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A GALVANIC CELL OXYGEN ANALYZER

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INTRODUCTION

In natural waters and wastes, electrode systems such as the dropping mercury electrode[1-3] and the rotating platinum electrode[4] have been employed. Other investigators[5,6] used materials of a high hydrogen overvoltage (alloys of Fe, Cr, Ni, Sn, Sb and Pb) as cathodes to give improved sensitivity and/or accuracy in the continuous voltammetric determination of dissolved oxygen.

Oxygen determinations using galvanic systems have been successfully used in gas streams. HERSCH[7] and BAKER *et al.*[8] reported systems composed of a silver cathode and a lead anode immersed in 24 wt.% potassium hydroxide, while KEIDEL[9] also developed a sensitive instrument for trace quantities of oxygen, but based upon a silver–cadmium galvanic couple. TÖDT[10] devised a corrosion indicator which was basically a galvanic cell for oxygen measurement. In all cases, one of the principle problems has been the effect of electroactive or surface active impurities which either react with or poison the sensing device. One way to avoid the effect of such impurities is to scrub the oxygen out of the sample by a carrier gas and to measure the oxygen content in the gas phase[7].

An alternate but simple approach is accomplished by covering the sensing electrode with a membrane permeable to oxygen but non-permeable to other substances in the test solution. An early attempt in this direction was reported by KAMIENSKI[11] who employed a protective adsorption film of hydrophilic colloid (silica gel) to cover a microplatinum electrode. More recently, CLARK *et al.*[12] described a procedure for recording dissolved oxygen in blood by the use of a micro-platinum electrode covered with a polyethylene membrane. This membrane is permeable to oxygen (and other gases), but practically non-permeable to ionic species of the solution. On this basis, REEVES, RENNIE AND PAPPENHEIMER[13] tested for oxygen in urine and SUGIOKA AND DAVIES[14] monitored oxygen tension in interstitial brain fluids in dogs. The use of a plastic membrane as a selective diffusion layer also suggested the possibility of voltammetric analysis in gases. SAWYER *et al.*[15] studied different kinds of Teflon and polyethylene membranes for the quantitative measurement of oxygen and sulfur dioxide in gas mixtures. Because of the temperature dependence of oxygen diffusion in the membrane, CARRITT AND KANWISHER[16] have incorporated a thermistor in their electrode system.

Because attempts to utilize these electrode systems for oxygen determination in natural waters and wastes were unsatisfactory, a study was made to develop a more suitable electrode system. The desired characteristics of an ideal electrode system include the ability for continuous monitoring for oxygen, long term stability, ruggedness and suitability for field use as well as unit plant processes, simplicity, ease of operation and maintenance. The resulting electrode system which has been used to advantage in several recent studies, appears to approach the desired characteristics more closely than those previously reported and its design constitutes the purpose of this report.

ELECTRODE MATERIAL

Previous studies in this laboratory on the electrolytic oxygen reduction on platinum electrodes, such as encountered in cell designs similar to that reported by CARRITT AND KANWISHER[16], showed evidence that the reaction was highly dependent on the previous history of the platinum surface. Recently LINGANE[17] showed that the reduction of oxygen on a platinum wire cathode is complex and involves the platinum–platinum oxide couple. In acid solutions the presence of platinum oxide film on the electrode surface is essential for the reduction of oxygen; in its absence the electrode reaction does not occur. Similar conclusions were substantiated by the recent studies of SAWYER AND INTERRANTE[18] on electrolytic oxygen reduction at the platinum and other electrodes. The latter authors postulated that the mechanism of the reaction proceeds through the reduction of the metal oxide which is in turn reformed by the reaction of the oxygen on the metal. If this latter reaction is slow, smaller kinetic-limited currents will be obtained. Significantly, SAWYER AND INTERRANTE reported that this phenomenon did not occur at the silver and gold electrodes. For this reason, silver was selected as the cathode material and performance characteristics more stable than with platinum were achieved.

Lead was selected as the anode material since its electrode potential is sufficiently negative to cause spontaneous reduction of oxygen but not so negative as to cause reduction of the supporting electrolyte. Also, its electrode reactions are quite reversible. With this design an external source of applied voltage is not needed and the instrument is therefore somewhat more suitable for field use. A 1 *M* potassium hydroxide solution was chosen as the supporting electrolyte because its conductivity is high, the residual current in the absence of oxygen is small and lead ions are soluble in it, thus maintaining a clean anode.

GALVANIC CELL OXYGEN ANALYZER

The cell design is shown in Fig. 1. A thin polyethylene membrane fixed in near contact with the electrode surface permits rapid diffusion of oxygen to the electrode's surface. The membrane and the thin layer of potassium hydroxide electrolyte solution constitute rigorously defined diffusion layers of constant thickness and exhibit a minimum "edge" effect. Because of the mechanical stability of this design and because of the smaller permeability of oxygen in the membrane as compared with the sample medium, the flux of oxygen and hence the current become independent of the degree of stirring in the test solution above a certain small threshold value. Two other advantages accrue from applying a polyethylene membrane over the sensing electrode. First, oxygen levels in non-conducting liquids and in gaseous streams may be measured. Second, the membrane forms a protective diffusion barrier separating the electrode system from the test sample which, because of its high selective permeability towards oxygen, permits measurements for oxygen in the presence of electroactive and surface active impurities that interfere in conventional voltammetry.

The current generated in this electrode system will depend at steady state on the rate of mass transfer of the electroactive species across the membrane and on the kinetics of the overall electrochemical process within the galvanic cell. When the silver cathode is used, the concentration of oxygen at the cathode surface is reduced to zero when the cell is placed in operation. Because the potassium hydroxide liquid layer is quite thin and because the permeability of oxygen in this layer is great, the rate of mass transfer across the membrane under total concentration polarization becomes the rate determining step at steady state.

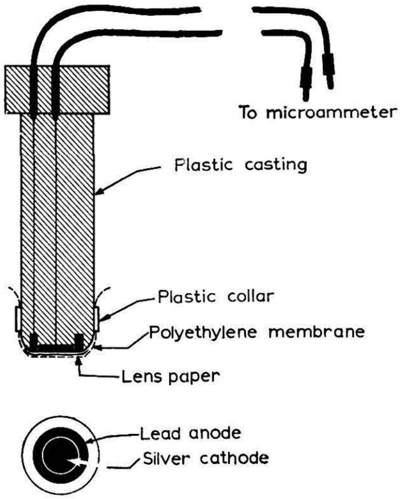

Fig. 1. The galvanic cell oxygen analyzer.

STEADY STATE MASS TRANSFER THROUGH MEMBRANES

The permeability (steady state) of homogeneous polymeric, non-rigid membranes to gases and vapors is usually described[19-21] by:

$$q = P_m \frac{C_1 - C_2}{b} \tag{1}$$

where C_1 and C_2 are the surface concentrations, moles cm^{-3}, in the phases on opposite sides of the membrane, q the flux, moles cm^{-2}sec^{-1}, P_m permeability coefficient of the membrane, cm^{2}sec^{-1}, and b the membrane thickness, cm.

The permeation process through plastic membranes involves first the solution of the permeating gas in the membrane material[19,20]. Customary equilibrium conditions are assumed to prevail at the membrane–phase boundary. Thus at low concentrations a linear relationship exists between the external gas concentration, C, and the corresponding equilibrium concentration, C_m, within the membrane surface.

$$C_m = kC \tag{2}$$

where k is the distribution coefficient.

Diffusion of the gas molecules *within* the membrane at steady state conditions may then be expressed as:

$$q = -D_m \frac{C_{m_1} - C_{m_2}}{b} \tag{3}$$

where D_m is the gas diffusion coefficient ($\text{cm}^2\text{sec}^{-1}$) in the membrane, at whose surfaces are maintained constant concentrations C_{m_1} and C_{m_2} moles cm^{-3}, respectively.

From eqns. 1–3 the relationship between the permeability coefficient, P_m, and the diffusion coefficient, D_m, is:

$$P_m = kD_m \tag{4}$$

THEORY OF DIFFUSION CURRENT FOR TWO-LAYER ELECTRODE SYSTEMS

Fig. 2 illustrates schematically the arrangement of the electrode and the pertinent concentration profiles. Separating the membrane from the silver cathode is a thin film of electrolyte solution. It is assumed initially that, with the analyzer immersed in a test solution of oxygen concentration C_s, equilibrium concentrations $C_{m,0}$, $C_{f,0}$ exist throughout the membrane and the electrolyte solution film respectively. The test solution is maintained homogeneous at all times by adequate stirring. On closing the cell circuit, the potential imposed on the cathode is sufficient to cause immediate and complete reduction of oxygen. As the time of electrolysis increases, the concen-

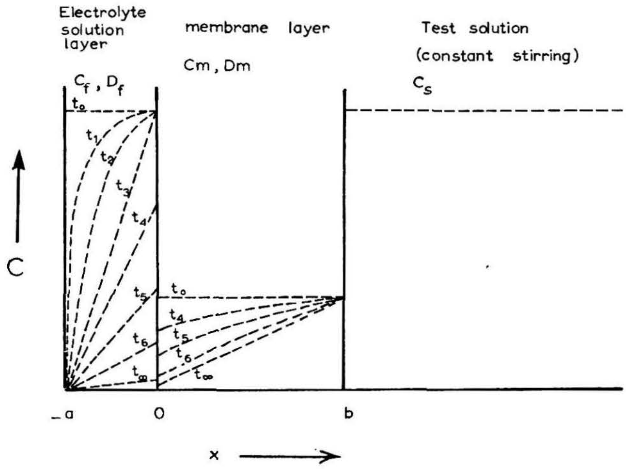

Fig. 2. Schematic diagram of theoretical steady state attainment. Concentration–distance profiles.

tration profile is continually modified until steady state, with a concentration profile corresponding to t_∞, is attained. The current is governed by the rate of diffusion of the electroactive species to the electrode surface[22] and is given by:

$$i_t = nFAD\left(\frac{\partial C}{\partial x}\right)_{x=-a} \tag{5}$$

where n is the number of electrons transfered in the electrode process, F the Faraday and A is the electrode surface area (silver).

In order to develop an expression for the diffusion current as a function of time, it is necessary to solve FICK's second law for linear diffusion

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{6}$$

under the appropriate initial and boundary conditions and substitute the flux value obtained into eqn. 5.

Eqns. 5 and 6 have been written in terms of concentrations of the electroactive species instead of the chemical potentials in order to simplify the discussion. The effect of this will be discussed later.

In the mathematical treatment of the diffusion problem, the following assumptions are considered:

(1) The diffusing substance enters through the membrane plane face and a negligible amount through the edges.

(2) The diffusion coefficient in the electrolyte solution film, D_f, and in the membrane layer, D_m, are constant parameters independent of concentration, time, and location within the appropriate phase.

(3) Initial conditions: $t = 0$

The equivalent equilibrium concentrations are given in terms of the following partition coefficients:

(a) $k_0 = \dfrac{C_{m,0}}{C_{f,0}}$ at $x = 0$

(b) $k_b = \dfrac{C_{m,0}}{C_s}$ at $x = b$

(4) Boundary conditions:

(a) $C_f = 0$ at $x = -a$

(b) $C_f = \dfrac{C_m}{k_0}$ at $x = 0$

(c) $D_f\dfrac{\mathrm{d}C_f}{\mathrm{d}x} = D_m\dfrac{\mathrm{d}C_m}{\mathrm{d}x}$ at $x = 0$

(d) $\dfrac{\partial C_f}{\partial t} = D_f\dfrac{\partial^2 C_f}{\partial x^2}$ $-a < x < 0$

(e) $\dfrac{\partial C_m}{\partial t} = D_m\dfrac{\partial^2 C_m}{\partial x^2}$ $0 < x < b$

(f) $C_m = k_b C_s$ at $x = b$

The subscripts f, m, and s signify the electrolyte solution film, the membrane layer, and the test solution respectively. The Laplace transform is used to solve eqn. 6 under the prescribed initial and boundary conditions. The transformation gives

$$\mathscr{L}C_f = \frac{C_{f,0}}{p}\left[1 - \frac{m \sinh z\sqrt{p} + l \sinh(-\delta)\sqrt{p}}{l \sinh w\sqrt{p} + m \sinh S\sqrt{p}}\right] \tag{7}$$

$$\mathscr{L}C_m = \frac{C_{f,0}}{p}\left[k_0 + \frac{2 \sinh \dfrac{x-b}{\sqrt{D_m}}\sqrt{p}}{l \sinh w\sqrt{p} + m \sinh S\sqrt{p}}\right] \tag{8}$$

where $\mathscr{L}C_f$ = the Laplace transform for C_f;
$\mathscr{L}C_m$ = the Laplace transform for C_m;
p = the Laplace transform constant;

$m = \left(\dfrac{1}{k_0} - \sqrt{\dfrac{D_m}{D_f}}\right)$;

$l = \left(\dfrac{1}{k_0} + \sqrt{\dfrac{D_m}{D_f}}\right)$;

$w = \left(\dfrac{a}{\sqrt{D_f}} + \dfrac{b}{\sqrt{D_m}}\right)$;

$S = \left(\dfrac{a}{\sqrt{D_f}} - \dfrac{b}{\sqrt{D_m}}\right)$;

$-\delta = \left(\dfrac{b}{\sqrt{D_m}} - \dfrac{x}{\sqrt{D_f}}\right)$;

$z = \left(\dfrac{x}{\sqrt{D_f}} + \dfrac{b}{\sqrt{D_m}}\right)$.

The inverse Laplace transformations of eqns. 7 and 8 yield the concentration of the diffusing substance at a distance x from the electrode surface at time t in the electrolyte solution film and in the membrane layer respectively:

$$C_f(x,t) = C_{f,0}[1 - (\gamma_1 + \gamma_2)] \tag{9}$$

where

$$\gamma_1 = \left(\frac{-\delta}{w}\right) + \frac{2}{\pi}\sum_{j=0}^{\infty}(-1)^j \frac{\sin j\pi\left(\dfrac{-\delta}{w}\right)}{j}\, e^{-\frac{j^2\pi^2 t}{w^2}}$$

$$+ \frac{m}{l}\frac{2\pi}{w^2}\int_0^t \left[\left\{\frac{S}{w} + \frac{2}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{n}\sin\left(\frac{n\pi S}{w}\right) e^{-\frac{n^2\pi^2(t-Z)}{w^2}}\right\}\right.$$

$$\left.\left\{\sum_{i=0}^{\infty}(-1)^{i+1}\, i\, e^{-\frac{\pi^2 i^2 Z}{w2}} \sin\left(\frac{i\pi(-\delta)}{w}\right)\right\}\right] dZ$$

$$\gamma_2 = \frac{m}{l}\int_0^t \frac{2\pi}{w}\sum_{j=0}^{\infty}(-1)^j\, j e^{-\frac{\pi^2 j^2(t-\varepsilon)}{w^2}} \sin\left(\frac{j\pi z}{w}\right) d\varepsilon$$

$$+ \left(\frac{m}{l}\right)^2 \frac{2\pi}{w^2}\int_0^t \left[\left\{\frac{S}{w} + \frac{2}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{n}\sin\left(\frac{\pi n S}{w}\right) e^{-\frac{n^2\pi^2(t-\varepsilon)}{w^2}}\right\}\right.$$

$$\left.\left\{\sum_{i=0}^{\infty}(-1)^{i+1}\, i \sin\left(\frac{i\pi z}{w}\right) e^{-\frac{i^2\pi^2\varepsilon}{w^2}}\right\}\right] d\varepsilon$$

$$C_m(x,t) = C_{f,0}[k_0 - 2\gamma_3] \tag{10}$$

where

$$\gamma_3 = \frac{1}{l}\left[\frac{\frac{b-x}{\sqrt{D_m}}}{w} + \frac{2}{\pi}\sum_{n=0}^{\infty}(-1)^n \sin\left(n\pi\frac{\frac{b-x}{\sqrt{D_m}}}{w}\right) e^{-\frac{n^2\pi^2 t}{w^2}}\right.$$

$$+ \frac{m}{l}\left\{\frac{2\pi}{w^2}\int_0^t \left(\frac{S}{w} + \frac{2}{\pi}\sum_{j=0}^{\infty}\frac{(-1)^j}{j}\sin\left(\frac{j\pi S}{w}\right) e^{-\frac{j^2\pi(t-Z)}{w^2}}\right)\right.$$

$$\left.\left.\left(\sum_{i=0}^{\infty}(1-)^{i+1}\, i\, e^{-\frac{i^2\pi^2 z}{w^2}} \sin\left(\frac{i\pi\frac{b-x}{\sqrt{D_m}}}{w}\right)\right) dZ\right\}\right]$$

Since the diffusion current is governed by the flux at the electrode surface, the problem at hand is to obtain an expression for the concentration gradient at any instant and at $x = -a$, from which, by means of eqn. 5, the current can be computed. Because of the complex nature of the general solution (eqns. 9 and 10), the following special conditions are considered.

(1) $\frac{a}{\sqrt{D_f}} = \frac{b}{\sqrt{D_m}}$

$$\left(\frac{\partial C_f}{\partial x}\right)_{x=-a} = \frac{C_{f,0}}{a}\left[\sum_{n=0}^{\infty}\left((-1)^n \frac{\left(\frac{1}{k_0} - \sqrt{\frac{D_m}{D_f}}\right)}{\left(\frac{1}{k_0} + \sqrt{\frac{D_m}{D_f}}\right)} + 1\right) e^{-\frac{n^2\pi^2 D_f t}{4a^2}} + \frac{\sqrt{\frac{D_m}{D_f}}}{1 + \sqrt{\frac{D_m}{D_f}}}\right] \tag{11}$$

(2) $\frac{a}{\sqrt{D_f}} \gg \frac{b}{\sqrt{D_m}}$

$$\left(\frac{\partial C_f}{\partial x}\right)_{x=-a} = \frac{C_{f,0}}{a}\left\{1 + 2\sum_{n=0}^{\infty} e^{-\frac{n^2\pi^2 D_f t}{a^2}}\right\} \tag{12}$$

(3) $\frac{a}{\sqrt{D_f}} \ll \frac{b}{\sqrt{D_m}}$

$$\left(\frac{\partial C_f}{\partial x}\right)_{x=-a} = \frac{C_{f,0}}{b}\left(\frac{D_m}{D_f}\right) k_0 \left\{1 + 2\sum_{n=0}^{\infty} e^{-\frac{n^2\pi^2 D_m t}{b^2}}\right\} \tag{13}$$

The series terms in eqns. 11–13 converge rapidly except at short time intervals. Thus these equations are most convenient at longer times of electrolysis. On the other hand by using the error function in solving for the equations for the specified conditions, an expression for the concentration gradient at the electrode surface is obtained which is valid for small values of t:

(1) $\frac{a}{\sqrt{D_f}} = \frac{b}{\sqrt{D_m}}$

$$\left(\frac{\partial C_f}{\partial x}\right)_{x=-a} = \frac{C_{f,0}}{\sqrt{\pi t D_f}}\left[1 + 2\sum_{n=0}^{\infty} e^{-\frac{4n^2a^2}{D_f t}}\right] \tag{14}$$

(2) $\frac{a}{\sqrt{D_f}} \gg \frac{b}{\sqrt{D_m}}$

$$\left(\frac{\partial C_f}{\partial x}\right)_{x=-a} = \frac{C_{f,0}}{\sqrt{\pi t D_f}}\left[1 + 2\sum_{n=0}^{\infty} e^{-\frac{n^2a^2}{D_f t}}\right] \tag{15}$$

(3) $\frac{a}{\sqrt{D_f}} \ll \frac{b}{\sqrt{D_m}}$

$$\left(\frac{\partial C_f}{\partial x}\right)_{x=-a} = \frac{C_{f,0}}{\sqrt{\pi t D_f}}\, k_0 \left(\frac{D_m}{D_f}\right)^{\frac{1}{2}}\left(1 + 2\sum_{n=0}^{\infty} e^{-\frac{n^2b^2}{D_m t}}\right) \tag{16}$$

The electrode system discussed in this paper falls under the condition $b/\sqrt{D_m} \gg a/\sqrt{D_f}$. Hence the transient current for *longer* time intervals of electrolysis can be calculated from:

$$i_t = nFA\,\frac{D_m k_0}{b}\,C_{f,0}\left\{1 + 2\sum_{n=0}^{\infty} e^{-\frac{n^2\pi^2 D_m t}{b^2}}\right\}$$

Alternatively, since

$$C_{f,0} = \frac{k_b}{k_0}\,C_s$$

and

$$P_m = k_b D_m$$

the equation may be written in terms of the permeability coefficient:

$$i_t = nFA\,\frac{P_m}{b}\,C_s\left\{1 + 2\sum_{n=0}^{\infty} e^{-\frac{n^2\pi^2 D_m t}{b^2}}\right\} \tag{17}$$

at *steady state*, the current is:

$$i_\infty = nFA\,\frac{P_m}{b}\,C_s \tag{18}$$

From eqns. 5 and 16 the transient current at *short* time intervals is:

$$i_t = nFA\left(\frac{P_m}{\pi t}\right)^{\frac{1}{2}} C_s\left\{1 + 2\sum_{n=0}^{\infty} e^{-\frac{n^2b^2}{D_m t}}\right\} \tag{19}$$

Eqn. 19 indicates that the current varies directly with the $\sqrt{P_m}$. At *very* small values of t, however, the electrolyte film will be of primary importance and the flux, and hence the current, will vary according to eqn. 15. Because of the nature of the assumption ($b/\sqrt{D_m} \gg a/\sqrt{D_f}$), eqn. 19 does not hold at extremely short times but only after times when diffusion in the membrane is governing.

EXPERIMENTAL

The cathode of the cell is a silver disc 0.6 cm in diameter surrounded by a ring-shaped lead anode (Fig. 1). The galvanic couple is imbedded in a solid polystyrene plastic in the shape of a probe, the tip of which is smoothed with a fine sand paper; the plastic membrane is fitted firmly against it by means of a plastic collar. Between the membrane and the surface of the galvanic couple, a thin disc of lens paper impregnated with 1.0 *M* solution of potassium hydroxide is placed covering both the cathode and the anode. A piece of insulating tape is then used to cover the edge of the membrane below the collar to prevent any possible contamination of the supporting electrolyte. The quantity of the electrolyte solution is estimated to be about 0.1 ml.

A 0–15 microammeter is satisfactory and, where desired, a recorder may be used. Current–time curves were obtained by the use of a Dumont Cathode Ray Oscilloscope, Type 350. Photographs of the oscillograms were made with a Polaroid Land Camera using a Polaroid film No. 42.

The polyethylene membrane used in this study was provided by Engineering Plastic, Inc., Gibsonville, N.C. It is postulated to have the following characteristics*:

density,	0.92 g/cm^3;
oxygen permeability,	0.15 g/24 h/100 sq. in./atm.;
carbon dioxide permeability,	0.70 g/24 h/100 sq. in./atm.;
water vapor permeability,	0.93 g/24 h/100 sq. in./atm.;
thickness,	1.0 mil.

The thickness of the polyethylene membrane was checked by measuring ten or fifteen layers with a micrometer graduated in thousandths of an in. The average deviation in a series of such measurements was less than 1%.

RESULTS AND DISCUSSION

The main design factors that influence the performance characteristics of the membrane-analyzer are as follows:

(1) the thickness and permeability of the plastic membrane;
(2) the geometry and the arrangement of the galvanic couple;
(3) the quantity of the electrolyte solution.

Membrane characteristics

A large number of membranes were tested. Some were found to be too impermeable for use. Others, such as polyethylene, polypropylene, teflon and natural rubber showed sufficient permeability towards oxygen and at the same time proved to be sufficiently impermeable to interfering ionic species in the test solution. Although these materials are actually made under widely variable manufacturing conditions, it was found that most of the commercially available polyethylene membranes are suitable.

During the mounting of the membrane it usually undergoes a certain amount of stretching which will change its thickness unevenly around the edges. However, if

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* *Alanthon-Polyethylene Resin*, a booklet published by E. I. DuPont De Nemour and Co., Inc., Wilmington, Delaware.

the surface of the galvanic couple and the embedding plastic are carefully smoothed, particularly around the edges, this effect can be greatly minimized. Reproducible stretching of the mounted membrane is easily acquired after few trials.

Cell geometry

The arrangement of the galvanic couple was found to have a significant effect on the sensitivity as well as on the analyzer response time. Previous studies in this laboratory using different electrode designs showed that the arrangement of the cathode and anode and the distance separating them are important design factors. In the design shown in Fig. 1, the exposed area of the analyzer facing the test sample is equal to that of the galvanic couple. This arrangement minimized any possible lateral diffusion of the electroactive species from the sides and around the edges of the analyzer, since the lead ring removes oxygen from this source and "guards" in this way the silver disc and yet does not contribute to the measured current.

Supporting electrolyte

The silver–lead galvanic cell analyzer showed suitable sensitivity with the different supporting electrolytes as illustrated in Table I. If the test sample contains a considerable amount of carbon dioxide, it may be advantageous to use 10% sulfuric acid as supporting electrolyte in the cell although this was not checked.

TABLE I

SENSITIVITY AND RESIDUAL CURRENT AT VARYING SUPPORTING ELECTROLYTES AT 25°

Supporting electrolyte	*Sensitivity ($\mu A/mg/l$)*	*Residual current μA*
1 *M* KOH	1.05	0.2
10% by vol. H_2SO_4	1.12	1.2
Sat. soln. KCl	0.64	1.0
Sat. soln. $KHCO_3$	0.95	0.3

By the use of potassium hydroxide electrolyte, the silver–lead electrode system showed maximum stability, low residual current, and no apparent change in sensitivity over a wide range of the hydroxide concentration. However, at potassium hydroxide concentrations below 0.05 *M* the analyzer showed lower response.

The quantity and the concentration of the electrolyte are important, however. As the cell discharges, the over-all concentration of the potassium hydroxide in solution falls. Also, the carbon dioxide present in test samples is capable of penetrating through the membrane and reacting with the hydroxides forming carbonates. This leads eventually to a marked lowering of the analyzer sensitivity. Previous studies in this laboratory showed that the larger quantities of the electrolyte solution are undesirable as the residual current is higher and the electrode response to changes in the oxygen concentration in the test sample is much slower. On using a total amount of electrolyte solution estimated to be 0.1 ml, the lead–silver electrode system showed minimum residual current, a very fast response, and a reasonable life time before need for cleansing and replenishing of electrolyte.

Sensitivity and linearity of response

At 25° the sensitivity, ϕ, was 1.05 μA/mg/l dissolved oxygen. Using a 1-mil thick polyethylene membrane and 1.0 *M* potassium hydroxide, this sensitivity remained unchanged throughout a period of 3 weeks of continuous monitoring of oxygen in tap water. Care should be taken to prevent damage and drying of the membrane. It is advisable to store the analyzer by submerging it in a saturated solution of sodium sulfite.

The effect of flow of the test sample on the sensitivity is shown in Fig. 3. From an initial low value with no stirring, the sensitivity rises rapidly with increasing stirring speed and then assumes a steady value. Adequate stirring of the test solution is necessary so that the oxygen concentration (C_s) at the membrane surface would be equal to that of the bulk of the solution.

The linearity of response at 25° ± 0.5° from zero oxygen to oxygen-saturated solutions is shown in the typical calibration curve of Fig. 4.

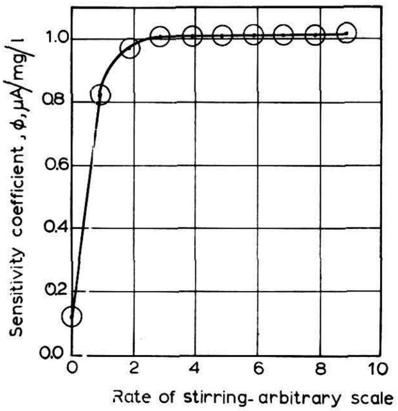


Fig. 3. Effect of stirring on sensitivity.

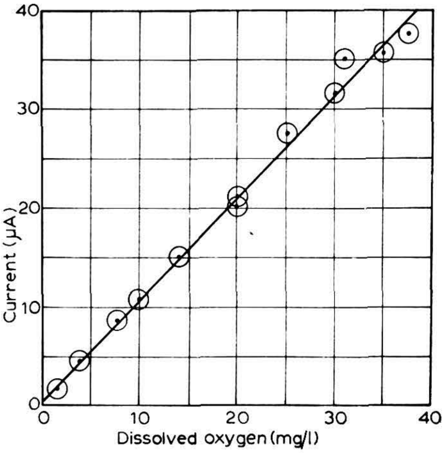


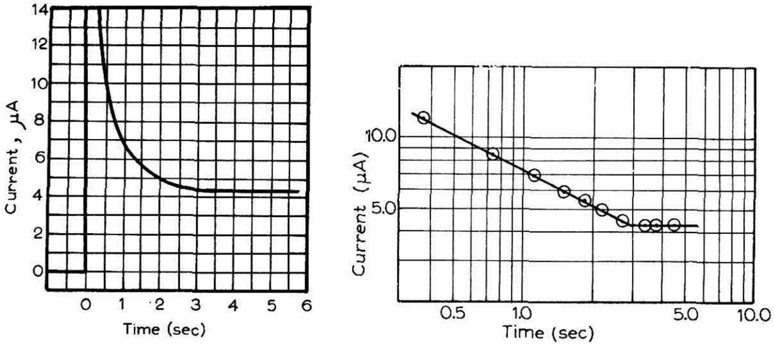
Fig. 4. Dissolved oxygen calibration curve.

Residual current

At zero oxygen concentration in a sample, residual currents are very low, ranging from 0.1 μA to 0.2 μA which corresponds to approximately 0.1–0.2 mg/l. It was originally believed that with each membrane change there would be a new value for the residual current. However, if the membrane is mounted properly and care is taken not to allow air bubbles to be trapped on the electrode surface, the residual current remains at a constant minimum value.

Transient current

During the attainment of a steady state, the current was found to vary inversely with the square root of time. In Fig. 5a the oscilloscope tracing shows the change of current at short time intervals. The logarithmic plot of this current *versus* time, Fig. 5b, yielded a straight line with a negative slope equal to 0.5 at short times, in agreement with eqn. 19. The time lag for the attainment of a steady state current was found to be about 3 sec.



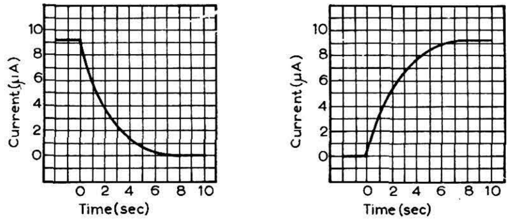
(a) (b)

Fig. 5. Transient current: a, current–time curve; b, steady state attainment.

Response time

The response time of the electrode system to changes in oxygen concentrations in aqueous samples is shown in Fig. 6. In Fig. 6a the analyzer was transferred from an air saturated water (8.8 mg/l D.O.) to a deoxygenated water sample. In Fig. 6b the reverse transfer was made. The time lag in response in each direction was 4.9 sec for 90% response, 5.6 sec for 95% response and 7.5 sec for 99% response.

The time lag in response is dependent, of course, on the membrane permeability and thickness and the amount of the electrolytic solution used.



a b

Fig. 6. Response time curve: a, change in concentration from air saturated water to a deoxygenated water sample; b, change in concentration from deoxygenated water to an air saturated water sample.

Temperature coefficient

One of the main characteristics of voltammetric membrane electrodes of this type is their relatively high temperature coefficient. Since the current in these electrode systems is solely dependent on the rate of transport of the electroactive species from the test sample to the electrode surface, the high temperature coefficient is mainly attributable to the permeability characteristics of the plastic membrane.

The lead–silver galvanic cell analyzer was calibrated over a range of oxygen concentrations at 10 temperatures between 5° and 35°. Linear calibrations were obtained in each case and the sensitivity (slope of calibration curve) is plotted as a function of temperature in Fig. 7a. The sensitivity coefficient, ϕ, μA/mg/l, was found to vary with temperature according to the classical law of an activated diffusion process:

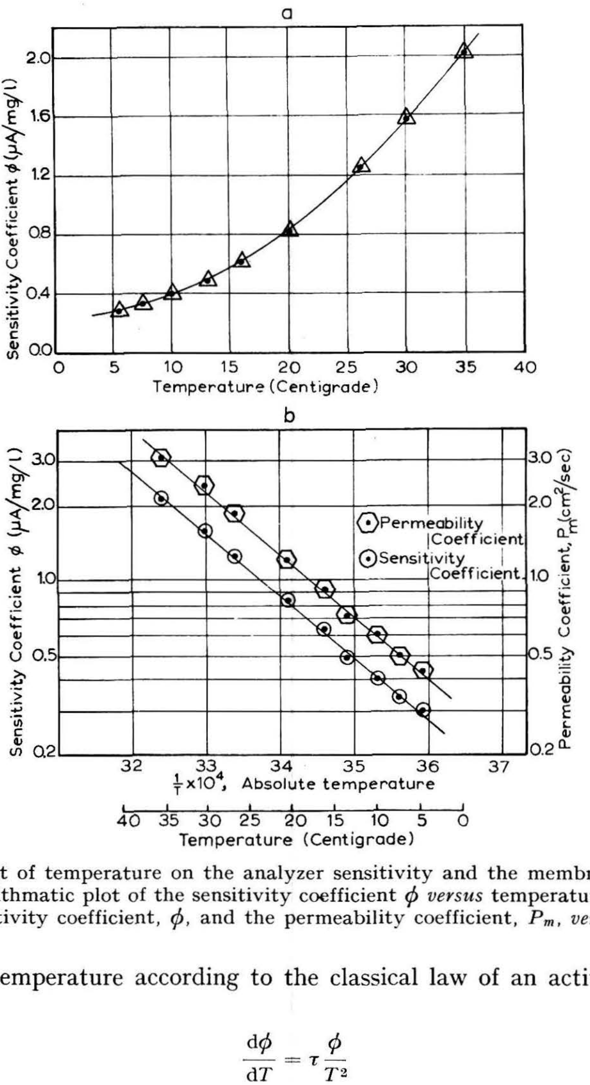


Fig. 7. The effect of temperature on the analyzer sensitivity and the membrane permeability coefficient: a, arithmatic plot of the sensitivity coefficient ϕ *versus* temperature; b, logarithmic plot of the sensitivity coefficient, ϕ, and the permeability coefficient, P_m, *versus* temperature.

$$\frac{d\phi}{dT} = \tau \frac{\phi}{T^2} \tag{20}$$

or alternatively

$$\ln \phi = -\frac{\tau}{T} + Q \tag{21}$$

where T is the absolute temperature. A logarithmic plot of the data is presented in Fig. 7b. By means of the plot, giving the change of the sensitivity ϕ with temperature as shown in Fig. 7a, it was then possible to use the analyzer successfully under various temperature conditions.

CARRITT AND KANWISHER[16] used thermistors in their membrane electrode system to compensate for the temperature effects. However, in this study no attempt was made for automatic temperature compensation by means of thermistors because the temperature effect, $d\phi/dT$, is proportional to the permeability coefficient, with the result that any change in the membrane permeability will result in different temperature effects. Plastic membranes even of the same thickness and structural material sometimes show different permeability coefficients from one batch to another depending on the degree of crystallization of the polymer caused by the particular manufacturing process employed. Also on mounting the membrane, a certain amount of stretching is unavoidable and its extent varies with each trial depending on personal technique. Evidently every time the membrane is replaced, there is a great possibility of having a different temperature coefficient and it was found that this factor must always be checked. Nomograph charts such as are shown in Fig. 7b are easy to use for this temperature compensation. One simply determines the sensitivity at a known temperature and plots this point on the Fig. 7b. After drawing a line through this point and parallel to the one already present, the sensitivity at any other temperature can now be read. It is easy to see that a single fixed thermistor *per se* cannot offer adequate temperature compensation.

Membrane permeability

The results of the temperature coefficient in the above section, as well as reported data on gas permeation through plastic membranes[20], indicate that the permeability coefficient increases exponentially with temperature according to:

$$P = P^0 \, e^{-\frac{E_p}{RT}} \qquad (25)$$

where E_p is the activation energy of permeation in cal/mole, P^0 the standard permeability coefficient, (corresponding to the frequency factor in the Arrhenius equation), R the universal gas constant in cal/mole deg., and T the absolute temperature.

The permeability coefficient is the product of the distribution coefficient, k, and the diffusion coefficient, D, and both (D and k) vary exponentially with temperature[19,20].

$$D = D^0 e^{-\frac{E_D}{RT}} \qquad (30)$$

where E_D is the activation energy of diffusion in cal/mole, and D^0 is the standard diffusion coefficient.

$$k = k^0 e^{-\frac{\Delta H}{RT}} \qquad (31)$$

where ΔH is the heat of solution at constant pressure in cal/mole, and k^0 is the standard partition coefficient.

It is important to note that P^0 and D^0 are rate constants while k^0 is an equilibrium constant. The energy of permeation, E_p, is then equal to:

$$E_p = E_D + \Delta H \qquad (32)$$

The experimentally determined permeability coefficient of polyethylene membranes for oxygen at varying temperatures is given in Fig. 7b. In calculating the permeability coefficient, P_m, from the sensitivity, ϕ, the assumption was made that the silver electrode surface area, A, is the effective area for mass transfer and that any edge transport effects are negligible.

The activation energy of permeation is calculated from

$$E_p = 2.303R \log \frac{P_{m_2}}{P_{m_1}} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{33}$$

where the subscripts refer to the temperatures, T_1 and T_2. For the polyethylene membranes used in this study the activation energy of permeation was found to be equal to 15,560 cal/mole in good agreement with reported literature values[1].

By means of steady state current measurements using this electrode system or similar designs, it is then possible to study rather easily the oxygen permeability of polymeric membranes. It is believed that this technique is much simpler and more accurate than differential pressure methods.

The salting effect. In the derivation of the theory of diffusion currents, it is assumed that the activity of oxygen is equal to its concentration. However, in cases where the test solution contains high salt concentrations, particularly electrolytes, the activity of the oxygen is not equal to the concentration. Although oxygen concentrations in salt solutions in equilibrium with air are lower than those in distilled water samples at the same temperature and oxygen partial pressure, the diffusion current was found to be the same in either case. Fig. 8 shows that the analyzer maintained the same response in air-saturated aqueous systems containing different salt concentrations. Since all solutions were in equilibrium with air under the same temperature and oxygen partial pressure, they had the same oxygen activity. However, the high salt concentration solutions contain lower oxygen concentrations as determined by the WINKLER method[1].

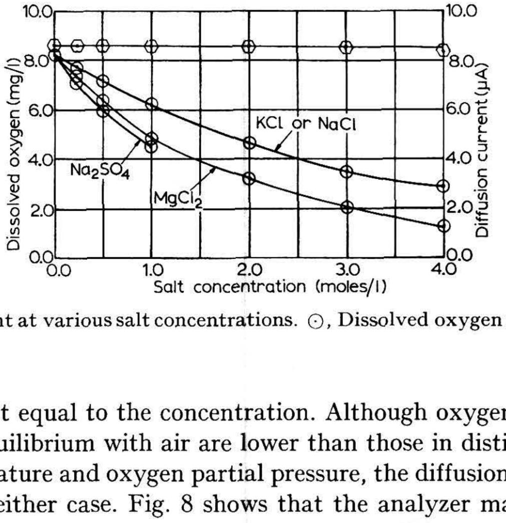


Fig. 8. Diffusion current at various salt concentrations. ⊙, Dissolved oxygen; ⬡, diffusion current.

In the case of high salt concentrations, the activity of oxygen is greater than its concentration, which means that its escaping tendency is greater than if the oxygen retains the same properties in the salt solution it possesses in distilled water. The diffusion current of the Galvanic Cell Oxygen Analyzer and similar membrane oxygen analyzers[15,16] measures the activity of oxygen rather than its concentration. Actually, it is more significant to define oxygen in solution in terms of activity since this is the effective concentration. For instance, activity determines the quantity of oxygen transferable across a respiratory membrane, the oxygen balance in a stream and the rate of corrosion of iron. In the present discussion, oxygen determinations are given in terms of concentration units because of their general acceptance.

When the analyzer is used in water samples containing high salt concentrations such as are encountered in sea water, the concentration of dissolved oxygen could be obtained by multiplying the cell sensitivity by a correction factor. This correction factor is simply the ratio of oxygen solubility in the salt solution to that in distilled water at the same temperature and pressure.

APPLICATIONS

Aeration studies

The galvanic cell oxygen analyzer has been used successfully for determining the role of oxygen transfer in several aeration experiments in laboratory and pilot plant studies.

In bubble aeration processes the electrode system was lowered directly into the aeration column to the desired level. The analyzer was inverted with the surface of the sensing electrode facing upward as in Fig. 9; with this arrangement, the electrode system could be placed directly in a stream of rising bubbles without interference. Disturbances by natural flow do not affect the analyzer sensitivity since its operating principle is based on achieving adequate stirring in the immediate vicinity of the membrane surface.

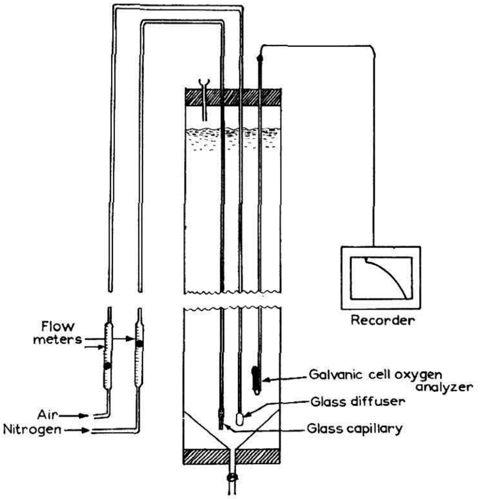


Fig. 9. Apparatus for studying aeration rates.

When attached to a recorder continuous smooth curves easily read over the normal range of dissolved oxygen concentration were obtained. This procedure permitted convenient measurement of the rate of oxygen transfer in the aeration column without requiring any change of the original volume as a result of sampling.

In aeration experiments where the effect of surface active agents on the rate of oxygen transfer was studied, no effect was found of these added impurities on the analyzer sensitivity.

Oxygen determination in lakes, rivers and other natural water bodies

The simplicity, ruggedness, portability, and ease of handling facilitate the use of the galvanic cell oxygen analyzer under variable field conditions. Being a completely submersible analyzer errors usually caused by sampling difficulties are eliminated since the oxygen is measured *in situ*. This is especially important for studies performed at different depths where changes in the physical and chemical characteristics of depth samples on bringing them to the surface are difficult to circumvent.

Evaluation of a vertical oxygen concentration profile in a fresh water lake

One of the first applications of the galvanic cell oxygen analyzer in the field consisted of obtaining a vertical oxygen profile in a thermally stratified lake. Preliminary tests were first made to evaluate the effect of water pressure on the instrument response. The analyzer was lowered into the lake to different depths and simultaneously samples were pumped up from these levels and analyzed for oxygen using the WINKLER method[1]. The results agreed closely and indicated no apparent effect of the hydrostatic head on the instrument response throughout the whole depth of the lake (28 ft).

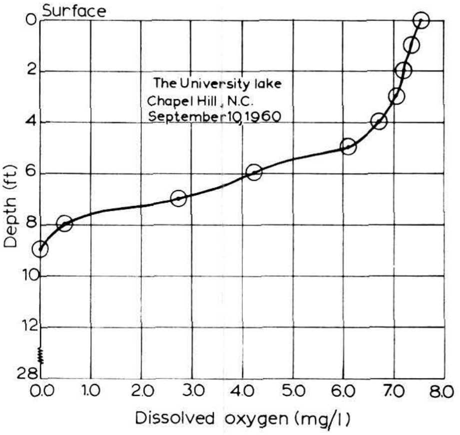


Fig. 10. Dissolved oxygen profile in a thermally stratified lake.

For temperature compensation the analyzer was tied to a telethermometer (Yellow Spring Instrument Co., Inc., Yellow Spring, Ohio) and then lowered in the lake to different depths. Temperature and dissolved oxygen were recorded simultaneously and by means of nomograph charts corrections for temperature were made.

Because the analyzer sensitivity is dependent to a certain extent on the flow characteristics of the test solution, it was then necessary to maintain a certain minimum amount of stirring around the tip of the electrode. In the lake with the analyzer completely submerged in water, a gentle shaking of the attached cable, either manually or by means of a simply automatic device, was sufficient to maintain adequate stirring. In other studies, sufficient stirring was achieved by suspending the analyzer from a moving boat.

Fig. 10 shows a typical dissolved oxygen profile in a thermally stratified lake.

Diurnal changes in dissolved oxygen in a fresh water lake

The oxygen analyzer attached to a telethermometer was lowered in the lake to a predetermined fixed level. The signals were transmitted by means of long cables to the shore where they were recorded continuously on a two channel recorder. In order to maintain a sufficient amount of flow across the membrane, the oxygen analyzer with the telethermometer was placed a few feet in front of a fresh water intake pipe. When the pumping station stopped withdrawing water from the lake during a few hours at night, this was shown clearly on the recorder charts by a decrease in analyzer sensitivity.

