une mesure beaucoup plus large de la composition cationique.

Influence de la nature de l'anion

Dans les milieux NaCl, NaI et Na₂SO₄, le *comportement électro-chimique de l'ion Ni est fondamentalement identique à celui observé en milieu perchlorate de sodium*, l'abaissement des ondes étant d'autant plus marqué que la force ionique est élevée. La relation (6) reste pratiquement vérifiée, quoique les valeurs du terme $(K\vec{\tau})$ dépendent quelque peu de la nature de l'anion. A concentration égale, elles croissent dans la série SO₄²⁻ < Cl⁻ et I⁻ < ClO₄⁻.

En milieu iodure concentré (de l'ordre de 3 M et plus) l'onde tend à se déplacer de manière appréciable vers les tensions négatives, et le début du palier se trouve relevé, en relation probable avec une accélération de la vitesse réactionnelle causée par une

légère adsorption spécifique des ions iodure, induisant des valeurs de ψ_0 plus négatives. (On pourrait s'attendre à observer une accélération plus importante encore dans les milieux cyanure et thiocyanate, si l'ion Ni n'y était complexé.)

En milieu chlorure très concentré (5 à 10 M en chlorure de lithium), l'onde se déplace de plusieurs décivolts dans le sens des tensions moins négatives, et se caractérise par un palier horizontal bien défini: des mesures spectrophotométriques ont permis d'établir que, dans de telles conditions, l'ion Ni est partiellement présent sous la forme d'un complexe chloruré (vraisemblablement NiCl_4^{2-})¹⁸.

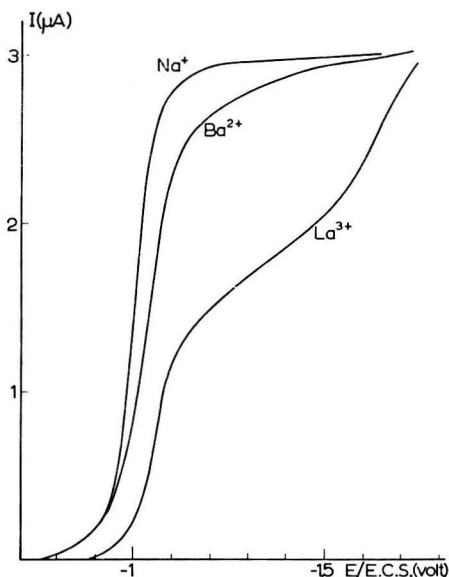


Fig. 6. Influence de la charge cationique de l'électrolyte-support MCl_x , à molarité égale (0.1 M).

Influence de la nature du cation

À molarité égale, les divers électrolytes-supports étudiés se caractérisent par des ondes d'autant plus abaissées que la charge électronique de leur cation est élevée. La Fig. 6, produite à titre d'exemple, permet de comparer les ondes polarographiques obtenues respectivement dans les milieux NaCl 0.1 M, BaCl_2 0.1 M et LaCl_3 0.1 M. L'interprétation de l'abaissement progressif est immédiate à la lumière du mécanisme proposé: les potentiels ψ_0 sont en effet d'autant moins négatifs que la charge du cation est élevée. Dans le cas des ions lanthane (et probablement également pour les ions baryum, dans une moindre mesure), il s'ajoute la possibilité d'une adsorption spécifique, dont l'effet tend à accentuer la décroissance observée.

Si l'on considère divers électrolytes-supports de même concentration et à charge cationique égale, on remarque des différences dans l'amplitude des courants qui, quoiqu'assez faibles, restent cependant aisément détectables. C'est ainsi que dans la série des chlorures de cations alcalins, les ondes de réduction du Ni s'abaissent graduellement dans la série $i_{\text{Li}^+} > i_{\text{Na}^+} > i_{\text{K}^+} > i_{\text{Cs}^+}$ (Fig. 7). Le fait qu'une

séquence renversée s'observe lors de la réduction de divers anions tels que $S_2O_8^{2-}$, $Cd(CN)_4^{2-}$ et $Hg(CN)_4^{2-}$ (qui sont repoussés électrostatiquement de l'électrode) permet de conclure à l'intervention d'un effet associé à la structure de la double-couche.

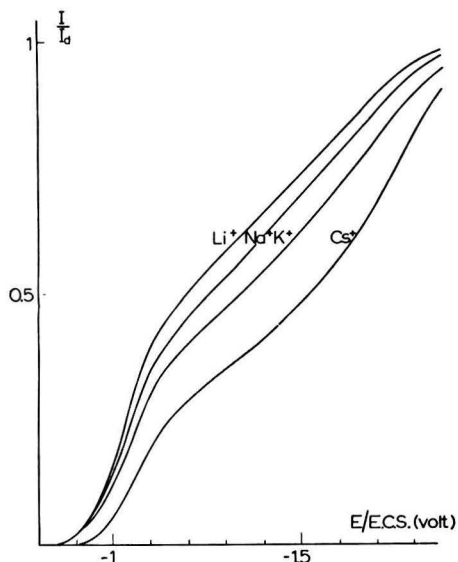


Fig. 7. Influence de la nature du cation à molarité et charge cationique égales; $[MCl] = 2 M$.

On sait par ailleurs que la densité de charge de l'électrode de Hg croît du Li au Cs pour un potentiel rationnel négatif donné. On peut déduire de l'ensemble de ces données, que l'excès superficiel cationique augmente à mesure que le nombre atomique croît. Cette corrélation est vraisemblablement due à l'action des forces d'adsorption à courte distance (ainsi que le suggère FRUMKIN¹⁹) et à l'accroissement des concentrations dans la partie diffuse de la double-couche, résultant du travail de polarisation associé au transfert des cations du sein de la solution vers une zone où règne un champ électrique intense²⁰. Quoique l'état actuel de nos connaissances en la matière reste d'ordre essentiellement qualitatif et qu'il soit difficile d'évaluer l'importance relative de ces deux facteurs, le caractère de généralité du phénomène nous paraît suffisamment étayé par l'expérience pour permettre d'expliquer l'abaissement progressif des ondes en termes d'une diminution parallèle de la tension ψ_0 .

Ainsi que l'on peut s'y attendre, l'addition de cations très tensioactifs tels que l'ion tétraéthylammonium amène un recul très accentué des ondes polarographiques. Cet accroissement de l'irréversibilité résulte vraisemblablement à la fois du déplacement des tensions ψ_0 vers des valeurs moins négatives, et de la diminution de la surface libre de l'électrode.

Comportement en milieu bromate

SANBORN ET ORLEMAN³ signalent que la réduction des ions bromate est fortement accélérée par la présence d'ions Ni, ce qu'ils attribuent à un processus de réduction

catalytique faisant intervenir des ions Ni monovalents. Les rendements en Ni métallique sont alors faibles, ce qui tend à confirmer le mécanisme avancé.

Il convient d'observer que ces expériences ont été effectuées en milieu non tamponné. Or, lors de la réduction des ions bromate, il apparaît une quantité importante d'ions hydroxyle. On sait par ailleurs que la tension de demi-onde de cette réaction varie considérablement avec le pH et est d'autant plus négative que le milieu est alcalin²¹. En présence d'ions Ni, le milieu est tamponné par suite de la formation locale d'hydroxyde de Ni: la réaction de décharge des ions bromate peut ainsi procéder à des tensions beaucoup moins négatives, tandis que le rendement en Ni métallique décroît. A l'appui de ce mécanisme, on signalera que l'addition d'autres cations dont la précipitation est susceptible de tamponner la solution au voisinage immédiat de l'électrode, entraîne un effet analogue.

CONCLUSIONS GÉNÉRALES

Il ressort de l'étude systématique de l'influence du milieu sur les ondes polarographiques de l'ion Ni que l'ensemble des faits expérimentaux peut être expliqué de manière satisfaisante si l'on admet que la *réaction de décharge proprement dite est précédée d'une réaction chimique de déshydratation, mettant en jeu des particules dont la concentration locale dépend des caractéristiques de la double-couche électrochimique.*

Malgré le caractère très approximatif du calcul des valeurs de ψ_0 , l'accord entre les données expérimentales et les prévisions théoriques est satisfaisant, puisqu'il n'a été observé aucune déviation suffisamment significative pour mettre en question la validité du mécanisme proposé.

Le comportement polarographique de l'ion Ni est remarquable, en ce que le courant limite observé à des concentrations en électrolyte-support pas trop élevées ($C_4 < 0.2 M$) n'est essentiellement qu'un *courant cinétique, accéléré par la présence de la double-couche au point que l'apport diffusif devienne le seul facteur limitatif.* Les „anomalies" observées en milieu concentré sont en fait représentatives du processus d'électrode fondamental, de moins en moins perturbé à mesure que la force ionique croît. En relation directe avec le mécanisme proposé, il convient de signaler que diverses recherches récentes, basées sur la résonance magnétique nucléaire²² et sur la mesure des temps de relaxation²³, ont permis d'établir que la vitesse d'échange des molécules d'eau de la sphère de coordination de l'ion Ni avec divers anions était exceptionnellement faible.

Un comportement polarographique analogue à celui du Ni peut en principe s'observer chaque fois que les conditions suivantes sont réalisées:

1. l'ion considéré doit être entouré d'une coque d'hydratation très stable, dont la structure fermée interdit toute réaction de décharge directe, sinon au prix d'une surtension très élevée;
2. l'ordre de grandeur de la quantité $K\vec{r}$ doit être inférieur à la valeur correspondant à la limite de sensibilité de la méthode utilisée;
3. la composition de la solution doit être ajustée de manière à réaliser une structure de double-couche qui *ralentisse* au maximum l'amplitude du courant cinétique, de manière à amplifier le facteur sensibilité.

Il semble permis de conclure de quelques expériences d'orientation, effectuées en l'absence d'anions spécifiquement adsorbables et en milieu très dilué, que la réduction de l'ion Cu(II) pourrait être limitée par une étape chimique de ce genre. De même,

en milieu perchlorate très concentré, l'ion Co^{2+} présente un comportement assez similaire à celui du Ni, avec toutefois des valeurs de $K\vec{\gamma}$ environ cent fois supérieures.

On remarquera pour conclure combien l'étude des courants cinétiques est en fait subordonnée aux théories descriptives de l'interphase métal-solution, pour le choix des conditions de milieu autant que pour l'évaluation rigoureuse des paramètres cinétiques réels de la réaction chimique déterminante, corrigés des perturbations de nature électrostatique. Réciproquement, l'étude des réactions perturbées peut constituer une méthode d'investigation extrêmement fructueuse, susceptible d'améliorer l'état actuel de nos connaissances concernant la structure fine de la double-couche électrochimique.

RÉSUMÉ

Le comportement polarographique de l'ion Ni en milieu non-complexant concentré est interprété en termes d'un courant cinétique de déshydratation, influencé par la double-couche électrochimique.

SUMMARY

The polarographic behaviour of Ni ion in concentrated non-complexing media is explained in terms of a dehydration kinetic current, influenced by the electrochemical double-layer.

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THÉORIE ET APPLICATIONS DE LA MÉTHODE CHRONOPOTENTIOMÉTRIQUE AVEC COURANT IMPOSÉ CROISSANT PROPORTIONNELLEMENT À LA RACINE CARRÉE DU TEMPS

I. INTRODUCTION GÉNÉRALE ET CAS DES RÉACTIONS DE DÉCHARGE DIRECTE

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INTRODUCTION

Les diverses méthodes électroanalytiques non stationnaires peuvent être classées en deux groupes distincts, selon que le paramètre imposé est la tension d'électrode ou le courant. Alors que l'on dispose actuellement de nombreuses méthodes à tension contrôlée (méthode potentiostatique à surface constante, polarographie classique, polarographie oscilloscopique à balayage en tension linéaire, „square wave polarography”, etc.), la seule méthode du second groupe**, dont la théorie détaillée ait pu être établie est la chronopotentiométrie à courant constant (ou méthode galvanostatique). La caractéristique essentielle de ce mode de polarisation réside dans le fait que le transfert massique est contrôlé uniquement par la densité de courant imposée, qui maintient à une valeur fixe le flux massique à l'électrode: l'état local des concentrations est ainsi indépendant du degré d'irréversibilité de la réaction de décharge. La concentration superficielle du dépolarisant tombe à zéro après une durée d'électrolyse (temps de transition τ) qui, pour une densité de courant donnée, est proportionnelle au carré de la concentration en solution¹. La grande simplicité des conditions-limites rend cette méthode particulièrement utile lorsqu'il s'agit d'établir la nature du mécanisme réactionnel déterminant et d'en évaluer les paramètres cinétiques²⁻⁵. La méthode possède par ailleurs diverses caractéristiques (simplicité technique, rapidité, précision, possibilité d'automatiser les mesures et d'utiliser des électrodes métalliques) qui expliquent son développement dans le domaine de la chimie électroanalytique⁶⁻⁹.

Il n'est toutefois pas démontré que le courant constant constitue le mode de polarisation présentant le maximum d'avantages: le fait que les temps de transition ne sont pas proportionnels aux concentrations et qu'ils ne constituent pas des grandeurs additives^{10,11} complique le calcul et peut amener des erreurs importantes s'il n'est pas tenu compte de l'entièreté de la courbe de polarisation.

* Associé au Fonds National de la Recherche Scientifique.

** Les autres méthodes à courant contrôlé proposées jusqu'ici sont limitées par un degré de complication des conditions locales tel que toute possibilité d'interprétation quantitative est virtuellement exclue.

L'objet de cette série de communications est de reconnaître les caractéristiques de la méthode chronopotentiométrique à surface constante et sans agitation, où le courant imposé croît proportionnellement à la racine carrée du temps compté à partir du début de l'électrolyse*. L'inconvénient d'ordre technique lié au plus grand degré de complication du circuit de polarisation est amplement compensé par le fait que les concentrations de surface varient linéairement avec le temps, ainsi qu'il le sera montré: il s'ensuit diverses conséquences d'ordre pratique (parmi lesquelles l'additivité des temps de transition, et leur proportionnalité aux concentrations) qui peuvent être mises à profit à la fois dans le domaine des applications analytiques et dans celui de l'étude des mécanismes réactionnels. A cet effet, on envisagera successivement les réactions de décharge directe (en considérant à part les réactions successives), l'influence de la géométrie du champ de diffusion, les processus contrôlés par une étape chimique antécédente, et les réactions catalytiques.

Dans cette première communication, on discutera des aspects techniques liés à l'imposition du courant de polarisation de la forme proposée. On établira ensuite l'expression mathématique des temps de transition et l'équation des courbes tension-temps, pour divers types de réactions en régime de diffusion linéaire. Les principales caractéristiques de la méthode seront finalement dégagées, et comparées à celles de la chronopotentiométrie galvanostatique.

LE CIRCUIT DE POLARISATION

Le dispositif expérimental est fondamentalement identique à celui utilisé en chronopotentiométrie classique. Il comprend une électrode de mercure M, dont la tension par rapport à l'électrode de référence R, est mesurée en fonction du temps, à l'aide du voltmètre à haute impédance V. Le courant, de forme $i = \varrho\sqrt{t}$ (ϱ étant le „facteur d'amplitude"), est fourni par le générateur I, et imposé à l'électrode de mesure par l'intermédiaire de l'électrode auxiliaire A (Fig. 1).

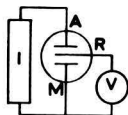


Fig. 1. Diagramme schématique du dispositif expérimental: I, générateur de courant de la forme $i = \varrho\sqrt{t}$; M, électrode de mesure; A, électrode auxiliaire; R, électrode de comparaison; V, voltmètre à haute impédance.

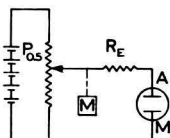


Fig. 2. Générateur de courant à résistance limitatrice: $P_{0,5}$, potentiomètre de raison 0,5; M, dispositif d'entraînement à vitesse constante; R_E , résistance limitatrice.

Divers types de générateurs peuvent être considérés selon la durée de l'électrolyse.

(a) Pour des durées de l'ordre de la minute, la solution la plus simple consiste à utiliser un système électromécanique comprenant un moteur à vitesse constante, couplé par un réducteur de vitesse à rapports fixes à un potentiomètre de précision $P_{0,5}$ bobiné de telle sorte que sa résistance soit proportionnelle à la racine carrée de l'angle de rotation du curseur (de tels potentiomètres existent sur le marché). La tension ainsi obtenue débite dans l'ensemble formé par la cellule et une résistance limitatrice

* La méthode où le courant croît linéairement avec le temps présente des caractéristiques moins intéressantes, en dépit de la simplicité plus grande de l'appareillage.

placée en série, destinée à contrôler la valeur du facteur d'amplitude ρ (Fig. 2).

De manière à éviter l'erreur sur le courant due à la variation de la contre-tension de la cellule, le courant imposé peut être asservi à la tension fournie par le potentiomètre $P_{0.5}$, à l'aide d'un circuit de comparaison commandant un potentiostat à réponse rapide P_s , équilibré pour un signal d'entrée nul (Fig. 3). Le facteur d'amplitude est ici aisément contrôlé par variation de la résistance de prélèvement R_L .

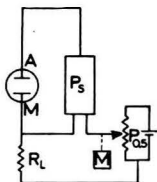


Fig. 3. Générateur de courant utilisant un potentiostat et une tension de référence variant en $\rho\sqrt{t}$: R_L , résistance de prélèvement; M, dispositif d'entraînement à vitesse constante; $P_{0.5}$, potentiomètre de raison 0.5; P_s , potentiostat équilibré pour un signal d'entrée nul.

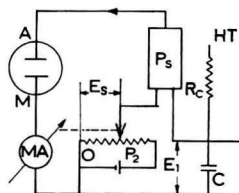


Fig. 4. Générateur de courant utilisant un potentiostat et une tension de référence variant linéairement avec le temps: P_2 , potentiomètre de raison 2, asservi mécaniquement au milliampèremètre MA; C, condensateur; R_c , résistance de charge; P_s , potentiostat équilibré pour un signal d'entrée nul.

On peut concevoir d'autres modes d'obtention d'une tension croissant avec la racine carrée du temps, notamment en utilisant un enregistreur du type „curve-follower”.

Une méthode de principe différent et d'utilisation plus souple, consiste à asservir une tension proportionnelle au carré du courant à une autre tension variant linéairement avec le temps. Cette opération peut s'effectuer (Fig. 4) à l'aide d'un milliampèremètre à équilibrage continu MA („continuous balance unit”), dont le potentiomètre d'équilibrage est couplé mécaniquement à un potentiomètre P_2 de loi quadratique ($R = k\alpha^2$, α étant l'angle de rotation du curseur), polarisé par une source de tension continue. La tension de sortie E_s , proportionnelle au carré du courant, est asservie à la tension pilote $E_1 = k \cdot t$, obtenue aux bornes du condensateur C chargé sous courant constant depuis l'instant initial par R_c . L'asservissement est réalisé à l'aide d'un potentiostat électronique équilibré à signal d'entrée nul, comme précédemment. L'ajustage du facteur d'amplitude ρ s'effectue aisément en agissant sur les valeurs de R_c et C, ou sur la sensibilité du milliampèremètre MA.

(b) Pour des durées d'électrolyse plus courtes (de l'ordre de la seconde ou moins), les dispositifs électromécaniques présentent trop d'inertie, et diverses solutions purement électroniques peuvent être envisagées. C'est ainsi qu'il est possible de réaliser un générateur de courant de la forme désirée en utilisant la technique des calculateurs électroniques. Une solution moins onéreuse, et susceptible d'une assez bonne précision, consiste à utiliser un oscilloscope dont l'écran est masqué par une came optique de géométrie appropriée. Le spot est astreint à se déplacer le long de la came, à l'aide d'un circuit feedback comprenant une cellule photoélectrique, qui commande l'amplificateur de déflexion verticale. Si une précision de l'ordre de quelques pourcents est acceptable, on peut songer à exploiter la propriété qu'ont divers tubes de radio, fonctionnant sous des tensions d'alimentation judicieusement choisies, de donner un courant anodique à peu près proportionnel au carré du signal de commande, mesuré à partir de la tension de cut-off (Fig. 5).

On peut également tirer parti du fait que la détection d'un signal alternatif de forme triangulaire fournit une tension proportionnelle au carré de la tension de polarisation continue qu'on lui superpose, pour des valeurs supérieures à la tension minimum de détection (l'aire de la surface hachurée de la Fig. 6 est en effet proportionnelle au carré du déplacement ΔV). On utilise un générateur à ondes triangulaires de fré-

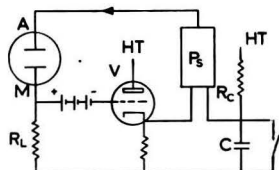


Fig. 5. Générateur de courant utilisant un potentiostat et une tension de référence variant linéairement avec le temps; R_L , résistance de prélèvement; V, tube à amplification de raison 2; C, condensateur; R_c , résistance de charge; P_s , potentiostat équilibré pour un signal d'entrée nul.

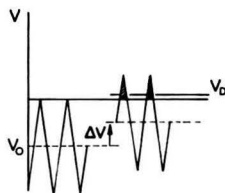


Fig. 6. Principe de la méthode basée sur la détection d'une onde en dents de scie: le signal détecté V_D est proportionnel au carré de la tension de polarisation ΔV .

quence suffisamment élevée, polarisé de manière à annuler exactement la tension de crête. Le signal, détecté et filtré, est ensuite asservi à une tension croissant linéairement avec le temps, par l'intermédiaire du potentiostat P_s contrôlant le courant d'électrolyse (Fig. 7).

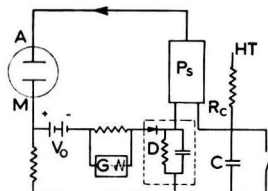


Fig. 7. Générateur de courant utilisant le principe de la détection d'une onde en dents de scie: G, générateur à onde triangulaire; D, système détecteur; C, R_c , circuit de base de temps; P_s , potentiostat équilibré pour un signal d'entrée nul.

La précision d'une telle méthode dépend principalement du degré de perfection géométrique de l'onde triangulaire et de la linéarité de la détection. Comme dans les montages de principe analogue précédemment proposés, le facteur d'amplitude ρ est aisément contrôlé par R_L , R_c ou C. On peut très probablement concevoir d'autres types de générateurs de courant, plus ou moins compliqués, et éventuellement susceptibles de présenter certains avantages (simplicité, précision) sur ceux auxquels s'est bornée cette brève revue, que nous avons limitée à quelques schémas-types.

Les expériences dont il sera fait mention dans cette série de communications ont été effectuées, sauf spécification contraire, avec le dispositif schématisé à la Fig. 3. Le potentiomètre de raison 0.5 possède une résistance totale de 200 Ω (type Aybc-19911 de la firme Novotechnik-Ruit bei Stuttgart). Sa réponse angulaire a été trouvée

correcte à moins de 0.5% de l'échelle totale, en tout point de la course. Selon la nécessité, ce potentiomètre peut être entraîné à un tour complet en 0.5, 1, 2, 4 ou 8 min, à l'aide d'un moteur synchrone couplé à un réducteur de vitesse de rapports appropriés. La tension aux bornes a été maintenue à 1.50 V. Le potentiomètre électronique P_s, du type „Standard” (Elektronische Werkstätten, Göttingen) fournit un courant de sortie de l'ordre de 100 mA pour un déséquilibre d'entrée de 1 mV, son temps de réponse étant inférieur à 0.1 msec. Les courbes tension-temps ont été enregistrées à l'aide d'un millivoltmètre enregistreur Brown ElekroniK série 153 × 18 (100 mV à fond d'échelle, parcourue en 1 sec), précédé d'un préamplificateur à haute impédance d'entrée avec sortie en cathode follower, muni d'un dispositif d'étalonnage en tension. R_L est une boîte de résistance à décades 0-10-100-1000 Ω. La cellule est constituée par un becher en Teflon d'un diamètre de l'ordre de 8.45 cm. L'électrode de mesure est formée d'une nappe de mercure dont la surface a été évaluée à 56 cm², en négligeant l'effet de ménisque. L'anode auxiliaire est constituée par un disque de platine disposé horizontalement au-dessus de la surface du mercure. On a utilisé comme électrode de comparaison une électrode à calomel saturé, connectée à la cellule par un siphon de Haber-Luggin, d'un diamètre intérieur de l'ordre du mm.

FORMULATION DU PROBLÈME ET CONDITIONS-LIMITES

On considère ici le cas d'une réaction simple, procédant par décharge directe, soit



où les particules A et B sont toutes deux solubles.

On suppose que les conditions suivantes sont réalisées: (1) la solution n'est pas agitée; (2) la composante d'apport par migration est annulée par la présence d'un large excès d'électrolyte-support; (3) la géométrie du système est telle que la diffusion vers l'électrode procède linéairement dans un volume semi-infini.

La densité de courant imposée étant de la forme

$$i = q\sqrt{t} \quad (1)$$

le flux de A à la surface de l'électrode est donné par la relation

$$q\sqrt{t} = nFD_A \left(\frac{\partial a(x,t)}{\partial x} \right)_{x=0} \quad (2)$$

où a et D_A sont respectivement la concentration (en mole cm⁻³) et le coefficient de diffusion (en cm² sec⁻¹) de la particule A, et x la distance comptée à partir de l'électrode; q est exprimé en A cm⁻² sec^{-1/2}.

Par ailleurs, la somme des flux de A et de B étant nulle à la surface de l'électrode

$$D_A \left(\frac{\partial a(x,t)}{\partial x} \right)_{x=0} + D_B \left(\frac{\partial b(x,t)}{\partial x} \right)_{x=0} = 0 \quad (3)$$

Dans le cas particulier (le plus fréquemment réalisé) où la solution est homogène en A (concentration a^0) et où la concentration en B est nulle en tout point avant que ne débute l'électrolyse, les conditions initiales s'écrivent

$$a(x,0) = a^0 \quad (4)$$

$$b(x,0) = 0 \quad (5)$$

Enfin, comme conséquence de la condition de semi-infinité:

$$a_{(\infty,t)} = a^{\circ} \quad (6)$$

$$b_{(\infty,t)} = 0 \quad (7)$$

EXPRESSIONS DES CONCENTRATIONS DE SURFACE

La résolution des équations secondes de FICK

$$\frac{\partial a(x,t)}{\partial t} = D_A \frac{\partial^2 a(x,t)}{\partial x^2} \quad (8)$$

$$\frac{\partial b(x,t)}{\partial t} = D_B \frac{\partial^2 b(x,t)}{\partial x^2} \quad (9)$$

s'effectue en introduisant les conditions (2) à (7), à l'aide de la méthode des transformées de LAPLACE (cf. Appendice).

Ce calcul donne*, pour les concentrations a et b , respectivement:

$$a(x,t) = a^{\circ} - \frac{q}{2nFD_A} \left\{ \sqrt{\pi D_A} \left(t + \frac{x^2}{2D_A} \right) \text{cfer} \frac{x}{2\sqrt{D_A t}} - x\sqrt{t} \exp \frac{-x^2}{4D_A t} \right\} \quad (10)$$

$$b(x,t) = \frac{q}{2nFD_B} \left\{ \sqrt{\pi D_B} \left(t + \frac{x^2}{2D_B} \right) \text{cfer} \frac{x}{2\sqrt{D_B t}} - x\sqrt{t} \exp \frac{-x^2}{4D_B t} \right\} \quad (11)$$

où cfer désigne le complément de la fonction d'erreur.

La Fig. 8 schématise la distribution instantanée des concentrations a et b après divers temps d'électrolyse pour les valeurs suivantes:

$$q = \frac{10^{-2}}{\sqrt{1.8}} \text{ A cm}^{-2} \text{ sec}^{-\frac{1}{2}}; n = 1; D_A = D_B = 10^{-5} \text{ cm}^2 \text{ sec}^{-1};$$

$$a^{\circ} = \frac{\pi}{4} \cdot 5 \cdot 10^{-5} \text{ soit } 3.93 \cdot 10^{-5} \text{ mol cm}^{-3}.$$

Ces valeurs ont été choisies de manière à permettre la comparaison avec le diagramme établi par DELAHAY² pour le régime galvanostatique: les deux systèmes se caractérisent par des temps de transition identiques, auxquels correspondent des densités de courant égales.

Les concentrations à la surface de l'électrode valent respectivement

$$a_{(0,t)} = a^{\circ} - \frac{qt}{2nF} \sqrt{\frac{\pi}{D_A}} \quad (12)$$

$$b_{(0,t)} = \frac{qt}{2nF} \sqrt{\frac{\pi}{D_B}} \quad (13)$$

* On remarquera que si B est une substance insoluble dont la formation ne perturbe pas la réaction d'électrode, le calcul conduit également à la relation (10), ainsi que l'on peut s'y attendre, puisque l'apport massique de A est exclusivement déterminé par le courant imposé.

La concentration $a(0,t)$ décroît linéairement avec le temps, pour s'annuler après une durée τ , qui constitue le temps de transition de la réaction, et vaut

$$\tau = \frac{2nF}{\rho} a^{\circ} \sqrt{\frac{D_A}{\pi}} \quad (14)$$

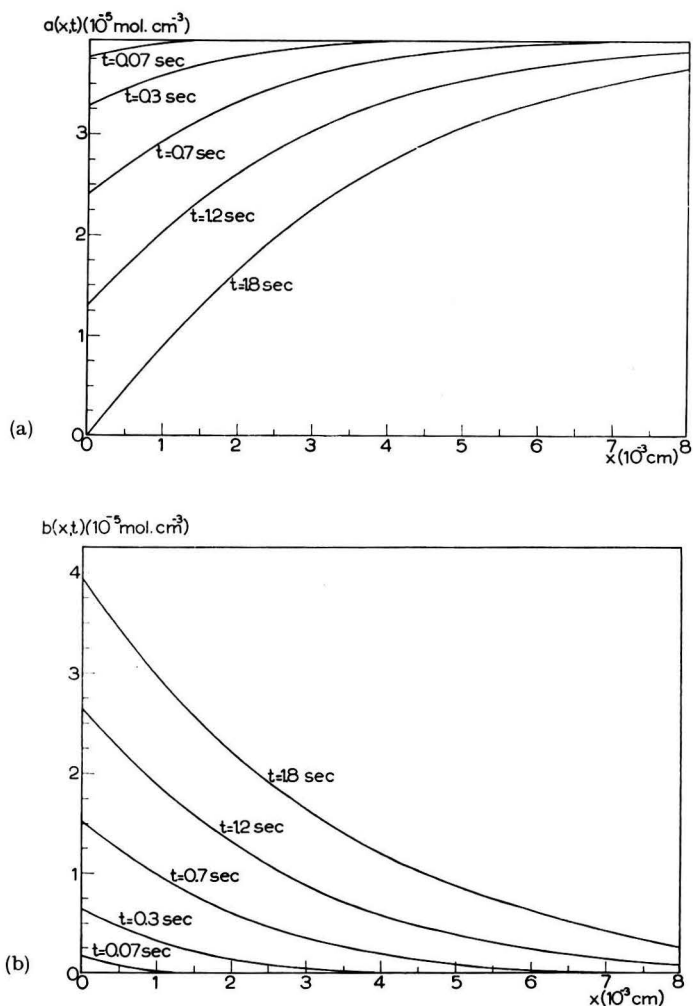


Fig. 8. Variation de la concentration de A (Fig. 8a) et de B (Fig. 8b) pour diverses durées d'électrolyse (cf. texte pour les données expérimentales).

Cette relation montre que les temps de transition sont directement proportionnels à la concentration de la particule dépolarisante et inversement proportionnels au facteur d'amplitude. Tout comme en régime galvanostatique, τ est aisément mesuré par voie potentiométrique. En effet, dès que t excède τ , le flux massique de A devient

insuffisant à assurer seul la densité de courant imposée: la différence est nécessairement comblée par une autre réaction d'électrode à laquelle correspond une tension de décharge différente. τ est ainsi détecté par l'occurrence d'un saut de tension, plus ou moins accusé selon la composition du système.

(12) peut également être mis sous les formes équivalentes

$$a_{(0,t)} = a^{\circ} \left(1 - \frac{t}{\tau} \right) \quad (15)$$

$$a_{(0,t)} = \frac{\rho}{2nF} \sqrt{\frac{\pi}{D_A}} (\tau - t) \quad (16)$$

dont il sera fait usage par la suite.

La validité de la relation (14) a été vérifiée pour les réactions de réduction de l'oxygène dissous et des ions Cd^{2+} , Eu^{3+} et CrO_4^{2-} . Les résultats produits ici à titre d'exemple, sont relatifs au dosage de l'ion chromate en milieu KOH molaire, après désoxygénation; à ce pH, la réduction procède par une réaction de décharge directe totalement irréversible, mettant en jeu 3 électrons au total.

Le dispositif expérimental utilisé est celui décrit précédemment. Les concentrations de chromate sont comprises entre 0.120 et 2.94 $\mu\text{mol cm}^{-3}$. Ainsi que le montre le graphique de la Fig. 9, les valeurs de τ sont bien proportionnelles aux concentrations.

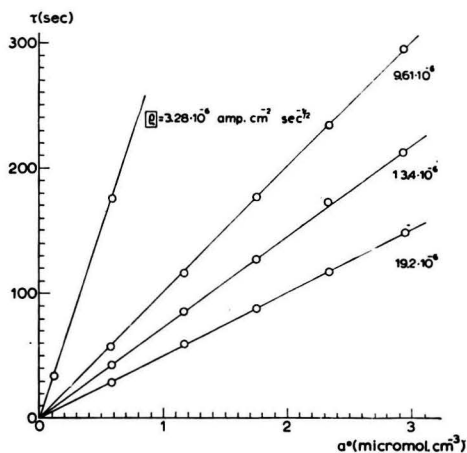


Fig. 9. Relation entre le temps de transition et la concentration, pour diverses valeurs du facteur d'amplitude (réduction de l'ion chromate en milieu KOH molaire).

Par ailleurs, les valeurs de l'expression $\rho\tau/a^{\circ}$ sont substantiellement indépendantes de ρ , τ et a_0 , ainsi qu'il ressort de l'examen des données consignées dans le Tableau I.

EQUATIONS DES COURBES TENSION-TEMPS

On considérera séparément le cas des processus réversibles et celui des processus totalement irréversibles.

Réactions réversibles: A et B sont solubles

B peut être une substance qui diffuse vers la solution, ou un métal amalgamé diffusant dans le mercure. Dans les deux cas, la courbe tension-temps s'établit à

TABLEAU I
VALEURS DE LA QUANTITÉ $\rho\tau/a^0$ POUR DIVERSES CONDITIONS EXPÉRIMENTALES
(les valeurs correspondantes de τ figurent entre parenthèses)

ρ ($\mu A\text{ cm}^{-2}\text{ sec}^{-\frac{1}{2}}$)	$a_0(10^{-6}\text{ mol cm}^{-3})$				
	2.94	2.35	1.76	1.18	0.59
19.2	$9.6 \cdot 10^2$ (148)	$9.5 \cdot 10^2$ (117)	$9.6 \cdot 10^2$ (88)	$9.7 \cdot 10^2$ (59.5)	$9.5 \cdot 10^2$ (29.2)
13.4	$9.7 \cdot 10^2$ (212)	$9.8 \cdot 10^2$ (172.4)	$9.7 \cdot 10^2$ (127.6)	$9.7 \cdot 10^2$ (85.5)	$9.8 \cdot 10^2$ (42.9)
9.61	$9.6 \cdot 10^2$ (295)	$9.5 \cdot 10^2$ (234)	$9.6 \cdot 10^2$ (177)	$9.5 \cdot 10^2$ (116)	$9.4 \cdot 10^2$ (57.3)

partir de la relation de NERNST, dans laquelle on introduit les valeurs de $a_{(0,t)}$ et $b_{(0,t)}$ données par les équations (12) et (13). Tenant compte des coefficients d'activité f_A et f_B , on trouve que

$$E = E_0 + \frac{RT}{nF} \ln \frac{f_A D_B^{\frac{1}{2}}}{f_B D_A^{\frac{1}{2}}} + \frac{RT}{nF} \ln \frac{a^0 - \frac{\rho\sqrt{\pi}}{2nF} t}{\frac{\rho\sqrt{\pi}}{2nF} t} \quad (17)$$

Posant $K = \rho\sqrt{\pi}/2nF$ et tenant compte de ce que la somme des deux premiers termes du membre de gauche de l'équation (17) n'est autre que la tension de demi-onde polarographique $E_{\frac{1}{2}}$, on a :

$$E = E_{\frac{1}{2}} + \frac{RT}{nF} \ln \frac{a^0 - Kt}{Kt} \quad (18)$$

Il vient finalement, en termes de temps de transition :

$$E = E_{\frac{1}{2}} + \frac{RT}{nF} \ln \frac{\tau - t}{t} \quad (19)$$

On déduit de cette relation qu'il y a identité entre la tension de demi-onde et la tension de demi-transition, atteinte lorsque $t = \frac{1}{2}\tau$. Le potentiel $E_{\tau/2}$ est indépendant de a_0 et de ρ .

On remarquera que l'équation (19) est formellement identique à celle d'une onde polarographique, si t et τ sont respectivement apparentés à I et I_d . Il s'ensuit que si l'on porte le logarithme décimal du rapport $(\tau - t)/t$ en fonction de la tension, les points expérimentaux doivent s'aligner sur une droite de pente 2.3 (RT/nF). Cette conclusion a été vérifiée, à la limite des erreurs de mesure près, dans le cas de la réaction de réduction de l'ion Eu(III) (Figs. 10 et 11), qui procède réversiblement sur l'électrode de mercure en milieu thiocyanate.

Réactions réversibles: A est seul soluble

Si A est l'ion du métal de l'électrode de mesure utilisée, l'activité de B peut être

tenue pour constante. Dans ce cas, on établit aisément que

$$E = E_0 + \frac{RT}{nF} \ln \left\{ i_A a^\circ \left(1 - \frac{t}{\tau} \right) \right\} \quad (20)$$

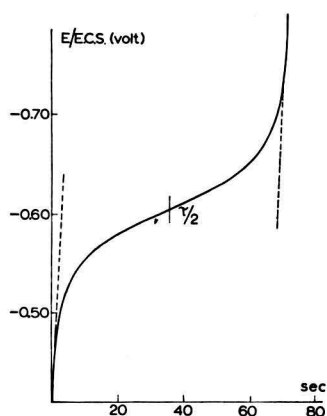


Fig. 10. Réduction de l'ion europium trivalent: courbe tension-temps. $[\text{Eu(III)}] = 2 \cdot 10^{-3} M$; $[\text{NaClO}_4] = 0.8 M$; $[\text{NaSCN}] = 0.2 M$; $\rho = 6.7 \cdot 10^{-5} \text{ A cm}^{-2} \text{ sec}^\dagger$.

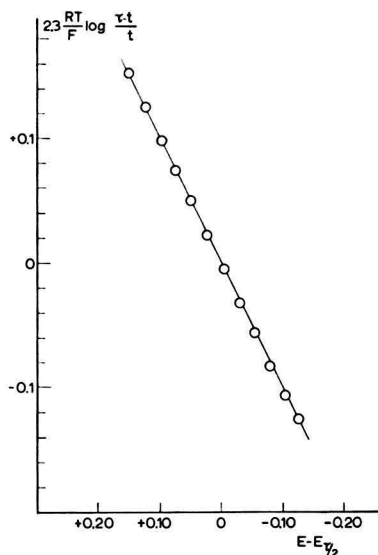


Fig. 11. Vérification graphique du critère de réversibilité: les points ont été calculés à partir de la courbe de la Fig. 10.

Tout comme pour la tension de demi-onde, la tension de demi-transition dépend de la concentration a° . Les points expérimentaux, portés dans un graphique ayant le logarithme décimal de la quantité $i - i/\tau$ pour ordonnée et la tension pour abscisse s'alignent sur une droite de pente $2.3 (RT/nF)$. Des droites parallèles sont obtenues si l'on fait varier a° .

Réactions totalement irréversibles*

Si la réaction procède de manière totalement irréversible, sa constante de vitesse (rapportée aux concentrations), pour une tension arbitraire E mesurée par rapport à une électrode de comparaison déterminée, est donnée par la relation

$$k_E = \frac{i_i}{nF a_{(0,t)}} \quad (21)$$

où t est l'instant où la tension considérée est atteinte.

Explicitant i_i et $a_{(0,t)}$ à l'aide des relations (1) et (16), on trouve, après simplification

$$k_E = 2 \sqrt{\frac{D_A}{\pi}} \frac{\sqrt{i}}{\tau - t} \quad (22)$$

* Le cas des réactions partiellement irréversibles sera considéré ultérieurement.

Le rapport $\sqrt{i}/(\tau - t)$ est par conséquent indépendant du facteur d'amplitude et de la concentration a° .

Si la relation de VOLMER est vérifiée, on a, dans le cas de l'irréversibilité totale,

$$k_E = k_0 \exp\left(\pm \frac{\alpha n_\alpha F}{RT} E\right) \quad (23)$$

où k_0 est la constante de vitesse pour la tension $E = 0$

α est le coefficient de transfert

n_α est le nombre d'électrons associés à l'étape déterminante, les signes + et - correspondant respectivement à une réaction d'oxydation et de réduction.

Dans ce cas, il vient

$$\log \frac{\sqrt{i}}{\tau - t} = \log \left\{ \frac{k_0}{2} \sqrt{\frac{\pi}{D_A}} \right\} \pm 2.3 \frac{\alpha n_\alpha F}{RT} E \quad (24)$$

En portant le logarithme décimal de la quantité $\sqrt{i}/(\tau - t)$ en fonction de la tension, la droite obtenue a pour pente $\pm 2.3 \alpha n_\alpha F/RT$ ce qui permet le calcul de la quantité αn_α .

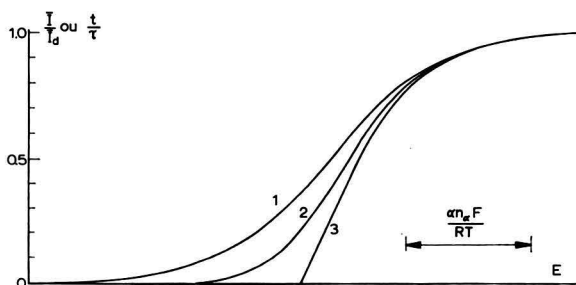


Fig. 12. Influence du régime d'électrolyse sur l'étalement des courbes de polarisation correspondant à une réaction totalement irréversible. Les courbes ont été amenées à coïncidence dans leur partie finale: (1) régime polarographique; (2) chronopotentiométrie en $i = \rho\sqrt{i}$; (3) chronopotentiométrie galvanostatique.

Ainsi que le montre le graphique de la Fig. 12 l'étalement en tension des courbes de polarisation est intermédiaire entre celui des courbes polarographique et galvanostatique.

CONCLUSIONS GÉNÉRALES

Comparée à la méthode galvanostatique, la méthode proposée s'en distingue essentiellement par le fait que les temps de transition sont ici directement proportionnels aux concentrations. Il en résulte notamment que l'image oscilloscopique obtenue en réalisant un balayage vertical linéaire et en imposant la tension d'électrode en déflexion horizontale est l'équivalent exact d'une onde polarographique. Les pics observés en polarographie oscillographique sont ici complètement éliminés; en outre l'amplitude de l'onde n'est pas influencée par le taux d'irréversibilité de la réaction.

Du fait de cette proportionnalité, l'évaluation immédiate des concentrations est possible, ce qui peut être particulièrement utile si la méthode est couplée à une volu-

métrie classique (ampérométrie chronopotentiométrique) ou pour diverses applications ressortissant au domaine de la régulation et du contrôle automatique.

Cette propriété mise à part, la méthode présente des caractéristiques très voisines de celles de la méthode galvanostatique. Comme pour cette dernière, l'interférence de la charge capacitive de l'électrode constitue le facteur essentiel de la sensibilité. Si le facteur d'amplitude est ajusté de manière à réaliser des temps de transition de l'ordre de plusieurs minutes, la sensibilité limite est comparable, sinon supérieure à celle de la polarographie classique. Il est de toute manière utile de prépolariser l'électrode à une tension aussi proche que possible de l'origine du palier de transition, de façon à ce que le temps mis à amener l'électrode aux tensions où survient la réaction étudiée n'introduise pas de retard appréciable entre l'enclenchement du courant et le début de l'électrolyse proprement dite. Aux très faibles concentrations (en dessous de 10^{-8} mol cm^{-3}) l'allongement des temps de transition dû au processus parallèle de charge capacitive peut être tel que le recours à une courbe de calibrage soit nécessaire. Tout comme en régime galvanostatique, il est possible d'éliminer automatiquement cette distorsion à l'aide d'un différentiateur électronique suivi d'un amplificateur en courant dont le signal de sortie, proportionnel à la vitesse de variation de la tension de l'électrode, est réinjecté à travers la cellule d'électrolyse.

Si l'on tente de circonscrire le champ des applications pratiques de la méthode, il apparaît que la complication relative du circuit de polarisation représente, en soi, un facteur défavorable dont l'importance est à évaluer, pour chaque problème particulier, en fonction de l'avantage résultant de la mesure rapide d'une grandeur directement proportionnelle à la concentration.

APPENDICE

Les équations différentielles ont été résolues à l'aide des transformées de LAPLACE définies par

$$\bar{f}(x,s) = \int_0^{\infty} f(x,t) \exp(-st) dt \quad (25)$$

Si l'on pose

$$\mu(x,s) = a^{\circ} - a(x,t) \quad (26)$$

les solutions de (8) et (9) prennent la forme suivante

$$\bar{\mu}(x,s) = \xi \exp\left(-\sqrt{\frac{s}{D_A}} x\right) \quad (27)$$

$$\bar{b}(x,s) = \delta \exp\left(-\sqrt{\frac{s}{D_B}} x\right) \quad (28)$$

Les constantes d'intégration de ces solutions sont déterminées à partir des transformées des conditions-limites

$$\xi = \left(\frac{\varrho}{nFD_A}\right) \sqrt{\frac{D_A}{s}} \int_0^{\infty} \sqrt{t} \exp(-st) dt = \left(\frac{\varrho}{nFD_A}\right) \frac{1}{2s^2} \sqrt{\pi D_A} \quad (29)$$

$$\delta = \sqrt{\frac{D_A}{D_B}} \xi \quad (30)$$

Les transformées inverses des équations résultantes

$$\bar{\mu}(x,s) = \left(\frac{\varrho}{nFD_A}\right) \frac{1}{2s^2} \sqrt{\pi D_A} \exp\left(-\sqrt{\frac{s}{D_A}} x\right) \quad (31)$$

$$\bar{b}(x,s) = \left(\frac{\varrho}{nFD_B}\right) \frac{1}{2s^2} \sqrt{\pi D_B} \exp\left(-\sqrt{\frac{s}{D_B}} x\right) \quad (32)$$

peuvent être évaluées en utilisant le théorème de convolution (14) et en tenant compte de ce que (15), la transformée inverse de $1/s \exp(-x/\sqrt{s/D})$ est cfer $(x/2\sqrt{Dt})$.

La solution de

$$\int_0^t \text{cfer}\left(\frac{x}{2\sqrt{Dt'}}\right) dt' \quad (33)$$

donne la transformée inverse de

$$\frac{1}{s^2} \exp\left(-\sqrt{\frac{s}{D}} x\right)$$

L'évaluation de (33) ne présente pas de difficultés notables: après intégration par parties on a

$$(33) = t \text{cfer}\left(\frac{x}{2\sqrt{Dt}}\right) - I \quad (34)$$

et

$$I = \int_0^t \frac{x}{2\sqrt{\pi Dt'}} \exp\left[-\left(\frac{x}{2\sqrt{Dt'}}\right)^2\right] dt' = \frac{x\sqrt{t}}{\sqrt{\pi D}} \exp\left[-\left(\frac{x}{2\sqrt{Dt}}\right)^2\right] - \frac{x^2}{2D} \text{cfer}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (35)$$

On peut dès lors écrire l'équation

$$\mu(x,t) = \frac{\varrho}{nFD_A} \left\{ \frac{\sqrt{\pi D_A}}{2} \left(t + \frac{x^2}{2D_A}\right) \text{cfer}\left(\frac{x}{2\sqrt{D_A t}}\right) - \frac{1}{2} x\sqrt{t} \exp\left[-\left(\frac{x}{2\sqrt{D_A t}}\right)^2\right] \right\} \quad (36)$$

ainsi que l'équation (11)

$$b(x,t) = \frac{\varrho}{nFD_B} \left\{ \frac{\sqrt{\pi D_B}}{2} \left(t + \frac{x^2}{2D_B}\right) \text{cfer}\left(\frac{x}{2\sqrt{D_B t}}\right) - \frac{1}{2} x\sqrt{t} \exp\left[-\left(\frac{x}{2\sqrt{D_B t}}\right)^2\right] \right\} \quad (37)$$

Tenant finalement compte de l'équation (26), la conversion de la fonction $\mu(x,t)$ dans l'équation (36) donne l'équation (10).

RÉSUMÉ

La méthode chronopotentiométrique où le courant imposé est de la forme $i = \varrho\sqrt{t}$ se caractérise par le fait que les temps de transition sont proportionnels aux concentrations, dans le cas des réactions de décharge directe. L'équation des courbes de polarisation est établie pour divers types de réactions. Les problèmes techniques liés à la réalisation du courant de la forme proposée sont brièvement discutés.

SUMMARY

The chronopotentiometric method, with an imposed current of the form $i = \varrho\sqrt{t}$,

gives, for direct discharge processes, transition times which are proportional to the concentrations. The equation for the potential-time curves is established for various types of reactions. The technical problems concerning the circuitry of the polarization unit are briefly discussed.

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THÉORIE ET APPLICATIONS DE LA MÉTHODE
CHRONOPOTENTIOMÉTRIQUE AVEC COURANT IMPOSÉ
CROISSANT PROPORTIONNELLEMENT À LA RACINE
CARRÉE DU TEMPS

II. CAS DES RÉACTIONS DE DÉCHARGE DIRECTE PROCÉDANT
EN RÉGIME DE DIFFUSION SPHÉRIQUE ET CYLINDRIQUE

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INTRODUCTION

Les principales caractéristiques de la méthode électro-analytique où le courant imposé est de la forme $i = q\sqrt{t}$ ont été définies dans une publication antérieure¹: on y a notamment établi qu'en régime de diffusion linéaire et pour un processus de décharge directe, les temps de transition sont proportionnels aux concentrations analytiques. L'objet de cette communication est d'établir les lois du transfert massique dans le cas où le champ de diffusion est sphérique ou cylindrique, de manière à pouvoir étendre les possibilités d'utilisation pratique de la méthode à divers types d'électrodes non planes, telles que le fil métallique de section cylindrique ou l'électrode à goutte pendante. Un problème identique a déjà été résolu et discuté dans le cas de la chronopotentiométrie galvanostatique^{2,3,4}: dans ce cas le terme de correction à apporter à la relation de SAND⁵ est d'autant plus important que la couche de diffusion est épaisse vis-à-vis du rayon de courbure de la surface de l'électrode: l'écart dépend par conséquent de la valeur du temps de transition et de celle du coefficient de diffusion de la particule électrolysée. Du fait de l'analogie existant entre la chronopotentiométrie galvanostatique et la méthode considérée ici, on peut s'attendre à ce que la résolution du problème mène à des conclusions similaires, quoique la forme des termes correctifs soit sans doute quelque peu différente. De manière à rendre possible le traitement mathématique, on admettra que le courant imposé est entièrement consommé par la réaction d'électrode, jusqu'au temps de transition. Cette condition revient à tenir pour négligeable la fraction de courant consommée par la charge capacitive de l'électrode.