Oxygen monitoring in rivers

The galvanic cell oxygen analyzer has been used successfully for monitoring oxygen in streams as a pollution control measure. An example of this case arose when waste from a paper mill was discharged in a river and it was necessary to evaluate the dissolved oxygen relationships downstream. Starting from a point slightly above the waste outlet, the analyzer was lowered in the river from a slowly moving boat and dissolved oxygen and temperature were recorded simultaneously throughout a distance of a few miles downstream. Results showed clearly the effect of the waste on the oxygen balance in the stream and provided valuable information concerning the effect of dilution and reaeration.

Several monitoring stations were then installed to provide a continuous record of dissolved oxygen. This information in turn was used to control the discharge of the plant effluent.

Studies on the rates of oxygen consumption in biological systems

Oxygen uptake rates in biological systems are usually estimated by the manometric method. This method, which is the oldest and best established, consists essentially of allowing the organisms (*e.g.* bacterial suspension) to respire in a closed flask connected to a calibrated manometer. The decrease in pressure inside the flask with time is noted and converted to oxygen uptake rates. Apart from the high cost of the equipment and the fair degree of skill needed for operating the instrument, another serious drawback exists. The measured rate is that of the decrease in the oxygen partial pressure in the gas phase rather than in solution. Hence the observed uptake rate involves the rate of oxygen transfer from the gas to liquid as well as the rate of oxygen consumption in the liquid phase. In cases of high rates of oxygen consumption, the manometrically observed rate is that of transfer of oxygen from gas to liquid rather than the true oxygen consumption of the biological system.

Voltammetric methods on the other hand are capable of detecting the change of oxygen concentration in the liquid phase. While the dropping mercury electrode and platinum electrodes have been applied for this purpose, mercury has been found to exert toxic effects on several biological systems and the adsorption of organic compounds on the electrode surface interfered with the electrode reaction[2–4].

The galvanic cell oxygen analyzer is more suitable for these types of studies and some applications, performed in this laboraotry, are given below.

The rate of oxygen consumption of the nymph of Tetragoneuria cynosura. The metabolic rate during the larval stage of *Tetragoneuria cynosura* was undertaken to identify the various factors influencing the metamorphasis of insects. While most metabolic studies of aquatic larvae employ manometric techniques or microchemical determinations to measure the uptake or evolution of metabolic gases, the galvanic cell oxygen analyzer provides a simpler technique.

A specially designed oxygen analyzer and the respiring nymph were placed in a small cell, and then sealed from contact to the atmosphere. As the nymph respired, the dissolved oxygen concentration in the cell and the corresponding electrode response was recorded continuously. Actually, the decrease of the oxygen concentration with time was due mainly to the respiration of the nymph and to a lesser extent to the electrode reaction. Electrolytic oxygen depletion in the cell could be however calculated from the following relation,

$$C_t = C_0 e^{-Kt} \tag{34}$$

where C_t is the concentration at time t, C_0 is the initial concentration, K is the rate constant in min^{-1} and t is the time in min. The K value was estimated for the electrode system according to,

$$K = 25.8 \frac{P_m A}{vb} \tag{35}$$

where P_m is the membrane permeability coefficient in $\text{cm}^2\text{sec}^{-1}$, A is the cathode surface area in cm^2, v is the volume of the test solution in cm^3, and b is the membrane thickness in cm.

For a 100 ml cell at 8 mg/l initial oxygen concentration, the decrease in the oxygen in solution by 1 mg/l due to the electrode reaction took about 83 h. Control experiments performed under the same conditions showed also that this effect proceeds at a very slow rate and could be neglected.

Being a completely portable instrument, the galvanic cell oxygen analyzer can

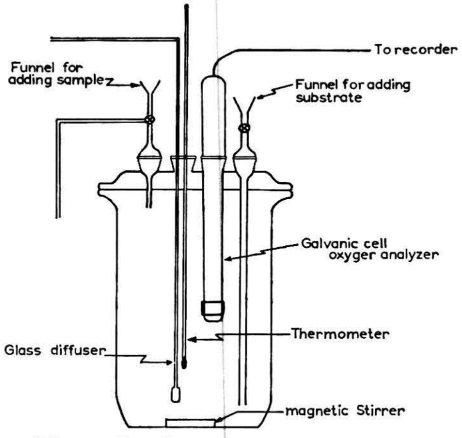


Fig. 11. Respirometer cell assembly.

easily be used for studying respiration rates of different organisms near their own natural environment.

Studies on oxygen utilization of domestic sewage. The oxygen analyzer has been used in this laboratory as the oxygen measuring system in a specially designed respirometer for determining oxygen uptake rates in activated sludge samples. Fig. 11 shows the respirometer cell assembly fitted with facilities for measuring oxygen in solution, for measuring temperature and for adding samples or substrates. The cell assembly was kept at constant temperature in a water bath and the oxygen content was recorded on a potentiometric recorder.

After a sample of the culture was added to the respirometer, it was aerated until stability was reached. The air was then turned off, the stirrer was started, and any change in oxygen concentration in the test solution was recorded. From the recorded data respiration rates were easily calculated.

Oxygen determinations in gaseous systems. Exploratory experiments performed in this laboratory on the application of the galvanic cell oxygen analyzer for oxygen determination in the gaseous phase showed that the current in this case was proportional to the partial pressure of oxygen (Fig. 12). The analyzer response time in gaseous samples was 2.7 sec for 90% response, 5 sec for 95% response, and 25–30 sec for 99% response.

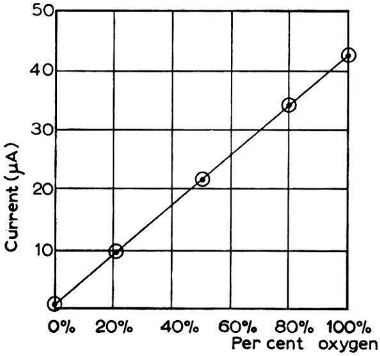


Fig. 12. Oxygen calibration curve in gaseous streams.

The principal difficulty in applying the membrane analyzer to anhydrous gaseous samples was that the electrolyte solution layer eventually dries out since the polyethylene membrane is slightly permeable to water vapor. However, laboratory experiments showed that for 72 h of continuous operation at 27° and at about 82% relative humidity there was no apparent change in the analyzer sensitivity.

APPENDIX

THE MATHEMATICAL TREATMENT OF THE DIFFUSION PROBLEM

According to the model given in Fig. 2, the problem is that of a linear finite diffusion in a two-phase medium. The Laplace transform is used to solve FICK's second law under the prescribed initial and boundary conditions.

By definition the Laplace transform is

$$\mathcal{L}(f) = \bar{f}(p) = \int_0^\infty \mathrm{e}^{-pt} f(t)\,\mathrm{d}t \tag{A-1}$$

The Laplace transform for the boundary condition *d*, is

$$\left(\frac{\partial^2}{\partial x^2}\mathcal{L}C_f\right) - \frac{p}{D_f}\mathcal{L}C_f = -\frac{C_{f,0}}{D_f} \tag{A-2}$$

and for the boundary condition *e*, is

$$\left(\frac{\partial^2}{\partial x^2}\mathcal{L}C_m\right) - \frac{p}{D_m}\mathcal{L}C_m = -\frac{C_{m,0}}{D_m} \tag{A-3}$$

The solution for the differential equation A-2 is then

$$\mathcal{L}C_f = A\mathrm{e}^{\sqrt{\frac{p}{D_f}}\cdot x} + B\mathrm{e}^{-\sqrt{\frac{p}{D_f}}\cdot x} + \frac{C_{f,0}}{p} \tag{A-4}$$

and the solution for the equation A-3 is

$$\mathcal{L}C_m = G\mathrm{e}^{\sqrt{\frac{p}{D_m}}\cdot x} + H\mathrm{e}^{-\sqrt{\frac{p}{D_m}}\cdot x} + \frac{C_{m,0}}{p} \tag{A-5}$$

The Laplace transform for the boundary condition *c*, is

$$D_f\left(\frac{\partial}{\partial x}\mathcal{L}C_f\right)_{x=0} = D_m\left(\frac{\partial}{\partial x}\mathcal{L}C_m\right)_{x=0} \tag{A-6}$$

From A-4 and A-5 we have

$$\sqrt{D_f}(A - B) = \sqrt{D_m}(G - H) \tag{A-7}$$

The Laplace transform for the boundary condition *b*, is

$$k_0(\mathcal{L}C_f)_{x=0} = (\mathcal{L}C_m)_{x=0} \tag{A-8}$$

and from A-4 and A-5 we have

$$k_0\left(A + B + \frac{C_{f,0}}{p}\right) = \left(G + H + \frac{C_{m,0}}{p}\right) \tag{A-9}$$

Since $C_{f,0}k_0 = C_{m,0}$ at $x = 0$ this simplifies equation A-8 to

$$(A + B) = (G + H)\frac{1}{k_0} \tag{A-10}$$

The Laplace transform for the boundary condition *f*, is

$$\mathcal{L}(C_m)_{x=b} = \frac{C_s}{p}k_b \tag{A-11}$$

and from equation A-5 we get

$$G\mathrm{e}^{\sqrt{\frac{p}{D_m}}\cdot b} + H\mathrm{e}^{-\sqrt{\frac{p}{D_m}}\cdot b} + \frac{C_{m,0}}{p} = \frac{C_s}{p}k_b \tag{A-12}$$

Since $C_s k_b = C_{m,0}$, equation A-12 is simplified to

$$G\,e^{\sqrt{\frac{p}{D_m}}\cdot b} + H\,e^{-\sqrt{\frac{p}{D_m}}\cdot b} = 0 \tag{A-13}$$

The Laplace transform for the boundary condition a, is

$$\mathscr{L}(C_f)_{x=-a} = 0$$

and from eqn. A-4 we get

$$A\,e^{\sqrt{\frac{p}{D_f}}\cdot -a} + B\,e^{-\sqrt{\frac{p}{D_f}}\cdot -a} + \frac{C_{f,0}}{p} = 0 \tag{A-14}$$

On solving the simultaneous eqns. A-7, A-10, A-13 and A-14 for A, B, G, and H we get,

$$A = \frac{1}{2}\frac{C_{f,0}}{p}\,\frac{l\,e^{\sqrt{\frac{p}{D_m}}\cdot b} - m\,e^{-\sqrt{\frac{p}{D_m}}\cdot b}}{l \sinh w\sqrt{p} - m \sinh S\sqrt{p}} \tag{A-15}$$

$$B = \frac{1}{2}\frac{C_{f,0}}{p}\,\frac{m\,e^{-\sqrt{\frac{p}{D_m}}\cdot b} - l\,e^{\sqrt{\frac{p}{D_m}}\cdot b}}{l \sinh w\sqrt{p} - m \sinh S\sqrt{p}} \tag{A-16}$$

$$G = \frac{C_{f,0}}{p}\,\frac{e^{-\sqrt{\frac{p}{D_m}}\cdot b}}{l \sinh w\sqrt{p} - m \sinh S\sqrt{p}} \tag{A-17}$$

$$H = \frac{C_{f,0}}{p}\,\frac{-e^{\sqrt{\frac{p}{D_m}}\cdot b}}{l \sinh w\sqrt{p} - m \sinh S\sqrt{p}} \tag{A-18}$$

Substitution of A and B in eqn. A-4 will give,

$$\mathscr{L}C_f = \frac{C_{f,0}}{p}\left[1 - \frac{m \sinh z\sqrt{p} + l \sinh(-\delta)\sqrt{p}}{l \sinh w\sqrt{p} - m \sinh S\sqrt{p}}\right] \tag{A-19}$$

Also the substitution of H and G in eqn. A-5, will give,

$$\mathscr{L}C_m = \frac{C_{f,0}}{p}\left[k_0 + \frac{2 \sinh \sqrt{\frac{p}{D_m}}(x-b)}{l \sinh w\sqrt{p} - m \sinh S\sqrt{p}}\right] \tag{A-20}$$

The general solution

The next step is to solve for the inverse Laplace transform. Eqn. A-19 may be rearranged as follows,

$$\mathscr{L}C_f = \frac{C_{f,0}}{p}\left[1 - \left\{\frac{l \sinh(-\delta)\sqrt{p}}{l \sinh w\sqrt{p} - m \sin hS\sqrt{p}} + \frac{m \sinh z\sqrt{p}}{l \sinh w\sqrt{p} - m \sinh S\sqrt{p}}\right\}\right] \tag{A-21}$$

The first term in eqn. A-21 will be treated as follows,

$$\frac{l \sinh(-\delta)\sqrt{p}}{pl \sinh w\sqrt{p} - m \sinh S\sqrt{p}} = \frac{l \sinh(-\delta)\sqrt{p}}{pl \sinh w\sqrt{p}\left(1 - \dfrac{m}{l}\dfrac{\sinh S\sqrt{p}}{\sinh w\sqrt{p}}\right)}$$

$$= \frac{l \sinh(-\delta)\sqrt{p}}{p \sinh w\sqrt{p}}\left(1 - \frac{m}{l}\frac{\sinh S\sqrt{p}}{\sinh w\sqrt{p}}\right)^{-1}$$

Since

$$\frac{m}{l}\frac{\sinh S\sqrt{p}}{\sinh w\sqrt{p}} < 1,$$

on expanding

$$\frac{\sinh(-\delta)\sqrt{p}}{p \sinh w\sqrt{p}}\left[1 + \frac{m}{l}\frac{\sinh S\sqrt{p}}{\sinh w\sqrt{p}} + \frac{m^2}{l^2}\frac{\sinh^2 S\sqrt{p}}{\sinh^2 w\sqrt{p}} + \dots\right] \tag{A-22}$$

The first two terms in the series will be considered only.

The inverse Laplace for $\dfrac{\sinh(-\delta)\sqrt{p}}{p \sinh w\sqrt{p}}$ is[23]

$$\frac{(-\delta)}{w} + \frac{2}{\pi}\sum_{j=0}^{\infty}(-1)^j \frac{\sin\left(\dfrac{j\pi(-\delta)}{w}\right)}{j} e^{-\left(\frac{j^2\pi^2 t}{w^2}\right)} \tag{A-23}$$

The inverse Laplace for $\dfrac{\sinh S\sqrt{p}}{p \sinh w\sqrt{p}} \cdot \dfrac{\sinh(-\delta)\sqrt{p}}{\sinh w\sqrt{p}}$ is derived as follows:

If $\bar{f}_1(y)$ and $\bar{f}_2(y)$ are the Laplace transforms of $f_1(t)$ and $f_2(t)$ respectively, $\bar{f}_1(y)$, $\bar{f}_2(y)$ are the Laplace transforms of

$$\int_0^t f_1(t-Z)\, f_2(Z)\mathrm{d}Z = \int_0^t f_1(Z) \cdot f_2(t-Z)\mathrm{d}Z$$

The inverse Laplace for $\dfrac{\sinh S\sqrt{p}}{p \sinh w\sqrt{p}}$, is

$$\frac{S}{w} + \frac{2}{\pi}\sum_{n=0}^{\infty}(-1)^n \frac{\sin\left(\dfrac{n\pi S}{w}\right)}{n} e^{-\left(\frac{n^2\pi^2 t}{w^2}\right)} \tag{A-24}$$

and the inverse Laplace for $\dfrac{\sinh(-\delta)\sqrt{p}}{\sinh w\sqrt{p}}$ is

$$\frac{1}{w}\frac{\partial\theta_4}{\partial(-\delta)}\left(\frac{(-\delta)}{2w} \middle| \frac{i\pi t}{w^2}\right)$$

where $\theta_4(\nu/\tau)$ is the theta function[23].

$$\theta_4 = \left(\frac{(-\delta)}{2w} \Big/ \frac{i\pi t}{w^2}\right) = 1 + 2 \sum_{i=0}^{\infty} (-1)^i \left(e^{-\frac{i\pi t}{w^2}}\right)^{n^2} \cos\left(2n\pi \frac{(-\delta)}{2w}\right) \frac{1}{w} \frac{\partial \theta_4}{\partial(-\delta)}$$

$$= \frac{2\pi}{w^2} \sum_{i=0}^{\infty} (-1)^{i+1} e^{-\frac{\pi^2 i^2 t}{i^2}} \sin\left(\frac{i\pi(-\delta)}{w}\right) \qquad \text{(A-25)}$$

From eqns. A-24 and A-25, the inverse Laplace for

$$\frac{\sinh S\sqrt{p}}{p \sinh w\sqrt{p}} \cdot \frac{\sinh (-\delta)\sqrt{p}}{\sinh w\sqrt{p}}$$

will be

$$\frac{2\pi}{w^2} \int_0^t \left(\frac{S}{w} + \frac{2}{\pi} \sum_{n=0}^{\infty} (-1)^n \frac{\sin\left(\frac{n\pi S}{w}\right)}{n} e^{-\frac{n^2\pi^2(t-Z)}{w^2}}\right) \left(\sum_{i=0}^{\infty} (-1)^{i+1}\, i\, e^{-\frac{i^2\pi^2 Z}{w^2}} \sin \frac{i\pi(-\delta)}{w}\right) dZ \qquad \text{(A-26)}$$

The combination of eqns. A-23 and A-26 gives the inverse Laplace for the first term in eqn. A-21, γ_1, which is defined previously in the text (eqn. 9).

The inverse Laplace for the second term in eqn. A-21

$$\frac{m \sinh z\sqrt{p}}{p(l \sinh w\sqrt{p} - m \sinh S\sqrt{p})}$$

is treated in the same manner and the inverse Laplace is given by γ_2 which is also previously defined in the text (eqn. 9).
Accordingly

$$C_f(x,t) = [1 - (\gamma_1 + \gamma_2)] \qquad \text{(A-27)}$$

The solution for the inverse Laplace for eqn. A-20 follows also the above treatment,

$$C_m(x,t) = [k_0 - 2\gamma_3] \qquad \text{(A-28)}$$

where γ_3 is defined in the text (eqn. 10).

The particular solution

(1) Case of $\frac{a}{\sqrt{D_f}} = \frac{b}{\sqrt{D_m}}$:

Under this particular condition $S = 0$, $w = 2a/\sqrt{D_f}$ and eqn. A-19 gives

$$\mathscr{L} C_f = \frac{C_{f,0}}{p} \left[1 - \frac{m \sinh z\sqrt{p}}{l \sinh \frac{2a}{\sqrt{D_f}}\sqrt{p}} - \frac{\sinh (-\delta)\sqrt{p}}{\sinh S\sqrt{p}}\right] \qquad \text{(A-29)}$$

The inverse Laplace for eqn. A-29 is,

$$Cf(x,t) = C_{f,0}\left[1 - \frac{m}{l}\left(\frac{2}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{n}\sin\frac{n\pi z}{\frac{a}{\sqrt{D_f}}}\,e^{-\frac{n^2\pi^2 t}{n}} + \frac{z}{\frac{a}{\sqrt{D_f}}}\right)\right.$$
$$\left. - \frac{(-\delta)}{\frac{a}{\sqrt{D_f}}} - \left(\frac{2}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{n}\sin\frac{n\pi(-\delta)}{\frac{a}{\sqrt{D_f}}}\,e^{-\frac{n^2\pi^2 t}{\frac{a}{\sqrt{D_f}}}}\right)\right] \qquad \text{(A-30)}$$

Similarly eqn. A-20 will give,

$$\mathscr{L}C_m = \frac{C_{f,0}}{p}\left[k_0 + \frac{2}{l}\,\frac{\sinh\sqrt{\frac{p}{D_m}}\,(x-b)}{\sinh 2\frac{a}{\sqrt{D_f}}\sqrt{p}}\right] \qquad \text{(A-31)}$$

and the inverse Laplace, using the theta function, will be

$$C_m(x,t) = C_{f,0}\left[k_0 + \frac{4}{\pi}\frac{1}{l}\sum_{n=0}^{\infty}\frac{(-1)^{n+1}}{n}\sin\left(\frac{n\pi(x-b)}{2a}\sqrt{\frac{D_f}{D_m}}\right)\left(1 - e^{-\frac{n^2\pi^2 D_f t}{4a^2}}\right)\right] \qquad \text{(A-32)}$$

The error function is used to solve for eqn. A-29, which gives

$$C_f(x,t) = C_{f,0}\left[1 - \frac{m}{l}\left\{\sum_{n=0}^{\infty} 1 - \frac{2}{\sqrt{\pi}}\operatorname{erf} y_1\right) - \sum_{n=0}^{\infty}\left(1 - \frac{2}{\sqrt{\pi}}\operatorname{erf} y_2\right)\right\}$$
$$\left. - \left\{\sum_{n=0}^{\infty}\left(1 - \frac{2}{\sqrt{\pi}}\operatorname{erf} y_3\right) - \sum_{n=0}^{\infty}\left(1 - \frac{2}{\sqrt{\pi}}\operatorname{erf} y_4\right)\right\}\right] \qquad \text{(A-33)}$$

where

$$y_1 = \tfrac{1}{2}\left[\frac{2a}{\sqrt{D_f}}(2n+1) - z\right]t^{-\frac{1}{2}}$$

$$y_2 = \tfrac{1}{2}\left[\frac{2a}{\sqrt{D_f}}(2n+1) + z\right]t^{-\frac{1}{2}}$$

$$y_3 = \tfrac{1}{2}\left[\frac{2a}{\sqrt{D_f}}(2n+1) - (-\delta)\right]t^{-\frac{1}{2}}$$

$$y_4 = \tfrac{1}{2}\left[\frac{2a}{\sqrt{D_f}}(2n+1) + (-\delta)\right]t^{-\frac{1}{2}}$$

(2) Case of $\frac{a}{\sqrt{D_f}} \gg \frac{b}{\sqrt{D_m}}$:

In this case $S = w = a/\sqrt{D_f}$ and eqn. A-19 gives

$$\mathscr{L}C_f = \frac{C_{f,0}}{p}\left[1 - \frac{m\sinh z\sqrt{p} + l\sinh(-\delta)\sqrt{p}}{l\sinh\frac{a}{\sqrt{D_f}}\sqrt{p} - m\sinh\frac{a}{\sqrt{D_f}}\sqrt{p}}\right] \qquad \text{(A-34)}$$

The inverse Laplace for eqn. A-34, using the theta function, is as follows

$$C_f(x,t) = C_{f,0}\left\{1 + \frac{m}{l-m}\frac{2}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{n}\sin\left(\frac{n\pi z\sqrt{D_f}}{a}\right)\left(1-e^{-\frac{n^2\pi^2 D_f t}{a^2}}\right)\right.$$

$$\left. - \frac{l}{l-m}\left(\frac{\frac{b}{\sqrt{D_m}}-\frac{x}{\sqrt{D_f}}}{\frac{a}{\sqrt{D_f}}} + \frac{2}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{n}\sin n\pi\left(\frac{\frac{b}{\sqrt{D_m}}-\frac{x}{\sqrt{D_f}}}{\frac{a}{\sqrt{D_f}}}\right)e^{-\frac{n^2\pi^2 D_f t}{a^2}}\right)\right\} \tag{A-35}$$

Similarly eqn. A-20 will give

$$\mathscr{L}C_m = \frac{C_{f,0}}{p}\left[k_0 + \frac{2\sinh\sqrt{\frac{p}{D_m}}(x-b)}{l\sinh\frac{a}{\sqrt{D_f}}\sqrt{p} - m\sinh\frac{a}{\sqrt{D_f}}\sqrt{p}}\right] \tag{A-36}$$

and the inverse Laplace, using the theta function, is as follows

$$C_m(x,t) = C_{f,0}\left[k_0 - \frac{2}{l-m}\frac{2}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{n}\sin\left(\frac{n\pi(x-b)}{a}\sqrt{\frac{D_f}{D_m}}\right)\left(1-e^{-\frac{n^2\pi^2 D_f t}{a^2}}\right)\right] \tag{A-37}$$

On using the error function to solve for eqn. A-34, it follows that

$$C_f(x,t) = C_{f,0}\left\{1 - \frac{m}{l-m}\left[\sum_{n=0}^{\infty}\left(1-\frac{2}{\sqrt{\pi}}\operatorname{erf} y_1\right) - \sum_{n=0}^{\infty}\left(1-\frac{2}{\sqrt{\pi}}\operatorname{erf} y_2\right)\right]\right.$$

$$\left. - \frac{l}{l-m}\left[\sum_{n=0}^{\infty}\left(1-\frac{2}{\sqrt{\pi}}\operatorname{erf} y_3\right) - \sum_{n=0}^{\infty}\left(1-\frac{2}{\sqrt{\pi}}\operatorname{erf} y_4\right)\right]\right\} \tag{A-38}$$

(3) Case of $\frac{a}{\sqrt{D_f}} \ll \frac{b}{\sqrt{D_m}}$:

Under this condition $S = w = b/\sqrt{D_m}$ and eqn. A-19 gives

$$\mathscr{L}C_f = \frac{C_{f,0}}{p}\left[1 - \frac{m\sinh z\sqrt{p} + l\sinh(-\delta)\sqrt{p}}{l\sinh\frac{b}{\sqrt{D_m}}\sqrt{p} - m\sinh\frac{b}{\sqrt{D_m}}\sqrt{p}}\right] \tag{A-39}$$

As in the previous cases the theta function is used and inverse Laplace will be

$$C_f(x,t) = C_{f,0}\left[1 - \frac{m}{l+m}2\pi\sum_{n=0}^{\infty}\frac{n(-1)^n}{n^2\pi^2}\sin\frac{n\pi z\sqrt{D_m}}{b}e^{-\frac{n^2\pi^2 D_m t}{b^2}}\right.$$

$$\left. - \frac{m}{l+m}\frac{z\sqrt{D_m}}{b} - \frac{l}{l+m}2\pi\sum_{n=0}^{\infty}\frac{n(-1)^n}{n^2\pi^2}\sin\frac{n\pi(-\delta)\sqrt{D_m}}{b}e^{-\frac{n^2\pi^2 D_m t}{b^2}} - \frac{l}{l+m}\left(\frac{(-\delta)\sqrt{D_m}}{b}\right)\right] \tag{A-40}$$

Eqn. A-20 under the same case will give

$$\mathscr{L}C_m = \frac{C_{f,0}}{p}\left[k_0 + \frac{2\sinh\sqrt{\frac{p}{D_m}}(x-b)}{l\sinh\frac{b}{\sqrt{D_m}}\sqrt{p} + m\sinh\frac{b}{\sqrt{D_m}}\sqrt{p}}\right] \tag{A-41}$$

and the inverse Laplace

$$C_m(x,t) = C_{f,0}\left[k_0 - \frac{2}{l+m}\frac{2}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{n}\sin\left(\frac{n\pi(x-b)}{b}\sqrt{\frac{D_f}{D_m}}\right)\left(1-e^{-\frac{n^2\pi^2 D_m t}{b^2}}\right)\right] \tag{A-42}$$

The solution of eqn. A-39, using the error function, is

$$C_f(x,t) = C_{f,0}\left\{1 - \frac{m}{l+m}\left[\sum_{n=0}^{\infty}\left(1-\frac{2}{\sqrt{\pi}}\operatorname{erf} y_1\right) - \sum_{n=0}^{\infty}\left(1-\frac{2}{\sqrt{\pi}}\operatorname{erf} y_2\right)\right]\right.$$

$$\left. - \frac{l}{l-m}\left[\sum_{n=0}^{\infty}\left(1-\frac{2}{\sqrt{\pi}}\operatorname{erf} y_3\right) - \sum_{n=0}^{\infty}\left(1-\frac{2}{\sqrt{\pi}}\operatorname{erf} y_4\right)\right]\right\} \tag{A-43}$$

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SUMMARY

A galvanic cell consisting of a silver–lead couple separated from the test sample by an oxygen permeable plastic membrane provides the basis of a simple oxygen analyzer. The current generated, while directly proportional to the amount of oxygen in the sample, also depends upon factors such as temperature, membrane thickness, kind and concentration of the supporting electrolyte, and the geometry of the cell. The analyzer has been used successfully with continuous recording devices and as a completely portable instrument with a readout on a microammeter for oxygen monitoring in natural waters and wastes. Oxygen content in non-aqueous systems and gaseous streams may be measured by the device.

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CHRONOPOTENTIOMETRIC REDUCTION OF THALLIUM(I) AT A SPHERICAL MERCURY ELECTRODE

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The equation derived by DELAHAY AND MAMANTOV[1] for transition times in chronopotentiometry at a spherical electrode,

$$\frac{CnFD}{i_0 r_0} = 1 - \exp\left(\frac{D\tau}{r_0^2}\right) \operatorname{erfc} \frac{(D\tau)^{\frac{1}{2}}}{r_0}$$

where C, D, i_0, r_0, τ, n, and F are respectively the bulk concentration of reducible substance, diffusion coefficient of the latter, current density, electrode radius, transition time, number of electrons, and the Faraday, was confirmed experimentally

TABLE I

THALLIUM(I) SULFATE IN 1 M SODIUM SULFATE

τ	*current* · $10^6 A$	*Concn.* Tl^+ (· 10^6 *moles/cc*)	$i_0\tau^{\frac{1}{2}}/C$ *Calculated*	$i_0\tau^{\frac{1}{2}}/C$ *Found*
1.62	21.8	1.89	313	313
1.67	181	17.1	315	307
1.78	20.9	1.89	315	315
1.90	20.3	1.89	316	316
2.18	18.9	1.89	318	315
3.30	15.6	1.89	321	320
3.63	128	17.1	322	318
3.65	67.9	9.08	322	323
4.82	113	17.1	327	325
5.07	12.5	1.89	329	319
5.35	56.8	9.08	331	326
6.72	98.1	17.1	334	333
7.00	10.9	1.89	336	326
7.05	95.1	17.1	336	330
8.63	46.3	9.08	339	338
9.18	9.7	1.89	342	334
10.9	80.5	17.1	345	348
11.0	41.9	9.08	345	346
11.4	8.9	1.89	347	341
12.0	40.7	9.08	349	350
13.2	75.8	17.1	350	363
13.6	38.3	9.08	353	350
14.3	8.2	1.89	353	352
15.7	7.8	1.89	357	354

Electrode radius: $5.90 \cdot 10^{-2}$ cm.

by these authors using a slowly dropping mercury electrode and transition times of 0.2 sec and less. By use of the hanging mercury drop electrode, longer transition times can be investigated.

The range of transition times from 1.5–16 sec has been studied at this electrode for reduction of thallium(I) in sodium sulfate supporting electrolyte, and data are given in Table I for three concentrations and current densities from $1.76 \cdot 10^{-4}$ to $40.5 \cdot 10^{-4}$ A/cm^2. Similar results were obtained with an electrode of radius $4.66 \cdot 10^{-2}$ cm.

The experimental values of $i_0\tau^{\frac{1}{2}}/C$ recorded in the table have been corrected by a blank quantity $i_0\tau^{\frac{1}{2}}$. This quantity was evaluated by determining the time required in 1 M sodium sulfate solutions for the electrode to reach the potential selected for measurement of transition times, using currents which gave blank values for τ over the range of transition times used with the thallium solutions. The numerical value of the correction is $(4.7 \pm 0.1) \cdot 10^{-5}$ A sec$^{\frac{1}{2}}$/cm^2. This represents a correction of less than 1% at a thallium concentration of $1.7 \cdot 10^{-5}$ moles/cc, less than 2% at $9 \cdot 10^{-6}$ moles/cc, but this rises to 7% at a concentration of $1.9 \cdot 10^{-6}$ moles/cc. Presumably this blank represents reduction of impurities and charging current.

In order to compute $i_0\tau^{\frac{1}{2}}/C$ from eqn. 1, the diffusion coefficient of thallium(I) in 1 M sodium sulfate is needed. A polarogram in this medium at the temperature used for the chronopotentiometry was recorded using a calibrated capillary, and this gave the value $1.19 \cdot 10^{-5}$ cm^2 sec^{-1} for the diffusion coefficient. Values for $i_0\tau^{\frac{1}{2}}/C$ calculated with this numerical value of D are given in Table I. Experimental values, within the limits of experimental error have an average deviation of ± 1.1% from theory.

EXPERIMENTAL

Apparatus

The circuit described by LINGANE[2] was used. Current was supplied by a 90 V battery (two 45 V Burgess 2308 B batteries) and passed through large dropping resistors to obtain the μA currents used. Current was measured potentiometrically as the IR drop across a precision resistor of appropriate size. The timer was a Standard Electric Co. Model S10, operated through a relay which also closed the electrolysis circuit.

The cathode was a hanging mercury drop electrode, as described by ROSS *et al.*[3]. Mercury drops were transferred to it from a calibrated dropping mercury electrode *via* a Teflon scoop. The radius of the hanging drop electrode was computed from the known rate of mercury flow from the capillary, and measured times of flow. The cell anode was a No. 18 platinum wire 5 mm long, in a compartment filled with 1 M sodium sulfate, separated by a fine sintered glass disc from the thallium solution. The cell was thermostatted at 30 ± 0.1°.

Procedure

The cell solution was deoxygenated by passing prepurified nitrogen through it for 15 min, and the nitrogen flow was then passed over the surface of the solution while measurements were made. The dropping mercury electrode was inserted in the solution, and two or three drops were collected in the scoop and transferred to the hanging drop electrode. After the dropping electrode had been withdrawn, the solution was stirred briefly, and after allowing two minutes for the solution to become quiet, electrolysis was started. The potential of the mercury electrode was followed on the oscilloscope, and electrolysis was interrupted when the potential was —1.0 V *vs.* S.C.E., on the rapidly falling portion of the wave. Transition times at each current were checked and found reproducible within ± 0.03 sec. The hanging drop mercury electrode was renewed for each trial while the time of mercury flow from the calibrated capillary was measured, to insure that the drop size remained constant.

SUMMARY

Transition times and current densities observed in chronopotentiometric reduction of thallium(I) in 1 *M* sodium sulfate at a hanging mercury drop electrode are in accord with the equation derived by DELAHAY AND MAMANTOV for a spherical electrode.

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DETERMINATION OF CHLORIDE ION IN DILUTE SOLUTIONS BY CATHODIC STRIPPING VOLTAMMETRY*

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INTRODUCTION

When a mercury electrode is made the anode in an electrolytic cell which contains a solution of chloride ions, the electrode becomes coated with a film of mercury(I) chloride (calomel). The calomel can be reduced in a subsequent cathodization and the quantity of electricity passed during cathodization measured. Cathodic stripping voltammetry is the implementation of the above electrolytic cycle under controlled conditions to obtain a measure of the chloride concentration in the solution.

The limits of detection obtained by stripping methods generally exceed those obtained directly. NIKELLY AND COOKE[1] and MAMANTOV, POPOFF, AND DELAHAY[2] have demonstrated the marked enhancement obtained with anodic stripping techniques for metals. Others[3] have employed a polarograph in the determination of chloride by cathodic stripping voltammetry with voltage-scan stripping.

We have applied a novel and simple instrument, the cathodic stripping coulometer, to the determination of chloride with voltage-step stripping. With this instrument it was possible to detect $2 \cdot 10^{-6}$ M chloride and to determine quantitatively concentrations in the range $4 \cdot 10^{-6}$ M–$3 \cdot 10^{-5}$ M.

THE CATHODIC STRIPPING COULOMETER

The cathodic stripping coulometer (Fig. 1) consists of circuits for applying selected voltages to the electrolytic cell and measuring the time of electrolysis, and for electronically integrating the cathodic electrolysis current. One pole of the fast-acting, double-pole voltage-stepping switch steps the voltage applied to the cell. The other pole shorts the integrator during anodic operation. The voltage divider, which is composed of resistors R-1, R-2, and R-3, is adjusted so that the working electrode terminal is always held at +0.4 V (anodic) or +0.1 V (cathodic) with respect to ground potential. One pole of the cell switch completes the circuit through the cell; the other connects the timer to the line during electrolysis. The negative input terminal of the stabilized operational amplifier is held at ground potential by means of negative feedback through the integrating capacitor. When current flows through the electrolysis cell, the iR drop through the input resistor (R-4) opposes the applied

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** Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

voltage. This diminishes the initial cathodic electrolysis current, which decays rapidly to a small (residual) value. The stripping current is integrated by the electronic integrator: a stabilized operational amplifier (combination of K2-X and K2-P, George A. Philbrick Researches, Inc., Boston, Mass.) with resistive input and capacitive feedback impedances. Current entering the integrator is accumulated in the feedback capacitor. In order to maintain its input at ground potential, the operational amplifier increases its output voltage in proportion to the charge (Q) developed in the capacitor. The measure of Q is the output voltage of the amplifier since $V = Q/C$, where C is the capacitance (farads), Q is the charge (coulombs), and V is the voltage across the capacitor. At any time the voltage can be read out without discharging the capacitor. The circuit shown gives a 100-V output when the accumulated charge is 2 millicoulombs. A panel meter in the read-out circuit gives continuous visual indication of the output; the resistors, R-5, R-6, and R-7 constitute a divider from which a fraction of the output voltage is taken for measurement with the precision potentiometer (Rubicon Company, Philadelphia).

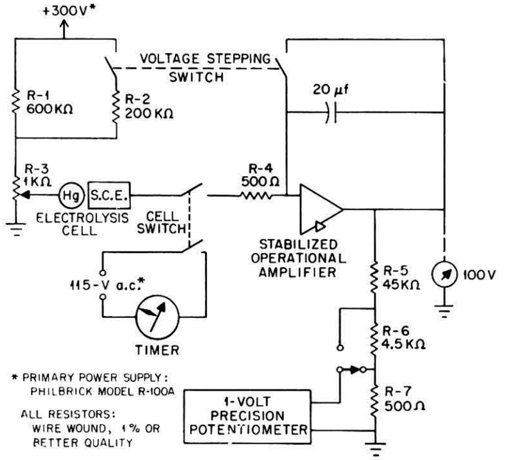

Fig. 1. Cathodic stripping coulometer.

After the input is disconnected the integrator retains the integral, Q, for a length of time which depends on the quality (leakage) of the feedback capacitor, the grid current in the input tube of the amplifier, the offset voltage inherent to the amplifier, and stray currents at the input. Useful comments on integrators are available from George A. Philbrick Researches, Inc.[4]. The capacitors used in the cathodic stripping coulometer were of high quality (Stabelex D, Industrial Condenser Corp., Chicago).

The input tube of the integrator (12AX7, Amperex, Hicksville, New York) was selected in order to minimize grid current. The offset of the amplifier was cancelled by a bias voltage applied at the reference input of the operational amplifier. Even though reasonable precautions (proper circuit layout and adequate shielding) are taken against leakage, grid current, offset, and stray noise, it is still necessary to correct for a small amount of drift. The drift decreases as the components become aged, but never disappears entirely. During the first few weeks of operation, it was necessary to adjust the bias of the integrator occasionally. Subsequently, the drift was checked weekly. The drift rate never exceeded 1 microcoulomb per minute.

After compensation for drift, the coulometer was tested by integrating known currents for known times. The readout value was within one percent of the input value.

ELECTROLYTIC CELL

The electrolytic cell is shown in Fig. 2. Its construction permits the removal of the reference electrode (a large S.C.E. of low resistance), which facilitates flushing the arm of the salt-bridge. Thus, contamination of the test solution by chloride diffusing from the S.C.E. is prevented. A 45-degree side-arm provides access for the introduction and withdrawal of samples and for cleaning the cell without disassembly. A closely-fitting Teflon cap serves as a bearing for the glass impeller. The impeller is a rounded spiral, roughly 12 mm in diameter, which is driven by a synchronous motor (Type K-2, Bodine Electric Company, Chicago, Ill.).

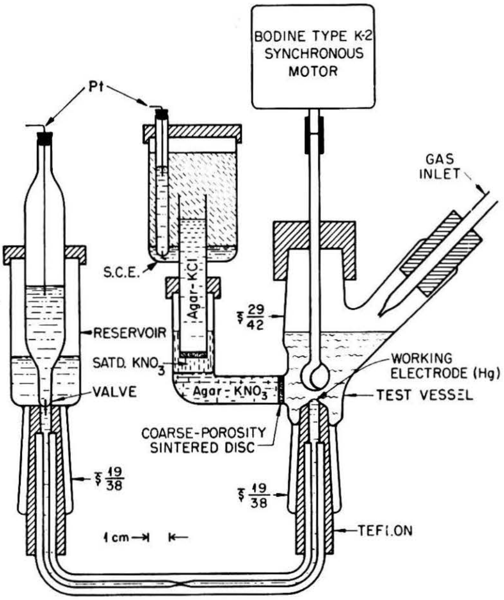

Fig. 2. Electrolytic cell, reservoir, and stirring apparatus.

The working electrode, a mercury pool 0.58 cm in diameter is patterned after those described by Arthur, Komayathy, Maness, and Vaughan[5], and by Nikelly and Cooke[1]. The mercury pool stands in a Teflon insert which also closes the bottom of the cell. The circle which joins the conical top of the insert and the axial hole for the the mercury column was made as smooth as possible. The insert extends into the cell for a distance of 8 mm to ensure that the electrode is centrally located in the sample solution. Connection to a mercury reservoir is made through a glass U-tube.

A valve which consists of a weighted glass plunger resting on a Teflon seat seals the end of the U-tube at the reservoir. A platinum wire sealed through the plunger tip provides electrical contact to the electrode. The mercury pool is renewed by spilling over mercury from the reservoir. A constriction in the connecting tube prevents a sudden flow of mercury when the valve is opened. The arrangement is simple and capable of handling samples by remote control. A solenoid lifter for the valve would be desirable for completely remote operation.

The area of the electrode, calculated on the assumption that the surface is a hemisphere, is 0.53 cm^2; it is reproducible to ± 0.016 cm^2 (95% confidence level — 10 trials).

REAGENTS

Triply-distilled mercury and analytical-reagent grade chemicals were used. A stock standard solution of potassium chloride, 1.00 *M*, was prepared by dissolving 74.55 g of the salt in distilled water and diluting to 1 liter. Test solutions of chloride, 0.1 *M* in supporting electrolyte, were prepared by dilution from the stock solutions. Nitric acid or 1:1 acetate buffer (pH 4.7) was used as the supporting electrolyte.

PROCEDURE

The instrument was warmed up for half an hour prior to use, during which time the cell switch was open and the voltage-stepping switch was closed.

A sample was delivered into the cell and a fresh electrode was prepared by allowing one drop of mercury to spill out from the reservoir. Next, the gas-inlet tube was introduced, nitrogen was admitted, and stirring was begun. The voltage stepping switch was opened, and the cell switch was closed, in that order, at the beginning of a 5-min period of deaeration. This ensured the stripping of any surface deposits reducible at 0.1 V *vs.* S.C.E.

After the pre-treatment period, the gas-inlet tube was removed from the solution and the voltage-stepping switch was closed, making the mercury the anode. At the end of the anodic period, the length of which is stated in the appropriate sections below, the voltage-stepping switch was again opened. The stripping period was terminated at an arbitrary time and the integral (*Q*) was read out with the potentiometer.

CALIBRATION CURVES

The concentration of a sample is determined by reference to a calibration curve, which is necessarily prepared under controlled conditions of cell geometry, electrolysis times, and stirring rate. Obviously, any factor which affects the mass-transfer process may be considered a parameter in the procedure; however, only the effects of the rate of stirring and of the time of anodization were considered in the calibration experiments. The distance between the stirrer and the working electrode is a significant variable.[1] Throughout the present investigation, the stirrer was placed as close as possible without agitating the electrode excessively.

The effect of stirring rate was observed with a plating time of 10 min and a stripping time of 30 sec. The samples were stirred continuously at rates of 300, 900, and 1800 rev/min. Calibration curves obtained at these stirring rates are shown in Fig. 3.

The effect of plating time is shown in Fig. 4. Solutions of several chloride concen-

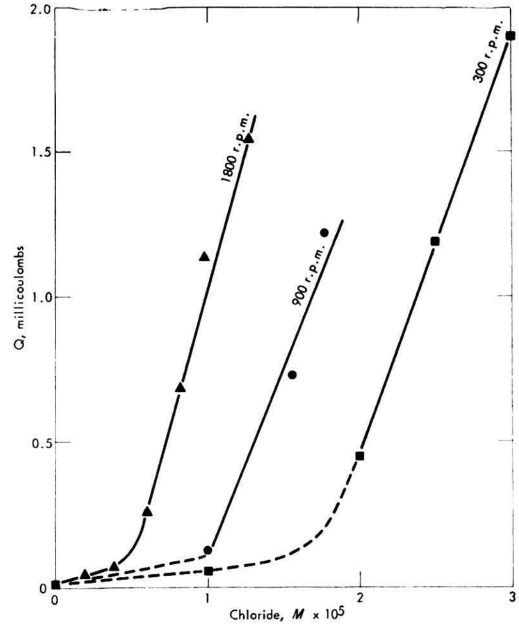

Fig. 3. Effect of stirring rate on the calibration curve. Conditions: 20-ml samples, 0.1 M HNO_3, plated 10 min at 0.4 V, stripped 30 sec at 0.1 V.

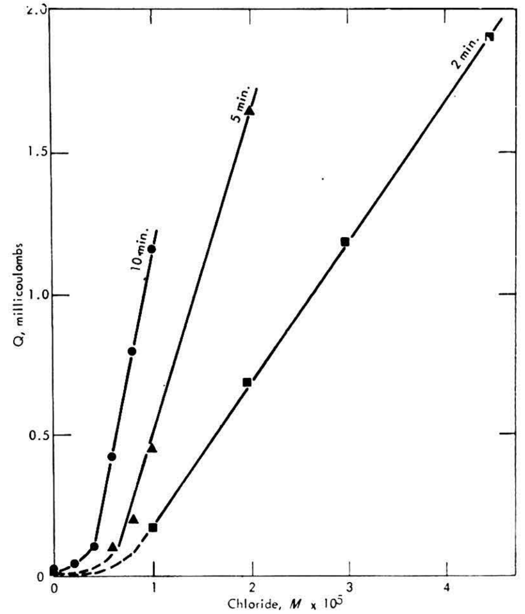

Fig. 4. Effect of plating time on the calibration curve. Conditions: 20-ml samples, 0.1 M HNO_3, plated at 0.4 V, stripped 15 sec at 0.1 V, stirring rate 1800 rev/min.

trations were electrolyzed for plating times of 2, 5, and 10 min. The stripping time was 15 sec; the stirring rate was 1800 rev/min.

The shape of the curves shown in Figs. 3 and 4 is characteristic for low concentrations of chloride: a region of little reponse is followed by a region of much greater (linear) reponse as one goes from lower to higher concentrations. The amount of chloride deposited does not increase continuously at higher concentrations; rather, a maximum amount is deposited at some concentration and, at greater concentrations the amount deposited diminishes progressively, as shown in Fig. 5. The curve shown in Fig. 5 was obtained with the input of the integrator modified to receive 1/100th of the total stripping current. Electrolysis conditions were: plating time, 5 min; stripping time, 3 min; stirring rate, 1800 rev/min.

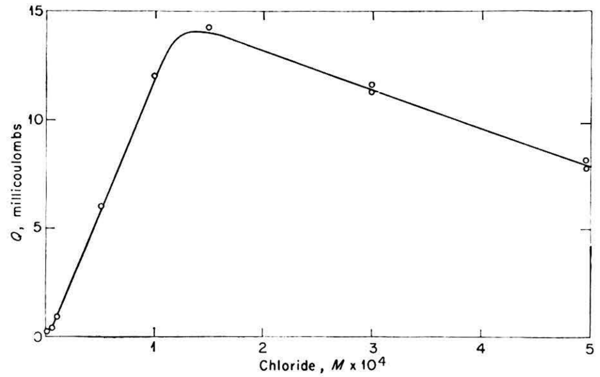

Fig. 5. Integrator read-out *vs.* chloride concentration. Conditions: 25-ml samples, 0.1 M HNO_3, plated 5 min at 0.4 V, stripped 3 min at 0.1 V.

QUANTITATIVE EVALUATION

The precision of a single determination of chloride by cathodic stripping coulometry was estimated in three sets of data. (1) A series of observations was made over a period of 1 week, electrolyzing a few samples each day. The chloride concentrations ranged from $7 \cdot 10^{-6}$ M to $3 \cdot 10^{-5}$ M; the plating time was 2 min; the stripping time was 15 sec. (2) A series was run over the course of 2 days, with a 10-min plating period and 15 sec of stripping. The chloride concentrations were $2 \cdot 10^{-6}$ M to $1 \cdot 10^{-5}$ M. (3) Because of an accident to the original cell, a series was run (2 days) in a similar, but larger (45-mm diameter) cell. The plating time of the latter series was 5 min and the stripping time was 30 sec. The chloride concentrations were from $6 \cdot 10^{-6}$ M to $1.8 \cdot 10^{-5}$ M. All the samples were 25 ml in volume and were stirred at 1800 rev/min. The data are shown in Table I. Approximate standard deviations were computed from these data, according to formulas for linear-regression analysis given in the monograph of Bennet and Franklin.[6] The standard deviations for the three series were (1) $6 \cdot 10^{-7}$ M for 2-min plating, over the concentration range, $1 \cdot 10^{-5}$ M to $3 \cdot 10^{-5}$ M in chloride, (2) $6 \cdot 10^{-7}$ M for 10-min plating in the range, $4 \cdot 10^{-6}$ M to $1 \cdot 10^{-5}$ M chloride, and (3) $5 \cdot 10^{-7}$ M for 5-min plating over the range of $6 \cdot 10^{-6}$ M to $1.8 \cdot 10^{-5}$ M chloride.

TABLE I

CALIBRATION DATA

(1) Plating 2 min		(2) Plating 10 min		(3) Plating 5 min	
Chloride ($M \cdot 10^5$)	Q (mcoul)	Chloride ($M \cdot 10^5$)	Q (mcoul)	Chloride ($M \cdot 10^5$)	Q (mcoul)
Blank[a]	0.02	Blank[a]	0.04	Blank[a]	0.06
1.00	0.10	0.20[a]	0.06	0.60	0.11
1.00	0.07	0.20[a]	0.06	0.60	0.13
1.00	0.12	0.20[a]	0.05	0.60	0.18
1.00	0.10	0.40	0.07	0.80	0.42
1.00	0.07	0.40	0.13	0.80	0.43
1.00	0.08	0.40	0.12	0.80	0.48
1.00	0.09	0.40	0.17	1.00	0.64
1.50	0.34	0.40	0.09	1.00	0.61
1.50	0.31	0.60	0.40	1.20	0.90
1.50	0.32	0.60	0.55	1.20	0.90
1.50	0.36	0.60	0.28	1.20	0.90
2.00	0.60	0.60	0.46	1.40	1.14
2.00	0.60	0.60	0.46	1.40	1.09
2.00	0.58	0.80	0.64	1.40	1.23
2.00	0.65	0.80	0.87	1.60	1.46
2.00	0.60	0.80	0.71	1.60	1.64
2.00	0.72	0.80	0.77	1.80	1.57
3.00	1.16	0.80	0.93	1.80	1.64
3.00	1.11	1.00	1.31	1.80	1.72
3.00	1.17	1.00	1.16		
3.00	1.19	1.00	1.07		
3.00	1.16	1.00	1.03		
3.00	1.17	1.00	1.28		
$S^b \sim 0.06$		$S^b \sim 0.06$		$S^b \sim 0.05$	

[a] Data not used in computation of precision.
[b] Standard deviation — see text.

CURRENT-STEP METHOD

The applicability of a current-step method, in which the deposition and dissolution of calomel is accomplished at constant current was investigated.

The accumulation of calomel in an amount proportional to the chloride concentration of the solution can be brought about by anodization at a suitable constant current. Then when a constant cathodic current is passed, the electrode which has been coated with calomel exhibits a potential–time characteristic much like the potential–time curves of chronopotentiometry; so long as some of the calomel remains, the electrode is depolarized and its potential remains substantially constant. The reduction of the last trace of the film is accompanied by polarization of the electrode, and its potential rises rapidly to more negative values at the transition time.

APPARATUS

An auxiliary electrode consisting of a stiff platinum wire, which dipped directly into the test solution was added to the cell assembly of Fig. 2. Constant current was obtained from the 300-V d.c. power supply through high-valued dropping resistors in series with the cell. The current-regulating and timing circuits were built up of Philbrick model K2-X amplifiers. Potential–time curves were observed with a cathode-ray oscilloscope; transition times were measured with a precision timer (model S-1, Standard Electric Time, Co., Springfield, Mass.)

PROCEDURE

A freshly-prepared electrode immersed in a previously deaerated sample was cathodized briefly. The current was then reversed (made anodic) for a period of 56 sec. A second reversal of current stripped off the calomel deposit. Stirring at 300 rev/min was continuous. The transition time for stripping was measured from the beginning of cathodization until the electrode potential reached zero V *vs.* S.C.E.

RESULTS AND DISCUSSION

The stripping transition time is related to the chloride concentration by curves similar to those of Figs. 3 and 4. The current passed during the anodic period (I_a) has a profound effect on the transition time, as is shown in Fig. 6. The curves of Fig. 6 were obtained by varying the anodic current from sample to sample and stripping at a fixed cathodic current (I_c). The resulting calibration curves are shown in Fig. 7. The choice of conditions is arbitrary — for example, an anodic current of 300μA yielded a linear calibration curve from 1.5 to $10 \cdot 10^{-4}$ *M* chloride.

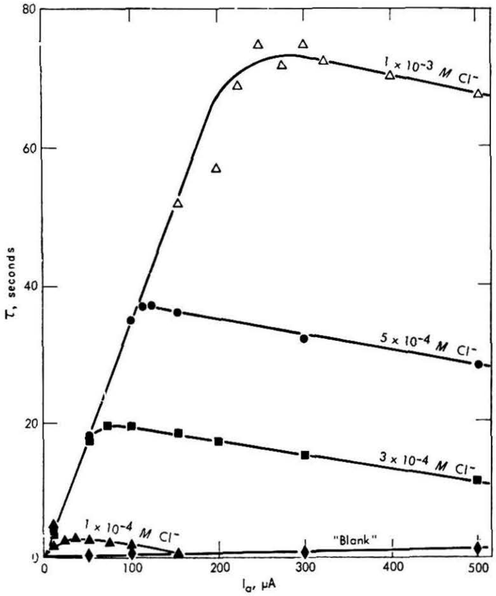

Fig. 6. Effect of plating current on cathodic transition time. Conditions: 25-ml samples, 0.1 *M* acetate, pH 4.7, stirred at 300 rev/min, stripped at 150 μA.

The results in this concentration range indicated a standard deviation of *ca.* $1.3 \cdot 10^{-5}$ *M*. At a higher rate of stirring, and with smaller currents, more dilute solutions — 1.5 to $5 \cdot 10^{-5}$ *M* — yielded an apparently linear calibration curve but the results were erratic.

The current-step technique appears less sensitive by an order of magnitude, and it involves more complicated procedure and instrumentation than the voltage-step technique.

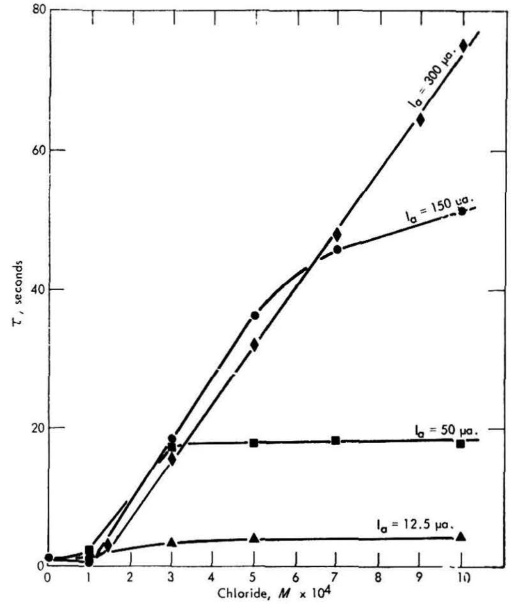

Fig. 7. Effect of plating current on the relationship between cathodic transition time and concentration. Conditions: 25-ml samples, 0.1 M acetate, pH 4.7, stirred at 300 rev/min, stripped at 150 μA.

SUMMARY

In cathodic stripping voltammetry, a mercury electrode is made first the anode and then the cathode in an electrolysis cell containing the chloride solution. The solution is stirred continuously during the electrolysis. Under the proper conditions, an amount of chloride which is proportional to the concentration of the solution deposits as calomel on the anode. The amount deposited is measured by integration of the current passed during electrolytic dissolution at constant voltage. A second (current-step) method, in which the deposition and dissolution are accomplished at constant current, with transition time of the dissolution giving the measure of chloride concentration, is discussed. A coulometric instrument for the determination of chloride ion at low concentrations ($2 \cdot 10^{-6} - 1 \cdot 10^{-4}$ M) by cathodic-stripping voltammetry is described.

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DAS OSZILLOGRAPHISCHE VERHALTEN UND DIE BESTIMMUNG VON RUTHENIUM UND OSMIUM

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Vom Gesichtspunkte der analytischen Chemie aus gesehen haben in der Gruppe der Platinmetalle Ruthenium und Osmium eine besondere Stelle. Sie können nämlich verhältnismässig leicht aus einer Mischung der Platinmetalle durch Destillation getrennt werden[1].

Dem polarographischen Verhalten von Ruthenium und Osmium wurde bisher wenig Aufmerksamkeit gewidmet. In den ersten Mitteilungen[2,3,4] wurden die katalytischen Wirkungen von Ruthenium auf die Wasserstoffabscheidung in saueren Lösungen untersucht, und erst im Jahre 1941 wurde in der Mitteilung von CROWELL, HEYROVSKÝ UND ENGELKEMEIR[5] das polarographische Verhalten von Osmium in gesättigten Lösungen der Hydroxyde alkalischer Erden beschrieben.

Die Entwicklung der Erforschung von Kernreaktionen, bei denen als eines der Spaltprodukte Ruthenium entsteht, hat zur gleichen Zeit das Interesse für die Möglichkeit seines schnellen Nachweises und seiner Bestimmung geweckt. Das spiegelt sich in den letzten Jahren in der Anzahl von Mitteilungen, die sich nicht nur mit der analytischen Chemie von Ruthenium und Osmium befassen, sondern auch mit ihrem polarographischen Verhalten[6–17].

Oszillopolarographisch wurde bisher nur das Verhalten von Platin, Palladium, Rhodium und Iridium untersucht [18–21]. In diesen Arbeiten wurde eine Reihe von Grundelektrolyten untersucht in denen sich die Platinmetalle durch depolarisierende Wirkungen kenntlich machen. Aus den durchgeführten Experimenten ist hervorgegangen, dass zum Nachweis von Palladium, Rhodium und Iridium nebeneinander sich eine 1 M Ethylendiaminsulphat Lösung am besten eignet. In dieser Lösung bieten alle drei Metalle deutliche Einschnitte, die sich durch die Potenziale (durch ihre Lage) genügend unterscheiden (Pd: $Q = 0.65$, pD $= 5.5$; Rh kathodisch $Q = 0.25$, pD $= 5.6$; anodisch $Q = 0.85$, pD $= 6.0$; Ir: der erste kathodische Dorn $Q = 0.3$, pD $= 4.6$, der zweite kathodische $Q = 0.75$, pD $= 6.4$). Dieser Elektrolyt wurde auch zur Bestimmung dieser drei Elemente nebeneinander sowie neben Platin und Gold verwendet, unter Anwendung der Methode der Komparationstitrationen[19].

Interessant ist das unterschiedene Verhalten von vierwertigem und zweiwertigem Platin in 1 M Ethylendiaminsulphat-Lösungen. Während sich zweiwertiges Platin ($PtCl_4^{2-}$) durch einen scharfen Dorn an dem anodischen Zweig der Kurve ($Q = 0.65$, pD $= 5.6$) kenntlich macht, bildet vierwertiges Platin ($PtCl_6^{2-}$) unter denselben Bedingungen nur die Andeutung dieses Dornes. Die Höhe des Dornes von zweiwertigem Platin wird mit abfallendem Wert der aufgezwungenen Gleichstromkomponente herabgesetzt. In dem angeführten Elektrolyt kann durch Vergleich mit dem Standard festgestellt werden, ob in einer analysierten Lösung von derselben Konzentration an vierwertigem Platin auch zweiwertiges Platin anwesend ist.

In 1 *M* Lösungen von Mineralsäuren (besonders der Chlorwasserstoffsäure) bilden Rhodium, Platin und Iridium einen scharfen Dorn an dem anodischen Teil der Kurve mit ungefähr demselben Depolarisationspotenzial von —1.2 V ($Q = 0.85$). An dem kathodischen Teil der Kurve entstehen bei höheren Konzentrationen den angeführten Metalle Einschnitte in der Gegend der Potenziale —0.3 V ($Q = 0.25$) und —1.2 V ($Q = 0.85$). Das Chlorwasserstoffsäure-Medium ist für den Nachweis und die Bestimmung von Rhodium besonders gut geeignet. Der Wert pD = 7.5 (Dorn an dem anodischen Teil der Kurve) zeugt von der hohen Empfindlichkeit der Bestimmung.

Es wurde durch eingehende Untersuchung festgestellt, das durch Herabsetzung der Konzentration der Chlorwasserstoffsäure der Charakter des Platindornes grundlegend geändert wird, und in 0.1 *M* HCl bereits verschwindet, oder nur durch einen gerundeten Ausläufer (bei hohen Platinkonzentrationen) kenntlich ist. Die abfallende Chlorwasserstoffsäure-Konzentration beeinflusst ebenfalls den Dorn am anodischen Teil der Kurve, der durch Chloroiridatlösungen verursacht wird. Bereits in 0.1 *M* HCl erinnert der Charakter des anodischen Kurventeils an die depolarisierende Wirkung von Chlororhodat. Da die Empfindlichkeit des derart durchgeführten "Iridiumnachweises" hundertmal niedriger ist im Vergleich zum Rhodium, konnte man voraussetzen dass die beobachtete Erscheinung durch eine Verunreinigung des Iridiums mit Rhodium herbeigeführt wurde. Das wurde durch Spektralanalyse bestätigt — das Präparat enthielt 1 % Rhodium.

Aus den verfolgten Abhängigkeiten ist hervorgegangen, das das Entstehen des Rhodiumdornes durch den katalytischen Einfluss von Rhodium auf die Reduktion von Wasserstoffionen bedingt ist. Die Tatsache das Rhodium noch in 5000-fachem Platinüberschuss im Medium von 0.1 *M* HCl und 0.6 *M* NaCl nachgewiesen werden kann wurde ausgenutzt um eine Methode der Bestimmung von Rhodium in Platin, Palladium und Gold[20] auszuarbeiten.

EXPERIMENTELLER TEIL

Reagenzien

Eine Lösung von vierwertigem Rutheniumsalz wurde aus metallischem Ruthenium bereitet (VEB Safina)[1,22]. Bei der Destillation wird Ruthenium(VII)-Oxyd in Vorlagen mit nur verdünnter Chlorwasserstoffsäure (1:1) absorbiert, wobei das Ru-(VII)-Oxyd überwiegend zu der Oxydationsstufe +4 (event. +3) reduziert wird.

Es muss dabei die vorgeschriebene Temperatur eingehalten werden, damit nicht die unlösliche braunschwarze Ru-(VII)-Oxyd Modifikation entstehe, die sich an den Apparaturwänden absetzen würde. Die Apparatur muss vordem vollkommen von allen Verunreinigungen und von Fett gesäubert werden.

Die in der ersten und zweiten Vorlage erhaltenen rotbraun gefärbten Lösungen wurde zusammen auf ein kleineres Volumen abgedampft und die entstandene Lösung fünf Minuten mit Chlorgas durchströmt, um das eventuell entstandene dreiwertige Ruthenium in die vierwertige Form zu überführen[23]. Durch nachfolgendes Abdampfen wurde eine Sirupartige Lösung erhalten, die genug Chlorwasserstoffsäure enthielt, damit nach Verdünnen mit Wasser der Hydrolyse vorgebeugt werde. Nach

Verdünnen mit Wasser entsteht entweder Hexachlororuthenium(IV)-Säure, oder bei niedrigerem Chlorwasserstoffsäure-Gehalt $Ru(OH)Cl_3$ 24.25. Die Sirupartige Lösung wurde mit Wasser so verdünnt, das 1 ml 13.7 mg Ru enthielt. Lösungen von niedrigerer Rutheniumkonzentration wurden durch genaues Verdünnen der Grundlösung bereitet.

Die entstandene Lösung wurde nach BRANDŠTETR[26] faktoriert nachdem das hydratierte Ru(IV)-Oxyd mit Ammoniumkarbonat gefällt wurde, und nach Glühen im Wasserstoffstrom wurde Ruthenium als Metall bestimmt.

Die Natriumruthenat-Lösung wurde nach Reduktion zur vierwertigen Form, die durch dreifaches Abdampfen mit HCl 1:1 erfolgte in derselben Weise faktoriert. Hexachloroosmium(IV)-Säure wurde aus metallischem Osmium (VEB Safina) bereitet[27]. Der Arbeitsgang ist mit dem bei Rutheniumsalzen beschriebenen identisch. Die Lösung wurde gravimetrisch faktoriert nachdem das hydratierte Osmium(IV)-Oxyd mit Natriumbikarbonat gefällt wurde, und nach dem Glühen im Wasserstoffstrom wurde Osmium als Metall bestimmt[20].

Lösungen der übrigen Platinmetalle wurden durch Lösen der entsprechenden Salze in redestilliertem Wasser bereitet. Eine $2.5 \cdot 10^{-2}$ M Nb^{5+} Lösung wurde durch Lösen einer Schmelze von 0.17 g Nb_2O_5 und 2.5 g $K_2S_2O_7$ in 20% $(NH_4)_2C_2O_4$ und Verdünnen mit destilliertem Wasser auf ein Volumen von 50 ml bereitet[28]. Die erhaltene Lösung hatte die Form eines Oxalatkomplexes. Die Ammoniumoxalatlösung, in der die Schmelze gelöst wird, muss genügend konzentriert sein, sonst tretet sofort Hydrolyse ein.

Die übrigen verwendeten Reagenzien waren meistens mit p.a. oder puriss. bezeichnet.

Apparatur

Alle in der vorliegenden Arbeit angeführten Messungen wurden am Polaroskop P 576 der Fa. Křižík mit mechanischem Tropfenabreisser durchgeführt. Die Messung der Einschnitttiefe wurde nach KALVODA[29] durchgeführt.

Die Depolarisationspotenziale wurden mittels Voltmeter Avomet (Metra-Blansko) unter Verwendung einer potenziometrischen Trommel nach BERAN[30] gemessen.

Der Q-Wert wurde nach HEYROVSKÝ UND KALVODA[31] gemessen.

Bei der Messung der Depolarisationspotenziale wurde als Vergleichselektrode eine abgetrennte gesättigte Kalomelelektrode verwendet, bei den übrigen Messungen eine Graphitelektrode. Die oszillopolarographischen Kurven wurden photographisch mit der Kamera Praktina IIA registriert, mit Objektiv Flexon (Lichtwert 2/50) und Zwischenring aus 20 cm Entfernung auf Agfa Isopan Rapid Film 25/10 Din, Expositionsdauer 1/15 Sek.

Die Messungen wurden bei Raumtemperaturen durchgeführt.

Die verwendeten volumetrischen Gefässe waren meistens amtlich geeicht.

Das oszillopolarographische Verhalten von Ruthenium und Osmium

Bei der Untersuchung des oszillopolarographischen Verhaltens von Osmium und Ruthenium wurde eine grosse Anzahl von verschiedenen Grundelektrolyten verwendet. Die erhaltenen Resultate sind in Tabelle I zusammengefasst, wo die Depolarisationspotenzialwerte der Einschnitte an den Kurven $dE/dt = f(V)$, die Q-quotienten und die durch pD-Werte ausgedrückten Beobachtungsgrenzen angegeben sind. Diese

TABELLE I

DEPOLARISATIONSPOTENZIALE, *Q*-QUOTIENTEN UND BEOBACHTUNGSGRENZEN DER OSMIUM- UND RUTHENIUM-EINSCHNITTE IN VERSCHIEDENEN ELEKTROLYTEN

Elektrolyt	*Ruthenium*			*Osmium*		
	E_{dep} (V)	Q	Mp (pD)*	E_{dep} (V)	Q	Mp (pD)*
1 *M* HCl	K 0.50	0.30	6.50	K 0.85	0.50	6.05
	K 1.20	0.75	6.50	K 1.05	0.60	5.70
	T 1.20	0.75	6.50			
1 *M* $HClO_4$	K 1.60	0.85	7.05	K 1.40	0.75	5.70
	T 1.60	0.85	7.05	+K 1.50	0.85	4.90
1 *M* H_2SO_4	T 1.10	0.80	5.90	K 0.30	0.30	5.60
				K 1.00	0.70	6.05
				A 0.30	0.30	5.60
1 *M* H_3PO_4	T 1.30	0.85	6.00	K 0.85	0.45	5.60
				K 1.15	0.70	5.90
1 *M* HNO_3				K 0.60	0.35	5.10
1 *M* Zitronensaüre	K 0.65	0.35	5.10	K 0.35	0.25	5.60
	A 0.15	0.15	5.10	A 0.20	0.15	5.60
1 *M* Oxalsäure	K 0.50	0.40	5.10	K 0.35	0.40	5.90
	A 0.10	0.10	5.40	A 0.25	0.30	5.90
1 *M* Essigsäure	K 0.35	0.25	5.70	K 0.55	0.35	5.90
	K 0.45	0.35	5.70			
	A 0.80	0.55	5.20			
1 *M* NaOH	K 0.55	0.35	5.10	K 0.25	0.30	5.60
				K 0.85	0.45	5.60
				K 1.55	0.85	5.90
				A 0.25	0.30	5.60
				A 0.85	0.45	5.90
				A 1.40	0.70	5.90
1 *M* $NaNO_3$	K 0.75	0.30	5.10	K 0.55	0.30	6.05
	A 1.40	0.60	4.30	K 1.50	0.70	5.60
				A 0.50	0.20	5.60
1 *M* NaCl	K 0.85	0.35	5.40	K 1.50	0.65	5.60
	K 1.75	0.75	5.40	K 1.75	0.75	5.30
	A 0.30	0.10	5.10	A 0.40	0.15	5.10
				A 1.25	0.55	5.10
1 *M* $(NH_4)_2SO_4$	—	—	—	—	—	—
1 *M* KCN	—	—	—	—	—	—
1 *M* KCNS	K 0.85	0.45	4.40	K 0.25	0.20	5.60
				K 0.40	0.30	5.60
				K 1.10	0.70	5.10
				A 0.40	0.30	5.30
1 *M* NH_4CNS	K 0.95	0.50	5.20	K 0.30	0.15	5.60
				K 0.40	0.35	5.60
				A 0.40	0.35	5.10

TABELLE I (Vortsetzung)

Elektrolyt	*Ruthenium*			*Osmium*		
	E_{dep} (*V*)	*Q*	*Mp* (*pD*)*	E_{dep} (*V*)	*Q*	*Mp* (*pD*)*
1 *M* en H_2SO_4	K 0.45	0.20	5.40	K 0.40	0.20	6.05
	K 1 50	0.75	5.40	K 1.50	0.65	6.20
	A 1.25	0.60	4.60	A 1.05	0.50	5.60
0.5 *M* $NaNO_3$				K 0.95	0.50	6.40
a 0.25 *M* en				K 1.33	0.70	6.10
				K 1.70	0.90	6.10
				A 0.40	0.25	5.75
				A 0.65	0.40	6.40
				A 0.90	0.55	6.40
				A 1.15	0.70	5.10
				+K 0.80	0.40	5.00
				+A 0.55	0.25	5.00
0.5 *M* TEA	—	—	—	K 1.10	0.50	5.60
				A 1.00	0.45	5.30
0.5 *M* TEA	K 0.50	0.30	4.80	K 0.55	0.30	5.30
a 0.5 *M* NaOH				K 0.95	0.50	5.60
				A 0.70	0.35	5.60
1 *M* KCl	—	—	—	K 1.45	0.75	5.30
				K 1.55	0.80	5.30
1 *M* KBr	K 1.75	0.95	5.30	K 1.25	0.65	5.60
				K 1.55	0.75	5.75
				A 1.00	0.50	5.30
1 *M* KJ	K 1.00	0.60	5.05	K 0.85	0.45	5.30
	K 1.50	0.90	5.05	K 1.10	0.55	5.00
0.6 *M* HCl	K 0.50	0.30	6.55	K 0.85	0.50	6.30
a 0.1 *M* NaCl	K 1.20	0.75	6.55	K 1.10	0.65	5.70
	T 1.20	0.75	6.55	+K 1.10	0.70	4.90
				+K 1.20	0.80	4.25
1 *M* $HClO_4$	K 1.60	0.85	6.95	K 1.25	0.70	6.05
a 0.1 *M* NaCl	T 1.60	0.85	6.95			

K — kathodischer Einschnitt.
A — anodischer Einschnitt.
T — Dorn an dem anodischen Teil der Kurve.
\+ — es wurde OsO_4 verwendet.
* Sämtliche hier angeführten Werte sind als negativ zu verstehen.

Werte wurden erhalten, indem an die Quecksilbertropfelektrode 0.2 mA Wechselstrom angelegt wurden.

Bei der Ermittlung der Depolarisationspotenziale der Einschnitte und Dorne wurde mit Lösungen gearbeitet, die 10^{-3} bis 10^{-5} *M* Ru^{4+} und Os^{4+} enthielten. Höhere Konzentrationen an Ruthenium oder Osmium verursachten in den meisten Elektrolyten eine Deformation der verfolgten Kurve der Funktion $dE/dt = f(V)$. Bei allen Messungen wurde ein mechanischer Tropfenabreisser verwendet, um der Möglichkeit vorzubeugen, dass Störungen durch den Einfluss von Reaktionsprodukten am Ausgang der Kapillare eintreten könnten, die besonders bei hohen Stromdichten nach dem Abtropfen entstehen.

Die Messung wurde innerhalb von 1 bis 5 Minuten nach dem Zusammenmischen der Lösungen bei Raumtemperatur durchgeführt.

Wie aus Tabelle I folgt, ist die Anwesenheit von Os^{4+} und Ru^{4+} in 1 *M* Kaliumkyanid und Ammoniumsulphat durch keinen Einschnitt kenntlich.

In Lösungen von 1 *M* Ammoniumrhodanid und 1 *M* Kaliumrhodanid bilden Ruthenium und Osmium keine bemerkenswerte Einschnitte. Es entstehen aber stark gefärbte Lösungen, die zum qualitativem Nachweis beider Elemente verwendet werden, wie TREADWELL anführt[32].

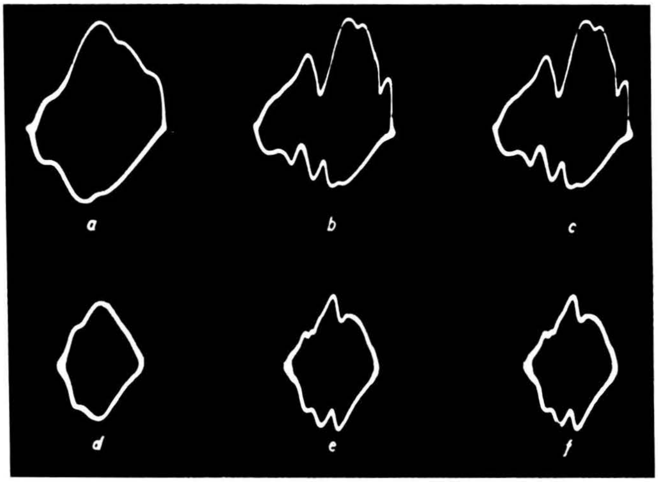

Fig. 1. Oszillopolarographische Kurven von Ruthenium und Osmium in Gegenwart von Ethylendiamin und Triethanolamin: (a)–(c) 0.25 *M* en + 0.5 *M* $NaNO_3$; (a) $1.5 \cdot 10^{-4}$ *M* Ru; (b) $1.5 \cdot 10^{-4}$ *M* Ru + $4 \cdot 10^{-4}$ *M* Os; (c) $4 \cdot 10^{-4}$ *M* Os; (d)–(f) 1 *M* TEA; (d) $1.2 \cdot 10^{-4}$ *M* Ru; (e) $1.2 \cdot 10^{-4}$ *M* Ru + $1.4 \cdot 10^{-4}$ *M* Os; (f) $1.4 \cdot 10^{-4}$ *M* Os; Tropfelektrode; Polaroskop.

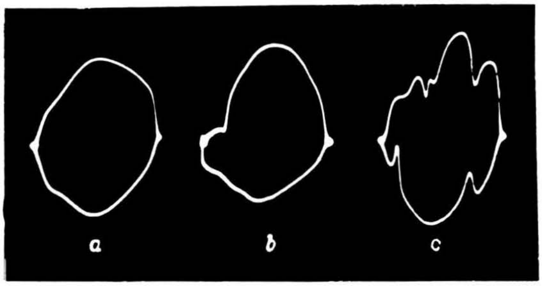

Fig. 2. Oszillopolarographische Kurven von Ruthenium und Osmium in Natriumhydroxyd: (a)–(c) 1 *M* NaOH; (b) $1.5 \cdot 10^{-3}$ *M* Ru; (c) $4 \cdot 10^{-4}$ *M* Os; Tropfelektrode; Polaroskop.

In 1 *M* Kaliumchlorid, 1 *M* Triethanolamin, 0.25 *M* Ethylendiamin und 0.5 *M* Natriumnitrat Lösungen bildet nur Osmium charakteristische Einschnitte (Fig. 1). Die geeignetsten Lösungen für den Nachweis und die Bestimmung von Osmium neben Ruthenium sind dann 0.25 *M* Ethylendiamin und 0.5 *M* Natrium-Nitrat.

Zum Nachweis von Osmium neben Ruthenium kann als Grundelektrolyt auch 1 *M* Natriumhydroxyd oder eine Mischung von 0.5 *M* Natriumhydroxyd und 0.5 *M* Triethanolamin verwendet werden. In diesen Elektrolyten bildet nämlich Ruthenium einen nur wenig empfindlichen Einschnitt dessen Potenzial von dem des Osmiumeinschnittes genügend entfernt ist (Fig. 2). Da in diesen Elektrolyten Ruthenium in grösseren Konzentrationen als hydratiertes Ruthenium(IV)-Oxyd ausgeschieden wird, kann der Nachweis von Osmium neben Ruthenium noch im Verhältniss von 1:30 vorgenommen werden.

In den übrigen neutralen Elektrolyten gibt es keinen grösseren Unterschied zwischen dem Verhalten von Osmium und Ruthenium.

Im Medium von 1 *M* Chlorwasserstoffsäure bildet Osmium einen empfindlichen kathodischen Einschnitt ($Q = 0.50$, pD $= 6.05$) neben dem sich bei höheren Konzentrationen noch ein zweiter Einschnitt bildet ($Q = 0.60$, pD $= 5.70$) der mit sinkendem Gleichstrom tiefer wird (Fig. 3).

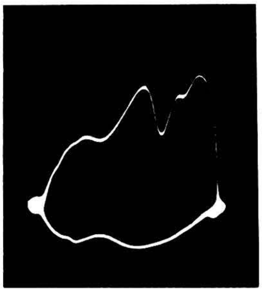

Fig. 3. Oszillopolarographische Kurve von Osmium in Chlorwasserstoffsäure: 1 *M* HCl und $2 \cdot 10^{-5}$ *M* Os; Tropfelektrode; Polaroskop.

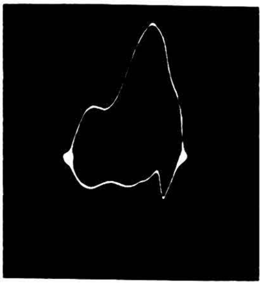

Fig. 4. Oszillopolarographische Kurve von Ruthenium in Chlorwasserstoffsäure: 1 *M* HCl und $2 \cdot 10^{-5}$ *M* Ru; Tropfelektrode; Polaroskop.

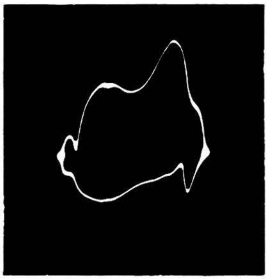

Fig. 5. Oszillopolarographische Kurve von Ruthenium in Perchlorsäure: 1 *M* $HClO_4$ und $2 \cdot 10^{-5}$ *M* Ru; Tropfelektrode; Polaroskop.

Ruthenium macht sich in diesem Medium durch einen kathodischen Einschnitt kenntlich ($Q = 0.75$, pD $= 6.50$) und besonders durch einen empfindlichen Dorn an dem anodischen Teil der Kurve ($Q = 0.75$, pD $= 6.50$) (Fig. 4). Ausser diesen zwei Effekten entsteht ein Einschnitt, der sich mit steigender Rutheniumkonzentration wenig vertieft ($Q = 0.30$, pD $= 6.50$). Ähnlich verhält sich Ruthenium auch im Medium von 1 *M* Perchlorsäure (Fig. 5). In diesem Fall ist die Empfindlichkeit des

Rutheniumnachweises sogar höher als im Medium von Chlorwasserstoffsäure. Dagegen kann der Osmiumeinschnitt in 1 *M* Perchlorsäure selbst zum qualitativen Nachweis nicht verwendet werden, denn in der Gegend des kathodischen Osmiumeinschnittes entstehen Deformationen der Kurve.

Die übrigen Mineralsäuren können nicht mehr als Elektrolyten verwendet werden, denn die Empfindlichkeit der Einschnitte ist kleiner.

Im Medium von 1 *M* Salpetersäure bildet nur Osmium einen Einschnitt, während beim Ruthenium, wahrscheinlich infolge der Bildung von sehr beständigen Ruthenium–Nitrosylverbindungen (besonders von Nitrosylnitriten)[33] keine Depolarisationswirkungen beobachtet werden.

In Lösungen, in denen das Verhalten von Os^{4+} und Ru^{4+} zum Nachweis und zur Bestimmung als geeignet erscheinen, wurde auch das Verhalten von Osmium(VIII)-Oxyd und Natriumruthenat untersucht. Es wurde experimentell bewiesen dass im Falle von Ru^{6+} im Medium von 0.6 *M* Chlorwasserstoffsäure oder 1 *M* Perchlorsäure die Quotienten Q und die Depolarisationspotenziale des Dornes an dem anodischen Teil der Kurve des Elektrolyten ($Q = 0.75$, $E_{\mathrm{Dep}} = -1.20$ V, bzw. $Q = 0.85$, $E_{\mathrm{Dep}} = -1.06$ V) mit den Depolarisationspotenzialen und Q-Quotienten, die bei Messungen mit Ru^{4+} erhalten wurden, identisch sind (Tabelle I). Die Empfindlichkeit des Nachweises ist aber niedriger: pD = 5.1.

Das oszillopolarographische Verhalten von Os-(VIII)-Oxyd ist praktisch mit dem Verhalten von Osmium in der +4 Oxydationsstufe identisch, die entstehenden Einschnitte sind aber in Säure-Medium zu den negativen Werten, in Ethylendiamin zu den positiven Werten verschoben. Die Empfindlichkeit des Nachweises ist ebenfalls niedriger.

Aus den durchgeführten Experimenten ist klar, dass das Ruthenium sich in Medien von Mineralsäuren ähnlich verhalten wird, wie das Rhodium, das von BERAN UND DOLEŽAL[18] untersucht wurde. Die Messung der Dornhöhe wurde auf ähnliche Weise vorgenommen wie von BERAN UND DOLEŽAL[20] beschrieben wird. Bei gegenseitig zusammenhängenden Messungen müssen die Polaroskopparameter konstant gehalten werden, d.h. der Wechselstrom, der Gleichstrom, Tropfdauer, horizontale und vertikale Verstärkung.

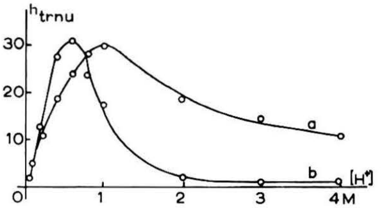

Fig. 6. Abhängigkeit der Höhe des Rutheniumdornes von der Wasserstoffionenkonzentration unter konstanter Ionenstärke: $3 \cdot 10^{-5}$ *M* Ru^{4+}, $\mu = 4$; (a) Perchlorsäure und Natriumperchlorat; (b) Chlorwasserstoffsäure und Natriumchlorid.

Wie aus Fig. 6 zu ersehen ist, beeinflusst ähnlich wie bei dem oszillopolarographischen Verhalten von Rhodium die Wasserstoffkonzentration die Dornhöhe von Ruthenium bei konstanter Rutheniumkonzentration und konstanter Ionenstärke. In Fig. 6 ist auch der unterschiedliche Einfluss der Chlorid- und der Perchlorationen auf die Kurve der Abhängigkeit der Dornhöhe von der Wasserstoffionenkonzentration sichtbar. Die Anwesenheit der Chloridionen hat sichtlich einen grösseren Einfluss auf die Verkleinerung des Dornes. Dies könnte dadurch erklärt werden, dass die Chloridionen mit Ruthenium einen Komplex bilden und dadurch die Bildung der Rutheniumform bremsen, die unmittelbar die beobachtete Erscheinung verursacht. Die Perchlorationen, die keinen Komplex bilden, haben auf die Verkleinerung des Dornes einen viel kleineren Einfluss. Die Höhe des Rutheniumdornes wird bei konstanter, 0.1 M, Wasserstoffionenkonzentration mit steigender Ionenstärke zuerst herabgesetzt, ab $u = 1$ steigt sie langsam an.

Bei dem Studium des Einflusses von Anionen steigt die Dornhöhe mit steigendem Atomgewicht des Elementes in der Reihe Chlorid, Bromid und Iodid, wie aus Fig. 7 zu ersehen ist.

Unter den übrigen Anionen unterdrücken Nitrat- und Rhodanidionen das Entstehen des Dornes, Sulphationen unterdrücken den Dorn beträchtlich (Fig. 7).

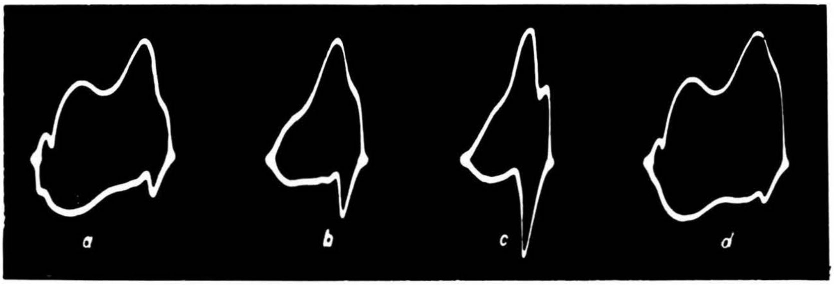

Fig. 7. Einfluss von Anionen auf den Rutheniumdorn in 1 M Perchlorsäure: (a)–(d) 1 M $HClO_4$ und $2 \cdot 10^{-5}$ M Ru; (a) 0.5 M NaCl; (b) 0.5 M NaBr; (c) 0.5 M NaI; (d) 0.1 M Na_2SO_4; Tropfelektrode; Polaroskop.

TABELLE II

ABHÄNGIGKEIT DER RUTHENIUMDORNHÖHE VON DER VALENZ DER ANWESENDEN KATIONEN UNTER KONSTANTER IONENSTÄRKE IN EINEM 1 M $HClO_4$ ENTHALTENDEN ELEKTROLYT

Kation	Na^+	Ca^{2+}	La^{3+}	Th^{4+}
Dornhöhe (mm)	7.5	4.5	3.5	2.5

Wenn die analysierte Lösung — 1 M Perchlorsäure und $1.2 \cdot 10^{-5}$ M Ru-Natrium-, Kalzium-, Lanthan(III)- oder Thorium(IV)-Nitrat enthält, dann wird bei konstanter Ionenstärke, die mit Natriumperchlorat eingestellt wird, mit steigender Valenz des Elementes die Höhe des Dornes herabgesetzt (Tabelle II).

Bei diesen Versuchen wurden Lösungen der entsprechenden Nitrate in $5 \cdot 10^{-2}$ M Konzentration angewendet, damit der eigene Einfluss der Nitrationen, die die Höhe des Rutheniumdornes herabsetzen, weitmöglichst beschränkt werde.

Der Einfluss von Gleichstrom und oberflächenaktiven Stoffen auf die Höhe des Rutheniumdornes ist ganz ähnlich wie bei dem Rhodium[18].

Auf Grund der durchgeführten Experimente kann das oszillopolarographisch verfolgte Verhalten von Ruthenium als identisch mit dem Verhalten von Rhodium betrachtet werden. Die lineare Abhängigkeit der Rutheniumdornhöhe von seiner Konzentration kann zu seiner Bestimmung verwendet werden (Fig. 8).

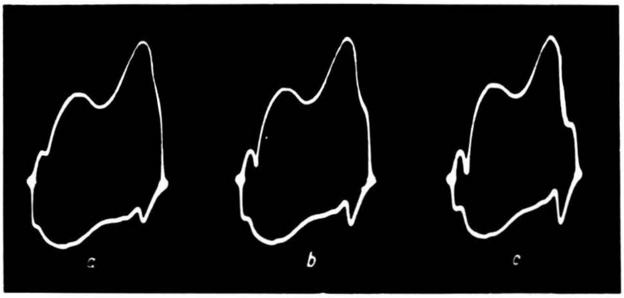

Fig. 8. Abhängigkeit der Dornhöhe von der Ruthenium Konzentration: (a)–(c) 1 *M* $HClO_4$; (a) 10^{-5} *M* Ru; (b) $2 \cdot 10^{-5}$ *M* Ru; (c) $4 \cdot 10^{-5}$ *M* Ru; Tropfelektrode.