RÉGIME DE DIFFUSION SPHÉRIQUE

En l'absence de convection et de migration, l'équation seconde de FICK représentative du régime de diffusion sphérique peut s'écrire:

$$\frac{\partial a(r,t)}{\partial t} = D \left[\frac{\partial^2 a(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial a(r,t)}{\partial r} \right] \quad (1)$$

où D est le coefficient de diffusion du dépolarisant A (en $\text{cm}^2 \text{sec}^{-1}$) et $a(r,t)$ est la

concentration instantanée (en mol cm⁻³) à une distance r , comptée en cm à partir du centre de l'électrode. On impose au système les conditions initiales et aux limites suivantes:

$$a(r,0) = a^{\circ} \quad (2)$$

$$a(\infty,t) = a^{\circ} \quad (3)$$

$$\left(\frac{\partial a(r,t)}{\partial r}\right)_{r=r_0} = \frac{\varrho\sqrt{t}}{nFD} \quad (4)$$

Dans ces relations a° est la concentration analytique de A (en mol cm⁻³) au sein de la solution, r_0 le rayon de l'électrode en cm, ϱ le facteur d'amplitude du courant¹ (en A sec^{-1/2} cm⁻²), F le faraday et n le nombre d'électrons échangés à l'électrode par particule de dépolarisant.

On choisit la variable

$$W(r,t) = rU(r,t) \quad (5)$$

où l'on pose

$$U(r,t) = a^{\circ} - a(r,t) \quad (6)$$

Cette variable $W(r,t)$ introduite dans (1) conduit à l'équation

$$\frac{\partial W(r,t)}{\partial t} = D \frac{\partial^2 W(r,t)}{\partial r^2} \quad (7)$$

dont la solution est obtenue grâce à la méthode des transformées de LAPLACE définies par

$$\bar{f}(r,s) = \int_0^{\infty} f(r,t) \exp(-st) dt \quad (8)$$

Si l'on tient compte des conditions initiales (2) et de convergence (3), la solution de l'équation issue de la transformée de (7) prend la forme

$$\bar{W}(r,s) = Q \exp\left(-\sqrt{\frac{s}{D}} r\right) \quad (9)$$

La constante d'intégration Q est déterminée en satisfaisant à la transformée de la condition limite (4):

$$\left(\frac{\partial \bar{U}(r,s)}{\partial r}\right)_{r=r_0} = -\frac{\sqrt{\pi} \varrho}{2nFDs^{3/2}} \quad (10)$$

La solution s'écrit finalement

$$\bar{U}(r,s) = \frac{\varrho\sqrt{\pi} r_0 \exp\left[-\sqrt{\frac{s}{D}}(r-r_0)\right]}{2nFDrs^{3/2}\left(\sqrt{\frac{s}{D}} + \frac{1}{r_0}\right)} \quad (11)$$

Le calcul de la transformée inverse de l'équation (11) s'effectue à l'aide du théorème de convolution⁶ et en utilisant la transformée inverse⁷ de l'expression

$$\frac{1}{\sqrt{s}} \frac{\exp \left[-\sqrt{\frac{s}{D}} (r - r_0) \right]}{\left(\sqrt{\frac{s}{D}} + \frac{1}{r_0} \right)} \quad (12)$$

On a ainsi:

$$U(r, t) = \frac{q\sqrt{\pi} r_0}{2nF\sqrt{D} r} \int_0^t \exp \left(\frac{r - r_0}{r_0} \right) \exp \left(\frac{Dt'}{r_0^2} \right) \text{cfer} \left(\frac{r - r_0}{2\sqrt{Dt'}} + \sqrt{\frac{Dt'}{r_0^2}} \right) dt' \quad (13)$$

où cfer représente le complément de la fonction d'erreur. La résolution par parties de cette intégrale conduit à la relation finale qui, si l'on tient compte de (6), peut s'écrire

$$a(r, t) = a^\circ - \frac{q\sqrt{\pi} r_0^2}{2nFD^{3/2} r} \left[2 \sqrt{\frac{Dt}{\pi}} \exp \left[-\left(\frac{r - r_0}{2\sqrt{Dt}} \right)^2 \right] - r \text{cfer} \left(\frac{r - r_0}{2\sqrt{Dt}} \right) + r_0 \exp \left(\frac{r - r_0}{r_0} \right) \exp \left(\frac{Dt}{r_0^2} \right) \text{cfer} \left(\frac{r - r_0}{2\sqrt{Dt}} + \sqrt{\frac{Dt}{r_0^2}} \right) \right] \quad (14)$$

La concentration à l'électrode vaut par conséquent:

$$a(r_0, t) = a^\circ - \frac{q\sqrt{\pi} r_0}{2nFD^{3/2}} \left[2 \sqrt{\frac{Dt}{\pi}} - r_0 + r_0 \exp \left(\frac{Dt}{r_0^2} \right) \text{cfer} \left(\sqrt{\frac{Dt}{r_0^2}} \right) \right] \quad (15)$$

Au temps de transition τ ,

$$a(r_0, \tau) = 0 \quad (16)$$

et dès lors,

$$a^\circ = \frac{q\sqrt{\pi} r_0}{2nFD^{3/2}} \left[2 \sqrt{\frac{D\tau}{\pi}} - r_0 + r_0 \exp \left(\frac{D\tau}{r_0^2} \right) \text{cfer} \left(\sqrt{\frac{D\tau}{r_0^2}} \right) \right] \quad (17)$$

Le développement en série du terme

$$r_0 \exp \left(\frac{Dt}{r_0^2} \right) \text{cfer} \left(\sqrt{\frac{Dt}{r_0^2}} \right)$$

dans l'équation (15) peut s'effectuer en considérant les cas limites où $\sqrt{Dt/r_0^2}$ est très grand ou très petit par rapport à l'unité.

(a) L'inégalité $\sqrt{Dt/r_0^2} > 1$ représente l'état le plus éloigné du régime de diffusion linéaire. Elle correspond au développement de la fonction $\exp(\xi)^2 \text{cfer}(\xi)$ pour $\xi > 1$ soit⁸

$$\exp(\xi)^2 \text{cfer}(\xi) \approx \frac{1}{\sqrt{\pi}\xi} \left[1 - \frac{1}{2\xi^2} + \frac{1 \cdot 3}{(2\xi^2)^2} - \frac{1 \cdot 3 \cdot 5}{(2\xi^2)^3} + \dots \right] \quad (18)$$

L'introduction du premier terme de cette série asymptotique dans la relation (15) conduit à l'équation

$$a(r_0, t) = a^\circ - \frac{q\sqrt{\pi} t}{2nF\sqrt{D}} \left[\frac{2}{\sqrt{\pi}} \left(\frac{r_0^2}{Dt} \right)^{1/2} - \left(\frac{r_0^2}{Dt} \right) + \frac{1}{\sqrt{\pi}} \left(\frac{r_0^2}{Dt} \right)^{3/2} - \dots \right] \quad (19)$$

En comparant les temps ainsi calculés aux temps t_i que l'on observerait en régime de diffusion linéaire et qui sont donnés¹ par

$$a(r_0, t) = a^\circ - \frac{q\sqrt{\pi}}{2nF\sqrt{D}} t_i \quad (20)$$

on peut écrire

$$\frac{t_i}{t} = \left[\frac{2}{\sqrt{\pi}} \left(\frac{r_0^2}{Dt} \right)^{1/2} - \left(\frac{r_0^2}{Dt} \right) + \frac{1}{\sqrt{\pi}} \left(\frac{r_0^2}{Dt} \right)^{3/2} - \dots \right] \quad (21)$$

où t et t_i représentent n'importe quelle durée d'électrolyse inférieure ou égale au temps de transition. Aux valeurs extrêmes de ce cas limite le rapport (21) tend vers zéro.

(b) L'inégalité $\sqrt{Dt/r_0^2} < 1$ réalisée dans les cas les plus usuels, correspond au développement de la fonction $\exp(\xi)^2$ cfer (ξ) pour des petites valeurs de ξ soit⁸

$$\exp(\xi)^2 \text{ cfer } (\xi) \approx 1 - \frac{2}{\sqrt{\pi}} \xi + \xi^2 - \frac{4}{3\sqrt{\pi}} \xi^3 + \frac{1}{2} \xi^4 - \frac{16}{30\sqrt{\pi}} \xi^5 \quad (22)$$

Les six premiers termes de cette série introduits dans l'équation (15) donnent

$$a(r_0, t) = a^\circ - \frac{q\sqrt{\pi} t}{2nF\sqrt{D}} \left[1 - \frac{4}{3\sqrt{\pi}} \left(\frac{Dt}{r_0^2} \right)^{1/2} + \frac{1}{2} \left(\frac{Dt}{r_0^2} \right) - \frac{16}{30\sqrt{\pi}} \left(\frac{Dt}{r_0^2} \right)^{3/2} + \dots \right] \quad (23)$$

Des relations (20) et (23) on tire l'équation

$$\frac{t_i}{t} = \left[1 - \frac{4}{3\sqrt{\pi}} \left(\frac{Dt}{r_0^2} \right)^{1/2} + \frac{1}{2} \left(\frac{Dt}{r_0^2} \right) - \frac{16}{30\sqrt{\pi}} \left(\frac{Dt}{r_0^2} \right)^{3/2} + \dots \right] \quad (24)$$

RÉGIME DE DIFFUSION CYLINDRIQUE

Dans les conditions de diffusion cylindrique, l'équation seconde de FICK s'écrit

$$\frac{\partial a(r, t)}{\partial t} = D \left[\frac{\partial^2 a(r, t)}{\partial r^2} + \frac{1}{r} \frac{\partial a(r, t)}{\partial r} \right] \quad (25)$$

Les variables conservent les significations qui leur ont été données dans le traitement du régime de diffusion sphérique. On choisit également les conditions initiales et aux limites (2), (3), (4) ainsi que la variable $U(r, t)$ définie par (6). D'autre part, à l'instar de RIUS, POLO ET LLOPIS², les grandeurs sans dimensions

$$T = \frac{Dt}{r_0^2} \quad (26)$$

et

$$R = \frac{r}{r_0} \quad (R > 1) \quad (27)$$

sont introduites dans l'équation (25); dès lors

$$\frac{\partial U(R, T)}{\partial T} = \frac{\partial^2 U(R, T)}{\partial R^2} + \frac{1}{R} \frac{\partial U(R, T)}{\partial R} \quad (28)$$

En tenant compte des transformées de LAPLACE (8) et de la condition initiale (2) on a

$$\frac{d^2 \bar{U}(R,s)}{dR^2} + \frac{1}{R} \frac{d\bar{U}(R,s)}{dR} - s\bar{U}(R,s) = 0 \quad (29)$$

La solution de cette équation différentielle doit obéir aux transformées des conditions (3) et (4) définies dans les nouvelles variables. Soit

$$\bar{U}(\infty, s) = 0 \quad (T > 0) \quad (30)$$

$$\left(\frac{d\bar{U}(R,s)}{dR} \right)_{R=1} = - \frac{\varrho r_0^2 \sqrt{\pi}}{2nFD^{3/2} s^{3/2}} \quad (T > 0) \quad (31)$$

La solution générale de l'équation (29) est de la forme

$$\bar{U}(R,s) = Z_0(j\sqrt{s} R) \quad (32)$$

avec

$$Z_0(j\sqrt{s} R) = MI_0(j\sqrt{s} R) + NK_0(j\sqrt{s} R) \quad (33)$$

$I_0(j\sqrt{s} R)$ et $K_0(j\sqrt{s} R)$ sont les fonctions modifiées de BESSEL de première et seconde espèces.

La condition de convergence (30) implique que $M = 0$, tandis que N est déterminé par la condition (31), qui concerne le flux à l'électrode. La solution de l'équation s'écrit donc

$$\bar{U}(R,s) = \frac{\varrho r_0^2 \sqrt{\pi}}{2nFD^{3/2}} \left(\frac{K_0(j\sqrt{s} R)}{s^2 K_1(j\sqrt{s})} \right) \quad (34)$$

Dans le cas où $R = 1$ et où $T \ll 1$, c'est-à-dire pour les grandes valeurs de s , on utilise la série asymptotique⁸

$$K_n(j\sqrt{s}) \approx \left(\frac{\pi}{2j\sqrt{s}} \right)^{1/2} \exp(-j\sqrt{s}) \left[1 + \frac{4n^2 - 1^2}{1! 8j\sqrt{s}} + \frac{(4n^2 - 1^2)(4n^2 - 3^2)}{2!(8j\sqrt{s})^2} + \dots \right] \quad (35)$$

et^{2,9}

$$\frac{K_0(j\sqrt{s})}{K_1(j\sqrt{s})} \approx 1 - \frac{1}{2j\sqrt{s}} + \frac{3}{8s} - \frac{3}{8s^{3/2}} + \dots \quad (36)$$

En tenant compte de la définition de $U(R,T)$, de (26), (27) et (36), la transformée inverse de (34) peut s'écrire

$$a(r_0, t) = a^\circ - \frac{\varrho \sqrt{\pi} t}{2nF\sqrt{D}} \left[1 - \frac{2}{3\sqrt{\pi}} \left(\frac{Dt}{r_0^2} \right)^{1/2} + \frac{3}{16} \left(\frac{Dt}{r_0^2} \right) - \frac{1}{5\sqrt{\pi}} \left(\frac{Dt}{r_0^2} \right)^{3/2} + \dots \right] \quad (37)$$

On a pour le temps de transition

$$a^\circ = \frac{\varrho \sqrt{\pi} \tau}{2nF\sqrt{D}} \left[1 - \frac{2}{3\sqrt{\pi}} \left(\frac{D\tau}{r_0^2} \right)^{1/2} + \frac{3}{16} \left(\frac{D\tau}{r_0^2} \right) - \frac{1}{5\sqrt{\pi}} \left(\frac{D\tau}{r_0^2} \right)^{3/2} + \dots \right] \quad (38)$$

Les équations (37) et (38) correspondent aux cas usuels où l'inégalité $\sqrt{Dt/r_0^2} \ll 1$ est assurée. Tenant compte de la relation (20), on obtient finalement

$$\frac{t_i}{t} = \left[1 - \frac{2}{3\sqrt{\pi}} \left(\frac{Dt}{r_0^2} \right)^{1/2} + \frac{3}{16} \left(\frac{Dt}{r_0^2} \right) - \frac{1}{5\sqrt{\pi}} \left(\frac{Dt}{r_0^2} \right)^{3/2} + \dots \right] \quad (39)$$

DISCUSSION

Il ressort de l'examen des équations (21), (24) et (39) que les temps d'électrolyse (temps de transition τ compris) mesurés en régime de diffusion sphérique et cylindrique sont supérieurs à ceux que l'on observerait en régime de diffusion linéaire, toutes autres conditions égales. Les Figs. 1 et 2 donnent les valeurs des termes d'ordre successif en $\sqrt{Dt/r_0^2}$ figurant dans les séries (24) et (39). Les sommes de ces différents termes sont également représentées. Pour les petites valeurs de la quantité $\sqrt{Dt/r_0^2}$, ces termes tendent vers zéro et on retrouve alors les temps t_i observés en régime de diffusion linéaire.

Il est intéressant de comparer les relations (24) et (39), aux équations correspondantes valables en chronopotentiométrie galvanostatique; celles-ci sont respectivement, pour la diffusion sphérique et cylindrique:

$$\sqrt{\frac{t_i}{t}} = \left[1 - \frac{\sqrt{\pi}}{2} \left(\frac{Dt}{r_0^2} \right)^{1/2} + \frac{2}{3} \left(\frac{Dt}{r_0^2} \right) - \frac{\sqrt{\pi}}{4} \left(\frac{Dt}{r_0^2} \right)^{3/2} + \dots \right] \quad (40)$$

$$\sqrt{\frac{t_i}{t}} = \left[1 - \frac{\sqrt{\pi}}{4} \left(\frac{Dt}{r_0^2} \right)^{1/2} + \frac{1}{4} \left(\frac{Dt}{r_0^2} \right) - \frac{3\sqrt{\pi}}{32} \left(\frac{Dt}{r_0^2} \right)^{3/2} + \dots \right] \quad (41)$$

Dans ces équations, les valeurs de t_i sont tirées de la relation de SAND⁵, soit

$$a(r_0, t) = a^\circ - \frac{2i_0}{nF} \sqrt{\frac{t_i}{\pi D}} \quad (42)$$

où i_0 est la densité du courant constant.

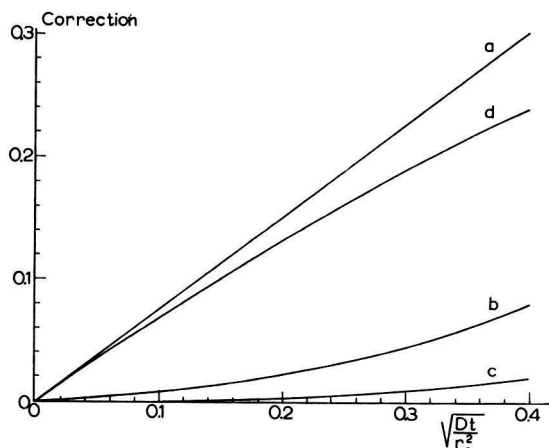


Fig. 1. Influence de la quantité $\sqrt{Dt/r_0^2}$ sur les termes de correction en régime de diffusion sphérique [équation (24)]: (a), terme du premier ordre en $\sqrt{Dt/r_0^2}$; (b), terme du second ordre; (c), terme du troisième ordre; (d), somme $a - b + c$.

Les accroissements de t résultent, dans tous les cas, de l'apport d'une quantité de matière plus grande que celle qui diffuserait perpendiculairement vers une électrode plane de surface identique. L'écart est d'autant plus considérable que la courbure

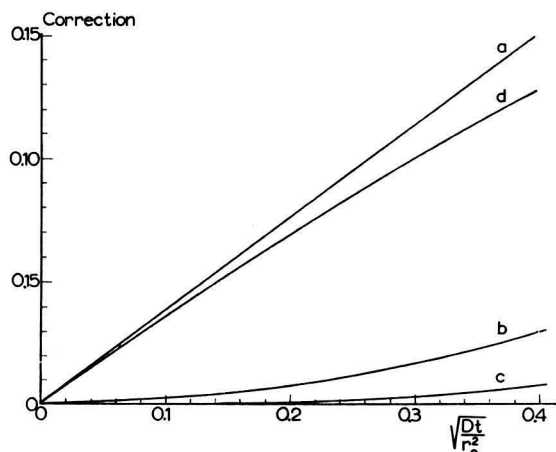


Fig. 2. Influence de la quantité \sqrt{Dt}/r_0^2 sur les termes de correction en régime de diffusion cylindrique [équation (39)]: (a), terme du premier ordre en \sqrt{Dt}/r_0^2 ; (b), terme du second ordre; (c), terme du troisième ordre; (d), somme $a - b + c$.

moyenne de l'électrode est grande et que l'appauvrissement local de dépolarisant ($\int_0^t i dt$) est important. A cet égard il est utile de considérer l'épaisseur équivalente 2δ de la couche de diffusion, grandeur représentative du degré d'appauvrissement en diffusion linéaire, et définie par la relation

$$2\delta = \frac{2 \int_0^t i dt}{nF[a^\circ - a(0,t)]} \quad (43)$$

On calcule aisément que, pour la méthode à courant variable,

$$\delta_{\varphi} \sqrt{i} = \frac{4}{3} \sqrt{\frac{Dt}{\pi}} \quad (44)$$

tandis qu'en chronopotentiométrie à courant constant

$$\delta_{i_0} = \frac{1}{2} \sqrt{\pi Dt} \quad (45)$$

La Fig. 3 représente ces épaisseurs équivalentes, ainsi que la distribution des concentrations $a(x,t)$ en régime de diffusion linéaire, dans le cas des deux méthodes chronopotentiométriques. Les valeurs suivantes y sont utilisées: $D = 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$; $n = 1$; $a^\circ = 3.93 \cdot 10^{-5} \text{ mol cm}^{-3}$; $t = 1.2 \text{ sec}$; $\varphi = 0.745 \cdot 10^{-2} \text{ A cm}^{-2} \text{ sec}^{-1/2}$; $i_0 = 0.635 \cdot 10^{-2} \text{ A cm}^{-2}$.

Ces valeurs ont été choisies de manière à réaliser dans les deux méthodes une même concentration $a(0,t)$ à l'électrode pour une durée d'électrolyse identique.

A partir des valeurs de δ , on constate que, pour la diffusion sphérique, le premier

terme de correction dans (24) et (40) est simplement δ/r_0 . D'autre part, en comparant ces équations avec les relations (39) et (41), on observe que ce terme est assez logiquement diminué de moitié si l'on passe au régime de diffusion cylindrique.

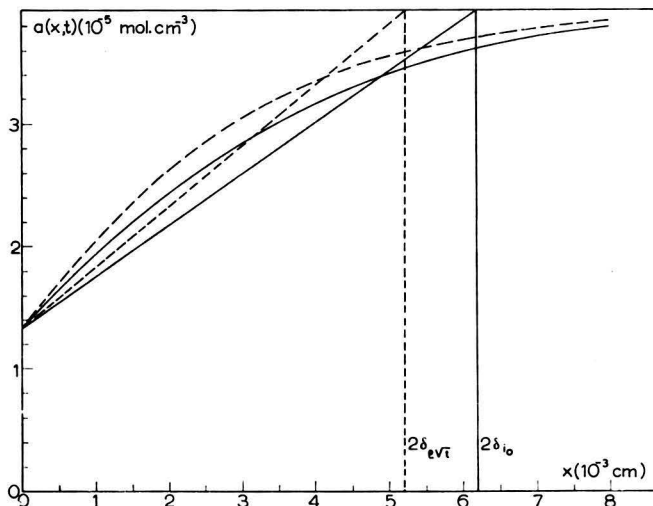


Fig. 3. Variation des concentrations et dimension des couches de diffusion pour la chronopotentiométrie sous courant constant (en trait continu) et la chronopotentiométrie sous courant variable (en traits interrompus) en régime de diffusion linéaire (les données expérimentales figurant dans le texte).

L'examen des équations (39), (41) et (24), (40) permet enfin de conclure que les termes de corrections calculés pour la chronopotentiométrie galvanostatique, et les facteurs du même ordre relatifs à la méthode considérée sont dans un rapport indépendant du type de régime de diffusion; ce rapport vaut respectivement $8/3\pi$ pour les termes du premier ordre en \sqrt{Dt}/r_0^2 , $3/4$ pour ceux du second ordre, et $32/15\pi$ pour ceux du troisième ordre. Le rapport des premiers facteurs

$$\frac{8}{3\pi} = \frac{\delta_e\sqrt{t}}{\delta_0} \quad (46)$$

représente le rapport coulométrique des quantités de dépolarisant consommées en régime de diffusion linéaire, après un même temps t , et pour une même concentration à l'électrode (Fig. 3).

La comparaison entre les relations (24) (39) (40) et (41) montre également que, pour de petites valeurs de \sqrt{Dt}/r_0^2 , les corrections dont il faut tenir compte dans la méthode proposée sont inférieures à celles calculées pour la chronopotentiométrie sous courant constant. Cette constatation est reflétée dans le Tableau I, où l'on a calculé les valeurs que doit prendre la quantité \sqrt{Dt}/r_0^2 pour que l'écart entre t et t_1 soit respectivement de 1% et 10%.

TABLEAU I

Régime	$\frac{t}{t_1}$	Chronopotentiométrie	
		à courant constant	à courant variable ($i = \rho\sqrt{t}$)
Diffusion	1.01	0.006	0.013
sphérique	1.10	0.055	0.133
Diffusion	1.01	0.011	0.026
cylindrique	1.10	0.114	0.270

CONCLUSION

Comparée à la chronopotentiométrie galvanostatique, la méthode proposée se caractérise par des corrections de courbure d'expression mathématique assez semblables; du fait de la moindre extension de la couche de diffusion, ces corrections sont légèrement inférieures, à durée d'électrolyse et courbure égales.

De manière à éviter de devoir tenir compte d'un trop grand nombre de termes correctifs, il est utile d'ajuster les conditions expérimentales de façon à ce que le rapport entre l'épaisseur équivalente de la couche de diffusion et le rayon de courbure soit amené à une valeur aussi réduite que possible; on remarquera cependant que, quel que soit le nombre des termes correctifs requis, les concentrations sont nécessairement proportionnelles au facteur d'amplitude, pour des temps de transition égaux: il est par conséquent toujours possible d'opérer par interpolation, à partir d'expériences effectuées à diverses valeurs du facteur d'amplitude.

De même qu'en chronopotentiométrie galvanostatique, le nombre des termes de corrections dont il faut tenir compte dépend de la valeur du coefficient de diffusion de la particule dépolarisante; les conclusions tirées par LINGANE⁹ d'expériences comparatives utilisant des ions de mobilité très différente peuvent dès lors être étendues aux régimes d'électrolyse considérés ici.

RÉSUMÉ

On établit les lois du transfert massique procédant en régime de diffusion cylindrique et sphérique, lorsque le courant imposé est de la forme $i = \rho\sqrt{t}$.

Les expressions trouvées sont comparées à celles obtenues en régime de diffusion linéaire, et aux expressions correspondantes établies pour la méthode galvanostatique.

SUMMARY

The mass transfer equations for cylindrical and spherical diffusion are established for an imposed current of the form $i = \rho\sqrt{t}$. The final expressions are compared with those obtained for linear diffusion, and with the corresponding relations for the constant-current method.

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POLAROGRAPHY OF 2-ETHYL-4-THIOCARBAMOYLPIRIDINE

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2-Ethyl-4-thiocarbamoylpyridine (ethionamide) has been found useful in the treatment of tuberculosis, particularly in cases of isoniazid resistance¹. In order to study its absorption from the gut and excretion by the kidney, KANE² described a polarographic method for the determination of its concentration in serum, cerebrospinal fluid and urine. The present paper describes the behaviour of this compound at the dropping electrode, including the reaction responsible for the polarographic wave (wave II described under RESULTS) used in the above analytical work.

EXPERIMENTAL

All reagents were AnalaR grade. Mercury was purified as described previously². De-aeration of solutions was accomplished by bubbling oxygen-free grade nitrogen through them. Maxima were suppressed by the addition of 0.002% polyethylene glycol 4000.

A laboratory-constructed, recording polarograph was employed utilising a synchronous-motor-driven Beckman helipot of linearity $\pm 0.1\%$ for applied voltage and an Ether-Wheelco W.S.P. recorder for measurement of current as the potential drop across a fixed resistor in series with the cell. The speed of response was 3.5 sec for full-scale traverse. No external damping was applied and it was assumed that the maximum excursion of the pen represented the current at the end of the drop-life. That the error introduced by this assumption was not considerable was shown by the comparison of results given below for the diffusion current constant for benzamide using both damped and undamped measuring instruments.

The cell consisted of a B.40 cone sealed off close to the ground glass. This was immersed in a Dewar flask of water at 25.0° for the recording of polarograms. A dip-type saturated calomel electrode³ served as the reference and non-polarised electrode. The dropping mercury electrode possessed the following characteristics: $m = 2.60$ mg/sec; $t = 3.0$ sec in 0.1 M KCl on open circuit.

pH measurements were made with glass electrodes and a Pye universal pH-meter.

Controlled potential electrolysis was carried out using a LINGANE-type⁴ potentiostat and a 2-chamber cell described previously⁵. Coulometric measurements were made using a hydrogen-oxygen coulometer.

Ultraviolet spectra were recorded on a Unicam SP. 700 spectrophotometer.

Polarograms were recorded in universal buffer solutions consisting of a mixture of hydrochloric, citric, phosphoric and aminoacetic acids to which varying amounts of KOH were added. These solutions covered the range 2–12 pH. $M/1$ and $M/10$ HCl

and $M/10$ KOH solutions were used to extend this to pH 0 and 13. Polarograms at a single concentration (0.46 mM) were recorded at pH intervals of about one unit over the range 1–13 pH and at varying concentrations at pH 0, 7 and 13. In addition polarograms at a single concentration were recorded at varying heights of the Hg reservoir at pH 0, 2.3, 7 and 13. The effect of temperature on polarograms at pH 0 and 2.3 was also investigated.

Attempts were made to measure the number of electrons/molecule added by coulometry using a macro-Hg cathode controlled at a potential corresponding to one of the limiting currents obtained polarographically.

RESULTS

Fig. 1 shows polarograms of 0.50 mM ethionamide in aqueous solution at pH 0, 7 and 13. For clarity, the polarograms are displaced along the current, but not the voltage, axis.

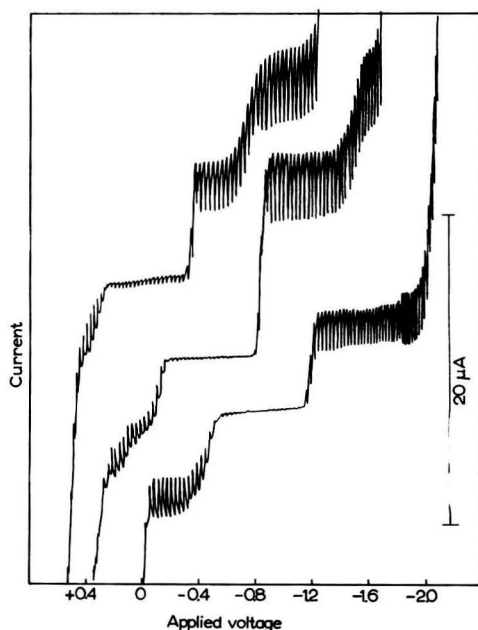


Fig. 1. Polarograms of 0.50 mM ethionamide: top, pH 0; middle, pH 7; bottom, pH 13.

In order to aid the interpretation of the polarographic properties of ethionamide, polarograms were also recorded of 0.50 mM solutions of 4-thiocarbamoyl-pyridine at pH 0, 7 and 13. These polarograms were very similar to those of ethionamide and it was assumed that the oxidation and reduction properties of the two compounds were completely analogous.

The polarograms may be divided for convenience into three regions of potential, *viz*:

(i) An oxidation wave, I, was obtained over the whole pH range studied. Except at highest pH values, it was not well-defined, possibly owing to adsorption effects, since the current-time curve for individual drops showed a complex form. This is quite noticeable in the pH 7 polarogram of Fig. 1.

(ii) A reduction wave, II, of constant height was obtained over the pH range 5–9. Below pH 5 it split into two waves III and IV, whose combined height was constant and equal to that of wave II. The wave height of III decreased with decreasing pH until at pH 0 the two waves were equal in height. The relative wave heights remained constant in more strongly acidic solutions up to 5 *N* sulphuric acid, the most strongly acid solution studied. Above pH 9 the wave height of II decreased with increase of pH until at pH 13 and above, its height was half that at pH 7.

(iii) In the region pH 5–11 a further reduction wave, V, whose height was half that of wave II, was revealed by displacement of the hydrogen wave with increase of pH. Beyond pH 11 this wave merged with the potassium wave of the buffer solutions.

Figs. 2 and 3 show the relationship between limiting current constant* and pH and half-wave potential and pH respectively.

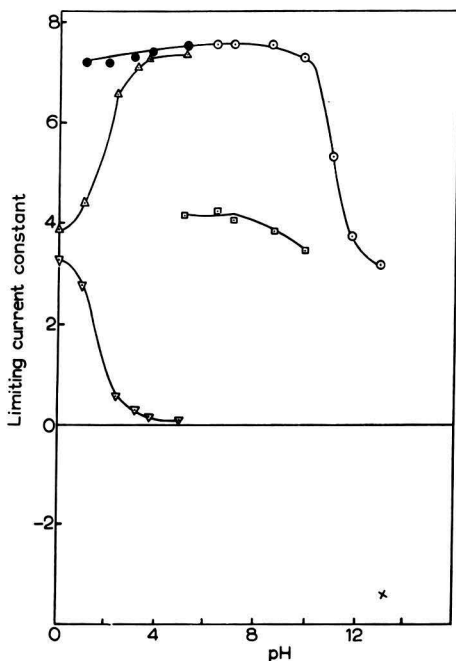


Fig. 2. Relationships between limiting current constants of ethionamide and pH. ×, Reduction wave I; o, II; Δ, III; ●, III + IV; ∇, IV; □, V.

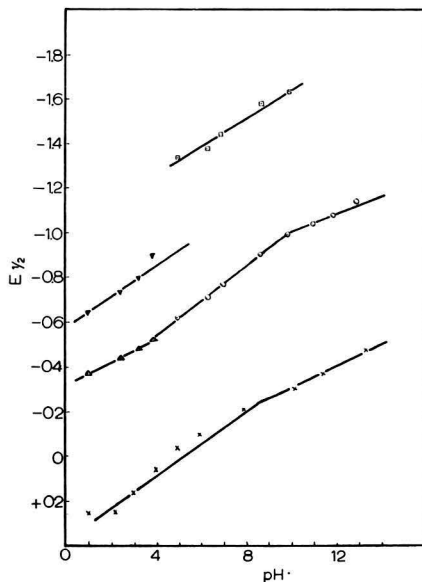


Fig. 3. Relationships between half-wave potentials of ethionamide and pH. Symbols as for Fig. 2.

At pH 0, 7 and 13, wave heights were proportional to concentration over the range 0.2–1.0 *mM*. At pH 0, 7 and 13, wave heights were proportional to the square-root of the Hg head on the dropping electrode, a necessary condition for diffusion-controlled currents. At pH 2.3, however, whereas $(i_{II} + i_{III})$ showed this same proportionality, the limiting current i_{III} was independent of the Hg head, indicative of a kinetic current. This limiting current was found to decrease with increasing temperature over the range 3–38° showing conclusively that it was not a diffusion-controlled current.

* Defined as $i_1/Cm^{2/3}t^{1/6}$.

The change of diffusion current with pH over the range 9–13 pH was found to be paralleled by a change in u.v. absorption spectrum indicating a change in the nature of the ethionamide molecule.

DISCUSSION

Number of electrons

The ILKOVIC equation may be written:

$$n = \frac{i_a}{706 D^{1/2} C m^{2/3} t^{1/6}}$$

$$= D' / 706 D^{1/2}$$

where $D' = i_a / C m^{2/3} t^{1/6}$ = diffusion current constant. Thus n can only be found if D is known. This can be deduced in two ways using "model" substances of similar molecular size and shape.

(i) From the NERNST equation

$$D_0 = 2.67 \cdot 10^{-7} A_0 / Z \text{ for an ion at } 25^\circ$$

where A_0 = ionic conductivity at infinite dilution;

Z = charge on the ion.

For 2 : 4 : 6-trimethylpyridine, ionising as the pyridinium hydroxide⁶

$$A_0 = 229 \text{ at } 25^\circ;$$

$$A_0 \text{ for OH}^- = 196 \text{ at } 25^\circ;$$

$$\therefore A_0 \text{ for the pyridinium ion} = 33,$$

$$\therefore D_0 = 9.07 \cdot 10^{-8} \text{ cm}^2/\text{sec},$$

$$\therefore n = 7.6 / (706 \cdot 3.01 \cdot 10^{-8}),$$

$$= 3.6,$$

$$= 4 \text{ to the nearest integer.}$$

(ii) For benzamidine

and

$$706 D^{1/2} = D' / n$$

$$n = 4 \text{ (KANE}^7)$$

D' was measured polarographically at pH 9.2 and found to be 7.8 using the recording polarograph. KANE'S⁷ average value at pH 9.2 of 6.7 multiplied by 7/6 to allow for the change from a damped to undamped operation also gives the value $D' = 7.8$.

$$\text{Hence } \therefore n \text{ for ethionamide} = 7.6 / 1.95,$$

$$= 3.9,$$

$$= 4 \text{ to the nearest integer.}$$

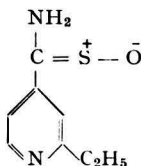
Attempts to measure n by a macro-coulometric method failed, values varying from $n = 5.5$ –8 being obtained for wave II. The reasons for this failure are not known.

From the relative values of limiting current constant in Fig. 2, the following values of n were therefore assigned:

$$\begin{array}{ll} \text{Wave I,} & n = -2 \\ \text{Wave II,} & n = 4 \\ \text{Wave III,} & n = 2 \text{ (below pH 1)} \\ \text{Wave IV,} & n = 2 \text{ (below pH 1)} \\ \text{Wave V,} & n = 2. \end{array}$$

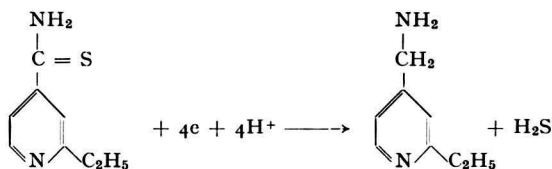
Nature of electrode reaction products

Wave I: The most likely sites for oxidation of a thiocarbamoylpyridine are one of the nitrogen atoms or the sulphur atom. It was found that 4-pyridylmethylamine did not yield an oxidation wave within the potential region available to the dropping Hg electrode and hence, the sulphur atom seemed the most likely site for oxidation, yielding



from ethionamide.

Waves II, III and IV: A possible 4-electron/molecule reduction reaction for ethionamide is:

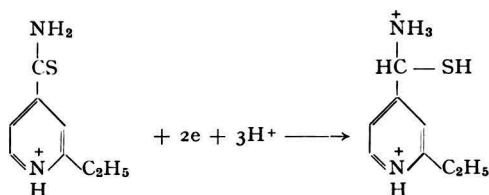


No sample of this amine was available, but an authenticated sample of 4-pyridylmethylamine was available. Polarograms were recorded of 0.50 *mM* solutions of 4-pyridylmethylamine and of 4-thiocarbamoylpyridine at pH 9.2 *vs.* a saturated calomel electrode. The half-wave potential of the second wave of the latter (−1.60 V) was identical with that of a single wave obtained for the former, and the wave heights were similar. This was regarded as confirmatory evidence for the 4-electron/mol. reduction outlined above.

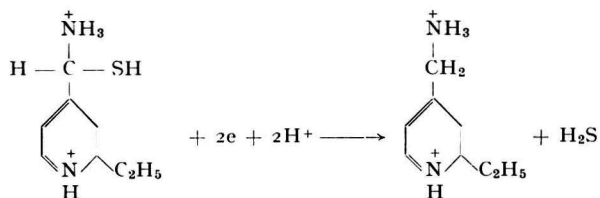
Supporting evidence for this reaction was the fact that, during the attempts to measure *n* by macro-coulometry, copious quantities of hydrogen sulphide were evolved.

The behaviour at low pH values suggested that a 2-electron reduction occurred to an intermediate compound. At pH values above 5 this was reduced further but at low pH values it was converted into a different form of more negative half-wave potential, thus giving rise to a kinetically-controlled wave. The nature of the intermediate and its conversion product can only be speculative and the following scheme is suggested as being not incompatible with the data:

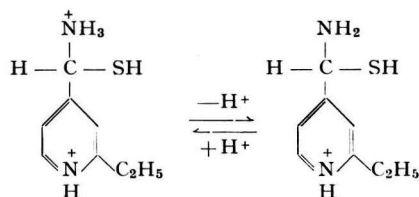
At very low pH (< 0) the wave III was:



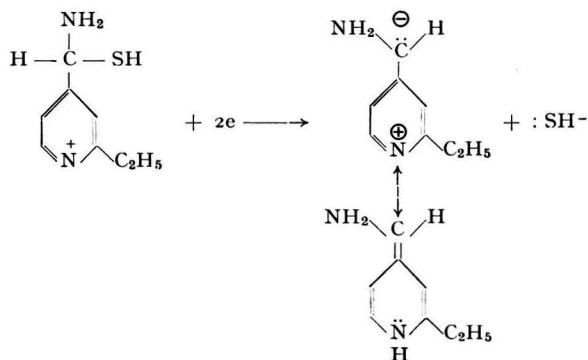
wave IV was:



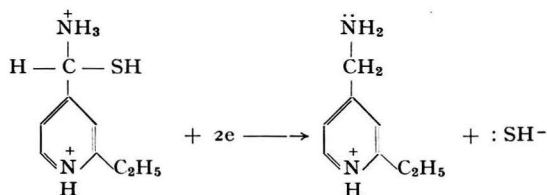
Between pH 0 and 4 there was a kinetic conversion



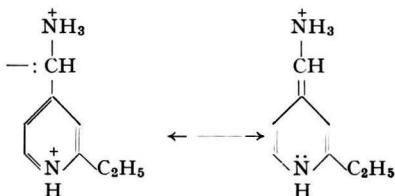
Considering the addition of two electrons to these two structures and assuming that hydrogen ions were added more slowly than electrons, we have



The half-wave potential being made more positive by the enhanced stability of the reduced form owing to resonance.



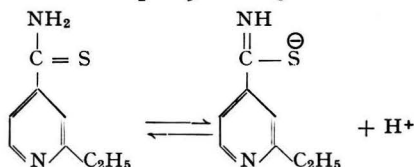
Here no resonance was possible and a more negative half-wave potential results. The tautomeric reduction product can possibly resonate *viz.*:



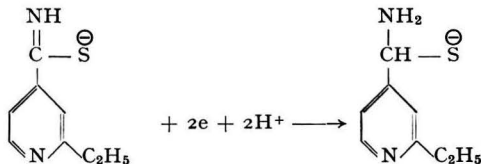
but the first form involves a triple charge separation and is unlikely to contribute substantially to the structure of the molecule and the second form has lost the resonance of the pyridine ring. Hence the 4-pyridylmethylamine structure is considered the more likely primary reduction product.

Some supporting evidence for a mechanism of this type was available from analysis of the waves. Upon plotting $\log i/(i_1 - i)$ vs. E at pH 0, 2.3 and 9.2, rectilinear curves were obtained for waves III and II (but not for wave IV) the slopes of the lines being -30 , -37 and -40 mV for the three pH values. These values were much closer to the value -30 mV required for a 2-electron/mol. wave than to the value of -15 mV required for a 4-electron/mol. wave. This suggested that over the whole of this pH range a 2-electron/mol. reduction was the potential determining step and that above pH 4, the 2-electron/mol. reduction product was immediately reduced further.

The behaviour in alkaline solution, in which the wave II was reduced in height to half that at lower pH values was accompanied by a change in u.v. absorption spectrum over the same pH range. It seemed reasonable to assume that the two phenomena were inter-connected and that between pH 9 and 13 the following reaction occurred:



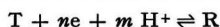
Presumably this thio-enolate was stable to reduction beyond the 2-electron/mol. stage:



Wave V: The wave V represented a 2-electron/mol. reduction, presumably of the pyridine ring. By analogy with acridines, a 1 : 4 reduction was considered most likely.

Relationship between half-wave potential and pH

A thermodynamically reversible oxidation-reduction system



whose current-voltage curves at the dropping Hg electrode are diffusion-controlled obeys the relationship⁸

$$E_{\frac{1}{2}} = E_0 - 0.059 \frac{m}{n} \text{pH at } 25^\circ.$$

TABLE I (Continued)

pH	Reaction	$-\frac{dE_{\frac{1}{2}}}{dpH}$ (mV)	
		Theory	Experiment
	<p>Wave I</p> $\text{R}-\text{C} \begin{array}{l} \text{S} \\ \text{NH}_2 \end{array} + \text{H}_2\text{O} \rightarrow \text{R}-\text{C} \begin{array}{l} \text{S}^+ \text{O}^- \\ \text{NH}_2 \end{array} + 2e + 2\text{H}^+$	59	76
4-9.5	<p>Wave II</p> $\text{R}-\text{C} \begin{array}{l} \text{S} \\ \text{NH}_2 \end{array} + 4e + 5\text{H}^+ \rightarrow \text{R}-\text{CH}_2 \cdot \overset{+}{\text{N}}\text{H}_3 + \text{H}_2\text{S}$	74	77
	<p>Wave V</p> $\text{R} \cdot \text{CH}_2 \cdot \overset{+}{\text{N}}\text{H}_3 + 2e + 2\text{H}^+ \rightarrow \text{RH}_2 \cdot \text{CH}_2 \cdot \overset{+}{\text{N}}\text{H}_3$	59	43
< 11	<p>Wave I</p> $\text{R}-\text{C} \begin{array}{l} \text{S} \\ \text{NH} \end{array} + \text{H}_2\text{O} \rightarrow \text{R}-\text{C} \begin{array}{l} \text{S}^+ \text{O}^- \\ \text{NH}_2 \end{array} + 2e + \text{H}^+$	30	41
	<p>Wave II</p> $\text{R}-\text{C} \begin{array}{l} \bar{\text{S}} \\ \text{NH} \end{array} + 2e + 2\text{H}^+ \rightarrow \text{R}-\text{CH} \begin{array}{l} \bar{\text{S}} \\ \text{NH}_2 \end{array}$	59	46

SUMMARY

2-Ethyl-4-thiocarbamoylpyridine yields one oxidation and one or two reduction waves, depending on pH, at the dropping mercury electrode over the pH range 0-13. One of the reduction waves is kinetically controlled. The nature of the electrode reaction products is discussed and probable electrode reactions are presented.

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REDOXOKINETIC AND IMPEDANCE TITRATIONS:
NEW ANALYTICAL TECHNIQUES

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INTRODUCTION

DOSS AND AGARWAL¹ discovered that, when a low frequency alternating field is applied between two platinum electrodes dipped in an aqueous solution containing a redox system, a d.c. potential develops at each of the electrodes, which can be measured with reference to a third electrode dipped in the same solution. This phenomenon has been termed the *redoxokinetic effect*, as it has its origin in the kinetics of the oxidation-reduction reactions at the electrode, and the d.c. potential, the *redoxokinetic potential*. The phenomenon is also referred to as *faradaic rectification*. Several attempts²⁻⁵ have been made to formulate a mathematical theory based upon the theory of absolute reaction rates for electrode processes⁶; the formulation recently effected by RANGARAJAN⁷ using Bessel functions appears to be a very general approach, as the results of other workers follow as special cases.

A method of titration based upon the measurement of the redoxokinetic potential (ψ) during the course of a titration (termed *redoxokinetic titration*) was developed by Doss *et al.*⁸ This takes advantage of the sudden change in ψ at the equivalence-point to locate the latter. This paper describes its application for the systems: ferrous ammonium sulphate *vs.* ammonium metavanadate, and lead nitrate *vs.* potassium ferrocyanide, the latter involving a precipitation reaction.

Since the above titrations were carried out under galvanostatic conditions, a measure of the a.c. potential across the platinum electrodes during the titration enabled calculation of the gross cell impedance to be made. It was found that the impedance also showed a sudden change at the equivalence-point⁹, and enabled the location of the endpoint in the above titrations. This method of titration is a slight modification of FRANCK'S method¹⁰ and a more appropriate name, *impedance titration*, is suggested.

EXPERIMENTAL

The circuit diagram is given in Fig. 1, which is self-explanatory. By the use of the variable series resistances R_1 , R_2 and R_3 , a constant current of 100 μ was maintained across the electrodes. Only two electrodes have been used in this set up, one of which is a platinum micro-electrode (E_1) and the other a platinum reference electrode having a large area (gauze electrode) (E_2). The gauze electrode just surrounded the experimental micro-electrode thereby minimizing the iR drop across it. Before each titration in the case of the ferrous-metavanadate system, the pretreatment of the electrodes

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as suggested by NARAYANAN *et al.*¹¹, was employed to enhance the reproducibility of the electrode surface. The solution to be titrated was placed in a beaker exposed to the atmosphere, and the electrodes suspended in it. Deaeration was not necessary. The compositions of the solutions in different experiments are given below.

Analytical grade chemicals were used for the preparation of the solutions.

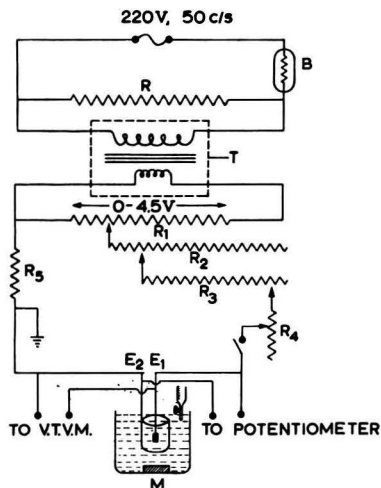


Fig. 1. Experimental set-up for redoxokinetic titration: B, current-stabilizing barretter (0.3 A); R, mains resistance (600 Ω , 20 W); T, step-down transformer (input 220 V, output 6 V); R_1 , R_2 , R_3 and R_4 , potentiometers (total resistance 200 Ω , 40, 10 and 1 k Ω , 3 W); R_5 (100 Ω , 0.5 W); E_1 , Pt micro-electrode (length 7.45 mm, mean dia. 0.48 mm); E_2 , gauge electrode (mean dia. 10 mm, cylindrical height 11.7 mm).

Titration of ferrous ammonium sulphate

(a) Solution in the beaker:

(i) 25 ml of 0.0176 M ferrous ammonium sulphate + 75 ml of 1.5–2 M sulphuric acid (supporting electrolyte);

(ii) 25 ml of 0.0084 M ferrous ammonium sulphate + 75 ml of 1.5–2 M sulphuric acid (supporting electrolyte).

(b) Solution in the burette:

Nearly 3 g of ammonium metavanadate dissolved in 100 ml of hot 1.5–2 M sulphuric acid and the volume made up to 250 ml and was diluted 10 times resulting in a solution equal to 0.0104 N with respect to vanadate.

Titration of potassium ferrocyanide

(a) Solution in the beaker:

(i) 20 ml of 0.5 M potassium ferrocyanide + 1 ml of ca. 1% freshly prepared potassium ferricyanide to maintain the redox system + 80 ml of ca. 10% ammonium nitrate (supporting electrolyte).

(b) Solution in the burette:

0.5 M lead nitrate.

After each addition the solution was well-stirred by a magnetic stirrer. At each

stage the redoxkinetic potential between E_1 and E_2 was measured by using a student's potentiometer (Kaycee type), the a.c. having been blocked by an inductance. The a.c. potential across the electrodes was measured by using a V.T.V.M. (Philips type G.M. 6015).

RESULTS

The typical values of the redoxkinetic potential (ψ) and the cell impedance (Z) in the course of various titrations are presented in Figs. 2-5.

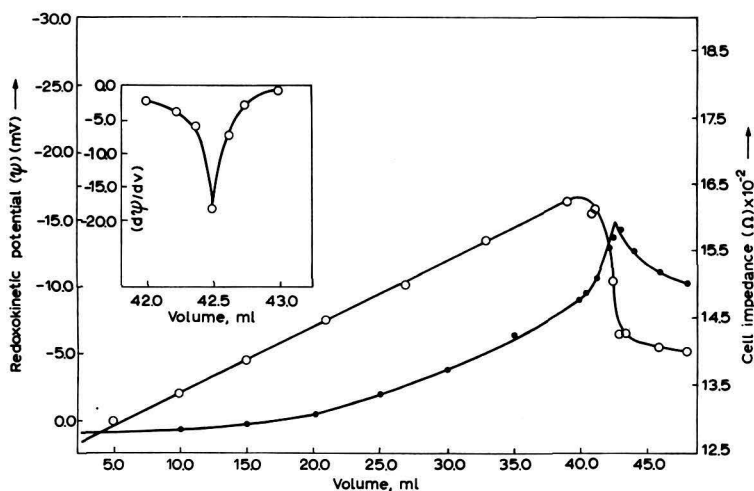


Fig. 2. Titration of 0.0176 *M* ferrous ammonium sulphate vs. 0.0104 *N* ammonium metavanadate: O, redoxkinetic potential; ●, cell impedance.