ZUSAMMENFASSUNG

Es wurde das oszillopolarographische Verhalten von Ruthenium und Osmium in verschiedenen Grundelektrolyten untersucht. Es wurden die Depolarisationspotenziale, *Q*-Quotienten und Empfindlichkeitswerte für den oszillopolarographischen Nachweis beider Metalle gemessen. Der letzte Teil der Arbeit wird der Bestimmung von Osmium selbst in Anwesenheit der Platinmetalle gewidmet.

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STUDIES ON REDUCTION WAVES OF COPPER AND LEAD IONS IN SODIUM BICARBONATE SUPPORTING ELECTROLYTE USING AN A.C. POLAROGRAPH

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INTRODUCTION

MEITES[1] has proved, by amperometric titration with potassium bicarbonate solution, that copper ion exists as the complex $[Cu(HCO_3)_5]^{3-}$ in solutions containing a large excess of potassium bicarbonate. According to the present study, using a.c. polarography of copper ions in potassium bicarbonate solution, copper ion does not exist as the complex proposed by MEITES, but instead as a complex co-ordinated with OH^- and HCO_3^- ions. A similar complex was also inferred in a sodium bicarbonate solution for lead.

APPARATUS AND REAGENTS

The d.c. and a.c. polarographs employed in the present work have already been described[2,3]. In the a.c. polarograph, R_s and C_s are respectively 0.5 kΩ and 0.2 μF. The reference electrode (1 *N* calomel electrode) is connected through an agar–agar bridge with the polarographic solution: the mercury flow from the capillary is 1.42 mg/sec; the drop time in 1 *M* potassium bicarbonate solution at —0.25 V *vs.* N.C.E. is 4.1 sec/drop. Specially purified grades of potassium bicarbonate, copper sulfate and lead nitrate were used.

THE CONCENTRATION OF POTASSIUM BICARBONATE AND pH (FOR COPPER ION)

Wave-form of the copper ion

The d.c. and a.c. polarograms of copper ion in potassium bicarbonate solution are illustrated in Figs. 1 and 2. Figure 1 shows the change of the d.c. and a.c. polarograms with the concentration of potassium bicarbonate used as supporting electrolyte. In 0.4 *M* potassium bicarbonate solution the polarogram gives only one wave, seen in (a) and (a′) in Fig. 1, but in 0.1 *M* solution two distinct waves are seen, as in (b) and (b′) in Fig. 1. If potassium hydroxide is added to the potassium bicarbonate solution, the wave-forms change in accordance with the pH value, *i.e.*, the polarogram shows only one wave, as shown in (a) in Fig. 2, over the pH range 8.8–10.8, while two distinct waves, shown in (b) in Fig. 2, are observed at a pH greater than 11. In 1 *N* potassium carbonate solution, the polarogram has a perfect shape consisting of two waves and approaches that[3] obtained in caustic alkali solution.

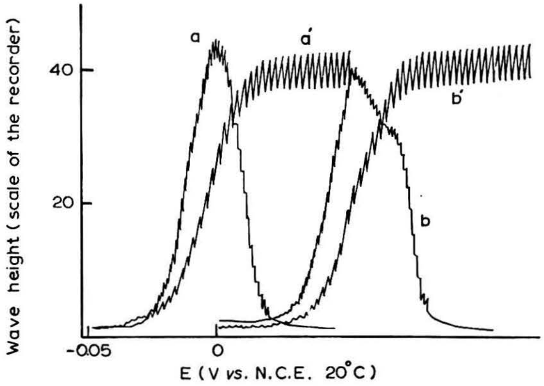

Fig. 1. Effect of $KHCO_3$ concentration on the reduction wave of copper: (a), a.c. polarogram in 0.5 *M* $KHCO_3$; (a'), d.c. polarogram in 0.5 *M* $KHCO_3$; (b), a.c. polarogram in 0.1 *M* $KHCO_3$; (b'), d.c. polarogram in 0.1 *M* $KHCO_3$.

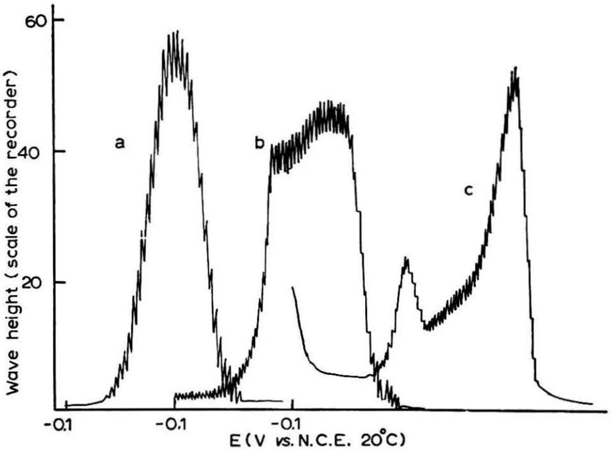

Fig. 2. Effect of pH of $KHCO_3$ solution on the reduction wave of copper: (a), pH 9; (b), pH 11; (c), in 0.5 *N* Na_2CO_3.

Peak potential of the copper ion

The polarogram of copper ion in potassium bicarbonate solution at concentrations > 0.4 *M* gives only one wave, provided that the pH of the solution is 9–10.8. Therefore, the analysis was carried out using the d.c. polarogram of copper ion in 0.5 *M* potassium bicarbonate solution, and it was found that the slope of $\log[i/(i_d - i)]$ *vs.* E varied with the change of the concentration of copper ion.

The slopes were 43 mV and 30 mV *vs.* a mercury pool, respectively, for 1 m*M* and 0.5 m*M* copper solutions. Since the latter slope approaches that of a reversible wave of a two-electron reaction, the following investigation was carried out to find the dependence of the peak potential on the concentration of potassium bicarbonate when the concentration of copper ion was 0.5 *M*. The peak potential moves towards a negative potential in accordance with the concentration of potassium bicarbonate, as shown in (a) in Fig. 3, and the potential shift ($\Delta E_{\frac{1}{2}}$) is 60 mV per unit concentration of potassium bicarbonate, the concentration of which is within the range 0.4–1 *M*. Therefore, the number (p) of HCO_3^- ions liberated at the surface of the electrode was calculated from the above value of the potential shift by using the following equation:

$$\frac{\Delta E_{\frac{1}{2}}}{\Delta \log C_x} = \frac{(p-q)}{n} 0.0591 \qquad (1)$$

where C_x is the concentration of potassium bicarbonate, q is the number of ligands co-ordinated on the reduced substance, and n is the number of electrons transferred in the electrode reaction (two electrons in this case).

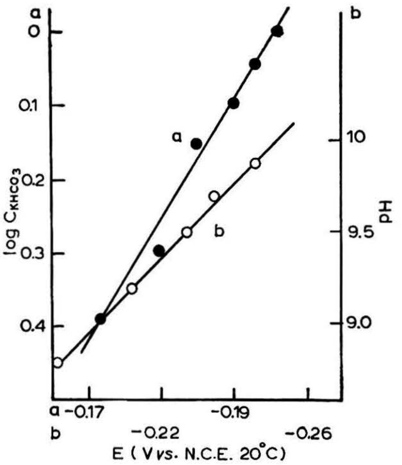

Fig. 3. Effect of $KHCO_3$ concentration and pH on the peak potential of 0.5 m*M* copper: (a), effect of $KHCO_3$ concentration; (b), effect of pH.

The results of the calculation give the value of p as 2, so it is concluded that the copper ion is co-ordinated with two HCO_3^- groups in 0.4–1 *M* potassium bicarbonate solution.

The peak potential of 0.5 m*M* copper ion in 1 *M* potassium carbonate solution shifts towards negative potentials in accordance with the pH value, as is shown in (b) in Fig. 3, so that the electrode reaction takes place with liberation of OH^- ions on the surface of the electrode. The peak potential shift was 50 mV per unit value of pH over the pH range of 9–10, so that the number of OH^- ions liberated on the electrode surface was calculated to be 2 by using eqn. (1). From the above results, the reduction wave of copper ion is concluded to be due to the following electrode reaction in potassium bicarbonate solution:

$$[Cu(OH)_2(HCO_3)_2]^{2-} + 2\,e \rightarrow Cu(Hg) + 2\,OH^- + 2\,HCO_3^- \qquad (2)$$

DISSOLUTION OF COPPER HYDROXIDE IN POTASSIUM BICARBONATE SOLUTION

The co-ordination of OH^- to copper ion in potassium bicarbonate solution was deduced from the peak potential shift in combination with the pH value. This conclusion can be also deduced from the following investigations. Figure 4 shows the titration curve of sodium carbonate with hydrochloric acid; the pH can be seen to change markedly at 8.3. At this pH, sodium carbonate is converted to sodium bicarbonate, and also the solution is unbuffered, as is seen in the titration curve, so it seems probable that the pH value changes with the introduction of OH^- ion. Therefore, the pH value should increase when copper hydroxide dissolves in the potassium bicarbonate solution at pH 8.3, since the co-ordinated OH^- group will be displaced by the HCO_3^- group, and liberated into the solution. However, in practice it was found that the pH value of the potassium bicarbonate solution did not alter on addition of freshly prepared and well washed copper hydroxide at pH 8.3, although its dissolution could be confirmed by the blue coloration of the solution. Therefore, copper ion dissolved in the solution is probably co-ordinated with OH^- and HCO_3^- groups, so that dissolution will occur according to the following equation:

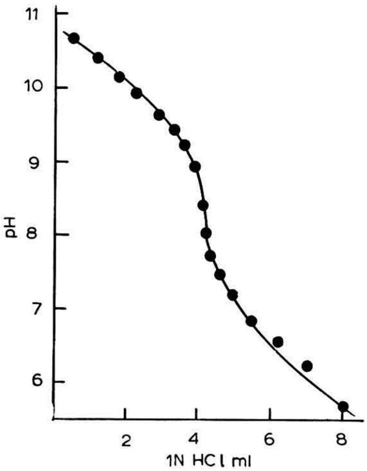

Fig. 4. Titration curve of 0.1 N $NaHCO_3$ with 1 N HCl.

$$Cu(OH)_2 + 2\ KHCO_3 = [Cu(OH)_2(HCO_3)_2]^{2-} + 2\ K^+ \quad (3)$$

THE CONCENTRATION OF POTASSIUM BICARBONATE AND pH (FOR LEAD ION)

The solubility of lead in 1 M potassium bicarbonate solution (pH 9) is about 0.25 mM, and increases with increasing pH. In the polarogram of 0.25 mM lead in 1 M potassium bicarbonate solution, the peak potential is located at —0.57 V. Also, the slope of $\log[i/(i_d - i)]$ *vs.* E in the d.c. polarogram is 30 mV *vs.* N.C.E., which confirms that the reduction wave is a reversible wave with a two-electron transfer.

The effect of the concentration of potassium bicarbonate on the potential of lead is shown in (a) in Fig. 5. The peak potential shifts towards a negative potential with an increase in the concentration of potassium bicarbonate, so that it can be inferred that the liberation of HCO_3^- takes place on the surface of the electrode. The potential shift was 58 mV per unit concentration of potassium bicarbonate, from which the number of HCO_3^- ions liberated is calculated to be 2, by using eqn. (1). Therefore, it is assumed that the reduction wave of lead in 0.5–1 *M* potassium bicarbonate solution is due to a complex co-ordinated with two HCO_3^- groups.

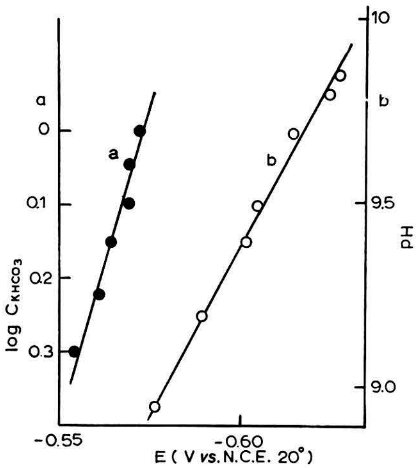

Fig. 5. Effect of $KHCO_3$ concentration and pH on the peak potential of lead: (a), effect of $KHCO_3$ concentration; (b), effect of pH.

The peak potential of the lead ion shifts towards negative potentials with an increase of pH, which can be varied by the addition of sodium hydroxide solution to the 1 *M* potassium bicarbonate solution. Therefore, the liberation of OH^- in the electrode reaction takes place on the surface of the electrode. The peak potential shift was 55 mV per unit value of pH over the pH range 9–10, which indicates that two OH^- groups are liberated in the electrode reaction.

Finally, it is concluded that lead ion is probably co-ordinated with two HCC_3^- and two OH^- groups, as $[Pb(OH)_2(HCO_3)_2]^{2-}$.

SUMMARY

According to the present study using a.c. polarography, copper and lead ions were found to exist as co-ordinated compounds such as $[Cu(OH)_2(HCO_3)_2]^{2-}$ and $[Pb(OH)_2(HCO_3)_2]^{2-}$, in solutions of potassium bicarbonate, the concentration of which ranged from 0.5–1 *M*, having a pH value 8.8–10.

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Short Communications

Utilisation d'un convertisseur tension-fréquence pour l'intégration coulométrique

On présente ici les résultats coulométriques obtenus à l'aide d'un convertisseur tension–fréquence (modèle 2210 de la Dymec Division de la Hewlett Packard Co.[1]). Une étude plus détaillée sera publiée par ailleurs[2].

L'introduction dans le circuit de coulométrie d'une résistance étalon (aux bornes de laquelle est branché l'appareil) permet de transformer le courant en une série d'impulsions dont la fréquence instantanée est proportionnelle à l'intensité. Le décomptage du nombre total d'impulsions pendant un temps donné permet donc de connaître la valeur de l'intégrale du courant prise sur ce temps (soit la quantité d'électricité).

Le coefficient de proportionnalité tension–fréquence est donné par le constructeur (à 0.06% près). Le nombre d'impulsions pouvant être compté exactement, la précision est en définitive limitée par la qualité de la résistance-étalon.

Des essais préliminaires permettent de contrôler les résultats attendus: on compare tout d'abord la fréquence délivrée par l'appareil — quand il est branché aux bornes d'un élément Weston — à la tension de cet élément.

Le coefficient de proportionnalité obtenu peut être réglé à une valeur s'approchant de $3 \cdot 10^{-4}$ de la valeur théorique et ce, avec une reproductibilité de $2 \cdot 10^{-5}$.

D'autre part, la mesure précédente n'étant effectuée que pour une seule tension, il semble intéressant de comparer les quantités d'électricité traversant la résistance étalon (et intégrées par le convertisseur) à celles que délivre un chrono-ampérostat (délivrant un courant connu pendant un temps déterminé). Aux limites de précision près, et même lorsqu'on fait varier le courant dans un rapport de trois cents fois, les deux séries de mesures sont entièrement concordantes.

Enfin, la comparaison de l'ensemble résistance–convertisseur–compteur à un coulomètre chimique (dissolution anodique de l'argent et titrage par le bromure) ne permet pas de mettre en évidence des écarts supérieurs à 0.2%.

Par ailleurs, il a été procédé à des essais sur le système mercure(I)/mercure(O) dans le but de doser coulométriquement le mercure(I). La réduction à potentiel contrôlé (+ 200 mV E.C.S.) permet en effet de connaître la quantité d'électricité nécessaire pour effectuer la réaction:

$$Hg_2^{2+} + 2\,e \longrightarrow 2\,Hg(O) \qquad (1)$$

La reproductibilité dans le montage utilisé, a d'abord été étudiée. Pour cela, on a comparé les quantités d'électricité nécessaires pour oxyder un peu de mercure métallique selon:

$$2\,Hg(O) - 2\,e \longrightarrow Hg_2^{2+}$$

et celles nécessaires pour réduire le mercure(I) ainsi formé, en mercure métallique. Les écarts relatifs entre les deux nombres n'ont jamais été supérieurs à 0.3% (conc. $> 5 \cdot 10^{-4}$ *M*).

Enfin un dosage coulométrique à forte concentration permettant de déterminer (à 0.3% près) le titre d'une solution inconnue de mercure(I), on peut par dilution de celle-ci étudier la limite de sensibilité du dosage (en opérant avec des quantités de plus en plus faibles de sel mercureux).

Le dosage est exact à moins de 2% jusqu'à une concentration de $3 \cdot 10^{-6}$ *M* et pour une concentration de $3 \cdot 10^{-7}$ *M*, la précision est encore de 14%.

L'ensemble de ces résultats est tel que l'appareil étudié nous a semblé apporter une solution rationnelle au problème de l'intégration précise des courants (même non constants) utilisés en coulométrie.

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[1] *Hewlett Packard Journal*, [2] 12 (1960).
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Reçu le 20 mars, 1962

* Actuellement stagiaire de l'O.E.C.E. (O.E.C.D.) au laboratoire de chimie analytique de l'Ecole Supérieure de Physique et de Chimie Industrielles, 10 rue Vauquelin, Paris, France.

The hanging mercury drop electrode

Hanging drop electrodes have been used by many workers in the field of polarography and electrode kinetics. GERISCHER[1] AND DELAHAY[2] adapted a method by which a few mercury drops, obtained with the usual dropping mercury electrode, were collected by a movable Teflon spoon and then attached on to a gold plated platinum electrode. SHAIN AND MARTIN[3] have used pure mercury drops supported from below. However, KEMULA's work deserves special mention for his exhaustive polarographic investigations with a pure mercury drop electrode. KEMULA has shown that the presence of platinum or gold in mercury can lead to unexpected errors. He has described[4] a simple method for obtaining stationary drops of pure mercury.

The electrode (Fig. 1) used in this laboratory is an improvement on the one devised by KEMULA. An "Agla" micrometer pipette has been adapted for this purpose. The syringe tube is provided with an air-tight ground glass plunger. A capillary, bent as shown in Fig. 1, is attached to the syringe. The plunger, pushed forward by rotation

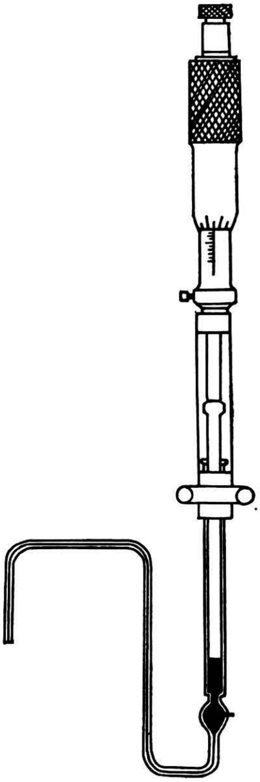

Fig. 1. Hanging mercury drop electrode.

of the micrometer head, forces the mercury out to form a drop at the tip of the capillary. The advantage of this method lies in the fact that a drop of any known size can be obtained by the rotation of the micrometer screw through the appropriate number of divisions. One complete rotation of 50 divisions pushed out liquid of volume equal to 0.01 ml. Further, it is possible to have the desired quantity of mercury in the reservoir, a small volume being preferred due to the possibility of complications resulting from temperature changes[4].

The drop so obtained was seen to hang on for more than an hour without any apparent change or increase in area. This has been confirmed by two independent measurements. The weight of the drop was determined after allowing it to hang on for different intervals of time, and compared with the calculated weight.

Adapting a circuit slightly different from the one used by DOSS AND GUPTA[5], the change of the alternating current with the polarising d.c. potential was recorded. A stationary mercury surface can quickly become contaminated. To avoid this complication, a circuit was adapted so that the drop was under a polarisation of —1.6 V, when any impurities present in solution are expected not to be adsorbed, and then quickly switched to the desired polarising potentials. Thus, one single drop could be used for study in the whole range of potentials, with reproducible results.

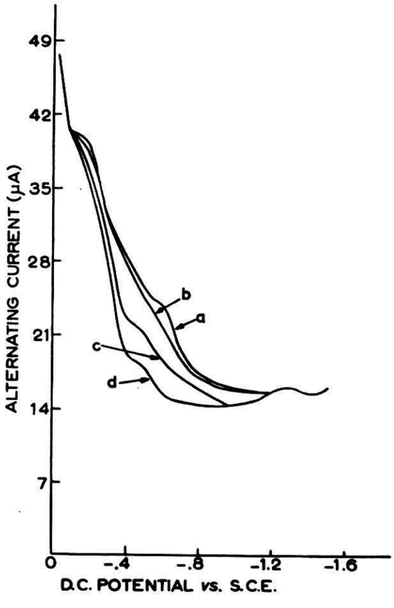

Fig. 2. Solution of 0.1 *M* Na_2SO_4, pre-electrolysed with a mercury pool cathode: a.c. ripple, 30 mV (rms); frequency, 50 c/sec; temperature, 27°; surface area of drop, 0.076 sq.cm. (a), 5 sec after switching on; (b), 10 sec after switching on; (c), 30 sec after switching on; (d), 60 sec after switching on.

To follow the variation of current with time, current magnitudes were noted at various intervals of time after switching to the desired polarising potential. Results obtained with 0.1 *M* Na_2SO_4 solution are given in Figs. 2 and 3. The current decreases with time in the range of potentials —0.2 to —1.1 V (with respect to the S.C.E.). However, the magnitudes of the changes are reproducible in the various experiments. This drift in current is not the result of a change in the size or shape of the drop, but is associated with an adsorption or an electrochemical process. GRAHAME had made similar observations during his studies on electrocapillarity, and attributed such drifts to traces of impurities that are not removed by chemical methods. BARKER[6] has remarked that with solutions treated with activated charcoal, the differential capacities remained constant over a period of 24 hours even with a stationary electrode. Experiments were done in this laboratory with solutions passed through a column of pure activated charcoal. The current was found to show very little drift over a period of a few minutes and then very slowly decreased. This reduction was largest at about the potential of the electrocapillary maximum.

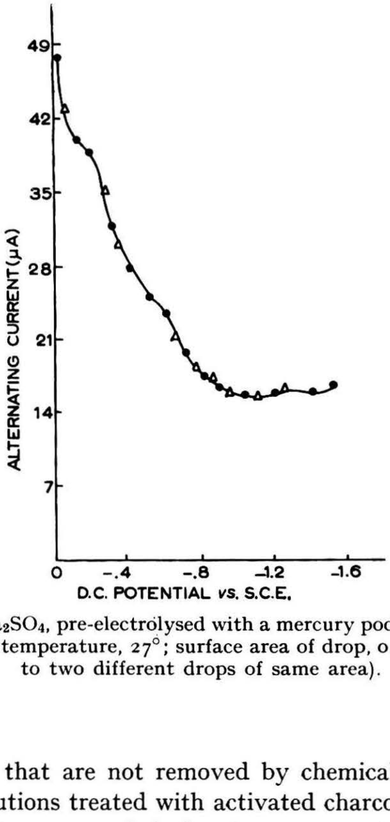

Fig. 3. Solution of 0.1 *M* Na_2SO_4, pre-electrolysed with a mercury pool cathode: a.c. ripple, 30 mV (rms); frequency, 50 c/sec; temperature, 27°; surface area of drop, 0.076 sq.cm. (●,△ correspond to two different drops of same area).

Differential capacity values calculated from the results compare well with the values reported by GRAHAME. This technique appears to be particularly suitable for tensammetric studies.

It is a pleasure to thank Professor K.S.G. Doss, Director, Central Electrochemical Research Institute, Karaikudi, for his suggesting the technique.

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Book Reviews

Dissociation Constants of Organic Acids in Aqueous Solution, by G. Kortüm, W. Vogel and K. Andrussow, Butterworths, London, 1961, xxii + 347 pages, £2.10s.

This monograph has been prepared at the request, and with the assistance, of the International Union of Pure and Applied Chemistry (I.U.P.A.C.) section of Analytical Chemistry, and its contents have already appeared in the issues nos. 2 and 3 of Volume 1 of "Pure and Applied Chemistry", the journal of the I.U.P.A.C.

The data, which refer to dissociation constants of organic acids in aqueous solution, should not be considered as a mere reproduction of classified information from a literature survey. The original data have, in fact, been critically examined in order to enable the user of the Tables to make the most reliable choice from the several available values of a given constant.

The assessment of reliability by the reviewers has been based on the examination of: (1) the experimental variables (nature of the system, reproducibility of measurements, purity of materials, constancy of temperature, etc.); (2) the methods of measurement, and the procedure for evaluating the quality of the measurement (concentration range, extrapolation to zero ionic strength, etc.). The conclusions which the reviewers have arrived at are expressed by four gradings: "very reliable", "reliable", "approximate", or "uncertain", according to whether the uncertainty in the K value is respectively, 0.1%, 1%, less than, or larger than, 10%.

Each line in the table starts with an order number, followed by the name and formula of the compound. The next line gives the dissociation constant(s), the temperature(s), some remarks on the concentration range, the ionic strength, etc., the experimental method, the critical evaluation as specified above, and finally the literature reference.

The text preceding the Tables gives a survey of the methods of determination (conductance, electrometric, catalytic and spectrophotometric measurements) showing in each case the actual equation by which the dissociation constant was evaluated. Although the text of the Tables is in German, the introductory chapters and the index of compounds are in both German and English.

The constants of over a thousand compounds collected in this way not only represent a valuable tool for many analytical procedures, but are also a helpful reference for all branches of chemistry. The people who have produced this very useful book are entitled to our gratitude.

Leonello Paoloni, Istituto Superiore di Sanità, Rome

The Determination of Stability Constants and Other Equilibrium Constants in Solution, by F. J. C Rossotti and H. Rossotti, McGraw Hill Book Company, N.Y. and London, 1961, xiv + 425 pages, £4. 17s.

"... A *complex* may be defined as a species formed by the association of two or more simpler species each capable of independent existence ...". With the further restriction of limiting themselves to complexes in solution, the Authors discuss the quantitative study of all the association equilibria which are encountered in every field of chemistry, from basic principles.

The book offers an excellent literature survey and a discussion of experimental techniques, and, at the same time, it has the character of a textbook useful for reference. The first five chapters, which consist of about a hundred pages, deal with fundamentals: definitions, basic principles common to all the experimental methods, and mathematical techniques for handling the results. These chapters are a necessary preliminary and allow the reader to turn eventually to the section which he thinks is suited to his needs. Nevertheless, anyone who must determine the association equilibrium constant of some process can examine in this book the advantages and disadvantages of several possible techniques.

The body of the book illustrates the different methods useful with mononuclear (BA_n) complexes: potentiometry, polarography and amperometry, solubility, liquid–liquid extraction, ion exchange, measurements of colligative properties, optical and spectroscopic measurements, formation and dissociation rates (fast reactions are not considered), conductivity, electrophoresis, dielectric polarization, and magnetic susceptibility.

The last chapters discuss polynuclear systems of both the B_q (self-association) and B_qA_p types, mixed complexes of the type $B_qH_jA_p$, and analogous complexes.

Each method is usually described in three parts: theory, measurements and interpretation of the results. The mathematical treatment is developed in the most general way, which perhaps makes some of the formulae look more complicated than they actually are. Nevertheless, the value of such a general treatment will soon be appreciated by the reader, as he progresses from the introductory chapters to the remainder of the book.

At the conclusion of his speech at the International Symposium on the Chemistry of Coordination Compounds in Rome (1957), Professor Sillén pointed out that "... before ... theoretical chemists and chemical physicists ... be through with their work, ... there will still have to be much hard and diligent work by experimental chemists". This book will certainly help to make their job easier, and improve the quality of their results.

LEONELLO PAOLONI, Istituto Superiore di Sanità, Rome

Photometric Titrations, by J. B. HEATRIDGE, Pergamon Press, Oxford and London, 1961, x + 122 pages, £2. 5s.

Photometric detection of end-points in titrimetry is less common than in other analytical methods, perhaps because the examples and the determinations performed using this method are scattered in many periodicals, a lot of which are not easily available or readable. This monograph fills, therefore, a gap existing in analytical literature, and can be considered as a laboratory manual for performing such titrations practically. In fact, the theoretical treatment occupies approximately twelve pages.

The first two chapters (34 pages) contain a short history and description of the method, sources of error, theory, and a description of some commercial instruments. The remaining 80 pages describe applications of the method in acid–base titrations, oxidation–reduction systems, complexometry, precipitation reactions, coulometry with a photometric end-point, and miscellaneous reactions.

A particularly useful feature of this monograph is, that for every titration the corresponding bibliographic references are given, so that a more detailed description can easily be found for every example.

Physical Chemistry, 2nd edn., by F. DANIELS AND R. A. ALBERTY, John Wiley, N.Y., 1961, x + 744 pages, $8.75.

This is a classical textbook on physical chemistry, particularly designed for a B.Sc. course. It is called the 2nd edn., although it is actually the tenth up-to-date, completely rewritten version of a text first published in 1927. The book is divided into 24 chapters and an appendix. The first third of the book (about 270 pages) is devoted to classical chemical thermodynamics. The next 110 pages are concerned with kinetics, followed by 100 pages devoted to electrochemistry. The remainder of the book is concerned with other topics *e.g.* quantum theory, molecular structure, spectroscopy, statistical mechanics, macromolecules, etc.

In comparison with the preceding edition, the three chapters devoted to kinetic theory, spectroscopy and statistical mechanics are new. In particular, the chapter on spectroscopy is very welcome because it is only rarely that a text book on physical chemistry for undergraduates treats such modern techniques as microwave electron magnetic resonance (EMR) and nuclear magnetic resonance (NMR). But, in the opinion of the reviewer, the inclusion of such topics as microwaves, EMR, NMR, etc. in the field of spectroscopy is a little confusing for students at the beginning of their course. It would, perhaps, be better to have "spectroscopy" limited to classical optical spectroscopy *i.e.* i.r., visible, u.v. and the Schuman region, which have a common background, founded on optical geometry, and to exclude all other techniques employing electromagnetic waves, but which utilize completely different measuring devices. Otherwise, no valid reason could be given for excluding from spectroscopy, for example, the investigation of crystal structures by X-rays, or the investigation of dipole moments or even ***ad absurdum*** the measurements of electrolytic conductance by means of a.c. methods. But this is a personal consideration only made while reading the book.

Otherwise this is an excellent book, very clearly written and very well produced, containing approximately 800 examples and exercises, giving the student practise in applying general laws, rules and equations to the solution of particular practical problems.

G. Milazzo, Istituto Superiore di Sanità, Rome

Methods for Emission Spectrochemical Analysis, E-2, 3rd edn., American Society for Testing Materials, 1961, xvi + 688 pages, $ 11.

This third edition of the A.S.T.M. publication on emission spectrochemical analysis contains 29 more methods than the 1957 edition, *i.e.* about one third more, and this is an indication of recent developments in this field. About one sixth of the book describes general practices, such as photographic processing, photometry, electrodes, reagents etc.; some seven pages contain a brief glossary of nomenclature, and about fifty pages are devoted to three appendices, the index and recommendations. The remaining 500 pages contain suggested and tentative methods for spectrochemical analysis of many elements in the most different materials.

As is usual in A.S.T.M. books, the methods are classified in proposed, suggested, tentative and standard methods. Owing to the rapid growth of knowledge in this field, most methods are only *suggested*, but they have usually been critically tested, so that confidence can be felt in their use.

The description of each method follows the normal A.S.T.M. scheme, so that no particular difficulty should be encountered in their use, and the characteristics of each one (precision, accuracy, limitations etc.) are given so that the reader can easily compare the methods given with others based on other analytical techniques.

Chromatographic Reviews, ed. M. Lederer, Vol. 3, Elsevier, Amsterdam, 1960, viii + 188 pages, Dfl. 25.

As with the two preceding volumes in the same series, this book constitutes a very useful review on different aspects of paper chromatography and electrophoresis. The reader is able to refer easily to the field which interests him. Moreover, the literature covered by the various contributors mostly dates from 1959 or the beginning of 1960.

The book contains a valuable report on multiple zones and spots in chromatography (by R. A. Keller and J. C. Giddings), one on starch column electrophoresis (by H. B. Bloemendal) and one on starch gel electrophoresis (also by H. B. Bloemendal); one on continuous electrophoresis and on two-dimensional chromatography (by Z. Pučar). There is an excellent collection of useful data for identification of phenol derivatives of biochemical interest (chapter V, by L. Reio), which forms a valuable supplement to the preceding work by the same author (which appeared in the first volume of this series). This work deserves a special mention, because it is a basic method, which will probably allow the identification of many metabolites, either of vegetable, microbiological or animal interest. Chapter VI discusses the chromatography of lipides on silicic acid (J. J. Wren). Recent advances in organic paper chromatography are summarized in chapter VII (M. Lederer), and the most recent electrophoretic separations of inorganic ions are described in chapter VIII (R. A. Bailey and L. Yaffe). The subjects treated in the final chapter have not previously appeared in the *Journal of Chromatography*.

This book is highly recommended to all those who are interested in paper chromatography and electrophoresis, and who use such techniques in the course of their work.

C. Casinovi, Istituto Superiore di Sanità, Rome

1. Fundamental electrochemistry

226 – Equilibrium distribution of ions and dipoles in an electric field. I. General equations. Application to electrostriction (in French). A. Sanfeld, A. Steinchen-Sanfeld and R. Defay (Free University, Brussels, Belgium). *J. chim. phys.*, 59 (1962) 132–138.
In the general case, where the dielectric constant depends on temperature, concentration and electric field, the authors establish the equations for chemical potentials and calculate the difference between the Helmholtz pressure and the Kelvin pressure. Finally, a general expression is proposed for the distribution of every dissolved constituent at every point of the system. The choice of activity coefficients is discussed, and also standard functions for the case of a system submitted to an electric field. An application of the effect of electrostriction is described. An expression is proposed for the calculation of the concentration of polarisable molecules, which is greater at the points where the electric field is more intense. [G.Mar.]

227 – Equilibrium distribution of ions and dipoles in an electric field. II. The plane diffuse layer (in French). A. Sanfeld, A. Steinchen-Sanfeld, H. Hurwitz and R. Defay (Free University, Brussels, Belgium). *J. chim. phys.*, 59 (1962) 139–147.
An application of general equations, for the distribution of ions and dipoles in an electric field, is made for the case of a diffuse layer in which every line of the field is perpendicular to the interface. The differential equation for the Kelvin pressure is integrated; the Helmholtz pressure is then computed, but the results differ according to whether the dielectric constant depends on the electric field or not. This effect has some influence on the distribution of constituents. The method requires the values of the derivatives of dielectric constant, in respect of the concentrations and the electric field. This evaluation is discussed, based on experimental values. For a partly ionised, tensio-active acid, the dissociation constant is smaller in the layer. (See preceding abstract). [G.Mar.]

228 – A calorimetric method for determination of ΔS for a chemical reaction from measurements on an electrochemical cell (in English). J. C. Eriksson and B. Söderqvist (Division of Physical Chemistry, Royal Institute of Technology, Stockholm, Sweden). *Acta Chem. Scand.*, 15 (1961) 1701–1706.
An equation is derived which may be used for the calculation of ΔS for a chemical reaction from fairly simple calorimetric measurements on an electrochemical cell. The lead accumulator is quoted as an example for the equation. Further application of the method, notably the determination of Peltier heats for electrodes, is discussed. [G.Ekl.]

229 – The rotating disc electrode in the polarography of molten salts (in Ukrainian). J. K. Delimarski, I. D. Pantshenko and G. W. Shilina (Institute of General and Inorganic Chemistry, Academy of Sciences, Ukrainian S.S.R.). *Dopodivi Akad. Nauk Ukr. R.S.R.*, (1961) 205–208.
By means of a rotating disc electrode it was possible to demonstrate the accuracy of Lewitsch's theory of convective diffusion. The salts investigated were chlorides of Ag, Cd, Tl and Pb (LiCl and KCl as supporting electrolytes). The relationship $i_d = K\omega^{0.58}$ was found between the limiting current and the angular velocity. By means of this relationship the value $0.9 \cdot 10^{-5}$ cm^2/sec was found (in agreement with results obtained by other methods) for the diffusion coefficient of Ag^+. [Ca.Cas.]

230 – Reference electrodes and overvoltage measurements in molten salts (in English). R. Piontelli (Laboratory of Electrochemistry, Chemical Physics and Metallurgy, Polytechnic, Milan, Italy). *Ann. N.Y. Acad. Sci.*, 79 (1959/1960) 1025–1071.
An exhaustive discussion on definitions, general concepts and practical applications of comparison electrodes in the field of overvoltage measurements in molten salts. Practical solutions and experimental measurements are also suggested. The following metals, mixed with alkali chlorides, and in the presence of their molten chlorides, do not show any overvoltage at a sufficiently high temperature; Pb, Cd, Sn, Zn, Mg, Al, Ni and Cu. [Ca.Cas.]

231 – A possible contribution made by conductance in dissociating systems (in English).

P. A. H. Wyatt (Department of Chemistry, The University, Sheffield, Great Britain). *Trans. Faraday Soc.*, 57 (1961) 773–779.
In solvents which are considerably self-dissociated, the conductance mechanism is thought to take place by an asymmetric dissociation in the electric field. A mathematical treatment is performed, involving the extent of dissociation and the ion-recombination rate constant. A re-interpretation is made of the conductance data of sulphuric acid. [Fr.Pan.]

232 – Diffusion in porous electrodes (in Russian). O. S. Ksenzhek (Institute of Chemical Technology, Dniepropetrovsk, U.S.S.R.). *Zhur. Fiz. Khim.*, 36 (1962) 243–248.
The macrokinetics of processes taking place in porous electrodes under such conditions that the determinating factor is the diffusion of the reactants in the pores, have been investigated. The intra-diffusion operating region of a porous electrode is characterized by diminished polarization, with increased values for the slope of the polarization curve. The application of porous electrodes may be effective for reactions with rate constants less than 10^{-3} cm sec^{-1}. [Ot.So.]

233 – Redox potentials of metal ions in complexes (in English). D. D. Perrin (Department of Medical Chemistry, Australian National University, Canberra, Australia). *Revs. Pure and Appl. Chem.*, 9 (1959) 257–285.
A review with 111 references of redox electric tensions and related properties of hydrated metal ions. Separate sections deal with metal electrodes, cyanide complexes, complexes with neutral ligands, complexes of Fe with organic anions and Cu complexes. Some biological applications are also dealt with. [Ca.Cas.]

234 – The causes of metals being displaced in the sequence of their standard electrode tensions in non-aqueous media (in Russian). E. J. Gorenbein (Academy of Sciences, Ukrainian S.S.R.). *Zhur. Obshcheĭ Khim.*, 29 (1959) 685–689.
Diskussion zur Veröffentlichung von Ju. K. Delimarski (*Zhur. Obshcheĭ Khim.*, [4] (1958)). Es werden die Ansichten des Autors über die Gründe der Platzänderungen der Metalle in der Reihe der Standardspannungen in nichtwässerigen Lösungen anhand neuester Ansichten über die Struktur des flüssigen Zustandes kritisiert. [Vi.Jes.]

235 – pH calculation for solutions in heterogeneous equilibrium systems of metal chlorides with sodium chloride of the type: M^{n+}–OH^-–Cl^-–H_2O (in Russian). N. V. Akselrud (Institute of Physical and Inorganic Chemistry, Academy of Sciences, U.S.S.R.). *Zhur. Neorg. Khim.*, 6 (1961) 239–241.
Im heterogenen Gleichgewichtssystem M^{n+}–OH^-–Cl^-–H_2O in Anwesenheit einer festen Fase an Salzen $M(OH)_yCl_{n-y}$, kann man das pH nach folgender Gleichung auswerten:

$$\mathrm{pH} = \frac{1}{y}\log S - \log K_w - \frac{n+1}{y}\log(\gamma_\pm)_0 + \frac{n+1}{y}\,0.05\log n - 0.20 -$$

$$\frac{0.95 - 0.05n}{y}\log c_{\mathrm{M}^{n+}} - \frac{1.05n + 0.05 - 0.93y}{y}\log c_{\mathrm{Cl}^-}$$

wo S den Löslichkeitsprodukt, K_w den Ionenprodukt des Wassers und $(\gamma_\pm)_0$ den mittleren Aktivitätskoeffizienten einer reinen Lösung des Metallchlorides mit derselben Konzentration des Chlors, wie im untersuchten System, vorstellt. Die pH-Werte, errechnet nach oben angegebener Gleichung, wurden mit den experimentellen Werten für eine ganze Reihe von heterogenen Systemen mit verschiedenen basischen Chloriden und Metallhydroxyden verglichen. Die Differenz zwischen den errechneten und experimentellen Werten überschreiten nicht den Wert ± 0.1.
Die oben angegebene Gleichung kann man auch zum Errechnen des Endpunkts der Fällung gebrauchen. In diesem Falle wird für die Konzentration der Metallionen ein Wert gebraucht, den man in der analytischen Chemie als praktische Abwesenheit der Ionen in einer Lösung bezeichnet, und zwar 10^{-6} Mol/Liter. [Vi.Jes.]

236 – Electrolytes in sulfuric acid (in English). R. J. Gillespie (McMaster University, Hamilton, Ontario, Canada). *Revs. Pure and Appl. Chem.*, 9 (1959) 1–32.
A review with 59 references containing single sections which deal with autodissociation of H_2SO_4 systems composed of acids and bases in H_2SO_4, acid–base reactions, cryoscopic and osmotic phenomena in H_2SO_4, conductivity, apparent molar volumes and viscosity. [Ca.Cas.]

237 – Solution energy of fluorides and the standard electric tension of fluorine in methanol (in French). B. Jakuszewski and S. Taniewska-Osińska (Institute of Physical Chemistry, University of Lodz, Poland). *Zeszyty Nauk. Uniw. Łódz., Ser. II*, (1959) 97–100.

The formula $-\Delta F = \Delta S + A$ (where ΔS is the entropy of solvation and A is a constant) was used in calculating the free energy ΔF of solvation of alkali halogenides. The constant A has the same value for K^+, Rb^+ and Cs^+, but different values for H^+, Li^+ and Na^+. The value $+2.43 \pm 0.01$ V was given for the standard electric tension of fluorine in methanol. [Ca.Cas.]

238 – **Use of the Hammett equation for the determination of ionization constants of phosphor-organic acids in 7% and 80% alcohol** (in Russian). T. A. Mastrjurova, T. A. Melentieva, A. E. Šipova and M. I. Kabačnik (Institute of Elementary Organic Compounds, Academy of Sciences, U.S.S.R.). *Zhur. Obshcheĭ Khim.*, 29 (1959) 2178–2182.
Die Bestimmung der pK-Werte erfolgte mit Hilfe der pH Konstanten teilweise neutralisierter Lösungen (30, 50 und 70%ige Neutralisation) mit einer Glaselektrode und einem elektronischem Potenziometer, die auf einen biphtalat-Puffer mit einem pH = 4.00 kalibriert wurden. Die Konzentration der gemessenen Lösungen betrug 5.10^{-3} M. Die Berechnung der pK-Werte erfolgte nach der Kumpler'schen Formel. Die Synthese der untersuchten organischen Phosphorsäuren erfolgte in bekannter Weise. Es wurden die σ-Konstanten für die, an das Phosphoratom gebundenen C_6H_5—O— und n-CH_3—C_6H_4—O— Gruppen bestimmt.
Anhand der Bestimmung der Ionisationskonstanten der Phosphorsäure im 7% und 80%igen Alkohol wurde bewiesen, dass in Übereinstimmung mit der Gammett-formel die Werte dieser linear von den σ-Konstanten abhängen. Es sind die Charakteristiken der untersuchten organischen Phosphorsäuren angeführt. [Vi.Jes.]

239 – **Test of the Fuoss–Onsager conductance equation and the determination of ion sizes in dimethylformamide** (in English). J. E. Prue and P. J. Sherrington (The University, Reading, Great Britain). *Trans. Faraday Soc.*, 57 (1961) 1795–1808.
The conductivity of various salts in dimethylformamide was measured, the following results being obtained; Li, Na, K, Rb, Cs, Tl, NH_4 and Ag perchlorates and potassium iodide are completely dissociated, in agreement with the predictions of the Fuoss–Onsager equation. Incomplete dissociation occurs with lithium chloride, silver nitrate and dimethylthallic iodide. By calculating limiting ionic conductances and Stokes law radii, the solvation of cations only was tested. A comparison was made with published data in various solvents. [Fr.Pan.]

240 – **Correlation between dissociation constants and polarographic half-wave electric tensions of some *iso*quinoline derivatives** (in Hungarian). K. Györbiró (Institute of Inorganic Chemistry, Technical University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 68 (1962) 26–27.
Es wurde ein charakteristischer Zusammenhang zwischen der polarographischen Halbstufenspannung und der Dissoziationskonstante einiger, zur Gruppe der Isochinoline gehörenden Basen, gefunden. Die Halbstufenspannung verschiebt sich nämlich mit zunehmender Stärke der Base in negative Richtung, und der Zusammenhang zwischen $E_{1/2}$ und Basenexponent ist beinahe linear. [J.Inc.]

See also abstracts nos. 308, 309, 360, 379, 386, 387, 409, 444.