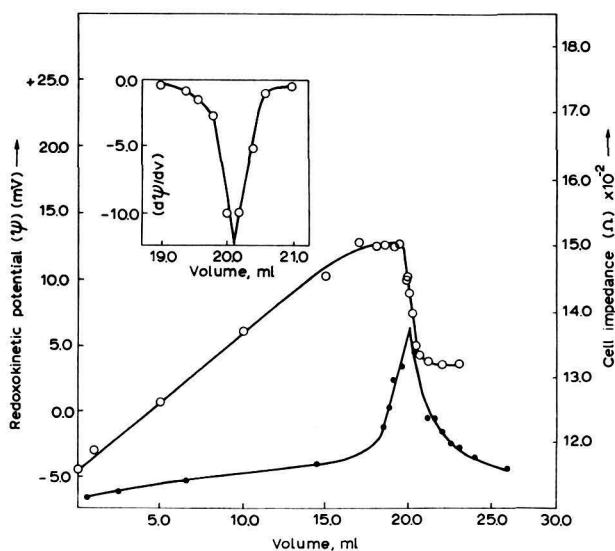


Fig. 3. Titration of 0.0084 *M* ferrous ammonium sulphate vs. 0.0104 *N* ammonium metavanadate: O, redoxkinetic potential; ●, cell impedance.

It should be noted that the characteristic feature of these titrations is the sudden change in ψ and Z at the equivalence-point, although variations in the general form of the curves is unavoidable, as the factors involved are kinetic parameters, which are difficult to reproduce at solid surfaces. The equivalence-point in the ferrous–vanadate system is characterized by a sharp inflexion of ψ , and a peak value of Z (Figs. 2 and 3)

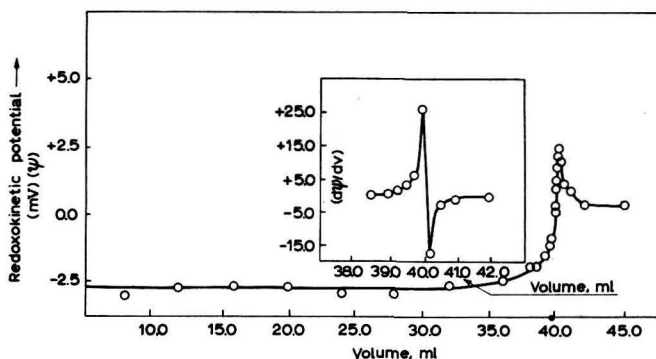


Fig. 4. Titration of 0.5 *M* potassium ferrocyanide vs. 0.5 *M* lead nitrate.

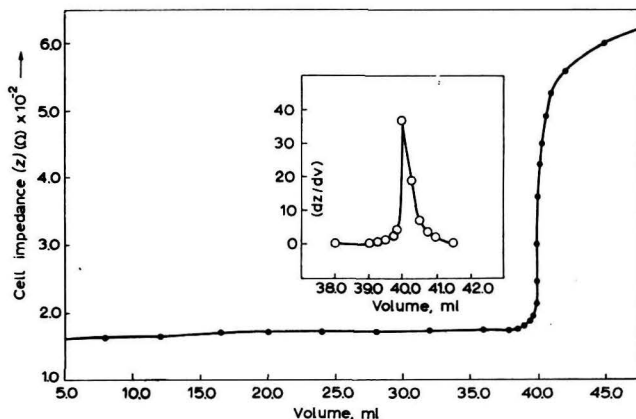


Fig. 5. Titration of 0.5 *M* potassium ferrocyanide vs. 0.5 *M* lead nitrate.

and in the case of the ferrocyanide–lead system both ψ and I show sharp inflexions at the equivalence-point (Figs. 4 and 5). The equivalence-point in the latter case corresponds to the formation of $\text{Pb}_2\text{Fe}(\text{CN})_6$, which is in agreement with previous findings¹². The insets show the corresponding derivative curves in arbitrary units. The results in all these cases agree closely with those of independent potentiometric titrations¹³. Table I summarizes the precision obtainable in various titrations, the examination of which shows that the methods may be used for precision determinations. Special implications and the theoretical aspects are under consideration.

TABLE I
PRECISION OBTAINABLE IN VARIOUS TITRATIONS

System No.	Titration	Technique	Concentration		Fig. No.	Curve No
1	Ferrous ammonium sulphate	Redoxo-kinetic	0.0176 M	±0.06%	2	1
			0.0084 M	±0.60%	3	1
	vs. ammonium meta-vanadate	Impedance	0.0176 M	±0.60%	2	2
			0.0084 M	±1.00%	3	2
2	Potassium ferrocyanide vs. lead nitrate	Redoxo-kinetic	0.5 M	±0.05%	4	—
			Impedance	0.5 M	±0.05%	5

ACKNOWLEDGEMENTS

The authors are grateful to the Director, Prof. K. S. G. Doss, for his keen interest and encouragement during the course of this investigation. One of them (K.S.N.) is indebted to the Council of Scientific and Industrial Research for the award of a Junior Research Fellowship, and the other (H.C.G.) is grateful to the University Grants Commission for the award of a travel grant.

SUMMARY

It is shown that the end-point in the titration of (i) Fe(II) salts with vanadate and (ii) ferrocyanides with lead can be determined accurately by taking advantage of the sudden change in the redoxokinetic potential and the cell impedance at the end-point. FRANCK'S¹⁰ technique of polarization titration has been slightly modified and a more appropriate name, *impedance titration*, is suggested.

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POLAROGRAPHIC RESOLUTION OF MIXTURES OF COMPLEXANS

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INTRODUCTION

The production and application of complexing agents of the complexan variety is receiving increasing attention and consequently the problem of detecting and even determining single constituents of mixtures of these aminopolycarboxylic acids must be considered. The analysis of mixtures of iminodiacetic acid and nitrilotriacetic acid which are obtained in the synthesis of the former is perhaps the most obvious example. Similarly mixtures of mono, di, tri and tetra acids are obtained in the synthesis of complexan compounds from aliphatic diamines *via* condensation with chloroacetic acid.

The resolution of such complexan mixtures by alkalimetric titration is not possible because of close similarity of pK_A values and consequent overlapping of individual titration curves. SIGGIA, EICHLIN AND RHEINHART¹ investigated titrations of a number of complexans with certain cations and REILLEY AND SCHMID² have used measurements at the mercury indicator electrode to characterise such metal chelates. It is possible that these methods could be adapted to investigate the composition of mixtures.

The anodic oxidation of EDTA at the dropping mercury electrode has been recorded³ but little information is available concerning other complexans. Moreover the voltage scale available (0 to + 0.3 V) for discrimination appears to be of too limited range to permit any useful differentiation of mixtures. However, the cathodic reduction of metal-complexan chelates takes place over a wider voltage range and since the half-wave potential of the chelate wave has been shown to bear a virtually linear relationship to the stability constant⁴, this presents perhaps the most favourable and sensitive method available for investigation of the problem. Of a number of metals investigated, copper(II) gave chelates which had both well-defined waves with all complexans and also a usefully wide range to permit differentiation.

A scheme of qualitative analysis for mixtures of these reagents has, however, already been proposed, which is based on separation of the mixture by zone electrophoresis on paper and identification of the components by measurement of polarographic half-wave potentials of the individual isolated copper(II) chelates⁴.

This communication describes a modified polarographic method which is capable of resolving many mixtures of known complexans without the necessity of previous isolation or group separation by electrophoresis. In principle, the solution is treated with just sufficient copper sulphate to form the Cu(II) chelates of all the complexans

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present and a derivative polarogram is recorded for the mixture. Where resolution is possible a separate peak is produced on the polarogram for each constituent. The $E_{\frac{1}{2}}$ value may be used to establish the identity of each complexan.

DISCUSSION

Our previous investigations have shown that at pH 2.5 in an acetate buffered medium the half-wave potentials of copper(II)-complexan chelates fall within the range 0 to -0.42 V vs. S.C.E. Initial experiments carried out on two and three component mixtures revealed that some of these, *e.g.* DHEG-DTPA-CHDTA*, showed three distinct waves when an excess of the mixture was added to a standard 0.002 M copper solution containing gelatin. Another, *e.g.* IDA-EDTA-CDTA, which on the basis of known $E_{\frac{1}{2}}$ values (*cf.* Table I) was expected to behave similarly, did not in fact show resolution into more than two waves, corresponding to IDA and CDTA.

TABLE I

CATHODIC HALF-WAVE POTENTIALS FOR DIRECT POLAROGRAMS OF VARIOUS Cu(II)-COMPLEXAN CHELATES AT pH 2.5

Chelate	$E_{\frac{1}{2}}$ values (-V vs. S.C.E.)
DHEG	0.02
IDA	0.06
MIDA	0.08
AADA	0.08
NTA	0.11
UDA	0.16
DTPA	0.21
EDTA	0.23
CPDTA	0.24
CDTA	0.32
CHDTA	0.42

Consequently, a systematic examination was made of controllable factors in an endeavour to find generally applicable conditions. Initially work was done on two component mixtures, an excess of which was added to a measured amount of 0.002 M copper(II) sulphate in 0.4 M acetic acid solution and containing 0.025% of gelatin. The pH was adjusted by addition of concentrated hydrochloric acid or 5 N sodium hydroxide to pH 2.5. The solutions were deoxygenated with hydrogen and the undamped polarogram was measured at $18 \pm 2^\circ$. Derivative polarograms were recorded on the same solution. A drop-rate of 2.5-3 sec was used. When a large (120%) excess of complexan solution was added it was found that usually only single derivative peaks were obtained (*cf.* Table II) and these corresponded not unnaturally to the stronger complexan.

* In the text which follows the following contractions are used in the interests of clarity: IDA, iminodiacetic acid; MIDA, methyliminodiacetic acid; NTA, nitrilotriacetic acid; UDA, uramil-N,N-diacetic acid; EDTA, ethylenediamine-N,N',N',N'-tetraacetic acid; DTPA, diethylenetriamine-N,N',N',N',N'-pentaacetic acid; DHEG, Di-(2-hydroxyethyl) glycine; AADA, *o*-carboxyphenyliminodiacetic acid; CPDTA, *trans*-cyclopentane-1:2-diamine-N,N',N',N'-tetraacetic acid; CDTA, *trans*-cyclohexane-1:2-diamine-N,N',N',N'-tetraacetic acid; CHDTA, *trans*-cycloheptane-1:2-diamine-N,N',N',N'-tetraacetic acid.

TABLE II

RESOLUTION OF COMPLEXAN MIXTURES BY DERIVATIVE POLAROGRAPHY OF Cu(II) CHELATES; LARGE EXCESS OF COMPLEXAN MIXTURE

Mixture	Theoretical peaks (-V vs. S.C.E.)	Observed peaks (-V vs. S.C.E.)
NTA-DTPA	0.11/0.21	0.24
CPDTA-DTPA	0.24/0.21	0.25
AADA-UDA	0.08/0.16	0.19
EDTA-CDTA	0.23/0.32	0.32
DTPA-CDTA	0.21/0.32	0.25(?) / 0.37
NTA-CPDTA	0.11/0.24	0.11/0.25
NTA-CDTA	0.11/0.32	0.11/0.37

Since it was obvious that the excess of complexan mixture was an important factor the above and some additional experiments were repeated, but with a 20% excess of reagent. Table III shows that resolution was now considerably improved.

TABLE III

RESOLUTION OF COMPLEXAN MIXTURES BY DERIVATIVE POLAROGRAPHY OF Cu(II) CHELATES; 20% EXCESS OF COMPLEXAN MIXTURE

Mixture	Theoretical $E_{\frac{1}{2}}$ values (-V vs. S.C.E.)	Observed $E_{\frac{1}{2}}$ values (-V vs. S.C.E.)
AADA-UDA	0.08/0.16	0.08/0.18
AADA-DTPA	0.08/0.21	0.08/0.27
NTA-DTPA	0.11/0.21	0.11/0.27
NTA-EDTA	0.11/0.23	0.11/0.28
EDTA-CDTA	0.23/0.32	No resolution (0.34)
UDA-CDTA	0.16/0.32	0.16/0.42
NTA-CDTA	0.11/0.32	0.10/0.37
NTA-CPDTA	0.11/0.24	0.11/0.30

These experiments reveal that separation is possible even for mixtures where the difference in $E_{\frac{1}{2}}$ values is only 80 mV. It must, however, be noted that whereas the value of $E_{\frac{1}{2}}$ for the derivative peak of the weaker complexan, *i.e.* the first peak, is accurate there is a considerable lag in the appearance of the second peak. In the case of the UDA-CDTA mixture this amounts to as much as 100 mV though the average value is *ca.* 50 mV. A check on the performance of the instrument on single components showed that normally the derivative peak lagged 20 mV behind the peak measured on the recorded (undamped) direct polarogram. Thus the discrepancy in the value of $E_{\frac{1}{2}}$ for the second wave can be partly accounted for on the basis of instrumental performance.

Since the decrease in the concentration of excess complexan to 20% was beneficial a method was now sought to reduce this even further so that just sufficient total complexan was present to chelate the Cu(II). Accordingly, the standard copper solution was lightly buffered at pH 6 and titrated with the complexan mixture to the extremely sensitive fluorescent end-point obtained with the *o*-dianisidine tetraacetic acid indicator recently proposed by BELCHER, REES AND STEPHEN⁵. In this manner the presence of the copper chelates of all complexans present in a mixture was ensured

and more reproducible results were obtained. It was first of all established by polarography that the copper(II) complex of the indicator was a very weak one and secondly that the extremely small amounts of it present at the end-point did not interfere in any way with individual single polarograms.

Since it is well known that the resolution between closely approaching derivative peaks on a polarogram may be somewhat improved by using a fairly fast capillary, the 3-sec capillary used in the previous experiments was now replaced by one dropping every 1.4 sec. The results obtained on 1 : 1 mixtures using the fast capillary and titrated mixtures are shown in Table IV.

TABLE IV
RESOLUTION OF COMPLEXAN MIXTURES BY DERIVATIVE POLAROGRAPHY OF Cu(II) CHELATES;
1.4-SEC CAPILLARY

Mixture	Theoretical $E_{\frac{1}{2}}$ values (-V vs. S.C.E.)	Observed $E_{\frac{1}{2}}$ values (-V vs. S.C.E.)
AADA-NTA	0.08/0.11	0.08/0.12
AADA-DTPA	0.08/0.21	0.08/0.24
AADA-EDTA	0.08/0.23	0.07/0.24
AADA-CPDTA	0.08/0.24	0.08/0.27
AADA-CDTA	0.08/0.32	0.08/0.38
NTA-DTPA	0.11/0.21	0.11/0.21
NTA-EDTA	0.11/0.23	0.11/0.23
NTA-CPDTA	0.11/0.24	0.11/0.26
NTA-CDTA	0.11/0.32	0.11/0.34
AADA-NTA-CDTA	0.08/0.11/0.32	0.08/0.11/0.35
IDA-NTA	0.06/0.11	0.12/0.15
IDA-EDTA	0.06/0.23	0.08/0.25
EDTA-CDTA*	0.23/0.32	0.22/0.31

* 1.2-sec capillary.

Examination of these results reveals resolution between waves that are separated (AADA-NTA) by as little as 30 mV. Moreover, it is noteworthy that whilst the $E_{\frac{1}{2}}$ value of the derivative peak of the stronger complexan still lags behind that of the direct polarogram of the single component it does so to a much more limited extent and lies close to the 20 mV instrumental difference previously noted. Unusually high results were obtained for the $E_{\frac{1}{2}}$ values of IDA in admixture with NTA and though this resolution is theoretically easier than that of AADA-NTA, because of the above phenomenon, a much poorer resolution was obtained (*cf.* Fig. 1). However, the separation appears to be consistently reproducible. It is difficult to account for this cathodic movement of the IDA-Cu(II) peak though the possibility of mixed complex formation should perhaps not be ruled out. The high values for CDTA can be related to the increased slope, *i.e.* non-reversibility, of the CDTA wave which is noticeable in many instances when this complexan is mixed with others.

Another important factor in determining the resolution of mixtures is of course the relative concentrations of the complexans particularly when the $E_{\frac{1}{2}}$ values lie close together. In order to find the limiting proportion, two mixtures were studied one having an $E_{\frac{1}{2}}$ separation of 80 mV (AADA-UDA) typifying weak complexan mixtures and the other with a separation factor of 120 mV (NTA-EDTA) typifying strong complexan mixtures. For each mixture the ratio of one complexan to the other

was varied stepwise as follows keeping the total amount of complexan in the system constant: 1 : 9, 2 : 8, 3 : 7, 4 : 6, 5 : 5, 6 : 4, 7 : 3, 8 : 2, 9 : 1. These two series of experiments were done with the 3-sec capillary.

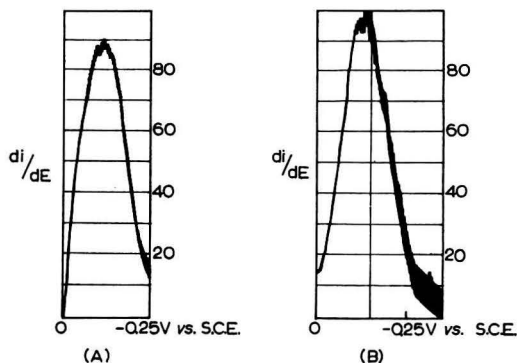


Fig. 1. Resolution of closely similar weak complexans by polarography of Cu(II) chelates at pH 2.50: (A) AADA-NTA, expected separation 30 mV; (B) IDA-NTA, expected separation 50 mV.

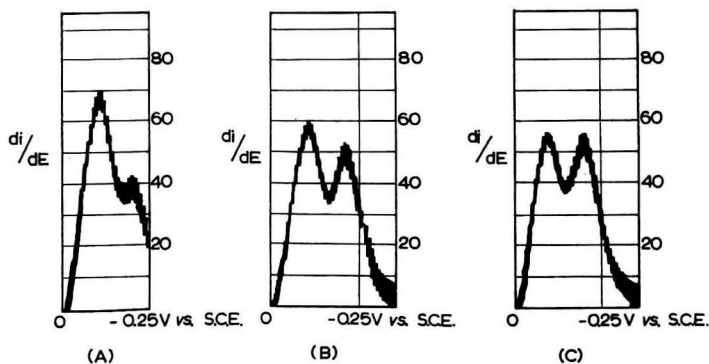


Fig. 2. Effect of relative proportions on resolution of weak complexans AADA-UDA: (A) AADA-UDA, 7 : 3; (B) AADA-UDA, 6 : 4; (C) AADA-UDA, 5 : 5.

In both systems, twin peaks were obtained except for the proportion 1 : 9 and 9 : 1 (*cf.* Figs. 2 and 3). Thus ratios of from 1 : 4 to 4 : 1 give good resolution with the mixture of strong or weak complexans. It is once more interesting to note that with the 9 : 1 mixture of AADA-UDA the peak obtained at -0.13 V is 30 mV more cathodic than the mean value for the other peaks recorded for AADA in this series of experiments. This again is similar to the performance of the very weak complexan IDA in admixture with NTA (*cf.* Table IV).

CONCLUSION

In the course of these experiments resolution was achieved for some twenty pairs of complexans. In addition some three-component mixtures were also successfully resolved, *e.g.* DHEG-DTPA-CHDTA (Fig. 4), DHEG-DTPA-CDTA (Fig. 5),

IDA-EDTA-CDTA and AADA-NTA-CDTA. It is doubtful if the scope of the method could be extended to the analysis of more complex mixtures than these.

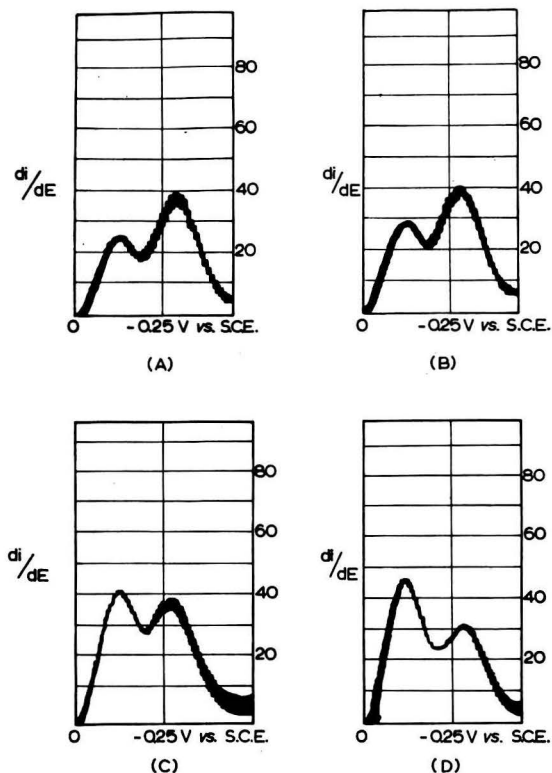


Fig. 3. Effect of relative proportions on resolution of strong complexans NTA-EDTA: (A) NTA-EDTA, 3 : 7; (B) NTA-EDTA, 4 : 6; (C) NTA-EDTA, 5 : 5; (D) NTA-EDTA, 6 : 4.

It may be concluded that with the equipment used, any two chelates having $E_{\frac{1}{2}}$ values differing by *ca.* 50 mV should be capable of clear resolution using a fairly fast capillary. The ratio of one complexan to the other should not greatly exceed 4 : 1 and in the case of complexans which closely approach each other's $E_{\frac{1}{2}}$ value the toleration may be less. In this study we related measured $E_{\frac{1}{2}}$ values from the derivative curves to the values obtained for direct polarograms of single complexans in a previous series of experiments⁴ and it is observed that in many instances the $E_{\frac{1}{2}}$ value for the stronger complexan is more cathodic. It would however, be more systematic to relate the $E_{\frac{1}{2}}$ values for mixtures to the $E_{\frac{1}{2}}$ values of derivative curves obtained on single components using the same drop-rate and damping. There appears to be no reason why the method should not be made semi-quantitative as well as qualitative since it will be seen from Figs. 2 and 3 that good proportionality exists between peak height and the amount of complexan present. Lastly it may be concluded that for unequivocal identification of strong complexans in admixture with others it is advisable to check

the $E_{\frac{1}{2}}$ value against a known mixture of the reagents analysed by the derivative method.

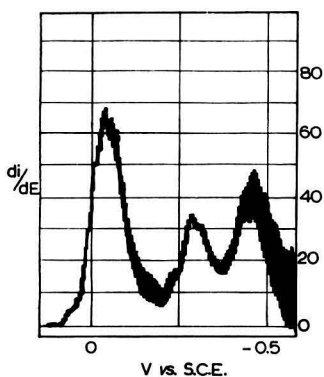


Fig. 4. Resolution of mixture, DHEG-DTPA-CHDTA.

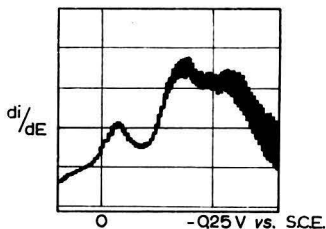


Fig. 5. Resolution of mixture, DHEG-DTPA-CDTA.

EXPERIMENTAL

Apparatus

Tinsley recording polarograph Mark 19;
EIL pH-meter 23A;
Agla syringe burette, 0.5 ml capacity;
Ultraviolet titration lamp.

Reagents

Copper sulphate solution (0.002 *M*), 0.025% with respect to gelatin. This solution should be freshly prepared every two days;
Complexan solutions, 0.1 *M* solution of sodium salts;
Hydrochloric acid, concentrated;
Sodium hydroxide, *ca.* 5 *N*;
o-Dianisidine-*N,N,N',N'*-tetraacetic acid, 1% dispersion in pulverised KNO_3 ;
pH 6 buffer, 20% ammonium acetate.

METHOD

10 ml of the copper sulphate solution were pipetted into a 20 ml beaker and 3-4 drops of pH 6 buffer were added. A microspatula-end of indicator was added and the beaker was placed under the u.v. lamp. The contents were then titrated by means of the syringe burette with 0.1 *M* complexan mixture solution till the appearance of fluorescence; the end-point was very slightly over-run to ensure a trace excess of complexan. To this solution 0.25 ml of glacial acetic acid was added and the pH was adjusted to 2.50 using concentrated hydrochloric acid.

The polarographic cell was then filled with the solution and deoxygenation with hydrogen was allowed to proceed for 5 min. The derivative polarogram was recorded against a saturated calomel electrode using circuit 2 of the instrument, zero counter-current, damping 2-4, sensitivity 1 or 1.2 μA f.s.d., chart scale of 4 in./V and a drop time of 1.4-1.2 sec under an open head of 76 cm mercury.

ACKNOWLEDGEMENTS

One of us (W.H.) is indebted to the Geigy Company (Manchester) for provision of a research scholarship. We are also grateful to Prof. R. BELCHER for his support and guidance.

SUMMARY

A method is described for the resolution of mixtures of complexans which is based on obtaining a polarogram of the mixture treated with an amount of copper sufficient to ensure that the copper(II) chelates of all the complexans coexist in solution. Resolution is possible when the $E_{1/2}$ values differ by only *ca.* 50 mV, *i.e.* a difference in log K value for the copper chelates of 2–3 units. The influence of proportion of components on the resolution is examined and it is indicated that semi-quantitative analysis is also possible where reasonable resolution is obtained.

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Short Communication

Sur le mouvement des anions minéraux en électrophorèse sur papier

On sait que le mouvement des substances en électrophorèse sur papier est influencé par l'électroosmose, l'évaporation pendant le passage du courant, l'adsorption sur papier et autres facteurs¹⁻⁴. Par conséquent les essais initiaux de la mesure de mobilité par le déplacement sur papier dans un champ électrique⁵ n'étaient pas couronnés de succès.

Nous étions donc frappés par une relation, disons empirique, entre le rapport du mouvement des anions minéraux monovalents et la mobilité de ces ions, une relation qu'on trouve dans les travaux de plusieurs auteurs différents⁶⁻⁹ se servant des techniques et des électrolytes très différents. La relation est illustrée dans la Fig. 1. Pour chaque ion la vitesse relative au Cl^- a été calculée et le même calcul a été fait pour les valeurs de mobilité. Malgré les imprécisions dûe sûrement en partie à la précision de mesures en électrophorèse sur papier il nous est possible de calculer la mobilité de quelques ions à partir des données électrophorétiques.

Exemples

(i) ClO_4^- se déplace 77 mm (GRASSINI ET LEDERER⁸) quand Cl^- migre 90 mm. Prenant 76.3 comme la mobilité de l'ion Cl^- à 25°¹⁰, la mobilité calculée à partir de l'électrophorèse est 65.5. Par mesure de conductivité on obtient 68.

(ii) Prenant les résultats de GROSS⁶ le perchlorate a une mobilité de 65.

(iii) Dans un autre travail⁷ l'ion ReO_4^- migre 59 mm et Cl^- 80 mm. Sa mobilité est donc 56.2 d'après l'électrophorèse et elle est 54.7 par mesure de la conductivité.

Une telle relation amène la supposition que l'adsorption sur papier est négligeable,

TABLEAU I

VALEURS DE R_F DE QUELQUES ANIONS MINÉRAUX AVEC 2% $(\text{NH}_4)_2\text{CO}_3$ COMME SOLVANT SUR PAPIER WHATMAN NO. 1

Anion	R_F
Cl^-	0.93
ClO_3^-	0.97
Br^-	0.88
BrO_3^-	0.88
I^-	0.85
IO_3^-	0.89
F^-	0.94
CNS^-	0.78
NO_2^-	0.90
NO_3^-	0.91
IO_4^-	environ 0.1

ainsi que nous avons confirmé par développement chromatographique avec un des électrolytes (Tableau I). Seul exception est l'ion periodate, qui présente aussi une

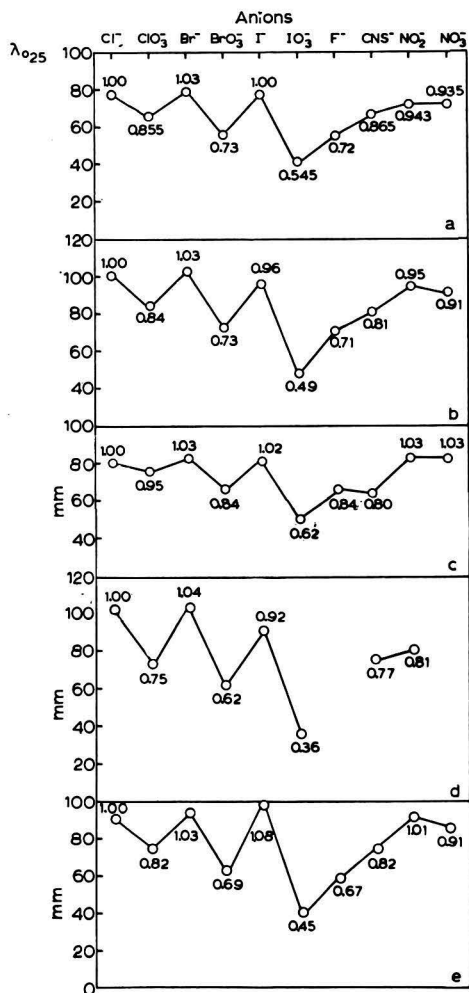


Fig. 1. (a) Mobilités ioniques à 25° d'après réf. 10; (b) migration des ions en 0.1 M (NH₄)₂CO₃ et 100 V/cm exprimé relative au mouvement de l'ion Cl⁻ (réf. 6); (c) migration des ions en 2% (NH₄)₂CO₃ avec 150 V dans une heure⁷; (d) migration dans 2% Na₂CO₃ avec 300 V dans une heure⁹; (e) migration dans 0.1 M NaOH avec 240 V dans une heure⁸.

anomalie en électrophorèse. Il nous reste encore à souligner que cette règle empirique s'applique uniquement aux ions de la même charge et que les ions bivalents et trivalents migrent avec des vitesses de la même grandeur que les ions monovalents.

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Book Reviews

Dictionnaire Chimique et Technique, Allemand-Français et Français-Allemand, par H. E. OSTEN, Ernst Arnold Buchdruckerei und Verlag GmbH, Dortmund-Mengede, Allemagne, 1959, 188 pages, D.M. 12.

Ce petit livre portatif est un dictionnaire de mots techniques intéressant la chimie, l'appareillage, les métaux, les techniques opératoires, l'énergie atomique. Il n'a pas la prétention d'être complet mais on y trouve les termes essentiels.

On sait avec quelle rapidité progresse la science, les expressions nouvelles voient constamment le jour; c'est pourquoi l'auteur a eu l'heureuse idée d'ajouter en les alternant, 188 pages blanches, si bien qu'il sera loisible à celui qui possédera cet ouvrage de le compléter des nouveaux mots qu'il découvrira au cours de ses recherches.

Un supplément placé en fin d'ouvrage comprend une liste des symboles (et non des formules comme le dit l'auteur) et des noms des principaux éléments puis la formule et le nom de quelques produits chimiques et réactifs courants (un peu plus de 200) et pour terminer quelques abréviations en allemand dans le domaine de la chimie.

De. Mo.

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Guide de Thermométrie—Méthodes, Réalisations des Mesures, by C. GOUX, Eyrolles-Gauthier Villars, Paris, 1959, 232 pages, N.Fr. 26.

This book is chiefly intended to give general information to manufacturing engineers. The author attempts to point out some of the errors in the present wide-spread, but often defective, methods of measuring temperature.

The contents of the book are divided into four parts. The first, very clearly written, reviews the principal methods of measuring temperature. The second reports on the diverse temperature scales, the thermodynamic scale and international scale of 1948 in particular. The third part is devoted to the choice of suitable methods. The meteorological factors influencing measurements (limits, accuracy, response time), the technological factors (distribution in time, geometrical properties, nature of sample) and finally, the modalities of working and combination of measuring systems are discussed. The last part indicates the precautions which should be observed in measuring temperature; errors are analysed and corresponding corrections proposed. Finally, some judicious advice is offered for the standardization and maintenance of apparatus.

This very clearly written book contains numerous details of information which will be of use to every one.

G. Mar.

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Electrochimie Théorique, par E. DARMOIS ET G. DARMOIS, Masson et Cie, Paris, 1960, 239 pages, N.Fr. 39.

Dans son introduction, le Pr. RIBAUD rend hommage à la mémoire d'EUGÈNE DARMOIS dont cet ouvrage est la dernière oeuvre scientifique. On connaît les très nombreux travaux de ce savant particulièrement axés sur l'étude des électrolytes, on n'est donc pas étonné de trouver dans ce traité, panorama de l'électrochimie, la marque de l'auteur, ses conceptions originales. Mme E. DARMOIS a pris une part active à la rédaction de ce traité. L'exposé y est clair, concis, bien ordonné, l'essentiel s'y trouve bien que ce livre ne compte que quelque 200 pages et 27 chapitres, dont nous ne citerons que quelques uns d'entre eux: les propriétés des électrolytes fondus, les électrolytes colloïdaux et applications, double couche au contact d'un métal et d'un électrolyte, électro-capillarité, phénomènes électrocinétiques, électroosmose, électrophorèse, F.E.M. de filtration,

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potentiel de membrane et applications, électrochimie des gaz, un bref résumé des applications analytiques de l'électrochimie, galvanoplastie et dépôts métalliques, techniques des différents dépôts galvaniques. Nous nous permettrons deux petites remarques, tout d'abord un manque de clarté de certaines formules provenant d'une mauvaise typographie particulièrement dans les puissances et les signes, puis le fait que les auteurs n'aient pas utilisé uniquement pour les systèmes acide-base la théorie du proton (BRÖNSTED) qui est la meilleure dans le domaine de l'électrochimie et qui est maintenant généralement adoptée en chimie minérale et analytique. Cet ouvrage est présenté de façon fort agréable, la typographie, à part les formules, y est parfaite, les figures sont soignées et la couverture souple est particulièrement robuste et bienvenue pour un livre qui doit être consulté très fréquemment.

De. Mo.

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Die Papierelectrophorese, 2nd edn., by C. WUNDERLY, H. R. Sauerländer & Co., Aarau and Frankfurt-am-Main, 1959, 202 pages, Fr. 18.80.

A few years after the first edition, the appliances and the various techniques related to paper electrophoresis have developed to such a point that this second edition is bound to be welcomed by everybody interested in this subject.

Of the five chapters, the first one is dedicated to a short historical review and to the definitions of terms used; the second to a concise but complete examination of the basic theories of the method; the third to the principal methods in use, with a compendium on column electrophoresis and other more direct methods; the real technique is referred to in detail in the fourth chapter. This chapter is in fact the most important and the most efficacious for those who wish to study the use of paper electrophoresis; the fifth is a detailed review of the results so far obtained, with special reference to biochemistry; the increase in experimental data is obvious in comparison to the first edition: this emphasizes the great possibilities offered by paper electrophoresis.

Two indexes follow, one of authors and one of subjects; the bibliographical references (over 1600) are placed at the bottom of the page, throughout the various chapters.

Ca. Cas.

J. Electroanal. Chem., 2 (1961) 178

Chromatographic Reviews: Progress in Chromatography, Electrophoresis and Related Methods, Vol. 2, edited by M. LEDERER, Elsevier Publishing Co., Amsterdam, 1960, 195 pages.

This book is a continuation of the first one published last year (for review see *J. Electroanal. Chem.*, 1 (1960) 341) and contains reviews already published in the *Journal of Chromatography*.

The first article that appears in this volume is dedicated to liquid-gas chromatography, and is conscientiously up-to-date with all the principal aspects of this technique.

In the second article, starch gel block electrophoresis is discussed in a satisfactory manner; readers seeking solutions regarding special separation problems in connection with proteins or nucleic acids, will find ample documentation on this subject.

In the study of proteic structures, one of the first objectives to aim at is the determination of the nature of the terminal amino-acids; for this purpose Sanger's method (dinitrophenylation) is very often used. The separation of the compounds that may result from the reaction and their identification are problems which are treated and solved concisely with a critical spirit.

Also the determination of the composition of the amino-acids in a protein based on the dinitro-fluorobenzene process (Levy's method) is described in detail.

The possibilities offered by chromatographic application in the survey of flavonoids are illustrated in the third review, in which extensive tables of R_F make it possible to study in a practical way the composition of the colour substances contained in plants.

The progress that has been made and the possible progress of the future in the clinical and anthropological fields are discussed in the fourth review (separation of human haemoglobins); the material collected in only ten years is due almost exclusively to the use of the new separation techniques and is already very extensive.

Finally, the principles of adsorption and precipitation chromatography are introduced and developed; their importance in numerous cases of inorganic chemistry are treated in the right manner, thus making findings, up till now only partly understood owing to incomprehension of their causes, easier to understand.

Ca. Cas.

J. Electroanal. Chem., 2 (1961) 178

Qualitative Analysis and Analytical Chemical Separations, by P. W. WEST AND M. M. VICK, 2nd edn., MacMillan, New York, 1959, xv + 301 pages, \$4.50.

The authors have ceased to use the hydrogen sulfide system (they also make little use of sodium or ammonium sulfide). On the other hand they do not follow the newer methods which are mainly performed by means of spot tests and some instrumental techniques, although they retain the schematic classification in groups because of its pedagogical advantages.

There are six groups of cations: (1) K^+ , Na^+ , NH_4^+ ; (2) Hg^+ , Ag^+ (insoluble chlorides); (3) Sn^{4+} , Sb^{3+} , BiO^+ , Fe^{3+} , Al^{3+} , Cr^{3+} (precipitated by benzoate buffer; (4) Pb^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Mg^{2+} (insoluble fluorides); (5) Mn^{2+} , Fe^{2+} , Hg^{2+} , Co^{2+} , Cu^{2+} , Ni^{2+} , Cd^{2+} (precipitated by NaOH); (6) Sn^{2+} , As^{3+} , Zn^{2+} .

The value of a scheme is chiefly proved by large scale use. For the mere reader there arise some questions, e.g. how the presence of AsO_4^{3-} and PO_4^{3-} influences the scheme; is Fe^{3+} also precipitated by the benzoate when oxalate is present; are $Mn(OH)_2$ and $Fe(OH)_2$ sufficiently insoluble after adding ammonia to the hydrochloric acid medium?

There are also some inconsistencies: on p. 18 Mn^{2+} is said to precipitate as $MnO(OH)_2$, while on p. 52 the same precipitate is formulated as $Mn(OH)_2$; on p. 80 AsO_4^{3-} is omitted after being mentioned on the preceding page and on p. 83.

Further, it seems doubtful that all sulfides give H_2S on warming with 6 M acetic acid. In the numbering of the anion tests on p. 83 there is an error.

The second part of the book can be considered as a concise text of general chemistry with special reference to equilibria. In the calculations of solubility products hydrolysis of some anions is not taken into account.

The contents of the third part are devoted to the occurrence, manufacture, refining and use of metals as well as some reactions. Several modern techniques are mentioned.

The statement of the authors, that over sixty institutions in the United States have introduced this book, may be a reason for taking notice of this new edition.

H.L.Ki.

J. Electroanal. Chem., 2 (1961) 179

Analyst's Pocket Book, by J. R. MAJER, Butterworths Scientific Publications, London, 1959, ix + 100 pages, 17s. 6d.

As indicated by the title, the aim of this small volume is to offer to the analyst a collection of the data and factors most frequently employed in analytical chemistry: atomic weights, chemical properties of chief elements, equivalents of volumetric solutions, equivalent weights of primary standards, indicators, etc. Moreover pH tables of common reagents are reported, together with those dealing with ionization constants of acids and bases, solubility products, preparation of some common laboratory reagents, solubility of inorganic compounds, concentrations of some important solutions of acids and bases, density of alcohol-water mixtures, conversion tables for different systems of measurement, logarithms and antilogarithms.

A scattered check of the data has shown that the numerical values agree with those currently reported in the literature.

F. Bu.

J. Electroanal. Chem., 2 (1961) 179

Scientific Russian Without Tears, by J. W. PERRY, Chicago Section of American Chemical Society, 86 East Randolph St., Chicago, Ill., 1959, 26 pages, \$1.00.

A very short booklet giving a very concise summary of the elements of the Russian language including the alphabet, grammar, verbs, some sentences and a short list of words useful to chemists. As an introduction to the Russian language, taking into account the suggestions given for future study, this booklet can be very useful.

Red.

J. Electroanal. Chem., 2 (1961) 179

Automatic Titrators, by J. P. PHILLIPS, Academic Press, New York, 1959, vii + 225 pages, \$6.00.

Automatic titration is rapidly growing in importance and a number of automatic titrators either commercially available or easily self-built have been described in the literature.

This volume of PHILLIPS provides a good survey of the subject and is particularly welcome since the papers concerning this subject are widely scattered in a number of periodicals.

This volume deals chiefly with the principles of automatic titrators so that for particular and detailed information it is always necessary to read the original papers, which are easy to find from the references.

After a short introduction (Chapter I), the general considerations and titrator design are dealt with (Chapter II) rather extensively. Chapters III, IV, V and VI are devoted to the different techniques suitable for automatic titrations: potentiometry; amperometry; conductometry; thermometry; photometry; coulometry. Chapter VII treats rather briefly the fully automatic and continuous titration; commercially available titrators and applications of automatic titration methods are briefly described in Chapters VIII and IX, respectively.

Good drawings make the text easier to understand.

G.Mi.

J. Electroanal. Chem., 2 (1961) 180

Principles of Electrolysis, by W. C. DAVIES, Royal Institute of Chemistry, London, 1959, vi + 30 pages, 3s. 6d.

A very short monograph issued by the Royal Institute of Chemistry for teachers, which aims to provide "concise and authoritative amounts of selected well-defined topics in chemistry".

It contains in a classical exposition some principles of electrochemistry which are perhaps more useful for those who wish to have a rapid and short account of electrochemistry than for "teachers" who should have these ideas already clear in their minds. The topics briefly treated are: electrolytic conduction; the electrode reaction; some examples of electrolytic processes; a summary of the principles and a short table of standard potentials.

Red.

J. Electroanal. Chem., 2 (1961) 180

Fluoreszenzmikroskopie, 2nd edn., by M. HAITINGER, Akademische Verlagsgesellschaft, Geest u. Portig K., Leipzig, 1959, viii + 168 pages, D.M. 22.

The original edition of HAITINGER's work on fluorescence microscopy has been revised by EISENBRAND AND WERTH and completely rewritten in many places. Since 1938, when the first edition was presented, the fluorescence microscopy field has become much broader so that now it is a very useful tool of research in medicine and biology.

The book is divided into many chapters which cover the subject from the basic principles of fluorescence to its application in microscopy and which describe the most modern available apparatus in this field.

The text is well divided: the first part deals with the various techniques of fluorescence in the field of histology and with the wider and more interesting use of fluorochromes. At present a very large number of substances are known that can be selectively fixed by cellular components so that different fluorescences can be produced.

The technique of fluorescence microscopy has reached such a degree of perfection that it can usefully be employed together with the technique of simple coloration in histology, which has already reached perfection. This becomes clear from reading the last two chapters, which discuss the progress of fluorescence microscopy in many problems of practical application.

The only criticism that can be made about this work is that it would have been better to extend the part that deals with the description of the most appropriate techniques in the various fields and to reduce the dissertation on theory, which appears to be too detailed.

Nevertheless the book, with its complete bibliography and a number of excellent illustrations in colour, has become, in this new edition, a very useful text for the research worker who wants to employ this new technique for studying living matter.

Au.Ma.

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1. Fundamental electrochemistry

229 – Instantaneous polarographic currents. I. Currents controlled by diffusion and by a slow electrode process (in German). J. Weber (Inst. of Physical Chemistry, Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 1424; *Chem. Listy*, 52 (1958) 1249. Einige Typen der momentanen polarographischen Ströme wurden mathematisch behandelt und diskutiert, vor allem unter Berücksichtigung der sphärischen Diffusion. Bei einem reversiblen Redox-System, bei welchem das Produkt der Elektrodenreaktion in die Lösung zurück diffundiert, ist der momentane Strom bei allen Potentialen um etwa 10% (bei üblichen polarographischen Bedingungen) grösser als der durch die Originalform der *Ilkovičsches* Gleichung gegebene. Die Korrektur auf die sphärische Diffusion verursacht, dass die Zeitabhängigkeit des momentanen Stromes zwischen 1 und 6 Sekunden die Form $i = \text{Konst. } t^{0.192}$ besitzt. Bei den Strömen, bei denen die Amalgambildung stattfindet, ist durch den Einfluss der sphärischen Diffusion der Strom erhöht, wenn das Potential negativer als das Normalpotential (E^0) ist, jedoch erniedrigt, wenn das Potential positiver als E^0 ist. Diese Differenz ist durch die Unterschiedlichkeit der Diffusionsräume der oxydierten und der reduzierten Form verursacht. Bei den durch einen langsamen Elektrodenvorgang geregelten Strömen ist die Korrektur auf die sphärische Diffusion in erster Annäherung vernachlässigbar. Der Zeitverlauf des Momentanstromes ist potentialabhängig und der Richtungskoeffizient der Abhängigkeit $\log i - \log t$ liegt zwischen 2/3 und 1/6. Bei kleineren Überspannung kann dieser Richtungskoeffizient im Potentialbereich des Stufenanstieges ein Maximum erreichen. [P.Zu.]

230 – Instantaneous polarographic currents. II. A study of the current-time curves at different potentials of the polarographic wave for reversible and irreversible processes (in German). J. Kůta and I. Smoleř (Polarographic Inst., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 2208-20; *Chem. Listy*, 52 (1958) 1259. Wegen der Übertragung der Konzentrationspolarisation müssen die Strom-Zeit-Kurven ($i-t$) am ersten, durch vorangehende Polarisation unberührten, Tropfen studiert werden. Die "ersten" $i-t$ -Kurven wurden bei verschiedenen Potentialen in dem Bereich des Stufenanstieges registriert. Für reversible Systeme, wie Fe(IV)/Fe(III) oder Ti(III)/Ti(IV) in Oxalat, für Chinon-Hydrochinon im Phosphatpuffer pH 6.8 usw. wurde in gesamten Potentialbereich eine lineare Abhängigkeit zwischen $\log i$ und $\log t$ gefunden. In Übereinstimmung mit der Theorie wurde für den Richtungskoeffizienten der Wert 0.195 gefunden. Bei reversiblen Vorgängen, bei welchen die reduzierte Form ein Amalgam bildet, ist durch die sphärische Diffusion der Strom erhöht, wenn das Potential negativer als das Halbstufenpotential ist, und erniedrigt, wenn das Potential positiver als das Halbstufenpotential ist. Beim Halbstufenpotential entspricht der Strom exakt der Originalform der *Ilkovičsches* Gleichung. Bei den irreversiblen Vorgängen mit grosser Überspannung nimmt der Exponent der parabolischen Zeitabhängigkeit von der Stufenferse (wo er 2/3 beträgt) beim Stromanstieg monoton ab, bis er beim Grenzstrom den Wert 1/5.3 erreicht. Bei irreversiblen Vorgängen mit geringer Überspannung erreicht der Exponent seinen Maximalwert im Potentialbereich des Stromanstiegs der polarographischen Stufe. Als Beispiel werden Zn^{2+} -Ionen in einer Sulfatlösung sowie Eu^{3+} in NaClO_4 und NaCl -Lösungen angegeben. Bei den Metallen der Eisen-Gruppe wurde ein unregelmässiger Verlauf der $i-t$ -Kurven beobachtet. Bietet also z.B. Ni^{2+} kein geeignetes Beispiel für eine irreversible polarographische Reduktion dar. [P.Zu.]

231 – Polarographic currents at a periodically alternating voltage. II. Theory of currents that are governed by the regeneration of the depolarizer due to a chemical reaction in solution (in German). J. Weber (Inst. of Physical Chemistry, Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 1770; *Chem. Listy*, 52 (1958) 1888. Die Ableitung der Gleichungen für den Momentanstrom für eine Elektrodenreaktion, bei welcher der Depolarisator durch eine chemische Reaktion aus den Elektrolysenprodukten regeneriert wird, wurde beschrieben. Unter der Voraussetzung eines reversiblen Elektrodenvorganges wurde die Berechnung für eine ebene Elektrode, weiter für eine kugelförmige Elektrode mit konstanter Oberfläche, sowie für eine tropfende Elektrode mit wachsender Oberfläche, abgeleitet. Die allgemein gültigen Gleichungen wurden für den Fall einer periodisch gewechselten rechteckigen Spannung spezialisiert. An der kugelförmigen stationären Elektrode ist der Mittelwert des Stromes von der Frequenz der rechteckigen Spannung unabhängig. Die speziellen Fälle, wo in der Lösung

entweder ein starkes Oxydations- oder Reduktionsmittel anwesend ist, wurden diskutiert. [P.Zu.]

232 – Kinetics of the electrode processes of complexes in polarography (in German). J. Koryta (Polarographic Institute, Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 2903; *Chem. Listy*, 52 (1958) 2253.

The method of determination of stability constants of complexes based on the shifts of half-wave potentials has been used so far for reversible systems which show polarographic diffusion currents. The author derived an equation which allows the computation of stability constants from shifts of half-wave potentials of kinetic currents controlled by the rate of a chemical process, provided that the electrode process is reversible:

$$(E_{1/2})_{\text{compl.}} = (E_{1/2})_{\text{Met.}} + RT/nF \ln i_d/i_1 - RT/nF \ln \sum_{j=0}^n k_0 \dots k_j [X]^j$$

Here $(E_{1/2})_{\text{compl.}}$ stands for the half-wave potential of the kinetic current, $(E_{1/2})_{\text{Met.}}$ that of the free metal, i_d for the diffusion current of the complex, i_1 for the kinetic limiting current of the first wave and k_j for the consecutive stability constant. The application of this equation was shown for waves of the cadmium complex with nitrilotriacetic acid (H_3X) in an acetate buffer. At $\mu = 0.1$ at 25° the value $\log K_{\text{Oax}} = 10.14$ was found. At concentrations higher than about $1.0 M$, acetate ion takes part in the complex formation. At higher pH-values, in buffers consisting of NH_3 and NH_4^+ , the complex CdX_2^{4-} is formed and at higher ammonia concentrations complexes of the type $Cd(NH_3)_nX^-$ (for $n = 1$ to 3) are formed. The possibility of formation of hydroxo-complexes and binuclear complexes is excluded. [P.Zu.]

233 – Theory of polarographic currents for a reversible electrode reaction accompanied by the adsorption of the electroinactive compound (in German). J. Koutecký and J. Weber (Institute of Physical Chemistry, Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 25 (1950) 1423.

The theory of polarographic diffusion currents derived for totally irreversible systems (*Z. Elektrochem.*, 63 (1959) 583) can also be applied for reversible systems and for those irreversible systems that are not substantially different from reversible ones. On the $i-t$ curves, showing the dependence of the instantaneous current on the time, an abrupt decrease in the current is observed at the moment when the surface of the mercury drop is covered by the adsorbed substance. Before this time, the curves have the same shape as in the absence of adsorption. For processes where the slowness of the electrode process is manifested by a small over-voltage only, the $i-t$ curves form a peak, decreasing after attaining a certain maximum value of current. The form of this decrease is less steep in the potential region near to the half-wave potentials. For reversible systems, only a decrease of the limiting current on the $i-E$ curves can be anticipated, the half-wave potential remaining constant. On the other hand for irreversible processes both a decrease in the limiting current and a shift of the half-wave potentials towards more negative value can be expected. [P.Zu.]

234 – The interpretation of the E.M.F.'s of cells with transference. M. Spiro (Chem. Dept., Univ. of Melbourne, Australia). *Trans. Faraday Soc.*, 55 (1959) 1207.

The defect in the Kerker concept of a stoichiometric transfer number, that it is a property of the cell rather than the electrolyte and hence varies from cell to cell, was overcome by considering the property of radical or ion constituents instead of an individual ion or the electrolyte as a whole. A general equation is derived relating the tension of a cell with transference to the transference number of an ion constituent in the solution. The equation holds if association and complex-ion formation occur in solution and also if the electrodes are reversible to a complex ion. [M.K.Hus.]

235 – Theory of the glass electrode. IX. The application of the ion-exchange theory to glass electrodes with different metallic functions (in Russian). B. P. Nikolskii, M. M. Schultz and N. V. Peshekhonova (Leningrad, U.S.S.R.). *Zhur. Fiz. Khim.*, 33 (1959) 1922.

The results of an experimental study of a glass electrode made of sodium aluminoborosilicate glass, presented in a previous communication (*Zhur. Fiz. Khim.*, 32 (1958) 19, 262) are discussed from the point of view of the simple ion-exchange theory of the glass electrode. Within the limits of experimental error the theory is confirmed for the case of transition of the glass electrode from the sodium to the potassium and lithium functions. Certain deviations of the experimental facts from theory, in the transition region, concerning exchange of glass sodium ions for solution hydrogen ions may be explained as for the glass ES-I, in accordance with the generalized ion-exchange theory, as being due to the bond energy differences of different groups of hydrogen atoms in the glass.

On the basis of the earlier studies it was impossible to deduce with certainty whether the bond differences between separate groups of ions refer only to hydrogen or also to metallic ions. The results of this work show that the transition of the glass electrode from one metallic electrode function to another obeys the simple ion-exchange theory in the transition region, *i.e.*, in contrast to hydrogen ions all ions of a given alkaline metal in glass are equivalent from any energy standpoint. [Ot.So.]

See also abstracts nos. 289, 293, 294, 431, 432, 438.

2. Apparatus and accessories

236 – Automatic compensation of errors, resulting in the measurement of polarographic currents due to a change in the resistance of a system (in German). J. Peizker (Polarograph. Inst., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 2405. A photoelectric compensator, enabling the potential of the reference electrode to be kept constant even when currents are flowing through the electrolytic cell for a long time has been designed. Such a device is important mainly in continuous analysis of industrial floating systems in which substantial changes in the resistance of the liquid to be analyzed cannot be excluded. A three-electrode system is used, in which the reference electrode is kept under conditions where there is no flow of current, using an electrode, the potential of which is regulated by the photocompensator. This device has been successfully applied with mercury dropping electrodes as well as with other types of electrodes. The circuits for measurement of small and large currents are given, together with a detailed circuit of the photocompensator. [P.Zu.]

237 – Polarograph with a new device for the recording of polarographic currents (in German). J. Peizker (Polarograph. Inst., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 2416; *Chem. Listy*, 52 (1958) 2195. The pen-recording polarograph with an electronic coordinatograph, designed originally by J. Ezr, has been improved. By including a photoelectric compensator in the circuit the electronic polarograph has been made to register true polarographic current-potential curves, even for a small area of the reference electrode and with high resistances in the polarographic circuit. It was thus possible to eliminate deformations in the recorded curves caused by the large resistance in Ezr's original apparatus. The curves registered with the modified apparatus were analogous to those obtained with a periodically damped galvanometer with a long swing period. All other advantages of Ezr's apparatus, *i.e.*, direct recording, elimination of the possibility of bad contacts in the precision potentiometer, etc.) remain unaffected. The photocompensation device can be applied successfully for improving other types of recording polarographs. The compensator can also be used separately as a potentiostat. [P.Zu.]

238 – On the impedance of galvanic cells (in English). J. H. Sluyters (Laboratory of Analytical Chemistry, State University, Utrecht, The Netherlands). *Thesis*, State University of Utrecht, 1959. A sinusoidal alternating current of constant amplitude and with a frequency ranging from 20–20,000 cycles/sec, is led through an electrolytic cell. A phase-sensitive voltmeter resolves the signal across the cell into its real and imaginary components, Z' and Z'' resp., which are directly and simultaneously readable on two meters.

It is shown, that at high frequencies of varying frequency ω , the rate constant of an electrode reaction, the ohmic resistance of the cell and the capacitance of the electrical double layer can be obtained from a plot of Z' against $\omega Z''$, provided the electrode reaction is not too fast. At low frequencies the cell impedance plotted in the complex plane yields a straight line of 45° slope, from which information can be gained both on the reaction rate constant and the diffusion coefficients of the reacting ions.

The theory is tested for the Hg–Hg₂²⁺ electrode in 1 M HClO₄ and the zinc amalgam–Zn²⁺ electrode in a base electrolyte consisting of 1 M NaClO₄ and 10⁻³ M HClO₄ at 25°. It was found, that for the Hg–Hg₂²⁺ electrode the reaction rate constant is too large to be measured with this technique. However, data on the diffusion coefficient of the Hg₂²⁺ ion could be obtained. For the zinc amalgam–Zn²⁺ electrode, the reaction rate constant, the transfer coefficient and the capacity of the double layer were calculated.

If the cell admittance is plotted in the complex plane it is shown that the influence of the double-layer capacity and the ohmic resistance in a.c. polarography can be accounted for in an easy way. The choice of the optimal frequency in a.c. polarography is discussed and experimental verification is given.

Finally the impedance of a galvanic cell with two plane parallel electrodes at a short distance is calculated. The result contains Randles' theory of electrode impedance as a special case and it is concluded that the contributions of both diffusion polarisation and ohmic resistance to the cell impedance become small at a very small electrode distance. A preliminary experimental verification was unsuccessful. [F.Vor.]

239 - Application of electrographic sampling in line-oven paper chromatography (in Hungarian).

A. Biró (Univ. Szeged, Hungary). *Magyar Kém. Folyóirat*, 66 (1960) 285.

For the investigation of metals, metal coverings and alloys a simple, easy-to-handle, portable electrographic sampling apparatus is described, with which sufficient samples may be taken in a few seconds for line-oven micro-analysis without any considerable damage of the material to be analysed. The apparatus consists of a plastic box, which contains a dry cell and a moving piston, and a separate needle electrode. The piston serves as a contact between the test materials and the anodic electrode. [Ja.Inc.]

240 - Simple and inexpensive polarograph cell. J. L. Moukman (Dept. of Natl. Health and Welfare, Ottawa, Canada). *Anal. Chem.*, 31 (1959) 1445.

A polarograph cell of borosilicate glass is described for use with a mercury pool anode. The total capacity is of the order of 5 ml. [Kl.Gr.]

241 - Controlled potential and derivative polarograph. M. T. Kelley, H. C. Jones and D. I. Fisher

(Anal. Chem. Div., Oak Ridge Natl. Lab., Oak Ridge, Tenn., U.S.A.). *Anal. Chem.*, 31 (1959) 1474.

Exact construction details of an apparatus for controlled and derivative polarography are given, especially suitable for high resistance media or for high currents in aqueous media. The $I-R$ drop is electronically corrected. The polarograph can be used for the analysis of reversible species as well as for irreversible ones at very low concentrations. The instantaneous currents, successive peak currents, successive average currents and derivative polarograms are recorded. Typical polarograms of the different species obtained with this apparatus are given. [Kl.Gr.]

242 - Determining serum protein gravimetrically after agar electrophoresis. R. D. Strickland, P. A.

Mack, F. T. Gurule, T. R. Podleski, O. Salome and W. A. Childs (Research Div., Veterans Adm. Hospital, Albuquerque, N. Mex., U.S.A.). *Anal. Chem.*, 31 (1959) 1410.

An apparatus for electrophoresis in agar and a micromethod for estimation of proteins gravimetrically has been developed. 11 protein compounds in human serum are determined. The construction and use of the electrophoresis apparatus is described. The separations are obtained in diethyl barbiturate buffer of 0.1 ionic strength at pH 8.6 with agar by applying a 2.5 V/cm potential gradient for 24 h. [Kl.Gr.]

243 - Stable apparatus for high-frequency analysis. K. Ishii, Sh. Hayashi and Sh. Fujiwara (Japanese Telegraph and Telephone Public Corp., Aoichō Minatoku, Tokyo, Japan). *Anal. Chem.*, 31 (1959) 1586.

Photochemical reactions in living leaves are studied by means of high frequency analysis. Construction details and wiring diagram of the apparatus are given. Shift of the tuning frequency is interpreted mathematically as a function of the dielectric and the resistive characters of the sample contained in the condenser of the tuning circuit. [Kl.Gr.]

244 - pH-measurements in strongly alkaline solutions at temperatures above 100°C (in German).

W. Vielstich (Institut für physikalische Chemie, Universität Bonn, Deutschland). *Z. Instrumentenk.*, 67 (1959) 154.

Glass electrodes are poorly suited for strongly alkaline solutions at higher temperatures. Even the hydrogen electrode has some disadvantages especially in respect of bad reversibility and long time of adjustment. In accordance with the tests carried out, Raney-nickel shows good reversible tensions depending upon the pH of the solution. Some hints on constructing the electrodes are given. Their properties are discussed by means of several diagrams. [Fr.Oe.]

245 - Technical questions in measuring pH (in German). U. Fritze (Farbenfabriken Bayer, Leverkusen, Deutschland). *Z. Instrumentenk.*, 67 (1959) 139.

A short discussion of the general and correct conception of pH is given. The impossibility of determining pH on the basis of thermodynamic calculations is pointed out here. This applies especially for non-aqueous solutions. For aqueous solutions a conventional set of standard buffers has been developed. Furthermore the electrical properties of a typical electrode assembly are briefly considered. A comparison is given of the different types of measuring- and reference-electrodes. Finally pH-meters are discussed. Examples are given in some detail of a number of industrial manufactured measuring devices. [Fr.Oe.]

246 – Lead dioxide electrode in acid–base titrations. I. M. Issa and A. A. Abdul Azim (Chem. Dept. Faculty of Science, Cairo Univ., Egypt). *Egypt. J. Chem.*, 2 (1959) 67.
An electrochemical study with PbO_2 electrodes prepared by electrodeposition from strongly acidic, weakly acidic and alkaline solutions was made. The E_h -pH curves obtained manifest two linear relations in the acid and alkaline ranges. E^0 values amounting to 1.45–1.50 and 1.55–1.63 V in the acid and alkaline solutions respectively, reveal that the electrode behaves in acid solutions as a $\text{PbO}_2/\text{Pb}^{2+}$ electrode. It is shown that a PbO_2 electrode prepared from alkaline solutions and washed in 0.1 M NaOH is suitable for acid–base titrations. [M.K.Hus.]

247 – Multilayer membrane electrodes. II. Preparation and use in double concentration cells. Harry P. Gregor and Harold Schonhorn (Dept. of Chemistry of the Polytechnic Institute of Brooklyn, U.S.A.). *J. Am. Chem. Soc.*, 81 (1959) 3911.
Es wird der Bau und die Verwendung einer Membranelektrode mit spezifischer Wirksamkeit für Erdalkalitionen beschrieben. Die Elektroden besitzen bei einer Fläche von $2 \text{ cm} \times 2500 \text{ \AA}$ ohm'sche Widerstände von 20 bis $60 \cdot 10^6 \Omega$, der spezifische Widerstand beträgt $2 \cdot 10^4 \Omega \text{ cm}$. Messungen mit verschiedenen konzentrierten Ca(II) -, Ba(II) - und Fe(III) -Salzen ergaben eine ideale Ionenselektivität für die betreffenden Kationen innerhalb des Ionenstärkebereichs von $3 \cdot 10^{-4}$ bis 15. [Ha.Re.]

248 – Application of the potentiostatic method to electrode processes with fast coupled chemical reaction. Kinetics of dissociation of monochloroacetic acid. Paul Delahay and Syotaro Oka (Coates Chemical Laboratory, Louisiana State University, U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 329.
Die der Ladungsüberführung in sogenannten „Kinetischen Prozessen“ vorausgehende chemische Reaktion wird mit Hilfe einer neuen potentiostatischen Methode untersucht. Auch solche Reaktionen, die für polarographische Messungen zu schnell ablaufen werden erfasst, die Strom-Zeit-Kurven werden mit Hilfe eines elektronischen Potentiostaten und eines Oszillographen, im Grenzstrombereich registriert. Geschwindigkeitskonstanten lassen sich aus den $i_d^{1/2} - t^{1/2}$ -Diagramm berechnen. Die Kinetik der Dissoziation der Monochloressigsäure in 50%-igen Äthanol-Wasser-Mischungen und einer Ionenstärke von 1 wurde nach dieser Methode näher untersucht. Für 25° wird für die Dissoziation eine Geschwindigkeitskonstante von $1.8 \pm 0.5 \cdot 10^6 \text{ sec}^{-1}$, und für die Rekombination $1.3 \pm 0.3 \cdot 10^{10} \text{ l. mol}^{-1} \text{ sec}^{-1}$, angegeben. [Ha.Re.]

249 – Graphite electrodes for zone electrophoresis. B. Paletta (Inst. med. Chem., Univ. Graz, Austria). *Angew. Chem.*, 72 (1960) 138.
Bei elektrophoretischen Arbeiten muss man den Messraum von unerwünschten Elektrolyseprodukten durch Zwischenschaltung verschiedenartigster Labyrinthensysteme abschirmen. Es wurde versucht mit einem Graphitelektrodensystem die starke Adsorptionsfähigkeit des Graphit-Pulvers zum Unschädlichmachen der Elektrodenverunreinigungen auszuwerten: Graphit-Pulver wird in ein Plexiglas-Kästchen gefüllt, welches nach einer Seite zu eine mit Cellophan-Haut überzogene Öffnung besitzt. Ein kompakter Plexi-Block mit einem eingesetztem Platinstift bildet eine Brücke zwischen dem Graphit-Pulver und den stromführenden Drähten. Das Kästchen taucht bis zum oberen Rand der Öffnung in den Puffer-Lösung ein, so dass Elektrolysenprodukte im Augenblick ihres Entstehens vom Pulver abgefangen werden. Das Graphit-Pulver kann mehrmals verwendet werden. [Ja.Inc.]

250 – Sur un appareillage de microtitrimétrie et ses applications. R. Berret (Centre de Recherches, Roussel-Uclaf). *Bull. soc. chim. France*, (1960) 271.
Description d'un appareillage de microtitrimétrie permettant d'effectuer des dosages, en présence d'indicateur ou par voie électrochimique, potentiométrie ou ampérométrie, sur des prises d'essais voisines de 2 mg par réduction des techniques classiques déjà éprouvées à des échelles pondérales supérieures. Des adaptations simples ont été, en particulier, réalisées dans le domaine des micro-indices fonctionnels (alcools, dérivés carbonylés, esters). [Bad.Lam.]

See also abstracts nos. 270, 278, 295, 299, 308, 318, 319, 359, 382, 385, 391, 414, 430, 436.

3. Polarography

251 – Rapid methods for analysis of metals and mineral raw materials. V. Polarographic determination of copper and bismuth in mineral raw materials and in iron (in German). J. Doležal and J. Novák (Inst. Anal. Chem., Charles University, Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 51; *Chem. Listy*, 52 (1959) 36.

Ein Eisenüberschuss kann bei der Kupferbestimmung mit Natriumhypophosphit reduziert werden. In 2 N HCl verläuft die Reduktion von 0.5 M FeCl₃ quantitativ nach dreiminütigem Kochen der Lösung in Anwesenheit von $1 \cdot 10^{-4}$ M Hg(NO₃)₂ als Katalysator. Mit Hilfe der polarographischen Reduktionsstufe, die der Reduktion des einwertigen Kupfers zu metallischen Kupfer entspricht, kann in 2 M HCl mit 0.5 M NaH₂PO₂ noch $5 \cdot 10^{-4}$ M Cu neben einem 10,000 fachen Überschuss von Eisen bestimmt werden. Bi und Pb können gleichzeitig bestimmt werden, falls sie nicht im Überschuss über Cu stehen. Mo und Ti stören, As jedoch nicht. Die Methode wurde zur Bestimmung von Kupfer in Erzen angewandt. [P.Zu.]

252 – Polarographic depolarization effects of thorium ions and of some other hydrolyzable cations (in German). J. Mašek (Polarograph. Inst., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 159; *Chem. Listy*, 52 (1958) 7.

In unbuffered solutions of potassium chloride three irreversible waves appear in the presence of thorium (IV). After addition of ethanol the third wave vanishes and addition of methylene blue causes a shift of the first wave to more positive potentials. The limiting current of the first and second waves is influenced by the rate of the chemical reaction. Addition of a hydroxide eliminates all three waves and acidification causes an increase in the first and a decrease in the third wave. No reduction wave was observed in buffered solutions. It has been proved that all three reduction waves correspond to the reduction of hydrogen ions originating from the aquocomplexes of thorium, and not to the electroreduction of the thorium ion to the metal state. In the first wave reduced protons are formed by hydrolysis of [Th(H₂O)_a]⁴⁺, in the second wave from another complex, and in the third, protons originate from [Th(H₂O)_{a-1}OH]³⁺. The relative amount of the last-mentioned complex is decreased by the addition of acid or alcohol. The behaviour of Al(III), Zr(IV) and Be(II) in aqueous and ethanolic solutions can be interpreted similarly. [P.Zu.]

253 – Potentiometric and polarometric titrations with tetraphenylborides. I. Argentometric determinations (in German). A. Heyrovský (Lab. of II. Dept. for Internal Medicine, Charles Univ., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 170; *Chem. Listy*, 52 (1958) 40.

Solutions of tetraphenylboranate can be titrated against a silver nitrate volumetric solution with formation of an insoluble compound Ag[B(C₆H₅)₄]. This reaction can be applied in both polarometric and potentiometric titrations. The volumetric determination can be performed over a wide range of pH and it is not influenced by the presence of acetone. The titrimetric method can be applied for indirect determinations of K⁺, NH₄⁺, Rb⁺, Cs⁺, Tl⁺ and of organic bases. After precipitation with a surplus of tetraphenylboranate it is possible to isolate the precipitate, dissolve it in acetone and titrate. It is also possible to determine directly the surplus of the tetraphenylboranate reagent by titration with a standard solution of AgNO₃. [P.Zu.]

254 – Relationship between the electronic structure and the polarographic behaviour of inorganic depolarizers. IV. Electrode processes in which the (n-2)f electrons participate (in German). A. A. Vlček (Polarograph. Inst., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 181; *Chem. Listy*, 52 (1958) 214.

Die Oxydation der Eu(II)-Ionen verläuft bei positiveren Potentialen als die Reduktion der Eu(III)-Ionen, also irreversibel. Der Unterschied der Halbstufenpotentiale der kathodischen und anodischen Stufen sowie die Steilheit der Stufen ist von der Zusammensetzung des Grundelektrolyten abhängig. Nur in den Lösungen der Äthylendiamintetraessigsäure ist es möglich eine reversible Stufe zu erhalten. Mit steigender Konzentration und Deformierbarkeit der Halogenide des Grundelektrolyten nähern sich die Halbstufenpotentiale der anodischen und kathodischen Stufe. Auch wenn nur eine Stufe ersichtlich ist, entspricht jedoch ihre Steilheit nicht der theoretischen. Beim Grenzstrom ist der Strom durch Diffusion bedingt, bei den Stufenfern besitzt der Strom jedoch einen kinetischen Charakter. Mit wachsender Tropfzeit verschiebt sich das Halbstufenpotential der kathodischen Stufe zu positiveren, das der anodischen zu negativeren Werten. Auch eine Temperaturänderung und Gelatinezusatz beeinflusst stärker die kathodische sowie auch die anodische Stufe. Der kathodische Prozess verläuft mit einem anderen Mechanismus als der anodische. Bei der Reduktion von Eu(III) entstehen zwei Formen von Eu(II) durch zwei parallele Mechanismen deren relativer Beitrag von der Elektrolytkonzentration und der Temperatur abhängig ist. Die Oxydation verläuft dagegen mit einem einfachen Mechanismus. Es wurde ein Reduktionsschema vorgeschlagen, in dem die Existenz des Ions Eu(II) in angeregtem Zustand angenommen wird. [P.Zu.]

255 – Polarographic reduction of trans-urocanic acid (in German). J. Kůta and E. Krejčí (Polarograph. Inst., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 258; *Chem. Listy*, 51 (1957) 2225.

Trans-urocanic (imidazol acrylic) acid is reduced polarographically over the pH range from 0 to 9

with consumption of two electrons, most probably in the double bond in the side-chain. The height of the reduction wave decreases with increasing pH, to give three successive steps in the form of a dissociation curve, the wave of the less protonized form being always at a more negative potential than that corresponding to the conjugate acid. The following values of pK' (corresponding to pH, when the heights of the waves of the acid and conjugated base are identical) were determined: $pK_1' = 5.6$ (in a veronal-acetate buffer), $pK_1 = 5.85$ (in a phosphate buffer); $pK_2' = 7.1$ (in a veronal-acetate buffer), $pK_2 = 7.35$ (in phosphate and Britton-Robinson buffer); $pK_3' = 8.5$ (in veronal-acetate buffer with 0.1 M $CaCl_2$). At higher pH values a decrease in the wave-height with time was observed (about 10% during one hour). The irreversibility of the electroreduction was proved using the curves $dE/dt - E$ and the commutator method according to Kalousek. The first dissociation curve was ascribed to the reduction and recombination of the cation, the second to the free acid and the third to the univalent anion. The second and third dissociation curves had the shapes required by the theory for dibasic acids. [P.Zu.]

256 - Polarographic determination of lead (in German). D. Weiss (Institute for Research of Ores, Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 282; *Chem. Listy*, 52 (1958) 1814.

0.5 bis 1.0 g des Erzes werden in 30 ml HCl erhitzt. Nach 5 Minuten fügt man 0.5 g $KClO_3$ hinzu und kocht weitere 3 Minuten. Falls Zinn anwesend ist, muss nach Zugabe weiterer Portionen von HCl und $KClO_3$ die Lösung bis zur Trockne abgedampft werden. Nach Zugabe von 10 ml konzentrierter HCl wird die Lösung bei 80° bis auf 10 ml eingeeengt. Nach Zugabe von 40–50 ml HCl (3:2) digeriert man den Rückstand 15 Minuten bei 90° und führt in einen 100 bis 500 ml Messkolben über. Man fügt soviel HCl (3:2) zu, dass das Kölbchen bis zu $3/4$ gefüllt ist; weiter 0.5 bis 1.0 ml gesättigter $HgCl_2$ Lösung, 5–10 ml 50%-ige Natrium Hypophosphit (Na_2HPO_3) Lösung und erhitzt bis sich die Lösung klärt. Nach Zugabe von $NaHCO_3$ lässt man das verschlossene Kölbchen 15 Minuten stehen. Nach Temperierung fügt man noch einmal festes Natriumbicarbonat und 5–10 ml 1%-iger Gelatinelösung hinzu, füllt zur Marke auf und verschliesst gut. Nach ein- bis zweistündigem Stehen wird die klare Lösung nach Beseitigung des Luftsauerstoffes polarographiert und die Bleistufe gemessen. Die Auswertung erfolgt durch Vergleich mit eine Probe von bekanntem Bleigehalt. [P.Zu.]

257 - Nitrosamines of secondary amines. III. A spectroscopic and polarographic study (in German). R. Zahradník, E. Svátek and M. Chvapil (Inst. Industr. Hygiene and Occup. Dis., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 347; *Chem. Listy*, 51 (1957) 2232. Polarographic curves and absorption i.r. and u.v.-spectra of nitrosamines derived from pyrrolidine, proline and oxyproline were recorded and discussed. A four-electron wave was observed at lower pH values, which was ascribed to the reduction of the protonized form of N-nitrosamine. The height of this wave decreased with increasing pH value in the form of a dissociation curve. At higher pH values a two-electron reduction wave was observed. The height and the half-wave potential of this wave is pH independent. The decrease of the height of the four-electron wave is due to the change of rate of recombination. This decrease is dependent on the kind of buffer used, so that participation of other proton donors as well as H_3O^+ is assumed. The product of the four-electron reduction is a hydrazine derivative, in the two-electron reduction process the splitting of the N–N bond occurs. The following values of half-wave potentials for the pH-independent two-electron wave were measured in 0.1 N NaOH (vs. S.C.E.): dimethylnitrosamine, -1.64 V; diethylnitrosamine, -1.67 V; diphenylnitrosamine, -1.16 V; N-nitroso pyrrolidine, -1.53 V; N-nitroso proline, -1.72 V; N-nitroso oxyproline, -1.75 V; N-nitrosopiperidine, -1.43 V; N-nitroso-morpholine, -1.32 V. pK-Values of N-nitrosamines were determined from the u.v. spectra. [P.Zu.]

258 - Polarographic behaviour of 4-amino-4'-methoxy-diphenylamine (Variaminblue) (in German). E. Bányai and P. Zuman (Polarograph. Inst., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem-Commun.*, 24 (1959) 522.

4-Amino-4'-methoxydiphenylamine is oxidized polarographically reversibly to quinone-*p*-anisil-diimine. This was shown by the wave-form, by the correspondence of the polarographic half-wave potentials with potentiometrically estimated redox-potentials, by the pH-dependence of the half-wave potentials as well as by the coincidence of the half-wave potentials of the oxidized and reduced forms. The oxidation was performed by potassium chromate or ferricyanide, or by oxygen in 1 N OH. The oxidation products were identified spectrophotometrically. The quinonediimine formed in this way undergoes a hydrolytic cleavage, shown by the formation of a wave for quinone-imine given at more negative potentials. The formation of semiquinones could not be proved, since in acid solution where it was described earlier the polarographic anodic wave was already masked by the current corresponding to the dissolution of mercury. [P.Zu.]

259 - Polarography of ferrocenmonoaldehyde (in English). P. Vrubleovský, R. Kubiček and F.

Šantavý (Chem. Inst., Faculty of Medicine, Palacký's University, Olomouc, Czechoslovakia) *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 645; *Chem. Listy*, 52 (1958) 974.

The polarographic waves of ferrocenmonoaldehyde were registered at various pH values. In acid solutions a single one-electron wave was observed, accompanied by an adsorption pre-wave. In less acid solutions another one-electron wave appears. The height of these waves decreases with increasing pH value in the form of a dissociation curve. At higher pH values a single two-electron wave was observed. The height of this decreases at pH higher than about 9 with increasing pH values. [P.Zu.]

260 - Polarographic current, controlled by the dissociation of an electroinactive species with formation of an electroactive and an electroinactive substance (in German). J. Čížek, J. Koryta and J. Koutecký (Inst. Phys. Chem., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 663.

The polarographic currents at any particular moment and also at limiting values were calculated for a system in which only the complex is present in the electrolysed solution in the absence of an excess of the complex-forming reagent. The complex B decomposes into the electroinactive complex-forming reagent (C) and into the electroactive metal ion (B) according to the equation: $B \rightleftharpoons C + A \xrightarrow{e} \text{products}$. The values of the quotient i/i_a calculated using the rigorous treatment were compared with values obtained using the approximate theory. The theoretical treatment was verified using the example of the reduction waves in solutions of the complex formed between nitrilotriacetic acid and Cd^{2+} ion (in the absence of an excess of nitrilotriacetic acid). Two waves are observed on the polarographic curves. The more positive wave corresponds to the reduction of the free metal ion, and the more negative to the irreversible reduction of the 1 : 1 complex. The total height is diffusion-controlled, the height of the more positive wave being limited by the rate of formation of the free metal ion, formed by the decomposition of the complex. The equilibrium in the solution is not completely shifted in favour of the complex particle. [P.Zu.]

261 - Kinetics of electrode processes. XVII. A simultaneous reversible and irreversible electron transfer at the dropping mercury electrode (in German). K. Micka (Polarograph. Inst., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 678; *Chem. Listy*, 52 (1958) 228.

The mathematical treatment of polarographic currents is given for a system in which the depolarizer is reduced (or oxidized) simultaneously by two routes, one of them being reversible and the other irreversible. Conditions are given under which such a process may occur. Chemical reaction of the products is considered. [P.Zu.]

262 - Application of the steady (hanging) mercury drop electrode for the study of electrode processes and for the identification of the electroactive products (in German). V. Cermák (Inst. Phys. Chem., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 831; *Chem. Listy*, 52 (1958) 413.

An eine polarographische Kapillare von innerem Durchmesser von 0.08 bis 0.09 mm wurde ein Glashahn angeschmolzen. Nach schliessen des Hahnes entstand eine ruhende Tropfenelektrode. Bei der Polarisierung durch eine anwachsende negative Spannung bis zu einem gewissen Wert und wieder zurück zu positiven Werten bzw. nach einer Vorpolarisation und nachfolgender Polarisierung mit veränderlicher Spannung wurden Kurven erhalten, welche charakteristische Stromspitzen aufweisen. Der Kurvenverlauf für diffusionsbedingte Ströme bei reversiblen Redoxsystemen, bei reversibler Amalgambildung, bei irreversiblen Reduktionsvorgängen sowie für einen Adsorptionsstrom wurden angegeben. Bei kinetischen Strömen entstehen keine Erschöpfungsspitzen. Die Methode wurde zur Aufklärung der Elektrodenvorgänge bei der Reduktion von Schwefeldioxyd und verwandten Verbindungen angewandt. Der Einfluss von Erschöpfungerscheinungen, wie z.B. die pH-Veränderung in der Elektrodenumgebung, wurden verfolgt. Die quantitativen Messungen an der ruhenden Tropfenelektrode sind durch Konvektionsströme, Änderungen des pH-Wertes an der Elektrode, Veränderungen der Elektrodenoberfläche (Filmbildung) und durch schwierige Reproduzierbarkeit der Elektrodenoberfläche kompliziert. [P.Zu.]

263 - A contribution to the polarographic study of stipitatic and puberulic acid (in German). F. Šantavý, B. Jámor and J. Domankos (Chem. Inst., Faculty of Medicine, Palacký's Univ., Olomouc, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 896; *Chem. Listy*, 52 (1958) 419.

Polarographic curves of stipitatic and puberulic acid were registered in buffers both in the presence and absence of boric acid over a wide range of pH-values. Changes were observed on the curves showing that several forms, having different numbers of protons, were involved. The dissociation of the OH-group was assumed; the strongly phenolic character of the OH-groups was interpreted as being due to the aromatic character of the seven-membered ring. [P.Zu.]

264 – Polarography of pterines. I. 2-Amino-4-hydroxy-6-methylpteridine (in German). J. Komenda (Inst. Phys. Chem., Faculty of Science, Masaryk University, Brno, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 903; *Chem. Listy*, 52 (1958) 1065.

6-Methylpterine (2-amino-4-hydroxy-6-methylpteridine) is reduced at the dropping mercury electrode and gives one two-electron wave on the polarographic curves. The height of this wave decreases at pH above 9 in the form of a dissociation curve with increasing pH value. Simultaneously a new wave is observed at more negative potentials. The total height of both waves remains constant. The value $k = 3 \cdot 10^{13} \text{ l mol}^{-1} \text{ sec}^{-1}$ was computed for the rate constant of the recombination reaction. In the medium pH range a decrease of the wave height was observed due to decrease in the solubility. Using the commutator method of Kalousek one cathodic-anodic wave was obtained in acid media. This would suggest that the process is reversible, but the slope of this wave does not correspond to the thermodynamic one. On the oscillographic $dE/dt-E$ curves depressions in the cathodic and anodic branch were observed at similar potentials. The reduction takes place in the pyrazine ring; this was proved by spectrophotometry of the reduction products. In solutions of lower pH values another wave occurs in the polarographic curves, the height of which is partially controlled by the rate of chemical reaction. Using the absorption spectra the dissociation of 6-methylpterine was studied and the constitution of the single dissociation forms discussed.

[P.Zu.]

265 – Carbamates, monothiocarbamates and dithiocarbamates. VIII. Polarographic study of the kinetics and mechanism of the cleavage of dithiocabamic acids in acid media (in German). R. Zahradník and P. Zuman (Polarograph. Inst., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 1132; *Chem. Listy*, 52 (1958) 231.

The polarographic anodic waves for dithiocarbamate, corresponding to the formation of a sparsely-soluble mercury salt, were used for the analyses of reaction mixtures in the kinetic study of the decomposition of dithiocarbamates in acid media. 1 ml of the acid reaction mixture was added to 4 ml 0.1 M sodium acetate. The resulting solution had a pH of 5.5. The mechanism of the decomposition reaction is discussed.

[P.Zu.]

266 – Polarographic behaviour of folic acid and some of its degradation products (in German). O. Hdrý (State Inst. for Control of Drugs, Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 1180; *Chem. Listy*, 52 (1958) 1058.

Folic acid is reduced in one two-electron wave at low pH values. At above 11 two waves appear, the more positive decreasing with increasing pH in the shape of a dissociation curve. The value of the pK' (i.e., pH value at which the heights of both waves are identical) is dependent on the buffer composition, so that as well as protons, other acids are also involved in the recombination reaction. In acid solutions two waves appear at more negative potentials, probably caused by catalytic hydrogen evolution. 2-Amino-4-hydroxy-6-pterinealdehyde is reduced in two waves. The first wave is accompanied by a low concentration independent wave ascribed to the adsorption of the oxidized form of the depolarizer. However, the two main waves are not strictly linear-dependent on the concentration of pterinealdehyde. The more positive wave was ascribed to the reduction of the pterine ring, the more negative one to the reduction of the carbonyl grouping. 2-Amino-4-hydroxy-pterine carboxylic acid is reduced in one wave, the shape of which is deformed by recombination between pH 11 and 12. The wave for the acid and base forms are not separated, although the slope of the wave is less. Reduction of the acid forms the dihydroderivative. The formation of pterine alcohol was investigated and the possibility of the analysis of folic acid and its degradation products discussed.

[P.Zu.]

267 – The application of oscillographic polarography in quantitative analysis. IX. Detection and determination of rhodium in the presence of platinum, palladium and gold (in German). P. Beran and J. Doležal (Inst. Anal. Chem., Charles University, Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 1341; *Chem. Listy*, 52 (1958) 2403.

In solutions of 0.1 M HCl and 0.6 M NaCl in the presence of rhodium ions, typical "thorns" are observed on the anodic part of the oscillographic $dE/dt-E$ curves. This effect is probably due to catalytic evolution of hydrogen. It was observed in the presence of 0.02% Rh in platinum metal and of 0.005% Rh in alloys of gold and palladium. The height of the "thorn" shows a linear dependence on the concentration of Rh between 0.25 and 12.5 μg in 10 ml of the electrolysed solution. The determination is carried out using a calibration curve. In the presence of Pt, Pd or Au the method of standard addition is to be preferred, as the presence of these metals influences the height of the "thorn".

[P.Zu.]

268 – Polarometric titration of thorium by Berillon (in German). J. Mašek (Polarograph. Inst., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 1343; *Chem. Listy*, 52 (1958) 740.

At pH 2, Berillon (sodium salt of 8-hydroxynaphthalene-3,6-disulpho-(1-azo-2')-1',8'-dihydroxynaphthalene-3',6'-disulphonic acid) shows a well-developed reduction wave at -0.20 V (S.C.E.). Metals that form coloured compounds with Berillon have no influence on the polarographic and oscillographic curves of Berillon. This is proof that in the formation of the complex the hydroxy groups (and possibly the sulpho groups) are involved but not the nitrogens of the azo group. Thorium(IV) on the other hand at pH 2 forms an insoluble precipitate with Berillon. This was used in polarometric titrations, in which the decrease in the Berillon wave was measured after addition of the analysed thorium solution until the equivalence-point was reached. 0.1 M to 0.01 M solutions of thorium(IV) salts were titrated at pH 2 using an applied potential of -0.8 V (S.C.E.). Equilibrium is attained in a stirred solution after two minutes. Zr(IV) ions and trivalent ions of the rare earths interfere. [P.Zu.]

269 – Polarographic study of the decomposition of narcotoline (in German). J. Holubek and J. Volke (Polarograph. Inst., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 1436; *Chem. Listy*, 52 (1958) 589.

Durch Spaltung des Narcotolins in 1 N Na_2CO_3 entsteht Cotarnolin, bei welchem mit Hilfe der polarographischen Methode bewiesen wurde, dass es sich um einen substituierten *o*-Oxybenzaldehyd handelt. Die Reduktion des Cotarnolins verläuft bei pH kleiner als 9 in einer zwei elektronigen Stufe. Bei höheren pH-Werten wurde eine Dissoziation der phenolischen Gruppe und eine nachfolgende Abnahme der Stufenhöhe – bis zu einer Einelektronenreduktion – gefunden. Der Unterschied zwischen der Spaltung des Narcotins und Narcotolins wurde diskutiert. Die Bildung der Ammoniumform des Cotarnolins in sauren Lösungen kann nicht ausgeschlossen werden. Nach Spaltung in ammoniakalischem Medium kann Narcotolin mit Hilfe der Cotarnolinstufe neben allen wichtigeren Opium-alkaloiden bestimmt werden. Die Bestimmung wird durch Narcein gestört, sein Gehalt kann jedoch vor der Spaltung des Narcotolins bestimmt werden. Die Menge des Narcotolins kann dann aus dem Unterschied der Höhe der Narceinstufe und der Gesamthöhe nach der ammoniakalischen Spaltung bestimmt werden. [P.Zu.]

270 – Measurements of average polarographic currents using a moving coil galvanometer (in German). J. Němec (Laboratorní přístroje, Research and Development, Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 1708; *Chem. Listy*, 52 (1958) 330.

A rigorous method is presented for the calculation of the average value of a polarographic current from oscillations, using an arbitrary dependence of the momentaneous current on time ($i-t$ curves) in a moving coil galvanometer. The average values can be obtained by drawing a line crossing the oscillations in such a way that the areas covered by the oscillations above and below the line were equal. The values estimated in this manner differ from those obtained in the usual manner (as the arithmetic mean value of the oscillations) only for curves with big and asymmetric oscillations, when the difference may be 3%. The conditions for the best choice of galvanometer sensitivity were given. [P.Zu.]

271 – Polarographic determination of tin in ores in the presence of lead (in German). D. Weiss (Institute for Research on Ores, Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 1715; *Chem. Listy*, 52 (1958) 1817.

0.5 g bis 2.5 g Erzes werden alkalisch mit Schwefel geschmolzen, mit Wasser ausgelaugt und alkalisiert. Die Lösung wird abfiltriert, wobei Zinn als Thiosalz quantitativ in das Filtrat übergeht. Nach dem Alkalisieren werden sulfidische Verbindungen mit H_2O_2 zu Sulfaten oxidiert, wobei Zinn ins alkalische Stannat übergeht. Nach Zerstörung des Wasserstoffperoxyds wird die Lösung mit HCl versetzt, bis ihre Konzentration 6 N beträgt. Nach nachfolgender Reduktion mit Eisen und Hypophosphit wird die Stufe des Zinns registriert. Wolfram und Vanad stören in Überschuss, Germanium stört, ist jedoch selten vorhanden. Arsen stört nicht. [P.Zu.]

272 – The application of amino acids in polarography of inorganic compounds. VII. Polarographic determination of copper and iron in nickel and aluminium and their salts (in German). J. Doležal and J. Novák (Inst. Anal. Chem., Charles Univ., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 1718; *Chem. Listy*, 52 (1958) 1353.

0.5 g der Nickel-Probe (bei Kupfergehalt grösser als 1% und Eisengehalt grösser als 2%) bzw. $4-5$ g der Probe (für kleinere Mengen) werden in Salpetersäure gelöst und auf 100 ml aufgefüllt. Zu 5 ml dieser Lösung fügt man 10 ml 2 M Äthylendiamintartrat und 2 ml 1 M $\text{K}_4\text{P}_2\text{O}_7$ hinzu, versetzt mit NaOH (stellt pH auf ca. 6 auf) und füllt zu 25 ml auf. Die Auswertung erfolgt mit Hilfe der Methode der Standardzugabe. Bei Aluminiumanalysen sind Einwägen von 1.2 bis 1.4 g am geeignetsten falls der Gehalt höher als 0.5% Cu bzw. 1% Fe ist. [P.Zu.]

273 – Relation between electronic structure and polarographic behaviour of an inorganic depolarizer. V. Cobalt carbonyl (in German). A. A. Vlček (Polarograph. Inst., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 1748; *Chem. listy*, 52 (1958) 1460.

Cobalt carbonyl, $\text{Co}_2(\text{CO})_8$, in an ethanolic saturated solution of lithium chloride at 2° shows a reduction wave with a half-wave potential of -0.35 V (S.C.E.). At higher temperatures rapid decomposition occurs. At the same potential the compound $\text{Co}(\text{CO})_4^-$, which is assumed to be the reduction product of $\text{Co}_2(\text{CO})_8$, shows an anodic wave. Nevertheless, this anodic wave is not ascribed to an oxidation process but to the formation of an insoluble compound with mercury. This was demonstrated by the correspondence of its half-wave potential with that of the reduction wave of $\text{Hg}(\text{Co}(\text{CO})_4)_2$ as well as by the similar effect of sodium sulfide on both waves. Both the waves for $\text{Hg}[\text{Co}(\text{CO})_4]_2$ and $\text{Co}(\text{CO})_4^-$ are complicated by adsorption phenomena. Using a platinum electrode, an anodic wave at $+0.12$ V was obtained for $\text{Co}(\text{CO})_4^-$. The electrode process corresponds to the reaction $\text{Hg} + 2 \text{Co}(\text{CO})_4^- \rightleftharpoons \text{Hg}[\text{Co}(\text{CO})_4]_2 + 2e$. The normal potential of the system $\text{Co}_2(\text{CO})_8/\text{Co}(\text{CO})_4^-$ was estimated to be between $+0.1$ V and -0.3 V (S.C.E.). It is assumed that in the molecule $\text{Co}_2(\text{CO})_8$ there is a free antibonding orbital with a strong electron affinity. The transfer of an electron to this orbital causes decomposition of the particle. In $\text{Co}(\text{CO})_4^-$ cobalt is in the oxidation state $+1$. [P.Zu.]

274 – Polarographic method for the direct measurement of rates of oxidation by chromic acid (in English). J. Krupička and J. Kadlec (Inst. Organ. Chem. and Biochem., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 1783; *Chem. listy*, 52 (1958) 2278.

In strongly acidic solutions of sulfuric and acetic acid chromic acid shows a limiting current which is directly caused by the dissolution of mercury. The height of this limiting current corresponds to a three-electron reduction to the oxidation state $+3$ and is a linear function of the concentration of the hexavalent chromium. This limiting current is suitable for the continuous analysis of reaction mixtures during the oxidation of alcohols by chromium(VI). Linear dependence of the limiting current on the Cr concentration was observed in 3.8 – 14.3 M H_2SO_4 and in acetic acid. Due to this high concentration of the supporting electrolyte, secondary maxima occurred. Therefore the curves were registered at low mercury flow rates, where the maxima are low. During the oxidation of isopropanol a new wave was found at 1.1 V which was ascribed to the reduction of chromium(III) bound in a complex. [P.Zu.]

275 – Polarography of steroids. III. Polarographic reduction of steroids with an aldehydic group in position 18 (in German). P. Zuman and V. Černý (Polarograph. Inst., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 1925; *Chem. listy*, 52 (1958) 1468.

Steroid compounds of the holarrhimin and holarrhidin groups show at pH 7–10 a polarographic reduction wave at -1.6 V, the half-wave potential and height of which are pH-independent. This wave was ascribed to the reduction of the aldehydic group, the hydration of which is sterically hindered. The alcohol, oxime, aldimine and semicarbazone show no reduction wave; the betainyl-hydrazone at pH 10 shows a reduction wave at -1.8 V. $3\text{-}\beta$ -dimethylaminoderivatives caused an abrupt change in the condenser current at -1.5 V in 0.1 M LiOH, whereas no such "false wave" was observed with $3\text{-}\alpha$ -dimethylaminoderivatives. The suppressive activity of the $3\text{-}\beta$ -dimethylaminoderivatives was substantially greater than that of the $3\text{-}\alpha$ -dimethylaminoderivatives. It assumed that these results can be explained by the adsorbability of the steroid molecule from behind. The bulky axial $3\text{-}\alpha$ -dimethylaminogroup hinders adsorption from behind. Dissociation constants of both amino groupings were determined using a potentiometric titration. [P.Zu.]

276 – Steric effects on catalytic hydrogen evolution in ammoniacal solutions of cobalt in the presence of threo- and erythro-phenylcystein (in German). P. Zuman (Polarograph. Inst., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 2027; *Chem. listy*, 52 (1958) 1349.

The catalytic wave of $3 \cdot 10^{-5}$ M erythro-phenylcystein in 0.001 M CoCl_2 , 0.1 M NH_3 and 0.1 M NH_4Cl is lower than the wave for the corresponding threo-derivative. Also the limiting value at concentrations about $1 \cdot 10^{-4}$ M is about double for erythro- compared with that for threo-phenylcystein. A difference in the pH-dependence of the wave height was also observed. The differences were explained on the basis of different stability constants of the cobalt-complexes, as well as on the basis of a difference in the acid dissociation constants. [P.Zu.]

277 – Polarographic determination of rhodium (in German). J. Seifert and J. Šimek (State Institute for Precious Metals). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 2046.

The red modification of rhodium(III) chloride gives well-developed diffusion-controlled polarographic waves with the following half-wave potentials (0.02% gelatine): 0.5 M $(\text{NH}_4)_2\text{HPO}_4$, -0.174 V; 0.5 M Na_2HPO_4 , -0.184 V; 0.5 M $(\text{NH}_4)_2\text{SO}_4$, $+0.026$ V; 0.5 M NH_4CNS , -0.386 V; 1.0 M HCl , -0.12 V. The yellow modification of rhodium(III) chloride gives no wave. The interfering platinum metals can be separated by hydrolysis at pH 6 in the presence of sodium bromate.

The accuracy of the polarographic determination is about the same as for the gravimetric procedure ($\pm 3\%$, in the presence of Pt $\pm 10\%$). The advantage of the polarographic determination lies in the gain in the time needed for the analysis. The time-consuming ignition of rhodium(III) hydroxide or rhodium metal in a stream of hydrogen and cooling in a stream of nitrogen or carbon dioxide can be omitted. [P.Zu.]

278 - Deformation of polarographic curves due to the ohmic resistance (in German). J. Peizker (Polarograph. Inst., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 2122; *Chem. listy*, 52 (1958) 1699.

Bei zu grossem ohmschen Widerstand im Messkreis bzw. bei Vorgängen an der Elektrodenoberfläche, die eine Erhöhung des Widerstandes im Stromkreis verursachen, entsteht eine Verzerrung der polarographischen Kurven. Solche Verzerrung an Kurven bei denen der Strom mit steigender negativer Spannung abnimmt, wurden durch elektrische Instabilität nach Kaufmann (*Ann. Physik*, 2 (1900) 150) erklärt. Durch Einschaltung eines ohmschen Widerstandes in den Stromkreis können polarographische Kurven, bei welchen der Strom mit steigender negativer Spannung abnimmt und die Kurve die Form eines runden Maximums besitzt (wie z.B. bei Perjodaten in alkalischer Lösung oder bei Ni^{2+} in Rhodanidlösungen), in Kurven mit scharfer diskontinuierlicher Stromabnahme übergeführt werden. Solche Kurven ähneln in der Form den wirbelbedingten Maxima. Auch bei runden wirbelbedingten Maxima kann durch Erhöhung des Widerstandes im Stromkreis ein diskontinuierlicher Stromverlauf erhalten werden. Im Gegensatz zu den früher erwähnten Beispielen weisen so hervorgerufene Maxima eine Hysteresis auf. Die diskontinuierliche Stromabnahme bei wirbelbedingten Maxima wird gleichfalls durch Instabilitätsbedingungen erklärt. Die periodischen Relaxationsschwingungen, die von Jenšovský (*Chem. listy*, 50 (1956) 1426) auf den $i-t$ -Kurven des Perjodats in alkalischer Lösung beobachtet wurde, sind durch zu hohen Widerstand der von Jenšovský benutzten Apparatur verursacht. Der diskontinuierliche Übersprung vom Bereich der positiveren Potential im Bereich der negativeren Potential kann an einem oder an mehreren Tropfen erfolgen. [P.Zu.]

279 - A contribution to the polarographic behaviour of tri- and tetravalent cerium (in German). J. Doležal and J. Novák (Inst. Anal. Chem., Faculty of Science, Charles Univ., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 2182; *Chem. listy*, 52 (1958) 582.

Cerium, which shows in neutral and acid solutions only an immediate rise in current due to mercury dissolution, gives in solutions of alkali metal carbonates of pH between 9 and 11.5 a well-developed wave corresponding to the reversible redox system Ce(IV)-Ce(III). At carbonate concentrations lower than 0.75 M and at a pH lower than 8.7 or higher than 12.7 the height of this wave decreases and a precipitate is formed. In 1.0 M K_2CO_3 the half-wave potential was found to be -0.114 V and in 2.0 M K_2CO_3 the value -0.158 V (S.C.E.) was determined. The electrode reaction proceeds according to the scheme: $[\text{Ce}(\text{CO}_3)_2]^- + 3 \text{CO}_3^{2-} \rightleftharpoons [\text{Ce}(\text{CO}_3)_5]^{3-} + e$. From the shifts of the half-wave potential with carbonate concentration, the difference of the logarithms of the stability constants of complexes with Ce(III) i.e., $\text{p}K_1$, and those of complexes with Ce(IV) denoted as $\text{p}K_2$ was determined: $\text{p}K_1 - \text{p}K_2 = -13.6$. In the oxidation of a Ce(III) complex with oxygen from the air a hydroxocomplex is formed as a byproduct. [P.Zu.]

280 - Influence of pH on the polarographic behaviour of cadmium amalgam (in German). Z. Záborský (Laboratory for Metallurgy, Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 2426.

In solutions of pH below 9 the height of the polarographic anodic wave, obtained with a cadmium amalgam, as well as the half-wave potential are independent of pH. At pH 9-10.5 the electrode process is influenced by the diffusion of hydroxyl ions towards the electrode and the wave is deformed. At pH above 11 the wave is shifted with increasing pH values towards more negative potentials. The shift of the half-wave potential is limited by the solubility product of cadmium hydroxide. The value of $dE_{1/2}/d \text{pH}$ and the logarithmic analysis of the wave are also in accordance with this assumption. For the solubility product at infinite dilution, the value $S = 1.6 \cdot 10^{-18}$ was computed from polarographic measurements. All the above findings were obtained in unbuffered solutions, where, with the exception of cadmium hydroxide, no other precipitates or complexes are formed. In media in which the pH value is regulated by use of a Britton-Robinson buffer, the dependence of the half-wave potentials of the anodic wave on the pH-value is more complicated due to the possibility of the formation of complexes of borates and phosphates with cadmium. [P.Zu.]