2. Apparatus and accessories

241 – **A simple pH meter also suitable for glass electrodes** (in English). E. Csanády. *Magyar Kém. Lapja*, 16 (1961) 578–580.
Es wurde über ein einfaches auch zu Glaselektroden anwendbares pH-Messinstrument berichtet. Die Kennzeichen des Instruments sind die folgenden: Messgenauigkeit (bei 2–10 pH-Intervall und bei 5.10^{-7} Ohm inneren Widerstand), 6 mV; optimale Stromempfindlichkeit, 10^{-13} A/Skalenteilung; Stabilität, 5%-ige Netzschwankung verursacht noch keine warnehmbare Nullpunktverschiebung. Das Schaltbild vom Instrument is gegeben. [J.Inc.]

242 – **Apparatus for measuring adsorption from solution on solid metal electrodes** (in English). M. Green, D. A. J. Swinkels and J. O'M. Bockris (John Harrison Laboratory of Chemistry, University of Pennsylvania, Philadelphia, Pa., U.S.A.). *Rev. Sci. Instr.*, 33 (1962) 18–21.

A description of an apparatus for measuring the adsorption of organic molecules on solid metal electrodes with controlled electric tension is given. The apparatus consists essentially of a metal tape which is passed through an electrolyte bath containing a tagged organic substance. This tape, after attaining adsorption equilibrium, passes into a cleaning chamber and the adsorption chamber. The tape electrode is polarized against a Pt-gauze auxiliary electrode, and the tension is measured *vs.* a S.C.E. The thickness of the adhering layer is then measured by a capacitance method. This apparatus has been used to investigate the adsorption of thiourea on nickel from 0.5 *M* sodium sulphate solution. [G.Mar.]

243 – Polarecord E 261, a device for rapid polarography and special electrochemical analytical methods (in German). S. Wolf. *Chemiker Ztg.*, 84 (1960) 429–430.
A method for fast polarography (60 sec) is described, which is based on increased Hg dropping, voltage scanning and recording rates. Under these conditions the limiting current is independent of electric tension, noise is reduced, second-type maxima are practically suppressed, the depleting effect is excluded, damping is reduced, etc. Conventional operating techniques are, however, possible. This apparatus can also be used as a d.c. millivoltmeter, connected to a coulometer, for coulometric titrations, and also for chronopotentiometry. [Ca.Cas.]

244 – A reference electrode for certain molten salt solutions (in English). G. W. Harrington and H. T. Tien (Department of Chemistry, Temple University, Philadelphia, Pa., U.S.A.). *J. Phys. Chem.*, 66 (1962) 173–174.
Instructions are given for the construction of a comparison electrode to be used in molten salt solutions. It consists of a Pyrex bulb about 15 mm diameter on the end of 5 mm o.d. tubing and filled with either mercury, cobalt amalgam or Li–K eutectic and containing 0.8 mole % $CoCl_2$. Contact is made by means of a platinum or tungsten wire. The electrode should be equilibrated in the molten solvent before use. [D.S.Ru.]

245 – Conductometric analysis and monitoring of acid concentration in working muddy products (in English). G. G. Eichholz and A. H. Bettens (Department of Mines and Technical Surveys, Mines Branch, Mineral Science Division, Ottawa, Canada). *Can. Mining Met. Bull.*, 53 (1960) 901–907.
A simple apparatus is described, by means of which conductometric measurements (with temperature compensation) are easily accomplished; its use for acid concentration analysis in muddy products encountered in mineral extraction is recommended. [Ca.Cas.]

246 – Electrical conductance cell assembly for use with aqueous solutions up to 800° and 4000 bars (in English). E. U. Franck, T. J. E. Savolainen and W. L. Marshall (Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A.). *Rev. Sci. Instr.*, 33 (1962) 115–117.
In this cell, one electrode is the wall of the cylindrical cell and the other electrode is a small platinum cylinder at the end of a platinum rod. This rod is insulated by a tube of Al_2O_3. In this assembly there are no concentrated mechanical forces at a high temperature. The temperature is controlled by a Chromel–Alumel thermocouple, around 400° to within 1° and around 700° to within 2°. The measurements of the pressure are made by a series of calibrated Bourdon gauges and are accurate to well within 1% between 100 and 4000 bars. The cell constant (about 0.3 cm^{-1}) was determined with a 0.010 *M* KCl solution at room temperature and at various pressures. [G.Mar.]

247 – A simple electrophoresis apparatus (in English). T. Santhanagopalan (Biochemical Laboratory, General Hospital, Pondichéry, India). *Current Sci. (India)*, 29 (1960) 97–98.
Description of an easily built paper electrophoresis apparatus for work in the 120–140 V range, which requires small amounts of buffer and is suitable for current biochemical and clinical investigations. [Ca.Cas.]

248 – Development of a simple high-resolution mobility analyser for small, charged particles (in English). G. Langer, J. Radnik and L. Templeton (Armour Research Foundation, Illinois Institute of Technology, Chicago, Ill., U.S.A.). *Rev. Sci. Instr.*, 33 (1962) 83–84.
This mobility analyser was constructed to determine the charge of monodisperse particles 0.06–0.1 μ in diameter. The aerosol, produced by a red hot platinum wire, is passed as a stable filament centered between a collector plate and a high voltage plate. When an electric tension is applied to the high voltage plate, the charged particles are deflected towards the collector plate. The current due to the charges is determined as a function of voltage to obtain mobility. [G.Mar.]

249 – Improved electrodes for the continuous measurement of sodium and potassium (in English). H. D. Portnoy, L. M. Thomas and E. S. Gurdjian (Department of Neurosurgery,

Wayne State University College of Medicine, Detroit, Mich., U.S.A.). *Talanta*, 9 (1962) 119–124.
A method for constructing sodium and potassium selective glass electrodes from NAS 11–18 and KAS 20–5 selective glasses is described. The electrodes gave the theoretical slopes for ten-fold dilution of the respective sodium or potassium ion activity using both a calomel comparison electrode with liquid junction and a Ag–AgCl electrode without liquid junction. They are capable of continuously recording the change of sodium and potassium activity. The pair of electrodes is able to distinguish a change of less than 0.5 mequiv/l of sodium and 0.5 mequiv/l of potassium when used in 130–150 mequiv/l of sodium and 2–6 mequiv/l of potassium containing biological solutions. [J.Inc.]

250 – Polarisation of the dropping mercury electrode by intermittent direct current in the presence of cadmium ions (in Hungarian). J. Dévay (Institute of Physics and Chemical Radiology, L. Eötvös University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 66 (1960) 203–207.
The effect of intermittent direct current on the polarisation of the dropping mercury electrode, in the case of the deposition of Cd^{2+} ions, was investigated by oscilloscopic measurements. It was found that the periodic current interruptions increase the depolarisation of the electrode in that range where the diffusion current changes with the electrode tension. [J.Inc.]

251 – Electrophoresis apparatus for measuring ζ potentials of alumina particles and related measuring methods (in Czech). J. Přikryl and J. Krajča. *Silikáty*, 4 (1960) 46–51.
An apparatus is described, whose cell is a slight modification of Tiselius' cell, permitting operation voltages up to 700 V. The ζ potential is measured from the migration of the sol–ultrafiltrate boundary. Reproducibility is ± 1–3 mV. [Ca.Cas.]

252 – Electrochemical oxygen meter (in English). R. R. T. Morgan (Atomic Energy Commission Research Establishment, Lucas Heights, New South Wales, Australia). *Nuclear Sci. Abstr.*, 16 (1962) 195. *Abstract No.* 1698.

253 – Butyltriethylammonium hydroxide as titrating agent for the potentiometric determination of weak acids in non-aqueous solvents (in German). P. Fijolka and I. Lenz (Plastics Institute, German Academy of Science, Berlin, Germany). *Plaste u. Kautschuk*, 7 (1960) 169–170.
Adipic acid and polyesters can be titrated potentiometrically in organic solvents with butyltriethylammonium. This has the advantage over sodium ethoxide that its salts are more soluble in the solvents used, but the 0.01 N solutions are not stable, and H_2O is formed during the titration. [Gio.Ser.]

254 – Tetramethylguanidine: a new solvent for titrating weak acids (in English). T. R. Williams and J. Custer (Chemistry Department, College of Wooster, Wooster, Ohio, U.S.A.). *Talanta*, 9 (1962) 175–177.
The use of 1,1,3,3-tetramethylguanidine as a solvent for titration of acidic compounds is described. The titrations may be carried out using a glass–calomel electrode pair and tetrabutylammonium or tetramethylammonium hydroxide as titrant in a titration cell, under a nitrogen atmosphere. The titrated phenol derivatives produced satisfactory tension inflexions in the region of the equivalence point. The commercially available solvent was purified only by distillation at 159–160°. [J.Inc.]

See also abstracts nos. 232, 258, 364.

3. Polarography

255 – Amperometric analysis and its recent developments (in Polish). E. Michalski (Institute of Inorganic Chemistry, University, Lodz, Poland). *Wiadomości Chemi.*, 14 (1960) 411–423.
A review on amperometric analysis, together with the author's own data on applications avoiding an external voltage source. [Ca.Cas.]

256 – High-speed cinematographic investigation at the dropping mercury electrode (in English). R. J. Newcombe and R. Woods (Department of Chemistry and Biology, College of Technology, Liverpool, Great Britain). *Trans. Faraday Soc.*, 57 (1961) 130–134.
A dropping mercury electrode was examined cinematographically in 0.1 *N* KCl, 8,000 exposures/sec being made. The current–time relationship was examined with an oscilloscope at the same time. At low dropping times a discontinuity was discovered, not previously reported in the literature, as drop coalescence occurred. The results of Smith (*Trans. Faraday Soc.*, 47 (1951) 63) concerning the area–time relationship were confirmed. [Fr.Pan.]

257 – Analytical chemistry at low concentrations (in English). J. T. Stock (Connecticut University, Storrs, Conn., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 3943. *Abstract No.* 30585.

258 – Measurement and approximate calculation of the resistance of the polarographic cell (in Hungarian). J. Dévay (Institute of Chemical Radiology, L. Eötvös University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 66 (1960) 207–210.
Es wurde eine oscilloscopische Methode zur Messung und eine annähernde Methode zur Berechnung des Widerstandes der polarographischen Zelle ausgearbeitet. Mit der Formel

$$R = \frac{4\varrho}{9\pi k t^{1/3}}$$

kann man die Berechnung mit der Genauigkeit von 10–15% ausführen, wo ϱ der spezifische Widerstand, t die Tropfzeit und k eine aus den Tropfenverhältnissen berechenbare Konstante ist. [J.Inc.]

259 – Determination of copper and iron in arsenic by means of ion exchange (in Russian). L. N. Rozanova and G. A. Katajev (Tomsk V. V. Kuibyshev State University, U.S.S.R.). *Zhur. Priklad. Khim.*, 32 (1959) 2574–2575.
As^{5+} befindet sich in saurer Lösung und wird von den Verunreinigungen durch eine Ionentauscherkolonne getrennt. Fe^{3+} und Cu^{2+} werden im Eluat in einem Seignettesalz-Puffer polarografisch bestimmt. Cu^{2+} gibt zwei Wellen ($E_{1/2} = -0.38$ V und -0.54 V). Fe^{3+} gibt auch zwei Wellen, die bei genügender Gelatine-Konzentration und Abwesenheit von Cl-Ionen in eine einzige Welle übergehen ($E_{1/2} = -1.62$ V). In der zu analysierenden Lösung wird zuerst das Kupfer bestimmt (-0.2 bis 0.8 V) und nach einem Zusatz von 5 Tropfen 0.5%-iger Gelatine-Lösung, das Eisen (-1.2 bis -1.8 V). Die Höhen der Wellen sind linear Konzentrationsabhängig. [Vi.Jes.]

260 – Polarographic determination of the formation constants of the oxalate complexes of copper(II) and cadmium(II) in light and heavy water (in English). D. L. McMasters, J. C. Di Raimondo, L. H. Jones, R. P. Lindley and E. W. Zeltmann (Department of Chemistry, Beloit College, Beloit, Wisc., U.S.A.). *J. Phys. Chem.*, 66 (1962) 249–252.
The over-all formation constant of copper(II) oxalate was found to be $1.87 \cdot 10^9$ ($\log K_2 = 9.27$) in light water and $3.27 \cdot 10^9$ ($\log K_2 = 9.51$) in heavy water.
The overall formation constants for cadmium(II) oxalate complexes were found to be as follows, in light water: $K_1 = 4.10 \cdot 10^2$, ($\log K_1 = 2.61$); $K_2 = 1.29 \cdot 10^4$, ($\log K_2 = 4.11$); $K_3 = 1.15 \cdot 10^5$, ($\log K_3 = 5.06$); and in heavy water: $K_1 = 4.60 \cdot 10^2$, ($\log K_1 = 2.66$); $K_2 = 1.60 \cdot 10^4$, ($\log K_2 = 4.20$); $K_3 = 1.49 \cdot 10^5$, ($\log K_3 = 5.17$).
The data were determined at 25.0 ± 0.05° and ionic strength 1.00 with sodium nitrate. [D.S.Ru.]

261 – Polarographic research on heavy metal chloride solutions in NaCl–KCl melts (in Ukrainian). J. K. Delimarski and W. W. Kusmovitch (Institute of General and Inorganic Chemistry, Academy of Sciences, Ukrainian S.S.R.). *Dopodivi Akad. Nauk Ukr. R.S.R.*, (1959) 55–59.
Polarographic investigations of heavy metals (Cu^+, Cu^{2+}, Ag, Zn, Cd, Tl, Pb, Co and Ni) dissolved as chlorides in molten NaCl–KCl mixtures at 660–680° demonstrated that the diffusion current is proportional to the molar fraction while the Heyrovský–Ilkovič law is obeyed. The half-wave electric tensions are almost constant (there is not, however, correspondence with the valence of simple ions). The following activation energies were calculated (in kcal/mol): Cu^+, 6.33; $CdCl_2$, 5.90; $PbCl_2$, 4.45; $NiCl_2$, 3.00. An increase in temperature increases the diffusion current more than the corresponding viscosity diminution would predict. [Ca.Cas.]

262 – Polarographic determination of copper impurity in metallic bismuth (in Russian). D. P. Malyuga and N. V. Blyuer. *Trudy Komissii Anal. Khim., Akad. Nauk S.S.S.R.*, 12 (1960) 224–226.
Copper can be determined polarographically in metallic bismuth in concentrations as low as 10^{-3}–10^{-4}%. Cu is separated by selective precipitation with dithio-oxamide from a solution containing potassium citrate and NH_4OH. The sample (2 g) is dissolved in HNO_3 (1 : 1), 10 ml of 20% K,

NH_4^+ or Na citrate are added, and the solution is diluted 10 fold with water. After adding aqueous NH_3 to make the solution alkaline to litmus, 4 ml of 0.5% dithio-oxamide solution are added. After 3 h the precipitate (containing Cu, Ni, Co, Zn, and Cd) is filtered off, washed with 1% NH_4Cl solution, dried on a crucible, moistened with 3–4 drops of conc. H_2SO_4, dried again and heated to 550°–600°. The residue is dissolved in conc. HCl and polarographed in 0.02 *N* NH_4Cl and 0.1 *N* aqueous NH_3. The error is ± 3%. [Gio.Ser.]

263 – Studies on the techno-analytical method using square wave polarography. II. Determination of copper, zinc and iron in aluminum alloy (in Japanese). N. Tajima and M. Kurobe (Toyoda Automatic Loom Works, Ltd., Kariya-shi, Japan). *Japan Analyst,* 10 (1961) 146–151.
A method for quantitative determination of several % of copper and 0.1–1% of iron and zinc in aluminum alloys by means of square-wave polarography was investigated. Copper and zinc from 0.1 g of sample were dissolved in hydrochloric acid–nitric acid mixture and evaporated to dryness. The residue was dissolved in 5 ml hydrochloric acid. This was made up to 50 ml with water and a portion was used for registering the polarogram. Copper and zinc were determined by the waves at −0.25 and −1.05 V respectively (*vs.* a mercury pool in each case). For determination of iron, another portion of the sample solution was evaporated to dryness, and the residue was dissolved in hydrochloric acid (1 : 1) and extracted with methyl isobutyl ketone. The solvent layer was treated with water to back-extract the iron. The extract was concentrated to about 2 ml to drive off the solvent. The remainder was made up to 25 ml with water, neutralized with 0.5 *N* sodium hydroxide, (using methyl red–methylene blue mixed indicator) and acidified with 1 ml of hydrochloric acid (1 : 10). 7.5 g sodium citrate were added and the solution was made up to 50 ml with water. Part of it was used for registering polarograms at −0.3 V (*vs.* a mercury pool) for the determination of iron from the wave height. This method is less affected by the presence of co-existing ions and the determination can be carried out within 1 h. [Ta.Fu.]

264 – Rapid determination of copper and bismuth in pure lead by a polarographic method (in Japanese). T. Iga, S. Yamashita and H. Uehara (Central Research Laboratory, Mitsui Mining & Smelting Co., Ltd., Mitaka-shi, Japan). *Japan Analyst,* 10 (1961) 227–231.
Since bismuth forms stable complexes with EDTA, NTA (nitrilotriacetic acid) and other chelating agents in nitric acid solution, the polarographic wave of bismuth complex can be shifted from the copper wave, even in the presence of large amounts of lead. The most suitable concentrations of nitric acid and NTA have been sought by the authors for the determination of copper and bismuth. The influence of interfering elements, *e.g.* tin and antimony, are eliminated by oxidation with a few drops of 1% potassium permanganate. By this method, copper and bismuth in pure lead can be determined directly and simultaneously.
The base solution is composed of 0.1 *N* HNO_3 + 0.005 *M* NTA + 0.04% CMC (sodium carboxymethyl cellulose) and the $E_{1/2}$ values of copper and bismuth are + 0.004 V and −0.14 V *vs.* S.C.E. respectively. The time required for an analysis is about 1.5 h. [Ta.Fu.]

265 – Polarographic investigations on the determination of surface active substances, on the mechanism of some indicators, and a method of Br^-–Ag^+ titration using an O_2 maximum (in Japanese). H. Watanabe, S. Miyazawa, K. Yamamoto and S. Hakomori (Laboratory of Analytical Chemistry, Tokyo Institute of Technology, Tokyo (first two authors) and Department of Chemistry, Faculty of Science, Tohoku University, Japan (last two authors)). *Japan Analyst,* 10 (1961) 284–290.
An attempt was made to estimate the quantities of surface active substances by a polarographic method using an O_2 maximum. Approximately 15 varieties of substance were tested and the limits of determination were sought. The relations between the amounts of surface active substance and the suppression of the O_2 maximum were obtained experimentally. Four types were found in the O_2 maximum suppressing characteristics, and the correlations between the characteristics and the chemical structure were explained for some compounds.
The method was applied for studying the mechanism of absorption and neutralization indicators. A method of Br^-–Ag^+ titration using an O_2 maximum was also presented. [Ta.Fu.]

266 – Polarographic method for the analysis of acid gold alloy plating solutions (in English). A. H. Craft and K. Schumpelt (Sel-Rex Corp., Nutley, N. J., U.S.A.). *Plating,* 48 (1961) 277–279.
Plating solutions (2 ml) of Au, Co, Ni and In are boiled with conc. H_2SO_4 (1 ml) until fuming (HNO_3 is added to destroy organic matter, if present). Au is precipitated. After cooling and dilution In is precipitated by adding diluted NH_3 to bromothymol blue end-point.
The precipitate of Au and In hydroxides is filtered off, and In is redissolved with 8.5 ml of HCl

(1 : 1). To the HCl solution (plus washings) 2 drops of 2% triton are added. The solution is diluted to 50 ml, N_2 is bubbled and the polarographic wave of In is recorded at −0.65 V. The Au is weighed after ignition in a crucible. Co and Ni are determined by polarography at −1.08 V and −1.3 V, respectively, in the first filtrate, after addition of 20 ml of NH_3–NH_4Cl (325 ml conc NH_3 and 367.5 g NH_4Cl in 2 l) and 15 drops of 0.2% triton, dilution to 50 ml and deaeration.
The method is compared to a standard electrolytic method, which was found not to give reproducible results for small quantities. [Gio.Ser.]

267 – Polarographic determination of Mg in spheroidal cast iron (in Polish). J. Marcinowska. *Przeglad Odlewnictwa*, 10 (1960) 53–57.
Dissolve 2 g of the sample in 1 : 1 HCl and a few drops of H_2O_2. After evaporating to dryness, dissolve the residue in very dilute HCl, and electrolyse the resulting solution for 1–1.5 h at 10 V with a Hg cathode (the cathodic surface must be continuously stirred). To 10 ml of the electrolysed solution, brought to pH 10 by means of NH_3–NH_4Cl, add alcoholic 8-hydroxyquinoline. Determine the excess of this reagent directly by polarography at 1.15 to −1.55 V (relative step at −1.39 V). By means of a calibration curve determine the excess of complexant; hence Mg can be calculated. Precision is 3–5%. [Ca.Cas.]

268 – Chelometric titrations with amperometric end-point detection (in English). R. T. Campbell and C. N. Reilley (Department of Chemistry, University of North Carolina, Chapel Hill, N.C., U.S.A.). *Talanta*, 9 (1962) 153–167.
Anodic chelate waves may be used as indicator waves in amperometric titrations of metal ions. By this method, mixtures of metal ions may be selectively titrated, if their stability constants differ by less than 10^4. A saturated calomel and a dropping mercury electrode were used. EDTA, HEDTA, DTPA, EGTA, triene and tetrene solutions were used as titrant. The titrations were carried out in various buffer solutions for stabilizing the required pH value. The results of titrations of Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+} and Bi^{3+} ions, alone and in the presence of each other, are presented. The interference of halide ions must be eliminated by suitable methods. [J.Inc.]

269 – Amperometric determination of zinc by the pyridine-rhodanide method (in Russian). A. T. Marunina (Institute of Chemical Technology, Kazan, U.S.S.R.). *Zavodskaya Lab.*, 28 (1962) 25–26.
Two aliquots of the sample solution are placed in titration beakers: a fresh 10% sulphite solution is added to the first, until the precipitate formed initially is redissolved, and the solution is titrated at an electric tension of −0.5 V against standard potassium thiocyanide solution. Pyridine is added to the second aliquot until the precipitate formed initially is redissolved, and the total zinc and copper is titrated using the same volumetric solution. The zinc concentration is determined by difference. Fe(II) and Mn do not interfere. Zinc can be determined in concentrations higher than $5 \cdot 10^{-3}$ g moles/l with a precision of 2% rel. The volumetric solution is 0.1 *M*. Zinc is titrated at an applied voltage of −1.2 V *vs.* S.C.E. [Ot.So.]

270 – Alternating current polarography for the determination of cadmium and thallium in various metal products (in Russian). P. G. Pats. *Zavodskaya Lab.*, 28 (1962) 18–20.
The method may be used to determine Tl and Cd in concentrations of 1 : 1,000 and 1 : 10,000 *i.e.* in the range of 10^{-1}–10^{-2}%. The relative error is 15–20%. Supporting electrolytes are: for Tl— 2% H_2SO_4 and 7% H_3PO_4 ($E_{1/2}$ is −0.6 V) and 1 *M* ammonium sulphate ($E_{1/2}$ is 0.37 V), and for Cd — 1 *M* ammonium sulphate or chloride ($E_{1/2}$ is −0.6 V). The presence of a thousand fold excess of copper does not interfere. [Ot.So.]

271 – Polarographic determination of the solubilities of indium hydroxide (in Russian). P. N. Kovalenko (Rostov State University, Rostov-on-Don, U.S.S.R.). *Zhur. Neorg. Khim.*, 6 (1961) 539–542.
Mit Hinsicht auf die Gewinnung von In aus Abfällen bei der Zn-Raffination, wurde das pH beim Beginn und Ende der Fällung von Indiumsulfatlösungen mit Ammoniak, und das Lösungsprodukt des Niederschlages in Abhängigkeit vom pH der Lösungen bestimmt. Die Methode wurde schon früher veröffentlicht. Die polarographischen Bestimmungen erfolgten in einer 0.1–0.05 *N* KCl-Lösung, bei Zusatz von Methylviolett oder Methylrot bei 20°. Es werden die Intensitäten des Diffusionsstromes, die Halbstufenspannungen und das Lösungsprodukt in Abhängigkeit von der Konzentration des In-Sulfates, sowie die Änderungen der Konzentration des In^{3+} mit dem pH erhalten. Durch Extrapolation der Lösungsprodukte auf die Nullkonzentration des In^{3+}, wird das Aktivitätsprodukt zu $1.41 \cdot 10^{-33}$ bestimmt. [Vi.Jes.]

272 – Determination of thallium(I) with iodate in the presence of mercuric ions and with

iodate and permanganate *via* bromide (in English). B. Sharma (Chemical Laboratories, Banaras Hindu University, India). *Bull. Chem. Soc. Japan*, 33 (1960) 277–279.
Amperometric titration with dead-stop end-point is found to be suitable for the oxidation of thallium(I) by iodate, in the presence of mercuric ions and at low acid concentration. Oxidation by permanganate and iodate in hydrochloric acid, *via* the bromide, is also quantitative and accurate. [H.H.Ba.]

273 – Studies on polarographic analysis: electrochemical masking (in Japanese). T. Fujinaga and Kosuke Izutsu (Chemistry Institute, Faculty of Science, University of Kyoto, Kyoto, Japan). *Japan Analyst*, 10 (1961) 63.
Reilley *et al.* used the effects of electrochemical masking with surface active substances (SAS) for the amperometric titration of metal ions with ethylenediaminetetraacetic acid (EDTA). In the present letter to the editors, the use of electrochemical masking for polarographic analysis is reported. By carefully selecting the supporting electrolyte and SAS, this method is applicable for the determination of trace elements in the presence of large quantities of other electroactive species, which are reduced at a more positive or at the same electric tension as that of the trace element. The polarogram of a solution containing $1 \cdot 10^{-2}$ *M* Cu^{2+} and $1.0 \cdot 10^{-4}$ *M* Tl^{+} in 0.1 *M* EDTA (pH 3.5) containing 0.02% Triton X-100 and saturated camphor, was registered. No copper wave appeared in advance of the Tl wave and a well-defined Tl wave was observed. By this method, concentrations of Tl as low as $1 \cdot 10^{-5}$ *M* in the presence of Cu^{2+} concentrations as high as $1 \cdot 10^{-2}$ *M* can be determined with good accuracy. [Ta.Fu.]

274 – The determination of some trace elements in silicate rocks (in English). R. E. Stanton, Alison J. McDonald and I. Carmichael (Department of Geology, Imperial College of Science and Technology, London, Great Britain). *Analyst*, 87 (1962) 134–139.
The paper describes methods for estimating Cd, Co, Cu, Pb, Ni and Zn. All but Cd are determined colorimetrically. Cd is determined by square-wave polarography. The rock was digested with hot $HF-HClO_4$ overnight and then fumed. The residue was warmed with dilute HCl until it dissolved, and the solution was buffered with a specially purified pH 11 buffer containing sodium citrate, hydroxylamine hydrochloride and NH_3. The buffered solution was extracted exhaustively with dithizone in CCl_4. The organic phase was evaporated to dryness and decomposed by heating with $H_2SO_4-HClO_4$ to fuming. The residue was dissolved in dilute HCl and a portion analysed for Cd with a Mervyn-Harwell square wave polarograph, after adding hydrazine hydrate and H_3PO_4. Polarographic results, but not the method, were presented for Cu, Pb and Zn, as well as for Cd. [P.O.Ka.]

275 – Polarographic properties of aqueous solutions of molybdosilicic acids (in English). W. Kemula and Sz. Rosolowski (Department of Inorganic Chemistry, University, Warsaw, Poland). *Roczniki Chem.*, 36 (1962) 179–181.
Contrary to polarographically inert α- and β-molybdosilicic acids, the γ-acid is reduced in a buffer solution (pH 1.30–3.83) containing hydrochloric acid, sodium formate and *n*-butanol. The polarographic wave has a kinetic character. In the pH range indicated above, the half-wave electric tension changes from −0.34 to −0.46 V *vs.* S.C.E. The wave having the best shape is obtained in 0.5 *N* buffer, and in the pH range 1.9–2.6. It can be used for polarographic determination of small amounts (0.01 μg/ml) of silicon. [Ad.Hu.]

276 – Determination of titanium and iron in titanium–zirconium and in iron ores and concentrates by a polarographic method (in Russian). L. N. Lyuibimova and V. G. Sotshevanov (Research Institute of Mineral Raw Materials, U.S.S.R.). *Zavodskaya Lab.*, 28 (1962) 15–17.
0.1–0.5 g of sample are melted with 2–4 g sodium peroxide and the melt is extracted with hot water. The extract is boiled to decompose excess peroxide and filtered. The precipitate of hydroxides is dissolved in H_2SO_4. Hydroxides are reprecipitated by ammonia, transferred to a 100 ml volumetric flask, 2 ml 1% gelatin solution are added and the hydroxides are redissolved by addition of the supporting electrolyte — 5 *M* H_3PO_4 and 1 *M* H_2SO_4. Fe is determined at 0 to −0.2 V and Ti at −0.2 to −0.8 V applied voltage (against a mercury pool). A calibration graph is used. [Ot.So.]

277 – Amperometric titration of titanium with EDTA; d.c. and a.c. methods (in Japanese). H. Takao and S. Musha (Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Japan). *Japan Analyst*, 10 (1961) 160–165.
The polarographic behaviour of a titanium–EDTA complex has been studied in various solutions, in order to apply the complex to the determination of titanium. In view of the facts that titanium reacts quantitatively with EDTA at pH 2 and the complex gives a well-defined wave with $E_{1/2}$ at −0.22 V. *vs.* S.C.E., the direct titration of titanium with standard EDTA solution has been studied.

In addition, the a.c. amperometric method, which uses both d.c. applied voltage and a 20 mv sine wave, was proposed. It was found that titanium in the concentration range of 10–70 p.p.m. can be determined by the latter method and 50–130 p.p.m. by the former one. In both cases the errors are less than ± 2.0%. [Ta.Fu.]

278 – Direct amperometric titration of zirconium with EDTA (di-sodium salt) with the rotating tantalum micro-electrode. V. A. Khadeev and F. F. Kvashina. *Khim. i. Khim. Tekhnol.*, 3 (1960) 251–257.
Zr can be titrated amperometrically with EDTA in a 1 *N* soln of H_2SO_4, HNO_3 or HCl, using a rotating tantalum electrode. EDTA is oxidised at + 1.2 V *vs.* S.C.E. The determination is very accurate, and no interference is observed with Cl^-, NO_3^-, acetate, Bo_3^{3-}, Be, Zn, Co, U, Th, Cd, Mo, Pb, Ni, Ce^{3+}, V^5, hydrazine sulphate or NH_4Cl. CrO^{2-}, Fe^{3+}, Sb, Bi, Sn^{4+}, Ta, W, Mn, F^-, Hg and Cu do interfere. Al^{3+}, Cl^- and tartaric acid reduce the interference of F^-, Hg and Cu. The Ta electrode can be used for 10 to 15 titrations, after which it must be ignited in an alcohol flame. [Gio.Ser.]

279 – Studies on analytical methods for trace impurities in high purity substances. XII. Determination of tin in high purity copper (in Japanese). M. Miyamoto (Nippon Mining Co. Ltd., Tokyo, Japan). *Japan Analyst*, 10 (1961) 438–443.
An analytical method for determining Sn in high purity copper by a.c. polarography has been established, which can determine as little as 0.1 p.p.m. To the solution of sample dissolved in HNO_3, manganese sulfate and potassium permanganate are added, and Sn is co-precipitated with manganese dioxide by boiling the solution. The precipitate is fused with ferrous sulfate and sodium peroxide and leached with water. Using the leached solution (now free from interfering ions) Sn is determined by a.c. polarography, after the addition of hydrochloric acid and gelatin. [Ta.Fu.]

280 – Voltammetric studies using complexing agents. I. Polarographic wave of Sn(IV) in oxalic acid–sodium bromide base solution as double complexing agents (in Japanese). T. Kitagawa (Department of Chemistry, Faculty of Science, Osaka City University, Osaka, Japan). *Japan Analyst*, 10 (1961) 603–606.
Stannic ion gives a well-defined wave with $E_{1/2} = -0.47$ V *vs.* S.C.E. from a base electrolyte consisting of 1 *M* Na Br, 0.2 *M* oxalic acid and 0.004% gelatin (pH, 2.0–2.3). This step results from the reduction of Sn(IV) to Sn(O) and this wave is diffusion controlled. Its diffusion current constant is 5.40 ± 0.02 and the temperature coefficient of this wave is about +2.0%. Under these conditions, the diffusion current is proportional to the concentration of Sn(IV) in the range of 10^{-3} *M*–10^{-4} *M*. [Ta.Fu.]

281 – Polarographic determination of lead in activated charcoal. J. Branžovský and O. Kusák (Industrial Chemistry School, Ostrava-Hrušov, Czechoslovakia). *Chem. průmysl*, 11 (1961) 134–135.
The samples are burned in the presence of $Mg(NO_3)_2$ and ethanol to prevent oxidation and reduction. The residue is treated with HCl and dried on a sand bath. The residue is heated with ammonium acetate (40%) and acetic acid (20%) and diluted to 250 ml with H_2O. 20 ml of the suspension are treated with 5 ml of 1 *M* ascorbic acid and 1 ml of 0.5% gelatin. After dilution to 100 ml and filtration to remove excess of Fe, the polarogram is recorded from −0.2 to −0.8 V. The method of standard additions is used for the evaluation. Samples containing from 0.007 to 0.07% of Pb can be analysed. [Gio.Ser.]

282 – New method for polarographic determination of trace elements in zinc (in Hungarian). R. Szegedi and I. Miklòs. *Fémipari Kutató Intézet Közleményei*, 2 (1959) 154–162.
The method is based on direct polarography of the solution resulting from dissolution of the sample (as metal) in HNO_3 and evaporation and re-dissolution in 0.1 *N* HNO_3. After degassing, an aliquot of the solution is polarographed from 0 V: Cu and Bi waves are fused together, while the Pb wave is separated. After addition of EDTA, the Cu wave is separated, while Bi and Pb waves are, in turn, fused. A simple subtraction gives the amount of Pb. [Ca.Cas.]

283 – The reproducibility of results on a stationary mercury drop in the determination of ultramicro concentrations of impurities (in Russian). M. S. Zacharov and A. G. Stromberg (Polytechnic Institute, Tomsk, U.S.S.R.). *Zavodskaya Lab.*, 28 (1962) 13–15.
It has been found possible to reproduce determinations of micro-concentrations (10^{-7} *M*) of Pb, Zn and Cu by the method of standard additions on one and the same mercury drop, hanging on platinum. Reproducibility requires the use of drops having equal dimensions. [Ot.So.]

284 – Composition and solubility product constant of lead(II) ethylenediaminetetraacetate plumbate(II) (in English). N. Tanaka, M. Kamada and G. Sato (Faculty of Science, Tohoku University, Sendai, Japan). *Bull. Chem. Soc. Japan,* 34 (1961) 541–545.
Polarographic measurements are used to determine the solubility product, $K = [Pb^{2+}][PbY^{2-}]$, where Y^{4-} represents EDTA anion. The constant, at ionic strength 0.2, is $3.54 \cdot 10^{-6}$ (mol/l)^2 at 15°, $4.34 \cdot 10^{-6}$ at 25° and $5.72 \cdot 10^{-6}$ at 35°. [H.H.Ba.]

285 – Determination of trace impurities in uranium metal. XIV. Determination of trace amounts of lead in uranium metal by a.c. polarography and spectrophotometry (in Japanese). K. Saito and T. Takeuchi (Institute of Techno-Analytical Chemistry, Faculty of Engineering, Nagoya University, Nagoya, Japan). *Japan Analyst,* 10 (1961) 152–156.
The sample was dissolved in hydrochloric acid and hydrogen peroxide. For the extraction of trace amounts of lead from large amounts of uranium, dithizone–benzene solution was used. To mask the trace impurities such as Cu, Ni, Fe and Zn in uranium during the extraction procedure, ammonium citrate, sodium sulfite, potassium cyanide and ammonium hydroxide were added initially to the sample solution. The lead extracted into the dithizone–benzene solution was transferred into 0.45 N perchloric acid by shaking and determined by a.c. polarography. For spectrophotometric determination, the absorbance of the extracted dithizone–benzene solution was measured at 520mμ. Good agreement was obtained between the results from the two methods. [Ta.Fu.]

286 – Oscillopolarographic determination of lead, cadmium and zinc in dolomitic limestones (in Polish). E. Görlich and Z. Kowalski (Department of Silicate Chemistry, Academy of Mining and Metallurgy, Kraków, Poland). *Chem. Anal. (Warsaw),* 6 (1961) 937–942.
A new device for very accurate regulation of the length of mercury streaming electrodes makes differential determination with two streaming electrodes possible. Using this equipment, a method of determining zinc, lead and cadmium in dolomitic limestones was developed. The sample was dissolved in hydrochloric acid, ferric hydroxide was precipitated with ammonia, and calcium chloride was added as a supporting electrolyte. It was found that, when calcium chloride concentration exceeds 15%, no mutual interference of metal ions was observed. The main advantage of the method compared to classical polarography is a very considerable time gain, due to elimination of deaeration of the solution, determination of zinc from the same solution (in spite of its high concentration) and simplicity in evaluating results. [Ad.Hu.]

287 – Determination of traces of lead, tin, bismuth and cadmium in metallic chromium and its alloys (in Russian). Z. S. Mukhina, A. A. Tikhonova and I. A. Zhemchuzhnaya. *Trudy Komissii Anal. Khim., Akad. Nauk. S.S.S.R.,* 12 (1960) 298–310.
Chromium is removed from the solution as $CrOCl_2$ and Pb, Sn, Bi, and Cd are precipitated with H_2S at pH 3 or with methyl violet iodide. Sn can be determined polarographically, Pb and Cd can be determined by colorimetry with dithizone or by polarography, with a sensitivity of 0.1 mg per g of alloy. Bi can be determined by colorimetry of the I–Bi complex, with a sensitivity of 10 μg per g of alloy. [Gio.Ser.]

288 – Polarographic determination of vanadium in high speed steel (in Japanese). H. Asaoka (Department of Commodities, Faculty of Commerce, Hitotsubashi University, Tokyo, Japan). *Japan Analyst,* 10 (1961) 255–259.
The author devised a method for analysing high speed steel containing more than 0.5% of vanadium by recording a composite cathodic–anodic wave of a mixture of vanadous and vanadic ion in *ca.* 1 N hydrochloric acid solution, and applied it to standard samples with excellent results. The recommended procedure is as follows: decompose 0.2 g of the sample by heating with 10 ml of HCl (1 + 1) and 15 ml of $HClO_4$ (60%) until dense fumes are evolved. Add 0.5 g of NaCl in several portions. After cooling the solution, dilute to approximately 180 ml with hot water. Add sufficient aqueous ammonia (1 + 1) to produce an iron precipitate, and boil the solution for a few minutes. Filter off the $Fe(OH)_3$ and dissolve it with 20 ml of hot HCl (1 + 3). Reprecipitate it in the same way to separate most of the Mo. Transfer the $Fe(OH)_3$ into a 100 ml conical flask with 20 ml of hot HCl (1 + 1), add 0.3 g of Al to this solution in several portions, heat gently to reduce the vanadium protecting it from air-oxidation. After cooling, dilute the solution to exactly 50 ml with air-free water. Record the polarogram of this solution. The vanadium wave appears at about −0.50 V *vs.* S.C.E. If the sample contains more than 1% tungsten, the tungsten should be filtered off before the $HClO_4$ treatment. [Ta.Fu.]

289 – Amperometric determination of As(III) and As(V) in ores (in Russian). V. A. Zakharov, A. P. Voiloshnikova and O. A. Songina (S. M. Kirov State University, Kazakhian S.S.R., U.S.S.R.). *Zavodskaya Lab.,* 28 (1962) 27–28.
0.1–0.5 g of the ore sample are dissolved as far as possible in conc. H_2SO_4 and transferred, together

with the undissolved residue, into a 50 or 100 ml volumetric flask, and made up to volume. To determine As(V), about one third of the solution is shaken with 5–7 ml of a 2% cadmium amalgam to remove copper and other heavy metals. An aliquot of 5–10 ml is made up to 25 ml with conc. HCl, containing 50 g NaCl/l, and titrated against 0.01–0.02 *N* potassium iodide solution with + 0.2 V applied voltage using a mercuric iodide electrode, or without applied voltage using a saturated calomel electrode. As(III) is determined by adding 3–5 ml 10 *N* tartaric acid to a 5–10 ml aliquot, and neutralising with NaOH to Tropaeolin OO. 0.5–1.0 g sodium bicarbonate are added. As(III) is oxidised by potassium chromate solution and titrated as above. [Ot.So.]

290 – Polarographic characterisation and microdetermination of arsenic and antimony in biological media after isolation as xanthates. L. Vignoli, B. Cristau and F. Gouezo (Laboratory of Pharmaceutical Chemistry and Toxicology, Faculty of Medicine and Pharmacy, University of Aix-Marseille, France). *Ann. fals. et fraudes*, 54 (1961) 132–141.
Organic matter is destroyed by boiling the samples with H_2SO_4 and HNO_3. After treatment with KI to reduce As^{5+} and Sb^{5+} to As^{3+} and Sb^{3+}, the solution is shaken with a solution of ethyl xanthate in CCl_4. The xanthates formed are extracted in CCl_4 phase; this is evaporated and the residue is decomposed with a mixture of H_2SO_4, $HClO_4$ and HNO_3 (7 : 2 : 1). The Sb and As are reduced to their hydrides and adsorbed on paper impregnated with $AgNO_3$. The paper is eluted with 1 *M* HCl containing 1 *M* tartaric acid, and the eluate is polarographed. The half-wave electric tensions of Sb and As are −0.19 V and −0.43 V respectively. From 10–125 μg of As and from 25–100 μg of Sb can be determined. In four different experiments the recovery was from 83–91%. [Gio.Ser.]

291 – Polarographic determination of the stability constant of a Bi–EDTA complex (in Hungarian). R. Szegedi and I. Miklos. *Repts. Research Inst. Non-Ferrous Metals*, 3 (1959) 422–431.
From half-wave electric tension and exchange equilibria determination, a value of 27.87 was calculated for the logarithm of the stability constant of the Bi–EDTA complex. [Ca.Cas.]

292 – Determination of the stability constant of the bismuth–DCTA complex (in English). A. R. Selmer-Olsen (University of Oslo, Chemical Institute A, Blindern, Norway). *Acta Chem. Scand.*, 15 (1961) 2052.
By a conventional polarographic method, the stability constant of the bismuth–DCTA complex was determined in solutions containing varying amounts of Bi, 1,2-diaminocyclohexanetetraacetic acid, DCTA, and Cu. Amperometric titrations showed that the composition of the bismuth–DCTA complex was 1 : 1. The stabilities of the copper and bismuth–DCTA complexes are of the same order. A mean value of the stability constant was found to be $K_{Bi-DCTA} = 1.3 \cdot 10^{24}$. [G.Ekl.]

293 – Polarographic determination of tellurium in copper and lead compounds (in Russian). A. I. Zelyanskaya and L. S. Gorshkova. *Trudy Inst. Fiz. Metal., Ural Filial Akad. Nauk S.S.S.R.*, (1960) 141–144.
To separate tellurium from copper, the solution, containing 10% aqueous NH_3 and 5 ml of $Na_4P_2O_7$ (for complexing Fe), is passed through a column of Wofatit R (NH_4^+ form) at a flow rate of 6–8 ml per min. The percolate is evaporated to 25 ml, diluted to 50 ml with a basic solution containing 1 *N* NH_3, 1 *N* NH_4Cl, 40 g/l of Na_2SO_3 and 0.1% gelatin, and polarographed.
The half-wave electric tension of Te in this solution is −0.9 V *vs.* S.C.E. and the wave is clearly defined. Se does not interfere. To separate Te from Pb, the solution is boiled and 20% $SnCl_2$ is added until Fe is reduced. An excess of 3–5 ml subsequently precipitates Te and Se completely. After 3–4 h on a warm plate, or 12 h at room temperature, the precipitate is removed, washed with 1–2% HCl, and dissolved in 5 ml of HCl containing 3–5 drops of HNO_3. The solution is neutralised with NH_3, diluted to 50 ml with the basic solution described above, and polarographed. [Gio.Ser.]

294 – Kinetics of cathodic and anodic polarization of uranyl ions in phosphorous acid solution (in Russian). J. P. Gokhstejn and Gao Caj-shen (V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow, U.S.S.R.). *Zhur. Neorg. Khim.*, 6 (1961) 157–161.
Mit Hilfe eines oszillographischen Polarographes wurde der Reduktionsmechanismus des UO_2^{2+} an einer Quecksilbertropfelektrode in 1 *M* H_3PO_4 und 0.25 *M* K_2SO_4 verfolgt. An den Strom–Spannung-Kurven wurde nur eine kathodische Welle erhalten, welche der Reduktion des sechswärtigen Urans auf vierwärtiges entsprach. Es wurden die Reaktionsgeschwindigkeitskonstanten und die Freienergie der Aktivierung errechnet. Es wurde erwiesen, das die erwähnte kathodische Reduktion irreversibel verläuft. [Vi.Jes.]