281 - Polarographic limiting currents for glyoxylic acid, controlled by the rate of dehydration (in German). J. Kůta (Polarograph. Inst., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 2532; *Chem. listy*, 52 (1958) 2267.

In 12.5 M H_2SO_4 besitzt die polarographische Reduktionsstufe der Glyoxalsäure einen Diffusions-

charakter. Mit abnehmender Acidität nimmt die Stufenhöhe ab und der kinetische Charakter zu, bis in Lösungen, die weniger als 5 M H₂SO₄ enthalten, zeigen die Stufen einen rein kinetischen Charakter. In Acetatpuffern bei pH 3.3 bis 5.9 weist die Gesamtstufenhöhe einen teilweise kinetischen Charakter auf und die Gesamthöhe ist pH-unabhängig. In Boratpuffern von pH grösser als etwa 8 wächst der Grenzstrom mit steigendem pH-Wert und steigender Pufferkonzentration an. Die Gesamtstufenhöhe in dem mittleren pH-Bereich hängt von der Pufferart ab. Bei pH 10, wo der Strom wieder höher ist, besitzt der Grenzstrom einen kinetischen, bei pH 12.3 einen teilweise kinetischen Charakter. In 0.01 M bis 0.1 M NaOH erreicht die Stufenhöhe ihren Maximalwert und der Grenzstrom ist beinahe diffusionsbedingt. Mit zunehmender OH⁻-Konzentration nimmt die Stufenhöhe in der Form einer Dissoziationskurve ab, und der kinetische Charakter wieder zu. Die pH-Abhängigkeit der Grenzströme wurde durch Begrenzung der Ströme durch acido-basisch katalysierte Dehydratation der Aldehydgruppe erklärt. Die Stufenabnahme in der alkalischen Lösung soll durch Protonabspaltung aus der hydratisierten Aldehydgruppe verursacht sein. Da die Gleichgewichtskonstanten der freien und hydratisierten Form (K_h) unbekannt sind, konnte nur das Produkt der Gleich- und Geschwindigkeitskonstanten der Dehydratation ($K_h k$) berechnet werden. In mittleren pH-Bereich wurde bei pH grösser als 5 eine Zerspaltung der Gesamtstufe in zwei Stufen beobachtet. Der Gesamtgrenzstrom bleibt dabei praktisch konstant. Die positivere Stufe wurde OHC-COOH, negativere dem Anion OHC-COO⁻ zugeschrieben. Der Verfasser nimmt an, dass das Anion weniger hydratisiert ist als die freie Säure. [P.Zu.]

282 – Catalysis of hydrogen evolution in the presence of some sulfur derivatives of hydantoin and pyrimidine (in German). P. Zuman and M. Kuik (Polarograph. Inst., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 24 (1959) 3861.

5,5-Diphenyl-2-thiohydantoin, 5,5-diphenyl-2,4-dithiohydantoin, 2-thiocytosine and 2,4-dithiopyrimidine show in ammoniacal cobalt(II) solutions a catalytic wave at the beginning of the limiting current of the cobaltous ion. With dithio derivatives another catalytic wave was observed at more negative potentials. Comparison of the pH-dependence, the influence of the buffer capacity, the ionic strength, the role of the cobalt and gelatine concentrations for the above-mentioned compounds with similar influences on the wave for cystine has shown that there are at least three different types of catalytic processes which cause an increase in the current at the limiting current of cobalt. The catalytic activity is greater for compounds with more sulfur atoms in the molecule and the catalytic activity has been found to increase in the order: —OH < —NH₂ < —SH. Derivatives of pyrimidine are more active than those of hydantoin. The structural changes can affect both acid dissociation constants and stability constants of the cobalt complexes. The formation of the cobalt complexes has been proved by the shift of the potentials of the cobalt wave. In buffer solutions of 2,4-dithiopyrimidine without a heavy metal, two catalytic hydrogen waves were obtained corresponding to two catalytically active groups of different acidities. [P.Zu.]

283 – Polarography of pterines. II. Hydroxyderivatives (in German). J. Komenda, L. Kišová and J. Koudelka (Inst. Theoret. and Phys. Chem., Masaryk Univ., Brno, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 25 (1960) 1020.

Polarographic behaviour of 2-amino-4-hydroxy-6-methylpteridine (I) was compared with that of 7-methylxanthopterin(II), 6-methylisoxanthopterin(III) and leukopterin(IV). II–IV are reduced with consumption of two electrons. For II an adsorption pre-wave was observed at lower pH values but with III and IV their low solubility at pH lower than about 9 hindered their study in acid media. With all the substances studied changes of the limiting currents with pH indicated the presence of several protonized forms which were reduced at different potentials. The acid–base equilibria are influenced by recombination causing the small currents to have kinetic character. For the recombination with formation of a cation, uncharged molecule and univalent anion, the following values of pK' (pH where the height of the acidic and basic forms are identical) were found for substance III: 10.1, 11.4 and 12.3. The normal steepness of the second dissociation curve and also the greater steepness of the first curve were in agreement with theory. The third dissociation curve was more steep than predicted by the theory. This was explained as being caused by changes in the environment of the mercury dropping electrode. For the sake of comparison the values of half-wave potentials at pH 5.0 and 10.0 are best suited: I, —0.52 and —0.89 V; II, —0.735 and —1.02 V; III, —0.91 and —1.345 V; IV, —1.13 and —1.47 V. The additivity of the substituent effects was proved. For II and IV oscillographic dE/dt -E curves were registered and the degree of reversibility of the electrode process discussed. [P.Zu.]

284 – Polarographic behaviour of acid monoazocompounds and their stability to light (in German). M. Kožený and V. Velich (Inst. Phys. Chem., College of Chemical Technology (Technische Hochschule für Chemie), Pardubice, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 25 (1960) 1031.

Half-wave potentials of acid monoazocompounds, prepared by the coupling of diazonium salts of

aniline and its derivatives with an R-acid, were measured at pH 2.0–8.0. The linear dependence of these values on the Hammett total polar substituent constant σ was verified. It was also shown that the relative bleaching times are a linear function of σ . The relationship between the reducibility of the substances studied and the stability to light both in solution and on woollen materials was demonstrated. The measurement of the half-wave potential of a group of related substances thus enables a suitable dyestuff to be chosen. [P.Zu.]

285 – Polarographic determination of methylglyoxal (in German). J. Krupička and J. J. K. Novák (Inst. Org. Chem. and Biochem., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 25 (1960) 1275.

Methylglyoxal is reducible at the dropping mercury electrode and the height of the limiting current is pH-dependent. The character of this dependence, *i.e.* an increase in acid media, followed by a decrease towards higher pH values and a bell-shaped increase in the alkaline region, is in accordance with the behaviour of a general acid–base catalysed system. It is assumed that the electron transfer is preceded by acid–base catalysed dehydration, the rate of which governs the height of the limiting current. Even at its maximum value at pH 11 the current possesses a kinetic character and corresponds to about 50% of the theoretical diffusion-controlled limiting current. The height of the wave is substantially lower in buffer solutions containing boric acid, which points to complex formation with the latter. The height of the wave for methylglyoxal decreases in alkaline solutions during standing of the solution. For analytical purposes a buffer solution consisting of 0.09 M Na₂HPO₄ and 0.01 M Na₃PO₄ proved best.

The decrease of current in this solution is relatively slow (about 50% in one hour), but for analytical purposes it is recommended to register the curves at fixed time intervals shortly after mixing. The calibration curve method is recommended for the evaluation of the curves. The pyruvic acid present up to 1–3% in samples, does not affect the results since its waves (even if of comparable height owing to their diffusion character) are at substantially more negative potentials. Polymers of methylglyoxal are inactive polarographically. [P.Zu.]

286 – A contribution to the oscillographic study of the depolarizing action of trivalent aluminium ions (in German). L. Treindl (Inst. Inorg. Phys. Chem., Faculty of Science, Komenský University, Bratislava, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 25 (1960) 1427.

Einschnitte auf den oszillographischen dE/dt - E -Kurven, die früher nur in der Anwesenheit von Li⁺ beobachtet wurden, wurden von den Autoren auch in 0.5 M MgCl₂ bei normaler Temperatur, bzw. in 0.5 bis 1.0 M CaCl₂, SrCl₂ und BaCl₂ entweder bei 50–70° oder in Lösungen, die 0.01 M NO₃⁻, NO₂⁻, JO₃⁻, BrO₃⁻ oder HCHO enthalten, festgestellt. Die Einschnitte auf den dE/dt - E -Kurven wurden mit der Quecksilbertropfelektrode jedoch nicht mit der strömenden Quecksilber-elektrode beobachtet. Mit hängender Quecksilbertropfelektrode wurden die Einschnitte auch bei Ca²⁺, Sr²⁺ und Ba²⁺ bei normaler Temperatur und ohne Zusatzstoffe beobachtet, falls die Elektrolyse mindestens 5 Minuten durchgeführt wurde. Das Potential des Einschnittes hängt vom Charakter des Erdalkalimetalls ab und ist vom Charakter des Zusatzstoffes (NO₃⁻, NO₂⁻, JO₃⁻ usw.) unabhängig. Bei hängender Tropfelektrode wächst die Tiefe der Al-Einschnitte mit der Elektrolysendauer, mit sinkendem pH-Wert nimmt sie ab. Durch verschiedene Potentiale der Einschnitte und Abhängigkeit deren Tiefe von der Erdalkalikonzentration bei konstanter Konzentration von Al abhängt, ist es möglich Konzentrationen von Ca²⁺, Sr²⁺ und Ba²⁺ abzuschätzen. In 10⁻³ M Lösungen der Erdalkalimetalle ist es möglich die Analyse von Mischungen von zwei und sogar von allen drei (bei günstigen Konzentrationsverhältnis) Ionen durchzuführen. Entstehung der Einschnitte wird durch Bildung von LiAlH₄ und analogen Hydriden erklärt. Bei Erdalkalimetallen wird die beendigte Entstehung von Einschnitten durch die langsame Bildung der Hydride erklärt. [P.Zu.]

287 – Polarography of aromatic heterocyclic compounds. VII. Reduction of nitriles of pyridine-carboxylic acids (in German). J. Volke, R. Kubíček and F. Šantavý (Polarograph. Inst., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Commun.*, 25 (1960) 1510. 2-Cyanpyridine is reduced on the mercury dropping electrode in acid media giving a four-electron polarographic wave which is complicated by adsorption. With increasing pH value this wave diminishes giving a dissociation curve with $pK' = 8.1$. On account of this wave a new four-electron wave appears at more negative potentials. 4-Cyanpyridine is similarly reduced to give a four-electron wave in acid solutions, but its reduction in alkaline media gives a two-electron wave. The gradual change from the four-electron to the two-electron process gives an unusual pattern which is observed over a wide range of pH values. A maximum is observed on the curves. In contrast to both the preceding substances 3-cyanpyridine is reduced polarographically in a single one-electron wave only. The height of this wave decreases in alkaline solutions and at pH 11 disappears altogether. Oscillographic dE/dt - E curves enable the individual isomers to be detected in mixtures of two or even three substances. Reduction on the pyridine ring is assumed. [P.Zu.]

288 – Polarographic investigation of thiosulphate complexes of cadmium in water-ethanol solutions. M. Pryszczyńska (Dept. of Gen. Chem., Politechnika, Szczecin, Poland). *Roczniki Chem.*, 33 (1959) 755.

The half-wave potentials of Cd^{2+} were determined in $\text{Na}_2\text{S}_2\text{O}_3$ and KNO_3 solutions containing 0, 25, 37.5 and 50% ethanol at constant ionic strength. The following species were identified, CdS_2O_3 , $\text{Cd}(\text{S}_2\text{O}_3)_2^{2-}$, $\text{Cd}(\text{S}_2\text{O}_3)_3^{4-}$, and their stability constants determined.

$\log K_1$, $\log K_2$ and $\log K_3$ values for different ethanol concentrations at 25° are as follows: 0% ethanol, 3.15, 4.88, 6.05; 25% ethanol, 3.93, 6.13, 8.58; 37.5% ethanol, 4.61, 7.36, 9.60; 50% ethanol, —, 8.30, 11.0 which were obtained by the Jacimirski method, and $\log K_1$ values: 3.21, 4.21, 4.70 and 5.52 for 0, 25, 37.5 and 50% ethanol respectively, obtained by the De Ford-Hume method. [Ad.Hu.]

289 – Investigation of the influence of oxygen on the reduction of cadmium and zinc ions at various types of mercury electrodes. W. Kemula, E. Goerlich, Z. Kowalski and B. Behr (Inst. Phys. Chem., Polish Academy of Science, Warsaw; Dept. of Mineral Raw Materials, School of Mining and Metallurgy, Kraków, Poland). *Roczniki Chem.*, 33 (1959) 797.

The influence of oxygen on the reduction of Cd^{2+} and Zn^{2+} at mercury electrodes was investigated. In this study streaming, dropping and hanging mercury electrodes were used. For the streaming electrodes the oscillographic curves were recorded using a voltage sweep rate from 14 to 896 V/sec for the Cd^{2+} and Zn^{2+} concentration range of 100–400 mg/l. It was confirmed that an additional reduction step for Cd^{2+} appeared only at higher concentrations and larger voltage sweep rates, but for Zn^{2+} the additional step was observed at lower concentrations and smaller voltage sweep rates. On cyclic voltammetric curves additional reduction and oxidation steps were observed for Cd^{2+} and Zn^{2+} only in the presence of oxygen. In the case of Cd^{2+} simultaneous suppression of the oxygen reduction current and a decrease of the double layer capacity was observed. Probably in this case, $\text{Cd}(\text{OH})_2$ precipitated on the electrode surface, was responsible for the additional steps, since for low Cd^{2+} concentrations and low sweep rates this compound is precipitated at some distance from the electrode. In the case of Zn^{2+} the mechanism of the additional step formation is different. It follows from the formation of this step at low sweep rates that it must be connected with the reduction of hydroxycomplexes present in the solution. The relatively slow precipitation of the hydroxide prevents this phenomenon occurring at the electrode surface. The measurements of the double layer capacity confirmed this conclusion. Under conditions when the additional steps on the cyclic voltammetric curves were observed the double layer capacity did not decrease, in contrast to what would be expected when a precipitate is formed on the electrode surface. Additional reduction steps were not observed in acidic or buffered solutions, and if the solution is not deaerated such conditions should be used in analytical work. [Ad.Hu.]

290 – The polarographic and spectrophotometric study of *p*-aminobenzaldehyde (in English). W. Kemula, E. T. Bartel and W. Rubaszewska (Dept. Inorg. Chem., University of Warsaw; Inst. Phys. Chem., Polish Academy of Science, Warsaw, Poland). *Roczniki Chem.*, 33 (1959) 1117.

The absorption spectrum of *p*-aminobenzaldehyde (PAB) was investigated at various pH values, and the thermodynamic dissociation constant was calculated at 20° to be equal to $K_a = 1.92 \cdot 10^{-2} \pm 0.08$; and $pK_a = 1.717 \pm 0.017$. The polarographic reduction of PAB which was investigated over the whole range of pH was analogous to *p*-dimethylaminobenzaldehyde. In alkaline solutions two well-developed waves were observed. From the change of their height, $pK' = 7.8$ was calculated, which corresponds to the pH value at which the diffusion current equals one half of the initial wave-height. At various pH values the half-wave potentials of the two waves are as follows: pH 0, 0.81, —; pH 7, 1.30, 1.52; pH 13, —, 1.61. From a comparison of the polarographic and spectrophotometric results it is found that pK' and pK of the aldehyde are similar to the corresponding values for *p*-dimethylaminobenzaldehyde. [Ad.Hu.]

291 – Microanalytical determination of adrenaline (in Dutch). J. A. C. van Pinxteren and M. E. Verloop (Pharmaceutical Laboratory, State University, Utrecht, The Netherlands). *Pharm. Weekblad*, 94 (1959) 169.

Adrenaline in amounts of 0.025–2 mg, is oxidized by adding an excess of potassium cyanoferrate(III) to a solution of the substance buffered by means of borax (pH between 7.6 and 9.3). Five minutes after mixing, the solution is acidified with sulfuric acid and the cyanoferrate(II) formed during the reaction is titrated with zinc sulphate using the bi-ampereometric ("dead-stop") indication method.

Official Netherlands Pharmacopeia adrenaline solutions containing metabisulphite to prevent oxidation are acidified and heated in a stream of nitrogen for ten minutes. [H.L.Ki.]

292 – Polarography of copper(II) thiocyanate solutions. I. M. Kolthoff and Y. Okinaka (School of Chemistry, University of Minnesota, Minneapolis, Minn., U.S.A.). *Rec. trav. chim.*, 79 (1960) 551.

In order to obtain clarification of the contradictory literature, the authors made a study of the current-tension curves from freshly-prepared and kept solutions of copper(II) in 0.1 *M* and 1 *M* thiocyanate containing 0.01% polyacrylamide.

In 0.1 *M* solution there are 4 waves corresponding to the reduction of Cu(II) to Cu(I), Cu(I) to Cu(O), an adsorption wave due to $\text{Cu}_2(\text{CNS})_2$ and a hydrogen wave. The first three waves decrease in height on aging of the solution but the fourth increases since hydrogen ions are formed by the hydrolysis of $(\text{CNS})_2$. In 1 *M* solution there are 3 waves the third of which is the hydrogen wave as the adsorption wave is absent. On keeping overnight, the first wave completely disappears.

[H.L.Ki.]

293 - Square wave electrolysis. I. The cyclic potential-step method. W. M. Smit and M. D. Wijnen (Lab. Anal. Chem., State University, Utrecht, The Netherlands). *Rec. trav. chim.*, 79 (1960) 5. In this first article of a series of four dealing with the application of a square wave alternating current for the determination of kinetic parameters of electrochemical processes, the authors present a mathematical treatment of the so-called cyclic potential-step method. The essential principle of this method is that a square wave voltage is applied to a polarisable electrode while the current response is visualised on the screen of a cathode-ray oscilloscope. In this way the transfer-coefficient (α), the standard exchange current density (j_0^*) and the influence of the shortcomings of the potentiostatic device can rapidly be obtained.

It is shown mathematically that the current response quickly approaches a constant pattern and may then afford as much information as a single record according to the "single" potential-step method. The derivations presented are free from restrictions concerning the reversibility of the system and the magnitude of the amplitude of the square wave.

[F.Vor.]

294 - Square wave electrolysis. II. The cyclic current-step method. M. D. Wijnen and W. M. Smit (Lab. Anal. Chem., State University, Utrecht, The Netherlands). *Rec. trav. chim.*, 79 (1960) 22. The authors present a mathematical treatment of a new method, the so-called cyclic current-step method, which is especially suitable for rapid determination of the exchange current j_0 . A square wave current is forced through a polarisable electrode and the voltage response is visualised and measured on the screen of a cathode-ray oscilloscope.

It is shown that the voltage response approaches a constant pattern when "coulomb-symmetry" is present. Even when the pattern is continuously changing due to the presence of coulomb-asymmetry the evaluation of j_0 may be easily achieved.

By means of the cyclic current-step method it is easily seen whether or not the influence of the double-layer capacity is negligible. Moreover, the method provides a ready means for the elimination of the ohmic part of the voltage response of the electrolytic cell.

[F.Vor.]

295 - Square wave electrolysis. III. Apparatus for the cyclic potential-step and cyclic current-step methods. M. D. Wijnen and W. M. Smit (Lab. Anal. Chem., State University, Utrecht, The Netherlands). *Rec. trav. chim.*, 79 (1960) 203.

The electrolytic cell consists mainly of a Pt micro-electrode, a Pt foil reference electrode with an area about 100 times as large as that of the polarisable electrode, and the solution to be examined. For the c.p.s. method the amplitude of the square wave voltage between the electrodes is held constant by the cell forming part of the feed-back circuit of a d.c. amplifier. For the c.c.s. method the electrolytic cell forms part of a bridge circuit in which the resistance in series with the cell is chosen to give a constant amplitude of the square wave current.

The apparatus used is thoroughly discussed and attention is paid to the following subjects: conditions for linear diffusion, reference electrode, potentiostatic conditions, time symmetry of the applied square wave and deviations from coulomb-symmetry.

[F.Vor.]

296 - Square wave electrolysis. IV. Results and discussion. M. D. Wijnen and W. M. Smit (Lab. Anal. Chem., State University, Utrecht, The Netherlands). *Rec. trav. chim.*, 79 (1960) 289.

The application of the c.p.s. and c.c.s. methods to the ferro-ferri system in 1 *M* H_2SO_4 and to the ferrocyanide-ferricyanide system in 1 *M* KCl is described. For the ferro-ferri system the values of j_0^* obtained by the two methods agree within 10%, of α within 3%. For the ferrocyanide-ferricyanide system the differences are respectively 8% and 10%.

With reference to deviations from values found in the literature, particularly for the ferro-ferri system, the authors point out the large influence of the experimental conditions. Suggestions for further investigations are given.

[F.Vor.]

297 - Recent trends in polarography (in German). J. Heyrovský (Polarograph. Inst., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Angew. Chem.*, 72 (1960) 427.

Es wurde über die konventionelle polarographische Methode, sowie die neu entwickelten polarographischen Methoden (square-wave-Polarographie, Tensammetrie, oszillographische Polarographie

usw.) und ihren Anwendungsmöglichkeiten in anorganischer und organischer Analyse, und in der Medizin berichtet. Die Polarographie hat sich zu einer analytischen Methode von extremer Empfindlichkeit entwickelt, ferner wird sie zunehmend für Strukturaufklärungen, zur Lösung chemischer Grundlagen-Probleme verwendet. [Ja.Inc.]

298 – Applications of polarography in organic chemistry (in German). H. W. Nürnberg (Inst. Phys. Chem., Univ. Bonn, Germany). *Angew. Chem.*, 72 (1960) 433.

Die Polarographie hat in den letzten Jahren steigende Bedeutung zur Lösung von Problemen der organischen Chemie gewonnen.

Er wird erst kurz über die Arbeitsmethoden allgemein berichtet, dann werden die zur analytischen Bestimmung ausnützbaren reversiblen Systeme (chinoide Systeme), ferner die nicht reversiblen Systeme (Aldehyde, Ketone, Säuren, Halogen-Verbindungen, stickstoffhaltige Verbindungen, ungesättigte Kohlenwasserstoffe, Schwefel- und Selen-Verbindungen, Heterocyklen), das Verhalten und die Reduzierbarkeit der verschiedenen Verbindungen besprochen. Polarographische reaktionskinetische Messungen erlangen auch ständig grössere Bedeutungen. Bei Halbwertszeiten die grösser als 15 sec sind, kann man mit einem Gleichspannungspolarographen simultan mit dem Reaktionsablauf die zeitliche Konzentrationsänderung eines polarographisch aktiven Reaktionsteilnehmers registrieren. Für Halbwertszeiten von 3–15 sec eignet sich die Verfolgung der zeitlichen Variation der Konzentration eines Teilnehmers durch kontinuierliche Aufnahme von $i-t$ -Kurven am Einzel-tropfen bei konstanter Spannung. Bei noch schnelleren Reaktionen geht man zur oszillographischen Polarographie über. Das Verhalten der kinetischen Grenzströme und die bestimmenden Faktoren werden theoretisch erörtert. Endlich werden die theoretischen Grundlagen der polarographischen Struktur- und Konstitution-Aufklärung und die Anwendungsmöglichkeiten besprochen. Bei irreversiblen Durchtrittsreaktionen stellt $E_{1/2}$ ein Mass für die Aktivierungsenergie und Aktivierungsentropie der elektrochemischen Reaktionen dar. (200 Zitate.) [Ja.Inc.]

299 – Rapid polarography (in German). S. Wolf (Phys. Chem. Lab., Metrohm A.G., Herisau, Switzerland). *Angew. Chem.*, 72 (1960) 449.

Es wurde eine neue gleichstrompolarographische Methode ausgearbeitet. Unter einer kontrollierten Quecksilber-Tropfelektrode erhöhter Tropffrequenz werden die Geschwindigkeiten für Spannungs- und Papierdurchlauf des Polarographen bedeutend erhöht (Aufnahmezeit ~ 1 min). Als polarographische Messgerät für die Untersuchungsbeispiele wurde der Polarecord E 261 R (Metrohm A.G.) benutzt. Der Polarographierstand mit Tropfkontroller E 354 stellt die einfache Ausführung einer kontrollierten Tropfelektrode dar. Durch einen Impulsgeber wird die Kapillare über ein Relais kurzzeitig angeschlagen. Da die Kapillare hierdurch aus ihrer Lage ein wenig ausgelenkt wird, fällt der Quecksilber-Tropfen ab. Am Gerät läst sich die Frequenz der Schläge zwischen 1 und 6 Impulsen/sec einstellen, was Tropfzeiten zwischen 1 und 0.17 sec entspricht. Die prinzipielle Form der erhaltenen Stufen ist bei der Rapid-Polarographie und der konventionellen Methode identisch. In nicht-wässrigen Medien ist die Methode auch anwendbar. Neben dem zeitlichen Gewinn bietet die Rapid-Polarographie weitere Vorteile, wie Unabhängigkeit des Grenzstromes von Spannung, starke Verringerung der Oszillationen des Grenzstromes, besseres Absetzen dicht aufeinanderfolgender polarographischer Wellen. Für theoretische Betrachtungen ist die Beschränkung des „Verarmungseffektes“ sowie das Ausbleiben von Maxima 2. Art von Interesse. [Ja.Inc.]

300 – Utilisation of ternary and ion-association complexes in chemical analysis. II. Polarographic determination of indium. M. Kopanica and R. Pribil (Chem. Inst., Czechoslov. Acad. Sci., Prague, Czechoslovakia). *Talanta*, 4 (1960) 158.

The formation and composition of the phenanthroline-thiocyanate complexes of indium, cadmium and other metals was investigated. The influence of EDTA on the formation of these complexes was observed. At pH 3 indium remains bound in the soluble EDTA complex, while cadmium, zinc, copper and other ions form water-insoluble complexes which can be separated from the aqueous phase into butanol. After separation and acidification it is possible to determine indium polarographically.

Procedure for the separation and determination of indium: Adjust the pH of the solution to a value of 3 by addition of formate buffer, then add 0.02 M EDTA solution in excess (compared to the indium content), 30% ammonium thiocyanate solution to make the total concentration 2–3%, and 0.05 M *o*-phenanthroline solution for as long as a precipitate is produced. Now add the same volume of butanol, stir for 3 min, and separate the two phases in a separating funnel. Repeat the stirring for 2 min. Separate again. Wash the butanol twice with 5 ml of water, add this water to the aqueous part, acidify with 12 ml conc. HCl, add 1 ml 1% glucose and dilute in a volumetric flask. Polarograph the indium within 2 h. Compare the wave-height with the wave-height of a standard indium solution prepared by the same procedure. In the analysis of cadmium samples with an indium content of 0.05–0.5% the error varies from ± 3 to $\pm 5\%$; when the indium content is 0.5 to 5% the error is $\pm 2\%$. It is also possible to separate zinc, copper, manganese, cobalt, nickel, iron(II) and molybdenum from indium in the same way. [Ja.Inc.]

301 – Peroxides. VIII. X-ray diffraction and polarographic study of *tert*-butylperesters and diacylperoxides of aliphatic monobasic acids. Leonard S. Silbert, L. P. Witnauer, Daniel Swern and C. Ricciuti (The Eastern Regional Research Laboratory, Philadelphia, Pa., U.S.A.). *J. Am. Chem. Soc.*, 81 (1959) 3244.

Für *t*-Butylperester wurden Halbwellenspannungen in dem Bereich von -0.82 bis -0.96 V und für Diacylperoxyde von -0.08 bis -0.12 V erhalten. Die Halbwellenspannungen für *t*-Butylperester und die Diffusionsstromkonstanten für Diacylperoxyde fallen mit steigender Kettenlänge. Es wird vorgeschlagen, die Beziehungen $i_d \cdot M^{1/2} = \text{const.}$ und $i_d \cdot M^{3/2} = \text{const.}$ für die Änderung der Diffusionsstromkonstanten mit der Kettenlänge bei Diacylperoxyden heranzuziehen. Mit Hilfe der Halbwellenspannungen ergibt sich eine absinkende Bindungsfestigkeit in der Reihe der Peroxyde in der Art: Di-*t*-Butylperoxyd > *t*-Butylperester \geq Hydroperoxyd > Diacylperoxyd > Persäure. [Ha.Re.]

302 – Kinetic currents in the polarographic reduction of cadmium nitilotriacetic acid complexes. Paolo Papoff (Institute of Physical Chemistry, University of Padua, Italy, and the Coates Laboratory, Louisiana State University, La., U.S.A.). *J. Am. Chem. Soc.*, 81 (1959) 3254.

In Acetattampfer werden die kinetischen Ströme bei der Reduktion von Nitilotriessigsäure untersucht. Er ergibt für die Bildung des Cd-Acetat-Komplexes eine korrigierte Geschwindigkeitskonstante für die Hinreaktion $\text{CdX}^- + \text{H}^+ = \text{Cd}^{2+} + \text{HX}^{2-}$ von $1.5-0.3 \cdot 10^6 \text{ Mol}^{-1} \text{sec}^{-1}$ bei einer Ionenstärke von 3 und $1.3-0.3 \cdot 10^6 \text{ Mol}^{-1} \text{sec}^{-1}$ für $\mu = 0.3$. Die Effekte an der Variation der Ionenstärke und aus der Änderung der Doppelschichtstruktur stimmen mit dem Mechanismus der Elektrodenreaktion überein. [Ha.Re.]

303 – A systematic polarographic study of the aromatic chloroethanes. Isadore Rosenthal and René J. Lacoste (The Research Laboratories, Rohm and Haas Co., Philadelphia, Pa., U.S.A.). *J. Am. Chem. Soc.*, 81 (1959) 3268.

Für die polarographische Reduktion von aromatischen Chloräthanen des Types $\text{C}_6\text{H}_5\text{CR} = \text{CCl}_4$ mit $\text{R} = \text{C}_6\text{H}_5$ oder H wurde eine allgemein gültige Regel gefunden, die besagt, dass entgegen der chemischen Reduktion die Vinylhalogen-Verbindungen dieses Types bei tieferen Potentialen reduziert werden als die entsprechenden gesättigten Verbindungen. Sie werden gleichfalls eher reduziert als die entsprechenden unsubstituierten Doppelbindungen. Die Reaktionsmechanismen an einer Reihe der genannten Verbindungen werden untersucht. [Ha.Re.]

304 – Polarographic reduction of copper chelates of 1,3-diketones. III. Solvent effects. E. R. Nightingale, Jr. and Henry F. Holtzclaw, Jr. (The Avery Laboratory of the University of Nebraska, U.S.A.). *J. Am. Chem. Soc.*, 81 (1959) 3523.

Der Einfluss des Lösungsmittels auf die polarographische Reduktion von Kupferchelaten einiger 1,3-Diketone wurde untersucht. Es wird gezeigt, dass sich das Halbwellenspannung linear mit der reziproken Dielektrizitätskonstante des Lösungsmittels ändert. Es wurde ferner beobachtet dass die Diffusionsstromkonstante von einigen Chelaten einer Stokes-Einstein-Beziehung folgt, wenn sie mit der Viskosität des jeweils verwendeten Lösungsmittels korrigiert wird. Für andere substituierte Diketone ist die Stokes-Einstein-Beziehung jedoch weniger zufriedenstellend. Abweichungen werden im Zusammenhang mit Grösse und Struktur des Chelatmoleküls diskutiert. [Ha.Re.]

305 – Bifurandione. IV. Polarographische Reduktion. E. A. Abrahamson (Central Research Dept., Experimental Station, E. J. Du Pont De Nemours). *J. Am. Chem. Soc.*, 81 (1959) 3692.

In Abhängigkeit vom pH-Wert wurde die polarographische Reduktion von *cis*- und *trans*- $\Delta^{2,2'}$ (5H,5'H)-Bifuran-5,5'-dion in Acetonitril-Wasser-Mischungen 1 : 1, und in 50%-igen Schwefelsäurelösungen untersucht. In der Acetonitril-Wasser-Mischung verschiebt sich das Halbwellenpotential pro pH-Einheit um ungefähr 0.06 mV innerhalb des pH-Bereiches von 0 bis 5.5. Über eine schrittweise Hydrolyse jedes Isomeren der beiden Lactonringe ergeben sich reduzierbare Produkte mit verschiedenen Halbwellenpotentialen. Sowohl in Acetonitril-Wasser, als auch in 50%iger Schwefelsäure ergibt sich die Reduktion als eine Zweielektrodenreaktion. [Ha.Re.]

306 – Polarographic behaviour of some 1,4-substituted-2,3,5-pyrrolidinetriones. E. A. Abrahamson (Central Research Dept., Experimental Station, E. I. Du Pont De Nemours). *J. Am. Chem. Soc.*, 81 (1959) 3919.

Die polarographischen Eigenschaften von 1,4 substituierten-2,3,5-Pyrrolidintrionen wurden mit Hilfe einer Quecksilbertropfenelektrode untersucht. Er wurde festgestellt, dass das polarographische Verhalten gewisse Parallelen zu Verbindungen wie Brenztraubensäure und Phenylglyoxylsäure hat, die sowohl in einer anionischen als auch in undissoziierter Form reduzierbar sind. Die Anwendung der Theorie von Delahay ergibt für die Rekombinationsgeschwindigkeit Werte in der Grössenordnung von 10^9 bis $10^{11} \text{ l} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$. [Ha.Re.]

307 – Polarographic and solubility studies on mercuric oxycyanide. Leonard Newman and David N. Hume (Dept. of Chemistry and Laboratory for Nuclear Science of the Massachusetts Institute of Technology). *J. Am. Chem. Soc.*, 81 (1959) 5901.

Beim Lösen von Quecksilberoxyd in wässrigen Quecksilbercyanidlösungen wurde ein Reaktionsprodukt HgOHCN gefunden. Die Gleichgewichtskonstante, K_m , der Reaktion $\text{Hg}(\text{CN})_2 + \text{Hg}(\text{OH})_2 = 2 \text{HgOHCN}$ wurde bei 23° und einer Ionenstärke der Lösungen bis zu 2.0 zu 260 ermittelt. Die polarographische Reduktion von Quecksilberoxycyanidlösungen ergab einen K_m -Wert von 280. Die polarographisch gemessene Dissoziationskonstante des Quecksilberhydroxyds ergab sich zu $4.0 \cdot 10^{-22}$, die Bildungskonstante des Quecksilberhydroxycyanides zu $7.3 \cdot 10^{-28}$. [Ha.Re.]

308 – A reversible dropping amalgam electrode. William M. MacNevin and Edward D. Moorhead (McPherson Chemical Laboratory, Ohio State University, U.S.A.). *J. Am. Chem. Soc.*, 81 (1959) 6382.

Mit einer Galliumamalgamtropfelektrode liessen sich mit gutem Erfolg anodische und zusammengesetzte polarographische Wellen erhalten. Die in 7.5 molaren KSCN -Lösungen erhaltenen anodischen, zusammengesetzten und kathodischen Wellen lassen deutlich eine reversible polarographische 3-Elektronenreaktion erkennen. Polarographische Irreversibilität lag in KNO_3 -Lösungen vor. Die Ga^{3+} -Reduktion in 7.5 molaren KCNS -Lösungen wird von der Diffusion bestimmt und $i_d/C_{\text{Ga}^{3+}}$ ist bis zu $0.3 \cdot 10^{-3}$ molaren Galliumlösungen eine Konstante. [Ha.Re.]

309 – A process for the determination of water following the Karl Fischer method. Part 4. Process for determining water in ketones. British Standards Institute (2 Park St., London, Great Britain). *Addendum No. 1* (1959) to *B.S. 2511*, 1954, 4 pp.

A description is given of an apparatus and of procedures for determining water in ketones by means of two methods; the first of these, whereby greater accuracy is obtained at very low water contents, comprises the use of a modified Karl Fischer reagent; the other consists in introducing methyl alcohol and pyridine into the reaction vessel. A description is also given of a single-burette method, using an electrometric end-point. [L.Tac.]

310 – Etude sur la détermination polarographique de la vitamine C dans les légumes et dans les fruits (en allemand). S. Krause et Z. Bozyk (Faculté de pharmacie de l'Académie de Médecine à Varsovie, Przemyslawstr. 25, Pologne). *Trav. chim. aliment. et hyg.*, 50 (1959) 228.

Les auteurs examinent l'influence de divers facteurs tels que le pH, la nature et les teneurs en substances tensio-actives, ainsi que la présence d'oxygène, sur le dosage polarographique de l'acide ascorbique dans les légumes et les fruits frais. Ils montrent que des polysulfures se forment au cours de la réduction par l'hydrogène sulfuré et que ces substances sont une source d'interférences pour les méthodes de dosage volumétrique. Aux pH 4.7 ou 6.2, l'acide déshydroascorbique est complètement réduit par SH_2 en un quart d'heure. Sur la base des résultats obtenus l'hypothèse est émise que l'acide déshydroascorbique n'est pas rencontré dans les fruits et les légumes. [De.Mo.]

311 – Microdosage de traces de plomb dans le sang, applicable à divers milieux biologiques. W. Haerdi et D. Monnier (Laboratoire de chimie minérale et analytique de l'Université de Genève, Suisse). *Trav. chim. aliment. et hyg.*, 50 (1959) 243.

Cette méthode comprend une minéralisation par voie humide, une séparation par extraction à la dithizone et une détermination polarographique du plomb. Une étude spéciale est faite concernant la pureté des réactifs. Le cadmium sert d'étalon interne. Les erreurs dues à l'appareillage ainsi que celles provenant des pertes et contaminations ont été étudiées. Le mode opératoire est donné en détail. Avec un polarographe ordinaire (Sargent), il est possible de doser $1 \mu\text{g}$ de plomb avec une erreur max. de 10% à partir de 3 à 10 ml de sang complet, le volume final étant de 0.5 ml. Le polarographe à rayons cathodiques permet de doser $0.05 \mu\text{g}$ de plomb par ml. [De.Mo.]

312 – Amperometric and conductometric studies on cadmium molybdate. R. S. Saxena and C. M. Gupta (Government College, Kota, India). *Rajasthan University Studies, Physical Sciences Section*, 6 (1960) 7.

The formation and composition of cadmium molybdate at pH 6–7 obtained by the addition of Na_2MoO_4 to cadmium salt has been studied by amperometric and conductometric titrations between the reactants at several dilutions. The polarogram of $0.001 M \text{CdSO}_4$ in $M \text{KNO}_3$ was studied on a manual polarograph. To suppress the maxima in C–V curves, 1% gelatine solution was added. To eliminate the migration component of the "limiting current" $M \text{KNO}_3$ and $M \text{KCl}$ were used as the supporting electrolytes. The value of $E_{1/2}$ for cadmium was calculated. Na_2MoO_4 did not yield any diffusion current in neutral media. The titrations were performed at an applied potential of -1.0 V . The amperometric titration curves gave an end-point corresponding to the formation of $\text{CdO} \cdot \text{MoO}_3$ in the pH range 6–7. The results of the amperometric titrations were confirmed by conductometric titrations. [R.S.Sa.]

313 – Polarographic studies on the concentration of oxygen in broth and oxygen uptake rate of mycelium in submerged fermentation of *Penicillium chrysogenum*. R. S. Gondhlekhar and R. S. Phadke (Hindustan Antibiotics, Pimpri, India). *J. Sci. Ind. Research (India)*, 19C (1960) 183. The oxygen levels in broth and the oxygen uptake rates of the mycelium from industrial fermentations of different strains derived from *Penicillium chrysogenum* Wis 51-20 and from the Russian strain are measured polarographically. The oxygen levels in the fermentations of strains producing pellety mycelium are lower than the strains giving the filamentous mycelium. The polarographic residual currents of the broth filtrates are abnormally high in fermentations with low yields. The storage of the broth sample at 5° lowers the mycelial weights and the oxygen uptake rates.

[R.S.Sa.]

314 – Polarographic determination of pentaerythrol trinitrate in the presence of nitroglycerine. W. M. Ayres and G. W. Leonard (Chem. Div., Research Department, U.S. Naval Ordnance Test Station, China Lake, Calif., U.S.A.). *Anal. Chem.*, 31 (1959) 1485.

Pentaerythrol trinitrate (I) in nitrocellulose propellants containing nitroglycerine, nitrocellulose, 2-nitrodiphenylamine(II) and dibutylphthalate as the major components can be determined, polarographically. A sample of the propellant is dissolved in acetone. One aliquot is polarographed without further treatment, the wave-height being proportional to the total nitrate. The second aliquot is allowed to react with sodium hydroxide in ethyl alcohol and polarographed. The wave-height is corrected for the content of (II), which is determined spectrophotometrically. The content of (I) is obtained from a standard curve. The first wave is then corrected for (I) and (II) and the nitroglycerine content obtained from a special standard curve.

[Kl.Gr.]

315 – Polarographic measuring devices (in German). H. Schmidt (Institut für physikalische Chemie, Universität Bonn, Deutschland). *Z. Instrumentenk.*, 67 (1959) 301.

The different stages of a polarograph are considered, *i.e.* the polarizing voltage source, the current-meter and/or recorder and the additional circuits to depress capacitance currents, and set-ups for derivative methods. Next the different means for measurement are discussed. Three main principles are pointed out: (a) methods using a d.c. voltage on the dropping mercury electrode; (b) methods with a.c. voltages on the mercury electrode; (c) oscillographic methods. A survey is given of the technical realization of these possibilities by reference to some modern polarographs.

[Fr.Oe.]

316 – Polarographic studies on some 12-heteropolyacids. III. The behaviour of silicomolybdic and phosphomolybdic acids in solutions of varying pH. H. K. El-Shamy, R. M. Issa and M. F. Barakat (Chem. Dept., Faculty of Science, Alexandria University, Egypt). *Egypt. J. Chem.*, 2 (1959) 91.

A polarographic study on the reduction of molybdenyl chloride solutions in hydrochloric, sulphuric and phosphoric acid supporting electrolytes and other various media was made. Using phosphate-citrate mixtures of varying pH values the relation between the polarographic behaviour of molybdenyl chloride with the pH was elucidated. The process is controlled by diffusion and is irreversible.

[M.K.Hus.]

317 – Propriétés chimiques et électrochimiques dans l'eutectique LiCl-KCl fondu. G. Delarue (Laboratoire de Chimie Analytique, Ecole de Physique et de Chimie Industrielles, Paris, Commissariat à l'Energie Atomique). *Bull. soc. chim. France*, (1960) 792.

L'auteur présente un résumé de sa conférence. Par la tracé des courbes intensité-tension, l'auteur montre que les oxydes solubles dans l'eutectique KCl-LiCl fondu (400°) sont dissociés: $MO \rightleftharpoons M^{2+} + O^{2-}$. La particule O^{2-} est oxydable chimiquement et électrochimiquement. De même les sulfures solubles sont dissociés et la particule S^{2-} est plus facile à oxyder que O^{2-} .

[Bad.Lam.]

318 – Anwendungsmöglichkeiten und Begrenzung der polarographischen Methode zur Verfolgung schneller chemischer Reaktionen in Lösung. J. Koryta (Polarographisches Institut, Tschechoslowakische Akademie der Wissenschaften, Prag, Tschechoslowakei). *Z. Elektrochem.*, 64 (1960) 23.

Für den Fall, dass der geschwindigkeitsbestimmende Schritt des Elektronenvorgangs eine schnelle chemische Reaktion ist, werden die Bildungsbedingungen und die Eigenschaften der Reaktionsschicht an der Elektrodenoberfläche besprochen. Die Grenzen der Geschwindigkeitskonstanten der chemischen Reaktionen, die sich aus polarographischen kinetischen Strömen ermitteln lassen, werden bestimmt. Der Fall in dem die Reaktionsschicht im Diffusionsteil der Elektroden Doppelschicht liegt, wird näher untersucht. Chemische Reaktionen, die den Elektrodenvorgang ohne komplizierende Einflüsse bestimmen, sind angeführt.

[Ha.Re.]

319 – Die durch oberflächenaktive Stoffe beeinflussten polarographischen Ströme. III. Untersuchungen an Strom-Zeit-Kurven der Elektrodenprozesse bei Anwesenheit oberflächenaktiver Stoffe.

Jaroslav Kuta und Ivan Smoler (Polarographisches Institut der Tschechoslowakischen Akademie der Wissenschaften, Prag, Tschechoslowakei). *Z. Elektrochem.*, 64 (1960) 285.

Durch an der Quecksilbertropfelektrode auftretende Momentanströme lässt sich der Einfluss von oberflächenaktiven Stoffen auf Elektrodenprozesse verfolgen. Stromstärke-Zeit-Kurven für ungeladene oberflächenaktive Stoffe lassen sich mit der Theorie von Weber, Kontecky und Koryta deuten. Abweichungen treten bei der Reduktion von Kationen bei Gegenwart von oberflächenaktiven Kationen auf. Eine Erklärung wird in der spezifischen Adsorption der oberflächenaktiven Kationen gefunden. Es wird eine einfache Formel angegeben, mit der es möglich wird die Bedeckung der Elektrode in den einzelnen Phasen der Tropfdauer aus dem Verlauf der Stromstärke-Zeit-Kurven zu ermitteln. [Ha.Re.]

320 – Über das polarographische Verhalten von Zirkonium- und Thorium Farbstoff-Komplexen. R. Patzak und M. R. Zaki (2. chem. Institut der Universität Wien, Österreich). *Mikrochim. Acta*, (1959) 274.

Das polarographische Verhalten der Solochrom-Violett-RS-Komplexe des Zirkoniums und des Thoriums wurde untersucht, und Proportionalität zwischen der Höhe der Reduktionswellen der Farbstoffkomplexe und der Konzentration der Metallionen im pH-Gebiet zwischen 2 und 3 festgestellt. Nach Überprüfung der pH-Abhängigkeit von Form und Lage der Reduktionswelle konnte eine Arbeitsvorschrift ausgearbeitet werden, die die gemeinsame Bestimmung des Zirkonium- und Thorium erlaubt und nach Maskierung des Thoriums mit Acetatoinen die selektive Zirkoniumbestimmung gestattet. [Ed.Bro.]

321 – Bestimmung von Uran und Thorium in natürlichen Wässern nach vorangehender Anreicherung an Amberlite I.R.A.-400 und Dowex-50. J. Korkisch, P. Antal und F. Hecht (Lehrkanzel für analytische Chemie im 2. chem. Institut der Universität Wien, Österreich). *Mikrochim. Acta*, (1959) 693.

Eine Methode zur Anreicherung und Bestimmung von Mikrogrammengen von Uran und Thorium in Wässern wird beschrieben. Die gleichzeitige Anreicherung dieser beiden Radioelemente erfolgt über der Ascorbinatkomplexe am Ionenaustauscher Amberlite I.R.A.-400 (Ascorbinatform). Die Trennung von einander und von den die Endbestimmung dieser Elemente störenden ebenfalls mit-adsorbierten Elementen Titan, Zirkon, Wolfram und Molybdän wird durch eine Kombination obigen Austauschers mit dem stark sauren Kationenaustauscher Dowex-50 (H⁺-Form) sowie durch geeignete Wahl der Eluierungsmittel bewirkt. Die Endbestimmung des Urans erfolgt unter Anwendung der katalytischen Nitratwelle auf polarographischen die des Thoriums auf spektrophotometrischen Wege mit Thoronol als Reagens. [Ed.Bro.]

322 – Über die Methodik der oszillographischen Polarographie in der chemischen Analyse. J. Dolešchal und J. Zyka (Inst. für analytische Chemie, Universität Prag, Tschechoslowakei). *Österr. Chem. Ztg.*, 60 (1959) 189.

Es wird ein Überblick über die Durchführungsmethoden der oszillographischen Polarographie und ihre Anwendungsmöglichkeiten in der analytischen Chemie gegeben. Insbesondere wird die Verwendung und Funktion des Polarskops beschrieben und auf die Methode der Komperation (Vergleichs-)Titration näher eingegangen. [Ed.Bro.]

323 – The time-dependence of the diffusion-controlled polarographic current. Joseph M. Markowitz and Philip J. Elving (Dept. of Chemistry, University of Michigan, U.S.A.). *J. Am. Chem. Soc.*, 81 (1959) 3518.

Ausgehend von der Annahme, dass zu Beginn der Tropfenbildung an der Quecksilbertropfelektrode der Raum um den sich bildenden neuen Tropfen frei von elektroaktiven Material ist, wurde das Diffusionsproblem für die Quecksilbertropfelektrode neu behandelt. Der erhaltene Ausdruck für die Strom-Zeit-Abhängigkeit führt, auch während der frühen Stadien der Tropfenbildung, zu gut mit experimentellen Messungen übereinstimmenden Ergebnissen. Es wird daher angenommen, dass der ionenfreie Raum um den sich bildenden Tropfen einen realen Bestandteil der physikalischen Situation darstellt. [Ha.Re.]

324 – The determination of the form of zinc in metallurgical products (in Russian). S. G. Trofimova and M. A. Abdeiev (Altai Institute of Ores and Metallurgy, Academy of Sciences of the Kazachian S.S.R.). *Zavodskaya Lab.*, 25 (1959) 1443.

Since there is no dependable method described in the literature for the determination of Zn in ferrite in the presence of ZnS, the authors have attempted to find a selective solvent for ferritic Zn. In the usual method of digesting the sample in a nickel crucible with an alkaline hydroxide under a layer of ethyl alcohol, part of the ZnS is dissolved and increases the result for ferritic Zn. The authors have found that a mixture of 3 N H₃PO₄ and 1 N HCl is most suitable as this dissolves

only 3% of the sulphide. In the solution obtained, Zn is determined polarographically, giving a good wave at potentials of 1.3 to 1.6 V. The character of the wave is independent of the presence of H_3PO_4 . [Ot.So.]

325 – The present state of the analytical chemistry of gallium, indium and thallium (in Russian). T. V. Tsherkashina and V. M. Vladimirova. *Zavodskaya Lab.*, 25 (1959) 1307.

A comprehensive review including gravimetric, volumetric, photometric, fluorimetric, polarographic and other methods for the determination of the elements mentioned. Special attention is given to the separation of the accompanying elements. 118 references up to 1958. [Ot.So.]

326 – The determination of Pb by an anodic amperometric method (in Russian). V. A. Kladeev and A. G. Nikurashina (University of Central Asia, U.S.S.R.). *Zavodskaya Lab.*, 25 (1959) 283.

The authors propose an anodic amperometric method for the titration of lead by $K_2Cr_2O_7$, which is decomposed, the polarographic current being caused by the oxidation of Pb to PbO_2 at the microanode. The determination has been carried out at pH about 4, the beginning of the level part of the diffusion current curve occurring at about 1 V and being dependent on pH. Even a one hundred-fold excess of Ca, Sr, Mg, Zn, Cu and Cd does not interfere. A table is included which shows the influence of various ions on the determination of Pb. The method has been used for the analysis of lead bronze which contained 4.33% Pb. [Ot.So.]