295 – Quantitative determination of uranium salts with the oscillographic polarograph (in Italian). S. Martini. *Nuclear Sci. Abstr.*, 16 (1962) 195. *Abstract No.* 1700.

296 – Polarography of large amounts of uranium (in Russian). B. P. Melent'ev and N. S. Gertseva. *Trudy Inst. Met. Akad. Nauk S.S.S.R.*, (1960) 198–201.
The polarographic determination of large amounts of uranium can be carried out on a dropping mercury electrode using as basic medium 9 *M* NaOH containing 6% mannitol. The half wave electric tension of U is −0.95 V *vs.* the mercury anode. 0.01–2 g/l of U can be determined with an error of 2–3%. At lower concentrations the error is higher, and at higher concentrations the wave form is less satisfactory. Cu and Cr do not interfere. The ratio of Fe to U must be less than 1 : 10. Using a basic medium of 50% ammonium hydrogen citrate, the half-wave electric tension is −0.6 V. 0.05–9 g/l can be determined, but a maximum appears at concentrations higher than 4 g/l. Using derivative polarography, up to 15 g/l of U can be determined, without interfering with the maximum. Cu, Fe, Mo, V, Ti and Pb do not interfere. [Gio.Ser.]

297 – In-line polarography of uranium in process wastes (in English). R. C. Propst (Du Pont de Nemours and Co. Ltd., Savannah River Laboratory, Aiken, S.C., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 3355. *Abstract No.* 25981.

298 – Polarographic investigation on manganese chloride in a NaCl–KCl melt (in Ukrainian). W. Kusmovitch (Institute for General and Inorganic Chemistry, Academy of Sciences, Ukrainian S.S.R.). *Dopodivi Akad. Nauk Ukr. R.S.R.*, (1961) 44–47.
The behaviour of Mn ions in a NaCl–KCl melt was investigated and the following $E_{1/2}$ values were measured; the first wave at 1 V, the second wave at 1.18 V (corresponding to the process $Mn^{4+} + 4e \rightarrow Mn$) and the third wave at 1.57 V (corresponding to the process $Mn(II) + 2e \rightarrow Mn$). [Ca.Cas.]

299 – Mechanism of the molybdate catalyzed reductions of perchlorate and nitrate ions at the dropping mercury electrode (in English). G. P. Haight, Jr. (Department of Chemistry, Swarthmore College, Swarthmore, Pa., U.S.A. and Kemisk Laboratorium A, Danmarks Tekniske Højskole, Copenhagen, Denmark). *Acta Chem. Scand.*, 15 (1961) 2012–2020.
Data on the catalytic waves found for molybdate in acid solutions containing nitrate and perchlorate have been re-examined and extended. Various theories of catalytic polarographic currents are applied. Conclusions from studies in homogeneous systems are introduced and the deductions tested. Given this assumption, it is possible to determine the order of magnitude of rate constants for the bimolecular reactions of Mo(IV) with nitrate, perchlorate, and chloride, and for the disproportionation of Mo(IV). [G.Ekl.]

300 – Determination of microamounts of chloride ions on the stationary mercury electrode (in Russian). Kh. Z. Braynina and E. M. Rosenblat (State Research Institute of Chemical Reagents, Donetsk, U.S.S.R.). *Zavodskaya Lab.*, 28 (1962) 21–23.
The method is based on the principle of electrochemically concentrated anions on the surface of the mercury electrode, in the form of a film of insoluble mercury salts, which is then cathodically reduced at continuously varying electrode electric tension. The value of the maximum measured cathodic current is directly proportional to the concentration of ions to be determined in the solution. Chloride ions have been determined in the concentration range $5 \cdot 10^{-6}$–$2 \cdot 10^{-4}$ *M*. [Ot.So.]

301 – Oxidation and reduction reactions using complex formation. VIII. Amperometric titration of Mn(II) using triphosphate as a complexing agent (in Japanese). T. Kitagawa (Chemistry Institute, Faculty of Education, Kobe University, Higashinada-ku, Kobe, Japan). *J. Chem. Soc. Japan; Pure Chem. Sect.*, 81 (1960) 83–85.
Manganese(II) ion can be titrated with a standard solution of permanganate in the presence of sodium triphosphate (TPA) as a complexing agent, at a pH within the range of 6.5–7.0 To determine the end-point, amperometric titration with one polarized rotating platinum electrode was applied, and the most suitable conditions were studied. It was shown that the titration can be carried out successfully under the following conditions: 1), at an applied electric tension of + 0.35 or +0.75 V (*vs.* S.C.E.); 2) in the presence of a few drops of 1% Triton X-100; 3), in the presence of 0.5–2 g of TPA (for 1.6–10 mg of Mn content). The relative error was shown to be 0.8%. [Ta.Fu.]

302 – Studies on the analytical applications of onium compounds. XIX. Amperometric titrations of permanganate and perchlorate with tetraphenylphosphonium chloride (in Japanese). H. Nezu (Department of Chemistry, Faculty of Science, University of Hiroshima, Hiroshima, Japan). *Japan Analyst*, 10 (1961) 571–575.
The investigation dealt with the application of tetraphenylphosphonium chloride as a quantitative

reagent for permanganate and perchlorate by amperometric titration. The titration of permanganate (10^{-3} F) in 0.5 F sodium sulfate could be carried out within an error of $\pm 2\%$. In this case, 1 ml of carbon tetrachloride was added to the cell, and it formed a layer on top of the mercury in the solution compartment of the cell, thus protecting the permanganate solution from the reducible metallic mercury. The titration of perchlorate (10^{-3} F) in 2 F potassium chloride could be made within an error of $\pm 2\%$. [Ta.Fu.]

303 – Studies on the analytical applications of onium compounds. XX. Amperometric titrations of several onium compounds with sodium tetraphenylborate (in Japanese). H. Nezu (Department of Chemistry, Faculty of Science, University of Hiroshima, Hiroshima, Japan). *Japan Analyst*, 10 (1961) 575–579.
The investigation dealt with the application of sodium tetraphenylborate as a quantitative reagent for triphenylsulfonium, triphenylselenonium, and tetraphenylphosphonium salts by amperometric titration. A silver–silver chloride comparison electrode was used. The titrations of triphenylsulfonium salt (10^{-3} M), triphenylselenonium salt (10^{-3} M) and tetraphenylphosphonium salt (10^{-3} M) were carried out within an error of $\pm 3\%$. The precipitation reactions were formulated as:
(1) $Ph_3SCl + Ph_4BNa = Ph_3SPh_4B + NaCl$
(2) $Ph_3SeCl + Ph_4BNa = Ph_3SePh_4B + NaCl$
(3) $Ph_4PCl + Ph_4BNa = Ph_4PPh_4B + NaCl$
The solubility products of these precipitates were estimated from the polarographic data, and were of the order of 10^{-8}. [Ta.Fu.]

304 – The use of iodine chloride for the amperometric titration of sodium sulphite, stannous chloride, rivanol (ethacridine lactate) and quinine hydrochloride. A. I. Gengrinovich, L. E. Korneva and A. M. Murtazaev. *Trudy Tashkent. Farm. Inst.*, 2 (1960) 355–358.
The compounds are titrated with ICl solution in 0.1 N HCl using a rotating platinum electrode without external electric tension. Na_2SO_3 and $SnCl_2$ are oxidised by ICl; ethacridine lactate forms a mono-iodo product, and quinine hydrochloride forms an addition product of ICl with the vinyl group. The current is due to I^+. The reaction of quinine hydrochloride is complete in 25–30 min, and that of the other compounds in 2–3 min. The method allows the determination of very small amounts of the compounds with great accuracy and reproducibility. [Gio.Ser.]

305 – Amperometric redox titration without external voltage. II. Titration of reversible systems by reversible titrants (in Polish). E. Michalski and N. Pawlik (Department of Inorganic Chemistry, University, Lodz, Poland). *Chem. Anal. (Warsaw)*, 6 (1961) 943–948.
When a reversible titration system is titrated with a reversible titrant, electroactive products are formed in the course of titration. Thus, in amperometric end-point detection without external voltage, the titration curves have no sharp inflexion points. Therefore, the reaction product should be bound in a stable complex or in a slightly soluble precipitate. According to these remarks, satisfactory results were obtained when ferrous ions were titrated with ceric ions in the presence of tartrate, citrate or pyrophosphate. In the last case, good results were obtained for 0.1 N but not for more dilute solutions. Potassium ferrocyanide was successfully titrated with ceric ion in the presence of zinc nitrate. No positive results were obtained in the titration of ferrous salts with iodine. [Ad.Hu.]

306 – Polarographic investigation of iron and tin chlorides in NaCl and KCl (in Russian). W. Kusmovitch (Institute of General and Inorganic Chemistry, Academy of Sciences, Ukrainian S.S.R.). *Dopodivi Akad. Nauk Ukr. R.S.R.*, (1961) 344–348.
In the molten system $FeCl_2$–NaCl–KCl, polarographic waves arise from cathodic processes only. The first one ($E_{1/2}$ 0.52 V) corresponds to the reaction $Fe^{3+} + 3e \rightarrow Fe$, the second one ($E_{1/2}$ 0.87 V), which appears at concentrations of 0.04 mol% or more, corresponds to the reaction $Fe^{2+} + 2e \rightarrow Fe$. A presumably two-electron reaction was demonstrated in the system $SnCl_2$–KCl–NaCl which gives asymmetric polarograms (corresponding to true concentration polarization). [Ca.Cas.]

307 – A reversible complex of cobaltodihistidine with molecular nitric oxide (in English). P. Silvestroni and L. Ceciarelli (Istituto di Chimica Generale, Università di Perugia, Perugia, and Istituto di Chimica Generale, Università di Roma, Rome, Italy). *J. Am. Chem. Soc.*, 83 (1961) 3905–3906.
Cobaltodihistidine (CoD_2, colorless) forms a violet 1 : 1 complex with nitric oxide in aqueous solution; the complex is reversibly decomposed by degassing or acidification. Prolonged treatment with nitric oxide results in an oxidation product, CoD_2^+. The behavior of the CoD_2 and CoD_2^+ species and the complex of the former with nitric oxide have been examined polarographically in phosphate buffer at pH 7.5 and histidine concentration 0.1 M. Nitric oxide-free solutions of CoD_2^+ yield a reduction wave ($E_{1/2} = -0.21$ *vs.* S.C.E.) corresponding to a one electron reduction to CoD_2.

In the presence of nitric oxide, two waves are obtained ($E_{1/2} = -0.16$ and -0.42). Nitric oxide-free solutions of CoD_2 yield an oxidation wave ($E_{1/2} = 0.20$); in the presence of nitric oxide this species yields an oxidation wave ($E_{1/2} = -0.16$) and a reduction wave ($E_{1/2} = -0.40$). The interpretation, given these polarographic results (with some additional vapor pressure, spectrophotometric, and coulometric data), indicates that CoD_2 exhibits with nitric oxide the same "carrier" properties which it shows with oxygen. [R.Mur.]

308 – Partition coefficients in mixed solvents. I. Ideal mixture of solvents (in English). W. Kemula, H. Buchowski and J. Teperek (Department of Inorganic Chemistry, University, Warsaw, Poland). *Bull. acad. polon. sci., Ser. sci. chim.*, 9 (1961) 595–599.
Partition coefficients of very dilute solutions of 1-nitropropane (I), *o*-nitrophenol(II) and *o*-nitroaniline(III) between water and *iso*octane–hexadecane mixtures have been measured by polarographic methods. *Iso*octane and hexadecane form nearly ideal solutions ($g^E < 2$ cal/mole). From thermodynamic considerations it follows that partition coefficients defined as ratios of mole fractions (${}^{x}k_{z} = x_{z}^{\alpha}/x_{z}^{\beta}$) obey the equation:

$$\log {}^{x}k_{z}^{\infty} = \sum x_{i}\varkappa_{z_{i}} \qquad (1)$$

when the solute (z) forms ideal solutions with the solvent, where x_i represents the mole fraction of solvent, and $\varkappa_{z_i}$ is constant. For Hildebrandt–Scatchard solutions the following equation seems more valid,

$$\log {}^{x}k_{z}^{\infty} = \sum \varphi_{i}\, x_{z_{i}} \qquad (2)$$

where φ_i represents the volume fraction. In case (I), partition coefficients obey eqn. (1), and in cases (II) and (III) they obey eqn. (2). [Ad.Hu.]

309 – Partition coefficients in mixed solvents. II. Non-ideal mixtures of solvents chloroform–carbon tetrachloride and chloroform–*n*-hexane (in English). W. Kemula, H. Buchowski and J. Teperek (Department of Physical Chemistry, University, Warsaw, Poland). *Bull. acad. polon. sci., Ser. sci. chim.*, 9 (1961) 601–604.
By the polarographic method the partition coefficients (${}^{x}k^{\infty}$) of *p*-nitrophenol between water and $CHCl_3$–CCl_4 and $CHCl_3$–*n*-hexane mixtures have been measured. The dependence of ${}^{x}k$ on the phase composition was studied. The chief cause for non-linearity of log ${}^{x}k_{z}^{\infty}$ is the non-ideal mixture of solvents ($g^E \neq 0$). The equation:

$$\log {}^{x}k_{z}^{\infty} = x_{1}\varkappa_{z_1} + x_{2}\varkappa_{z_2} + g_{(12)}^{E}/4.575T$$

is valid for both mixtures studied. The equation fails when changes of solute solvation accompany changes of phase composition. This was shown for iodine solutions in CCl_4–benzene mixtures. [Ad.Hu.]

310 – Polarographic determination of tetraethylthiouram disulphide in chloroprene latex (in Czech). J. Kresta and O. Mikl. *Chem. prumysl*, [36] 11 (1961) 52–55.
Tetraethylthiouram disulfide can be extracted from the latex by means of methanolic (95%) solutions of LiCl (0.2 *M*) and Na acetate (0.025 *M*). Before polarography KOH (0.5 *M*, 0.06 ml) is added. The presence of S and other substances does not interfere; the error (95% confidence) is within ± 3.6%. [Ca.Cas.]

311 – Polarographic reduction of the phenyl substituted ethenes. I. Relation of postulated mechanism to theoretical behaviour patterns. P. G. Grodzka and P. J. Elving (Michigan University, Ann Arbor, Mich., U.S.A.). *Nuclear Sci. Abstr.*, 16 (1962) 13. *Abstract No.* 94.

312 – Polarographic reduction of phenyl substituted ethenes. II. Electrochemical kinetic parameters and mechanism in dimethylformamide. P. G. Grodzka and P. J. Elving (Michigan University, Ann Arbor, Mich., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1962) 13 . *Abstract No.* 95.

313 – Polarography of some organo-mercury compounds with —C ≡ C— bonds (in Japanese). K. Okamoto (Takamine Laboratory, Sankyo Co. Ltd., Shinagawa-ku, Tokyo, Japan). *J. Chem. Soc. Japan; Pure Chem. Sect.*, 81 (1960) 125–129.
The polarographic reductions of a series of organo-mercury compounds with —C≡C— bonds were studied in unbuffered and buffered aqueous solutions containing dioxane, tetraethylammonium ion and phosphate ion. Most of the compounds studied showed two or three irreversible reduction waves. The first wave seemed to correspond to rupture of a C–Hg bond. Two others were caused by rupture of the C–halogen bond and by the reduction of the —C≡C— bond or aromatic nucleus, that is, naphthalene, furan, etc. It was deduced from the relation between the limiting current and mercury height or temperature that these reduction waves are diffusion con-

trolled. The number of electrons concerned in these electrode reactions was calculated by the Ilkovič equation, using the values of diffusion coefficients estimated by the Stokes–Einstein equation. The reduction mechanisms were discussed. [Ta.Fu.]

314 – Simultaneous determination of formaldehyde and acetaldehyde in pentaerythritol production processes (in Polish). D. Sikorska and K. Hetmańska (Analytical Department, Institute of the Organic Chemicals Industry, Warsaw, Poland). *Chem. Anal.* (*Warsaw*), 5 (1960) 1063–1068.
Some known methods of determining formaldehyde and acetaldehyde, *viz.* by mercuric chloride, by manganometric and by ammonium sulphate methods were tested and found inaccurate. A new method was devised. It consists of determining the sum of both aldehydes in the condensation reaction with hydroxylamine hydrochloride, followed by titration of free hydrochloric acid formed. The formaldehyde content was determined polarographically in 0.1 *M* LiOH as supporting electrolyte, after deaeration with nitrogen. Acetaldehyde was found by difference. [Ad.Hu.]

315 – Polarographic investigation of glyoxylic acid (in Russian). V. D. Bezuglij, V. N. Dmitrieva, T. S. Tarasjuk and N. A. Izmajlov. *Zhur. Obshcheĭ Khim.*, 30 (1960) 2415–2421.
Auf bekanntem elektrolytischem Wege erhaltene Glyoxylsäure wird auf der Hg-Tropfelektrode in stark sauren gepufferten Lösungen mit einer Welle reduziert. Oberhalb pH 3.5 erscheint eine weitere Welle, wobei sich die Höhe des ersteren verringert und bei pH 5.0 ganz verschwindet. Bei pH 5.7 wird eine dritte Welle erhalten wobei die zweite bei pH 7.2 verschwindet. Es wurden die Halbstufenspannungen der drei Wellen und ihre Abhängigkeit vom pH der Grundlösung angegeben. Die Werte des Grenzstromes sind stark temperaturabhängig. Die Aktivationsenergie der Dehydrierung dei Glyoxylsäure wird in Abhängigkeit vom pH zu 16,900 bis 10,500 kcal/Mol bestimmt.
[Vi.Jes.]

316 – Pre-oxidation by iodine monochloride–potassium hydroxide and use of iodine monochloride end-point in the determination of hydrazine, thiocyanate, thiosulfate and glucose (in English). B. Sharma (Chemical Laboratories, Banaras Hindu University, India). *Bull. Chem. Soc. Japan*, 33 (1960) 279–282.
Pre-oxidation with hypoiodite (iodine monochloride–potassium hydroxide) and back-titration with iodate, permanganate or ceric sulfate, using an amperometric dead stop end-point, is suitable for determination of hydrazine, thiocyanate, thiosulfate and glucose. [H.H.Ba.]

317 – On the polarographic behaviour of geometric syn- and anti-isomers of oximes. N. Tütülkoff and I. Bakărdžiev (Chair of Chemistry, Faculty of Medicine, Sofia, Bulgaria). *Doklady Bolgar. Akad. Nauk*, 12 (1959) 133–136.
By investigating the polarographic behaviour of syn- and anti-isomers of furan-, pyrrol- and thiophene-2-aldoximes it was demonstrated that for α(syn) forms in water–organic solvents (MeOH, EtOH, PrOH) the ratio between the limiting currents of the first and second step decreases as the concentration of the organic solvent is raised; this ratio is independent of the presence of the β-form and increases with temperature. [Ca.Cas.]

318 – Polarography of benzenoid halogenated hydrocarbons and of their derivatives (in Czech). P. Zuman (Polarographic Institute, Czechoslovak Academy of Sciences, Prague, Czechoslovakia). *Chem. listy*, 56 (1962) 219–241.
The author discusses the monohalogeno-hydrocarbons from the point of view of the mechanism of their reduction, the influence of the solvent cation and constitution on their polarographic behaviour. In the case of iodoanilines, iodophenols and iodobenzoic acids, the influence of preceding recombination reactions is noted. In the case of polyhalogeno-derivatives, the interaction of halogens and the influence of substituents are stressed, and the course of a step-wise reaction is described. For iodinium compounds, various mechanisms described are compared, and also the influence of composition. Lastly, the polarographic behaviour of iodoso and iodoxy-benzene is described. Analytical possibilities are discussed for all classes of compounds. [Ot.So.]

319 – Electron spin resonance and polarographic investigation of substituted nitrobenzene negative ions (in English). A. H. Maki and D. H. Geske (Department of Chemistry, Harvard University, Cambridge, Mass., U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 1852–1860.
Polarographic half-wave electric tensions and current constants have been obtained for 14 *para*-substituted and 8 *meta*-substituted nitrobenzene derivatives in acetonitrile solvent. The initial reduction wave, corresponding to generation of the mononegative radical ion, was found to be reversible for most of the derivatives studied. The $E_{1/2}$ values for the *meta* compounds gave a linear correlation with σ^n and σ^0 values of the substituents. *Para* resonance energies of the *p*-amino and *p*-nitro compounds were obtained from the gross deviations of the sigma values of these substitu-

ents from the *meta* correlation line. Electron spin resonance spectra for the electrolytic *in situ* generation of the radical ions of the *para* derivatives were also obtained. The ^{14}N coupling constant of the nitro group was found to decrease as $E_{1/2}$ of the parent molecule is decreased by *para* substitution. The conclusion was reached from ring proton coupling constant measurements, that the total electron spin magnetization in the four central ring π-orbitals is approximately constant; *para* substitution merely effects a redistribution of the magnetization among these ring positions. Evidence based on hyperfine structure is presented for hindered rotation of the aldehyde group in the *p*-nitrobenzaldehyde anion, and a maximum rotational frequency of $2.8 \cdot 10^6$ c.p.s. is estimated. Comparison of the ^{19}F hyperfine coupling constant of *p*-fluoronitrobenzene with the *para* proton coupling constant of nitrobenzene leads to the ratio $a_F/a_H = 2.12$; from this ratio it is estimated that $Q_F = -47.5$. [R.Mur.]

320 – Polarographic determination of diphenylamine (in Japanese). S. Usami (Toyama Plants, Kurashiki Rayon Co., Ltd., Toyama-shi, Japan). *Japan Analyst*, 10 (1961) 137–141.
A simple quantitative determination of diphenylamine was investigated by using a polarogram of *p*-anilino-phenyl quicksilver acetate, formed from the reaction of diphenylamine and mercuric acetate. 3–4 m*M* mercuric acetate and diphenylamine (less than 60% by molar ratio to the mercuric acetate being present) were reacted in 10% acetic acid–90% methanolic solution for 7.5 h at 50°, resulting in quantitative formation of the mercury addition compound of diphenylamine. This mercury addition compound gave a two-step wave in the polarogram at around −0.3 and −0.8 V. *vs.* S.C.E. when Triton X-100 was used as a maximum suppressing agent and 0.1 *M* sodium nitrate was used as a supporting electrolyte. There were proportional relations between the concentration of diphenylamine and each of the heights of the first and second waves. The second wave was used for quantitative determination since it was more stable than the first wave. Analytical data were obtained with the coefficient of variation, 1.1–1.8%. The time required for completion of the reaction of diphenylamine with mercuric acetate can be shortened by decreasing the concentration of acetic acid in the solution, or by reducing the molar ratio of diphenylamine to mercuric acetate. [Ta.Fu.]

321 – Conformational analysis. XIV. The use of the polarograph for the determination of the conformations of the 2-halocyclohexanones (in English). A. M. Wilson and N. L. Allinger (Department of Chemistry, Wayne State University, Detroit, Mich., U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 1999–2001.
The polarographic characteristics of a number of 2-chloro- and 2-fluorocyclohexanones have been evaluated. In systems of relatively fixed conformation, such as the 2-halo-4-*t*-butylcyclohexanones, the epimer with halogen in the axial position is more readily reduced. The compound 2-chlorocyclohexanone, which contains comparable amounts of two conformations, yields a reduction potential characteristic of the more easily reducible axial form. [R.Mur.]

322 – Polarographic investigations on autoxidation of 1,2,4-trihydroxynaphthalene. II. Enzymatic and non-enzymatic oxidation of therapeutically active plant substances (in German.) G. Schenk, K. J. Fetter and R. Müller (Institute of Pharmacology, Berlin, Germany). *Arch. Pharm.*, 292, 64 (1959) 62–70.
It was polarographically demonstrated that 1,2,4-trihydroxynaphthalene gave rise to 2-hydroxy-1,4-naphthoquinone by autoxidation, one mole of O_2 being consumed and one mole of H_2O_2 being formed per mole of the hydroquinol. The half-wave electric tension for the parent substance, or of the resulting quinol (6.54 mol/l) was found to be +0.248 V, while its diffusion constant was $8.4 \cdot 10^{-6}$ cm^2 sec^{-1} (at 25°). [Ca.Cas.]

323 – Polarography of aromatic compounds. XII. The catalytic wave of 2-methyl-1,2-di-3′-pyridylpropan-1-one (in English). J. Volke (Polarographic Institute, Czechoslovak Academy of Sciences, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Communs.*, 27 (1962) 483–485.
It has been proved that the more negative polarographic wave of the substance investigated does not correspond to the reduction of the pyridine ring, as has been supposed until now, but that the wave is of catalytic origin. [Ot.So.]

324 – Polarographic determination of some derivates of acridine. II (in Russian). L. B. Rabina, Z. V. Puskareva, N. M. Voronina and N. M. Chvorova (Sverdlovsk Agricultural Institute, U.S.S.R.). *Zhur Obshcheĭ Khim.*, 30 (1960) 3480–3486.
Es wird das polarographische Verhalten von 27 Akridinderivaten in Acetat- und Ammoniak-Puffern (pH 4.48 und 9.25) verfolgt. Es sind die Halbstufenspannungen (zur normal-Kalomelelektrode) und die Werte des Grenzdiffusionsstromes in beiden Puffern angeführt. Der Mechanismus der polaro-

graphischen Reduktion und die biologische Aktivität der geprüften Derivate werden diskutiert. [Vi.Jes.]

325 – Electrochemical reduction of pyrimidine, cytosine and related compounds; polarography and macroscale electrolysis (in English). D. L. Smith and P. J. Elving (Michigan University, Ann Arbor, Mich., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 3936. *Abstract No.* 30531.

326 – Direct polarographic determination of pyridoxal in the presence of pyridoxal-5-phosphate (in English). O. Manoušek and P. Zuman (Central Research Institute of the Food Industry and Polarographic Institute, Czechoslovak Academy of Sciences, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Communs.*, 27 (1962) 486–487.
A new method is described for the determination of pyridoxal in the presence of pyridoxal-5-phosphate, which is based on the separation of waves of a trivalent pyridoxal-5-phosphate anion and a monobasic pyridoxal anion. A medium of 0.1–0.15 *M* NaOH is used. A simultaneous determination of both substances is possible only at comparable concentrations. Accuracy of the method is 2–3%. [Ot.So.]

327 – Electrochemical reduction of purine, adenine and related compounds by polarography and macroscale electrolysis (in English). D. L. Smith and P. J. Elving (Michigan University, Ann Arbor, Mich., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 3760. *Abstract No.* 29164.

328 – Polarographic determination of phenothiazine (in Japanese). S. Usami (Toyama Plants, Kurashiki Rayon Co., Ltd., Toyama, Japan). *Japan Analyst*, 10 (1961) 626–629.
Phenothiazine is used as a polymerization inhibitor of vinyl acetate. Polarographic determination of phenothiazine alone or in vinyl acetate has been investigated. Phenothiazine was treated in a methanolic solution containing 3.5% by vol. of nitric acid for 3 h at 30°, and the polarogram obtained by using this solution directly as an electrolyte showed a reducing wave at approximately −0.68 V which was directly proportional to the concentration of phenothiazine. This reducing wave was of a sulphinyl (—SO—) group formed by the oxidation of a thio (—S—) group in phenothiazine, and was affected neither by a micro amount of diphenylamine present in phenothiazine nor by vinyl acetate. A simple method for the determination of micro amounts of phenothiazine in vinyl acetate was given. [Ta.Fu.]

329 – Steric effects in organic polarography (in German). P. Zuman (Polarographic Institute, Czechoslovak Academy of Sciences, Prague, Czechoslovakia). *Acta Chim. Acad. Sci. Hung.*, 18 (1959) 141–153.
Polarography of various sydnones (in 0.17 *M* NaOH against a S.C.E.) showed that steric hindrance, caused by coplanarity of the two rings in *o*-substituted derivatives, causes a shift in the half-wave electric tension (up to 0.105 V) towards more negative values, which is lacking in the polarograms from coplanar derivatives (*e.g.* 3-4-dihydroquinolo-(1,2,c)-sydnone). In aldehydes belonging to dehydro-N,N′-tetramethyl- holarrhimine series, the shift in the half wave electric tension (from the value normal for other aldehydes) is interpreted as due to steric hindrance of hydration. Differentiation between erythro- and threo-phenylcysteine is possible on examination of their catalytic step; influence of conformation on the adsorption step is more or less evident in the hexaclorocyclohexanes and holarrhimine derivatives. [Ca.Cas.]

330 – Polarographic investigation of the alkaloid of Vinca minor (in Hungarian). T. Damokos (Institute of Inorganic Chemistry, Technical University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 67 (1961) 538–541.
The possibilities of the polarographic determination of vincamine (the alkaloid of Vinca minor) were investigated. It was found that the alkaloid can be determined only after conversion to a polarographically active product by photolysis.
Procedure: from the sample prepare a solution containing 0.5 *N* sulphuric acid and 40–800 μg/ml vincamine. Add 3 ml of this solution to 4 ml of propylene glycol. To this solution add 3 ml of 10% $NaHCO_3$ solution and mix well to eliminate the bubbles of carbon dioxide. Register the polarogram from −1.5 V, and determine the quantity of alkaloid using a calibration curve. [J.Inc.]

331 – Determination of berberine by amperometric titration (in Japanese). H. Watanabe (Yamagata Technical High School, Yamagata-shi, Japan). *Japan Analyst*, 10 (1961) 268–270.
An amperometric titration method was tried for berberine hydrochloride, using silicotungstic acid as a precipitating agent. With H_2SO_4 (0.1–0.2 *N*) as supporting electrolyte, and using a dropping

mercury electrode, the titration was made with silicotungstic acid under an applied voltage of $E_c = -0.85$ V *v.s.* S.C.E.
The results showed that one mole of silicotungstic acid combined with four moles of berberine hydrochloride. 2–20 mg of berberine hydrochloride were determined with ± 2.0% average error. [Ta.Fu.]

332 – Polarographic determination of dinitrophenyl amino acids (in Russian: English summary). I. A. Waintraub (Protein Chemistry Laboratory, The University, Kishinev, U.S.S.R.). *Biokhimiya*, 25 (1960) 688–692.
After paper chromatographic separation, the dinitrophenyl amino acid spots are eluted by means of 1 ml of a buffer (pH 8.2–8.3, contact time 20 min) and polarographed after addition of 10–20 mg Na_2SO_3 (contact time 3–4 min). Errors are within 4% for concentrations in the range $5 \cdot 10^{-6}$–$2 \cdot 10^{-4}$ *M*, and within 10% in the range $< 10^{-6}$ *M*. [Ca.Cas.]

333 – Microdetermination of impurities in monosodium glutamate with a high-sensitivity polarograph. I. Determination of L-cystine (in Japanese). J. Seto (Ajinomoto Co. Inc., Kawasaki Factory, Kawasaki-shi, Japan). *Japan Analyst*, 10 (1961) 133–137.
Monosodium glutamate (M.S.G.) often contains L-cystine, which shows a prominent peak in high-sensitivity square wave a.c. polarograms. The cystine in M.S.C. was confirmed by comparing its summit electric tension with that of the standard cystine solution in the supporting electrolyte of high-purity M.S.G. The summit electric tension of cysteine wave, observed after the reduction of cystine with sodium sulfite, also coincided well with that of pure cysteine added to M.S.G. By the method of standard additions, the cystine content in a commercial M.S.G. sample was found to be 0–0.12%. Traces of lead did not interfere with the determination. [Ta.Fu.]

334 – Microdetermination of impurities in monosodium glutamate with a high sensitivity polarograph. II. Square-wave polarographic determination of impurities in monosodium glutamate (in Japanese). J. Seto (Ajinomoto Co. Inc., Kawasaki Factory, Kawasaki-shi, Japan). *Japan Analyst*, 10 (1961) 401–406.
Application of square-wave polarography to the determination of Pb, Zn and Ca in monosodium glutamate (MSG) and other amino acids is criticized. Minute quantities of Pb can be determined (1) after dithizone-extraction, (2) after ashing, and (3) by dissolving the amino acid sample in ($HClO_4$–NaCl) supporting electrolyte, in which L-cystine does not interfere. Zn is concentrated into a HCl solution by using dithizone extraction, and the solution is then neutralized and polarographed in CH_3COONH_4–KSCN base solution. Application of the Pribil–Roubal method of determining Ca gives a good result also with square-wave polarography. With an ordinary grade product of MSG, the contents of the impurities determined are: Pb, 1.1–2.4 p.p.m.; Zn, less than 2 p.p.m.; Ca, 220–240 p.p.m. [Ta.Fu.]

335 – Polarographic determination of tubocurarine in pharmaceutical specialities (in Italian). G. Alessandro and F. Dal Brollo (Farmitalia, Milan, Italy). *Farmaco, Ed. pract.*, 16 (1961) 138–143.
To 2 ml of a solution of tubocurarine (30–70 mg in 100 ml) in H_2O, 0.1 ml of HNO_3 (density = 1.4) is added, and the solution is boiled for 1 min. After cooling, 1 *N* NaOH is added until the colour changes to pink–violet, and the solution is diluted to 10 ml with McIlvain buffer, pH 7. The solution is deaerated and the polarographic wave of tubocurarine is recorded. The half-wave electric tension is 0.43 V and the current is proportional to the concentration between 0.2 and 0.8 mg per ml, with a maximum error of 0.3%. The method is suitable for solutions to be injected and for suppositories. The latter are dissolved in $CHCl_3$, the $CHCl_3$ solution is extracted with 0.1 *N* H_2SO_4 and an aliquot of the extract is treated as described above. [Gio.Ser.]

336 – Polarographic micro-determination of parathion and malathion in admixture. D. E. Ott and F. A. Gunther (Department of Entomology, University of California, Riverside, Calif., U.S.A.). *Analyst*, 87 (1962) 70–72.
The method is a combination of Bowen and Edward's (*Anal. Chem.*, 22 (1950) 706) method for parathion and Jura's (*Anal. Chem.*, 27 (1955) 525) method for malathion. The first is based on direct polarographic reduction of the insecticide whilst the second is indirect, based on reduction of fumaric acid produced by hydrolysis of the insecticide. A Sargent Model XXI polarograph was used in conjuction with an H-cell. For parathion, a solution was used which was 0.05 *N* in KCl, 0.1 *N* in acetic acid and containing 0.01% w/v gelatin and 50% w/v acetone. Dissolved O_2 was removed with N_2 and the polarogram recorded from 0–1.0 V *vs.* S.C.E., at a sensitivity of 0.003–0.015 μA/mm and maximum damping. Wave height was proportional to concentration from 3–65 μg/ml parathion with a deviation of ± 1 μg/ml for individual points. At a concentration of 16 μg/ml parathion, the addition of up to 55 μg/ml malathion caused no significant change of wave heights. For malathion, 5 ml of an acetone solution were hydrolysed by addition of 1 ml of 0.1 *N* NaOH,

and bubbling N_2 for 3 min. 4 ml of a solution which was 0.1 *N* in KCl, 0.2 *N* in acetic acid and which contained 0.02% gelatin were added. O_2 was removed by N_2 and the polarogram was recorded from −0.9–1.4 V *v.s.* S.C.E. at a sensitivity of 0.006 μA/mm. Wave height was proportional to concentration from 9–73 μg/ml and deviation of individual points was ± 0.3 μg/ml. The lower limit for determining malathion in the presence of 16 μg/ml parathion is 25 μg/ml. [P.O.Ka.]

See also abstracts nos. 229, 240, 243, 250, 405, 414, 456.

4. Potentiometry

337 – Stability of metal-ion complexes in solution. III. Potentiometric methods for computing stability constants of polynuclear three component complexes ($M_q(OH)_pA_2$) (in Polish). L. Pajdowski (Department of Inorganic Chemistry, University, Wroclaw, Poland). *Wiadomości Chem.*, 15 (1961) 529–542.
A review with 23 references.

338 – Automatic titration in process stream analysis (in Japanese). S. Oka (Measuring and Instruments Division, Shimadzu Seisakusho, Kyoto, Japan). *Japan Analyst*, 10 (1961) 513–518.
An automatic titrator was developed for continuously measuring and controlling some manufacturing processes in the chemical industry.
This titrimetric analyzer performs batch type analysis, which eliminates some of the inaccuracies and sample flow-control problems usually associated with continuous sampling. The sequence of operations is controlled by a multiple switch programmer and a number of valves and relays. The instrument introduces precisely a definite volume of solution to be analyzed into a titration cell, by means of an automatic pipette. The titration cell has an indicator electrode to detect the equilibrium point; the solution in the cell is agitated by a magnetic stirrer. Addition of the titrant is automatically stopped when the electric tension of the indicator electrode has reached its equilibrium value. The titrant is added at a controlled flow rate, while a valve in the titrant flow-line is opened. The titration device, of course, has an anticipator. The volume of titrant consumed is then transposed to an electrical signal and measured by a pen-and-ink recorder. These operations are automatically repeated every 7 min.
Good selectivity and reproducibility over a wide field of electrochemical analysis are important features. Details of instrumentation and results of basic experiments are described. [Ta.Fu.]

339 – Static and asymmetric potentials in cells with magnesia electrodes at high temperatures (in English). M. Coll-Palagos and C. R. Masson (Atlantic Regional Laboratory, Halifax, Nova Scotia, Canada). *Trans. Faraday Soc.*, 57 (1961) 1621–1627.
The electric tension of the cell

$$\mathrm{Fe\ (l)}\ \left|\ \begin{array}{l}\mathrm{FeO}\\ \mathrm{Fe_2O_3}\\ \mathrm{MgO}\end{array}\ \right|\ \mathrm{MgO(s)}\ \left|\ \begin{array}{l}\mathrm{CaO,\ SiO}\\ \mathrm{MgO,\ Fe_2O_3}\\ \mathrm{FeO}\end{array}\ \right|\ \mathrm{Fe\ (l)}$$

was measured at 1550°, corrections being necessary for static and asymmetry tensions. The magnesia electrode behaves as an oxygen electrode, whose characteristics depend on the partial pressure of O_2. An interpretation is suggested involving anion vacancies and excess electrons. [Fr.Pan.]

340 – Quantitative studies in complex chemistry. I. Electrometric methods (in English). H. J. de Bruin and T. M. Florence (Atomic Energy Commission Research Establishment, Lucas Heights, N.S.W., Australia). *Nuclear Sci. Abstr.*, 16 (1962) 199. *Abstract No.* 1729.

341 – Determination of sodium in aluminium alloys using a sodium glass electrode (in Russian). R. S. Chernyak (Institute of Aviation Technology, Moscow, U.S.S.R.). *Zavodskaya Lab.*, 27 (1961) 536–537.
The alloy is treated with mercury dichloride, the precipitate obtained is electrodialyzed and sodium

ions enter the dialyzed solution. This is then analyzed using the electric tension difference between sodium glass electrodes immersed in the sample solution and in a reference solution. Determinations in the range of $10^{-2}\%$ are possible. [Ot.So.]

342 – Metal-polyelectrolyte complexes. IX. The poly-N-ethyleneglycine-copper (II) complex (in English). D. H. Gold and H. P. Gregor (Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, N.Y., U.S.A.). *J. Phys. Chem.*, 66 (1962) 246–249.
Weak bonding effects were demonstrated between sodium and potassium ions and synthetic polyampholyte poly-N-ethyleneglycine. In Cu(II) solutions complexes showed spectrophotometric absorption maxima in the 680–780 mμ region. Three glycine ligands were bound to the copper ion indicating 6-fold co-ordination. Potentiometric titrations in the presence of Cu(II) indicated the simultaneous bonding of two glycine units with a formation constant $k_1k_2 = 12.04$, and a third unit bound with a constant $k_3 = 2.88$. [D.S.Ru.]

343 – Differential electrolytic potentiometry. V. The precision and accuracy of applications to argentimetry (in English). E. Bishop and R. G. Dhaneshwar (Washington Singer Laboratories, The University, Exeter, Great Britain). *Analyst*, 87 (1962) 207–213.
A small constant current is passed between two indicator electrodes and the electric tension between them is measured. At one electrode a small amount of titrant is generated and its electric tension is shifted in one direction, whilst at the other electrode a corresponding amount of titrant is consumed, and its electric tension is shifted in the opposite direction. The difference in electric tension during a titration follows the first derivative of the zero current potentiometric curve. To test the method in argentimetric titrations, Ag or Ag–AgCl indicator electrodes were used and $Hg-Hg_2SO_4$ or glass electrodes were used as comparison electrodes. Results of differential electrolytic titrations were compared with those of zero-current potentiometric titrations for the titration of Cl^-, SCN^-, Br^- and I^-. Agreement between the two methods was within ± 0.04% in all cases and end-point discrimination was very much superior in the differential electrolytic titration. [P.O.Ka.]

344 – The silver electrode as an indicating electrode in chelatometric potentiometric titrations (in German). F. Štráfelda (Institute of Chemical Technology, Prague, Czechoslovakia. *Collection Czechoslov. Chem. Communs.*, 27 (1962) 343–349.
An equation is derived for the electric tension of a silver electrode at the equivalence point in the potentiometric titration of Ag^+ ions by EDTA, and the influence of pH on the course of the titration curves is discussed. Potentiometric indication with a silver electrode is proposed for the standardisation of solutions of pure silver salts in the concentration range 10^{-2} *M* to $5 \cdot 10^{-4}$ *M* in media buffered by sodium tetraborate. [Ot.So.]

345 – Study of selenocyanic complexes of silver in miscellaneous and methanol solutions (in Russian). A. M. Golub and V. V. Skopenko (T. G. Shevchenka State Institute, Kiev, U.S.S.R.). *Zhur. Neorg. Khim.*, 6 (1961) 140–143.
Durch potentiometrische Untersuchungen mittels einer Kette des Types: $Ag \mid AgNO_3, KCNSe \mid KNO_3 \mid KCl, Hg_2Cl_2 \mid Hg$, ist bei verschiedener Konzentration des KCNSe in Gemischen aus Methanol und Wasser das Studium der Selencyanidkomplexe des Silbers durchgeführt worden (bei Konzentrationen von 35, 56, 74, 83, 92 und 100 Vol. % Methanol). Es ergab sich, dass in den Lösungen mit niederer Konzentration des Methanols (bis 60%) die Komplexionen $Ag(CNSe)_3^{2-}$ überwiegen. In Lösungen mit höherer Konzentration entsteht der Komplex $Ag(CNS)_4^{3-}$.
Es wurde erwiesen, das bei niederer Konzentration des Methanols die Abhängigkeit des Logarithmus der Dissoziationskonstante vom reziproken Werte der Dielektrizitätskonstante nicht linear verläuft, im Gegensatze zu dem linearen Verlauf dieser Abhängigkeit bei höheren Konzentrationen. [Vi.Jes.]

346 – A pH study of some bivalent metal-5-sulphosalicylic acid complexes (in English). V. S. K. Nair (Chemistry Department, College of Advanced Technology, Birmingham, Great Britain). *Talanta*, 9 (1962) 27–31.
The stabilities of 5-sulphosalicylate complexes of several metal ions were investigated at 25° and at constant ionic strength (~0.1) by pH-titration, using a glass and a Ag–AgCl electrode in a cell without liquid junction. The log *K* values obtained (K = formation constant) are as follows: Mn^{2+}, $pK_1 = 5.25$, $pK_2 = 3.4$; Co^{2+}, $pK_1 = 6.47$, $pK_2 = 4.3$; Ni^{2+}, $pK_1 = 6.61$, $pK_2 = 4.2$; Cu^{2+}, $pK_1 = 9.35$, $pK_2 = 6.92$. The increasing order of p*K* values was found to be the same as that shown by the reciprocal of the cationic radius, and by the second overall ionisation potential of the metals. [J.Inc.]

347 – Studies on the hydrolysis of metal ions. 37. Application of the self-medium method to the hydrolysis of beryllium perchlorate (in English). B. Carell and Å. Olin (Department of

Inorganic Chemistry, Royal Institute of Technology, Stockholm, Sweden). *Acta Chem. Scand.*, 15 (1961) 1875–1884.
The hydrolysis of beryllium perchlorate has been studied in the concentration range $B = 0.04$–$1\ M$ by potentiometric measurements of log H at 25°. The same set of complexes as found by Kakihana and Sillén at low beryllium concentrations, namely Be_2OH^{3+} and $Be_3(OH)_3{}^{3+}$, can also explain the present data.

$$3\ Be^{2+} + 3\ H_2O \rightleftharpoons Be_3(OH)_3{}^{3+} + 3\ H^+$$
$$\log \beta_{3,3} = -8.66 \pm 0.03\ (B = 0.04\text{–}1\ M)$$

$$2\ Be^{2+} + H_2O \rightleftharpoons Be_2OH^{3+} + H^+$$
$$\log \beta_{1,2} = -3.22 \pm 0.05\ (B = 0.04\text{–}0.32\ M), -3.18 \pm 0.03\ (B = 0.64\ M), -3.15 \pm 0.03\ (B = 1\ M).$$

[G.Ekl.]

348 – The value of the electric tension of fluorite powder electrodes in the presence of flotation reagents (in Polish). A. Waksmundzki and J. Szczypa (Department of Physical Chemistry of Surface Phenomena, Polish Academy of Sciences, Lublin, Poland). *Przemysl Chem.*, 40 (1961) 330–332.
The effect of electrode preparation and cell design on the value and reproducibility of the electric tension of fluorite powder electrodes has been examined. It was found that the reproducibility of the electric tension depends on the measuring technique and electrode preparation, uniform packing of the powder and its contact with air. When the electrode powder was freshly washed with ethanol and water the electric tension increased. In constant conditions of electrode preparation, the relation between electric tension and concentration of sodium oleate collector at pH 8, 8.5 and 9 was examined. These relationships show a maximum at the collector concentration corresponding to maximum flotation efficiency of fluorite. [Ad.Hu.]

349 – Potentiometric determination of boron in steel and alloys (in Russian). P. Ya. Yakovlev and G. V. Kozina (Research Institute of Iron Metallurgy, U.S.S.R.). *Zavodskaya Lab.*, 26 (1960) 1342–1343.
1 g of the sample is dissolved in 30 ml HCl (1:1) under reflux, hydrogen peroxide is added and the mixture is boiled. Metals are precipitated by sodium hydroxide and removed by filtration. The filtrate is neutralised by HCl, made up to volume and an aliquot is taken. The solution is now brought to pH exactly 6.9, invert sugar is added, and the solution is titrated by 0.02 *N* NaOH until pH 6.9 is again reached. The volumetric solution is standardised by a standard boron solution prepared from recrystallized boric acid. A blank must be taken. [Ot.So.]

350 – Electrochemical properties of bentonite suspensions. IV. Potentiometric titration of various acid forms of askangel (in Russian). I. A. Usskow and J. T. Usskova (Shevshenko University, Ukrainian Academy of Soil Science, Kiev, U.S.S.R.). *Kolloid. Zhur.*, 21 (1959) 492–498.
Results of potentiometric titrations of electrodialysed askangel and its acid forms, prepared from this material by means of excess mineral acid or by ion-exchange resins (in the H^+ form), showed that the same value was obtained for the exchange strength only in the case of the acid forms, irrespective of the alkali used. It is demonstrable that in the untreated form, both H and Al ions are adsorbed on its surface. [Ca.Cas.]

351 – Complex formation of aluminium with 7-iodo-8-hydroxyquinoline-5-sulphonic acid (ferron) (in English). F. J. Langmyhr and Å. R. Storm (University of Oslo, Chemical Institute A, Blindern, Norway). *Acta Chem. Scand.*, 15 (1961) 1461–1466.
The two dissociation constants of ferron were determined in the presence of 0.10 *M* potassium chloride by potentiometric methods. Potentiometric titrations of mixtures of ferron (H_2A) and aluminium indicated the presence of different complexes. The stability constants of the complexes not containing hydroxyl were found to be $\log K_{MA} = 7.6$, $\log K_{MA_2} = 7.1$ and $\log K_{MA_3} = 5.6$ at 25.0 ± 0.1° and in the presence of 0.10 *M* potassium chloride. Under the same conditions the log *K* for the equilibrium $[AlA_2{}^-]/[Al(OH)A_2{}^{2-}][H^+]$ was calculated to be 5.0. [G.Ekl.]

352 – Potential of aluminium in aqueous chloride solutions. I (in English). T. Hagyard and J. R. Williams (Department of Chemical Engineering, The University, Canterbury, New Zealand). *Trans. Faraday Soc.*, 57 (1961) 2288–2294.
An oscillographic examination of the variation in electric tension for a fresh aluminium surface in aqueous KCl and/or $AlCl_3$ showed three consecutive processes: (a), anodic behaviour of Al (a rise of tension up to -1.6 V, time constant $< 10\ \mu$sec); (b), H^+ discharge (tension falling to between -1.2 and -1.5 V according to pH, time constant 1 msec); (c), formation of an oxygen or oxide film in the presence of dissolved O_2 (tension falling further to -0.48 V, time constant ~ 5 sec). [Fr.Pan.]

353 – **Potential of aluminium in aqueous chloride solutions. II** (in English). T. Hagyard and M. J. Prior (Department of Chemical Engineering, The University, Canterbury, New Zealand). *Trans. Faraday Soc.*, 57 (1961) 2295–2298.
Experimental work was performed with very small Al electrodes in *N* KCl solutions. Erratic results were always found, so that only a partial description of some phenomena can be made: no general conclusions can be drawn. [Fr.Pan.]

354 – **Studies on the hydrolysis of metal ions. 35. The hydrolysis of the lanthanum ion, La^{3+}** (in English). G. Biedermann and L. Ciavatta (Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm, Sweden). *Acta Chem. Scand.*, 15 (1961) 1347–1366.
The hydrolysis equilibria of the La(III) ion have been studied at 25° by hydrogen ion concentration measurements, using a glass electrode. The total [La(III)] was varied between 0.1–1.0 *M*, whilst the concentration of the ClO_4^- ion was held constant at 3 *M* by the addition of $LiClO_4$. The data, which indicate a slight hydrolysis in the log H range −6.5 to −8.1, can be explained by assuming the equilibria:

$$La^{3+} + H_2O \rightleftharpoons LaOH^{2+} + H^+;\ \log \beta_{1,1} = -10.1 \pm 0.1 \qquad (I)$$

$$2\ La^{3+} + H_2O \rightleftharpoons La_2OH^{5+} + H^+;\ \log \beta_{1,2} = -9.95 \pm 0.1 \qquad (II)$$

$$5\ La^{3+} + 9\ H_2O \rightleftharpoons La_5(OH)_9{}^{6+} + 9\ H^+;\ \log \beta_{9,5} = -71.45 \pm 0.1 \qquad (III)$$

Equally good agreement with the data is obtained by replacing equilibrium (III) with:

$$6\ La^{3+} + 10\ H_2O \rightleftharpoons La_6(OH)_{10}{}^{8+} + 10\ H^+;\ \log \beta_{10,6} = -78.75 \pm 0.1 \qquad (IV)$$

No other mechanism involving the formation of only three hydrolysed species could be found which would explain the experimental data.
The experimental conditions necessary for accurate results to be obtained, when the hydrolysis equilibria must be studied in poorly buffered solutions, are discussed in some detail. [G.Ekl.]

355 – **The stability of lanthanum, cerium, praeseodymium and neodymium complexes with aspartic acid** (in Russian). I. M. Batjev, S. V. Lapionov and V. M. Shulman. *Zhur. Neorg. Khim.*, 6 (1961) 153–156.
Es wurde die Bestimmung der Stabilitätskonstanten komplexer Verbindungen des Lantans, Cers, Praseodyms und Neodyms mit Asparaginsäure durchgeführt (Typen Ma^+ und MA_2^-). Die Bestimmung wurde mit Hilfe einer potentiometrischen Titration der erwähnten Komplexe mit 0.1 *N* KOH durchgeführt. Man verwendete eine Glaselektrode und arbeitete in Stickstoffatmosphäre bei Ionenstärke 0.1. Die erhaltenen Resultate wurden nach Bjerrum und Schwarzenbach ausgewertet. Es ergab sich, das die Stabilität der erwähnten Komplexe in der Reihenfolge La < Ce < Pr < Nd wächst. [Vi.Jes.]

356 – **Complex formation between Tl^{3+} and 1,10-Phenanthrolin (Ph) or 2,2'dipyridyl (Dp)** (in Russian). F. Ja. Kulba, Ju. A. Makashev and V. E. Mironov (Leningrad Lensoviet Institute of Chemical Technology, U.S.S.R.). *Zhur. Neorg. Khim.*, 6 (1961) 630–635.
Komplexbildungen werden in den Systemen Tl^{3+} und 1,10-Phenanthrolin (Ph) oder 2,2'-Dipyridyl (Dp) potentiometrisch und durch Redox-Spannungsmessung Tl^+/Tl^{3+} bei verschiedenen Verhältnissen der organischen Amine und 25° verfolgt. Die Konzentrationen des Tl^{3+} und Tl^+ werden im Intervall $0.5 \cdot 10^{-3}$–$2.0 \cdot 10^{-3}$ bei konstantem Verhältnis $c_{Tl^+}/c_{Tl^{3+}} = 1.0$ geändert. Die experimentellen Elektrodenspannungen Pt/Tl^+, Tl^{3+} und Tl/Tl^+ stimmen mit den aus der Nernst'schen Gleichung berechneten überein. Bei $[H^+] = 0.5$ und einer Ionenstärke $k = 1.0$ werden in wässeriger Lösung die Ionen $[TlPh]^{3+}$, $[TlPh_2]^{3+}$, $[TlDp]^{3+}$ und $[Tl\ Dp_2]^{3+}$ gebildet. Ihre Instabilitätskonstanten betragen $2.7 \cdot 10^{-12}$, $0.5 \cdot 10^{-10}$, $4.0 \cdot 10^{-10}$ und $0.8 \cdot 10^{-16}$. [Vi.Jes.]

357 – **Oxidation states of the elements and their electric tensions in fused salt solutions; the actinide elements** (in English). D. M. Gruen, R. L. McBeth, J. Kooi and W. T. Carnall (Argonne National Laboratory, Lamont, Ill., U.S.A.). *Ann. N.Y. Acad. Sci.*, 79 (1959/1960) 941–949.
A summary of current knowledge on the oxidation states, electric redox tensions and stabilities of the following actinide elements in molten chlorides and nitrates are given: Ac, Th, Pa, Np, Am, Cm and trans-curide. [Ca.Cas.]

358 – **Application of powder electrodes in a new method of determining the reinforcing properties of carbon black** (in Polish). A. Potocki (Department of Chemical Technology, Laboratory of Rubber Technology, Polytechnic, Gdańsk, Poland). *Przemysl Chem.*, 40 (1961) 694.
Powder electrodes prepared from various types of carbon black exhibit a characteristic value of electric tension, which can be used for describing the properties of carbon black. [Ad.Hu.]

359 – Determination of carbon in the converter process using electric cells (in Russian). B. M. Ljepinskich and O. A. Jesein. *Zhur. Priklad. Khim.*, 32 (1959) 313–317.
Die angewandte Einrichtung ermöglicht die gleichzeitige Messung der thermoelektrischen Spannungen zwischen Wolfram und Graphit, d.h.:

$$\mathrm{C} \mid \mathrm{Fe, C}_{\text{gesättigt}} \mid \mathrm{W} \qquad \text{(I)}$$

weiter die elektrische Spannung der Zelle:

$$\mathrm{C} \mid \underset{\text{Schlacke (fest)}}{\mathrm{MgO, CaC_2, B_2O_3}} \ \underset{\text{(flüssig)}}{\mathrm{Fe, C}} \mid \mathrm{W} \qquad \text{(II)}$$

und zuletzt die der Zelle:

$$\mathrm{Fe, C} \mid \mathrm{MgO, CaC_2, B_2O_3} \mid \mathrm{Fe, C}_{\text{gesättigt}} \qquad \text{(III)}$$

Nach einer Korrektion auf die thermoelektrische Spannung (C–W) stimmten die gemessenen Spannungen der Konzentrationszelle (III) mit den berechneten in gewissen Grenzen überein. Die Spannung der Zelle ist eine Funktion der Konzentration des Kohlenstoffes im flüssigen Stahl. Versuche in einem 50-kg Konverter bestätigten die Möglichkeit die Änderungen des Kohlenstoffgehaltes im flüssigen Stahl qualitativ zu beurteilen. [Vi. Jes.]

360 – Equilibrium electrode tension of Zr in miscellaneous molten salt solutions of chloride and fluoride (in Russian). M. V. Smirnov, V. J. Pomarov and A. N. Baraboshkin (Ural Electrochemistry Institute, Academy of Sciences, U.S.S.R.). *Doklady Akad. Nauk S.S.S.R.*, 133 (1960) 409–412.
In einer Quartzglaszelle mit einer Chlor-Vergleichselektrode wird die Gleichgewichtsspannung des Zr in equimolaren KCl–NaCl Schmelzen mit einem Gehalt von 0.17–1.05% Zr und 2.04–15.82% an Fluor gemessen. Die Gleichgewichtsspannung wird in Abhängigkeit von Temperatur und der Konzentration an freien F-Ionen angegeben. Anhand der Ergebnisse und theoretischer Überlegungen über die Komplexbildung in der Schmelze wird für die Gleichgewichtsspannung,

$$E = -3.50 + 5.4 \cdot 10^{-4}\, T + \frac{1.984}{n}\, 10^{-4}\, T.\mathrm{lg}\, \frac{[\mathrm{Zr}]}{[\mathrm{F}^-]^m}$$

erhalten, (m, mittlere Anzahl der an das Zr-Atom gebundenen F-Ionen im Komplexe; n, mittlere Valenzzahl des Zr in der Schmelze). Für Näherungsberechnungen im Bereiche $75 > [\mathrm{F}]:[\mathrm{Zr}] > 10$ wird $m = 5$ und $n = 3.2$ empfohlen. [Vi. Jes.]

361 – Stability of complexes of several carboxylic acids formed with bivalent metals (in English). M. Yasuda, K. Yamasaki and H. Ohtaki (Chemical Institute, Nagoya University, Chikusa, Nagoya, Japan). *Bull. Chem. Soc. Japan*, 33 (1960) 1067–1070.
Stability constants are given (from pH titration measurements) for the complexes of lead, copper, cadmium, zinc and nickel with acetic, benzoic, *o*-methoxybenzoic, succinic, itaconic, glutaric, adipic, phthalic, malonic, maleic, citraconic, diglycolic and thiodiglycolic acids. The stabilities followed the order $\mathrm{Pb} > \mathrm{Cu} > \mathrm{Cd} > \mathrm{Zn} > \mathrm{Ni}$. [H.H.Ba.]

362 – Determination of antimony in technical alloys. M. E. Gárate and F. Burriel-Marti (Central Laboratory, R.E.N.F.E., Madrid, Spain). *Rev. univ. ind. Santander*, 3 (1961) 13–16.
Antimony alloys can be dissolved easily by mixtures of HNO_3 and HF diluted with water. The composition of the mixtures can be varied according to the type of alloy. Sb is present in the solution as Sb^{3+} and can be determined by titration with $KBrO_3$. The titration is carried out potentiometrically using a Pt wire cathode and a normal calomel anode. Only arsenic interferes. [Gio.Ser.]

363 – The formation constants of the tantalum fluoride system. II. Tantalum electrode potential studies (in English). L. P. Varga and H. Freund (Department of Chemistry, Oregon State University, Cornwallis, Oreg., U.S.A.). *J. Phys. Chem.*, 66 (1962) 187–189.
The electrical tension of the cell, $\mathrm{Ta} \mid \mathrm{Ta}^{5+}, \mathrm{HF}(1\ M\mathrm{ClO_4}^-) \mid \mathrm{H_2}, \mathrm{Pt}$ was determined and the relation:

$$E_{\mathrm{cell}} = 0.769 + 0.182 \log(\mathrm{F}^-) + 0.013\, [\log (\mathrm{F}^-)]^2$$

was obtained. The existence of $\mathrm{TaF_9}^{4-}$ is suggested. [D.S.Ru.]

364 – Electrochemical device for measuring oxygen (in English). J. R. Neville (Physiology–Biophysics Brand School of Aerospace Medicine, U.S.A.F. Brook Air Force Base, Texas, U.S.A.). *Rev. Sci. Instr.*, 33 (1962) 51–55.
This paper describes an electrochemical device, especially designed for measuring oxygen in gases.

The design involves a gold indicator electrode and a cadmium comparison electrode in an insulated housing. The cell is filled with a solution of KCl and encapsulated with a gas-permeable membrane of polyethylene. The device requires no applied polarizing voltage and the cell gives a current proportional to the oxygen partial pressure. The functional characteristics of the apparatus are discussed. [G.Mar.]

365 – A method for high precision assay of uranium metal (in English). J. A. Duckitt and G. C. Goode (U. K. Atomic Energy Authority, A.W.R.E., Aldermaston, Berks., Great Britain). *Analyst*, 87 (1962) 121–124.
The method is based on solution of the metal in hot 88% w/w H_3PO_4 to give U(IV), aeration to oxidise traces of U(III), followed by dilution with 5% v/v H_3PO_4 in 3 M H_2SO_4 to prevent precipitation. An excess of standard $K_2Cr_2O_7$ oxidised the U(IV) to U(VI) and the excess was back-titrated potentiometrically with standard ferrous ammonium sulphate using a Cambridge electro-titration unit, fitted with Pt indicator and calomel comparison electrodes and delivering the titrant from a polythene weight burette. The standard deviation of the method was 0.02%. The presence of up to 5% of Fe or Cr caused no interference, neither did the presence of up to 250 p.p.m. of Mo or V, 500 p.p.m. of Ni, Co, Zn or 1000 p.p.m. of Cu. [P.O.Ka.]

366 – Measurement of the uranium–uranium(III) potential in LiCl–KCl eutectic (in English). D. M. Gruen and R. A. Osteryoung (Argonne National Laboratory, Lemont, Ill., and Rensselaer Polytechnic Institute, Troy, N.Y., U.S.A.). *Ann. N.Y. Acad. Sci.*, 79 (1959/60) 897–907.
Measurements were conducted in a specially designed, fused silica cell (for particulars, see the text), operated under high vacuum to protect samples from oxygen. The comparison electrode was a silver–silver chloride electrode. An average value of -1.475 ± 0.005 V (at 450°) was obtained for $x\ E°_{MU}$ (with respect to the Ag–AgCl electrode) and of -130 kcal for ΔH in the reaction $U + 3\ AgCl(s) = UCl_3 + 3\ Ag$. Graphs and tables summarising experimental results are given. [Ca.Cas.]

367 – Hydrogen fluoride solvent system. VI (in English). A. F. Clifford and E. Zamora (Department of Chemistry, Purdue University, Lafayette, Ind., U.S.A.). *Trans. Faraday Soc.*, 57 (1961) 1963–1967.
Electric tension measurements for the system: $Pt \mid TlF_3(s) \mid TlF(HF) \mid Cu\ F_2(s) \mid Cu$, in liquid HF, gave $E° = 0.9282$ V and $\Delta G° = -42.8$ kcal/mole at 0°. The constants of the equilibria: $TlF \rightleftarrows Tl^+ + F^-$ and $TlF_3(s) + F^- \rightleftarrows TlF_4^-$ are respectively $4.7 \cdot 10^{-4}$ and $1.3 \cdot 10^{-2}$. The molar solubilities of TlF_3, and CuF_2 (at zero ionic strength) are $2.1 \cdot 10^{-4}$ and $< 2.10^{-5}$. [Fr.Pan.]

368 – Complex compounds of Rh with thiosulphate and ethylenediamine (in Russian). I. I. Cernjajev and A. G. Maiorova (N.S. Kurnakov Institute of General and Inorganic Chemistry, Moscow, U.S.S.R.). *Zhur. Neorg. Khim.*, 5 (1960) 1074–1084.
Durch Zusammenwirken von $[Rh_3NH_3Cl_3]$, $Na_2S_2O_3 \cdot 5H_2O$ und Äthylendiamin in wässerigem Medium wurde ein gelbes Pulver erhalten, dessen Zusammensetzung laut Analyse einem Tetramer entspricht: $[Rh_4 1\,3S_2O_3 2NaS_2O_3 8En]Na_{10}(NH_4)_6\ 11.5H_2O$.
Die molare Leitfähigkeit der wässerigen Lösung dieses Produktes wird bei 25° bestimmt. Anhand der Ergibnisse wird vorausgesetzt, dass sich 2 Na-Atome in der inneren komplexen Sphäre befinden und mit Thiosulfat das Radikal NaS_2O_3 bilden. Die Bindung des Thiosulfat-Radikales und ihre Menge wurden potentiometrisch geklärt. [Vi.Jes.]

369 – Complex formation of ferric iron with 7-iodo-8-hydroxyquinoline-5-sulphonic acid (ferron) (in English). Å. R. Storm and F. J. Langmyhr (University of Oslo, Chemical Institute, A, Blindern, Norway). *Acta Chem. Scand.*, 15 (1961) 1765–1771.
The complex formation of ferric iron with 7-iodo-8-hydroxyquino-line-5-sulphonic acid (ferron) was studied by potentiometric and spectrophotometric methods. Titrations of mixtures of the ligand and metal ion with standard alkali indicated the presence of complexes. By spectrophotometry, absorption curves and curves of continuous variation at different pH values were plotted. The photometric measurements confirmed the results obtained by potentiometry as to the number of complexes present, and showed that in the visible range the three complexes have absorption maxima which are only 10–15 mμ apart. (See abstract no. 351.) [G.Ekl.]

370 – Miscellaneous dihalogeno-bis-dimethylglyoxamate cobaltic acids (in Russian). A. V. Ablov and N. M. Samus (Kishinev State University, Moldavian S.S.R.). *Zhur. Neorg. Khim.*, 5 (1960) 852–860.
Es wurden Dihalogen-Derivate der bis-Dimethylglyoximatokobaltisäure synthetisiert. Br, Cl, und I wurden in den Produkten potentiometrisch bestimmt. Zur Einwage (0.3 g) des Komplexes wird

50–70 ml Methanol zugesetzt, langsam erwärmt und 1–2 g metallisches Na zugefügt. Nach beendeter Reaktion wird gekühlt, 100 ml Wasser zugegeben, mit HNO_3 angesäuert und potentiometrisch mit Ag-Elektrode und $AgNO_3$-Losüng titriert. [Vi. Jes.]

371 – The stability of cobalt complexes with some vitamins (in Russian). A. A. Grinberg and Ch. Ch. Chakimov. *Zhur. Neorg. Khim.*, 6 (1961) 144–152.
Es wurde die Stabilitätskonstante der komplexen Verbindungen des Kobalts mit *p*- und *m*-Aminobenzoesäure, Thiaminchlorid und Novocain bestimmt. Die Bestimmungen wurden mit potentiometrischer Titration der betreffenden komplexen Kobaltsalze mit einer 0.1 *N*-HNO_3, in Stickstoffatmosphäre bei Ionenstärke 1 durchgeführt. Die erhaltenen Resultate wurden nach der Bjerrum-Methode ausgewertet. Im Zusammenhang mit dem Werte der Stabilitätskonstante ist die Frage der biologischen Aktivität einiger Verbindungen verfolgt worden. [Vi. Jes.]

372 – Determination of the solubility product $Co(OH)_3$ and the standard redox electric tension Co^{2+}/Co^{3+} (in Russian). M. M. Selivanova, V. A. Shneider and R. I. Rjabova. *Zhur. Neorg. Khim.*, 6 (1961) 21–26.
Noyes und Dealh geben für die Redox standard elektrische Spannung für $Co^{2+} \rightleftarrows Co^{3+} + e$ den Wert +1.84 V an, und Latimer für den Löslichkeitsprodukt des $Co(OH)_3$ den Wert $2.5 \cdot 10^{-43}$ (bei 25°). Mit Hilfe des Isotopen ^{60}Co ist für den Löslichkeitsprodukt der Wert $3 \cdot 10^{-41}$ (25°) ermittelt worden und aus diesem Werte ein tieferer Wert der Redox standard elektrischen Spannung und zwar: $U_{0Co2+/Co3+} = 1.30$ V. [Vi. Jes.]

373 – Electrode potentials in molten lithium sulphate–potassium sulphate eutectic (in English). C. H. Liu (Brookhaven Material Laboratory, Upton, N.Y., U.S.A.). *J. Phys. Chem.*, 66 (1962) 164–166.
A molten solvent consisting of 80 mole % lithium sulphate in potassium sulphate was used to measure the standard electrical tension of several metals at 625°. The silver(I)–silver (0) system was used as reference.

Electrode system	*Standard eletrical tension*
Pd(II)–Pd(0)	0.541
Rh(III)–Rh(0)	0.387
Cu(II)–Cu(I)	0.051
Ag(I)–Ag(0)	0.000
Cu(I)–Cu(0)	−0.202

The Nernst equation was obeyed in all cases. [D.S.Ru.]

374 – Simultaneous micro-determinations of organic halogens and sulfur with potentiometric and chelatometric titrations (in Japanese). K. Hozumi and K. Mizuno (Faculty of Pharmacy, Kyoto University, Kyoto-shi, Japan). *Japan Analyst*, 10 (1961) 383–387.
Modifications of Stragand-Safford's silver absorption method for determining organic halogens or sulfur had been proposed by some workers, who suggested the possibility of separating halogens and sulfur gravimetrically by dissolving silver sulfate in hot water. In practice, the separations were not quantitative.

More reliable results were obtained from successive applications of potentiometric titration to halogenide ions and chelatometric titration of sulfate ion, after the sample had been decomposed and absorbed into concentrated alkali solution on the surface of small glass beads which filled an absorption funnel. The titrations are performed as follows: slowly wash the alkali solution from the absorption funnel into a 50 ml beaker using 20 ml water. After treatment with one drop each of hydrogen peroxide and hydrazine, acidify the solution slightly. Titrate the halogenide ions with 0.002 *N* $AgNO_3$ using silver–amalgamated silver bimetallic electrodes. Add 5.00 or 10.00 ml of 0.005 *M* $BaCl_2$, and evaporate the solutions to less than 5 ml within 20 min. After further additions of 15 ml water, 15 ml methanol and 2 ml ammonia, titrate the sulfate ion with 0.005 *M* EDTA using 1 ml phthalein complexone as indicator. [Ta.Fu.]

375 – Potentiometric titration of nitrogen-containing silicon organic derivatives in non-aqueous media (in Russian). A. P. Kreschov, W. A. Dresdov and J. C. Wlassowa. *Izvest. Vysshikh Ucheb. Zavedenii, Khim. Technol.*, [1] 3 (1960) 80–84.
Various aminosilane derivatives can be titrated with good accuracy (error less than 1.5%) in acetonitrile and nitromethane or their mixtures with benzene and dioxane, by acetic solutions of $HClO_3$. [Ca.Cas.]

376 – Potentiometric titration of alkylchlorosilanes by means of organic bases in acetonitrile (in Russian). A. P. Kreschov, W. A. Dresdov and J. G. Wlassova. *Izvest. Vysshikh Ucheb. Zavedenii, Khim. Technol.*, [1] 3 (1960) 85–87.
Trimethylchlorosilane, dimethyldichlorosilane, methyltrichlorisilane and $SiCl_4$ have been successfully titrated by means of bases, such as pyridine, dimethylaminoantipyrine or nitron, both visually and potentiometrically. In the second case a particular cell was developed, and the voltage hump was increased by adding suitable solvents (benzene, toluene, chlorobenzene and carbon tetrachoride), whose effects were studied. [Ca. Cas.]

377 – Determination of glycerol in fruit pastilles. W. J. W. Lloyd (Beecham Foods Ltd., Product Research Division, Brentford, Middlesex, Great Britain). *Analyst*, 87 (1962) 62–64.
The method was very similar to that of Sporek and Williams (*Analyst*, 79 (1954) 63), separating glycerol by chromatography and analysing the eluate by oxidation with periodic acid, followed by titration of the formic acid thus liberated. The differences from Sporek and Williams' method consisted in using less water for initial extraction and a longer column for chromatography. This prevented the eluate from splitting into two phases. Instead of using phenol red as indicator, titrations were performed potentiometrically using a glass electrode and a Pye automatic titrator. The end-point was in the pH range 8.7—10.2 and 9.6 was taken as the standard end-point. Alternatively, thymolphthalein (pH range 9.3–10.5) could be used as indicator. [P.O.Ka.]

378 – Dissociation constants of some sulpho-carboxylic acids and the rate of hydrolysis of potassium-1-ethoxycarbonylethane-2-sulphonate (in English). R. P. Bell and G. A. Wright (Physical Chemistry Laboratory, The University, Oxford, Great Britain). *Trans. Faraday Soc.*, 57 (1961) 1377–1385.
Potentiometric titrations were performed on the acids of the series $COOH(CH_2)_nSO_3^-$ in order to evaluate the acid dissociation constants. The following values of p*K* were found: 4.20, 4.74, 4.91, 5.04 and 5.21, respectively, for $n = 1, 2, 3, 4$, and 10. The distribution of charge in the ions was estimated to give an interpretation for the possibility of the SO_3^- group to act as an electron-attracting or an electron-repelling group, respectively, at short or longer distances. The rate of acid hydrolysis of the ethyl esters in the above series (*n* being 1 or 2) was also widely investigated. [Fr.Pan.]

379 – Investigations on the influence of phenyl substituents in the benzene ring on the non-neighbouring functional group. I. Benzoic acid derivatives (in Polish). W. Polaczkowa, N. Porowska and B. Dybowska (Department of Organic Chemistry, Polytechnic, Warsaw, Poland). *Roczniki Chem.*, 35 (1961) 1263–1271.
With the aim of estimating the effect of phenyl groups on the properties of the functional group in position 5 of 1,2,3-triphenylbenzene, the apparent dissociation constants of some benzoic acids have been determined at 23° in 60% (by volume) aqueous ethanol solutions. The measurements were performed by titration of 0.001 *N* solutions of acids with ethanolic KOH, after deaeration with nitrogen. The following p*K* values were obtained: benzoic acid, 5.73; *m*-toluic acid, 5.85; *p*-toluic acid, 5.94; 3,5-dimethylbenzoic acid, 5.97; 3,4,5-trimethylbenzoic acid, 6.15; 3,5-dimethyl-4-ethylbenzoic acid, 6.11; *p*-phenylbenzoic acid, 5.69; *m*-phenylbenzoic acid, 5.64; 3,4-diphenylbenzoic acid, 5.64; 3,5-diphenylbenzoic acid, 5.60; and 3,4,4-triphenylbenzoic acid, 5.61.
The value of σ for a phenyl substituent in the *para* position was obtained using the value $\varrho = 1.66$, calculated from Hammett's equation for ionisation in the stated conditions. The plot of log K/K_0 against σ shows the additivity of σ values of methyl substituents in positions 3,4 and 5, and the lack of additivity for phenyl substituents in positions 3,4 and 3,4 and 5. These results indicate that phenyl groups in the above-mentioned positions do not exert a resonance effect on the carboxyl group and only a weak inductive effect is observed. [Ad.Hu.]

380 – Chelate stabilities of certain oxine-type compounds. III. Schiff bases (in English). T. J. Lane, C.S.C. and A. J. Kandathil (Department of Chemistry, University of Notre Dame, Notre Dame, Ind., U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 3782–3784.
The acid dissociation constants for three types of Schiff bases (four different compounds of each type) which are structurally similar to 8-hydroxyquinoline and the successive formation constants of chelates formed with copper(II), nickel(II) and cadmium(II) have been determined in 50 volume% water–dioxane at 25° by potentiometric titration. The factors affecting the values of these constants for this series of ligands are discussed. The measured formation constants are lower than those of the corresponding 8-hydroxyquinoline chelates and higher than those for the 4-hydroxybenzimidazoles. [R.Mur.]

See also abstracts nos. 230, 232, 233, 241, 244, 249, 253, 254, 394.

5. Conductometry

381 – Studies on the separation of anions with anion exchange resins. I. Determination of selective coefficients of monovalent anions by the conductive method (in Japanese). K. Takiura and Y. Takino (Pharmaceutical Faculty, University of Osaka, Osaka, Japan). *Japan Analyst*, 10 (1961) 483–488.
The progress of the ion exchange reaction of an OH-type resin (Dowex 2) gives a continuous increase in the concentration of OH ion and a proportional increase in conductivity of the solution. Constant OH ion concentration and conductivity are reached at the equilibrium point of the exchange reaction. Accordingly, an estimate of the rate of increase in conductivity should give an exchange velocity. According to the authors' work, the ion exchange reaction took place as soon as the resin was immersed, and an equilibrium was reached within 5 min. The concentration of OH ion could be found by a simple calculation from the value of conductivity at the equilibrium stages. Furthermore, a calculation of the selective coefficient (anion exchange equilibrium constant), K_{OH}^{Anion} (25°), was made. The results were:

$$BO_2^- < F^- < AsO_2^- < IO_3^- < BrO_3^- < Cl^- < (OH)^- < CN^- < NO_2^- < NO_3^- < ClO_3^- < Br^- < I^- < NCS^-.$$

The procedure for this method is simpler than the conventional titrimetric methods, the range of application is wide and there is the merit of being able to confirm the point where the equilibrium is just reached. [Ta.Fu.]

382 – Investigation of the $(Cu(SCN)_2)^-$–$SeCN^-$–CH_3COCH_3 system (in Polish). A. Łodzińska and D. Babicka (Department of Inorganic Chemistry, Copernicus University, Toruń, Poland). *Roczniki Chem.*, 35 (1961) 1195–1202.
The photometric method of continuous variation, also photometric titration and conductivity measurements were used for investigation of the $[Cu(SCN)_2]^-$–$SeCN^-$–CH_3COCH_3 system. The following results were obtained: the Cu–SCN complex in acetone decomposes in the presence of $SeCN^-$ ions, giving complexes with varying composition, of the general formula $Cu_x(SCN)_y(SeCN)_z$, where x and $y > z$. Taking into account that decolorisation of Cu–SCN^- complexes proceeds in the presence of small amounts of $SeCN^-$, a transformation into a colorless complex, devoid of $SeCN^-$ ions, can take place. In dilute solutions both reactions presumably proceed simultaneously. [Ad.Hu.]

383 – Electroconductivity, viscosity and density in the system $SnCl_4$–C_2H_5OH–C_6H_6(I) and $SnCl_4$–C_3H_7OH–C_6H_6(II) (in Russian). T. Sumarokova and Ju. Nevskaja (Chemistry Institute, Academy of Sciences, Kazakhian S.S.R.). *Zhur. Obshcheĭ Khim.*, 30 (1960) 3526–3531.
Mit der schon veröffentlichten Methode (*Izvest. Sektora Platiny i Drug. Blagorod. Metal. Inst. Obscheĭ i Neorg. Khim. Akad. Nauk S.S.S.R.*, 27 (1952) 127), wurde das System (I) bei 40° und 60° und bei Konzentrationen des Benzens 50 und 70 Mol % analysiert. Die Konstante B ($\eta = A$ exp. (B/RT)) erreicht einen Maximalwert bei 30–33 Mol % $SnCl_4$, was die Existenz des schon beschriebenen $SnCl_4 . 2C_2H_5OH$ bestätigt. Die Leitfähigkeit des Systems (I) ist sehr hoch und ihr Maximalwert bei 22–26 Mol % $SnCl_4$ weist auf die Existenz der Verbindung $SnCl_4 . 3C_2H_5OH$ hin. Analogisch wurden im System (II) die Verbindungen $SnCl_4 . 2C_3H_7OH$ und $SnCl_4 . 3C_3H_7OH$ erhalten. Die Existenz des von C.V. Rogov beschriebenen $SnCl_4 . 4C_2H_5OH$ wird nicht bestätigt. [Vi.Jes.]

384 – Investigation of the formation of compounds of higher order in the system $CaCr_2O_7$–$K_2Cr_2O_7$–H_2O (in Russian). A. Ja. Deitč. *Zhur. Neorg. Khim.*, 5 (1960) 503–505.
Bei 30° wurden die Dichte, die spezifische Leitfähigkeit, die Viskosität und die optische Dichte des Systems $CaCr_2O_7$–$K_2Cr_2O_7$–H_2O untersucht. Die Leitfähigkeit wurde in gewohnter Weise in einer Zelle mit platinierten Platinelektroden bei einer Frequenz von 20 Hz und einer Spannung von 10 V gemessen. Als Nullinstrument wurden ein Telephon und parallel ein hochohmiger Galvanometer gebraucht. Die Abweichungen der Leitfähigkeit von der Additionskurve als auch die übrigen Eigenschaften weisen auf die Existenz der Verbindung $K_2[Ca(Cr_2O_7)_2]$ hin. [Vi.Jes.]

385 – Investigation of reactions of KCNS, NH_4CNS and NaI with water in acetone (in Russian). E. Ja. Gorenbein and I. S. Prosjanik. *Zhur. Neorg. Khim.*, 5 (1960) 2847–2848.
Mit der Methode isomolarer Serien (I. Ostromyslenski) werden die Leitfähigkeiten der Systeme Aceton–Wasser–(KCNS, NH_4CNS, NaI) gemessen (Tongenerator, 500 Hz). Die $\Delta\chi$-Werte weisen auf die Bildung der Hydrate $KCNS . H_2O$, $NH_4CNS . 3H_2O$ und $NaI . H_2O$. Aus wässrigen Lösungen der Salze werden Hydrate dieser Zusammensetzungen nicht erhalten. Die experimentellen Grundlagen genügen nicht zum eindeutigen Beweise der Existenz dieser Hydrate. [Vi.Jes.]

386 – Kinetics of ionic conductance. I. Energies of activation and the constant volume principle (in English). S. B. Brummer and G. J. Hills (Department of Chemistry, Imperial College, London, Great Britain). *Trans. Faraday Soc.*, 57 (1961) 1816–1822.
The mechanism of ionic migration in liquids is discussed. The theory of transition states appears to be the best one when determining the limiting equivalent ionic conductance, basing it on the constant volume principle. [Fr.Pan.]

387 – Kinetics of ionic conductance. II. Temperature and pressure coefficients of conductance (in English). S. B. Brummer and G. J. Hills (Department of Chemistry, Imperial College, London, Great Britain). *Trans. Faraday Soc.*, 57 (1961) 1823–1837.
The authors measured the conductance of KCl, $NaNO_3$ and tetra-alkylammonium picrates in water, methanol and nitrobenzene over the range 20°–60° and 1–900 atm. The experimentally found temperature and pressure coefficients are used for the mathematical treatment discussed in the first part, to draw attention to the possible description of limiting conductance using the transition state theory. [Fr.Pan.]

388 – Conductometric determination of small amounts of alkali carbonate in admixture with excess hydroxide. Z. Hoštálek and F. Kůtek (Department of Inorganic Chemistry, Institute of Chemical Technology, Prague, Czechoslovakia). *Chem. průmysl*, 11 (1961) 177–180.
A new graphical method is described for evaluating the titration of small samples of alkali carbonates, containing a large excess of hydroxide, with HCl. It is based on determination of displacement of the entire titration curve after the end-point. The theoretical basis is that the conductivities of the alkali carbonates, when present in small amounts, are very similar to those of the chlorides formed during the titration. [Gio.Ser.]

389 – Electroconductivity in the tricomponent reciprocal system of nitrates and nitrites of potassium and barium (in Russian). P. I. Procenko and A. Ja. Malachova (Rostov State University, Rostov-on-Don, U.S.S.R.). *Zhur. Neorg. Khim.*, 5 (1960) 2307–2310.
Mit Hilfe der visuellen polithermischen Methode wurde die Liquidus-Fläche des Systems K, Ba || NO_3, NO_2 bestimmt. Mit der schon früher veröffentlichten Methode (*Zhur. Obshcheĭ. Khim.*, 24 (1954) 207; 22 (1952) 1916; 24 (1952) 1734) wurden die Leitfähigkeiten der Schmelze bei 320° gemessen. Die Verbindung $KNO_2 \cdot 2\ Ba(NO_2)_2$ dissoziiert in der Schmelze vollständig, daher wird im Gebiete ihrer Zusammensetzung auf dem Leitfähigkeitsdiagramm keine Diskontinuität erhalten. Zwischen dem Liquidus des ternären Phasendiagrammes und den Isothermen der spezifischen Leitfähigkeit wird keine Korrespondenz gefunden. [Vi.Jes.]

390 – Equilibria in solution in reactions of trivalent cations with bidentate ligands (in Russian). A. K. Babko and L. J. Dubovenko (T. G. Shevchenka State Institute, Kiev, U.S.S.R.). *Zhur. Neorg. Khim.*, 6 (1961) 136–139.
Es wurden konduktometrische Untersuchungen einiger Oxalatkomplexe des Types $M_2(C_2O_4)_3$ duchgeführt. Aus den experimentellen Daten folgt, dass für 0.1 *M* Lösungen des Aluminiums, Eisens und Chroms eine mehr also 50%-ige Dissoziation eintritt und zwar nach der Gleichung:

$$M_2(C_2O_4)_3 \rightleftharpoons MC_2O_4^+ + M(C_2O_4)_2^-$$

Es wird gezeigt, dass in den Systemen M^{3+}–$C_2O_4^{2-}$ kein Konzentrationsbereich existiert, in welchen die Gruppen $M_2(C_2O_4)_3$ überwiegen. Die Stabilität der Komplexionen wächst in der Reihenfolge Al < Fe < Cr. [Vi.Jes.]

391 – Conductometric research on $AlCl_3$ or $AlBr_3$ in ether using $LiAlH_4$ (in English). T. Heyashi and T. Ishida (College of Engineering, Department of Applied Chemistry, Osaka University, Japan). *Bull. Univ. Osaka Prefect.*, A7 (1959) 55–60.
Conductometric curves obtained in ether solutions of $AlCl_3$ or $AlBr_3$ using $LiAlH_4$ are interpreted in terms of the following equations, (Hal = Cl or Br):

$$Al(Hal)_3 + 3\ LiAlH_4 = 4\ AlH_3 + 3\ LiHal$$
$$2\ AlHal_3 + AlH_3 = 3\ Al(Hal)_2$$

[Ca.Cas.]

392 – Investigation of the solubility of glasses and of products of crystallization in the system Li_2O–SiO_2 (in Russian). M. Matvejev and V. Velja. *Zhur. Priklad. Khim.*, 33 (1960) 34–42.
Zur Charakterisierung der Lösungsfähigkeit synthetischer glasartiger Lithiumsilikate und ihrer Kristallisationsprodukte wird die Leitfähigkeit ihrer wässrigen Eluate gemessen. Die Ergebnisse weisen auf eine unbedeutende Hydrolyse und auf ein gleichartiges Lösungsmechanismus beider Produkte hin. Es wurden Silikate der Zusammensetzung Li_2O. (2–6) SiO_2 geprüft. Die Leitfähigkeit ihrer wässrigen Lösungen ist erheblich niedriger als die der Na-Silikate. Die Einstellung des Gleich-

gewichtes ist auch langsamer. Die Arbeit hat eine Bedeutung für die synthetische Produktion der Li-Silikate auf nassem Wege im Autoklave. [Vi.Jes.]

393 – The electrical conductivity of solutions of metals in their molten halides. III. Cerium-cerium trichloride (in English). H. R. Bronstein, A. S. Dworkin and M. A. Bredig (Chemistry Division, Oak Ridge Material Laboratory, Oak Ridge, Tenn., U.S.A.). *J. Phys. Chem.*, 66 (1962) 44–48.
The conductivity of Ce–Ce Cl_3 solutions at 855° was found to rise from 1.20 for pure salt to 5.35 ohm^{-1} cm^{-1} at 9.0 mole % Ce. The presence of the equilibrium $Ce^{3+} + e^- \rightleftharpoons Ce^{2+}$ is suggested as being responsible for the increase. Careful cell design eliminated contact with ceramic materials, which may have been responsible for the lower results of previous investigators. [D.S.Ru.]

394 – Complex compounds of thorium with malonic acid (in Russian). O. E. Zvjagincev and L. G. Chromenko (N. S. Kurnakov Institute of General and Inorganic Chemistry, Moscow, U.S.S.R.). *Zhur. Neorg. Khim.*, 6 (1961) 593–601.
Es wurden die Leitfähigkeiten der wässrigen Lösungen von Thoriumnitrat und Äpfelsäure und ihrer Na-Salze mit einer Kohlrausch-Brücke und Oscillograph als Nullindikator bestimmt. Die wässrigen Lösungen von Thoriumnitrat und Äpfelsäure wurden mit NaOH Lösungen potentiometrisch titriert. In den Lösungen bilden sich zwei Komplexverbindungen im Verhältnisse Th : Mal = 1 : 1 und 1 : 2. Die Struktur weiterer Komplexe wird diskutiert. Die Konstante der Instabilität des Komplexes $(ThMal)^{2+}$ wird zu $5.2 \cdot 10^{-7}$ bestimmt. [Vi.Jes.]

395 – Electrolytic conductance of salts of several cyanocarbon acids (in English). J. E. Lind, Jr., and R. M. Fuoss (Sterling Chemistry Laboratory, Yale University, New Haven, Conn., U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 1828–1830.
The conductances of tetraethylammonium salts of the cyanocarbon acids 1,1,2,3,3-pentacyanopropene (I) and 1,1,2,4,5,5-hexacyano-3-azapentadiene (II) have been measured in several solvents. Both compounds exhibited a lack of association in acetonitrile solvent; compound(I) was also studied in water and gave a similar result. Association was evident in ethylene dichloride solvent; association constants were 2600 for (I) and 2000 for (II). These association values and the large contact distances derived from them show that the negative charge is highly distributed in the anions of both acids, as would be expected from resonance considerations. [R.Mur.]