327 – Polarography of organic compounds (in Russian). A. L. Markman (Polytechnical Institute of Central Asia, U.S.S.R.). *Uzbekii Khim. Zhur. Akad. Nauk. Uzbek. S.S.R.*, No. 5 (1959) 50.

A comprehensive review summarising the results of Uzbekian scientists in the field of organic polarography. [Ot.So.]

328 – Adaptation of the Geokhi (I) oscillographic polarograph for determining the instantaneous tension between test and reference electrodes (in Russian). Ya. P. Gokhstein (Moscow). *Zhur. Fiz. Khim.*, 34 (1960) 1138.

A wiring diagram of the adaptation is presented accompanied by a very brief description. The values of the tension peaks obtained for Cd^{2+} , Pb^{2+} , Cu^{2+} , Sb^{3+} and Bi^{3+} in various media corresponded to the theoretical values. [Ot.So.]

329 – Study of the determination of thiamine by derivative polarography (in Russian). V. D. Skobetz and E. M. Skobetz (Ukrainian Academy of Agricultural Sciences, U.S.S.R.). *Ukrain. Khim. Zhur.*, 25 (1959) 114.

The author determines thiamine by the method of derivative polarography in an acid medium. This method was chosen since it indicates relatively ill-defined waves. A dropping mercury electrode with forced dropping was used. Thiamine was polarographed in 0.1 N KCl and was found to give one wave only at $E_{1/2} = -1.32$ V. The height of the maximum is proportional to the concentration. In 0.1 N KCl at pH under 2 (on addition of HCl) another wave appears (-1.25 V). [Ot.So.]

330 – The use of classical and derivative polarography in the analysis of products of the coke industry (in Russian). A. G. Pazdeeva and N. Kh. Tscherkasev (Eastern Research Institute for Coal Chemistry, Nizhnii Tagilsk, U.S.S.R.). *Zhur. Priklad. Khim.*, 32 (1959) 1973.

Pyridine and its homologues together with pyridine bases have been studied by classical and derivative polarography. It was found that the maximum wave-height is proportional to the concentration. Half-wave values for the pyridine derivatives lie in the range of -1.80 V (pyridine) to -1.9 V (2,4-lutidine). The medium employed was 0.1 M KCl. [Ot.So.]

331 – Polarographic and photometric determination of 6-mercaptopurine (in Czech). J. Vacheck (Pharmaceutical and Biochemical Research Institute, Prague, Czechoslovakia). *Českoslov. farm.*, 9 (1960) 126.

Two methods for the determination of 6-mercaptopurine, a polarographic and a photometric one, have been worked out. The polarographic method is based on the formation of an anodic wave in a buffer of pH 7.1 at $E_{1/2} = -0.26$ V (S.C.E.). The wave-height is linear up to a concentration of $2.7 \cdot 10^{-4}$ M. The wave-height is independent of pH, but $E_{1/2}$ shifts to more negative potentials with increasing pH. The presence of hypoxanthine and glucose does not interfere. [Ot.So.]

332 – Polarographic determination of 6-azauracil (in Czech). F. Icha (Penicillin Natl. Corp., Control Laboratory, Roztoky and Prague, Czechoslovakia). *Českoslov. farm.*, 8 (1959) 384.

6-Azauracil shows in the pH range 1.95 to 10.0 a well-defined wave corresponding to the uptake of two electrons during the reaction. The wave-height decreases with increasing pH and finally disappears with the simultaneous appearance of a less distinct negative wave. Best results are

obtained in a Britton-Robinson buffer solution of pH 7-8, where the height of the first wave is directly proportional to the concentration. The half-wave value is -1.18 V. Nine ml of buffer solution are added to 1 ml of the sample and after bubbling with nitrogen the polarogram is registered from -0.8 V. A standard prepared from the pure substance (m.p. 272°) is run simultaneously. [Ot.So.]

333 - The occurrence, constitution, detection and (determination) of anthracene derivatives in drugs. V (in Czech). L. J. Kraus (State Institute for the Control of Drugs, Prague, Czechoslovakia). *Českoslov. farm.*, 8 (1959) 520.

The fifth part of a comprehensive review. Among the chemical methods of analysis, a polarographic method for the determination of aloin in Aloe and its preparations is mentioned which is based on its polarographic determination in a medium of ethanol, water and acetate buffer of pH 4 after removal of oxygen. Four more polarographic methods for the determination of pure anthracene derivatives are mentioned. A separation of hydroxy-anthraquinone derivatives by paper electrophoresis is described, using a barbital buffer of pH 8.6 and a potential of 400 V. [Ot.So.]

334 - Analytical study of N,N'-(bis-methylquinolyl-methylsulphate-6)-urea (Acaprin-Bayer). I. Gravimetric and volumetric determinations (in Czech). V. Špinková and J. Zýka (State Institute for the Control of Drugs, Prague and Department of Analytical Chemistry, Charles University, Prague, Czechoslovakia). *Českoslov. farm.*, 8 (1959) 551.

A polarometric titration is proposed, in which the sample is dissolved in HCl and titrated with a 0.05 M volumetric solution of HgCl_2 . The mercury drop electrode and saturated calomel electrode were directly connected to a sensitive galvanometer.

An electrometric titration of the solution obtained on acid hydrolysis of the sample served as a reference method. A 0.1 M NaNO_2 solution was used, and the electrodes were of platinum and graphite. [Ot.So.]

335 - Polarographic determination of ephedrine (in Czech). G. Buděšínský and T. Čavanák (State Institute for the Control of Drugs, Prague, Czechoslovakia). *Českoslov. farm.*, 8 (1959) 205.

A polarographic method for the determination of ephedrine has been worked out using the fact that polarographically inactive ephedrine can be oxidised to benzaldehyde by boiling for one minute with bromine which is easily reduced polarographically. This method is about 30 times more sensitive than Allport's colorimetric method for ephedrine determination. The sample is dissolved in phosphate buffer (pH 6.5-7). 2 N KCl is added and the oxidation carried out by boiling with water, the excess bromine being removed by thorough bubbling with nitrogen. The polarogram is registered starting at 0.8 V (S.C.E.). The height of the benzaldehyde wave is linearly proportional to the concentration of ephedrine over the range 0.1 to 1.0 mg. By this method ephedrine has been determined in the presence of various current tablet ingredients. [Ot.So.]

336 - Determination of hydrocyanic acid in food products by the method of oscillographic polarography (in Czech). V. Jedlička and A. Pašek (Central Research Institute of the Food Industry, Prague, Czechoslovakia). *Českoslov. farm.*, 8 (1959) 138.

This rapid method for the identification and determination of residual hydrocyanic acid is based on oscillographic polarography with alternating current, using the mercury drop electrode. A 0.1 M NH_4Cl solution is used as the supporting electrolyte with a pH of 5.65. In this electrolyte the determination is not affected even by high contents of carbon disulphide (or its electroreduction products) which otherwise has a very similar oscillographic effect. The potential difference between the hydrocyanic acid wave and the nearest wave of carbon disulphide is -0.35 V. The method has also been applied to the determination of residual hydrocyanic acid in biological material. The calibration curve has the shape of a parabola and is suitable for rapid determinations in the range 0-100 μg HCN/ml. [Ot.So.]

337 - A contribution to the polarographic determination of iron (Fe^{2+} and Fe^{3+}) in galenic preparations (in Czech). M. Mandák, L. Zathurecký, L. Molnár and J. Tomáška (Dept. of Galenic Pharmacy, Pharmaceutical School, Bratislava, Czechoslovakia). *Českoslov. farm.*, 9 (1960) 66.

A polarographic method of determination for Fe^{2+} and Fe^{3+} when present together in Sirupus ferri iodati and Sirupus ferri chlorati has been developed. An anodic-cathodic arrangement is used, the medium being an alkaline solution of triethanolamine. The total iron content, as well as the ratio of Fe^{2+} to Fe^{3+} are evident from a single polarogram, the part of the wave below the zero line corresponding to Fe^{2+} and the part above the line to Fe^{3+} . [Ot.So.]

338 - Polarographic determination of 2-methyl-4-amino-5-acetamidomethylpyrimidine and of 2-methyl-4-amino-5-aminomethylpyrimidine sulphate (in Czech). M. Konupčík and O. Manoušek (Technical Control Dept., Farmakon, Natl. Corp., Olomouc and Central Research Institute of the Food Industry, Prague, Czechoslovakia). *Českoslov. farm.*, 9 (1960) 78.

A new polarographic method has been worked out for the determination of the substances mentioned, which is useful in the synthesis of thiamine. The accuracy of the method is 3-4%. The substances may be determined together in a mixture by use of a derivative method, the precision then being less.

The wave of the first-mentioned substance can be registered in solutions of acids and buffers up to pH 9. The wave is best defined in an acetate buffer of pH 4.7. the half-wave value being -1.32 V. Under the same conditions the half-wave value of the second substance is -1.27 V. For the simultaneous determination of both by derivative polarography an acetate buffer of pH 4.5-5 is most suitable. [Ot.So.]

339 - Amperometric titration of Cu, Pd and Co by α -nitroso- β -naphthol on a rotating tantalum electrode (in Russian). V. A. Khadeev and L. A. Glazunova (V. I. Lenin State University of Central Asia, U.S.S.R.). *Uzbekii Khim. Zhur. Akad. Nauk Uzbek. S.S.R.*, No. 3 (1959) 24.

The authors have studied the polarographic determination of the reagent on Pt and Ta microelectrodes in the cathodic and anodic regions. The reagent gives two waves in acetic and ammoniacal media, an anodic and a cathodic wave. Half-wave values are $+0.4$ and $+0.45$ V in ammoniacal and -0.15 and $+0.6$ V in acetic media. The titration of Cu is carried out on a Ta microelectrode at $+0.9$ V. The error is not larger than a few tenths %. 0.2 mg Cu may be titrated in 40 ml of solution. The influence of a number of ions is described. The titration of Pd is similar to Cu. The titration of Co does not give good results using either Pt or Ta electrodes. [Ot.So.]

340 - Polarographic study of vinyl acetylene hydrocarbons (in Russian). A. A. Petrov and V. V. Petrov (Technological Institute "L'ensoviet", Leningrad, U.S.S.R.). *Zhur. Obshchei Khim.*, 29 (1959) 3987.

A systematic study of the dependence of the reactivity of hydrocarbons on their structure has been made. The authors have studied polarographically 12 different vinyl acetylene hydrocarbons, and they report in tabular form the half-wave tensions, I_d and concentration. In all cases only one wave was obtained. The galvanometer sensitivity was $1 \cdot 10^{-9}$ A/mm/m. The electrolyte was 0.1 M tetrabutylammonium iodide in a 75% solution of dioxane in water. The temperature was regulated to $25 \pm 0.1^\circ$. Oxygen was not removed and the half-wave values were determined with a precision of ± 0.02 V. It was found that substitution of hydrogen atoms in the alkyl groups increases the half-wave values, especially if the substitution takes place next to two multiple bonds. [Ot.So.]

341 - The importance of trivalent iron in pulse-polarography (in Russian). B. Y. Kaplan (Chemical Laboratory, Geological Directory of the Central Districts, U.S.S.R.). *Zavodskaya Lab.*, 25 (1959) 669.

When there is a large amount of Fe^{3+} present in the solution, the pulse-polarographical peaks occur at higher values and, at the same time, are shifted towards negative values. The author, in an attempt to find the cause of this raising of the peaks constructed a pulse-polarograph which prevented this effect. The author found a high conductivity of the mercury drop electrode in the presence of large amounts of Fe^{3+} . A method has been established for the determination of Pb in ores containing acid-soluble Pb. The sample is dissolved in boiling HCl and 500 mg Fe^{3+} are added. After addition of H_3PO_4 the pulse-polarogram is registered. The results differ very little from control samples. This method has no analogy in classical polarography. [Ot.So.]

342 - Amperometric titrations with solutions of mercaptobenzthiazole (in Russian). J. J. Usatenko and G. E. Bekleshova (Dept. of Anal. Chem., Dnepropetrovsk Chemicotechnological Institute, U.S.S.R.). *Ukrain. Khim. Zhur.*, 25 (1959) 512.

0.05 M and 0.005 M solutions of 2-mercaptobenzthiazole in 0.1 M KOH are used as the titrating agents. The compound is easily oxidised on a rotating platinum microanode. The heights of the waves on the voltage-current curves are proportional to the concentration. Oxidation begins at -0.2 V (S.C.E.). The centre of the wave occurs at a tension of $+0.4$ V. Using these results metals which form precipitates with the said compound can be determined. For the determination of Ag, the sample is dissolved in water, NH_4NO_3 is added and the solution is titrated with the reagent which is added from a microburette using an external tension of $+0.5$ V. Results are satisfactory over the range 0.05 - 10 mg Ag. Cu has been titrated in the following media: 0.1 M solutions of KNO_3 , NaCl, NH_4Cl , $(NH_4)_2SO_4$ and NH_4OH . In all cases the equivalence-point is very clear. [Ot.So.]

343 - Polarographic determination of trivalent antimony; the influence of the pH of the solution (in Russian). I. A. Vokoshenko (Technological Institute of the Food and Freezing Industry, Odessa, U.S.S.R.). *Ukrain. Khim. Zhur.*, 25 (1959) 576.

A polarograph of the type SGM-8 was used for the experiments having a galvanometer of $2.9 \times$

10^{-9} A/mm sensitivity. Oxygen was eliminated by bubbling with hydrogen. $SbCl_3$ was obtained by dissolving Sb_2O_3 in conc. HCl using redistilled water. A solution of pH 2 was obtained by diluting 1 ml $0.1 M SbCl_3$ to 100 ml in $3.3 N HCl$ and 10 ml $1 M Na_2SO_4$, and further variations of the pH were carried out by additions of HCl and NaOH. It was found that on varying the pH two kinds of waves may be obtained for Sb(III). $E_{1/2}$ of the first wave shifts to negative values when the pH changes from 5 to 7. $E_{1/2}$ of the second wave does not change on varying the pH from 9 to 10 and remains equal to $-0.88 V$. The height of the first wave depends on the pH and on the medium. The author has investigated the dependence of $E_{1/2}$ on pH and of $I_{1/2}$ on pH and concludes that the wave of half-wave value $-0.88 V$ is caused by the reduction of the SbO^+ ion on the mercury drop electrode. [Ot.So.]

344 – Polarographic study of the azoderivatives of barbituric and thiobarbituric acid (in Russian). K. R. Voronova and A. G. Stromberg (Polytechnic Institute, Tomsk, U.S.S.R.). *Zhur. Obshchei Khim.*, 29 (1959) 3117.

The authors have investigated the relationship between structure and ability to be reduced on the mercury drop electrode. A visual polarograph of the type UFAN was used, having a galvanometer of 10^{-9} A/mm sensitivity and a time constant of 20 sec. The anode was a saturated calomel electrode. The temperature was regulated to 25° by a toluene thermostat. 14 azoderivatives of barbituric acid, and 13 derivatives of thiobarbituric acid were investigated. All the half-wave values are within the range 560–700 mV. Derivatives of thiobarbituric acid are reduced more reversibly than derivatives of barbituric acid. Derivatives containing a naphthalene ring are more easily reduced if the ring contains a sulpho group. The reducibility of derivatives containing a benzene ring is decreased by introduction of either a sulpho or a carboxyl group into the ring. [Ot.So.]

345 – The reduction of furfural on the mercury drop electrode (in Russian). J. E. Exter (Agricultural Institute, Odessa, U.S.S.R.). *Zhur. Obshchei Khim.*, 29 (1959) 17.

The determination of furfural on the mercury drop electrode has already been described previously by some authors. The results vary, probably because the authors did not take into account the influence of the buffers and medium used. The author has investigated the degree of reduction, magnitude of the diffusion current, half-wave tension of furfural in relation to aqueous and aquo-alcoholic media, composition of the buffer and pH. The furfural employed was distilled at $161-162^\circ$. Solutions contained 30, 40 and 60% ethyl alcohol in water and an automatic polarograph SGM-8 was used, the galvanometer sensitivity being $3.3 \cdot 10^{-9}$ A/mm. Drop times were 2.3 to 2.35 sec. Oxygen was eliminated by addition of a few drops of saturated Na_2SO_3 solution. The medium used was $0.1 N NH_4Cl$. With increasing ethyl alcohol concentration the magnitude of the diffusion current dropped because of the higher viscosity, and the half-wave tension shifts in the direction of negative values because of a change in the dielectric constant of the solvent. In a further series of experiments the influence of pH on the polarographic constants was investigated. Oxygen was removed by bubbling of hydrogen for 30 min. The buffers used were: (a) acetate, pH 3.6–5.3; (b) citrate–phosphate, pH 3.6–7.4; (c) phosphate, pH 6–7.4. From the results it may be concluded that two waves are obtained only at pH 4.3, 4.6, 5.0, and 5.3 with buffers (a) and (b). In all other cases only one wave is obtained. In buffers (a) and (c) the half-wave value is more negative than in (b). [Ot.So.]

346 – Determination of small concentrations by Pzdreev's method of oscillographic polarography (in Russian). Yu. M. Kargin (Kazanian State University, U.S.S.R.). *Zavodskaya Lab.*, 25 (1959) 273.

The method described involves the simultaneous electrolysis of two solutions which are identical except that one contains the material to be determined. The curve on the cathode-ray screen corresponds to the theoretical curve of the difference in the electrical current densities. The author has worked out a method for the quantitative determination of small concentrations of Cd, Pb Bi and Zn. Cd and Pb are determined in a medium of $0.1 M HCl$, Bi in $0.4 M CH_3COOH + 0.4 M CH_3COONa + 0.01 M$ trilon and Zn in a medium of $1 M NH_4OH + 1 M NH_4Cl + 0.1 M KNaC_4H_4O_6$. The sensitivity of the analysis is $1 \cdot 10^{-6} M$ and errors in the concentration range $5 \cdot 10^{-6} M$ are 5–8%. [Ot.So.]

347 – Determination of copper in steel by amperometric titration with sodium diethyldithiocarbamate (in Russian). J. J. Usatenko and F. M. Tulupa (Chemico-Technological Institute, Dnepropetrovsk, U.S.S.R.). *Zavodskaya Lab.*, 25 (1959) 280.

In studying the electrochemical properties of sodium diethyldithiocarbamate, the authors found that it is oxidised on a rotating platinum microanode and that it gives two waves (two limiting currents). The first wave appears at a tension of $0.4 V$, the second at $0.8 V$ (S.C.E.). Using these facts the authors determined those metals that form insoluble compounds with the reagent, copper being among these.

The pure salts were titrated using a microburette of 5 ml capacity with a galvanometer of 0.2 mA/degree sensitivity and a resistance of 700 ohms. Trilone B was used for masking 10-fold excesses of Zn or Ni and 20-fold excesses of Fe, its concentration not exceeding 0.02 *M*. Pb(NO₃)₂ was used as the indicator. Pb ions form a compound with the reagent after the equivalence point of copper but before the equivalence-points of Mn, Cd, Fe, Co, Ni and Zn with the reagent have been reached, so that the metals mentioned do not interfere. [Ot.So.]

348 – Polarographic determination of aluminium (in Russian). V. D. Bezuglii (Dental Materials Works, Kharkov, U.S.S.R.). *Zavodskaya Lab.*, 25 (1959) 277.

Aluminium has been determined in a medium of calcium gluconate, with which it forms a complex compound. The author investigated the influence of pH on the character and height of the Al wave. When the pH varies from 4.7 to 3.5 the wave-height remains unchanged. At pH 3.32 the formation of a hydrogen wave which distorts the aluminium wave is observed. The optimum pH is therefore 3.5 to 5. Additions of CaCl₂ do not interfere and make it possible to use more concentrated gluconate solutions with better buffering capacity. The best medium is a mixture of 5% Ca gluconate and 3–5% CaCl₂. *E*_{1/2} is then –1.57 to –1.60 V (S.C.E.). The wave-height is a linear function of Al concentration and small amounts of Na⁺ and K⁺ do not interfere although Fe²⁺ does. The method described may be used for the determination of Al in the presence of Zn using either a calibration curve or the method of standard additions. [Ot.So.]

349 – Polarographic determination of Tl and Pb in Cd (in Russian). V. A. Zimmergagl and Z. A. Kromova (Institute of General and Inorganic Chemistry, Academy of Sciences, U.S.S.R.). *Ukrain. Khim. Zhur.*, 25 (1959) 501.

Tl is extracted from molten Cd by molten SnCl₂, whereupon it is easily determined polarographically. The sensitivity of the method is 0.001%. This method of analysis is more rapid and simple than the electrolytic or dithizone methods. Only a single extraction is necessary for the complete extraction of Tl. For the analysis, 1–20 g Cd are melted under a molten layer of potassium and sodium acetate to remove Zn. After washing the Cd is melted in a test-tube of refractory glass under a layer of SnCl₂ and NH₄Cl. The SnCl₂ is dissolved in hot water, HNO₃ added and the solution evaporated to dryness. This is repeated, hydrazine sulphate being added in the second evaporation. Polarograms are then registered in a medium of citric acid and ammonia. [Ot.So.]

350 – Polarographic determination of microgram amounts of rhenium (in Russian). K. S. Pakhomo-va and L. P. Volkova (State Institute of Mineral Raw Materials, U.S.S.R.). *Zavodskaya Lab.*, 25 (1959) 1291.

The determination of rhenium has been studied in NaCl, KCl and LiCl solutions at pH 9.5. In these solutions the Re wave may be obtained at concentrations of 0.2 µg/ml. Na₂S is added to solutions of ReO₄⁻ and the polarographic medium is 1–5 *N* NaCl. Fe, Mn, As, Sb, Bi, Se, Co and W do not interfere when present in concentrations less than 1 mg/ml, Mo less than 0.2 mg/ml and Cr less than 0.001 mg/ml. The method has been used for the determination of Re in molybdenites. It cannot be used for materials containing more than 0.001 %Cr and nitrates. Sensitivity is 0.2 µg Re per ml. Re may be determined in the concentration range 10⁻⁴ to 5 · 10⁻¹% in samples of 0.05–3 g. [Ot.So.]

351 – Amperometric determination of fluorine (in Russian). V. F. Malcev and V. P. Novak. *Zavodskaya Lab.*, 25 (1959) 1296.

The authors have developed a method for the determination of fluoride ions present either alone or in complexes. The method is based on the titration of fluoride ions with FeCl₃ when excess Fe³⁺ ions cause a diffusion current. A rotating platinum electrode of 400–600 rev/min and a saturated calomel electrode are used. For the determination of free fluoride, an aliquot of the sample is taken, 5 ml ethyl alcohol and 1–2 g NaCl are added, the pH is brought to 5–6 by 2% HNO₃ or 2% NaOH and the volume is brought to about 20 ml. This solution is titrated with a solution containing 0.010 to 0.12 g Fe³⁺ per litre at 0.5 V tension. To determine the total fluoride, 5 ml of the sample is diluted with water, 10 ml 20% NaOH are added and the solution is heated to 50–70°C. After cooling the solution is made up to 100 ml, part of it is filtered and the filtrate is titrated as in the case of free fluoride. [Ot.So.]

352 – Automatic determination of gas humidity with Fisher's reagent (in Russian). A. N. Korol, N. B. Znamenskaya and L. P. Losev. *Zavodskaya Lab.*, 25 (1959) 1305.

A method has been worked out for the determination of the humidity of cracking gases. The gas is bubbled through a known volume of Fisher's reagent (anhydrous pyridine, metallic iodine and dry SO₂ in absolute methyl alcohol). I₂ and SO₂ react to form HI and H₂SO₃ in the presence of water and these are neutralised by pyridine. Two Pt electrodes are placed in the Fisher's reagent and a certain tension passed between them. The equivalence-point is then determined by the dead-stop method. The water content of the gas is then determined from the known volume and

concentration of Fisher's reagent and the volume of the gas. The introduction of gas up to the equivalence-point is controlled by an electronic instrument, whose wiring diagram is appended to the original paper. [Ot.So.]

353 – Polarographic determination of metal ions in the system acetic acid–water (in Russian). P. K. Migal and B. G. Agas'eva (Kishinev State University, Kishinev, U.S.S.R.). *Zhur. Obshchei Khim.*, 29 (1959) 8.

Cd, Zn and Pb were determined in the acetic acid–water medium. The concentration of the acid was 0–80 mol. %. Six concentrations of each ion were studied in each mixture, ranging from 0.2 to 1 mmole/l. A saturated calomel comparison electrode was used and measurements were carried out at $25 \pm 0.2^\circ$. The results were analogous to the results of Migal's earlier paper. The dependence of the diffusion current constant on the acetic acid concentration showed peaks which correspond to the formation of hydrated complexes. [Ot.So.]

354 – Polarographic determination of metal ions in the system muriatic acid–water (in Russian). P. K. Migal and B. G. Agas'eva (Kishinev State University, Kishinev, U.S.S.R.). *Zhur. Obshchei Khim.*, 29 (1959) 3.

The aim of this work was the study of the influence of the solvent composition on the polarographic behaviour of metal ions. The polarographic behaviour of Cd, Zn and Pb ions in a medium of muriatic acid and water was studied. The supporting electrolyte was 0.1 M KCl but Pb was polarographed without a supporting electrolyte. The concentration of the acid ranged from 0 to 100%. In each mixture 6–7 ion concentrations were studied over the range of 0.2 to 0.9 mmoles/l. The comparison electrode was a saturated calomel electrode containing 75% HCOOH. Tensions were determined accurately to ± 0.005 V. The authors include graphs of the dependence of the diffusion current on a concentration for the various ions and show that this dependence is linear. The constant of the diffusion current varies in relation to the concentration of HCOOH present. The authors also give a table showing the dependence of the diffusion current constants of the various ions on the HCOOH concentration. The error of the determinations varied from 4 to 7%. The graph of the dependence of the diffusion current constant on the composition of the medium has two peaks at 33 and 50 mol. % HCOOH. The authors conclude that these correspond to hydrated complexes with 1 and 2 molecules of water. [Ot.So.]

355 – Polarographic oxidation of phenol on the rotating platinum anode (in Russian). V. I. Ginzburg (Moscow, U.S.S.R.). *Zhur. Fiz. Khim.*, 33 (1959) 1594.

A study has been made of the polarographic oxidation of phenol on stationary and rotating platinum anodes. The reasons for the poisoning of the anode, leading to the removal of the diffusion limits, have been established. Optimal conditions for the preparation of the platinum anode and the determination of the voltametric curves to obtain reproducible waves for phenol, corresponding to large limiting currents, have been found.

The effect of the electrode history, the speed of rotation of the electrode, the rate of application of the tension and the temperature of the solution on the limiting current value, residual current, half-wave value and other polarographic characteristics has been studied. The oxidation of phenol on an activated rotating platinum electrode has been found to proceed irreversibly with diffusion limits. It is suggested that the electrode stages of the process include the participation of surface oxides of platinum, a free radical of phenol ether being formed, and end in the formation of capillary active polymers. A new polarographic method for the analysis of small amounts (under $1 \cdot 10^{-5}$ M) of phenol on a rotating platinum electrode has been developed. [Ot.So.]

356 – Electrochemical study of copper–cadmium amalgams (in Russian). A. I. Zebreva, E. E. Spersanskaya and M. T. Kozlovskiy (Alma-Ata, U.S.S.R.). *Zhur. Fiz. Khim.*, 33 (1959) 2715.

No effects indicating interaction between cadmium and copper are observed in the electrolytic oxidation of copper–cadmium amalgams, or when employing the latter as dropping amalgam electrodes (anode), in contrast to the previously described behaviour of copper–zinc amalgams. Despite the excess of copper salt in the solution, not all the cadmium is removed from the amalgam at the moment of the tension jump on cementation of copper by cadmium amalgam; however, the ratio between copper and cadmium in the amalgam does not remain constant. This effect is observed to a much lesser degree on titrating cadmium amalgam with copper salts. The above-mentioned phenomena are explicable from the point of view of the cementation theory derived from the polarization curves. [Ot.So.]

357 – A study of the Karl-Fisher titration (in German). G. T. Walker. *Seifen-Ole-Fette-Wachse*, 85 (1959) 256.

Two methods of preparing the Karl-Fisher solution are given with some specifications on its titration and its application. The reagent is standardized against 10 ml of a standard aqueous solution (0.5% water in dry methanol) and is added until the galvanometer deflection appears

and remains for at least 30 sec.; the value obtained must be corrected for the vessel humidity, which is checked by titration with 5 ml of dry methanol. The sample to be analysed can be in methanolic solution or can be added in the solid state. The water content of petroleum derivatives or fats is found by placing the sample in the still of a dry distillation apparatus, which contains dry benzene (predistilled to give a negative reaction with the Karl-Fisher reagent). The benzene sample solution is distilled, collecting 40 ml fractions of the distillate, which are made up to 50 ml with dry benzene: an aliquot is the nitrated with the Karl-Fisher solution. The distillation is discontinued when the 40 ml fraction does not react with the reagent. The water amount can be calculated from the total quantity of the Karl-Fisher solution required for all the 40 ml fractions. [G.de An.]

358 - Characteristics of irreversible waves and kinetic currents at the rotated dropping mercury electrode. Y. Okinaka and I. M. Kolthoff (School of Chemistry, University of Minnesota, U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 324.

Im Vergleich zur konventionellen Quecksilbertropfelektrode sind die Halbwellenpotentiale von irreversiblen Wellen an einer rotierenden Quecksilbertropfelektrode erheblich negativer. Unter der Annahme, dass bei der rotierenden Elektrode eine gestörte Diffusionsschicht vorliegt, konnten die Abweichungen mathematisch erfasst werden. Eine Überprüfung erfolgte durch eine experimentelle Untersuchung der Reduktion von Nickelionen in Natriumperchloratlösung bei Gegenwart von Polyacrylamid und von Kupferionen in Perchlorsäurelösung bei Gegenwart von Triton X-100. Durch weitere Messungen an Vanadium- und Kupfersalzen wird gezeigt, dass eine an der konventionellen Quecksilbertropfelektrode reversible Welle an der rotierenden Elektrode eine irreversible Charakteristik erhalten kann. Der Ausdruck für den kinetischen Strom bleibt bei der rotierenden Elektrode der gleiche wie er für die konventionelle Elektrode abgeleitet wurde. Messungen mit Glucose und Brenztraubensäure ergaben, dass die Dicke der Reduktionsschichten bei beiden Elektroden die gleiche ist, und bei der rotierenden Elektrode unabhängig von der Drehzahl bleibt. [Ha.Re.]

359 - Application of polarography using the a.c. bridge-polarograph (in Japanese). T. Takahashi, H. Shirai and E. Niki (Inst. Ind. Sci., University of Tokyo, Japan). *Repts. Inst. Ind. Sci., Univ. Tokyo*, 8 (1959) 122.

After giving a description of the apparatus (Takahashi and Niki, *Talanta*, 1 (1958) 245) the linearity of the response is tested and the behaviour of the following ions is examined in different supporting solutions: Pb^{2+} in H_3PO_4 , HNO_3 , KNO_3 , HCl and KCl solutions; Cd^{2+} in H_3PO_4 , $KCNS$, KCl , KBr , KNO_3 and NH_4Cl/NH_4OH solutions; In^{3+} in KNO_3 , KCl and HCl solutions; W^{6+} , Ti^{4+} and Mo^{6+} in H_3PO_4 solutions; Ni^{2+} and Zn^{2+} in $KCNS$ solutions and some Cd^{2+} , Cu^{2+} Pb^{2+} , Zn^{2+} and Fe^{3+} chelates.

The influence of oxygen on the polarograms obtained with the different solutions is also investigated and discussed. Hydrogen is not suitable for removing oxygen from the solutions since it modifies the polarograms; therefore nitrogen is used for this purpose. [G.de An.]

360 - Polarographic determination of dissolved oxygen and of a microorganism's respiration intensity using the rotating platinum electrode (in Russian). T. I. Grinjur (Sci. Research Inst. for Antibiotics, Moscow, U.S.S.R.). *Lab. Delo*, 5 (1959) 31.

In order to control nutritive solutions and to follow the growth of micelia cultures in the antibiotics industry the solution under investigation is collected in a round-bottomed flask which contains 1/10 or 1/5 of its volume of saturated aqueous phenol solution. The flask has a stopper through which two glass tubes with stop-cocks are inserted; one of them reaches the bottom of the flask and is connected to the fermentation kettle. After sampling, the stop-cocks are closed and the solution is well stirred. It is then transferred to a 3-4 ml molybdenum glass electrolysis vessel provided with a platinum microelectrode, which has a diameter of 1.5-2 mm and rotates at not less than 600 rev/min; three tubes with stop-cocks allow the connection with a S.C.E. through a KCl-agar bridge and the inside of the vessel. The electrolysis cell containing the solution is maintained at a temperature suitable for the microorganism culture and three current intensities (I_c , I_n , I_o) are measured at 0.8 V: I_c = current intensity in the solution without any treatment; I_n = current intensity in the solution after saturation with air; I_o = current intensity in the solution after saturation with a gas such as nitrogen, hydrogen or carbon dioxide. The oxygen content C expressed as a percentage of the oxygen content of the solution saturated with air is given by

$$C = 100(I_c - I_o)/(I_n - I_o)$$

while the true oxygen content C_1 of the solution corrected for added phenol is

$$C_1 = (C - a)/(100 - a)$$

where a is the phenol content of 100 ml of the solution.

The microorganism's respiration intensity can be deduced from the diminution of the oxygen content. [G.de An.]

361 – Oxydation de la méthionine par PbO₂ (in French). M. Convers (Laboratoire de Chimie Analytique, Ecole de Physique et Chimie Industrielles, Paris, France). *Bull. soc. chim. France*, (1960) 105. Par une étude voltamétrique à une électrode de PbO₂, de l'oxydation de la méthionine d'une part, et de la réduction de PbO₂ d'autre part, l'auteur peut prévoir les conditions d'oxydation chimique de la méthionine par PbO₂. [Bad.Lam.]

362 – Determination of mercury, copper and zinc by derivative polarography. Application to solutions of uranyl sulphate containing corrosion products. R. G. Ball, D. L. Manning and O. Menis (Oak Ridge Natl. Lab., Tenn., U.S.A.). *U.S. Atomic Energy Commission Rept. ORNL-2717*, (1959). Zn is extracted from the solution with chloroform as the diethyldithiocarbamate complex, which is then taken up in dilute HCl and polarographically measured (coefficient of variation for 2–20 µg/ml Zn = 2%).

Mercury and copper are also determined polarographically, serious interference by Fe being eliminated by the use of Na citrate–NH₄ carbonate as the supporting electrolyte (for high Fe contents) or nitrilo-triacetic acid (for low Fe contents). EDTA is also satisfactory as the complexing agent in the absence of Fe (in the range 2–20 µg/ml, the coefficient of variation is 4%). [Ca.Cas.]

363 – Polarographic determination of tin in Zircaloy-2. T. Bruce and R. W. Ashley (Atomic Energy of Canada Ltd., Chalk River, Ont., Canada). *Atomic Energy of Canada Ltd. Rept. CRDC-840*, (1959).

The alloy is dissolved in HF (or HBF₄) and HBr, KBr is added as the supporting electrolyte and Triton X-100 as the maximum suppressor and the polarogram is then recorded. [Ca.Cas.]

364 – Analytical chemistry. J. Haslam and D. C. M. Squirrel. *Ann. Repts. Progr. Chem. (Chem. Soc. London)*, 56 (1953) 372.

Report on the most recent papers concerning different methods of chemical analysis. The papers considered were published mainly in 1959, some in 1958 but none in 1960. 6 pages are devoted to electrical methods: potentiometry and polarography. There are 256 references of which 33 concern the methods mentioned above and only 3 concern other electrochemical methods. [Red.]

See also abstracts nos. 229–233, 236, 237, 240, 241, 371.

4. Potentiometry

365 – The Hammett equation for ionisation of the ortho-substituted derivatives of benzoic acid (in Polish). M. J. Malawski and T. Drapała (Dept. of Organic Chemistry, University of Warsaw; Dept. of General Chemistry, School of Agriculture, Warsaw, Poland). *Roczniki Chem.*, 33 (1959) 879.

A series of 4'-substituted biphenyl-(2)-carboxylic acids was obtained and their ionisation constants calculated from potentiometric measurements in 50% (vol.) ethanol–water solutions. The results plotted against Hammett's substituent constant gave a linear relationship. [Ad.Hu.]

366 – Some properties of acid neutralization curves (in Polish). W. Wyczałkowska (Dept. of General Chemistry, School of Agriculture, Warsaw, Poland). *Roczniki Chem.*, 33 (1959) 1389.

Neutralization curves of medium strength acids were investigated. The Auerbach–Smolczyk equation was transformed into the equation:

$$z = \frac{a(Kc - c_h^2 - c_h^K)}{c_h^2 + c_h^K + c_h a c + a c K}$$

where c = stoichiometric acid concentration, K = dissociation constant of the acid, c_h = hydrogen ion concentration, $z = av/V$, where $a = nc$, n = base concentration, v = added volume of base and V = initial acid volume. Consideration of this equation leads to the conclusion that for small c/K values, when $z = 0.5$, $\text{pH} = \text{p}K$ as a limiting case. For larger c/K values (*i.e.*, for stronger acids) $\text{pH} = \text{p}K$ when z is within the range 0 to 0.5. For $c/K = 2$, $\text{pH} = \text{p}K$ when $z = 0$ as a second limiting case. These conclusions were proved by chloroacetic acid titrations at different concentrations. [Ad.Hu.]

367 – Potentiometric investigation of adsorption layers on powdered carbon (in Polish). W. Tomassi (Dept. of Physical Chemistry, Politechnika, Warsaw, Poland). *Przemysl Chem.*, 38 (1969) 76. Several carbon preparations were studied potentiometrically after adsorption of certain sub-

stances from aqueous and ethanolic solutions and also from the gas phase. From aqueous solution, acetic acid, ammonia and chlorine were adsorbed, from ethanol solution, ethyl acetate and from the gas phase, ammonia and chlorine. In the range of not too high concentrations the electrode potential π depends on the surface concentration Γ of the adsorbed substance

$$\pi = a\Gamma^b$$

where a and b are constants. From potential measurements some conclusions can be deduced about the state of the powdered solid phase. [Ad.Hu.]

368 – Application of powder electrode potential measurements and catalytic properties investigation to the characterisation of lead powders for storage batteries (in Polish). K. Appelt, M. Elbanowski and A. Janko (Central Laboratory of Cells and Accumulators, Poznań, Poland). *Przemysl Chem.*, 38 (1959) 156.

Lead powders prepared in different ways were investigated by means of measurements of the adsorption potential of powder electrodes (*Przemysl Chem.*, 36 (1957) 9, 500), and by the determination of the catalytic properties of indigocarmine by peroxidative oxidation. Identical potential values were obtained for powder electrodes from tetragonal lead oxide with a deformed lattice and for electrodes from a commercial lead powder. [Ad.Hu.]

369 – Determination of normal potentials of dehydrogenated and non-dehydrogenated Raney nickel preparations (in Polish). Z. Siedlecka (Dept. of Physical Chemistry, Politechnika, Warsaw, Poland). *Przemysl Chem.*, 38 (1959) 211.

The normal potentials of powder electrodes made of Raney nickel containing various initial aluminium amounts were determined. The potential did not vary considerably and was more negative when the initial aluminium content in the alloy was greater. Completely dehydrogenated nickel electrodes showed more negative potentials than those prepared from non-dehydrogenated nickel. When nickel was partially dehydrogenated the electrode potentials shifted after some time to the potential values of the non-dehydrogenated electrodes. All measurements were performed in the cell, Ni/NiSO_{4(aq)}/Hg₂SO_{4(s)}, Hg, at 25°. [Ad.Hu.]

370 – Electrochemical research on paraffin membranes. VI. H. J. C. Tendeloo and F. H. van der Voort (Laboratory of Physical and Colloid Chemistry, Agricultural University, Wageningen, The Netherlands). *Rec. trav. chim.*, 79 (1960) 639.

The tension of cells of the type Ag/AgCl–electrolyte 1–membrane–electrolyte 2–S.C.E. is measured. The membrane consists of pure paraffin, some Arlcel 85 and sometimes stearic acid, calcium stearate or a mixture of these substances. A marked effect due to the anion present in the salt solutions is observed. It is assumed that the electrode should be considered as an adsorption electrode and that the adsorption process is accompanied by ion exchange.

The measurements lead to the conclusion that exchange of ions takes place preferably at those spots where it is possible to exchange ions of equal valency. [H.L.Ki.]

371 – Electrochemical methods of ultramicroanalysis. I. P. Alimarin and M. N. Petrikova (V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, Moscow, U.S.S.R.). *Rec. trav. chim.*, 79 (1960) 491.

The authors review earlier work on reduction and oxidation executed in a capillary vessel on the platform of a microscope with a volume of about 1 mm³ and current of 10⁻⁴–10⁻⁵ A. It is also possible to execute potentiometric as well as amperometric titrations on the same scale with an accuracy within 2%. The introduction of an ultramicro glass electrode for measuring the pH in such small volumes is new. A drop of the solution is placed in an open capillary. The bulb of the glass electrode (diameter 0.3 mm) is introduced into one side of it and the capillary end of a calomel electrode placed at the other side. The whole is constructed on the platform of a microscope provided with two manipulator mechanisms. [H.L.Ki.]

372 – Standard potential of the silver bromide–silver electrode in anhydrous methanol at 25°C. C. L. de Ligny and A. A. Wieneke (Laboratory of Analytical Chemistry, State University, Utrecht, The Netherlands). *Rec. trav. chim.*, 79 (1960) 268.

The value of the standard tension of the silver–silver bromide electrode found in the literature (–0.1328 V) leads to a difference of about 0.04 pH units when using it for the calculation of pH measurements in anhydrous methanol. Supposing the literature value for the silver–silver chloride electrode (–0.0103 V) to be correct, the authors determined the standard tension of the silver–silver bromide electrode. This appears to be –0.1375 V.

In this article all necessary experimental details are given. [H.L.Ki.]

373 – The dissociation constants of some aliphatic amines in water and methanol–water mixtures.

C. L. de Ligny (Laboratory of Analytical Chemistry, State University, Utrecht, The Netherlands). *Rec. trav. chim.*, 79 (1960) 731.

It is shown that in calculations the dissolved amounts of base and salt have to be corrected for hydrolysis. The molal activity coefficient is calculated by the Gronwall-La Mer-Sandved equation. The pK values show a minimum at 60–80% methanol. [H.L.Ki.]

374 – The liquid-junction potentials between some buffer solutions in methanol and methanol-water mixtures and a saturated potassium chloride solution in water. C. L. de Ligny and M. Rehbach (Laboratory of Analytical Chemistry, State University, Utrecht, The Netherlands). *Rec. trav. chim.*, 79 (1960) 727.

From measurements of the tension of the cell: H₂/standard buffer in methanol-water/KCl (saturated in water) comparison electrode, it is possible to calculate the liquid-junction tensions. The results obtained for oxalate and succinate buffers agree. [H.L.Ki.]

375 – The pH of some standard solutions in methanol and methanol-water mixtures. I. Theoretical. C. L. de Ligny, P. F. M. Luykx, M. Rehbach and A. A. Wieneke (Laboratory of Analytical Chemistry, State University, Utrecht, The Netherlands). *Rec. trav. chim.*, 79 (1960) 699.

Some complications arise when the method of the National Bureau of Standards is applied to solutions other than water. The authors derive a correction term for the incomplete dissociation of the added halides. It is also necessary to estimate the value of the molal activity coefficient of the halogen ion. It appears that the optimum concentration for the buffer solution is 0.01 M; only univalent salts should be present. [H.L.Ki.]

376 – The pH of some standard solutions in methanol and methanol-water mixtures. II. Experimental Part. C. L. de Ligny, P. F. M. Luykx, M. Rehbach and A. A. Wieneke (Laboratory of Analytical Chemistry, State University, Utrecht, The Netherlands). *Rec. trav. chim.*, 79 (1960) 713.

The following buffers were chosen as standard solutions: 0.01 M oxalic acid + 0.01 M ammonium hydrogen oxalate; 0.01 M salicylic acid + 0.01 M sodium salicylate; 0.01 M succinic acid + 0.01 M lithium hydrogen succinate. The results of the measurements are tabulated and compared with previously published data. In practice one should standardize the pH-meter which should be equipped with glass and calomel electrodes with a standard buffer prepared in exactly the same solvent as the unknown solution, in order to eliminate the considerable liquid-junction tension. [H.L.Ki.]

377 – A new reducing agent: reduction of vanadium(IV) and uranium(VI) with ferrous ion in catechol solutions. J. W. Miller (Research Div., Phillips Petr. Co., Bartlesville, Oklahoma, U.S.A.). *Talanta*, 4 (1960) 292.

In a study of the polarographic behaviour of vanadium, iron and uranium as their catechol complexes a powerful reducing system was observed. According to the polarographic data the reduction tension of the ferrous-catechol/ferri-catechol system at pH 9.5 is -0.97 V vs. Ag/AgCl. It appears that the ferrous complex will reduce water too. In ammoniacal solution in the presence of excess catechol, ferrous ions reduce vanadium and uranium rapidly to the V(III) and U(IV) species respectively. The analytical application of this reaction has been examined briefly. The direct titration of uranyl-catechol with ferrous ion to a potentiometric or amperometric end-point indicated the stoichiometry mentioned above. Similar behaviour was also noted in the case of the vanadyl-catechol complex. [Ja.Inc.]

378 – The determination of sulphur in organic compounds with metallic silver as absorbent. J. P. Dixon (Shell Research Ltd., Chester, England). *Talanta*, 4 (1960) 221.

In the determination of microgram quantities of sulphur by absorption on silver of the sulphur oxides given after combustion of sulphur compounds, the interfering factors were isolated and eliminated. For complete oxidation the "empty tube combustion technique" was used for efficient absorption on electrolytically prepared silver. The extraction of silver sulphate was carried out with deionised water. For preventing the formation of silver oxide on cooling from 450° to below 100°, the silver was blanketed with nitrogen.

The recommended apparatus consists of a rotameter, a preheater (900°) filled with copper oxide wire, and a scavenging tube filled with "Carbosorb". The latter is connected with a combustion tube, with a baffle tube (900°) and finally with an absorption tube (400–450°). During the combustion period the oxygen flow through the whole apparatus was 50 ml/min. After combustion the silver was covered with boiling water and nitrogen allowed to agitate the liquid. After washing with water, alcohol and ether, the solution was titrated potentiometrically with 0.1 N potassium iodide, using a micro-glass and silver electrode pair and a syringe burette.

The minimum limit of determination is 10–15 µg of sulphur, using a 25 mg sample, and the reproducibility about 3%. [Ja.Inc.]

379 – Lithium chloride in non-aqueous potentiometric titrations. E. L. Grove (School of Chemistry University of Alabama, U.S.A.). *Talanta*, 4 (1960) 205.

The use of lithium chloride for improving instrument stability in non-aqueous potentiometric titrations was investigated. Its use was found undesirable in the titration of aluminium oxinate or pyridine with 0.1 *N* perchloric acid in glacial acetic acid or in chlorobenzene. The real usefulness of lithium chloride was found to be in the titration of weak acids with sodium methoxide in neutral or weakly basic solvents. In the titration of benzoic and stearic acids lithium chloride improved the stability of the pH-meters, using a glass-calomel electrode combination and caused an increase in $\Delta E/\Delta V$ (the change of tension per increment of titrant) near the end-point when solvent mixtures with high ratios of benzene to methanol and dimethylformamide were used. [Ja.Inc.]

380 – A potentiometric study of 2-substituted benzimidazole ligands. T. J. Lane and John M. Daly (Dept. of Chemistry, University of Notre Dame, Notre Dame, Ind., U.S.A.). *J. Am. Chem. Soc.*, 81 (1959) 2953.

Für verschiedene 2-substituierte Benzimidazole ($R = -CH_2OH, -COOH, -CH_2-COOH$ und $-CH_2-CH_2-COOH$) wurden in 50%igen Dioxan-Wasser-Mischungen die Säuredissoziationskonstanten gemessen. Die Stabilitätskonstanten von Mn(II), Zn(II), Fe(II), Pb(II), Co(II), Ni(II) und Cu(II)-Komplexen wurden bei 3°, 25° und 40° bestimmt. Die Stabilität der Komplexe steigt in der Reihe $Mn < Fe < Co < Ni < Cu < Zn$ an. Die thermodynamischen Ergebnisse stimmen für 2-Benzimidazoleessigsäure und 2-Benzimidazolpropionsäure mit Beobachtungen von George überein. [Ha.Re.]

381 – Essais de pureté des produits pharmaceutiques à l'aide des microméthodes (en allemand). H. Lehner (Institut de recherches, Dr. Wander A.G., Berne, Suisse). *Chimia*, 13 (1959) 248.

A propos des contrôles effectués sur les produits pharmaceutiques l'auteur cite quelques méthodes d'électroanalyse telles que: les titrations potentiométriques, ampérométriques, coulométriques ainsi que la méthode polarographique. Il donne l'exemple du dosage de traces de Xanthone dans le "Spalial" en présence d'une base quaternaire (0.1 à 0.01%) et la détermination de traces d'ions chlore par potentiométrie (la sensibilité est de $5 \cdot 10^{-5} M$). [De.Mo.]

382 – Electrode de verre avec adjonction de dioxyde de germanium (en allemand). W. Simon, G. H. Lyssy, P. F. Sommer et D. Wegmann (Laboratoire de chimie organique de l'École Polytechnique Fédérale, Zürich Suisse). *Helv. Chim. Acta*, 42 (1959) 1581.

Cet article est une suite d'un premier travail (*Helv. Chim. Acta*, 41 (1958) 2099). Les auteurs substituent, dans 5 électrodes de verre connues, 0.5, 1.0, 2.0, 4.0, 8.0 et 16.0 mol% de SiO_2 par du dioxyde de germanium. Les verres renfermant 0.5 à 2% de GeO_2 présentent de réels avantages sur les électrodes ordinaires. Des graphiques donnent les erreurs dues aux ions et la résistance des électrodes pour des verres de diverses natures. Au dessus de 4 mol% de GeO_2 , l'erreur due aux ions et la résistance de l'électrode est peu changée par rapport à l'électrode de verre ayant les mêmes caractéristiques. [De.Mo.]

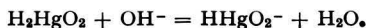
383 - Reduction of acid potassium permanganate by iodide, nitrite and bromide. B. P. Gyani and S. N. Prasad (Science College, Patna, India). *J. Indian Chem. Soc.*, 37 (1960) 85.

The reduction of $KMnO_4$ solution by KI, KNO_2 and KBr in the presence of different concentrations of H_2SO_4 and HCl, has been studied by potentiometric titrations with each of the reactants alternately used as the titrant. Sufficient time was allowed for equilibrium to be attained. No titration was completed in less than 6 h. When $KMnO_4$ is reduced, the E_0 is positive at all stages and hence the reduction is always instantaneous.