396 – The donor properties of triphenylarsine oxide (in English). D. J. Phillips and S. Y. Tyree, Jr. (Department of Chemistry, University of North Carolina, Chapel Hill, N.C., U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 1806–1810.
The coordination of triphenylarsine oxide with chromium(III), manganese(II), iron(III), cobalt (II), nickel, copper(II), zinc, mercury(II), tin(IV) and antimony(III) and (V) has been investigated. A series of new compounds was prepared and characterized by conductivity measurements in nitrobenzene, molecular weight determinations, magnetic susceptibility measurements and infrared spectra. [R.Mur.]

397 – Determination of the dissociation equilibria of water by a conductance method (in English). H. C. Duecker and W. Haller (National Bureau of Standards, Washington D.C., U.S.A.). *J. Phys. Chem.*, 66 (1962) 225–229.
The temperature coefficients of conduction were determined for water fractions containing varying quantities of impurities at 18° and 25°. The activation energy of conduction of very dilute aqueous solutions is expressed as a function of electrical conductivity. The theoretical conductivity is calculated to be $0.0373 \cdot 10^{-6}$ ohm^{-1} cm^{-1} at 18°. The dissociation constants for water, the equivalent conductance of ions and the density calculated from this value agree with those determined from the electrical tension of galvanic cells. [D.S.Ru.]

398 – Ion association in polyvalent symmetrical electrolytes. II. The conductance of manganese(II) sulfate and MnBDS in methanol–water mixtures (in English). C. J. Hallada and G. Atkinson (Department of Chemistry, University of Michigan, Ann Arbor, Mich., U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 3759–3762.
Conductance measurements have been performed on magnanese *m*-benzene disulfonate (MnBDS) in water–methanol mixtures ranging from 0–100% methanol, and on manganese(II) sulfate in water–methanol mixtures ranging from 0–40% methanol at 25°. The conductance data are examined using the extended Fuoss–Onsager theory, and the K_A, Λ° and a° parameters obtained. In contrast to manganese sulfate, MnBDS is essentially unassociated in water (99.6 ± 0.6% unassociated at $3 \cdot 10^{-3}$ M). The parameter a° is examined as a function of mole fraction of methanol, and K_A as a function of the dielectric constant of the solvent; the variation of these parameters indicates the non-ideality of the solvent system. [R.Mur.]

399 – Preparation and properties of $(C_5H_5)_2$ *M* compounds of Mn and Re. I. $(C_5H_5)_2$ Mn (in English). G. Wilkinson, J. M. Birmingham and F. A. Cotton (Harvard University, Cambridge, Mass., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 3339. *Abstract No.* 26013.

400 – The acid dissociation of γ-butyrolactam in water at 25° (in English). R. L. Hansen (Central Research Department, Minnesota Mining and Manufacturing Co., St. Paul, Minn., U.S.A.). *J. Phys. Chem.*, 66 (1962) 369–370.
The conductometric method of Ballinger and Long has been used to determine the acid dissociation constant of γ-butyrolactam. The value $K_{HA} = 2 \pm 1 \cdot 10^{-15}$ mole/l was obtained at 25°.
[D.S.Ru.]

401 – The donor properties of pyridine N-oxide (in English). J. V. Quagliano, J. Fujita, G. Franz, D. J. Philips, J. A. Walmsley and S. Y. Tyree (Department of Chemistry, University of North Carolina, Chapel Hill, N.C., and Florida State University, Tallahassee, Fla., U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 3770–3773.
The coordination of pyridine N-oxide with a variety of acceptors (cobalt(II), nickel(II), copper(II), zinc(II), iron(II), iron(III) and tin(IV)) has been investigated. New compounds, prepared in the form of perchlorates, nitrates and halides, have been characterized by infrared spectra, magnetic susceptibility and conductance measurements in non-aqueous solvents. Of the compounds prepared, all perchlorate salts and some nitrate and halide salts have only pyridine N-oxide directly coordinated to the metal. In some cases, nitrates are also coordinated. [R.Mvr.]

See also abstracts nos. 231, 239, 245, 246.

6. Electrolysis

402 – Studies on electrolytic analysis using chelating agents. IV. Determination of copper in the presence of bismuth, antimony and arsenic using tartrate–DTPA electrolyte (in Japanese). G. Nakagawa (Nagoya Institute of Technology, Showa-ku, Nagoya, Japan). *J. Chem. Soc. Japan; Pure Chem. Sect.*, 81 (1960) 102–104.
A method for the electrolytic determination of copper in the presence of bismuth, antimony and arsenic was investigated. For the separation of copper from antimony and arsenic(III), diethylene triamine penta-acetic acid(DTPA) solution was not very favourable as the electrolyte, because antimony and arsenic(III) DTPA chelates were not stable enough to prevent their electrodeposition. However, using tartrate–DTPA electrolyte, more favourable results were obtained. In this medium, at pH 4–5, the quantitative separation of copper from both antimony and arsenic(III) was attained at the cathodic electric tension of −0.40 to −0.45 V *vs.* S.C.E. Arsenic(V) was codeposited with copper from neither DTPA nor tartrate–DTPA electrolyte. The following procedure was recommended for the electrolytic determination of copper co-existing with bismuth, antimony and arsenic: to a sample solution containing copper, bismuth, antimony and arsenic, add 0.4 *M* sodium tartrate, twice as much DTPA as total moles of bismuth, antimony and arsenic, and 1.5 g hydrazine hydrochloride. Dilute the solution to about 150 ml and adjust its pH to 4–5: heat to 70–80°. Deposit the copper on a platinum gauze cathode, maintained at the cathodic electric tension of −0.40 to −0.45 V *vs.* S.C.E. [Ta.Fu.]

403 – The separation of magnesium from dimethylformamide and pyridine (in German). H. J. Bittrich, R. Landsberg and W. Gaube (Institute of Physical Chemistry, Technical High School for Chemistry, Merseburg, Germany). *J. prakt. Chem.*, [4] 12 (1961) 191–197.
Attempts to separate Mg from $MgBr_2$ solutions in pyridine were unsuccessful, even after addition of water; separation can be achieved from $MgCl_2$ solutions in dimethylformamide, using a Hg cathode as an amalgam, but not a solid cathode. Current yields increase with the water content. From the knowledge of the complexes formed in this medium and from analogy with reactions with metallic Na, the following cathodic reactions can be derived (DMF = dimethylformamide):

$$\mathrm{Mg(DMF)_6Cl_2} \rightleftarrows \mathrm{Mg(DMF)_6Cl^+} + \mathrm{Cl^-} \qquad \text{(I)}$$

$$\mathrm{Mg(DMF)_6Cl^+} \rightleftarrows \mathrm{Mg(DMF)_6{}^{2+}} + \mathrm{Cl^-} \qquad \text{(II)}$$

$$\mathrm{Mg(DMF)_6{}^{2+}} + 2\ \mathrm{e^-} + x\mathrm{Hg} = \mathrm{MgHg}_x + 6\ \mathrm{DMF} \qquad \text{(III)}$$

whilst at solid cathodes other reactions, followed by hydrolysis, take place. [Ca.Cas.]

404 – Electrochemical separation of magnesium on a microscale (in Hungarian). E. Csongor (Kossuth Scientific Societies, Experimental Physics Institute, Debrecen, Hungary). *Magyar Fiz. Folyóirat*, 7 (1959) 517–520.
Mg can be electrochemically deposited on a metal surface quantitatively, avoiding the use of binders. [Ca.Cas.]

405 – Determination of small amounts of lead in metallic bismuth. S. I. Sinyakova and E. K. Gol'braikh. *Trudy Komissii Anal. Khim., Akad. Nauk S.S.S.R.*, 12 (1960) 187–190.
Lead can be determined in metallic bismuth containing ~ 0.2% of lead by electrolytic separation as PbO_2 and purification with thiourea. The sample (1 g) is dissolved in HNO_3 (1 : 1), diluted twofold and electrolysed at 70°–80° at 0.25–0.3 A, using a Pt-gauze anode and a Pt-spiral cathode. After 2 h the electrodes are washed, the PbO_2 is dissolved in HNO_3 (1 : 1) in the presence of H_2O_2, and the solution dried on a quartz dish. The residue is dissolved in 1 *N* HNO_3 and the solution saturated with thiourea. Large crystals of $2\ Pb(NO_3)_2.11CS(NH)_2)_2$ are formed if sufficient thiourea is added. After 1 h at 0° the crystals are filtered off, washed with 1 *N* HNO_3, saturated with thiourea, dried and ignited at 300° for 20 min. The residue is wetted with HNO_3, evaporated, dissolved in 1–2 ml of 20% ammonium acetate and diluted with 10 ml of water. Pb is determined in the solution by polarography or by the iodimetric method. The error is ± 7%. [Gio.Ser.]

406 – Determination of nickel and molybdenum when present together (in Russian). G. P. Protsenko and P. N. Kovalenko (State University, Rostov, U.S.S.R.). *Zavodskaya Lab.*, 28 (1962) 23–25.
Electrolytic separation of nickel and molybdenum is carried out in sulphuric acid medium at pH 3.3–4.1 at 2.4 V and 0.8–0.3 A/cm^2, for one h. Molybdenum precipitates as $2\ Mo_2O_3 . 13H_2O$ together with copper, whose concentration must therefore be determined separately. The electrolyte is used for successive determination of nickel after filtration. [Ot.So.]

407 – Electrolytic generation of radical ions in aqueous solution (in English). L. H. Piette, P. Ludwig and R. N. Adams (Department of Chemistry, University of Kansas, Lawrence, Kan., U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 3909–3910.
The authors report the E.P.R. detection in aqueous solution of cation and anion free radicals of aliphatic nitrocompounds produced by *in situ* electrolysis at a mercury electrode. The E.P.R. spectra indicate the generation of the mononegative ions of *o*,- *m*-, and *p*-nitroaniline and nitrophenol, *p*-nitroanisole, *p*-nitrodimethylaniline and nitrobenzene. The radical ions were removed by a first order reaction ($t_{1/2}$ about 2 sec) upon cessation of the electrolysis. Cation radicals of *p*-phenylenediamine, N,N-dimethyl-*p*-phenylenediamine, *o*-tolidine, N,N'-tetramethylbenzidine, *p*-aminodiphenylamine and several derivatives of chloropromazine have also been detected in aqueous solution. [R.Mur.]

408 – Electron spin resonance studies of electrolytically reduced tetra-cyanoethylene derivatives (in English). P. H. Rieger, I. Bernal, and G. K. Fraenkel (Department of Chemistry, Columbia University, New York, N.Y., U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 3918–3919.
The electrolytic reduction products of tetracyanoethylene, 1,1,2,2,-tetracyanocyclopropane, and 1,1,2,2-tetracyanoethane have been studied by electron spin resonance. Tetracyanoethylene is immediately reduced to the anion radical simply by dissolution in the solvent N,N-dimethylformamide; an electric tension of -0.2 V (*vs.* Ag–$AgClO_4$ comparison electrode, 0.1 *M* $AgClO_4$ and DMF solvent) is required to reduce this compound in acetonitrile solvent. The E.S.R. spectrum of the reduction product in these two solvents is the same. Reduction of the 1,1,2,2-tetracyanocyclopropane derivative occurs at -1.4 V and of 1,1,2,2-tetracyanoethane at -2.5 V in DMF to yield an E.S.R. spectrum identical to that of the reduction product of tetracyanoethylene, indicating identical reduction products of these three compounds. Further oscillopolarographic evidence is given for this conclusion. [R.Mur.]

409 – On the mechanism of the electro-oxidation of alcohols and aldehydes on platinum (in Russian). A. K. Korolev and A. I. Shlygin (State University, Vladivostok, U.S.S.R.). *Zhur. Fiz. Khim.*, 36 (1962) 314–317.
Data are presented on the electro-oxidation and oxidation of *n*-propyl alcohol. It has been shown that electron exchange takes place between the electrode and alcohol molecules, and that the electro-oxidation reaction proceeds according to the electron-radical mechanism. The limiting stage of the electro-oxidation process has been shown to vary, and a comparison of the behaviour of ethyl and *n*-propyl alcohols during electro-oxidation and oxidation was made. [Ot.So.]

See also abstracts nos. 325, 327, 443, 444, 449, 450.

7. Coulometry

410 – Principles and uses of coulometric analysis (in English). A. G. C. Morris. *S. African Ind. Chemist*, 13 (1959) 166–171.
A literature survey with 161 references.

411 – Controlled potential coulometry in metallurgical analysis (in English). G. W. C. Milner and J. W. Edwards (U.K.A.E.A. Research Group, A.E.R.E., Harwell, Great Britain). *Nuclear Sci. Abstr.*, 15 (1961) 3754. *Abstract No.* 29115.

412 – Coulometric titration by electrogenerated tin(II) ion (in English). T. Takahashi and H. Sakurai (Institute of Industrial Science, University of Tokyo, Tokyo, Japan). *Talanta*, 9 (1962) 74–76.
As an electrogenerated reducing agent, tin(II) has been investigated and was found applicable in the coulometric titrations. In a simple coulometric apparatus (consisting of constant current source, titration cell, potentiometer for end-point detection and time measuring apparatus) titrations were carried out using 3 *M* KCl, NH_4Cl or HCl electrolyte solutions. Satisfactory results were obtained using 3 *M* KCl and 0.3 *M* tin(IV) chloride for the determination of cerium(IV) ion, iodine and bromine, with an error of only a few %. [J.Inc.]

413 – Internal coulometric method for determining oxygen dissolved in water (in Italian). G. Barbi and S. Sandroni (National Centre for Nuclear Research at Ispra, via Cerva 31, Milan, Italy). *Nuclear Sci. Abstr.*, 15 (1961) 3755. *Abstract No.* 29119.

414 – Amperometric determination of small quantities of Fe^{3+} by electrolytically generated NO_2^+ (in Italian). G. Barbi (National Centre for Nuclear Research at Ispra, via Cerva 31, Milan, Italy). *Nuclear Sci. Abstr.*, 16 (1962) 195. *Abstract No.* 1699.

415 – The determination of iron in metals and minerals by controlled potential coulometry (in English). G. W. C. Milner and J. W. Edwards (Analytical Chemistry Group, Atomic Energy Research Establishment, Harwell, Great Britain). *Analyst*, 87 (1962) 125–133.
A laboratory-constructed potentiostat in conjunction with the A.E.R.E. coulometer and cell (*A.E.R.E. Report No.* 3772, Harwell, 1961) were used in this work. 10 μg to 10 mg pure Fe dissolved in pure aqueous HCl or H_2SO_4 gave recoveries in the range 99.6–101.5%, replicate determinations showing coefficients of variation from ± 2.2% at lowest concentrations to ± 0.03% at highest concentration. Silicate minerals with low Ca contents were dissolved in H_2SO_4–HF mixtures, the HF being removed by fuming. Solution of the resultant salts in *N* H_2SO_4 gave solutions suitable for coulometry. For silicates with high Ca content, $HClO_4$–HF mixtures were used for dissolution, and after fuming the salts were dissolved in *N* HCl for coulometry. For plastic and flint clays, a Na_2CO_3 fusion on the residue left after H_2SO_4–HF digestion was necessary. Details were given for methods of dissolving a range of non-ferrous and ferrous alloys in order to determine the contents coulometrically. The main interfering element in alloy analysis was Cu, which could be removed by pre-electrolysis. [P.O.Ka.]

8. Electrophoresis

416 – Electromigration in ion-exchange papers (in English). T. Yamabe, M. Seno and N. Takai (Institute of Industrial Science, University of Tokyo, Tokyo, Japan). *Bull. Chem. Soc. Japan*, 34 (1961) 738.
A note on the use of ion-exchange papers in electrophoresis. The migration rate is slower, and tailing less, than with ordinary paper. [H.H.Ba.]

417 – Zone and boundary diffusion in electrophoresis (in English). J. R. Boyack and C. G. Giddings (Department of Chemistry, University of Utah, Salt Lake City, Utah, U.S.A.). *J. Biol. Chem.*, 235 (1960) 1970.
A more general theoretical approach for predicting the extent of zone spreading in zone elec-

trophoresis and ultracentrifugal sedimentation, when the effect is larger than expected from molecular diffusion effects. The theory is also applicable to complex reaction systems. [Ca.Cas.]

418 – **Isotope enrichment by electromigration in a mixture of molten $RbNO_3$ and $LiNO_3$** (in English). A. Lunden (Chalmers Institute of Technology, Gothenburg, Sweden). *Ann. N.Y. Acad. Sci.*, 79 (1959/1960) 988.
By means of electromigration for 107 h in the system cathode–$LiNO_3$–$RbNO_3$–anode in a cell of a particular design (for details see the text) the ratio for isotopes 85 and 87 of Rb was increased from 2.62 to 3.21. [Ca.Cas.]

419 – **Separation of rare earths by means of paper electrophoresis** (in English). Han-kuo Huang and Shu-chuan Liang (Department of Chemistry, Academia Sinica, Peking, China). *Sci. Record (Peking)*, 3 (1959) 469–476.
By adopting the Wieland–Fischer technique (*Naturwissenschaften*, 35 (1948) 29) in rare earth electrophoresis, the following data were collected: separation of Pr, Nd and Sm dissolved in dilute HNO_3 is possible within 4 h in 0.05 *M* citric acid, with added phenol (1 g/l) at 400 V tension, a proportionality between migration rate and applied voltage being observed. The migration decreases as the paper strip becomes narrower, without affecting separation. Sc and Th form complexes which migrate towards the anode, while complexes which migrate towards the cathode are formed by Sm, Nd, Y, Pr, Ce and La (migration rates are in the order given). If disodium-EDTA (0.05 *M*) is used, the maximum resolving power is obtained at pH 7. Nd and Y are best separated using citric acid–EDTA. At pH 2.7, in 0.025 *M* citric acid–0.01 *M* EDTA the rare earths migrate in the order; Ce, La, Pr, Nd, Sm, Sc, Y, and Th, whereas at pH 6.1 a different order, Sc, La, Y, Pr+Nd, Sm, Ce and Th is observed. Some advantages over chromatographic separations are claimed. [Ca.Cas.]

420 – **Paper electrophoresis of hexane hexaols and of mild oxidation products of *meso*-inositol** (in French). M. Traisnel and P. Balatre (Laboratoire de Pharmacie Galénique, Faculté de Médecine et Pharmacie, Lille, France). *Bull. soc. chim. biol.*, 42 (1960) 151–157.
Separation of linear polyols of *scyllo-meso-inosose* and *epi-meso-inosose* can be achieved by means of paper electrophoresis in borate buffers; spots are revealed with bromothymol blue. [Ca.Cas.]

421 – **Chromatography of dinitrophenols** (in Japanese). W. Funasaka and Tsuguo Kojima (Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan). *Japan Analyst*, 9 (1960) 33–37.
Attempts have been made to separate *p*-nitrophenol, 2,4- and 2,6-dinitrophenol and 2,4,6-trinitrophenol by paper chromatography and by paper electrophoresis. In paper chromatography, when a mixture of nitrophenols was developed with amyl alcohol–benzene mixture containing citric acid buffer solution on a filter paper strip impregnated with the same buffer solution, or when it was developed with amyl alcohol–benzene–acetic acid on a filter paper strip impregnated with sodium acetate, good separations were obtained. In paper electrophoresis, migration in acetic acid–sodium acetate buffer solution at pH 3.2–3.6 for 1.5 h at 500 V gave a complete separation.
With the aim of separating 2,6-dinitrophenol and 2,4,6-trinitrophenol in 2,4-dinitrophenol, separation by column electrophoresis has been investigated, and it was confirmed that the determination of 0.25% of 2,6-dinitrophenol and 2,4,6-trinitrophenol was possible. 2,6-Dinitrophenol in a commercial 2,4-dinitrophenol was also determined. [Ta.Fu.]

422 – **Separation of uronic acids by paper electrophoresis** (in English). A. Haug and B. Larsen (Norwegian Institute of Seaweed Research, NTH, Trondheim, Norway). *Acta Chem. Scand.*, 15 (1961) 1395–1396.
A rapid and convenient method for qualitative and quantitative analysis of mixtures of uronic acids is described. The electrophoresis was carried out with a current of 0.5 mA cm^{-1}. A solution of anilintrichloroacetate in glacial acid was used as location reagent. After dipping, the strips were heated for 2–3 min at 100°. It was found to be convenient to examine the strips in u.v. light. [G.Ekl.]

423 – **Paper electrophoresis of carbohydrates in sulphonated phenylboronic acid buffer** (in English). P. J. Garegg and B. Lindberg (Svenska Träforskningsinstitutet, Stockholm Ö, Sweden). *Acta Chem. Scand.*, 15 (1961) 1913–1922.
The paper electrophoresis of some carbohydrates in sulphonated phenylboronic acid buffers is described. These allow electrophoresis to be run at neutral pH values and are therefore useful for the separation and characterisation of alkali-labile carbohydrate derivatives. Specific configurations

are required for the hydroxyls for complex formation, and information of structural significance can be obtained for unknown carbohydrates. The new buffers are a useful complement to those previously described, especially for the separation of glycitols. [G.Ekl.]

424 – An electrophoretic method for de-salting amino acids (in English). J. C. Nichol (Oak Ridge National Laboratory, Biology Division, Oak Ridge, Tenn., U.S.A.). *Science*, 129 (1959) 1549–1550.
10–30 μl of the solution (containing amino acids and/or peptides) to be desalted are placed at the centre of a paper strip, whose ends dip into two different ammonium formate buffer solutions at values of pH respectively below and above their isoelectric points: owing to the pH-gradient so formed, amino acids and peptides migrate when 50 V are applied until they reach the point of common isoelectric pH value, while salts migrate at the electrodes. Elution with water then permits recovery of the substances, the formate being eliminated by vacuum sublimation. The method is also applicable to nucleotides. [Ca.Cas.]

425 – Electrophoretic separation of single-stranded deoxyribonucleic acid from double stranded deoxyribonucleic acid (in English). K. Matsubara and Y. Takagi (Department of Biochemistry, Medical School, Kanazawa University, Ishikawa, Japan). *Biochem. et Biophys. Acta*, 55 (1962) 389–392.
Deoxyribonucleic acid (I) can be separated from ribonucleic acid (II) by electrophoresis. In this paper it is shown that single-stranded (I) migrates with a velocity intermediate between double-stranded (I) and (II). The electrophoresis was carried out on starch gel, buffered with 0.05 *M* borate buffer (pH 8.5), using a Kyowa zone-electrophoresis apparatus (Kyowa Scientific Instrument Co., Tokyo, Japan) at 2.4Vcm^{-1}, 8.1 mA cm^{-2} at 5° for 18.5 h. The nucleic acids were determined by cutting the starch into 1 cm segments, eluting with 5 ml of water, and measuring the u.v. absorption at 260 μm. Results are shown of the separation of different types of (I) and of the influence on the mobility of (I) of various treatments. [Gio.Ser.]

426 – Tracer electrophoresis. V. The mobility and charge of human serum albumin at low concentration and low ionic strengths (in English). Estella K. Mysels and K. Mysels (Department of Chemistry, University of Southern California, Los Angeles, Calif., U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 2049–2055.
Open tube electrophoresis of human serum albumin with ^{131}I-tagged albumin tracer has been used to obtain electrophoretic data over a wide range of protein and buffer concentrations. ζ-Potentials and charges calculated from this data are found to agree with titration charges, assuming a radius of 34 Å for the hydrodynamically equivalent sphere and provided a moderate expansion of the sphere (supported by viscosity data) is allowed for at very low ionic strength. [R.Mur.]

427 – The application of paper electrophoresis for controlling the homogeneity of seed proteins (in Russian: English summary). Yu. Ya. Hofman and I. A. Weintraub (Laboratory of Protein Chemistry, State University, Kishinev, U.S.S.R.). *Biokhimiya*, 25 (1960) 1049–1054.
Quantities as small as 4% of vicilin in pea legumin can be detected by paper electrophoresis if the mixture to be resolved is placed on the paper near to the equilibrium position of the protein being studied. It is also demonstrable that vicilin consists of two components, having slightly different mobilities. [Ca.Cas.]

428 – A rapid modified starch electrophoretic method for haemoglobin (in English). J. W. McCoo and S. L. Leikin (Children's Hospital, 2125 13th St. N.W., Washington D.C., U.S.A.). *Am. J. Clin. Pathol.*, 35 (1961) 349–352.
Potato starch washed with 0.05 *M* barbitone buffer at pH 8.6 was suspended in the same buffer and poured into a plastic mould 6 in. × 2.5 in. × 5/16 in. The starch gel was allowed to settle for 10 min and the excess buffer was blotted out. Near one end of the block, three slits were made with a spatula and about 50 μl of a 10% haemolisate were placed in each slit. The mould had a cellulose sponge wick on each side, which were immersed in vessels containing 800–1000 ml of buffer and the two platinum electrodes. The whole assembly was covered with a triangular evaporation chamber and the electrophoresis was carried out for 4.5–6 h with an applied voltage of 260–310 V and a current of 20–30 mA. [Gio.Ser.]

See also abstracts nos. 247, 251.

9. Other methods

429 – Determination of alkali metals and halides in zirconium dioxide by high voltage electrodialysis (in Russian). S. V. Elinson and A. T. Rezova. *Zavodskaya Lab.*, 26 (1960) 1209–1210.
An electrodialyser, capable of employing voltages up to 2000 V and currents up to 300 mA is described. Platinum electrodes are built into the side chambers, 6–8 cm apart. The sample is placed in the central chamber and distilled water is placed in the side chambers. The aqueous suspension of the sample is dialysed until the current drops to 4–5 mA, the water in the side chambers being changed two or three times. The side chamber liquors are then analysed for the metal and halide by conventional methods. [Ot.So.]

430 – A low frequency polaroscope (in Ukrainian: English summary). O. W. Gorodisski (Institute of General and Inorganic Chemistry of the Ukrainian Academy of Sciences, S.S.R.). *Dopodivi Akad. Nauk Ukr. R.S.R.*, (1959) 995–997.
Schematic description of an apparatus in which solid electrodes are used, the main feature being an additional, unpolarized comparison electrode; the duration of polarization is 10 sec. More reproducible results are obtained, as exemplified by a determination of $PbCl_2$ in a sodium chloride–potassium chloride melt, by means of a Pt electrode. [Ca.Cas.]

431 – Adsorption and dielectric studies of the alumina–ethyl chloride system at 35° (in English). R. A. Yount (Department of Chemistry, University of North Carolina, Chapel Hill, N.C., U.S.A.). *J. Phys. Chem.*, 66 (1962) 326–328.
The dielectric constant and loss were determined at frequencies between 100 c and 100 kc for varying quantities of ethyl chloride. The dielectric loss increased to the monolayer completion, then remained unchanged with further adsorption. The dielectric constant increased with increasing adsorption and with decreasing frequency. [D.S.Ru.]

432 – The dielectric constant of water between 0°–40° (in English). G. A. Vidulich and R. L. Kay (Metcalf Research Laboratory, Brown University, Providence, R.I., U.S.A.). *J. Phys. Chem.*, 66 (1962) 383.
Considerable disagreement has existed in previous reports on the dielectric constant for water and its temperature coefficient. The following values were obtained using the bridge method, with a newly designed dielectric cell: 0°, 87.90; 20°, 80.20; 25°, 78.37; 40°, 73.19. They are compared with results from previous publications. (C. G. Malmberg and A. A. Maryott, *J. Research National Bureau Standards*, 56 (1956) 1; J. Wyman and E. N. Ingalls, *J. Am. Chem. Soc.*, 60 (1938) 1182; B. B. Owen, R. C. Miller, C. E. Milner and H. L. Cogan, *J. Phys. Chem.*, 65 (1961) 2065). [D.S.Ru.]

433 – Polarometric determination of O_2 and H_2O_2 dissolved in H_2O (in Italian). G. Barbi (National Centre for Nuclear Research at Ispra, via Cerva 31, Milan, Italy). *Nuclear Sci. Abstr.*, 15 (1961) 3355. *Abstract No.* 25980.

434 – Complex ions in molten salts: a galvanostatic study (in English). D. Inman and J. O'M. Bockris (John Harrison Laboratory of Chemistry, University of Pennsylvania, Philadelphia, Pa., U.S.A.). *Trans. Faraday Soc.*, 57 (1961) 2308–2313.
The electric tension–time curves at constant current were recorded oscillographically in a molten $Cd(NO_3)_2$–$NaNO_3$–KNO_3 solution. Complex formation occurred when Cl^-, Br^-, or I^- ions were added. By determining the values $E\tau/4$ the following formation constants were evaluated at 263°: ligand Cl^-, $K_1 = 100$, $K_2 = 7$, $K_3 = 35$; ligand Br^-, $K_1 = 100$, $K_2 = 65$, $K_3 = 8$; ligand I^-, $K_1 = 500$, $K_2 = 60$, $K_3 = 53$, $K_4 = 78$. [Fr.Pan.]

435 – Identification of nucleic acid components by electrodialysis combined with circular paper chromatography (in Russian: English summary). E. K. Alymova, G. D. Bolgova and A. T. Astvazaturian (Chair of Biochemistry and Chair of Pharmacology, State Medical Institute, Rostov-on-Don, U.S.S.R.). *Biokhimiya*, 26 (1961) 221–224.
By means of electrodialysis, nucleic acid hydrolysates can be fractionated in cationic (purine bases), anionic (pyrimidine nucleotides) and neutral components (carbohydrates). Pyrimidine bases can be obtained in the same way, after hydrolysis of the corresponding nucleotides. [Ca.Cas.]

436 – Electrocapillarometric identification of toxic substances in biological materials (in Russian). A. W. Wassin and J. P. Kwitin (Veterinary Research Institute, Saratov, U.S.S.R.). *Veterinariya*, 37 (1960) 83–85
The method is suitable for identification of toxic substances (such as P, As and heavy metals) in

very minute amounts; the sample to be investigated is placed, as a dry powder, on a water impregnated paper strip, held on a glass plate by means of Al clamps. A d.c. source, 120 V, is connected to the paper ($i = 2$A) and after 3–30 min a suitable reagent is applied, according to the nature of the substance to be recognized, near the cathode or the anode; *e.g.* $AgNO_3$ can easily differentiate between arsenites, which have tetra- or octahedric crystals, and phosphorus compounds, which have rod shaped crystals. [Ca.Cas.]

See also abstract no. 248.

10. Related topics

437 – **Chemical and electrochemical properties in molten LiCl–KCl eutectic** (in French). G. Delarue (Saclay Nuclear Research Centre, Gif-sur-Yvette, Seine-et-Oise, France). *Nuclear Sci. Abstr.*, 15 (1961) 3358. *Abstract No.* 26011.

438 – **Electrochemical radiation dosimetry** (in English). I. H. S. Henderson (Canada Defence Research Chemical Laboratory, Ottawa, Canada). *Nuclear Sci. Abstr.*, 15 (1961) 3767 *Abstract No.* 29218.

439 – **Evaluation of ζ potential with correction for cell constant and surface conductance** (in English). B. N. Ghosh and P. K. Pal (University College of Science and Technology, Calcutta, India). *Trans. Faraday Soc.*, 57 (1961) 116–122.
Calculations were performed, using data of previous authors, on the zeta-potential of gelatine gel, a correction being made for the variation of cell constant with the content of solid matter. New equations are deduced, giving results in agreement with the data by Biefer and Mason (*Trans. Faraday Soc.*, 55 (1959) 1239). [Fr.Pan.]

440 – **Determination of the relative effective area of electrodes by polarization measurements** (in English). G. Wranglén and Å. Warg (Division of Applied Electrochemistry and Corrosion, Royal Institute of Technology, Stockholm, Sweden). *Acta Chem. Scand.*, 15 (1961) 1411–1412.
The relative effective area ratio of electrodes has been determined for nickel nets by using the Tafel equation. For one net and a package of five nets with an area five times greater two parallel polarization curves were obtained, from which the surface area ratio was calculated. The area ratio experimentally found was 4.94 : 1, in good agreement with the real value, 5 : 1. [G.Ekl.]

441 – **Electro-osmosis in membrane ion-exchangers** (in English). V. Subrahmanyan and N. Lakshminarayanaihah (Physical Chemistry Department, University of Madras, Guindy, Saidapet, Madras, India). *Current Sci. (India)*, 29 (1960) 307–308.
The quantity of water transported by electro-osmosis across as ion-exchange membrane is independent of current when the membrane is in equilibrium with NaCl solutions (0.1, 0.5, 1.0 *N*); a strong inverse dependence was found in 0.01 *N* NaCl. [Ca.Cas.]

442 – **Transference numbers of polyprotic acids by the moving boundary method. I and II** (in English). M. Kerker, J. Keller, J. Siau and E. Matijevič (Clarkson College of Technology, Potsdam, N.Y., U.S.A.). *Trans. Faraday Soc.*, 57 (1961) 780–784.
The transference number of H_2SO_4 in the range 0.003–0.1 *N* at 25° can be represented by the expression:

$$T = 0.8038 - 0.0033 \log N$$

as found by using the moving-boundary method. The relation between molar concentration and the transference quantity τ for three heteropoly acids is shown below, such that $\tau = T/n$, where n is the basicity of the acid.

τ	*Acid*
$0.2080 + 0.0005 \log M$	$H_4SiW_{12}O_{40}$
$0.1448 + 0.0025 \log M$	$H_6P_2W_{18}O_{62}$
$0.1480 + 0.0101 \log M + 125 M^2$	$H_7PW_{12}O_{42}$

[Fr. Pan.]

443 – Application of activated carbon anodes for electrolysis of sodium chloride solutions (in Polish). W. Tomassi and J. Wójtowicz (Department of Physical Chemistry, Polytechnic, Warsaw, Poland). *Przemysl Chem.*, 40 (1961) 556–560.
The electric tensions of activated carbon anodes have been measured during electrolysis of 5 *N* NaCl compared to the electric tension of a graphite rod anode. The tension of the powder anode depends on the applied pressure and the mass of carbon used. The tension distribution was not uniform over the height of the electrode layer. [Ad.Hu.]

444 – Application of activated carbon anodes for electrolysis of sodium chloride solutions. II. Current and tension field in the adsorption powder electrode (in Polish). J. Wójtowicz (Department of Physical Chemistry, Polytechnic, Warsaw, Poland). *Przemysl Chem.*, 40 (1961) 688–694.
An equation was given, describing non-stationary current and electric tension distributions in the electrode layer. Its derivation was based on some simplifying assumptions concerning the structure and electrochemical properties of the adsorption powder electrode. The theoretical conclusions were compared with experimental results discussed previously (W. Tomassi and J. Wojtowicz, *Przemsyl Chem.*, 40 (1961) 556). An equation for ionic current during the equalizing discharge, which occurs in the electrode after the electrolysis, was given and discussed. [Ad.Hu.]

445 – The effect of sinusoidal alternating current on electrode processes. VI. The effect of alternating current on the corrosion of a Hg–Zn metal pair, for an anode process (in Hungarian). T. Erdey-Gruz, J. Dévay, R. Szegedi and I. Vajasdy (Institute of Physical Chemistry and Radiology, L. Eötvös University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 67 (1961) 512–517.
Die Korrosion der Zn-Anode wurde in einer Hg- und Zn-Elektroden und 5%-ige KCl-Lösung enthaltenden, einfachen Messzelle unter Wechselstromeinfluss untersucht. Es wurde gefunden, dass die Korrosion und der vom Galvanelement gelieferte Strom erhöht werden, wenn durch die Anode ein Wechselstrom fliesst. Die Zunahme der Korrosion ist desto grösser, je grösser die Intensität und je kleiner die Frequenz des Wechselstromes ist. Die Erscheinung kann man mit der asymetrischen Polarisierbarkeit der Anode erklären. Die Polarisation der Anode wird nämlich vom Wechselstrom herabgesetzt. Nach den oszilloskopischen Untersuchungen konnte man auch feststellen, dass die Konzentrationspolarisation an der Zn-Elektrode vom Wechselstrom beeinflusst wird. [J.Inc.]

446 – The effect of sinusoidal alternating current on electrode processes. VII. The effect of the non-uniform distribution of alternating current on corrosion of the zinc electrode (in Hungarian). T. Erdey-Gruz, J. Dévay and R. Szegedi (Institute of Physical Chemistry and Radiology, L. Eötvös University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 67 (1961) 535–537.
Durch in einer Zn-Elektroden und 5%-ige KCl-Lösung enthaltenden Messzelle durchgeführte Messungen wurde festgestellt, dass die elektrolytische Korrosion von Zn durch die ungleichmässige Verteilung des Wechselstromes auf der Metalloberfläche beeinflusst wird. Je grösser die Intensität und je kleiner die Frequenz des Wechselstromes ist, desto grösser ist die Wirkung des Wechselstromes. Die Erscheinung kann durch von der asymmetrischen Polarisierbarkeit der Elektrode verursachte Spannungsverschiebung in negative Richtung erklärt werden. Diese Verschiebung verändert nämlich die Spannungsdifferenz zwischen den einzelnen Oberflächenteilen. [J.Inc.]

447 – Porous systems in electrokinetic investigations (in Polish). Z. Sokalski and Z. Drzewiecki (Department of Physical Chemistry, Polytechnic, Gliwice, Poland). *Przemysl Chem.*, 40 (1961) 637–643.
The electrokinetic tension measurements and flow tension measurements in systems containing a porous substance were used to find the characteristics of porous materials of the silica type. The results obtained by the flow method were compared with those determined from electro-osmotic measurements. [Ad.Hu.]

448 – Cathodic precipitation of chromium in polychromate solutions obtained by preliminary electrolysis of sodium bichromate (in Russian). C. C. Saveljev and A. I. Levin. *Zhur. Priklad. Khim.*, 32 (1959) 321–326.
Mit Hinsicht auf eine Verbesserung der Technologie der Gewinnung von CrO_3 wurde die Elektrolyse von Natriumbichromatlösungen untersucht. Es wurde mit einer Hg-Kathode, einer Pb-Anode und einem Porzellandiaphragm gearbeitet. Die Änderungen der Konzentration im Anodenraum wurden potentiometrisch mit einer PbO_2 Indikator- und einer Kalomel-Vergleichselektrode

verfolgt. Es wurde die Ausbeute von CrO_3 in Abhängigkeit von der Konzentration der Ausgangslösung, von der Stromdichte und der Dauer der Elektrolyse gemessen. Die elektrischen Spannungen der Elektroden und der Diaphragmenoberfläche wurden während der Elektrolyse verfolgt. Es ist möglich aus Lösungen, die $Na_2Cr_2O_7$ und freie Polychromsäuren enthalten, elektrolytisch metallisches Cr zu gewinnen. [Vi.Jes.]

449 – Electrochemical preparation of chlorine and copper using powder electrodes. I. Electrolysis of hydrochloric acid (in Polish). W. Tomassi and H. Jankowska (Department of Physical Chemistry, Polytechnic, Warsaw, Poland). *Przemysl Chem.*, 40 (1961) 624–626.
Experiments have been performed to electrolyze 10% hydrochloric acid solutions with carbon rod anodes and activated carbon powder cathodes. The chlorine yield was 60% and 90% for anode current densities of 100 and 500 A/m^2 and electrolysis voltage 1.2 and 2.0 V, respectively. A method of continuous electrolysis at reduced voltage was described. The activated carbon cathodes undergo spontaneous regeneration by losing hydrogen, after three days exposure in the air.

450 – Electrochemical preparation of chlorine and copper using powder electrodes. II. Deposition of copper (in Polish). W. Tomassi and H. Jankowska (Department of Physical Chemistry, Polytechnic, Warsaw, Poland). *Przemysl Chem.*, 40 (1961) 679–680.
Continuous electrolysis of copper hydrogen sulphate with carbon powder anodes was described. Electrolysis was carried out at 100A/m^2 cathode current density. The copper yield was 100%. Currents of 0.2 and 1.0 A were used, and the voltage, 0.75 and 1.25 V, was maintained constant. [Ad.Hu.]

451 – Contributions to the mechanism of anaerobic microbiological corrosion. I. Interpretation of the effects of sulphate-reducing bacteria on the basis of polarisation curves (in Hungarian). J. Horváth (Institute of General and Physical Chemistry, Szeged University, Hungary). *Magyar Kém. Folyóirat*, 68 (1962) 5–9.
Electrochemical model tests were carried out, using a cell with mild steel electrodes in a liquid culture medium, for detecting the mechanism of anaerobic microbiological corrosion of iron and steel caused by sulphate-reducing bacteria. It was found that the rapid corrosion in the presence of sulphate-reducing bacteria can be attributed to strong cathodic and anodic depolarisation. The cathodic and anodic polarisation curves obtained before and after bacterial inoculation are interpreted on the basis of bacterial activity and the precipitation of solid ferrous sulphide. [J.Inc.]

452 – Contributions to the mechanism of anaerobic microbiological corrosion. II. Correlations between pH, corrosion rate and the precipitation zone of solid corrosion products of iron and steel (in Hungarian). J. Horváth (Institute of General and Physical Chemistry, Szeged University, Hungary). *Magyar Kém. Folyóirat*, 68 (1962) 54–59.
Correlations between pH and the rate of anaerobic microbiological corrosion were interpreted on the basis of electrochemical model tests and theoretical calculations. It was found that the dependence of corrosion rate on pH is due partly to physico-chemical and partly to bacteriological factors. Anaerobic microbiological corrosion caused by sulphate reducers is most intense at pH 7. Correlations between pH, corrosion tension, and corrosion currents are discussed on the basis of polarisation diagrams. [J.Inc.]

453 – Contributions to the mechanism of anaerobic microbiological corrosion. III. Study of the correlations between oxidation tension, pH and composition of corrosion products on the basis of Pourbaix diagrams (in Hungarian). J. Horváth and M. Novák (Institute of General and Physical Chemistry, Szeged University, Hungary). *Magyar Kém. Folyóirat*, 68 (1962) 60–65.
A tension–pH diagram was constructed for the ternary system $Fe-S-H_2O$ for studying the mechanism of anaerobic microbiological corrosion. The correlations between pH and oxidation tension were discussed in connection with the growth of sulphate-reducing bacteria. On the basis of the proportions of the FeS, $Fe(OH)_2$ and Fe_3O_4 corrosion products, the corrosion rate dependence on the pH was discussed. [J.Inc.]

454 – Electrochemical oxidation of cyanide in sewage (in Polish). P. Szafrowski and B. Kotulski (Research Laboratory, Chemical Works, Oświęcim, Poland). *Przemysl Chem.*, 40 (1961) 339–341.
The most favourable conditions for electrochemical oxidation of hydrogen cyanide in industrial sewage have been established. The current density, time of process performance, hydrogen cyanide concentration and temperature were carefully examined. The process of oxidation was performed in the presence of considerable amounts of sulphuric acid and ammonium sulphate. The consumption of electric energy amounts to 0.028 kWh per 1 g of HCN. [Ad.Hu.]

455 – Influence of solvent and electrolyte on the action of hydrochloric acid on *n*-propanol in *n*-propanol–water mixtures (in German). S. Kilpi und Eva Lindell (Chemical Institute, Helsinki University, Finland). *Acta Chem. Scand.*, 15 (1961) 1999–2011.
Die Geschwindigkeitskoeffizienten k_1 und k_2 der Einwirkung von HCl auf *n*-Propanol bzw. der Solvolyse des gebildeten Propylchlorids wurden in wasserarmen Propanol–Wassergemischen bei verschiedenen Temperaturen bestimmt. Die Zunahme des Ionenabstands beim Steigen des Wassergehalts und die dabei stattfindende Veränderung der Aktivierungsenergie und Aktivierungsentropie wurden in Beziehung zu der Solvatation diskutiert. Beim Darstellen der Elektrolytwirkung mit der Debye-Hückelschen Gleichung wurde statt 2Bm ein empirisch entwickelter elektrostatischer Ausdruck verwendet, mit dem die Wirkung der Veränderung der Dielektrizitätskonstante und des Ionenabstands auf den Aktivitätskoeffizienten thermodynamisch berechnet werden kann. Der Ionenabstand von HCl ist nach den Messungsresultaten in konzentrierter Lösung gleich 1.84 A entsprechend dem Wert des Ionenabstands in nichtsolvatisiertem Zustand. [G.Ekl.]

456 – Investigation of reduction of anthraquinone derivatives in a homogeneous phase (in Hungarian). F. Péter and Gy. Lepenye (Institute of Practical Chemistry, Technical University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 68 (1962) 45–49.
Es wurde die mit Natriumdithionit durchgeführte Reduktion von fünf verschiedenen Anthrachinon-Derivaten (Gelb 5 GK, Rotbraun 5 RF, Goldorange 3 G, Oliv R, Orange 7 RK) untersucht und alle Reaktionen wurden erster Ordnung gefunden. Der Zusammenhang zwischen den mit Polarograph gemessenen Halbstufenspannungswerten und den berechneten log *k* Werten (*k* ist die Geschwindigkeitskonstanten) wurde entsprechend der Formel nach Dimroth (*Angew. Chem.*, 46 (1933) 571) als linear gefunden. [J.Inc.]

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