It is observed that acid $KMnO_4$ may be quantitatively reduced to Mn^{2+} by iodide and nitrite when the conditions are suitable ($N/10$ to $5 N H_2SO_4$); 5.0 and 2.5 moles of KI and KNO_2 respectively are required per mole of $KMnO_4$. On the other hand, reduction by KBr ($N/10$ to $2 N H_2SO_4$) stops short at the MnO_2 stage. The complete reduction to Mn^{2+} may perhaps be attained at 2 to 3 *N* H_2SO_4 , but further increase in acid concentration (up to 8 *N*) leads to evolution of oxygen and the consumption of KBr again drops steadily. In the KI titration, there is an initial inflection at 0.5 mole KI and in the KNO_2 titration, at 1.5 moles but each of these shifts to larger amounts as the H_2SO_4 concentration increases. With HCl, the titration of KI is not possible beyond $N/10$ HCl, due to evolution of chlorine. The first inflection remains steady at $1/2$ mole of KI and the second one is at a point somewhat less than 5 moles. With KNO_2 ($N/10, N/20, N/30$ HCl) two inflections were obtained corresponding to 1.5 and 2.5 moles. With KBr, the inflection remained steady at 3.0 moles in all the HCl solutions. The mechanism of reduction has been explained. [R.S.Sa.]

384 – The solubility and amphoteric properties of mercuric oxide. T. M. Salem (Chem. Dept., Ain Shams University, Cairo, Egypt). *J. Indian Chem. Soc.*, 36 (1959) 83.

The solubility and amphoteric properties of mercuric oxide have been examined from the mean of 10 determinations. At 35°, the solubility in water has been found to be 3.47×10^{-4} g mol Hg/l. The solubility at first decreases, then increases with increase of alkali hydroxide concentration. The isoelectric point of this oxide is between pH 7.5 and 8. At lower pH, the oxide in solution dissociates mainly as a base which may be $\text{Hg}(\text{OH})_2$. At higher pH, the dissociation is mainly as an acid H_2HgO . It is observed that HgO possesses weak acid properties and that the isoelectric point should be on the alkaline side near the neutral point according to the expected reaction



A potentiometric method has been used for the determination of small amounts of Hg using KI solution and amalgamated platinum as an indicator electrode. An amount of mercury as small as 0.5 mg/100 c.c. can be determined with an accuracy of not less than 1%. [R.S.Sa.]

385 – A semi-flowing junction method for the measurement of liquid-junction potentials. P. B. Mathur (Electrochemical Laboratories, Karaikudi, India). *Indian J. Appl. Chem.*, 22 (1959) 173. A semi-flowing method, where one liquid is kept stationary and the other moving, is described. The technique is simple and gives a very sharp junction. The apparatus consists of a U-tube AB attached to another bent tube C by means of an 0.2 cm thick capillary. The tubes AB and C are first filled with a solution and then C is corked. The liquid is then taken out from A and B. Afterwards an equilibrium is established. The junction tensions between the water and the saturated solutions of the electrolytes are measured, keeping the electrolyte solutions as the stationary phase and water as the flowing phase. Highly reproducible results are obtained with solutions which are anodic with respect to water, while the tensions of the cathodic solutions fall with time. The latter has been explained to be due to the tendency of these salts to become adsorbed over the electropositive metals thus rendering the electrode polarized. [R.S.Sa.]

386 – Complex compounds of aluminium with mandelic acid. S. N. Srivastava and Manohar (St. Johns College, Agra, India). *J. Indian Chem. Soc.*, 37 (1960) 299.

From pH and conductance measurements it is concluded that mandelic acid is a good chelating agent for aluminium. To constant volumes of aluminium chloride, varying amounts of chelating agent were added so as to make three sets of mixtures containing the reagents in the ratios 1 : 1, 1 : 2 and 1 : 3. To these mixtures, varying quantities of NaOH solutions of known strength were added and the pH and specific conductances of the mixtures were determined and plotted on a graph against the volume of the alkali added. For comparison, AlCl_3 and mandelic acid were titrated potentiometrically and conductometrically with standard alkali solution under the same conditions. The chelate of composition 1 : 1 is formed at a lower pH value, while 1 : 2 and 1 : 3 chelates, which occur at pH 6.5 and 7.8 respectively, are more stable than 1 : 1 chelate. The chelation takes place easily on account of the close proximity of the acidic and the electron-donating groups, a fact which is essential for formation of the ring containing the metal ion. [R.S.Sa.]

387 – Chloramine-T as a volumetric reagent: determination of organic derivatives of hydrazine. B. Singh, S. S. Sahota and R. P. Singh (Punjab University, Chandigarh, India). *J. Indian Chem. Soc.*, 37 (1960) 392.

In the presence of HCl, chloramine-T solution has been used as a volumetric reagent for the determination of semicarbazide hydrochloride, benzal semicarbazone, *o*-nitro, *m*-nitro, *o*-hydroxy, *p*-methoxy, *p*-chloro and *o*-chloro-benzal semicarbazones, acetone semicarbazone, benzoyl-hydrazine, benzalazine, 4-phenyl-semicarbazide hydrochloride, thiosemicarbazide, phenylhydrazine hydrochloride and *B*-formylphenylhydrazine by means of visual titrations and also by a potentiometric titration method.

In visual titrations iodine monochloride-chloroform was used as the indicator. To a known amount of each substance was added water (25 ml), HCl (2.5 to 4.5 *N*), 0.02 *M* iodine monochloride (5 ml) and chloroform (5 ml) and the solution titrated with 0.05 *M* chloramine-T solution. The end-point was very sharp. In the potentiometric method, HCl (5.0 to 5.5 *N*) was added to the solution of the substance, one drop of 0.005 *M* KI was added as a catalyst and the mixture was titrated potentiometrically against 0.05 *M* chloramine-T using platinum as the indicator electrode. At the equivalence-point a sharp jump in tension was observed in each case. The results were very accurate. [R.S.Sa.]

388 – La valeur du pH comme mesure de l'acidité (en allemand). K. Schwabe (Institut d'électrochimie, Haute École technique de Dresde, Allemagne). *Chimia*, 13 (1959) 385.

L'auteur montre qu'il n'y a de mesure de pH que lorsque les protons interviennent. Les valeurs données par les méthodes potentiométrique, colorimétrique et catalytique ne sont pas comparables. Le pH, rapporté à une activité moyenne de $a_{\pm} = 1$ dans l'eau montre la même évolution que le

pH_t conventionnel quand on passe d'une solution aqueuse à un solvant organique. Les valeurs, de pH_t peuvent servir d'élément de comparaison de l'acide dans l'eau et dans le solvant organique, comme le montrent les recherches polarographiques, bien que pH_t ne représente pas une valeur acceptable de point de vue thermodynamique. La valeur du pH imaginée il y a 50 ans par Sørensen garde un intérêt pratique pour la mesure de l'acidité mais sa signification physique a perdu de son importance. Le développement de la thermodynamique et celui de la théorie des électrolytes sont venus remettre en question bien des considérations qu'on croyait solidement établies.

[De.Mo.]

389 – Titration of ketimines in glacial acetic acid. P. L. Pickard and F. A. Iddings (Chem. Div., Celanese Corp. of America, Clarkwood, Tex., U.S.A.). *Anal. Chem.*, 31 (1959) 1228.

Solutions of ketimines in acetic acid are titrated with perchloric acid. Accuracy and precision are within 1%. Potentiometric or visual end-point detection is used. The potentiometrical end-point detection uses a platinum glass electrode system in conjunction with a Beckman Model H pH-meter. S-shaped curves are obtained. Few impurities other than amines or ammonia interfere. 0.1 N solution of perchloric acid in acetic acid is used as titrant. Potassium acid-phthalate is taken as a standard. Procedure: ketimine samples are weighed into a small bottle containing a few ml of acetic acid. The sample is rinsed into a volumetric flask and diluted to the mark with acetic acid. Aliquots are taken for titration.

[Kl.Gr.]

390 – Automatic titration of peroxides in petroleum products. J. S. Matthews and J. F. Patchan (Gulf Research and Develop. Co., Pittsburgh, Pa., U. S.A.). *Anal. Chem.*, 31 (1959) 1003.

The method described involves oxidation of iodide and the continuous reduction of iodine with standard thiosulfate solution. The reaction is indicated by the use of an automatic potentiometric titrator. It is applicable to low or high concentrations of diacyl type peroxides and hydroperoxides. Olefinic and sulfur compounds do not interfere. The accuracy is within 3% on peroxide numbers above 1 and within 0.1% on peroxide numbers of lower values. A Beckman automatic titrator is used. Procedure and apparatus are described.

[Kl.Gr.]

391 – Redox potentials in melts: the system titanium chloride + lithium chloride + potassium chloride. I. A. Menzies, G. J. Hills, L. Young and J. O'M. Bockris (Chem. Dept., Imperial College, London, Great Britain). *Trans. Faraday Soc.*, 55 (1959) 1500.

In halide melts, titanium tetra, tri and dichlorides are well characterized stable compounds at room temperature. Analytical studies have been made of the equilibria between titanium metal and these chlorides dissolved in alkali metals. This study deals with the electrochemical investigation of this system. Potentiometric titration of TiCl₃ with hydrogen is reported. The all-glass high temperature cell together with the method of preparation of LiCl + KCl eutectic and the experimental technique is also given.

[M.K.Hus.]

392 – The kinetics of anodic processes at very low current densities. II. The anodic dissolution of tin. S. E. Khalafalla, A. M. Shams El-Din and H. Kotb (Chem. Dept., Faculty of Science, Cairo University, Egypt). *Egypt. J. Chem.*, 2 (1959) 1.

Through dissolution characteristics of the metal in acid solutions at constant current, the kinetics of the Sn/Sn²⁺, Sn⁴⁺ electrode were studied. The tension-time curves at different current densities showed two slopes. For the Sn/Sn²⁺ electrode process, the rate constant lies between 2.5 · 10⁻² and 3.6 · 10⁻³ cm sec⁻¹. By calculation, the transfer coefficient was found to equal 0.52.

[M.K.Hus.]

393 – Microtitration of weak organic acids in non-aqueous solvents. B. K. Maurmayer, Muhel Margosis and T. S. Ma (Dept. of Chem., Brooklyn College, New York, U.S.A.). *Mikrochim. Acta*, (1959) 177.

Phenole lassen sich in Dimethylformamid titrieren. Enthalten sie Chloratome bzw. Hydroxyl- oder Carbonylgruppen kann gegen Thymolblau titriert werden. Sind Amino- oder Alkylgruppen enthalten, wird gegen Azoviolett titriert. Verbindungen mit einem pK_s bis etwa 9 durch visuelle Endpunktbestimmung bis 10.5 auf potentiometrischen Weg. Pyridin eignet sich als Lösungsmittel für visuelle Titrationen schwacher Säuren mit einem pK_s bis etwa 10.5. Methylisobutanon hingegen für saure Verbindungen mit einem pK_s von etwa 9 und weniger wobei Thymolblau als Indikator dient. Hydrazide werden besser potentiometrisch titriert. Die visuelle Endpunktbestimmung ist hier nicht gut geeignet.

[Ed.Bro.]

394 – Neue Schnellmethode zur Mikroanalytischen Bestimmung von Chlor, Brom und Fluor in organischen Substanzen. F. Ehrenberger (Analyt. Laboratorium der Farbwerke Höchst A.G., vormals Meister Lucius und Brüning, Frankfurt a.M.-Höchst, Deutschland). *Mikrochim. Acta*, (1959) 192.

Die organische Substanz wird im Wasserstoffstrom vergast und in einer kleinen Knallgasflamme verbrannt. Die Verbrennungsprodukte werden mit dem in der Knallgasflamme entstehenden Wasserdampf in eine Vorlage geführt und in Lauge absorbiert. Da das Volumen der Vorlagelösung auf ungefähr 30 ml gehalten werden kann, sind die potentiometrischen Titraktionen von Chlor und Brom mit 0.02 *N* AgNO₃ bzw. Fluor mit 0.01 *N* Thoriumnitratlösung gut durchführbar.

[Ed.Bro.]

395 – Acidimetric titration of metal acetates in glacial acetic acid. A. T. Casey and K. Starke (Dept. of Chem., University of Melbourne, Carlton, Victoria, Australia and Dept. of Chem., University of Kentucky, Lexington, Ky., U.S.A.). *Anal. Chem.*, 31 (1959) 1060.

Acetates of 18 metals can be titrated potentiometrically in glacial acetic acid. Al, Fe and Cr give unusual results. The metals are dissolved as acetates or nitrates. In the latter case the nitrate radical is decomposed with acetic anhydride. A Beckman Model G pH-meter with a glass and a saturated calomel electrode is used. As a titrant 0.1 *N* perchloric acid in glacial acetic acid or dioxane is used. Representative titration curves are shown in the paper. The potential break is not sharp enough to determine the end-point accurately. The more precise method of plotting dE/dV gives better results. Procedure and reagents are described.

[Kl.Gr.]

396 – The determination of chlorides in solutions used in the zinc-manufacturing industry, by a method of non-compensating potentiometric titration (in Russian). Z. I. Ivanova and P. N. Kovalenko (State University of Rostov, U.S.S.R.). *Zavodskaya Lab.*, 25 (1959) 290.

The solution analysed may contain 120 to 0.2 mg Cl⁻. The error in the determination is ± 0.3 to $\pm 3.7\%$. The indicating electrode is metallic mercury and the comparison electrode is tungsten. A Hg²⁺ solution is used as the titrating agent instead of AgNO₃ at pH 3 to 8. Tolerated concentrations of Zn, Mn, etc. are given. For a description of the method, see earlier abstracts.

[Ot.So.]

397 – A contribution to the determination of 1,4-dihydrazino-phthalazine (in Czech.). F. Jančík, B. Buděšínský and J. Körbl (Pharmaceutical and Biochemical Research Institute, Prague, Czechoslovakia). *Českoslov. farm.*, 9 (1960) 304.

The possibilities of the oxidimetric determination of 1,4-dihydrazino-phthalazine in the form of the dichloride or sulphate have been investigated. The results show bromatometric titration to be the most suitable, although there is a side reaction which must be suppressed as far as possible by judicious choice of conditions. Direct potentiometric titration with 0.1 *N* potassium bromate is used, or an excess is added and back-titrated in the usual way, adding potassium iodide and titrating with 0.1 *N* sodium thiosulphate. The authors do not give a description of the potentiometric arrangement.

[Ot.So.]

398 – Oxidations with potassium permanganate in the presence of fluoride. II. Potentiometric titration of mercury(I) and the redox potential of Mn(+7)/Mn(+3) system. I. M. Issa and M. Hamdy (Faculty of Science, Cairo University and Assiut University, Egypt). *Anal. Chim. Acta*, 22 (1960) 558.

Mercury(I) can be titrated potentiometrically with permanganate in the presence of fluoride and sulphuric acid. The optimum conditions are 2.5–10 ml of 9 *N* acid and 10–100 ml of 2% sodium fluoride at a temperature of 25–40°. Larger amounts can be determined than in the visual method, although copper(II) is a suitable indicator screen in the titration of fairly large amounts. The reverse titration is also satisfactory; the optimum conditions are 1.5–4 ml of 9 *N* acid and 25–75 ml of 2% fluoride at 25–40°. The formal redox tension of the Mn⁷⁺/Mn³⁺ couple is 1.4 V, in the presence of 1.38 *N* H₂SO₄ and 0.12 *N* NaF.

[P.Mec.]

399 – Bromometric determination of organic compounds (in Czech). A. Berka and J. Zýka (Dept. of Anal. Chem., Charles University, Prague, Czechoslovakia). *Českoslov. farm.*, 8 (1959) 17.

In indirect bromometric determinations based on substitution and addition reactions, the iodometric determination of the excess reagent can be substituted by hydrazinometric titration. Either direct titration with a volumetric hydrazine sulphate solution with potentiometric indication is used, or else an excess of this solution is added and back-titrated with a volumetric bromate solution using methyl red as the indicator. With potentiometric indication, a sharp potential change is observed in the vicinity of the equivalence-point (150 mV for 0.05 ml volumetric solution).

[Ot.So.]

400 – Titration of periodates in the presence of iodate with hydrazine sulphate (in Czech). A. Berka and J. Zýka (Dept. of Anal. Chem., Charles University, Prague, Czechoslovakia). *Českoslov. farm.*, 8 (1959) 137.

It has been found that the reduction of periodate to iodate by hydrazine sulphate is quantitative in suitably buffered solutions, and the method was used for the direct potentiometric titration

in solutions of sodium bicarbonate, sodium tetraborate and sodium acetate. The method is especially suitable for the rapid and accurate determination of excess reagent (preferably at pH 7.5-9) in oxidations of organic compounds with periodate. The presence of even a large excess of iodate does not interfere. Platinum and saturated calomel electrodes are used. [Ot.So.]

401 - Titrations with quinol and similar reducing agents. XV. Potentiometric microdetermination of gold in drugs (in Czech). J. Doležal, M. Höfer and J. Zýka (Dept. of Anal. Chem., Charles University, Prague, Czechoslovakia). *Českoslov. farm.*, 8 (1959) 557.

Results of the potentiometric, reductometric determination of gold by quinol have been investigated and it was found that about $1 \mu\text{g Au}$ can be determined in solutions of pH 2-7. These results have been applied to the determination of gold in pharmaceutical products. Aliquots of aqueous solutions of the decomposed samples were directly titrated with a 0.01 N hydroquinone solution using a platinum wire electrode and a saturated calomel electrode. The tension change was very sharp. [Ot.So.]

402 - A contribution to the reductometric determination of copper in some pharmaceutical products (in Czech). A. Berka and J. Zýka (Dept. of Anal. Chem., Charles University, Prague, Czechoslovakia). *Českoslov. farm.*, 8 (1959) 576.

The potentiometric determination of copper in some pharmaceutical products and the indirect determination of reducing sugars is based on the fact that cupric salts can be reduced to the cuprous state by quinol solutions in media containing sufficient ammonium chloride, acetate and thiocyanate, even without an inert atmosphere. The inflexion value is in the vicinity of 220 mV and the tension change at the equivalence-point is 50 mV for 0.02 ml of the volumetric solution. A platinum wire electrode and a saturated calomel electrode are used. Titration with 0.1 N hydrazine sulphate solution carried out under the same conditions shows no advantages over the hydroquinone method. The inflexion tension in the case of hydrazine sulphate occurs at 180 mV. [Ot.So.]

403 - Titrations with quinol and similar reducing agents. XVI. Potentiometric microdetermination of gold in urine (in Czech). J. Doležal, J. Höfer and J. Zýka (Dept. of Anal. Chem., Charles University, Prague, Czechoslovakia). *Českoslov. farm.*, 8 (1959) 578.

A sensitive and simple method has been successfully applied to the determination of gold in the urine of patients who have been treated with preparations containing gold. The urine was decomposed by evaporation with nitric acid and aqua regia followed by ignition. The residue was diluted with water, the pH brought to 4.5 by addition of HCl and the solution, after heating to the boiling point, was titrated with a 0.001 N hydroquinone solution. The electrodes were platinum wire and saturated calomel. [Ot.So.]

404 - Nitrite titration of some pharmaceutically important pyrazole derivatives (in Czech). M. Matrká, Z. Ságner and V. Štěrba (Research Institute of Organic Syntheses, Pardubice-Rybitví, Czechoslovakia). *Českoslov. farm.*, 9 (1960) 122.

Attention has been paid to the reactions of some pharmaceutically important pyrazolone derivatives with nitrous acid, with a view to their determination. The results show that the nitrosation of antipyrine is not quantitative. This is caused by the slow rate of the reaction, and by a further subsequent reaction occurring during the titration. A 0.2 M NaNO_2 solution was used which was prepared by dissolving the pure chemical in water. Its titer was determined using sulphanilic acid as the standard. Potentiometric titrations were carried out using a PEHAVI potentiometer, with a bright platinum electrode and a saturated calomel electrode. Tension changes were sufficiently sharp. The reactions of the pyrazolone derivatives are discussed in great detail. [Ot.So.]

405 - Bromometric determination of beta-naphthoxyethanol (in Czech). F. Buben and F. Jančík (Pharmaceutical and Biochemical Research Institute, Prague, Czechoslovakia). *Českoslov. farm.*, 9 (1960) 309.

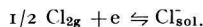
A method for the determination of beta-naphthoxyethanol has been developed which is based on substitution by bromine, which under unchanged conditions of acidity forms the monoderivative only. The solution of beta-naphthoxyethanol in glacial acetic acid is acidified with HCl, and after addition of KBr titrated potentiometrically with 0.1 N KBrO_3 solution, using platinum and saturated calomel electrodes. The establishment of the tension is very rapid and the tension change at the equivalence-point is 350-400 mV for 0.03 ml of the solution. The error in the determination does not exceed $\pm 0.3\%$. [Ot.So.]

406 - A potentiometric method for the determination of aluminium in refractory nickel-base alloys (in Russian). A. A. Goulova and L. J. Polak. *Zavodskaya Lab.*, 25 (1959) 285.

Based on the work of Tshirkov (*Zavodskaya Lab.*, 14 (1948) 783) a method has been developed for

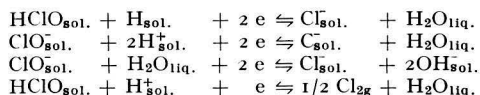
the rapid determination of Al in refractory alloys. This method does not require the separation of Al from the other components of the alloy. 0.25 g of the alloy, containing 3 to 6% Al, is dissolved in 30 ml aqua regia and evaporated and the residue after dissolving in 15 ml HCl is reduced by the addition of a few Zn grains. After filtration through glass wool the filtrate is neutralised by NH_3 till a precipitate is formed which is then dissolved with a few drops of warm HCl. The determination is carried out at pH about 6. An electrode pair of Al-nichrome is immersed in the solution to a depth of 1 to 2 cm. The solution is then titrated under agitation with a 0.25 N NaF solution to the first sharp tension change. [Ot.So.]

407 – The potential of the chlorine electrode at various temperatures (in Russian). I. E. Flis, K. P. Mitschenko and N. V. Troitskaya (Leningrad, U.S.S.R.). *Zhur. Fiz. Khim.*, 33 (1959) 1744. Potentiometric measurements were carried out with glass and platinum electrodes in acid hypochlorite solutions. Using the experimental data obtained, the normal oxidation tensions of the system $\text{Cl}_2\text{g} - 2\text{Cl}_{\text{sol}}^-$ were calculated for 10, 25, 35 and 50°. The calculations for 25° are in good agreement with reported data. Equations have been obtained for the temperature dependence of $\varphi_{\text{Cl}_2/\text{Cl}^-}$ and $\Delta Z^\circ_{\text{Cl}_2/\text{Cl}^-}$; the values of ΔZ° , $d\varphi^\circ/dT$ and ΔH_{AS} for the equilibrium



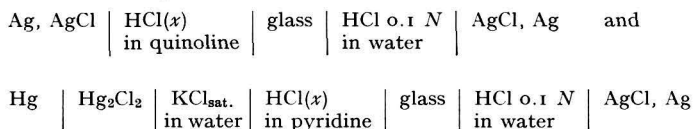
were also calculated for the same temperatures.

The values of φ° and ΔZ° were calculated for the equilibria:



The temperature dependence of the standard tensions of these equilibria were expressed by corresponding equations. [Ot.So.]

408 – The hydrogen function of the glass electrode in non-aqueous solutions of basic nature (in Russian). F. N. Kozlenko (Lvov, U.S.S.R.). *Zhur. Fiz. Khim.*, 33 (1959) 1866. The tensions of the following cells were determined:



The concentration coefficients of activity for HCl solutions in quinoline were calculated from the tension values and the standard tensions of the first cell and the relation $\log \gamma^* - \sqrt{m}$ was plotted, the slope of which coincides in the limit with the theoretical value. On the basis of the known dissociation constant for HCl in pyridine, the activities, a_{H^+} , were calculated and a graph was plotted of the relation between E of the second cell and $-\log a_{\text{H}^+}$. A straight line was obtained with a slope of 59 mV. The data obtained permit a conclusion to be drawn as to the existence of a hydrogen function of the glass electrode in the non-aqueous basic media investigated. [Ot.So.]

409 – Recherches sur le comportement électrochimique des membranes. I. Membranes poreuses: les membranes de paraffine. P. Cloos et J. J. Fripiat (Laboratoire des colloïdes des sols tropicaux I.N.E.A.C. et Laboratoire de chimie biologique et colloïdale du sol I.R.S.I.A., Institut Agronomique de l'Université de Louvain, Héverlé, Belgique). *Bull. soc. chim. France*, (1960) 423. Le comportement électrochimique des membranes proposées par Tendeloo et Krips et composées de paraffine, d'oxalate de calcium et de trioléate sorbitique, a été étudié dans différentes solutions d'électrolytes.

Il a été observé que les tensions mesurées dépendent de la nature de la solution intérieure et extérieure et que l'allure de la variation de la tension en fonction de la concentration dépend de la nature du cation et de l'anion de la solution extérieure. En outre, les membranes ont manifesté des effets de "mémoire". Les auteurs concluent qu'elles sont à classer dans la catégorie des membranes poreuses, peu chargées et qu'elles sont perméables aux anions aussi bien qu'aux cations. La théorie de Kobatake, fondée sur les principes de la thermodynamique des phénomènes irréversibles, a été vérifiée pour ces membranes. [Bad.Lam.]

410 – Volumetric determination of mercury with alkaline permanganate. I. M. Issa, M. Hamdy and A. El-Hadidy (Chem. Dept., Faculty of Science, Cairo University, Egypt). *Egypt. J. Chem.*, 2 (1959) 59.

Analysis was carried out by mixing an aliquot of Hg^{2+} solution with a known excess of KMnO_4 -alkali mixture in the presence or absence of telluric acid. This was followed by the addition of a known excess of cold acidic ferrous iron solution and then back potentiometric titration of the excess Fe^{2+} with KMnO_4 was carried out. It was shown that the tension of the redox system has the same nature in alkaline and acidic solutions, i.e., $E_{\text{OH}} = E_{\text{H}} - 2.303 m/n \cdot RT/F \cdot \text{pH}$. In the case where the oxidation of mercurous oxide takes place through OH^- with the release of 2 e, E_{OH} equals $E_{\text{H}} - 0.059 \times 14$. This indicates that if the value of the $\text{HgO}/\text{Hg}_2\text{O}$ couple in acid medium is equal to that of the $\text{Hg}_2^{2+}/\text{Hg}^{2+}$ system, the tension in the alkaline solution is ~ 0.1 V. [M.K.Hus.]

411 – Measuring devices for determining the pH value using electrode assemblies of high resistance (in German). H. J. Wolf (Fa. Metrohm A.G., Herisau, Switzerland). *Z. Instrumentenk.*, 67 (1959) 147.

A detailed discussion of different methods of measuring pH is given. The comparison concerns the following methods: (a) Direct current amplifiers: The set-up may contain one or several stages. In the latter case a strong feed-back improves the stability and even an automatic drift compensation is possible. (b) Alternating current amplifiers: The modulation of the d.c. voltage of the electrode assembly can be carried out by a chopper, a vibrating condenser or electronically. A device of high accuracy is the two channel-amplifier, the properties of which are comparable to those of a compensation circuit.

The importance of making a comparison of direct-reading and compensation methods is shown. Apart from the accuracy required, the purpose of the application will determine the selection of the method. Numerous diagrams provide clear details of the methods discussed. [Fr.Oe.]

412 – Potentiometric titration of dark coloured products in the food industry (in Polish). A. Sroczyński and M. Boruch (Dept. of Starch and Syrup Technology, Politechnika, Łódź, Poland). *Przemysł Spożywczy*, 13 (1959) 225.

The advantages of potentiometric titration compared to visual titration with indicators are discussed. Methods for the acidity and alkalinity determination of potato syrup, glucose, wine, beer and other products are described. [Ad.Hu.]

See also abstracts nos. 246, 247, 253, 364, 423, 470.

5. Conductometry

413 – Selenocyanomercurates of heavy metals with coordination numbers 3 and 4 (in Polish). A. Swinarski, A. Łodzinska, M. Cacha and K. Bieniak (Dept. of Inorganic Chemistry, Kopernik University, Toruń, Poland). *Roczniki Chem.*, 33 (1959) 899.

On the basis of gravimetric analyses and conductometric titrations it was found that in solutions $\text{Hg}(\text{SeCN})_3^-$ ions can be present in equilibrium with precipitates containing the same ions. In a saturated solution the concentration of $\text{Hg}(\text{SeCN})_3^-$ was found to be equal to $2.5 \cdot 10^{-2}$ mol/l. The Zn^{2+} and Cu^{2+} salts were found to have the general formula $\text{Me}[\text{Hg}(\text{SeCN})_3]_2$, but in the case of Co^{2+} the salt $4\text{Co}[\text{Hg}(\text{SeCN})_3]_2 \cdot \text{Co}(\text{CH}_3\text{COO})_2$ exists. Salts of Ni^{2+} , Pb^{2+} and Cu^{2+} with coordination number 4 have the general formula $\text{Me}[\text{Hg}(\text{SeCN})_4]$ except the Ni^{2+} compound with the composition $\text{Ni}[\text{Hg}(\text{SeCN})_4] \cdot \text{Hg}(\text{SeCN})_2$. These experiments confirmed the suppositions that the cation influences the type of precipitate formed and that in the case of highly-polarizing cations simple complex can be formed. [Ad.Hu.]

414 – Radio-frequency methods in analytical chemistry. M. F. C. Ladd and W. H. Lee (Chem. Dept. Battersea College of Technol., London, Great Britain). *Talanta*, 4 (1960) 274.

The theory of radio-frequency measurements of chemical importance is outlined and suitable apparatus discussed. The practical applications of the radio-frequency technique in acid-base titrations, chloride and sulphate determinations and miscellaneous titrations are summarized in tables. Finally the applications of dielectric constant measurements are discussed. (166 references.) [Ja.Inc.]

415 – Equivalent and ionic conductances for mixtures of potassium and lithium chlorides in aqueous solution at 25°C. G. S. Kell and A. R. Gordon (Dept. of Chemistry, University of Toronto, Canada). *J. Am. Chem. Soc.*, 81 (1959) 3207.

Leitfähigkeiten von KCl - LiCl -Mischungen wurden bei einer Ionenstärke von 0.01 mit Hilfe einer Direktstrommethode gemessen. Gleichzeitig wurden die Überführungszahlen der einzelnen in der

Lösung anwesenden Ionen bestimmt. Die Äquivalentleitfähigkeit der Mischlösungen war kleiner als nach der Onsager-Fuoss-Theorie für den Mischungseffekt zu erwarten gewesen wäre. Das Gleiche wurde bei früheren Messungen bei höheren Konzentrationen beobachtet. In den Mischlösungen sinkt der Anteil des Kaliumions an der Leitfähigkeit etwas, der des Lithiumions wird dagegen etwas grösser als in den reinen Salzlösungen. [Ha.Re.]

416 – Hydrogen halides in acetonitrile. I. Ionisation processes. George J. Janz and Steven S. Danyluk (Dept. of Chemistry, Rensselaer Polytechnic Institute). *J. Am. Chem. Soc.*, 81 (1959) 3846.

In wasserfreiem Acetonitril wurden bei 25° die Leitfähigkeiten von HCl, HBr und HJ-Lösungen gemessen. Die Leitfähigkeit einer frisch bereiteten Lösung steigt mit der Zeit an und erreicht einen konstanten Maximalwert in der gealterten Lösung. Der Zeiteffekt wird in Bezug auf die Eigenschaften des Lösungsmittels, des gelösten Stoffes und des Wassergehaltes untersucht. Er ergab sich eine Wechselschichtung zwischen gelösten Stoff und Lösungsmittel in der Art, dass Salze vom Nitril-Typ und Iminohydrohalogenide gebildet werden. Da sich nach einer bestimmten Zeit ein Gleichgewicht einstellt, erreicht die Leitfähigkeit einen konstanten Endwert. [Ha.Re.]

417 – Hydrogen halides in acetonitrile. II. Solid substrates. George J. Janz and Steven S. Danyluk (Dept. of Chemistry, Rensselaer Polytechnic Institute). *J. Am. Chem. Soc.*, 81 (1959) 3850.

Die sich aus Acetonitril und Halogenwasserstoffen bildenden Substanzen des Typs $\text{CH}_3\text{CN}\cdot 2 \text{HX}$ werden spektroskopisch und mit Hilfe von Leitfähigkeitsmessungen untersucht. $\text{CH}_3\text{CN}\cdot 2 \text{HCl}$ hat die Struktur eines Nitriliumsalzes $(\text{CH}_3\text{CNH}^+)(\text{Cl}_2)^-$, während für $\text{CH}_3\text{CN}\cdot 2 \text{HBr}$ und $\text{CH}_3\text{CN}\cdot 2 \text{HJ}$ eine Iminohydrohalogenstruktur $\text{CH}_3\text{C}(\text{X})=\text{NH}_2^+\text{X}^-$ wahrscheinlicher erscheint. Es wurden physikalische Eigenschaften dieser Stoffe, sowie Ergebnisse aus Leitfähigkeitsmessungen und spektroskopischen Untersuchungen angegeben. [Ha.Re.]

418 – Hydrogen halides in acetonitrile. III. Electrical conductance. George J. Janz and Steven S. Danyluk (Dept. of Chemistry, Rensselaer Polytechnic Institute). *J. Am. Chem. Soc.*, 81 (1959) 3854.

In wasserfreiem CH_3CN wurden bei 25° die elektrischen Leitfähigkeiten von gealterten Lösungen von HCl, HBr und HJ gemessen. Die molaren Leitfähigkeiten von HCl-Lösungen sind kleiner als 1. Für HBr ergibt sich 10–20 und für HJ-Lösungen wurden Leitfähigkeiten von 35–50 erhalten. Die Leitfähigkeiten lassen sich nicht mit Hilfe der Leitfähigkeitsgleichungen für schwache Elektrolyte und assoziierte Ionen wiedergeben, da den ionischen Prozessen molekulare Lösungsmittel-Stoff-Wechselwirkungen überlagert sind. Es wird eine empirische Beziehung zur Darstellung der molaren Leitfähigkeiten in Abhängigkeit von der Konzentration der gelösten Halogenwasserstoffe angegeben. [Ha.Re.]

419 – Comments on the determination of α -acids in hops by conductimetric methods, with regard to their value in the brewing industry. (Observations on a paper bearing the aforesaid title by B. Trolle and R. Djurtoft.) B. D. Hartong, H. E. Jansen and P. Mendlik (Phoenix Brewery, Rotterdam, The Netherlands). *Brauwissenschaft*, 12 (1959) 43.

It is claimed that the statement contained in the aforesaid paper (*Brauwissenschaft*, 11 (1958) 283) according to which CHCl_3 is superior to benzene as an extraction medium for α -acids, is not correct. Also the statement that the α -acids constitute "about" 50% of the total acids is inaccurate, as the variations actually fluctuate between 45 and 75%. [L.Tac.]

420 – Relationship between basicity of acids and conductance in aqueous solutions. C. K. Ganguli and S. C. Rakshit (Laboratory, Indian Bureau of Mines, Delhi, India). *J. Indian Chem. Soc.*, 36 (1959) 13.

The failure of Ostwald's empirical relation $\lambda_{1024} - \lambda_{32} = 10.8 b$ connecting basicity (b) of the acids and the equivalent conductance (λ) of their sodium or potassium salts at 1024 and 32 l dilution, in many cases has been ascribed to the selection of two arbitrary dilution limits, over which the conductance of sodium salts of any two monobasic or polybasic acids may not exhibit identical types of decline.

From Onsager's conductance equation, simplified relations for unsymmetrical electrolysis have been obtained. It has been considered preferable to select the more fundamental dilution limits of infinity and 100 l. A new basicity rule has been derived "the difference in equivalent conductances of sodium salts of any acid at infinity and 100 l dilution is nearly 8.3 times the basicity of the acid" and the rule shows good agreement for a number of acids. A similar generalisation has also been made for the acidities of alkalis "the difference in equivalent conductivities of a chloride of an alkali at infinity and 100 l dilution is nearly 8.7 times the acidity of the alkali". This has been fairly well corroborated by experimental data. The Ostwald's basicity rule has been modified in the light of Onsager's equation as $\lambda_{1024} - \lambda_{32} = 11.58 b$. [R.S.Sa.]

421 – Behaviour of electrolytes in mixed solvents. IV of Conductance. $MgCl_2$ and K_2SO_4 in dioxane-water mixtures at 35° . P. B. Dass, P. K. Dass and D. Patnaik (Ravenshaw College, Cuttack, India). *J. Indian Chem. Soc.*, 36 (1959) 761.

The conductance of $MgCl_2$, a bimonovalent salt and that of K_2SO_4 , a monovalent electrolyte in 10, 20 and 30% dioxane-water mixtures have been measured at 35° with a view to ascertaining the effect of solvent composition on the diameter of the ion pairs, $MgCl^+$ and KSO_4^- . Adopting the method of Jenkin and Monk (*J. Chem. Soc.*, (1951) 68) the dissociation constants of these ion pairs have been calculated. The mean values of $K \times 10^2$ for $MgCl^+$ in 20 and 30% dioxane-water mixtures are 4.96 and 2.06 respectively; whereas for KSO_4^- they are found to be 12.53, 9.44 and 5.02 in 10, 20 and 30% dioxane-water mixtures. The values of the ionic diameters calculated by the two different methods of Stokes and Bjerrum, are in good agreement. The composition of the solution, which might affect the ion atmosphere, does not affect appreciably the diameter of the ion pairs, $MgCl^+$ and KSO_4^- . [R.S.Sa.]

422 – Physico-chemical studies on the composition of complex thiosulphates of metals. I. Composition of cadmium thiosulphate by conducto- and thermometric titrations and by Job's method of continuous variation. M. S. Bhadravar and J. N. Gaur (Lohia College, Churu, India). *J. Indian Chem. Soc.*, 36 (1959) 103.

The composition of cadmium thiosulphate has been studied by conductometric and thermometric titrations between $Na_2S_2O_3$ and $CdCl_2$ at different concentrations, both by the direct and the reverse methods and also by applying Job's method of continuous variation. The results show that the reaction between cadmium salt and sodium thiosulphate takes place in the ratio 1 : 1, suggesting the formation of CdS_2O_3 . The dissociation constant of CdS_2O_3 at a molar concentration of $CdCl_2$ ($c = 0.01$) has been calculated to be $3.0 \cdot 10^{-3}$. [R.S.Sa.]

423 – The apparent dissociation constants of diethyldithiocarbamic acid. K. P. Soni and A. M. Trivedi (M. G. Science Institute, Ahmedabad, India). *J. Indian Chem. Soc.*, 37 (1960) 349.

Both pH and conductometric measurements have shown that sodium diethyldithiocarbamate is a diacidic base which has not been apparently reported before. Solutions of 1, 2, 5 and 10 mM/l of the sodium salt were titrated against $HClO_4$, HCl and CH_3COOH of suitable normalities both conductometrically and potentiometrically. The conductimetric titration shows two breaks in the curves indicating that the acid formed is dibasic. This has also been confirmed by pH measurements, as the end-point was obtained when nearly double the equivalents of the titrant acid was added.

The values of the two acidic dissociation constants as found by the Bjerrum method by tension measurements are: $pK_1 = 7.5$ ($-SH$ group) and $pK_2 = 8.4$ ($-NH^+(C_2H_5)_2$). The behaviour of diethyldithiocarbamic acid has been compared with that of ampholytes. [R.S.Sa.]

424 – Spectrophotometric and conductometric studies of metal complexes of 3-hydroxy-1-p-sulphonatophenyl-3-phenyltriazine. IV. Iron complex. R. N. Mathur and N. C. Sogani (Government College, Ajmer, India). *J. Indian Chem. Soc.*, 37 (1960) 117.

Fe^{3+} forms a bluish black, water-soluble complex with 3-hydroxy-1-p-sulphonatophenyl-3-phenyltriazine. The formula of the complex, established conductometrically and spectrophotometrically by applying Job's continuous variation method, slope ratio method and molar ration method, has been found to be FeR_3 ($R =$ Reagent) in the pH range 2.0 and 4.3. At higher pH values FeR^{2+} and FeR_2^+ are indicated. The dissociation constant of FeR_3 at 20° has been calculated to be $2.38 \cdot 10^{-12}$ and its stability constant is $4.2 \cdot 10^{11}$. The standard free energy of the formation of the complex has been calculated from the relation $\Delta F^\circ = RT \ln K$ and works out to be -15.59 kcal/mole at 20° . [R.S.Sa.]

425 – Beryllium fluorides. II. Formation of beryllium fluorides in solution. A. K. Sen Gupta (University College of Science, Calcutta, India). *J. Indian Chem. Soc.*, 37 (1960) 291.

Beryllium is known to be capable of combining with one or more fluoride ions to furnish several simple and complex fluorides. The conductometric titration of beryllium nitrate with KF shows breaks in the curves at $Be:F$ ratios of 1:1, 1:2 and 1:4, corresponding to the formation of BeF^+ , BeF_2 (slightly dissociated) and BeF_4^{2-} ions. The break corresponding to the formation of the latter is, however, not sharp, although its formation has been confirmed by conductometric titration of KF and BeF_2 . These titration curves show the absence of BeF_2^- , BeF_3^- and BeF_4^- ions. The conductometric titration curve obtained by titrating HF with beryllium fluoride shows only one break corresponding to tetrafluoberyllic acid H_2BeF_4 which has been corroborated by the method of thermometric titrations. [R.S.Sa.]

426 – Benzoyl chloride as a polar solvent. V. Conductometric titration in benzoyl chloride. R. C. Paul, J. S. Johar and G. Singh (Punjab University, Hoshiarpur, India). *J. Indian Chem. Soc.*, 37 (1960) 195.

Acid-base neutralisation reactions between solvo-acids like titanium tetrachloride, stannic chloride, zirconium tetrachloride, tellurium chloride and antimony pentachloride, on the one hand, and solvo-bases like pyridine, quinoline, α , β and γ -picolines and dimethylaniline, on the other, have been carried out in benzoyl chloride, and the course of the reactions has been followed conductometrically. The composition of the neutralisation complexes has been established. The conductances of the solutions of solvo-acids and solvo-bases as well as their neutralisation has been explained on the basis of the ionisation of benzoyl chloride as: $BzCl = Bz^+ + Cl^-$.

For example, when $SnCl_4$ in C_6H_5COCl is added to a solution of α -picoline, a light yellow precipitate begins to separate and the conductance of the solution falls progressively till at the point, where the acid/base ratio becomes 0.5, the conductance is at a minimum and the precipitation is complete. The change in conductance has been attributed to the addition and removal of ionic species from the reaction medium. [R.S.Sa.]

427 – Rapid determination of aluminium with high frequency titration. E. Pungor and E. E. Zapp (Institute of Inorg. and Anal. Chem., L. Eötvös Univ., Budapest, Hungary). *Egypt. J. Chem.*, 2 (1959) 81.

A high-frequency method for the determination of aluminium in mg amounts was developed. An excess of a standard barium hydroxide solution reacts with acid aluminium solution and back-titration with acetic acid is performed. At the end of the titration Al is present in the form of aluminate. [M.K.Hus.]

428 – Acid ionisation of alcohols. II. Acidities of some substituted methanols and related compounds. P. Ballinger and F. A. Long (Dept. of Chemistry, Cornell University, U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 795.

Säuredissoziationskonstanten von verschiedenen einfachen Alkoholen in Wasser bei 25° wurden mit Hilfe von Leitfähigkeitsmessungen ermittelt. Es wurden für die Alkohole: $CH \equiv C-CH_2OH$, $C(CH_2OH)_4$, $CH_2OH-CHOH-CH_2OH$, CH_2OH-CH_2OH , CH_3OCH_2OH , CH_3OH , $CH_2=CHCH_2OH$ und CH_3-CH_2OH in der gleichen Reihenfolge folgende Dissoziationskonstanten $K_{HA} \times 10^{16}$ angegeben: 280, 79, 40, 17, 15, 2.9, 3, 1. Unter den gleichen Bedingungen werden für die pK_{HA} -Werte der Alkohole $R-CH_2OH$ mit $R=CCl_3-$, CF_3- , CHF_2CF_2- , $CHCl_2-$, $CH \equiv C-$, CH_2Cl- , CH_3-OCH_2- , $HOCH_2-$, $H-$, $CH_2=CH-$, CH_3- , wiederum in der gleichen Reihenfolge die Zahlenwerte: 12.24, 12.37, 12.74, 12.89, 13.55, 14.31, 14.8, 15.1, 15.5, 15.5 und 15.9 angegeben. Die relativen Aciditäten von Methanol-Wasser und Äthanol stehen in Wasser als Lösungsmittel in einem Verhältnis 3 : 2 : 1. Für die Alkohole CF_3-CH_2OD und CH_2Cl-CH_2OD werden pK_{DA} -Werte von 13.02 und 14.99 angegeben. [Ha.Re.]

429 – Transference numbers and conductances of multivalent salts in aqueous solution: zinc sulfate and zinc perchlorate. James L. Dye, M. Patricia Faber and David J. Karl (Kedzie Chemical Laboratory, Michigan State University, U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 314.

In wässrigen Lösungen bei 25° wurden Überführungszahlen gemessen. Leitfähigkeitsmessungen an $Zn(ClO_4)_2$ -Lösungen ergaben bereits bei sehr verdünnten Lösungen erhebliche Abweichungen von der Onsagergleichung. Die Abweichungen lassen sich nicht durch Annahme einer paarweisen Ionenassoziation oder Hydrolyseerscheinungen erklären. Leitfähigkeitsmessungen an $ZnSO_4$ -Lösungen dagegen lassen sich gut mit Hilfe der Onsager-Fuoss-Theorie unter Zuhilfenahme einer Ionenassoziation und einer höheren Näherung der Elektrophoresgleichung wiedergeben. Es wird angenommen, dass die Neigung des Zn^{2+} zur Ausbildung einer Kovalentenbindung bewirkt, dass eine Beschreibung des Leitfähigkeitsverhaltens durch eine Theorie, die nichtpolarisierbare Ionen voraussetzt, nicht möglich ist. [Ha.Re.]

430 – Leitfähigkeitsmessungen in Phosphoroxchlorid. 1. V. Gutmann und M. Baaz (Institut für anorganische und allgemeine Chemie, T. H. Wien, Österreich). *Monatsh. Chem.*, 90 (1959) 239. Es wird eine experimentelle Anordnung beschrieben, mit der sich ein sehr reines Phosphoroxchlorid der Leitfähigkeit $\kappa = 2 \cdot 10^{-8} \text{ ohm}^{-1}\text{cm}^{-1}$ darstellen lässt und Leitfähigkeitsmessungen unter völligem Luftabschluss durchgeführt werden können. Weiters werden Leitfähigkeitsmessungen an Triäthylammoniumchlorid in konzentrierten und verdünnten Lösungen sowie im Bereich der Eigenleitfähigkeit des Lösungsmittels diskutiert. [Ed.Bro.]

431 – Leitfähigkeitsmessungen in Phosphoroxchlorid. 2. Tetraalkylammoniumsalze. M. Baaz und V. Gutmann (Institut für anorganische und allgemeine Chemie, T.H. Wien, Österreich). *Monatsh. Chem.*, 90 (1959) 256.

An einer Reihe typischer Ionenverbindungen wird die Abhängigkeit der Grenzleitfähigkeit und der Dissoziationskonstante von der Ionengröße untersucht. Indirekte Methoden ergeben gut übereinstimmende Werte für die Ionenbeweglichkeiten. Für die Tetraalkylammoniumionen und das Perchloration gilt die Waldensche Regel, aber auch das Chloridion zeigt keine anomale Beweglich-

keit. Bei den R_4N^+ , Cl^- und ClO_4^- -Ionen sind die Bjerrumschen Parameter den Stokesschen Radien proportional; das abweichende Verhalten der Br^- und J^- -Ionen wird durch Solvolyse erklärt. [Ed.Bro.]

432 – Leitfähigkeitsmessungen in Phosphoroxchlorid. 3. Triäthylamin. M. Baaz und V. Gutmann (Institut für anorganische und allgemeine Chemie, T.H. Wien, Österreich). *Monatsh. Chem.*, 90 (1959) 276.

Am Beispiel des Triäthylamins wird das Leitfähigkeitsverhalten eines gekoppelten Dissoziationsgleichgewichtes mit nichtleitender Zwischenstufe ($A \rightleftharpoons B \rightleftharpoons C + D^-$) untersucht. [Ed.Bro.]

433 – Leitfähigkeitsmessungen in Phosphoroxchlorid. 4. Antimonpentachlorid. M. Baaz und V. Gutmann (Institut für anorganische und allgemeine Chemie, T.H. Wien, Österreich). *Monatsh. Chem.*, 90 (1959) 426.

Die Existenz des $SbCl_6^-$ -Ions in Lösungen von $SbCl_5$ in $POCl_3$ bei Gegenwart starker Cl^- -Ionen-donoren wird durch Leitfähigkeitsmessungen sichergestellt; das Komplexion ist relativ stabil und nicht zu Polyionen assoziiert. $SbCl_5 \cdot POCl_3$ zeigt das Dissoziationsverhalten eines gekoppelten Gleichgewichtes und liegt dementsprechend in Lösungen teilweise als Koordinationsverbindung vor ($Cl_5SbOPCl_3$). Die Änderung des Leitvermögens frisch hergestellter $SbCl_5$ -Lösungen mit der Zeit kann durch die Dissoziation von Neutralkolloiden erklärt werden. Sie gehen in einen Gleichgewichtszustand über, der fast dem in Lösungen von $Cl_5SbOPCl_3$ entspricht und von diesem nach kurzer Zeit erreicht wird. [Ed.Bro.]

434 – Détermination rapide de la teneur en aluminium par titrage en haute fréquence. E. Pungor et E. E. Zapp (Institut de Chimie Minérale et Analytique de l'Université Eötvös de Budapest Hongrie). *Bull. soc. chim. France*, (1960) 121.

Par addition d'hydroxyde de Ba les auteurs réalisent successivement la neutralisation de l'acidité libre, la précipitation de $Al(OH)_3$, la formation d'aluminate de Ba, et l'alcalinisation de la solution par un excès de $Ba(OH)_2$. Cet excès est titré en retour par de l'acide acétique. Ces différentes réactions sont suivies par conductimétrie haute fréquence et permettent le dosage de l'aluminium. [Bad.Lam.]

435 – Etude de l'acidité de surface des silicates et alumino-silicates par titration en milieu non-aqueux. J. J. Fripiat, G. Vancompernelle et A. Servais (I.N.E.A.C. Laboratoire des Colloïdes des sols tropicaux, Institut Agronomique, Université de Louvain Heverlé, Louvain, Belgique). *Bull. soc. chim. France*, (1960) 250.

Le problème posé par l'étude de l'acidité de surface des silicates et alumino-silicates dans un état normal d'hydratation est celui des titrations de fonctions acides faibles: il y a intérêt à les effectuer en milieux non-aqueux. Les auteurs ont utilisé un dispositif de conductimétrie haute-fréquence et passent en revue l'application de ces principes et de ces méthodes à la titration d'un silicagel à différents états d'hydratation, à la titration de montmorillonites et de kaolinites acides et de catalyseurs de cracking.

L'appareil, dont le schéma est donné par les auteurs, est un oscillateur du type multivibrateur; son domaine de fréquence s'étend de 50 kc à 40 Mc. [Bad.Lam.]

436 – Electrode-less high-frequency measurement of the electroconductivity of solutions (in Russian). S. V. Usikov (Leningrad, U.S.S.R.). *Zhur. Fiz. Khim.*, 33 (1959) 2007.

A new method of measuring the electroconductivities of liquid media from the active conductivities ratio determined at high frequencies without the use of electrodes has been developed. In relation to this a technique is proposed for measuring the limiting resistance. The method permits investigation into the electroconductivity of liquids at different frequencies. The nature of the change in the high frequency electroconductivity obtained by the new method from the low frequency conductivity has been ascertained. The electrical circuit of the apparatus as well as a model of a flow cell are included. [Ot.So.]

437 – Electrochemical investigation of HCl solutions in solvents of low dielectric constants (in Russian). E. M. Ryzhkov and A. M. Sukhotin (Leningrad, U.S.S.R.). *Zhur. Fiz. Khim.*, 34 (1960) 986.

A new procedure has been developed for measuring the electroconductivity of electrolytes in mixed solvents, permitting the effect of solvent composition on the conductivity to be completely elucidated. The equivalent electroconductivity of hydrogen chloride in butanol-hexane mixtures of dielectric constant 1.90 to 17.3 has been determined over a wide range of HCl concentrations. The dissociation constants of HCl in solutions have been calculated. The dependence of K_{diss} upon the dielectric constant is described in terms of the electrostatic theory. This shows that the undissociated hydrogen chloride in such solutions (in the low concentration range) comprises chiefly ionic pairs and not covalent molecules. [Ot.So.]

438 – The chemical effects of pressure. 5. The electrical conductivity of water at high shock pressures. H. G. David and S. D. Hamann (C.S.I.R.O. Division of Industrial Chemistry, High Pressure Lab., Sydney University, Australia). *Trans. Faraday Soc.*, 55 (1959) 72.

Water becomes highly ionised when it is compressed by intense shock waves. A number of measurements at shock pressures between 33,000 and 127,000 atm have shown that the specific conductance rises steadily, reaching $\sim 1 \Omega^{-1}\text{cm}^{-1}$ at the highest pressure. Most of the change is due to an increase in the ionic product of water, possibly by a factor as great as 10^{12} at 127,000 atm. The experimental method is given in some detail. [M.K.Hus.]

See also abstracts nos. 312, 386.

6. Electrolysis

439 – Hydrogen evolution during the electrolysis of acid solutions of Zn salts (in Russian). A. F. Nikiforov and V. V. Stendes (Chemico-technological F. E. Dzerzhinski, Dniepropetrovsk, U.S.S.R.). *Ukrain. Khim. Zhur.*, 25 (1959) 18.

The authors have investigated the dependence of the rate of hydrogen evolution on current density during the electrolysis of acid ZnSO_4 and ZnCl_2 solutions with various concentrations of Cu, Co, Ni and Sb impurities in the electrolyte. The authors prove that at current densities lower than a critical value, hydrogen is evolved partly by the dissolution of Zn and partly by external polarisation. At current densities equal to, or higher than the critical value, hydrogen is formed only by external polarisation. [Ot.So.]

440 – The mechanism of the influence of anions on the value of the distribution coefficient in the simultaneous electrolytic precipitation of Co and Ni (in Russian). A. I. Iosilevitch and G. A. Tziganov (Institute of Chemistry, Academy of Sciences of the Uzbekistan S.S.R.). *Uzbekii Khim. Zhur. Akad. Nauk Uzbek. S.S.R.*, No. 5 (1959) 45.

The authors have found already from previous research that by using solutions with different anions it is possible to vary the distribution coefficient in the simultaneous electrolytic precipitation of Co and Ni. The same result is obtained by the addition of compounds having a different anion to the electrolyte. It has been found that there is no direct dependence of the distribution coefficient on the cathode tension at which the electrolysis is carried out. The authors have tried to discover the mechanism of this effect, and have found that the main cause is the difference in the chemical affinities of the two ions. This is proved by experiments in which the potential of anodic dissolution of Co and Ni in electrolytes with various anions is measured. [Ot.So.]

441 – Non-stationary processes in the electrolytic precipitation of Cu and Cd at high current densities (in Russian). G. A. Yemelyanenko and E. Y. Baibarova (State University of Dniepropetrovsk, U.S.S.R.). *Ukrain. Khim. Zhur.*, 25 (1959) 727.

The authors have investigated the case of the non-stationary diffusion of ions from the surface of a cathode which is chemically polarised. Discharge of the ions is accompanied by dehydration. It is shown that at constant current as well as constant tension the relations $it^{1/2} - i : it^{1/2} - E$ agree with experimental data.

In the electrolytic precipitation of Cu and Cd at high current densities it is shown that in this case there exists simultaneously concentration and chemical polarisation. Electrolysis at controlled cathode tensions showed that Cu and Cd are obtained in powder form in the case when precipitation of the metal influences the electrode process. [Ot.So.]

442 – Electrolysis of sodium zincate solutions. V. V. Stender and V. D. Zholudev. *Zhur. Priklad. Khim.*, 32 (1959) 1296.

The authors show that in the electrolysis of zincate solutions, zinc is precipitated in sponge form because of the insufficient supply of reducible particles at the cathode. Since during the electrolysis of zincate solutions it is difficult to obtain strong layers of zinc, and on the other hand it is easy to obtain powdered zinc, the authors propose a method for the preparation of powdered zinc for use in the cementation of metals. The authors include a table of the activity of zinc in the cementation of Cd and the surface area of zinc powders obtained by electrochemical and thermal methods. [Ot.So.]

See also abstract no. 474.

7. Coulometry

443 – Automatic coulometric micro-determination of unsaturation with kinetic proof of real equivalence-point. W. Walisch and M. R. F. Ashworth (Institute for Organic Chemistry, Analytical Section, University of the Saar, Saarbrücken, Germany). *Mikrochim. Acta*, (1959) 497.

Eine für kinetische Zwecke entwickelte coulometrische Methode wurde auf die „Bromtitration“ ungesättigter Verbindungen angewandt. Die Reproduzierbarkeit ist bei monoolefinischen KW u. ähnlichen Verbindungen besser als $\pm 0.3\%$. Die Anordnung ermöglicht die Feststellung ob die Addition vollständig abgelaufen ist und ob der Titrationswert nicht durch eine Nebenreaktion verfälscht wird. An Beispielen wird gezeigt wie an Gemischen olefinischer Verbindungen die Bestandteile ausreichend verschiedener Reaktivität enthalten, die einzelnen Anteile nebeneinander bestimmt werden können. [Ed.Bro.]

444 – Coulometric titrations. V. A. Mirkin. *Zavodskaya Lab.*, 25 (1959) 292.

A comprehensive review of the results obtained in the field of coulometric titrations in the last three years. The bibliography contains 67 literature references. [Ot.So.]

445 – Determination of neptunium by controlled-potential coulometry. R. W. Stromatt (General Electric Co., Hanford Atomic Products Operation, Richland, Wash., U.S.A.), *U.S. Atomic Energy Commission Rept. HW-59447*, (1959).

The total Np is determined as follows: it is oxidised to Np(VI) with Ce(IV), reduced (together with excess reagent) to Np(V), and then coulometrically reoxidised to Np(VI), this last step being used to calculate the Np concentration.

The various oxidation states of the metal can be measured as follows: determine Np(VI) by quantitative coulometric reduction to Np(V); re-oxidise the Np(V) to Np(VI), the difference between these two results giving the Np(V) concentration in the sample; the Np(IV) concentration can be similarly calculated as the difference between Np(V) + Np(VI) and the total Np found above. Substances undergoing oxido-reductions at the tensions used interfere and must be eliminated or masked; Pu, Fe and U do not interfere seriously. The electrolysis cell used consists of a Pt electrode in 1 N H₂SO₄. 2 μ g of Np can be detected; the coefficient of variation of the method ranges from 1% (20 μ g of Np in the cell) to 0.05% (more than 1 mg of Np in the cell). [Ca.Cas.]

8. Electrophoresis

446 – Method for detecting small quantities of synthetic food colours by micro-electrophoresis.

P. P. Legrand. *Ann. fals. et fraudes*, 52 (1959) 5.

For detecting synthetic food colours a technique which has already been described previously (cf. *Ann. biol. clin. (Paris)*, no. 12 (1956); *Ann. fals. et fraudes*, 51 (1958) 5) is applied. An 8 ml aliquot of aqueous solution of the dyestuff (concentration 1 μ g/ μ l, containing naphthol yellow S as an internal standard) is distributed along a transverse line in the centre of a paper strip; electrophoresis is then continued at a pH value of 8.6 until the naphthol yellow S has moved 5 cm towards the anode (approximately 8 h), and then the paper is rapidly dried in an air draught and inspected in daylight and u.v. light. Synthetic food colours are mostly electro-negative at a pH value of 8.6; the following dyes are, however, electropositive: auramine, malachite green and Paris violet. As far as naphthol yellow S and 26 other synthetic dyes are concerned, diagrams have been provided and detailed discussions have been made. It is possible to separate mixtures of three or four colours, even when they are closely similar with respect to their mobilities. If the mobilities are close to those for naphthol yellow S, as is the case for certain yellow colours, a comparison is made with the main strip of a comparison strip produced from a solution of the unknown dye alone. [L.Tac.]

447 – Physico-chemical studies on indigenous seed proteins. IV. Peptization of red gram (*Cajanus indicus*) proteins and their characterization by electrophoresis. Saroj Tawde and K. V. Giri (Institute of Science, Bangalore, India). *J. Sci. Ind. Research (India)*, 19C (1960) 190.

The effect of the extraction period and pH of extractant, and the influence of various anions, cations and detergents on the solubilization of red gram (*Cajanus indicus*) proteins have been investigated. Electrophoretic analysis of meal protein in buffers of varying pH and ionic strength have also been carried out. Maximum separation of the components, one major and two minor, has been found to take place between pH 7 and 8.6 and at ionic strength 0.1. [R.S.Sa.]

448 – Process for analysing plant-virus preparations by electro-phoretal means. P. M. Townsley (Chem. Div., Can. Dept. of Agriculture, Vancouver, B.C., Canada). *Can. J. Biochem. and Physiol.*, 37 (1959) 119.

In this process use is made of a buffer consisting of tri(hydroxymethyl)methylamine maleate (pH value = 7.0) with 0.7% agar, and a final buffer molarity of 0.02. At a temperature of 0° the juice is extracted from the leaves and immediately applied to the origin. A voltage of 150 V and a current of 14 mA are applied during the electrophoresis. The following procedures are applied for locating the tomato mosaic virus and the potato virus X: autoradiography, and serological and protein-staining methods. [L.Tac.]

449 – Process for the determination of steroid glucuronides in human plasma by recovery, characterization and measurement methods. G. L. Cohn and P. K. Bondy (Dept. of Internal Med., Yale University, New Haven, Conn., U.S.A.). *J. Biol. Chem.*, 234 (1959) 31.

A description is given of a method for assessing the tetra-hydrocortisone and tetrahydrocortisol glucuronides in human plasma. Paper electrophoresis and paper chromatographic methods are used for separating the conjugated steroids from the non-conjugated ones. The carbazole reaction is then utilized for determining each glucuronide. A description is also provided of a method based on the dilution of isotopes; when applied in conjunction with [$4\text{-}^{14}\text{C}$]-tetrahydrocortisone glucuronides, it is useful for correcting the results up to 100% isolation. [L.Tac.]

450 – Die Papierelektrophorese von Phenolen. H. Berbalk und I. Szabolcs (Institut für organische Chemie, T.H. Wien, Österreich). *Monatsh. Chem.*, 90 (1959) 198.

Es wird über die Papierelektrophorese ein- und mehrwertiger, teilweise auch substituierter Phenole, sowie einiger saurer Kupplungskomponenten für Azsolfarbstoffe berichtet. Nachweismittel und Wanderungswerten unter vergleichsbaren Versuchsbedingungen werden angegeben, des gleichen wird versucht, Zusammenhänge zwischen Konstitution und Laufweite zu finden. [Ed.Bro.]

451 – Study of the proteins in despeciated serum by means of electrophoresis (in Czech). T. I. Pristoupil (Institute of Haematology and Blood Transfusion, Prague, Czechoslovakia). *Českoslov. farm.*, 9 (1960) 161.

In studying modified proteins, the results obtained in cell and paper electrophoresis of solutions of despeciated serum of various origins were compared. By means of paper electrophoresis, hitherto only insufficiently used in studying these preparations, characteristic changes were found in the protein fractions, depending especially on pH and NaCl and formaldehyde concentrations used during the modification of the proteins. For cell electrophoresis a veronal-citrate and a veronal-citrate-oxalate buffer of pH 8.6 and ion strength $\mu = 0.1$ was used. Electrophoresis was carried out at 158 V and 13 A for 2 h. Paper electrophoresis was carried out in a veronal-citrate-oxalate buffer of pH 8.6 and ionic strength usually 0.075, at 17.5 V/cm and 0.6 mA/cm in a horizontally arranged cell according to Pechar. [Ot.So.]

452 – Paper electrophoretic determination of serum lipoproteins (in Russian). N. N. Madievskaja and A. J. Brailovshij (Ukrain. Sci. Research Inst. for Skin and Venereal Diseases, U.S.S.R.). *Lab. Delo*, 5 (1959) 6.

The electrophoresis is performed on strips (2.5 × 24 cm) of No. 4 Volodarski (Leningrad) paper. 0.03 ml of serum are used for the lipoprotein determination and 0.02 ml for the comparative protein determination. The working conditions are: electrolytic solution, Veronal buffer (pH = 8.6, ionic strength = 0.05–0.1); tension, 4.6 V/cm; duration, 20 h; drying, 15 min at 80°; lipoprotein development, 3 h at 37° in a solution of Sudan II in 60% ethanol and washing for 10 min in 30% ethanol (twice) and for 5 min in distilled water (twice); protein development, 15 min in bromophenol-blue solution and washing for 10 min in 0.5% acetic acid (4 times); drying, in the dark at room temperature; lipoprotein elution, the strips are cut into 24 pieces and each of them is eluted for 2 h in test-tubes containing 3 ml of 20% acetic acid in 96% ethanol; protein elution, the strips are cut into 48 pieces, which are eluted for 30 min in 0.02 N sodium hydroxide solution; colorimetric lipoprotein determination, blue filter; colorimetric protein determination, green filter. Paper strips without serum are used as a blank. [G.de An.]

453 – Paper ionophoresis and chromatography of phosphate esters and organic acids. V. C. Runeckles and G. Krotkov (Queen's University, Kingston, Ontario, Canada). *Arch. Biochem. Biophys.*, 80 (1959) 94.

The authors describe a modification of an earlier method (*Arch. Biochim. Biophys.*, 70 (1957) 442); they propose to use for the electrophoresis a buffer solution of 2.5% pyridine–0.25% acetic acid, a tension of 20 V/cm and a duration of 3½ h. For two-dimensional paper chromatography a solution

of ethyleneglycolmonomethylether-pyridine-acetic acid-water 8 : 4 : 1 : 1 with 0.15% (w/v) 8-hydroxyquinoline is proposed. [G.de An.]

454 - Electrophoretic determination of plasma fibrinogen (in Russian). S. M. Ševčenko (Child Clinic and Lenin Medical Inst., U.S.S.R.). *Lab. Delo*, 5 (1959) 25.

0.01 ml of serum or plasma are placed on paper strips (28 × 2 cm) at 8.5 cm from the cathodic end. The electrolytic solution is a Veronal buffer (pH = 9.3; 7.36 g sodium Veronal, 3.86 g sodium acetate, 1100 ml distilled water) and 210 V are applied for 18 h. After drying for 30 min at 110° the strips are developed with 0.02% acid-blue or 10B amido-black solution in methanolic 10% acetic acid and then they are washed in a 4% phenol solution in 10% acetic acid. From the initial point the following substances are seen on the strips: fibrinogen, γ -, β -, α_2 -, α -globulins, albumins. Fibrinogen can be eluted with 0.1 N NaOH and determined colorimetrically with the aid of an orange or green filter. [G.de An.]

455 - Mobility of different haemoglobin derivatives by high-frequency electrophoresis (in German).

W. Künzer and E. Ambs (Univ. Würzburg, Würzburg, Germany). *Klin. Wochschr.*, 37 (1959) 249. The electrophoresis is conducted for 5-7 h with a tension of 1200-2000 V and a current intensity of 40-60 mA using Veronal buffer (pH = 8.6) as the electrolyte. From the starting point the following can be seen: meta-, O-, CO-, cyan-haemoglobin. A second band may be obtained owing to the formation of meta-haemoglobin from O- and CO-haemoglobin; this can be avoided by working with haemoglobin cyanderivatives. Both adult and foetus haemoglobin can be recognized in umbilical cord blood. [G.de An.]

See also abstracts nos. 242, 333.

9. Other methods

456 - The influence of gold in a mercury electrode on some electrode processes. W. Kemula, Z. Galus and Z. Kublik (Dept. of Inorganic Chemistry, University of Warsaw, Poland). *Roczniki Chem.*, 33 (1959) 1431.

Using the hanging drop electrode of Kemula and Kublik (*Anal. Chim. Acta*, 18 (1958) 104) prepared from pure mercury and 0.001, 0.01, and 0.1% gold amalgams, the influence of the gold in the mercury on the electrode processes was investigated. Cyclic polarisation with different voltage sweep rates was applied and voltammetric or oscillographic curves were recorded. When the gold concentration in the amalgam exceeded 0.001% an influence on the zinc electrode reaction was observed which increased with increasing gold concentration. This can be explained by the formation of relatively stable AuZn. In anodic processes this compound is not oxidized at the reversible zinc oxidation potential and thus decrease or even disappearance of the anodic dissolution current can be observed. The influence is less pronounced for cadmium but the same general trend is exhibited as for zinc. From a reversible process on the mercury electrode it changes to an irreversible and kinetic one on the amalgam electrode. From these experiments it follows that neglect of intermetallic compound formation in mercury electrodes hung on gold or gold-plated wires may sometimes lead to erroneous conclusions. [Ad.Hu.]

457 - Dielectric investigations on molecular sieves (in German). F. Oehme (Inst. Entw. Chem. Phys. Anal. Meth., Weilheim/Obb., Germany). *Angew. Chem.*, 72 (1960) 489.

Die Linde Molekularsieve sind Silikate von Zeolith Struktur, welche mit Nichteletrolyt Molekülen Käfig-Einschlussverbindungen bilden. Die Möglichkeit eines Einschlusses wird massgeblich durch den Moleküldurchmesser bestimmt. Zur Prüfung des Absorptionsvermögens wurden dielektrische Messungen durchgeführt. Die Absorption von Wasser, Methanol, Äthanol, Acetaldehyd usw. in Benzol und Xylol Lösungen wurde bei verschiedenen Temperaturen untersucht. In Ermangelung gesicherter thermodynamischer Daten kann die von Debye definierte Relaxationszeit als relatives Mass für den Molekülradius verwendet werden, soweit es sich um Moleküle näherungsweise kugelförmiger Gestalt mit starr eingebauten Dipolen handelt. Eine Übertragung der Eyring-schen Theorie auf das eingeschlossene, rotationsgehemmte Molekül lässt aus der Verschiebung des Gebietes anomaler dielektrischer Dispersion eine Berechnung der Adsorptionsenthalpie zu. [Ja.Inc.]

458- Réduction catalytique et électrolytique de la cyanamide sur le nickel finement pulvérisé (en

allemand). G. Trümpler et H. E. Klauser (Ciba, Institut de chimie physiologique, Bâle, Helvetia). *Helv. Chim. Acta*, 42 (1959) 407.

La cyanamide se réduit difficilement sur une cathode de Hg, elle est aisée en présence de nickel actif. Les auteurs traitent: (a) De la réduction catalytique directe de la cyanamide par H₂ en présence de nickel Raney. (b) De la réduction catalytique directe de la cyanamide par H₂ en présence de nickel électrolytique finement divisé. (c) De la réduction électrolytique de la cyanamide sur des électrodes de Ni électrolytique finement divisé. La réduction a et b qui s'effectue en milieu tamponné (pH 7), conduit pratiquement à la formation de la formamidine, qui donne par saponification de l'acide formique. On contrôle la réduction en mesurant l'hydrogène absorbé et on titre l'acide formique. Le rendement de la méthode c, peut atteindre dans certaines conditions 90 à 95%. Les auteurs donnent une explication de la réduction catalytique et du fait que celle-ci est plus aisée que la réduction électrolytique spécialement sur le Hg. [De.Mo.]

459 – The modification of dielectric absorption in molecular crystals by impurities and plastic deformation. H. K. Welsh (Division of Electrotechnology, National Standards Lab., Sydney, Australia). *Trans. Faraday Soc.*, 55 (1959) 52.

The magnitude of the dielectric absorption in ethyl and methyl esters of long chain fatty acids increases with increasing impurity content and plastic deformation but decreases with annealing. It is possible to analyse the absorption curves as a doublet rather than as curves arising from a continuous distribution of relaxation times. A discussion regarding the identification of the molecular processes involved in these absorptions is given. [M.K.Hus.]

460 – Dielectric properties of some polycrystalline stannates and cerates. Blodwen Piercy (Electrical Engineering Dept., Imperial College, London, Great Britain, and Radio and Electrical Engineering Division, National Research Council, Ottawa, Canada). *Trans. Faraday Soc.*, 55 (1959) 39.

A measurement of the dielectric constant and loss of several stannates and cerates in sintered form was carried out over a range of frequency and temperature. In all specimens the dielectric dispersion was small at and below room temperature and large at elevated temperatures, the latter being caused by space charge polarisation of electrons. Small absorption maxima were frequently observed and are related either to a small electronic space charge or localised ion jumps. Below room temperature and with BaSnO₃, a negative temperature coefficient of capacity was observed. [M.K.Hus.]

461 – Die Erfassung schneller chemischer Reaktionen im potentiostatischen Ablauf einer Elektrodenreaktion. H. Gerischer (Max-Planck-Institut für Metallforschung, Stuttgart, Deutschland). *Z. Elektrochem.*, 64 (1960) 29.

Am Beispiel der Reaktion $[\text{Cd}(\text{CN})_4]^{2-} \rightleftharpoons [\text{Cd}(\text{CN})_3]^- + \text{CN}^-$ wird gezeigt, dass die potentiostatische Methode für die Analyse einer Elektrodenreaktion mit vorgelagerter chemischer Reaktion sehr geeignet ist. Es wird auf die Schwierigkeiten hingewiesen, die sich bei der Interpretation der so erhaltenen Geschwindigkeitskonstanten chemischer Reaktionen ergeben. Die potentiostatische Methode erlaubt die Erfassung von Reaktionen mit τ bis etwa 100 sec. Die Geschwindigkeitskonstanten der untersuchten Reaktionen werden angegeben. [Ha.Re.]

462 – Untersuchung der Adsorptionserscheinungen an Rhodium, Iridium, Palladium und Gold mit der potentiostatischen Dreiecksmethode. F. G. Will und C. A. Knorr (Physikalisch-Chemisches Institut und Elektrochemisches Institut der Technischen Hochschule München, Deutschland). *Z. Elektrochem.*, 64 (1960) 270.

Mit Hilfe einer neuen potentiostatischen Dreiecksmethode werden die Wasserstoff- und Sauerstoffadsorptionsschichten an den Edelmetallen Rhodium, Iridium, Palladium und Gold in Abhängigkeit von der Bezugsspannung gemessen. Die maximale Wasserstoffbedeckung an der aufgerauten Metalloberfläche beträgt an Rhodium 62%, and Iridium 45% und an Gold 3%. Die Wasserstoffbedeckung ist abhängig von der Spannungsgeschwindigkeit und der Vorbehandlung der Elektrode. Die Sauerstoffbelegung beginnt bei den verschiedenen Metallen bei verschiedenen Spannungen und nimmt bis 2,2 V ständig zu. Bei Iridium erfolgt oberhalb 1,6 V über eine einatomare Schicht hinaus kein weiteres Anwachsen der Sauerstoffbelegung. Die charakteristischen Messwerte sind zusammengestellt. [Ha.Re.]

463 – An electrometric method for the study of solutions (in Russian). O. K. Kudro and J. D. Vdovenko (Polytechnic Institute of Kiev, U.S.S.R.). *Ukrain. Khim. Zhur.*, 25 (1959) 25.

A rapid method of chemical analysis has been developed using results obtained by the author in an earlier work, *i.e.*, $C = ai \tau^{1/2}$, where C = electrolyte concentration (moles/l), i = current density (A/cm²), τ = time of electrolysis from the start to the moment when a black film appears

on the electrode (sec), a = constant dependent on the nature of the electrolyte. The authors propose an automatic instrument for the determination of electrolyte concentrations over a broad range of temperatures and concentrations. The authors have found that at high current densities some surface-active compounds affect electrolysis, in agreement with the adsorption theory; this is proved by the fact that at negative tension values the surface-active compounds are desorbed on the cathode. [Ot.So.]

464 – Determination of cholinesterase activity in blood and organs by automatic titration. J. Jensen-Holm, H. H. Lausen, K. Milthers and K. O. Møller (Copenhagen Univ., Denmark). *Acta Pharmacol. Toxicol.*, 15 (1959) 384.

Excess acetylcholine (as iodide) is added to the sample and the pH maintained constant by automatic addition of standard alkali (0.1 N NaOH); the amount of base required, after deduction of the blank value (due to spontaneous hydrolysis of the substrate and non-specific acid liberation from the sample), expressed in μ moles/ml/min, gives the activity. [Ca.Cas.]

See also abstracts nos. 243, 248.

10. Related topics

465 – Investigation of the electronic properties of tungsten trioxide. I. The electronic conductivity of tungsten trioxide within the temperature range 100–700°C (in English). J. Dereń and E. Polaczkowa (Dept. of Surface Phenomena, Institute of Physical Chemistry, Polish Academy of Science, Kraków; Dept. of Inorganic Chemistry, Academy of Mining and Metallurgy, Kraków, Poland). *Bull. acad. polon. sci., Sér. des sci. chim., géol. et géogr.*, 7 (1959) 313.

The electroconductivity of WO_3 pellets was investigated over the temperature range 100–700°. In general $\log \sigma$ did not change linearly with $1/T$. When the temperature increased to 350°, a maximum and a subsequent minimum were observed. When the sample was cooled its conductivity was less and showed a pronounced minimum. In this region a stationary value was obtained after several tens of minutes. Above 350° $\log \sigma$ increased and decreased regularly and momentarily upon heating or cooling of the samples. Several factors were investigated: the effect of pressure (1 atm– 10^{-5} mm Hg); sintering of the sample in 1100°; and various atmospheres, *i.e.*, pure air with added water vapour, CO_2 and ethyl alcohol. [Ad.Hu.]

466 – Investigation of the electronic properties of tungsten trioxide. II. Current–voltage characteristics of tungsten trioxide within the temperature range 100–700°C (in English). J. Dereń and E. Polaczkowa (Dept. of Surface Phenomena, Institute of Physical Chemistry, Polish Academy of Science, Kraków; Dept. of Inorganic Chemistry, Academy of Mining and Metallurgy, Kraków, Poland). *Bull. acad. polon. sci., Sér. des sci. chim., géol. et géogr.*, 7 (1959) 321.

Various WO_3 samples were investigated under various conditions and current–tension curves were obtained using both alternating and direct current. In most cases a linear or slightly curved $i-V$ relation was obtained. The non-linearity was supposed to be caused by processes taking place on the surface of intergranular necks. In several cases an anomalous shape of the $i-V$ curve, namely two symmetrical loops, was observed. This occurs in the temperature range over which conductivity decreases with increasing temperature. Dielectric constant changes were also measured as a function of the temperature. Three sections were noted: below 300°, dielectric constant is practically independent of temperature; 300–500°, it increases slightly but distinctly; and above 500°, the increase is very pronounced. [Ad.Hu.]

467 – Investigation of the electronic properties of tungsten trioxide. III. The influence of surface processes on the electric conductivity of WO_3 (in English). J. Dereń and E. Polaczkowa (Dept. of Surface Phenomena, Institute of Physical Chemistry, Polish Academy of Science, Kraków; Dept. of Inorganic Chemistry, Academy of Mining and Metallurgy, Kraków, Poland). *Bull. acad. polon. sci., Sér. des sci. chim., géol. et géogr.*, 7 (1959) 327.

On the basis of previous experiments (*cf.* Abstracts Nos. 281 and 282) the influence of surface phenomena on the electronic properties of WO_3 was shown and discussed. In the range 100–350° WO_3 can be characterized as a n -type semiconductor. In this region, lattice defects, sintering, the addition of various gases to the air atmosphere influence the conductivity strongly. Varying

contributions of the surface to the total conductivity were reflected of sintering of samples. The effect of chemisorption was also discussed. At higher temperatures WO_3 is an intrinsic conductor and the surface effect does not influence the conductivity to such an extent. [Ad.Hu.]

468 – Desorption kinetics of cathodic hydrogen from thin nickel layers (in English). B. Baranowski (Institute of Physical Chemistry, Polish Academy of Science, Warsaw, Poland). *Bull. acad. polon. sci., Sér. des sci. chim., géol. et géogr.*, 7 (1959) 891.

The kinetics of the cathodic hydrogen desorption from electrolytic nickel layers was investigated for cases in which the H : Ni atomic ratio was equal to 0.7 (layer thickness to 30μ). It was found that neither diffusion nor phase boundary processes are rate-controlling processes for the over-all desorption. Thus it was assumed that the rate-determining process takes place within the nickel layer (volume process). Its character is not yet clear. Desorption proceeds according to a first order reaction equation and is characterized by an activation energy of 13–14 kcal/mole. Two stages of desorption were observed, which could be explained assuming two hydrogen phases to be present in the nickel layers. [Ad.Hu.]

469 – Dependence of the cathodic hydrogen content in thin nickel layers on the current density and saturation temperature (in English). B. Baranowski (Institute of Physical Chemistry, Polish Academy of Science, Warsaw, Poland). *Bull. acad. polon. sci., Sér. des sci. chim., géol. et géogr.*, 7 (1959) 897.

Three regions of current density which govern the hydrogen content in electrolytic layers of nickel were observed. For small densities the atomic ratio H : Ni = 0.03 was attained. Increase of density causes an abrupt change of the hydrogen concentration to the ratio H : Ni = 0.6–0.8, but no further increase of this ratio was observed. Investigating the temperature dependence it was found that at low temperatures the atomic ratio depends slightly on temperature changes but remains of the order of 0.6. At higher temperatures a sudden decrease was observed below the ratio 0.1. These facts support the existence of two phases of hydrogen layers which is similar to the behaviour of the H–Pd system. [Ad.Hu.]

470 – An equation for the potentiometric adsorption isotherm (in Polish). W. Tomassi (Dept. of Physical Chemistry, Politechnika, Warsaw, Poland). *Przemysl. Chem.*, 38 (1959) 285.

The empirical equation $\pi = a\Gamma^b$ was discussed, where π is the potential of the powder electrode with the powdered substance covered by an adsorption layer, and Γ is the surface concentration of the adsorbed substance. In all the cases studied this equation was obeyed. It was shown that a theoretically deduced formula must have a different mathematical form. The physical meaning of the constants a and b was discussed. Using the supposed mechanism of the process, an equation $\pi = A + B \log \Gamma$ was derived for a carbon electrode with adsorbed chlorine. The physical meaning of A and B and methods for their theoretical computation were given. [Ad.Hu.]

471 – Electrochemical method for the determination of the depolarizing ability of pyrolusite (in Polish). K. Appelt and H. Puroł (Central Laboratory of Cells and Accumulators, Poznań, Poland). *Przemysl. Chem.*, 38 (1959) 292.

A method for the determination of the depolarizing ability of pyrolusite was described. It was based on the direct testing of pyrolusite under standard conditions in a $\text{Zn-MnO}_2\text{-NH}_4\text{Cl-C}$ cell system. This method is simple and rapid and the results are reproducible and accurate. The sample preparation, the composition of the pyrolusite and the electrolyte, and the grain size did not influence the results, which were directly comparable with the depolarizing ability of pyrolusite in dry cells. This method has made possible the investigation of the best composition of various depolarizing mixtures used in practice. [Ad.Hu.]

472 – Adsorption rate of hydrogen dissolved in water on platinized platinum electrodes (in Hungarian). I. Telcs, F. Nagy and I. Nyitrai (Central Inst. Chem., Hungarian Academy of Sciences, Budapest, Hungary). *Magyar Kém. Folyóirat*, 66 (1960) 190.

The investigation of the adsorption rate of hydrogen in aqueous solution onto a platinized platinum electrode led to the following conclusions. The velocity of adsorption is governed by the velocity of diffusion through the liquid film adhering to the surface of the electrode. The rate constant of adsorption changes with the speed of stirring, rapidly at low rates, asymptotically tending towards a limiting value at high stirring rates. The energy of activation of the adsorption rate was found to about 2.0 kcal/mole. [Ja.Inc.]

473 – Glow discharge electrolysis of potassium iodide. B. S. R. Sastri (Central Electrochemical Research Institute, Karaikudi, India). *J. Sci. Ind. Research (India)*, 19B (1960) 317.

Aqueous solutions of KI at varying concentrations (0.2–2.5 M) have been subjected to glow dis-

charge electrolysis at currents ranging from 50 to 90 mA and with one electrode (anode) in the vapour above the electrolyte. A certain minimum concentration of the substrate has been found necessary to retain the iodine in solution. Iodine and hydrogen are the initial products of glow discharge electrolysis of KI solutions, and hydrogen peroxide appears at higher concentrations. The characteristic features of glow discharge electrolysis, as observed from the behaviour of the glow when the glow discharge electrode is made the anode or the cathode, are suggestive of point-to-plate discharges. [R.S.Sa.]

474 – Electrodeposition of copper from the pyrophosphate bath. S. K. Pannikar and T. L. Ramachar (Institute of Science, Bangalore, India). *J. Sci. Ind. Research (India)*, 19A (1960) 265.

The plating of copper from complex pyrophosphate solutions has been investigated. The optimum conditions for obtaining satisfactory deposits on steel are: bath composition, copper 31.8, pyrophosphate 190.8, ammonium citrate 20 g/l; pH, 8.05; temperature, 60°; and limiting current density 10 A/sq. cm; agitation of the bath is important. Under these conditions, efficiencies close to 100% are obtained. High cathode polarization and a linear relationship between tension and log current density have been observed. The throwing power of the plating solution measured with a modified Haring-Blum cell is in the range 59–84% as per field formula using the weight of deposits and 23–62% using the Gardan equation involving the cathode tension and resistivity. The anode tension curves show the phenomenon of electropolishing of copper. The pyrophosphate bath is comparable to the high efficiency cyanide bath for copper plating with the added advantage of higher permissible current density. [R.S.Sa.]

475 – Behaviour of graphite in an electrostatic and high tension separator. K. K. Majumdar (Atomic Energy Establishment, Bombay, India). *J. Sci. Ind. Research (India)*, 19B (1960) 314.

The behaviour of natural graphite in electrostatic and high tension separators has been studied with different polarities, position of electrodes and r.p.m. of the grounded rotor in a carpco laboratory high tension separator. The results show that high tension separation is superior to electrostatic separation. Even in high tension separation, by employing a combination of convective and electrostatic fields, a better separation is effected than by using a pure convective field. Better separation is also possible when the electrode is made positive than when it is made negative. [R.S.Sa.]

476 – Calculations of dipole moments of H₂Se and AsH₃. D. V. G. L. Narasimha Rao (Physics Dept., Andhra University, Waltair, India). *Trans. Faraday Soc.*, 55 (1959) 19.

From the bond angle, the moment of H₂Se is explained on the basis of *s,p*-hybridization alone and about 7% ionic character is assumed for the As–H bonds to account for the observed moment of AsH₃. [M.K.Hus.]

477 – Untersuchung des Auf- und Abbaues der Wasserstoff- und Sauerstoffbelegungen an Platin mit einer neuen instationären Methode. F. G. Will und C. A. Knorr (Physikalisch-Chemisches und Elektrochemisches Institut der Technischen Hochschule München, Deutschland). *Z. Elektrochem.*, 64 (1960) 258.

Ein Verfahren zur Untersuchung von Adsorptionserscheinungen an Platin wird beschrieben. Zwischen einer Versuchselektrode und einer Bezugslektrode liegen eine Gleichspannung und eine Dreiecksspannung variabler Amplitude und Frequenz, die von einem elektronischen Potentiostaten vorgegeben sind; der Zellenstrom wird oszillographisch registriert. Eine Steigerung der Frequenz der Dreiecksspannung bewirkt bei Wasserstoffbespülung der Elektrode einen Übergang von der stationären, durch Transportvorgänge bestimmten Kurve, zu einer instationären von Umladungsvorgängen bestimmten Kurve. Der Auf- und Abbau von Wasserstoff- und Sauerstoff-Adsorptionsschichten lässt sich durch graphische Integration der Strom-Zeit-Kurven quantitativ ermitteln. Reaktionshemmungen lassen sich durch Variation der Dreieckfrequenz untersuchen. Besonders grosse Hemmungserscheinungen wurden beim Abbau der Sauerstoffadsorptionsschichten beobachtet. [Ha.Re.]

478 – Zum Mechanismus der elektrolytischen Chromabscheidung durch Reduktion von Chromsäure. M. Käppel und H. Gerischer (Max-Planck-Institut für Metallforschung, Stuttgart, Deutschland). *Z. Elektrochem.*, 64 (1960) 235.

Es wird ein neuer Mechanismus der elektrolytischen Chromabscheidung angegeben, bei dem der letzte Schritt in der Reduktion einer monomolekularen oxydischen Deckschicht zum metallischen Chrom besteht. Die Fremdionenwirkung wird durch eine parallel ablaufende Auflösungsreaktion gedeutet, die das Dickenwachstum der Oxydschichten verhindert. Gleichzeitig inhibieren die Anionen die Wasserstoffentwicklung und erhöhen somit die Stromausbeute für die Chromab-

scheidung. Die experimentellen Messungen der elektrolytischen Chromabscheidung aus wässrigen Chromsäurelösungen erfolgten mit Hilfe einer potentiostatischen Methode. [Ha.Re.]

479 – Zur Potentialverteilung im Elektrolyten vor zweiphasigen Metalloberflächen. Christa Ilshner-Gensch (Versuchsanstalt der Friedrich Krupp Widia-Fabrik, Essen, Deutschland). *Z. Elektrochem.*, 64 (1960) 275.

Mit Hilfe einer verschiebbaren Potentialsonde wurde die Potentialverteilung vor einem ebenen Lokalelementmodell gemessen. Die Stromdichteverteilung im Elektrolyten wurde auf graphischem Wege abgeschätzt. Durch Verwendung von Elektrolyten verschiedener Leitfähigkeit konnten die asymmetrischen Verhältnisse nahe der Phasengrenze, die durch unterschiedliche Polarisationsparameter von Anode und Kathode hervorgerufen werden, erfasst werden. Ergebnisse einer Näherungsrechnung, die auf vereinfachenden Annahmen über die Form der Stromlinien beruhen, stimmen gut mit den Messwerten überein. [Ha.Re.]

480 – Über den Einfluss des Lösungsmittels auf organische Reaktionen. I. Podkowska und A. Tarnawski (Institut für physikalische Chemie der T.H. Gleiwitz, Polen). *Monatsh. Chem.*, 90 (1959) 179. Es wurde Phenol mit gasförmigen NO_2 in organischen Lösungsmitteln und wässrigen Lösungen mit verschiedenen Dielektrizitätskonstanten nitrirt. Es wurde festgestellt, dass mit Ansteigen der Dielektrizitätskonstante die relative Menge an Paraisomeren in den Reaktionsprodukten zunimmt. Ferner versuchte man die funktionelle Abhängigkeit zwischen dem „summarischen Dipolmoment“ der Reaktionsprodukte und der Dielektrizitätskonstante des Lösungsmittels festzustellen. [Ed.Bro.]

481 – Über eine elektrochemische Darstellung von Sauerstoff-Difluorid. A. Engelbrecht und E. Nachbaur (Institut für anorganische und analytische Chemie der Universität Innsbruck, Österreich). *Monatsh. Chem.*, 90 (1959) 367.

Die Elektrolyse von Fluorwasserstoff mit wechselndem Wassergehalt wird als Methode der präparativen Darstellung von OF_2 untersucht. Die dabei erzielten maximalen Ausbeuten liegen um 60% OF_2 , der Rest des Anodengases besteht aus O_2 mit Spuren O_3 . Eine Bestimmung der spez. Leitfähigkeit im System Wasser–Fluorwasserstoff ergibt ein relatives hohes Maximum bei etwa 74% HF. [Ed.Bro.]

482 – Die Elektrofluorierung von Guanidin-Hydrofluorid in wasserfreiem Fluorwasserstoff. A. Engelbrecht und E. Nachbaur (Institut für anorganische und analytische Chemie der Universität Innsbruck, Österreich). *Monatsh. Chem.*, 90 (1959) 371.

Die Elektrofluorierung von Guanidin-Hydrofluorid in wasserfreiem Fluorwasserstoff wird als Methode zur präparativen Herstellung von NF_3 untersucht; die Vorteile dieser Methode gegenüber einer Elektrolyse von Ammoniumbifluorid-Schmelzen sind vor allem viel bessere Stromausbeuten an NF_3 und die Erleichterungen in der Durchführung, welche sich aus der niederen Arbeitstemperatur ergeben. Ein erheblicher Nachteil ist die gleichzeitige Bildung von CF_4 und die ausserordentliche Schwierigkeit der präparativen Trennung dieses Gasgemisches. Partialdrucke von HF über gesättigten Lösungen von Guanidin-Hydrofluorid in HF werden bestimmt und das Debye-Scherrer-Diagramm von Guanidin-Hydrofluorid aufgenommen. [Ed.Bro.]

483 – Über die Bedeutung der Dielektrizitätskonstante beim Mischpunkt des ternären Systems Propanol-(2)-Wasser-Benzol. C. V. Suryanarayana und K. M. Somasundaram (Phys.-chem. Laboratorium d. Universität Annamalai, Annamalainagar, Süd-Indien). *Monatsh. Chem.*, 90 (1959) 375.

Um zu verstehen, warum ein heterogenes System, bestehend aus zwei mit einander nicht mischbaren Flüssigkeiten ohne Vermischung existiert, wurden die physikalischen Eigenschaften eines Systems studiert, dessen Phasengrenzfläche nach Zusatz einer optimalen Menge eines dritten, mit den beiden ursprünglichen heterogenen Komponenten vollständig mischbaren Komponente gerade im Verschwinden war. Es wurde gefunden, dass in diesem Zustand $\Sigma L_k \cdot \kappa_k = L_{1,2,3}$ gilt, worin L_k die Volumspolarisation κ_k der Molenbruch der Komponente k und $L_{1,2,3}$ die Volumspolarisation der Mischung bedeuten. Die Gültigkeit der Gleichung lässt sich auf einen mit den Lücken innerhalb der Substanz in Zusammenhang stehenden Volumsfaktor Φ zurückführen; dieser ist der Schlüssel für das Verständnis der gegenseitigen Mischbarkeit von Flüssigkeiten. [Ed.Bro.]

484 – Die Wechselwirkung zwischen Chlorwasserstoffgas und Äthanol in flüssiger Phase unter dem Einfluss von Wechselstromfeldern. Prakashchandra Gupta (Dept. of Chemistry, College of Science, Hindu-Universität, Banaras (Varanasi), Indien). *Monatsh. Chem.*, 91 (1960) 152.

Während eine in einem Siemens-Ozonisator gefüllte Alkohol-HCl-Mischung auch nach 6-stündiger

Behandlung unter Wechselstrom von 50 bzw. 500 Hz und 12 bis 15 kV praktisch unverändert bleibt, bilden sich bei der Einwirkung von Wechselstrom auf Alkohol-HCl-Mischungen in U-förmigen oder zylindrischen Elektrolysenzellen chlorierte und nichtchlorierte Oxydationsprodukte des Alkohols in Abhängigkeit vom Elektrodenmaterial (Pt-Draht und Kohlestäbchen). Die Abhängigkeit der Natur der Reaktionsprodukte vom Elektrodenmaterial wird diskutiert.

[Ed. Bro.]

485 – Solubility and solubility product (in Russian). N. V. Akselrod and B. V. Spivakovskii (Institute of General and Inorganic Chemistry, Academy of Sciences of the U.S.S.R.). *Ukrain. Khim. Zhur.*, 25 (1959) 14.

The authors deal with the inconsistencies between the experimentally observed solubilities of little-soluble hydroxides and sulfides and the solubilities calculated from the solubility product. The difference between the two values is caused by the slight dissociation of the hydroxide or sulfide (Ni, Zn, Be, Al, Fe and Co). The authors calculate in a simple manner the dissociation constants and solubility products and give their results in the form of two tables.

[Ot. So.]

486 – Anodic oxidation of zirconium. I. L. Rosenfeld, E. N. Latseva and E. I. Kalinina (Moscow). *Zhur. Fiz. Khim.*, 34 (1960) 995.

The anodic oxidation of zirconium in basic (borate and carbonate) and acidic (nitric, sulphuric and phosphoric) solutions has been investigated. The nature of the change in the terminal voltage was elucidated. The thickness of the films was determined as a function of the duration of the anodizing process. The current efficiency was found for the process in borate and carbonate solutions.

[Ot. So.]

487 – The hydrogen overvoltage on active galvanic nickel precipitates (in Russian). A. M. Mizzakarimov and G. A. Czyganov (Institute of Chemistry, Academy of Sciences of Uzbekistan S.S.R.). *Uzbekii Khim. Zhur. Akad. Nauk Uzbek. S.S.R.*, No. 4 (1959) 29.

The possibility of reducing the hydrogen and oxygen overvoltages on electrodes by the use of galvanic Ni films formed in the presence of some additives containing S and N is known. The mechanism of the formation of such films is, however, unknown. The authors have investigated the influence of gallic acid, anabasin and pyridine on this phenomena. The compositions of the solutions and the conditions of the experiments are given. The authors report polarisation curves of nickel precipitation obtained in electrolytes containing the said additives. Hydrogen overvoltage curves on the active surfaces have also been obtained.

[Ot. So.]

488 – Three anomalies in the electrochemical precipitation of chromium (in Russian). A. Vagramyan and D. N. Usatshev (Institute of Physical Chemistry, Academy of Sciences, U.S.S.R.). *Izvest. Akad. Nauk U.S.S.R.*, (1959) 1207.

In the electrolytic reduction of chromic acid in the presence of H_2SO_4 the following anomalies were observed:

- the electroreduction Cr(VI)–Cr(III) is most rapid at low tension (less than 1 V) and is greatly retarded at higher tensions;
- agitation of the electrolyte strongly decreases cathodic polarisation at low tensions, whereas at higher tensions it has no influence;
- when, in a certain tension range (0.65–1.0 V) the electrode tension is increased, the polarisation current falls.

The authors suppose the anomalies to be caused by the formation of a film on the surface of the electrode. Since the formation of the film is observed only in the presence of H_2SO_4 it is concluded that H_2SO_4 does not destroy the film, but instead supports its formation.

[Ot. So.]

489 – The value of the redox tension of Co^{2+}/Co^{3+} , the solubility product and their mutual interaction (in Russian). V. L. Kheyfets, A. L. Rotinyan and E. S. Kozitch (Institute for the Nickel, Cobalt and Zinc Industries, Leningrad, U.S.S.R.). *Zhur. Obshchei Kim.*, 29 (1959) 1052.

The authors insert into the Nernst equation the tension of the oxygen electrode at equilibria pressure for the tension of the system Co^{2+}/Co^{3+} (since the Co^{3+} ions decompose water) and for the concentration of Co^{3+} ions they insert the solubility product of $Co(OH)_3$; this is possible if we take into account a solution in equilibrium with the solid phase $Co(OH)_3$. In this way the equation is derived

$$\varphi_{Co^{3+}/Co^{2+}}^0 = \varphi_{O_2}^0 - \frac{2.3 RT}{F} \log \pi_{so} i_{Co(OH)_3} + \frac{6.9 RT}{F} \log K_w + \frac{4.6 RT}{F} pH + \frac{2.3 RT}{F} \log \alpha_w^{2+}$$

This equation is verified by investigating the dependence of $a_{Co^{2+}}$ on pH. The agreement with experimental data is good.

[Ot. So.]

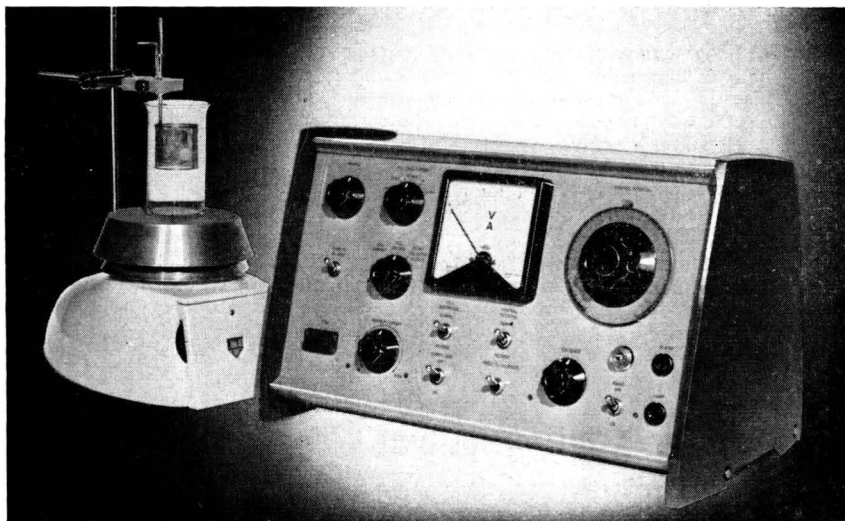
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Wadsworth Controlled Potential Electro-Depositor

ELECTRO-DEPOSITION has long been recognised as an analytical and separative technique for solutions containing metallic ions. The method may be applied where the ionic concentrations of the metals present in solution vary widely, separation being best achieved where the potential of the working electrode relative to the solution is controlled, using a reference

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control attained may be judged from the fact that the incremental error in electrode potential as a function of cell current has a mean value of 1.6 millivolts/ampere; thus when the electrolysis current has fallen to the low levels obtaining towards the end of a deposition, extremely close control is established. It is noteworthy that the potential defined by the built-in potentiometer cannot be exceeded as cell current cuts off at zero potential error.

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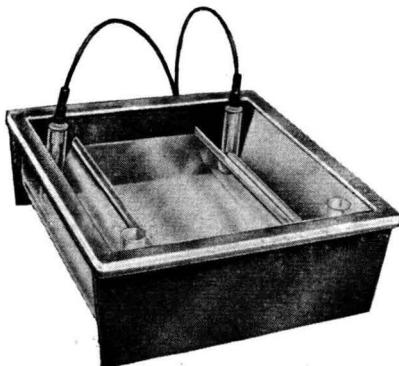
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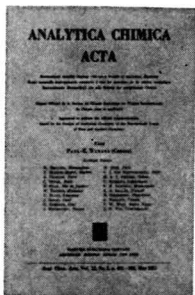
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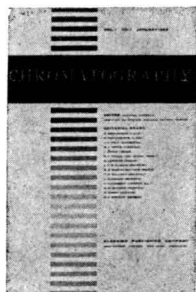
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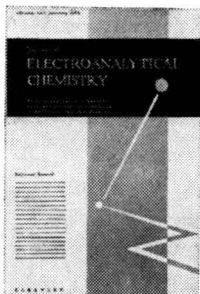


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